Structural Properties of Scandium Inorganic Salts

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Abstract.

The structural properties of reported inorganic scandium (Sc) salts were reviewed, including the halide (Cl, Br, and I), nitrate, sulfate, and phosphate salts. Additional analytical techniques used for characterization of these complexes (metrical data, FTIR and Sc-45 NMR) were tabulated. A structural comparison of Sc to select lanthanide (La, Gd, Lu) salt complexes was briefly evaluated.

1. Introduction.

1.1 Need for this review. Scandium (Sc) occupies an interesting spot in the periodic table. As defined by IUPAC, Sc is lumped in with the lanthanides due to its presence in lanthanide (Ln) containing ore deposits, a +3 charge, and supposed similar reactivity.[1] In contrast, due to its high Lewis acidity and small size, the chemistry of Sc^{3+} is also associated with Al^{3+} . [2, 3] This ‘confusion’ may be a result of the relative lack of chemistry developed for Sc^{3+} in comparison to the rest of these metals. This void is often due to the high cost of Sc precursors, erroneously believed to be due to its rarity. Sc is actually the 34th most abundant element in the earth’s crust (50th overall, more abundant than B). While available, Sc is widely dispersed into many different ores, with one of the highest levels found in thortveitite $(\text{Sc,Y})_2(\text{Si}_2\text{O}_7)$ at 21%. Therefore, it is not fiscally rewarding to directly mine this element and it is often isolated as an expensive by-product of other refining efforts (i.e., recovery from uranium tailings).[4] Recently, the structures of some ‘simple’ homoleptic Sc salts were disseminated which highlighted the lack of fundamental Sc^{3+} chemistry present in the literature.[5] Based on this lacuna, a review of the structures available for Sc with an emphasis on common inorganic salts was undertaken to determine other unexplored ‘gaps’ in Sc chemistry.

1.2 Past reviews. Reviews concerning the structural properties of Sc complexes are limited and often buried within reports that showcase the lanthanide and actinide derivatives.[6-8] A majority of Sc reviews focus on its health benefits and risks, [9-11] extraction methods, [4, 12] catalytic behavior,[13-16] and alloys[17-20]. Of particular note concerning the

limited number of Sc structural reviews are those that cover the organometallic/coordination complexes by Willey et al.[21], non-cyclopentadienyl ancillaries by Piers and Emslie[22], and anhydrous Sc halide complexes with neutral donor ligands by Mishra [23].

1.3 Range of review. The scope of this review focuses on structurally characterized inorganic salts of Sc. It is noteworthy that a wide assortment of structure types are available for organic Sc salts (i.e., carboxylate, triflates, and alkyl sulfonates); however, these are beyond the scope of this report and could be the focus of another review. The acids investigated include inorganic salts from the following groups – (i) hydrohalic acids, (ii) nitric acid, (iii) sulfuric acid, and (iv) phosphoric acid. The scope of this review will mainly be on homoleptic Sc^{3+} complexes, with some attention to related heteroleptic complexes. The Crystal Structure Determination, Cambridge Crystallographic Data Centre (CSD/CCDC) [24, 25], and Inorganic Crystal Structure Database (ICSD) [26] were used for this review. Colored structure depictions were obtained from OLEX2 [27] and Table 1 identifies the color scheme used.

2. Inorganic Salts.

2.1. Halide. While the simple reaction of acid and metal is a successful approach for the synthesis of aqueous halo Ln salts, the same cannot be said for the smaller Sc atom. The various structures obtained from the reactions with the hydrohalic acids are discussed

below, along with various hydroxide (OH) and solvate complexes obtained from these reactions. It should be noted that a number of unsolvated ScX_n [28-35] and ScOX [36, 37] complexes are not included in this review.

2.1.1. Chloride. Reports on the halogenation of Sc^0 via the addition of concentrated HCl (aq) reveals that reaction conditions play a significant role in the final product formed. For instance, the addition of HCl (aq) to Sc^0 at a constant temperature of 0°C produces $[\text{Sc}(\text{H}_2\text{O})_6]3(\text{Cl})$ (Figure 1). [38] A similar maximally hydrated species was isolated as $[\text{Sc}(\text{H}_2\text{O})_7]3(\text{Cl})$ from the hydration of ScCl_3 (Figure 2). [39] These monomeric complexes have either an octahedral (OC-6) geometry or a coordination number of 7 (CN-7) based on the number of waters bound to the metal and the chloride (Cl) ions located in the outersphere. Although a reproducible synthetic route has not been discerned, another monomeric Sc-Cl hydrate salt has been observed as the dual innersphere hydrate $[\text{Sc}(\text{Cl})_2(\text{H}_2\text{O})_4](\text{Cl})\cdot\text{H}_2\text{O}$. [38]

<<Insert Figure 1 here>>

<<Insert Figure 2 here>>

Without any external influence on reaction temperature (i.e., the mixture is heated by the exothermic nature of the reaction), the resulting product is the hydroxy-hydrate complex $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Cl})2(\text{H}_2\text{O})$ (Figure 3). [5] The dimeric complex consists of two capped trigonal prismatic Sc atoms connected by bridging hydroxy ligands, coordinated water molecules, and outersphere Cl ions. This complex presumably forms due to the loss of HCl (g) from the warm solution. $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Cl})2(\text{H}_2\text{O})$ [40] has also been reported from a number of other reaction systems: the slow evaporation of an aqueous solution of

$[\text{Sc}(\text{H}_2\text{O})_6]3(\text{Cl})$, [38] and as a minor component from the slow crystallization of $[\text{ScCl}_3(\text{diglyme})]$ under ambient atmospheric conditions[41-43]. The interconversion of $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Cl})2(\text{H}_2\text{O})$ to $[\text{Sc}(\text{H}_2\text{O})_6]3(\text{Cl})$ is easily achieved through the addition of concentrated HCl (aq) followed by slow evaporation; the reverse conversion is possible through the addition of base.[38] Another OH bridge species was noted for the perchlorate structure $[\text{Sc}(\mu\text{-OH})(\text{ClO}_4)_3(\text{H}_2\text{O})]_2$, which formed regardless of method used to dehydrate $\text{Sc}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$. Each OC-6 Sc metal center has three $\kappa^1\text{-ClO}_4$ ions, two $\mu\text{-OH}$ ligands, and one coordinated H_2O molecule. [43]

<<Insert Figure 3 here>>

Rapid drying of the reaction mixture at high temperatures ($< 100\text{ }^\circ\text{C}$) yields the 4:2 salt complex $[\text{ScCl}_4(\text{H}_2\text{O})_2][\text{ScCl}_2(\text{H}_2\text{O})_4]$ as shown in Figure 4. [38] This molecule consists of two OC-6 Sc atom types: 4 bound Cl atoms on one and 2 bound Cl atoms on the other. The remainder of the coordination sphere was filled by H_2O molecules. Attempts to dry the hydrate with thionyl chloride in THF led to $[\text{ScCl}_3(\text{THF})_2(\text{H}_2\text{O})]$. [38] This complex was also isolated from the controlled hydrolysis of $[\text{ScCl}_3(\text{THF})_3]$. [44] [45] ScCl_3 can also be solvated by various ligands and the reported $[\text{ScCl}_3(\text{Solv})_n]$ complexes include THF (Figure 5, $n = 3$) [44], (DME)(NCCH₃)[42] ($n = 1, 1$) and (dimethyldiglycol)[42] ($n = 1$). Crown ether salts of $\text{ScCl}_3 \cdot 6(\text{H}_2\text{O})$ have also been reported, such as: $[\text{ScCl}_3(\text{H}_2\text{O})_3] \cdot (18\text{-crown-6})$, [46, 47] and $[\text{ScCl}_3(\text{H}_2\text{O})_3] \cdot (\text{Cl})(1,4,10,13\text{-tetraoxa-7,16-diazoniumcyclo-octadecane})$ [48] as shown in Figure 6. Other ScCl_3 complexes (i.e., pincer type ligands, heterometallic scandium alkoxides, multidentate amines as well as O,N ligands, C₆₀ based complexes, and numerous crown-ethers) have been reported but discussion of them is beyond the scope of this review.

<<Insert Figure 4 here>>

<<Insert Figure 5 here>>

<<Insert Figure 6 here>>

2.1.2. *Bromide.* In general, the Sc bromide (Sc-Br) system has fewer structural variations reported in comparison to the Cl system (*vide infra*). Both outersphere and innersphere bromide (Br) atoms are present in these structures which are discussed below.

