Tris{2,4-bis(2-pyridyl)-1,3,5-triazapentanedienato}manganese(III), a complex derived from a unique metal ion-assisted transformation of pyridine-2-amidoxime

Vasilios Duros^a, Harikleia Sartzi^{a,b1}, Simon J. Teat^c, Yiannis Sanakis^{d,*}, Olivier Roubeau^{e,*}, Spyros P. Perlepes^{a,f,*}

^a Department of Chemistry, University of Patras, 26504 Patras, Greece

^b WestCHEM, Department of Chemistry, The University of Glasgow, C12 8QQ Glasgow, UK

^c Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

^d Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, NCSR "Demokritos", 15310 Aghia Paraskevi Attikis, Greece

^e Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, Facultad de Ciencias, Plaza San Francisco, s/n, Zaragoza 50009, Spain

^f Institute of Chemical Engineering Sciences, Foundation for Research and Technology-Hellas (FORTH/ICE-HT), Platani, P.O. Box 1414, 26504 Patras, Greece

* Corresponding authors: Tel.: +30 210 6503345 (Y.Sanakis); +34 976 762461 (O.Roubeau); +30 2610 996730 (S.P.Perlepes).

E-mail addresses: sanakis@ims.demokritos.gr (Y. Sanakis); roubeau@unizar.es (O. Roubeau); perlepes@patras.upatras.gr (S.P.Perlepes).

¹ Present address.

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ABSTRACT

A novel metal ion-mediated reaction of pyridine-2-amidoxime has led to an 1:3 mononuclear Mn(III) complex containing the 2,4-bis(2-pyridyl)-1,3,5-triazapentanedienate(-1) ligand; the high-spin Mn^{III} in the complex is “EPR silent” at X-band.

Upon coordination of a ligand (L) to a metal center (M), the former's properties (acidity, electrophilic or nucleophilic character, susceptibility to reduction or oxidation, etc.) can be significantly altered and therefore its reactivity can be enhanced or inhibited; coordination to M can even enable a reaction that would otherwise not take place. Thus the reactivity chemistry of coordinated ligands is a “hot” research theme in contemporary transition-metal chemistry [1]. Oxime (C=N–OH) and oximate (C=N–O[−]) groups can bind an M in a variety of coordination modes and are thus ideal candidates for reactivity chemistry [2]. Nucleophilic reagents can add to the C-atom (a reaction that is promoted by coordination of the N-atom), whereas electrophilic reagents can attack the O[−] or the N-sites [2].

Scheme 1. Structural formulae and abbreviations of the ligands discussed in the text. The initially used ligand is pyridine-2-amidoxime, (py)C(NH₂)NOH, and the anionic ligand present in the Mn(III) complex is 2,4-bis(2-pyridyl)-1,3,5-triazapentanedienate(-1), bptzpd[−]; py is the general abbreviation for the 2-pyridyl moiety.

Our groups have a long-standing interest in the reactivity chemistry of coordinated organic ligands [3] and especially in metal-mediated reactions of 2-pyridyl oximes (Scheme 1, left), (py)C(R)NOH [4]. Pyridine-2-amidoxime (IUPAC name: *N*-hydroxy-pyridine-2-carboxamidine, (py)C(NH₂)NOH; R=NH₂ in Scheme 1) occupies a special position amongst the 2-pyridyl oximes [5] because the amine functionality can (i) coordinate to a metal centre, (ii) be deprotonated favouring various bridging behaviours and cluster formation, and (iii) form H-bonds leading to interesting supramolecular architectures. However, its metal-assisted reactivity remains totally unexplored. In the present work, we report a reaction of (py)C(NH₂)NOH with a Mn(II) source that leads to a Mn(III) complex in which a novel transformation of the ligand has been observed.

The reaction of MnF₂, (py)C(NH₂)NOH and LiOH in an 1:2:2 molar ratio in MeCN/DMSO at room temperature gave a dark brown (indicative of Mn^{II} oxidation) solution that upon slow evaporation gave dark red (essential black) crystals of