2.1.2.1. *Innersphere.* Only two complexes possess Br atoms that are innersphere, $[\text{ScBr}_3(\text{THF})_3]$ [49] (see Figure 7) and $[\text{Br}_3(\text{NH}_3)\text{Sc}(\mu\text{-Br})_2\text{ScBr}(\text{NH}_3)_3]$ [50, 51]. The former mononuclear OC-6 structure was obtained by the solvation of anhydrous ScBr_3 . [49] The latter dinuclear complex was isolated from a sealed tube reaction of $(\text{NH}_4)\text{Br}$ with Sc^0 . [50, 51] For this complex, one OC-6 Sc atom is surrounded by three NH_3 molecules and three Br ligands, both in a meridional arrangement. The other Sc atom has only one NH_4 ligand and five Br ions. Other ligands led to a single outersphere Br ion, such as was noted for $[(\text{C}_6\text{H}_5)_3\text{PO}]_4\text{ScBr}_2(\text{Br})\cdot\text{OEt}_2$. [52] The complexation of $\text{ScBr}_3\cdot 6\text{H}_2\text{O}$ with 6,6'-bis(2,2-dimethyl-1-yl)-2,2'-bipyridine led to a pentagonal bipyramidal geometry around Sc metal center (see Figure 8). This was realized by the binding of two hydroxides and two N atoms of the ligand, while retaining two coordinated Br atoms (an additional Br anion was located in the outersphere). [53]

<<Insert Figure 7 here>>

<<Insert Figure 8 here>>

2.1.2.2. *Outersphere.* The maximally hydrated $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{Br})$ was isolated from the addition of HBr (aq) to Sc^0 [38] and from the hydration of ScBr_3 . [39] The product is similar to the Cl based complex reported by the same group, with a fully hydrated CN-7 Sc metal

center, as all of the Br ions are located in the outersphere. Analogous to the Cl salt, the centrosymmetric dimeric cationic species $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_2\text{4}(\text{Br})$ [41] [54, 55] was isolated from the reaction of Sc_2O_3 with HBr (aq). It also consists of two edge-sharing (hydroxy-bridged) symmetrically equivalent ' $\text{Sc}(\text{H}_2\text{O})_5(\mu\text{-OH})_2$ ' polyhedra and two outersphere Br anions balancing the charge. $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_2\text{4}(\text{Br})$ can also be prepared from the addition of NaOH (aq) to $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{Br})$ or from simply heating an aqueous solution of $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{Br})$. [38] Three outersphere Br atoms were also observed in $[(\text{Me})_3\text{AsO})_6\text{Sc}]_3(\text{Br})$ which was isolated from the reaction of $[\text{ScBr}_3]_n(\text{H}_2\text{O})$ with Me_3AsO . [52]

2.1.3. Iodide. Analogous to the Cl and Br salts, the hydrated iodide (I) salt $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{I})$ [39] and the hydroxy iodide salt $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_4(\text{I})$ [55] (Figure 9) are reported. These complexes were prepared from the hydration of ScI_3 [39] and from the reaction of scandium oxide in HI (aq) [55], respectively. Similarly, $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{I})$ was produced from the addition of HI (aq) to Sc^0 . $[\text{Sc}(\text{H}_2\text{O})_7]_3(\text{I})$ which can then be converted to $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]_4(\text{I})$ via addition of base. [38] As expected for the hard Sc^{3+} cation and a soft I^- anion, the majority of solvated Sc iodide (Sc-I) complexes have the I^- ions residing in the outersphere. This means the *OC*-6 coordination sphere of the Sc atoms are typically saturated by the solvent used, forming $[\text{Sc}(\text{solv})_6]_3(\text{I})$ complexes where *solv* = dimethylsulfoxide (Figure 10), [56] 1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one, [57, 58] 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane, [59] or NH_3 [60]. These complexes are synthesized from the reaction of a Sc precursor (ScCl_3 or $[\text{ScCl}_3(\text{THF})_3]$) mixed with the ligand or from a solid state reaction of Sc^0 with NH_4I [60]. The use of 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane in the presence of ScI_3 resulted in a complex

with two innersphere and one outersphere I anions. The lack of a sufficient number of hard donors to saturate the Sc center in this complex allows the soft I atoms to coordinate. This is also one of the first examples of a coordinated selenoether donor where the macrocycle coordinates to the metal ion through the S and O atoms [59] (shown in Figure 11).

<<Insert Figure 9 here>>

<<Insert Figure 10 here>>

<<Insert Figure 11 here>>

2.2. Nitrate. The majority of structurally characterized scandium nitrate (Sc-NO_3) salts [5, 61-74] are prepared from the reaction of $[\text{Sc}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}]$ with varying ratios of the desired ligand followed by heating to refluxing temperatures in acetonitrile [62] [64] or a short chain alcohol [46] [61] [63]. In some instances, hydrothermal routes are used as well.[69]

2.2.1. Mixed spheres. Surprisingly, the structure of the hydrated Sc-NO_3 salt was only recently reported.[5] The $[(\text{H}_2\text{O})_4\text{Sc}(k^2\text{-NO}_3)_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$ complex was isolated from the reaction of nitric acid and $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_2 4\text{Cl} \cdot 2\text{H}_2\text{O}$ at elevated temperatures. The product is an *CN*-8 monomeric salt with two chelating NO_3 ligands, four bound water molecules, an outersphere NO_3 ion, and an outersphere water molecule (see Figure 12 – two molecules are [located](#) in the unit cell). Other similarly structured hydrated NO_3 salts have been reported with co-ligands, such as 15-crown-5 [46] and cucurbit(6)uril[68]. A single outersphere NO_3 was noted for the $[\text{Sc}(k^2\text{-NO}_3)_2(\text{L})_n]\text{NO}_3$ species when $n = 4$, $\text{L} = \text{OP}(\text{C}_6\text{H}_5)_2(\text{CH}_3)$ [63] ; $n = 3$, $\text{L} = \text{OAs}(\text{C}_6\text{H}_5)_3$ [65]; $n = 4$, $\text{L} = \text{urea}$ [73] (see Figure 13).

2.2.2. Innersphere. The majority of the remaining Sc-NO₃ structures adopt a chelating NO₃ arrangement with a co-crystallized ligand (**L**) either solved in the lattice or bound to the scandium. For the co-crystallized species, [(H₂O)_nSc(*k*²-NO₃)₃]**•L**, the ligand is typically a co-crystallized crown ether: *n* = 3, **L** = 18-crown-6 [66, 67], see Figure 14); *n* = 2, **L** = benzo-15-crown-5, [70] [71] [74] and **L** = 12-crown-4. [46] The CN-9 Sc atom in [(H₂O)₃Sc(*k*²-NO₃)₃](18-crown-6) is described as a capped square antiprism observed with a multilayer sandwich structure.

Additional water free Sc-NO₃ monomers have been reported with a bound polyamine ligand forming [(**L**)_nSc(*k*²-NO₃)₃] where *n* = 1: **L** = terpyridyl[62], amino, and bispyridyl triazine[64]. For the terpyridyl complex, only *k*²-NO₃ ligands were observed generating a CN-9 geometry around the Sc metal center. Uniquely, the triazine complex has a *k*¹-NO₃ present, yielding a Sc atom CN-8 arrangement, that was described as irregular due to the 0.29 Å displacement above the plane of the ligand. [64]

<<Insert Figure 12 here>>

<<Insert Figure 13 here>>

<<Insert Figure 14 here>>

2.2.3. Outersphere. A subset of Sc-NO₃ complexes contain only outersphere NO₃ ions. One example is a CN-8 tetrakis(*κ*²-biuret) complex[75] with a squashed, square-antiprismatic geometry. The 4,5-imidazole dicarboxylate [76] Sc-NO₃ polymer has OC-6 ScO₆ species and triangular dodecahedron CN-8 Sc atoms with four *κ*²-(O,N) ligands. As mentioned above, OC-6 complexes include [Sc(**L**)₆]3(NO₃) where **L** = (O)P(CH₃)₃[77] and (O)As(CH₃)₃ [65]. Another monomeric outersphere NO₃ complex involves a hydrated 2,6-diacetylpyridine,

bis(semicarbazone)[78] complex. This is also the only Sc-NO₃ complex with a reported outersphere hydroxide ion. The Sc metal center is forced into a *CN*-7 (Figure 15), which was described as pentagonal bipyramidal due to the remarkable planarity of the ligand (deviation of 0.023 Å for 20 atoms).

<<Insert Figure 15 here>>

The remaining outersphere Sc-NO₃ complexes are polymeric. These include a 4,4'-bipyridine-N,N'-dioxide[79] ligand (see Figure 16), 2,5-dihydroxyterephthalato,[80] and a tetramethyl, tetraazaspiro, undecane, dione[81] complex, each with an outersphere NO₃. The last two salts have bound water molecules that complete the *OC*-6 coordination sphere of each Sc metal center.

<<Insert Figure 16 here>>

2.2.4. Hydroxide. The room temperature reaction of [(H₂O)₅Sc(μ-OH)]₂4(Cl)2(H₂O) with concentrated HNO₃ (aq) produced [(*k*²-NO₃)(H₂O)₃Sc(μ-OH)]₂2(NO₃) (Figure 17). [5] The 'Sc₂(μ-OH)₂' central core is retained with a chelating NO₃ ligand and outersphere NO₃ ions, forming *CN*-7 Sc metal centers. This product was also generated from the reaction of Sc(NO₃)₃•xH₂O with Zn⁰ in water or from the treatment of Sc(NO₃)₃ (aq) with NaOH (aq) [82]. Again, the co-crystallization of 12-crown-4 ether yielded a similar hydrated complex. [46] The introduction of the tetradentate ligand 1,2-bis(pyridine-α-carbaldimino)ethane allowed for the synthesis of the hydrate free [Sc₂(NO₃)₂(μ-OH)₂(κ⁴-(N)1,2-bis(pyridine-α-carbaldimino)ethane)₂2(NO₃)2·MeCN complex. [62] The *CN*-8 metal center completes its distorted dodecahedron coordination by binding a *k*²-NO₃ and a bridging OH. Another reported Sc-NO₃ dimer, [(phen)(*k*²-NO₃)₂Sc(μ-OMe)]₂ [61] (Figure 18), had bridging

methoxide ions, bidentate phenanthroline, and two bidentate NO_3 ions. A chelating bis-2,3-pyridinedicarboxylate ligand was found to bridge hydrated *CN-7* Sc metal centers with chelating $\kappa^2\text{-NO}_3$ ions.[69]

<<Insert Figure 17 here>>

<<Insert Figure 18 here>>

2.3. Sulfate. The scandium sulfate (Sc-SO_4) salts reported in this review do not include the ubiquitous organic sulfonic salts; hence, only a handful of inorganic salts have been disseminated. [5, 83-86] The solid state synthesis of a NaCl melt of ScCl_3 in the presence of Li_2SO_4 was found to generate a ' $\text{Sc}_2(\text{SO}_4)_3$ ' polymer that has ScO_6 octahedra and sulfate (SO_4) tetrahedra connected through a variety of vertices.[86] Another homoleptic salt was recently reported and was isolated from the sulfuric acid treatment of $[(\text{H}_2\text{O})_5\text{Sc}(\text{OH})]_24(\text{Cl})2(\text{H}_2\text{O})$ to form $(\text{H})[\text{Sc}(\mu_3\text{-SO}_4)_2]\cdot 2\text{H}_2\text{O}$ (Figure 19). [5] The product was found to adopt a polymeric structure with *OC-6* ScO_6 centers bound by four bridging SO_4 moieties. The water molecules do not bind to the Sc atom but rather hydrogen bond to the SO_4 moieties.