$[\text{Mn}^{\text{III}}(\text{btpzpd})_3] \cdot 0.5\text{MeCN}$ (**1**·0.5MeCN), where btpzpd^- is the monoanion of 2,4-bis(2-pyridyl)-1,3,5-triazapentanediene (Scheme 1, right), in 55% yield [6]. We have not noticed the formation of any other product from this reaction system. A high $(\text{py})\text{C}(\text{NH}_2)\text{NOH}:\text{MnF}_2$ molar ratio (e.g. 3:1 or 4:1) increases only slightly the yield (up to 60%). The same reaction in a concentrated MeOH solution in the presence of NEt_3 , i.e., in the absence of MeCN, gives the same product in a powdered form, upon slow evaporation at room temperature over a period of 3 months in a lower (~20%) yield. Excluding MnF_2 from the above reaction mixtures in, at least, 50 experiments, we have obtained no evidence (IR, ^1H NMR) for the formation of Hbtpzpd or its lithium “salt”, $\text{Li}(\text{btpzpd})$. The difference between “blind” and metal-mediated conditions leads us to believe that the $(\text{py})\text{C}(\text{NH}_2)\text{NOH} \rightarrow \text{btpzpd}^-$ transformation is metal ion-assisted. Remarkably, two $\text{Cu}(\text{II})/\text{btpzpd}^-$ complexes [7], namely $\{[\text{Cu}_3(\text{O}_2\text{CMe})_2(\text{btpzpd})_2](\text{ClO}_4)_2\}_n$ and $[\text{Cu}(\text{btpzpd})_2]$, and the $\text{Pd}(\text{II})$ compound $[\text{Pd}(\text{btpzpd})_2]$ [8] have been prepared and structurally characterized. Scheme 2 illustrates the three metal ion-assisted transformations (including the one that gave **1**) that have led to the formation of coordinated btpzpd^- . It is clear that complexes containing the btpzpd^- ligand have been synthesized by three different metal ion-assisted (promoted) transformations.

A detailed mechanistic description for the observed $(\text{py})\text{C}(\text{NH}_2)\text{NOH} \rightarrow \text{btpzpd}^-$ transformation is not yet possible. It is noteworthy to indicate that it does not proceed in the absence of the Mn salt, thus showing the essential role of the Mn ion (most probably Mn^{III} or Mn^{IV}). Also, the transformation does not require MeCN and thus it is not based on the nucleophilic addition of the oxime to the nitrile [9]. Suffice it to propose that the transformation involves metal-ion assisted nucleophilic attack of $(\text{py})\text{C}(\text{NH}_2)\text{NOH}$ [or better of $(\text{py})\text{C}(\text{NH})\text{NOH}$] to another $(\text{py})\text{C}(\text{NH}_2)\text{NOH}$ molecule, followed by NH_3 elimination and a series of steps that lead to the deprotonated, coordinated 2,4-bis(2-pyridyl)-imidoylamidine (btpzpd^-). It should be mentioned at this point that no definite mechanism has been proposed for the two other transformations that lead to the btpzpd^- ligand [7, 8].

Complex **1**·0.5MeCN crystallizes in the trigonal space group $R\bar{3}$ [10]. Its structure consists of well-separated $[\text{Mn}^{\text{III}}(\text{btpzpd})_3]$ molecules and lattice MeCN molecules. The Mn^{III} atom, which sits on a 3-fold axis of symmetry, is coordinated by three N,N'-bidentate chelating (or 1.11000 using Harris notation) btpzpd^- ligands (Scheme 2, top); the btpzpd^- donor atoms are the nitrogen atoms of the 1 and 5 positions of the triazapentanedienate backbone (N1 and N2), each of which possessing a H atom (the H atoms on N1 and N2 were found in difference Fourier maps). A clear Jahn-Teller distortion, expected for a high-spin $3d^4$ $\text{Mn}(\text{III})$ system, is not observed in **1**·0.5MeCN, because the metal is found at a position of high symmetry [11]. The metal coordination geometry is well described as moderately distorted octahedral. The complex is a racemic mixture of its Δ and Λ enantiomers of the chiral neutral compound by virtue of the (centrosymmetric) space group operations. All six atoms (Mn1, N1, C1, N3, C2, N2) of the chelating ring are nearly coplanar within 0.07(2) Å; the 2-pyridyl arms are twisted by 6.58° (the N4-containing ring) and 7.59° (the N5-containing ring) from this plane. The 2-pyridyl rings of a given btpzpd^- ligand form an angle of 1.299(3)°. The C1-N1, C1-N3, C2-N3 and C2-N2 distances are in the range 1.239(10)-1.338(9) Å (the mean distance is 1.296(10) Å), supporting delocalization throughout the NCNCN π -skeletal system [8, 9, 12]. The corresponding ranges in complexes $[\text{Pd}(\text{btpzpd})_2]$ [8] and $[\text{GaMe}_2\{\text{HNC}(\text{CF}_3)\text{NH}\}]$ [12] are 1.301-1.350 and 1.274-1.354 Å, respectively.

Scheme 2. Metal ion-assisted transformations of different organic ligands that lead to complexes containing the coordinated 2,4-bis(2-pyridyl)-1,3,5-triazapentanedienate(-1) ion (bptzpd⁻); the coordination modes of bptzpd⁻ in the resultant metal complexes are also shown. Reaction conditions and references: (i) MnF₂, LiOH, MeCN/DMSO, 20°C [this work]; (ii) [Cu₂(O₂CMe)₄(H₂O)₂]/NaClO₄, dry MeOH, reflux [9]; (iii) Na₄EDTA, H₂O/CHCl₃, 20°C [9]; (iv) PdCl₂/(Me)(Et)C=NOH, *n*-PrNH₂, MeOH/CHCl₃, 100°C [8].

The short Mn1-N bond lengths [1.913(6), 1.936(6) Å] are similar to those reported for the few, structurally characterized low-spin Mn(III) [t_{2g}⁴] complexes possessing six N donor atoms [13]. For example, the mean Mn^{III}-N bond lengths in the low-spin complexes [Mn^{III}(pzTp)₂](SbF₆), [Mn^{III}(Tp)₂](SbF₆) and [Mn^{III}(Tp*)₂](SbF₆) are 1.974(4), 1.984(5) and 1.996(4) Å, respectively, [13a]; pzTp⁻, Tp⁻ and Tp*⁻ are the tridentate chelating ligands tetrakis(pyrazolyl)borate(-1), hydrotris(pyrazolyl)borate(-1) and hydrotris(3,5-dimethylpyrazolyl)borate(-1), respectively. This raises the possibility that compound **1** is a low-spin Mn(III) complex at 100 K, the temperature at which the crystal structure was solved.

The crystal structure of the complex is stabilized through intermolecular π - π stacking interactions (Fig. 2), which form a 3D lattice in the crystal. The π interaction is an offset or slipped stacking, i.e. the rings are parallel displaced.

Complex **1** is only the fourth structurally characterized complex of bptzpd[−] with any metal [7, 8] and the first with Mn; as illustrated in Scheme 2, all four complexes have been prepared by metal ion-assisted transformations of three different organic ligands. The free Hbptzpd compound is not known in organic chemistry.

The room-temperature effective magnetic moment (μ_{eff}) of **1** is 4.99 B.M., in agreement with its high-spin character ($S=2$) **at room temperature**.

Fig. 1. Partially labeled plot of the molecule that is present in the structure of **1**·0.5MeCN. Most H atoms have been omitted for clarity. Only one of the two enantiomers that are present in the crystal is shown. Selected bond lengths (Å) and angles (°): Mn1–N1 1.936(6), Mn1–N2 1.913(6), C1–N1 1.320(9), C1–N3 1.338(9), C2–N3 1.286(10), C2–N2 1.239(10); N1–Mn1–N2 85.1(3), N1–Mn1–N1' 93.3(2), N1–Mn1–N2'' 93.2(3), N2–Mn1–N2' 88.5(3), N1–Mn1–N2' 173.4(3), N1–C1–N3 127.2(7), C1–N3–C2 122.2(7), N2–C2–N3 124.1(8). Symmetry codes: (') 1-*y*, *x*-*y*, *z*; (') 1-*x*+*y*, 1-*x*, *z*.

Fig. 2. Stacking interactions present in the crystal of **1**. Only two molecules are shown; these interactions form a 3D architecture. Ring A is the N5C8C12C11C10C9 ring and ring B the N4C3C7C6C5C4 one. Metric parameters: Centroid-centroid distance 3.616(6) Å, displacement angle (angle between the ring normal of the pyridyl plane and the centroid vector) 19.08°, slippage 2.13 Å (i.e. a shift of ca. 1.5 C-C bond length from the face-to-face perfect alignment), plane-plane distance 3.418(5) Å. Symmetry codes: (A and B) $-1/3+y, 1/3-x+y, 4/3-z$; (A' and B') $1-y, x-y, z$.

Fig. 3. Dual mode X-band EPR spectra of a powdered sample of complex **1**. EPR conditions: T , 4.2 K; microwave power, 20 mW; modulation amplitude, 10 G_{pp}; microwave frequency, 9.60 GHz (perpendicular mode), 9.33 GHz (parallel mode).