<<Insert Figure 19 here>>

The four remaining reported Sc-SO_4 complexes are also polymeric[24, 25] [26] but were isolated as salts with amine cations [83-86]: (EDA),[85] hexamethylenediammonium (HMA),[83] 4, 4'-bipyridinium (bipy),[84] or guanidinium [83]. Two of these *OC-6* ScO_6 species utilize water molecules to fill the coordination sphere: $(\text{H}_2\text{bipy})^{2+2-}[(\mu_3\text{-SO}_4)(\mu\text{-SO}_4)\text{Sc}(\text{H}_2\text{O})]_n$ [84] and $(\text{HMA})^{2+2-}[(\mu\text{-SO}_4)_2\text{Sc}(\text{H}_2\text{O})+\text{O}]_n$ [83]. The remaining two

complexes, $[\text{Sc}(\mu\text{-SO}_4)_3]_n \cdot \text{H}_2\text{O}$ [83] and $(\text{EDA})[\text{Sc}(\mu_3\text{-SO}_4)_3] \cdot 3\text{H}_2\text{O}$ (Figure 20), [85] possess lattice water molecules.

<<Insert Figure 20 here>>

2.4. Phosphate. As observed for the SO_4 salts, no outersphere scandium phosphate (Sc-PO_4) [5, 87-93] complexes have been reported. [24, 25] Except for the homoleptic salts [5], all of the Sc-PO_4 salts reported [24, 25] were synthesized from hydrothermal processes or melts.

2.4.1. Homoleptic. While there are a number of structures noted for Sc-PO_4 salts, [88] [94-98] [99] [100, 101] [102] the acidification of $[(\text{H}_2\text{O})_5\text{Sc}(\text{OH})]_2\text{4}(\text{Cl})$ with phosphoric acid led to the isolation of *another structure* type, $[\text{Sc}(\mu\text{-PO}_4)_6 \cdot 15\text{H}]_n$ (Figure 21). [5] Crystallization of this complex was initially difficult due to poor volatility and formation of oils; however, it was found that slow thermal drying in an oven yielded high quality crystals. $[\text{Sc}(\mu\text{-PO}_4)_6 \cdot 15\text{H}]_n$ was determined to be a polymer with octahedral Sc atom centers.

<<Insert Figure 21 here>>

It should be pointed out that a number of *additional* Sc-PO_4 structural reports have been generated from powder X-ray studies of Sc-PO_4 salts. [94-98] Another species, ScPO_4 , was isolated from a flux method in a Pt crucible. [99] The structure of ' $\text{Sc}_2(\mu\text{-HPO}_3)_3$ ' was reported from the hydrothermal processing of ScCl_3 and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$. [100] This structure consists of units of bridging HPO_3 tetrahedra and distorted ScO_6 octahedra. Finally, a mixture of Sc_2O_3 with $(\text{NH}_4)_2\text{HPO}_4$ was heated in a crucible to generate ' $\text{Sc}(\text{PO}_3)_3$ ', which was found to *be isotopic* with $\text{Lu}(\text{PO}_3)_3$. [102].

2.4.2. *Amines.* Another subset of reported Sc-PO₄ structures were generated from solvothermal routes that employed amines. There are two alkali metal (Rb and K) polymers reported that use a tetraphosphatodiborate ligand but the inclusion of another metal eliminated them from this discussion.[91, 92] The remaining complexes are polymers with amine cations ranging from simple di-ammonium to cyclohexylammonium to diazoniabicyclo-octane.

2.4.3. *Non-fluorinated.* The structures reported for all of the non-fluorinated species are polymeric Sc-PO₄ ammonia salts. In some instances, the cation simply resides within the cavities of the polymer. [87, 88, 93] For these complexes the ScO₆ octahedra are formed by bridging phosphate (PO₄) moieties forming pillared sheet structures or 8-membered ring channels down the *a*-axis. [88] In one report, ribbons of ScO₆ phosphate chains are linked by hydrogen bonded fully protonated ethylenediammonium ions.[87] See Figures 22 and 23 for the structures of an intercalated cation noted for (H₃NC₄H₈NH₃)₃[(Sc(OH₂))₆Sc₂(μ-HPO₄)₁₂(μ-PO₄)₂] [87] and an interacting chain structure for (H₃NC₂H₄NH₃)₃[Sc₃(OH)₂(μ-PO₄)₂(μ-HPO₄)₃(μ-H₂PO₄)]. [87]

<<Insert Figure 22 here>>

<<Insert Figure 23 here>>

2.4.4. *Fluorinated.* The remaining Sc-PO₄ complexes are fluorinated and the majority form polymeric complexes with ammonium salts. [87] [89] [90] For these structures, the Sc atoms are in an OC-6 geometry with coordinated F atoms. This limits the PO₄ interaction and results in protonation of the O atoms. Figure 24 shows the first reported Sc-PO₄ open framework that consisted of fully connected PO₄ groups.[90] Again, there are instances of

the cations linking various chains by hydrogen bonding. The chains are composed of bridging PO_4 moieties and F ions in $(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Sc}_4(\mu\text{-F}_2)(\mu\text{-PO}_4)_4]4(\text{H}_2\text{O})$, [90] $(\text{C}_6\text{H}_{11}\text{NH}_3)[\text{Sc}(\mu\text{-F})(\mu\text{-HPO}_4)(\mu\text{-H}_2\text{PO}_4)]$, [87] and $2n(\text{C}_4\text{H}_8(\text{NH}_3)_2)[\text{Sc}_5(\mu\text{-F}_4)(\mu\text{-HPO}_4)_8]n(\text{H}_3\text{O})$ [87]. For the $[\text{C}_4\text{H}_8(\text{NH}_3)_2]^{2+}$ species, a layered structure of ScO_6 octahedra and tetrameric arrangements of ScO_4F_2 octahedra are further connected by protonated diaminobutane molecules (see Figure 25).

<<Insert Figure 24 here>>

<<Insert Figure 25 here>>

3. Properties.

A brief discussion of the structural properties and analytical information concerning these complexes is warranted. The majority of the structural data was obtained from CSD and ICSD. [25] [26] Analytical data (metrical, FTIR, and Sc-45 NMR) were transferred from the original publications and are tabulated in Table 2.

3.1. Metrical information. With these structures collated, it was of interest to elucidate the general metrical ranges for the different complexes. The distances from Sc to either Cl, Br, or I in the hydrated complexes were tabulated and as would be expected, the larger halide (X) had longer distances. Of these complexes, coordination to Sc only occurred with Cl atoms (which explains the large range): Sc---X: 2.444-4.921 Å for Cl; 4.401-4.896 Å for Br; and 4.640-5.122 Å for I. The Sc-O (H_2O) distances were found to vary from 2.074-2.226 Å. In comparison, the Sc-O distances of the $\text{Sc}(\mu\text{-OH})$ complexes[38] had a much smaller variation, ranging from 2.045-2.084 Å.

The nitrate, sulfate, and phosphate Sc-O distances were found to adopt a wide range of distances (2.017 – 2.617 Å). The Sc-SO₄ complexes have the most uniform and strongest binding ligands for this series with reported distances of 2.017-2.105 Å. The S-O phosphate lengths are comparable to Sc-SO₄ distances with an observed range of 2.022-2.154 Å. The greatest disparity of Sc-O lengths was the Sc-NO₃ complexes with a 2.166 - 2.617 Å range. This implies that the Sc-NO₃ complexes have the weakest interaction and may explain why there are so many outersphere NO₃ ions present in the reported structures, in comparison to the other salts. Bite angle comparison of the nitrate (O-N-O), sulfate (O-S-O), and phosphate (O-P-O) ligands revealed that the Sc-PO₄ angles were very flexible ranging from 101.34-120.09 °. The SO₄ angles were the most consistent with a tight range of 106.61-110.50 °. The longer nitrates had a minimum angle of 111.95 ° and a maximum angle of 116.47 °.

Distances between the central Sc metal atoms and the central atom of nitrate (Sc---N), sulfate (Sc---S), or phosphate (Sc---P) were also tabulated. The shortest distance observed was for the Sc-NO₃ complexes with a range of 2.62-2.85 Å. The Sc-SO₄ complexes again led to a more uniform range of 3.34-3.47 Å but this may be due to the significantly smaller number of structures available. The Sc-PO₄ salts had a similar range, 3.26 - 3.59 Å, to the Sc-SO₄ salts and the longest reported distance. Outersphere distances of the Sc---N varied significantly and were not further analyzed due to lack of meaningful variance. Comparison of three types of Sc-O bonds lengths with Sc---L (L= N, S, and P) distances revealed an inversely proportional relationship (i.e., the shorter the Sc-O distance the longer the Sc---L distance).

The angles of these Sc-L species were also investigated. With the exception of $\sim 180^\circ$, the O-Sc-O angles for the nitrate, sulfate, and phosphate complexes are provided in Table 2. The smallest angle and variance observed was for the Sc-NO₃ complexes with a range of $51.30 - 57.61^\circ$. Larger angles, 85.26° and 95.61° , were observed in the Sc-SO₄ salts. The largest range and largest angle was observed in the Sc-PO₄ complexes ($63.35 - 104.76^\circ$). The large O-P-O angle variance prevented adequate correlation between Sc-O bond length and PO₄ ligand bite angle.