X-band EPR spectra of a powdered sample of **1** at 4.2 K recorded in parallel or perpendicular modes are shown in Fig. 3. Similar signals were observed in a frozen CH₂Cl₂ solution of the complex. The perpendicular mode spectrum gives rise to signals (labeled 1 and 2) in two regions of the magnetic field. No signals are observed in the parallel mode spectrum. The behaviour of the EPR signals suggests half-integer spin minor species (Mn(IV), $S=3/2$; Mn(II), $S=5/2$), arising from low-concentration impurities. Spectra recorded at higher temperatures do not reveal any new signals attributable to Mn(III) ($S=2$) species. High-spin Mn(III) complexes are characterized by relatively large zero-field splitting with $|D| > 0.5 \text{ cm}^{-1}$ [14]. Low-spin Mn(III) complexes are extremely rare and the relevant EPR literature is very limited; in one case extremely large zero-field splitting values were reported [13c]. For integer spin systems with large $|D|$, EPR signals at X-band from the non-Kramers doublets of the system can be observed for appropriate values of the rhombic (E/D) and higher order zero-field splitting terms [15]. Most importantly, such signals are enhanced when the EPR experiment is carried out in parallel mode [15]. Indeed, several mononuclear high-spin Mn(III) complexes ($S=2$) have been shown to exhibit characteristic dual mode X-band EPR signals [16]. To the best of our knowledge no dual mode X-band EPR studies for low-spin Mn(III) complexes ($S=1$) have been reported so far. In any case, the data for **1** indicate that the Mn^{III} ion is “EPR silent” at X-band due to unfavorable values of zero-field parameters (E/D and/or higher order terms). This may occur in two distinct cases [15]. In a strict axial symmetry ($E/D=0$) and for negligible higher order terms, the *intra*-doublet transitions (possessing $\Delta M_S \neq \pm 1$ character) are strictly forbidden. Alternatively, for relatively large E/D values and/or significant higher order terms, the separation of the non-Kramers states is larger than the microwave energy at X-band and the resonant condition cannot be fulfilled. At present we cannot exclude either possibility. High Field-High Frequency EPR spectroscopic studies are required in order to determine the electronic properties of a Mn^{III} ion in such cases [13c, 16a].

In summary, the use of pyridine-2-amidoxime in a reaction with MnF₂ has led to a novel transformation of this oxime ligand, showing that metal-mediated reactions of 2-pyridyl oximes are still in their infancy; indeed, ongoing studies in our groups reveal that we have scratched only the surface of this research area. Current efforts involve the deeper elucidation of the (py)C(NH₂)NOH $\rightarrow$ bptzpd⁻ transformation (including the investigation of the role of F⁻ ions in the transformation), the determination of the room temperature, single-crystal structure of **1** (to probably “see” the high-spin form of the complex, if the present structure represents the low-spin form), the variable-temperature magnetic study of **1** (to probably reveal a spin-crossover behaviour) and the synthesis of other 3d-metal/ bptzpd⁻ complexes starting from (py)C(NH₂)NOH.

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Appendix A. Supplementary data

CCDC-1017311 contains the supplementary crystallographic data for **1**·0.5MeCN. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche/>.

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quantity of MnO₂ and the dark brown filtrate was allowed to slowly concentrate by solvent evaporation at room temperature for a period of one month. Well-formed, essentially black prismatic crystals of the product appeared which were collected by filtration, washed with Et₂O (2×1 mL) and dried in air. Typical yields were in the 50-60% range. The air-dried solid was analyzed as solvent-free, **1**. *Anal.* Calc. for C₃₆H₃₀MnN₁₅ (**1**): C, 59.41; H, 4.16; N, 28.88. Found: C, 59.71; H, 4.09; N, 29.13%. Representative IR bands (KBr, cm⁻¹): 3285mb [$\nu(\text{NH})$], 1595s [$\nu(\text{C}^{\equiv\equiv\text{N}}$)], 645s [$\delta(\text{py})$], 427m [$\gamma(\text{py})$].

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GRAPHICAL ABSTRACT

A novel manganese-assisted transformation of pyridine-2-amidoxime has been observed, leading to a mononuclear octahedral Mn(III) complex containing the 2,4-bis(2-pyridyl)-1,3,5-triazapentanedienate(-1) ligand.