Scandium coordination environments for these complexes are also tabulated below in Table 2. The majority of Sc-Cl complexes were *CN-7*. The remaining scandium halide (Br and I) structures had *CN-7* environments. All of the reported Sc-PO₄ and Sc-SO₄ structures have *OC-6* octahedral metal centers. In contrast, a range of *OC-6* to *CN-9* was observed for Sc-NO₃ complexes; however, the majority of the complexes were found to adopt a *CN-8*. Only two *CN-9* Sc-NO₃ structures have been reported.[67] [62] This clearly shows the ability of this rather small cation to allow the coordination of a larger number of ligands.

3.2. FTIR spectroscopy. Listing the stretching frequencies of the anions from the wide variety of Sc salts discussed above was attempted to delineate bonding modes. Surprisingly, only the [(H₂O)₅Sc(μ -OH)₂Sc(H₂O)₅]Br₄•2H₂O and [(H₂O)₅Sc(μ -OH)₂Sc(H₂O)₅]I₄ report the FTIR spectrum.[55] Sc-O stretching frequencies were assigned at $1154-1155$ and $861-971\text{ cm}^{-1}$. [55] Further, less than half of the reported Sc-NO₃ complexes were characterized via FTIR spectroscopy. Coordinated and non-coordinated NO₃ molecules have similar reported stretching frequencies in the $1550-1700$, $1478-1502$, and $810-838\text{ cm}^{-1}$ regions. [43, 46, 59-63, 66, 74, 76, 77] Stretching frequencies unique to

coordinated NO_3 molecules are observed at 1510-1538 and 1009-1304 cm^{-1} . [59] It should be noted that some of the complexes were not further characterized as insufficient material was isolated. $(\text{H}_2\text{en})\text{Sc}_2(\text{SO}_4)_4 \cdot (\text{H}_2\text{O})_{0.72}$ is the only Sc- SO_4 complex characterized by FTIR spectroscopy. [85] Although there are more reported structures of Sc- PO_4 than Sc- SO_4 , none of them were characterized via FTIR spectroscopy.

3.3 Sc-45 NMR spectroscopy. As is often noted in Sc based papers, the ^{45}Sc nucleus is primed for NMR experiments due to its inherent properties: 100% naturally abundant, spin (I) of 7/2, high observed frequency, with a moderate quadrupole moment (Q) of $0.22 \times 10^{-28} \text{ m}^2$, and a chemical shift range of 250 ppm. Furthermore, Schurko *et al.* indicated in their comprehensive report on solid-state ^{45}Sc NMR spectroscopy that the coordination environment of the metal is associated with the chemical shift. [103] A correlation between the NMR tensor characteristics and the coordination of the Sc metal center is also reported to exist. Unfortunately, many of the reported halide, SO_4 , NO_3 , and PO_4 complexes were not fully characterized via ^{45}Sc NMR spectroscopy.

The only scandium halide structure with reported ^{45}Sc NMR data was $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_2\text{Cl} \cdot 2\text{H}_2\text{O}$. A singlet at δ 18.5 was observed in the solid state spectrum. Solution characterization in water required concentration and temperature variance to identify a $[\text{Sc}(\text{OH})\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}$ and $[\text{Sc}(\text{OH})(\text{H}_2\text{O})_6]2(\text{Cl})$ equilibrium. Of all of the structurally characterized Sc- NO_3 complexes, only $[(\text{H}_2\text{O})_4\text{Sc}(\kappa^2\text{-NO}_3)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ was characterized in the solid and solution state by ^{45}Sc NMR spectroscopy. Multiple peaks, attributed to different phases, packing inequivalence, and/or loss of crystallinity under the MAS conditions, were observed. In solution, a single resonance at δ -15 was noted in

concentrated HNO_3 (aq) but shifted to δ 0.4 in D_2O . The δ 0.4 singlet was also observed for $[(\text{H}_2\text{O})_3\text{Sc}(\kappa^2\text{-NO}_3)(\mu\text{-OH})]_2(\text{NO}_3)_4$ dissolved in water. Due to the similarity in shifts for these two complexes (and those discussed below), the 0.4 ppm shift is believed to be the formation of the fully hydrated species (i.e., $\text{Sc}(\text{H}_2\text{O})_6^{+3}$). [5]

A number of $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and Ph_3AsO reactions were surveyed in ethanol and acetone[65] where two resonances assigned as $[(\text{Ph}_3\text{AsO})_3\text{Sc}(\text{NO}_3)_2](\text{NO}_3)$ and $[(\text{Ph}_3\text{AsO})_2\text{Sc}(\text{NO}_3)_3]$ were reportedly observed. The dichloromethane recrystallized product from a 1:1 $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}:\text{Ph}_3\text{AsO}$ reaction in acetone was used to identify $[(\text{Ph}_3\text{AsO})_2\text{Sc}(\text{NO}_3)_3]$ at δ 14.0. A broad line at δ 31.9 is assigned as $[(\text{Ph}_3\text{AsO})_3\text{Sc}(\text{NO}_3)_2](\text{NO}_3)$, which was isolated from the 1:3 $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}:\text{Ph}_3\text{AsO}$ reaction in ethanol. No changes to this resonance are noted in the presence of excess ligand.[65] $[(\text{Ph}_3\text{PO})_2\text{Sc}(\text{NO}_3)_3]$ was another complex unaffected by excess ligand (Ph_3PO) with a singlet at δ -7.5. [63] In contrast, $[(\text{Ph}_2\text{MePO})_3\text{Sc}(\text{NO}_3)_3]$ had two peaks at δ -3.5 and -33 at 300 K, which in the presence of excess Ph_2MePO led to an intensity increase for the lower frequency. [63] $[\text{Sc}(\text{OAsMe}_3)_6](\text{NO}_3)_3$ dissolved in MeNO_2 had a broad peak at δ 58 with a superimposed sharp feature at δ 56.[65] The addition of excess OAsMe_3 led to the complete conversion to the δ 56 species $[\text{Sc}(\text{OAsMe}_3)_6]^{3+}$. The δ 58 peak was attributed to a coordinated NO_3 complex.

The two remaining Sc-NO_3 complexes that were characterized by ^{45}Sc NMR spectroscopy had outersphere crown ether molecules. [46] Both were dissolved in acetone with $[\text{Sc}(\text{H}_2\text{O})_2(\text{NO}_3)_3] \cdot (12\text{-crown-4})_2$ observed at δ -1, whereas $[\text{Sc}(\text{H}_2\text{O})_4(\text{NO}_3)_2]\text{NO}_3 \cdot 15\text{-crown-5}$ had a peak at δ 2. With a range of CN-7 complexes observed at δ -15–31.9 and a

CN-8 range of δ -7.5–0.4, the chemical shift of these NO_3 complexes appear to be more dependent on the ligands employed than the CN.

The only Sc- SO_4 complex characterized via ^{45}Sc NMR spectroscopy was $(\text{H})[\text{Sc}(\mu_3\text{-SO}_4)_2]\cdot 2\text{H}_2\text{O}$. The solid state spectrum had a single peak with a classic second-order quadrupolar broadened powder pattern. The quadrupolar coupling constant (QCC) was found to be δ 6.2 MHz. The δ -1.1 chemical shift noted for concentrated sulfuric acid singlet was shifted to δ 9.8 upon dissolution in water. The shift was believed to be the result of a fully hydrated species (i.e., $\text{Sc}(\text{H}_2\text{O})_6^{+3}$) that was also similarly observed for $[(\text{H}_2\text{O})_4\text{Sc}(\kappa^2\text{-NO}_3)_2]\text{NO}_3\cdot\text{H}_2\text{O}$. [5]

$[\text{Sc}(\mu\text{-PO}_4)_6 12\text{H}]_n$ is the only reported Sc- PO_4 complex with solution and solid state ^{45}Sc NMR data. [5] In fact, $[\text{Sc}(\mu\text{-PO}_4)_6 12\text{H}]_n$ is the only Sc- PO_4 complex with reported solution resonances. In concentrated H_3PO_4 (aq) a singlet was observed at δ -8.4, whereas in water a singlet at δ 31.1 was noted. The δ 31.1 singlet was not identified and was unique when compared to other similar Sc salts dissolved in water. Two peaks at δ -11.5 and -6.8 were observed in the solid-state spectrum. The multiple peaks were attributed to the presence of different phases, packing inequivalence, and/or loss of crystallinity under the MAS conditions. [5]

The solid-state ^{45}Sc NMR of a number of Sc- PO_4 complexes displayed broad spectra that reflected crystallographic observations. For instance, $(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3[(\text{Sc}(\text{OH}_2))_6\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$ contained a single broad peak assigned as three overlapping signals at δ 1. [87] In contrast, $(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3[\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$, $\text{C}_6\text{H}_{11}\text{NH}_3[\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$, and $(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_4(\text{H}_3\text{O})_2[\text{Sc}_{10}\text{F}_8(\text{HPO}_4)_{16}]$ had two broad peaks in the solid state spectra. [87] The reported resonances are provided in

Table 2 and span from δ 35.4 to -15.5. Several overlapping resonances at δ 26.3, 10.3 and -3 were also reported for $\text{Sc}(\text{HPO}_4)_2 \cdot 0.5(\text{N}_2\text{C}_2\text{H}_{10})$ with the two up-field resonances associated with the PO_4 complex and the latter with residual Sc_2O_3 in the sample.[93]

Four unique scandium environments were observed in the spectrum of $(\text{C}_6\text{N}_2\text{H}_{14})\text{Sc}_4\text{F}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ at δ 33, 34, 63, and 90.[90] The resonance assignments were based on feature characteristics, a ^{45}Sc multiple quantum MAS experiment, and $^{45}\text{Sc}/^{19}\text{F}$ REDOR NMR spectroscopy. A ScO_6 species was readily identified at δ 90 with its absence in the difference spectrum and an extremely broad peak in the 3QMAS spectrum. The largest intensity drop in the $^{45}\text{Sc}/^{19}\text{F}$ REDOR NMR spectroscopy experiments aided in the ScO_4F_2 species characterization peak at δ 34. The remaining peaks (δ 33 and 63) were in isotropic dimension and are attributed to the two symmetric Sc atoms as seen in the crystal structure. The four scandium sites were then extracted from the slices in the 3QMAS spectrum as δ 25, 34, 46, and 127.

The Sc-PO_4 solid state NMR spectra ranged from δ -15.5 to 90. As all of the structures contained octahedral Sc metal centers correlation between CN and observed resonance was not assigned.

4.0. Comparison to select Lanthanide (La, Gd, Lu) Salts.

As Sc is often included with the Ln series, it was of interest to compare and contrast the basic structure types reported (i.e., halides, nitrates, sulfates, phosphates). The same databases[24, 25] were used to locate selected early, middle, and late Ln salts: lanthanum (La), gadolinium (Gd), and lutetium (Lu). This allows a quick, general overview as a full evaluation of all Ln cations would require a much more comprehensive study. The structures found for these cations and Sc are listed in Table 3.

Monomers, dimers, and polymers were reported for the Ln halide complexes. Comparison of these structure types, mono and dimeric Sc halide salts reveals that Gd [104, 105] and Lu [106] adopted a similar two innersphere and one outersphere Cl atom structure. [38] The four remaining unique Sc-Cl salts are $[\text{Sc}(\text{H}_2\text{O})_6]3(\text{Cl})$ [38], $[\text{Sc}(\text{H}_2\text{O})_7]3(\text{Cl})$ [39], $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Cl})2(\text{H}_2\text{O})$ [5] [40], and $[\text{ScCl}_4(\text{H}_2\text{O})_2][\text{ScCl}_2(\text{H}_2\text{O})_4]$ [38]. There is a reported La-Cl dimer [107] with coordinated water molecules; however the La complex contained bridging Cl atoms rather than the bridging OH ligands noted for $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Cl})2(\text{H}_2\text{O})$. This Sc dimer is also in contrast to the reported continuous networks of $[\text{Ln}(\text{OH})_2\text{Cl}]$ (where Ln = Gd, Lu) isolated from the hydrothermal treatment of the respective $[\text{LnCl}_3]n(\text{H}_2\text{O})$. [108] Finally, the reported La-Cl polymer differs from the Gd and Lu polymers via coordinated water molecules. [109]

The hydrated Lu-Br salt was the only the only structure that was similar to the Sc-Br salt observed, where each structure has three outersphere Br ions. [38] [39] [110] There is only one other reported Sc-Br salt, $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})]_24(\text{Br})$, which is surprisingly unique to Sc. [38] [41] [54, 55] The final reported Ln-Br (Ln = La, Gd, Lu) salt is a La-Br dimer with coordinated water molecules, bridging Br atoms, and outersphere Br ions. [55, 110] Hydrated I salts with outersphere I ions are reported for the investigated Ln cations. [38] [39] [111] As with the other halide salts, the hydroxy Sc-I salt $[\text{Sc}(\mu\text{-OH})(\text{H}_2\text{O})_5]4(\text{I})$ is known. [38] [55] The corresponding La dimer $[\text{La}(\mu\text{-OH})(\text{H}_2\text{O})_5]4(\text{I})$ is the only Ln hydroxy halide salt observed and is similar to the three Sc hydroxy halide structures. [112] Finally, $[\text{La}_6(\text{H}_2\text{O})_{23}(\text{OH})_{10}]\text{I}_8 \cdot 8\text{H}_2\text{O}$ and $[\text{La}_7(\text{OH})_{18}\text{I}_3]$ are the remaining reported Ln-Br salts and are only observed for the La cation. [113] [114] These salts were prepared from hydrothermal routes using Ln_2O_3 and HI (aq). As can be noted from the halide system, the structures

reported for the 'simple' Sc-X-H₂O ligand system can be significantly varied from those of the Ln series.

The NO₃, SO₄, and PO₄ salt structures reported for La, Gd, and Lu were also compared to the corresponding Sc structures. The Sc-NO₃ monomer [(H₂O)₄Sc(κ^2 -NO₃)₂](NO₃)•2(H₂O) is unique when compared to the other Ln-NO₃ monomers which reportedly possess only κ^2 -NO₃ molecules. [115] [116] [117] [118] [119] The last Ln-NO₃ structure, polymeric OH Ga-NO₃ [120], is in contrast to the only other Sc-NO₃ salts reported as [(κ^2 -NO₃)(H₂O)₃Sc(μ -OH)]₂(NO₃). [5] [82] All disseminated Ln-SO₄ salt structures were polymers. As noted (*vide infra*) the Sc-SO₄ salts were also polymeric. Comparison of these polymers revealed that there are four structure types: hydrated, anhydrous, outersphere water, and hydroxy polymers. With the exception of a bound water Lu-SO₄ polymer, anhydrous and coordinated water SO₄ polymeric structures are reported for the investigated metals. [83] [86] [121] [122] [123-125] [126] [127] [128] [129, 130] Only La [131] has a structure similar to the outersphere hydrated polymer noted for Sc. [5] Finally, both La [132] and Gd [133] report a OH Ln-SO₄ polymer that is not observed for Sc. There are numerous reports of anhydrous M-PO₄ [99] [134] [135] [136] [137] [138] and MO₉P₃ [96] [102] [139] [140] [141] [142] (M = Sc, La, Gd, and Lu) polymers. Of the various M-PO₄ polymer types reported, five structures are unique to Sc. [5] [95] [97] [98] Two of these unique polymers are hydrated with outersphere hydronium ions or coordinated water molecules. [88] [143] The presence of the hydronium ion was unique to Sc salts, whereas coordinated water molecules were observed in separate Ln-PO₄ polymeric salts. [144] [145] [146] [147] [147]

While more work is obviously necessary for the structural identity of the fundamental Ln salts, significant differences in the structure types and behavior of the Sc atom is obvious even when compared to a small subset of similar Ln (La, Gd, and Lu) salts.

This may be due to the size of the cation but the lack of the *f*-orbitals will also play a role in dictating the final structural arrangement.

5.0. Summary and conclusion

This review covers the reported structural properties of various inorganic Sc salts. The structures of the 'simple' scandium halide (chloride, bromide, and iodide) salts have been presented and as can be discerned a wide variety of structure types are available. The Cl atoms were found in both the innersphere and outersphere, whereas the larger halide (Br, I) hydrated Sc salts have mainly outersphere ions. Bridging hydroxy halide complexes were noted for all of the Sc halide salts. The structures of Sc-NO₃, Sc-SO₄, and Sc-PO₄ complexes were isolated with innersphere anions, outersphere anions, hydroxy anions, and fluorine atoms. The majority of these salts were isolated as polymers with the acid moieties acting as bridges between the various Sc metal centers. Although a library of Sc salt structures exists, many of these products are not characterized via FTIR and ⁴⁵Sc NMR spectroscopy. As can be noted from this review, there are substantial differences in Sc and the selected Ln complexes evaluated. Additional work is clearly necessary in the development of the fundamental structures concerning the properties of both scandium and the lanthanide cations.

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Table 1. Color scheme used for structural depictions in Figures 1 – 14 and 16 - 25.

Table 2. Analytical data for the Sc salts. Abbreviations used (distorted included): *OC-6* = octahedral, *pbp* = pentagonal bipyramidal, *mct* = monocapped trigonal prism *ddh* = dodecahedron, *sap* = square anti-prism, *tbp* – trigonal bipyramid.

Table 3. Single Crystal structural data comparison of Sc-L complexes to select Ln-L complexes.

Table 1. Color scheme used for structural depictions in Figures 1 – 14 and 16 - 25.

Element	Color	Depiction
Sc	dark blue
Br	crimson
C	grey
Cl	green
F	light green
I	purple
N	light blue
O	red
P	pink
S	yellow

Table 2. Analytical data for the Sc salts. Abbreviations used (distorted included): (IS) = innerspher, (OS) = outersphere, *CN* = coordination number, *OC*-6 = octahedral, *pbp* = pentagonal bipyramidal, *mct* = monocapped trigonal prism *ddh* = dodecahedron, *sap* = square anti-prism, *tbp* – trigonal bipyramid.

Sc ligand	Distance (Å)/ Angle (°) ^a	CN <i>geometry</i>	(δ) ⁴⁵ Sc (solv)	FTIR (cm ⁻¹)	[REF] (code) ^{b,c}
halides					
Cl					
H ₃₇ Cl ₂ O ₇ Sc	Sc-OH: 2.059-2.065 Sc-OH₂: 2.173-2.205 Sc-Cl(OS): 4.893-4.921	7	38.7, 8.9 (H ₂ O) 18.5 ^d	3361, 2387, 2347, 2291, 1701, 1637, 1262, 1094, 909, 801, 672, 536 [38]	[5] (196168) ^b
H ₁₄ Cl ₃ O ₇ Sc	Sc-OH₂: 2.098-2.209 Sc-Cl(OS): 4.264-5.853	7 <i>pbp</i>			[39] (91460) ^b
H ₂₆ Cl ₄ O ₁₄ Sc ₂	Sc-OH: 2.066-2.068 Sc-OH₂: 2.176-2.208 Sc-Cl(OS): 4.507-4.897	7			[41] (39838) ^b
H ₂₆ Cl ₄ O ₁₄ Sc ₂	Sc-OH: 2.060-2.074 Sc-OH₂: 2.074-2.210 Sc-Cl(OS): 4.977-4.901	7			[40] (281125) ^b
H ₁₂ Cl ₃ O ₆ Sc	Sc-OH₂: 2.105-2.113 Sc-Cl(IS): 2.444 ScCl(OS): 4.620	6 <i>OC</i> -6		3656, 2981, 2890, 1474, 1461, 1384, 1254, 1153, 1072, 958, 816 [38]	[38]
H ₁₂ Cl ₆ O ₆ Sc ₂	Sc-OH₂: 2.101-2.131 Sc-Cl(IS): 2.437-4.437	6 <i>OC</i> -6		3653, 2981, 2887, 2361, 2331, 1478, 1468, 1390, 1257,	[38]

				1153, 1069, 955, 816 [38]	
Br					
H ₁₁ Br ₂ O ₆ Sc	Sc-OH: 2.048-2.083 Sc-OH₂: 2.160-2.222 Sc-Br(OS): 4.691-5.238	7			[54] (172188) ^b
H ₁₄ Br ₃ O ₇ Sc	Sc-OH₂: 2.094-2.209 Sc-Br(OS): 4.395-6.010	7 <i>pbp</i>			[39] (91461) ^b
H ₂₆ Br ₄ O ₁₄ Sc ₂	Sc-OH: 2.063-2.069 Sc-OH₂: 2.182-2.211 Sc- Br(OS): 5.090-6.777	7 <i>pbp</i>		3700-3200 (OH), 2306, 1592(H ₂ O), 1155 (ScOH), 885 (μ-OH + Sc-O), 547-317, 203- 116	[55] (421755) ^b
H ₂₆ Br ₄ O ₁₄ Sc ₂	Sc-OH: 2.047-2.076 Sc-OH₂: 2.170-2.208 Sc- Br(OS): 4.646-5.076	7			[41] (39839) ^b
H ₂₂ Br ₄ O ₁₂ Sc ₂	Sc-OH: 2.051-2.076 Sc-OH₂: 2.160-2.213 Sc-Br(OS): 4.860-4.893	7			[38]
H ₁₄ Br ₃ O ₇ Sc	Sc-OH₂: 2.095-2.203 Sc-Br(OS): 4.401-4.896	7			[38]
I					
H ₁₆ I ₃ O ₈ Sc	Sc-OH₂: 2.107-2.218 Sc-Br(OS): 10.435-12.688	7 <i>pbp</i>			[39] (91462) ^b

$\text{H}_{22}\text{I}_4\text{O}_{12}\text{Sc}_2$	Sc-OH: 2.045-2.081 Sc-OH₂: 2.152-2.222 Sc-I(OS): 4.779-5.215	7 <i>mct</i>		3700-3200 (OH), 1603 (H ₂ O), 1154 (ScOH), 971-861 (μ -OH + Sc-O), 474-311 (Sc-O), 272-102	[55] (421752) ^b
$\text{H}_{22}\text{I}_4\text{O}_{12}\text{Sc}_2$	Sc-OH: 2.051-2.084 Sc-OH₂: 2.161-2.226 Sc-I(OS): 5.099-5.122	7			[38]
$\text{H}_{14}\text{I}_3\text{O}_7\text{Sc}$	Sc-OH₂: 2.100-2.201 Sc-I(OS): 4.640-5.138	7			[38]
NO₃					
$\text{H}_{10}\text{N}_3\text{O}_{14}\text{Sc}$	Sc-OH₂: 2.103-2.185 Sc-ONO₂: 2.2550(12)-2.3383(12) Sc-N: 2.6795(15)- 2.7361(15) O-N-O: 113.84-114.12 O-Sc-O: 55.29-56.54	8 <i>ddh</i>	-15 (HNO ₃) 0.4 (H ₂ O) (-19.3, -38.3, -40.6) ^d		[5] (196170) ^b
$\text{H}_7\text{N}_2\text{O}_{10}\text{Sc}$	Sc-OH: 2.053-2.076 Sc-OH₂: 2.114-2.183 Sc-ONO₂: 2.2669(15)-2.3229(15) Sc-N: 2.7230(17) O-N-O: 114.17 O-Sc-O: 55.758	7 <i>pbp</i>	0.4 (H ₂ O)		[5] (196169) ^b

$\text{H}_{14}\text{N}_4\text{O}_{20}\text{Sc}_2$	Sc-OH: 2.051-2.073 Sc-OH₂: 2.116-2.182 Sc-ONO₂: 2.268-2.327 Sc-N: 2.726 O-N-O: 114.17 O-Sc-O: 55.574	7 <i>pbp</i>			[82] (251134) ^b
$\text{C}_{36}\text{H}_{41}\text{N}_{27}\text{O}_{33.5}\text{Sc}$	Sc-O: 2.269(5)-2.356(5) Sc-N: 2.748(5) O-N-O: 113.501 O-Sc-O: 54.921	8 <i>sap</i> ^e			[68] (NELHIW) ^c
$\text{C}_{12}\text{H}_{30}\text{N}_3\text{O}_{18}\text{Sc}$					[66] ^f (JAKVOG) ^c
$\text{C}_{12}\text{H}_{30}\text{N}_3\text{O}_{18}\text{Sc}$	Sc-O: 2.2495(5)-2.3634(5) Sc-N: 2.6858(7)-2.7285(8) O-N-O: 114.544-115.48 O-Sc-O: 54.078-55.791	9 capped <i>sap</i>			[67] (JAKVOG01) _c
$\text{C}_{14}\text{H}_{24}\text{N}_3\text{O}_{16}\text{Sc}$					[70] ^f (SEZFOS) ^c
$\text{C}_{14}\text{H}_{24}\text{N}_3\text{O}_{16}\text{Sc}$					[71] ^f (SEZFOS01) ^c

$C_{14}H_{24}N_3O_{16}Sc$	Sc-O: 2.1657(18)-2.255(2) Sc-N: 2.6206(16)-2.669(2) O-N-O: 113.765-114.554 O-Sc-O: 56.745-57.612	8 <i>ddh</i>			[74] (SEZFOS02) ^c
$C_{16}H_{36}N_3O_{19}Sc$	Sc-O: 2.2007(15)-2.2682(14) Sc-N: 2.6422(19)-2.679(3) O-N-O: 113.839-115.117 O-Sc-O: 56.983-57.575	8 <i>sap</i> ^e	-1.0 (br) (Me ₂ CO)	3580br, 2665m, 1650m, 1587m, 1305w, 1168w, 1157w, 1088w, 1024w, 972m, 931m, 897m, 852m, 813w, 770m, 637w, 560w, 519w	[46] (TUVYOY) ^c
$C_{10}H_{28}N_3O_{18}Sc$	Sc-O: 2.184-2.249 Sc-N: not reported	8 <i>ddh</i> ^e	2.0 (Me ₂ CO)	3400br, 3200br, 1645br, 1537m, 1279m, 1121m, 1098m, 1056w, 1023m, 964w, 944m, 833m, 808m, 757m	[46] (TUVYUE) ^c
$C_8H_{30}N_4O_{24}Sc_2$	Sc-O: 2.2607(19)-2.3660(14) Sc-N: 2.732(2) O-N-O: 114.68 O-Sc-O: 55.233	7 <i>pbp</i> ^e			[46] (TUVYIS) ^c

$C_{15}H_{11}N_6O_9Sc$	Sc-O: 2.234(3)-2.482(4) Sc-N: 2.674(4)-2.753(3) O-N-O: 113.08-115.923 O-Sc-O: 52.706-56.869	9		(1510, 1502, 1304, 1020, and 12) ^b	[62] (DITFOB) ^c
$C_{15}H_{16}N_9O_{10}Sc$	Sc-O: 2.213(3)-2.617(4) Sc-N: 2.654(4)-2.849(4) O-N-O: 114.123-114.692 O-Sc-O: 51.301-57.5	8 <i>irregular</i>			[64] (DUCVIG) ^c
$C_{36}H_{30}N_3O_{11}P_2Sc$	Sc-O: 2.204(7)-2.311(7) Sc-N: 2.670(11)-2.722(12) O-N-O: 111.948-114.369 O-Sc-O: 55.176-57.049	8 <i>tbp</i>	-7.5 (CH ₂ Cl ₂)	1562, 1437, 1299, 1282, 1167 (PO), 1140, 1123, 1009, 808, 747, 725, 692, 542	[63] (DOTPEH) ^c

$C_{42}H_{36}N_3O_{11}P_2Sc$	Sc-O: 2.2506(18)-2.3371(16) Sc-N: 2.687(2)-2.725(2) O-N-O: 113.316-115.255 O-Sc-O: 55.55-57.537	8 <i>tbp</i> ^e			[72] (WEFMEB) ^c
$C_{53.3}H_{54.6}N_3O_{13}P_4Cl_{2.6}Sc$	Sc-O: 2.312(7)-2.426(7) Sc-N: 2.741(7)-2.809(7) O-N-O: 114.441-116.468 O-Sc-O: 53.318-54.831	8 <i>tbp</i>	-3.5 ((CH ₂ Cl ₂)	1591 w, 1299m, 1153s (PO), 1125m, 1108m, 1073m, 1037w, 996w, 889s, 831w, 818w, 811s, 744s, 694s, 507s, 479m, 453m, 425w, 400w, 277m	[63] (DOTPIL) ^c
$C_{54}H_{47}As_3N_3O_{13}Sc$	Sc-O: 2.251(5)-2.266(6) Sc-N: 2.662(6)-2.686(7) O-N-O: 113.892-115.002 O-Sc-O: 56.282-56.806	7 <i>tbp</i>	31.9 (CH ₂ Cl ₂ /CDCl ₃)	3065w, 1521s, 1485m, 1441s, 1362s, 1298m, 1163w, 1089s, 1026m, 999m, 948w, 899br s, 832w, 812m, 743s, 691s, 478s, 418m, 368s, 357s	[65] (HUWFEK) ^c

$C_4H_{16}N_{11}O_{13}Sc$	Sc-O: 2.2970(6)-2.4361(6) Sc-N: 2.7721(7)-2.7727(7) O-N-O: 113.892 O-Sc-O: 56.806	8 <i>ddh</i> ^e			[73] (URSCNI) ^c
$C_8H_{20}N_{15}O_{17}Sc$	Outersphere	8 <i>sap</i>			[75] (BIZKAX) ^c
$C_{20}H_{18}N_9O_{24}Sc_3$	Outersphere	8, 6 triangular <i>ddh</i> , <i>OC-6</i>		3394s, 1624s, 1478w, 1357m, 1393m, 1131w, 981w, 838m, 616w, 510m	[76] (WUBGIL) ^c
$C_{18}H_{54}As_6N_3O_{15}Sc$	Outersphere	6 <i>OC-6</i> ^e	58.0 (MeNO ₂ /CD ₃ NO ₂)	3010w, 1648w, 1364s, 1269m, 1111 m, 1048w, 925s, 873vs, 848s, 836sh, 648s, 396s, 303m	[65] (HUWFAG) ^c
$C_{18}H_{54}N_3O_{15}P_6Sc$	Outersphere	6 <i>OC-6</i>			[77] (GUVNIU) ^c
$C_{11}H_{20}N_9O_8Sc$	Outersphere	7 <i>pbp</i>		1700, 1645, 1600, 1550	[78] (ACPYZS) ^c
$C_{30}H_{24}N_9O_{15}Sc$	Outersphere	6 <i>OC-6</i>			[79] (FITGUL) ^c
$C_{24}H_{18}NO_{25}Sc_3$	Outersphere	6 <i>OC-6</i>			[80] (ICISAP) ^c
$C_{33}H_{72}N_{18}O_{30}Sc_2$	Outersphere	6 <i>OC-6</i> ^e			[81] (YOCBID) ^c

$C_{32}H_{36}N_{14}O_{14}Sc_2$	Sc-O: 2.296(3)-2.333(3) Sc-N: 2.732(3) O-N-O: 115.041 O-Sc-O: 54.816	8 <i>ddh</i>		(1500, 1295, 1015, 810) ^g	[62] (DITFUH) ^c
$C_{26}H_{22}N_8O_{14}Sc_2$	Sc-O: 2.2506(18)-2.3371(16) Sc-N: 2.687(2)-2.725(2) O-N-O: 114.18-115.251 O-Sc-O: 55.148-56.034	8 <i>ddh</i> ^e		(1538, 1522, 1510, 1303) ^a	[61] (BOFHEK) ^c
$C_7H_5N_2O_8Sc$	Sc-O: 2.35(5)-2.238(4) Sc-N: 2.655(5) O-N-O: 114.223 O-Sc-O: 56.96	7 <i>pbp</i>		3197m, 1635m, 1583s, 1416s, 1113m, 831m	[69] (NORQES) ^c
SO₄					
$H_5O_{10}S_2Sc$	Sc-O: 2.046(3)-2.060(3) Sc-S: 3.404-3.427 O-S-O: 107.62-109.03 O-Sc-O: 85.257-91.243	6 <i>OC-6</i>	-1.1(H ₂ SO ₄) 9.8 (H ₂ O) -15.8 ^d	3377, 2949, 2607, 2488, 1638, 1286, 1175, 1070, 1008, 887, 851, 678, 615, 575, 456, 415 [38]	[5] (196172) ^b

$\text{H}_{10}\text{O}_{17}\text{S}_3\text{Sc}_2$	Sc-OSO₃ : 2.029-2.080 Sc-OH₂ : 2.092-2.122 Sc-S : 3.364-3.438 O-S-O : 107.30-108.30 O-Sc-O : 87.669-94.460	6 <i>OC-6</i>		3183, 3360, 1636, 1665, 1058-1081, 1127, 1223, 600, 643, 672, 469, 572	[83] (413609) ^b
$\text{O}_4\text{SSc}_{0.7}$	Sc-OSO₃ : 2.057-2.071 Sc-S : 3.412-3.413 O-S-O : 108.03-110.50 O-Sc-O : 87.669-94.460	6 <i>OC-6</i>			[86] (411221)
$\text{C}_2\text{H}_{11.44}\text{N}_2\text{O}_{16.72}\text{S}_4\text{Sc}_2$	Sc-O : 2.068(2)-2.0824(19) Sc-S : 3.355-3.380 O-S-O : 108.044-109.579 O-Sc-O : 86.805-95.613	6 <i>OC-6</i>		3115w, 1509w, 1347vw, 1221m, 1101s, 1077s, 1064s, 1053s, 769w, 659m	[85] (TEWCOO) ^c
$\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_{20}\text{S}_4\text{Sc}_2$	Sc-O : 2.049(7)-2.059(7) Sc-S : 3.363-3.381 O-S-O : 106.993-109.027 O-Sc-O : 89.3-94.755	6 <i>OC-6^e</i>			[84] (SECBIM) ^c

$C_6H_{48}N_{18}O_{30}S_6Sc_2$	Sc-O: 2.0783(15)-2.0806(15) Sc-S: 3.388-3.466 O-S-O: 108.114 O-Sc-O: 89.367-90.633	6 <i>OC-6^e</i>			[83] (SANKAU) ^c
$C_6H_{30}N_2O_{22}S_4Sc_2$	Sc-O: 2.017(3)-2.105(3) Sc-S: 3.340-3.473 O-S-O: 106.609-107.428 O-Sc-O: 90.8	6 <i>OC-6^e</i>			[83] (SANJUN) ^c
PO₄					
$H_6O_{12}P_3Sc$	Sc-O: 2.06157(7) Sc-P: 3.462 O-P-O: 115.405 O-Sc-O: 88.15-91.871	6 <i>OC-6^e</i>	-8.4 (H ₃ PO ₄) 31.1 (H ₂ O) (-11.5, -6.8) ^d	1643, 1552, 1484, 965, 890, 751, 682, 605, 504, 406 [38]	[5] (196171) ^b
$O_{36}P_{12}Sc_4$	Sc-O: 2.072-2.082 Sc-P: 3.420-3.519 O-P-O: 118.63 O-Sc-O: 88.51-92.72	6 <i>OC-6</i>			[95] (1719) ^b
O_9P_3Sc	Sc-O: 2.057-2.109 Sc-P: 3.313-3.521 O-P-O: 116.19-118.59 O-Sc-O: 81.92-97.14	6 <i>OC-6</i>			[96] (20430) ^b

H ₆ O ₁₂ P ₃ Sc	Sc-O: 2.062-2.077 Sc-P: 3.448-3.477 O-P-O: 116.27 O-Sc-O: 86.83-92.47	6 <i>OC-6</i>			[97] (20432) ^b
O ₉ P ₃ Sc	Sc-O: 2.070-2.077 Sc-P: 3.415-3.512 O-P-O: 118.60 O-Sc-O: 84.46-92.81	6 <i>OC-6</i>			[98] (200309) ^b
O ₄ PSc	Sc-OPO₃: 2.154 Sc-P: 3.592 O-P-O: 101.34-113.68 O-Sc-O: 63.35-92.79	8			[99] (201132) ^b
H ₄ O ₆ PSc	Sc-OPO₃: 2.025-2.063 Sc-OH₂: 2.117-2.181 Sc-P: 3.457 O-P-O: 107.65-111.03 O-Sc-O: 91.26-96.57	6 <i>OC-6</i>			[143] (240988) ^b
O ₉ P ₃ Sc	Sc-O: 2.036-2.108 Sc-P: 3.302-3.507 O-P-O: 116.24-120.09 O-Sc-O: 82.12-98.02	6 <i>OC-6</i>			[102] (420120) ^b
H ₅ O ₉ P ₂ Sc	Sc-O: 2.050(3)-2.132(3) Sc-P: 3.435-3.488 O-P-O: 111.268-112.857 O-Sc-O: 86.675-94.535	6 <i>OC-6</i>		3438, 2375, 2010, 1698, 1125, 1000, 750	[88]

$\text{H}_4\text{O}_6\text{PSc}$	Sc-O: 2.022(7)-2.090 Sc-P: 3.409-3.469 O-P-O: 108.4-110.547 O-Sc-O: 91.113-96.34	6 <i>OC-6</i>			[88]
$\text{C}_{12}\text{H}_{66}\text{N}_6\text{O}_{62}\text{P}_{14}\text{Sc}_8$	Sc-O: 2.023(4)-2.097(5) Sc-P: 3.371-3.446 O-P-O: 108.519-114.113 O-Sc-O: 88.031-97.302	6 <i>OC-6</i>	15 ^d		[87] (CANZOH) ^c
$\text{C}_2\text{H}_{14}\text{N}_2\text{O}_{16}\text{P}_4\text{Sc}_2$			10.3,26.3, -3.0 ^d		[93] ^f (UGIGAS) ^c
$\text{C}_2\text{H}_{14}\text{N}_2\text{O}_{16}\text{P}_4\text{Sc}_2$	Sc-O: 2.0557(14)-2.1448(16) Sc-P: 3.360-3.419 O-P-O: 108.182-113.606 O-Sc-O: 81.341-98.572	6 <i>OC-6</i>			[88] (UGIGAS01) ^c
$\text{C}_8\text{H}_{58}\text{N}_8\text{O}_{42}\text{P}_8\text{Sc}_6$	Sc-O: 2.062(3)-2.109(3) Sc-P: 3.365-3.513 O-P-O: 108.08-112.957 O-Sc-O: 86.25-101.826	6 <i>OC-6</i>			[88] (EQUCOI) ^c

$C_6H_{37}N_6O_{26}P_6Sc_3$	Sc-O: 2.075(5)-2.132(5) Sc-P: 3.366-3.471 O-P-O: 109.544-111.999 O-Sc-O: 86.11-93.11	6 <i>OC-6</i>	35.4, 8.8 (broad) ^d		[87] (CANZIB) ^c
$C_6H_{17}FNO_8P_2Sc$	Sc-O: 2.072(3)-2.099(3) Sc-P: 3.327-3.411 O-P-O: 109.699-112.585 O-Sc-O: 87.495-92.613	6 <i>OC-6</i>	23.8, -15.5 (quadrupolar line shapes) ^d		[87] (CAPBAX) ^c
$C_6H_{22}F_2N_2O_{20}P_4Sc_4$	Sc-O: 2.034(2)-2.120(2) Sc-P: 3.262-3.452 O-P-O: 107.38-110.974 O-Sc-O: 84.738-104.759	6 <i>OC-6</i>	25, 34, 46, 127 ^d		[90] (FIVQIL) ^c
$C_4H_{22}F_6N_4O_8P_2Sc_2$	Sc-O: 2.087(2)-2.1179(17) Sc-P: 3.423-3.469 O-P-O: 107.893-112.006 O-Sc-O: 81.402-91.619	6 <i>OC-6^e</i>			[89] (FAQGIO) ^c

$C_8H_{39}F_4N_4O_{33}P_8Sc_5$	Sc-O: 2.056(8)-2.108(12) Sc-P: 3.351-3.593 O-P-O: 115.405 ^h O-Sc-O: 86.448-95.439 ^h	6 <i>OC-6</i>	10, 0 (broad, overlap) ^d		[87] (CANZUN) ^c
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^aAngles of approximately 180 ° were omitted. ^bICSD CCode. ^cCCDC refcode. ^dsolid state. ^ebased on structure – not assigned by author. ^fduplicate structure of descending row. ^gfor $[Sc(NO_3)_3(bpce)(H_2O)_2]$. ^hdisorder angles omitted.

Table 3. Single Crystal structural data comparison of Sc-L complexes to select Ln-L complexes. (IS) = innerspher, (OS) = outersphere.

ligand	Sc	[REF] (CCode)	La	[REF] (CCode)	Gd	[REF] (CCode)	Lu	[REF] (CCode)
Cl	Monomer 2(IS), 1(OS) 3(OS)	[38] [38] [39] (91460)			Monomer 2(IS), 1(OS)	[104, 105] (300016) (15396)	Monomer 2(IS),1(OS)	[106] (300013)
	OH dimer μ -OH, 2(OS)	[5] [40] (196168) (281125)	Dimer μ -Cl, 2(OS)	[107] (300011)				
	Dimer 4(IS), 2(IS)	[38]						
			Polymer μ -Cl	[109] (75266)	Polymer 2 μ -OH, 1 μ -Cl	[108] (260831)	Polymer 2 μ -OH, 1 μ -Cl	[108] (260838) (260841)
Br	Monomer 3(OS)	[38] [39] (91461)					Monomer 3(OS)	[110] (87630)
	OH dimer μ -OH, 2(OS)	[38, 41, 54, 55] (39839) (172188) (421755)	Dimer μ -Br, 2(OS)	[55, 110] (421754) (87625)				

I	Monomer 3(OS)	[38] [39] (91462)	Monomer 3(OS)	[111] (91454)	Monomer 3(OS)	[111] (91457)	Monomer 3(OS)	[111] (91459)
	OH dimer μ -OH, 2(OS)	[38] [55] (421752)	OH Dimer 2 μ -OH, 1(IS)	[112] (416012)				
			OH Polymer 10 μ -OH, 8(OS) 18 μ -OH, 3(OS)	[113] (419186) [114] (1524)				
NO₃	Monomer 2(IS), 1(OS)	[5] (196170)	Monomer (IS)	[115] (25030)	Monomer (IS)	[116] [117] [118] (71846) (262813) (402753)	Monomer (IS)	[119] (87623) (87624)
	OH Dimer 1(IS), 1(OS)	[5] [82] (196169) (251134)			Polymer OH	[120] (63551)		
SO₄	Polymer <i>Coordinated H₂O</i>	[83] (413609)	Polymer <i>Coordinated H₂O</i>	[123-125] [126] [127] (24707) (68005) (87632) (158301) (411953)	Polymer <i>Coordinated H₂O</i>	[129, 130] (73204) (74829)	Polymer <i>Coordinated H₂O</i>	[124] (87634) (87636)
	Polymer <i>No H₂O</i>	[86] (411221)	Polymer <i>No H₂O</i>	[121] [122] (408962)	Polymer <i>No H₂O</i>	[128] (74818)		

				(420714)				
	Polymer H ₂ O (OS)	[5] (196172)	Polymer H ₂ O (OS)	[131] (2264)				
			Polymer <i>OH</i>	[132] (413562)	Polymer <i>OH</i>	[133] (261284)		
PO₄	Polymer <i>No H₂O</i>	[99] (201132)	Polymer <i>No H₂O</i>	[134] [135] [136] (21066) (79747) (201479)	Polymer <i>No H₂O</i>	[135] [137] (79753) (201841)	Polymer <i>No H₂O</i>	[135] [99] [138] (2505) (79761) (201133)
	ScO₉P₃ Polymer <i>No H₂O</i>	[96] [102] (20430) (420120)	LaO₉P₃ Polymer <i>No H₂O</i>	[139] (202640)	GdO₉P₃ Polymer <i>No H₂O</i>	[140] [141] (155301) (416843)	LuO₉P₃ Polymer <i>No H₂O</i>	[142] [141] (162217) (416842)
	Sc₂H₂₀O₂₀P₅ Polymer <i>No H₂O</i>	[5] (196171)	La₃O₁₀P₃ Polymer <i>No H₂O</i>	[148] (31564)	GdO₁₄P₅ Polymer <i>No H₂O</i>	[149] [150] [151] (84236) (156410) (411262)	LuO₁₄P₅ Polymer <i>No H₂O</i>	[152] (241229)
	Sc₃H₂₀O₄₀P₁₀ Polymer <i>No H₂O</i>	[97] (20432)	La₂H₁₀O₂₀P₅ Polymer <i>Coordinated H₂O</i>	[144] (240963)	GdH₇O₁₀P₂ Polymer <i>Coordinated & (OS) H₂O</i>	[145] (51412)	Lu₁₃O₁₂₀P₄₀ Polymer <i>No H₂O</i>	[153] (260036)
	Sc₃O₃₀P₁₀ Polymer <i>No H₂O</i>	[95] [98] (1719) (200309)			GdH₉O₁₀P₂ Polymer <i>Coordinated H₂O</i>	[146] (65514)		

	ScH₄O₆P Polymer <i>Coordinated H₂O</i>	[88] [143] (240988)			GdH₉O₁₁P₂ Polymer <i>Coordinated H₂O</i>	[147] (153521)		
	Polymer H ₃ O ⁺ (OS)	[88]						

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Figure 4. Structure plot of $[\text{ScCl}_4(\text{H}_2\text{O})_2][\text{ScCl}_2(\text{H}_2\text{O})_4]$. [38]

Figure 5. Structure plot of $[\text{ScCl}_3(\text{THF})_3]$ (CCDC 1131918).

Figure 6. Structure plot of $[\text{ScCl}_3(\text{H}_2\text{O})_3 \cdot (\text{Cl})](1,4,10,13\text{-tetraoxa-7,16-diazoniumcyclo-octadecane})$ (CCDC 248348).

Figure 7. Structure plot of $[\text{ScBr}_3(\text{THF})_3]$ (CCDC 730384).

Figure 8. Structure plot of complexation of $[(\kappa^4\text{-}(O,N,N',O')6,6'\text{-bis}(2,2\text{-dimethylpropan-1-ol}))\text{ScBr}_2\text{H}_2\text{O}](\text{Br})(\text{H}_2\text{O})$ (CCDC 253182).

Figure 10. Structure plot of complexation $[\text{Sc}(\text{DMSO})_6]3(\text{I})$ (CCDC 249315).

Figure 11. Structure plot of $[\text{ScI}_2([\text{18}] \text{aneO}_4\text{S}_2)](\text{I})\text{MeCN}$ (CCDC 940228).

Figure 12. Structure plot of $[(\text{H}_2\text{O})_4\text{Sc}(\kappa^2\text{-NO}_3)_2](\text{NO}_3)\cdot(\text{H}_2\text{O})$ (CCode 196170). There are two molecules per unit cell.

Figure 13. Structure plot of $[\text{Sc}(k^2\text{-NO}_3)_2(\text{urea})_4]\text{NO}_3$ (CCDC 1278542).

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Figure 14.
Structure plot
 $[(\text{H}_2\text{O})_3\text{Sc}(k^2\text{-O}_3)_3](18\text{-crown-6})$
25).

Figure 15. Structure plot of diaqua(2,6-diacetylpyridine, bis(semicarbazone) scandium cation (CCDC 1100980). Reprinted from [78] with permission from Elsevier.

Figure 16. Structure plot of Scandium 4,4'-bipyridine-N,N'-dioxide nitrate complex (CCDC 241335).

Figure 17. Structure plot of $[(\text{H}_2\text{O})_3\text{Sc}(\kappa^2\text{-NO}_3)(\mu\text{-OH})]_24(\text{NO}_3)$ (CCode 196169).

Figure 18. Structure plot of $[(\text{phen})(k^2\text{-NO}_3)_2\text{Sc}(\mu\text{-OMe})]_2$ (CCDC 675741).

Figure 19. Structure plot of $(\text{H})[\text{Sc}(\mu_3\text{-SO}_4)_2]2(\text{H}_2\text{O})$ (CCode 196172).

Figure 20. Structure plot of (EDA)[Sc(μ_3 -SO₄)₃] 3(H₂O) (CCDC 227969).

Figure 21. Structure plot of $[\text{Sc}(\mu\text{-PO}_4)_6 15\cdot\text{H}]_n$ (CCode 196171).

Figure 22. Structure plot of $(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3[(\text{Sc}(\text{OH}_2))_6\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$ (CCDC 261858).

Figure 23. Structure plot of $(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3[\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ (CCDC 1278162).

Figure 24. Structure plot of $(\text{C}_6\text{H}_{14}\text{N}_2)\text{Sc}_4\text{F}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ (CCDC 266503). Disorder in triethylenediamine is presented.

Figure 25. Structure plot of $(\text{C}_6\text{H}_{11}\text{NH}_3)[\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$ (CCDC 261859).

Graphical abstract

The structural properties of reported inorganic scandium (Sc) salts were reviewed, including the (a) halides, (b) nitrate, (c) sulfate, and (d) phosphate salts. Examples shown.