Amine-imine compounds of nickel(II) and copper(II) incorporating 1,2-ethanediamine and 1,3-propanediamine

Neil F. Curtis^a, Olga P. Gladkikh^a, Ward T. Robinson^b, Raymond J. Butcher^c

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Nickel(II) compound

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Crystal structures

[(2,8,8,10-tetramethyl-3,7,11-triazatridec-2,10-diene-13-amine)nickel(II)]

[(15-amino-4,4,9,9,11-pentamethyl-5,8,12-triazatetradec-11-ene-2-one)copper(II)]

Abstract

Reaction with acetone of $[M(en)(tmd)](ClO_4)_2$ (en = 1,2-ethanediamine, tmd = 1,3-propanediamine) for $M = Ni(II)$ forms 7*RS*-(2,8,8,10-tetramethyl-3,7,11-trimethyltridec-2,10-diene-13-amine)nickel(II) perchlorate with square-planar Ni(II). For $M = Cu(II)$ the reaction forms 5*RS*,8*RS*-(15-amino-4,4,9,9,11-pentamethyl-5,8,12-tetraazapentadec-11-ene-2-one)copper(II) perchlorate 0.33 water with a N_4O pentadentate ligand. The structures of these products are reported.

1. Introduction

A variety of compounds are formed by reactions of nickel(II) and copper(II) amine compounds with acetone [1]. Reaction of a coordinated primary amine group with acetone initially forms a coordinated N-isopropylidene imine function, $M-N=C(CH_3)_2$, im. These are usually readily hydrolysed, so compounds with these functions are seldom isolated. The coordinated imine group can undergo an aldol-like reaction with a second acetone molecule to form a coordinated β -amino ketone function, $M-NH-C(CH_3)_2-CH_2-(C=O)-CH_3$, β ak, which can be stabilized by coordination of the ketone oxygen. The ketone function can undergo an imine forming reaction with a suitably placed coordinated primary amine group, which then links the two amine groups by a β -amine imine bridge, $-NH-C(CH_3)_2-CH_2-(C=N)-(CH_3)$, β aib. Formation of two such links leads to formation of a diamine-dimine macrocycle.

Fig. 1. Showing species formed by reaction of nickel(II) and copper(II) bis(1,2-ethanediamine) compounds with acetone. Labels used for compounds described in this communication combine a label for the diamine (1,2-ethanediamine = en and 1,3-propanediamine = tmd) and derived functions, as e.g. en-im for an N-isopropylidene group formed by en, en- β ak for a β -amino ketone group formed by en, en_2 - β aib for two en residues linked by a β -amine imine group and en_2 - β aib-im for a tetradentate ligand with two en groups linked by a β -amine imine group, with an N-isopropylidene function.

1.1. Reactions of (1,2-ethanediamine)nickel(II) compounds with acetone

The reaction of $[\text{Ni}(\text{en})_2](\text{ClO}_4)_2$ with acetone forms the bis(β -amino ketone) compound $[\text{Ni}(\text{en-}\beta\text{ak})_2](\text{ClO}_4)_2$, see Fig. 1 [2,3]. This is stable as the solid, and in solvents such as acetone or acetonitrile. At higher temperatures, as in refluxing methanol or the original report of the reaction [4], $[\text{Ni}(\text{en-}\beta\text{aib-im})](\text{ClO}_4)_2$ is formed. One β -amino ketone function has reacted with a primary amine group to form a βaib link, and the other has been partially hydrolysed to leave an N-isopropylidene imine group, leading to a cation with a tetradentate ligand, with a β -amine imine bridge and an imine group. The structure of $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]\text{ZnCl}_4\cdot\text{H}_2\text{O}$ has been reported [3]. The unsupported imine function of this cation is relatively resistant to hydrolysis, only slowly hydrolysing in boiling water to form $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib})]^{2+}$. In pyridine both ketone functions of $[\text{Ni}(\text{en-}\beta\text{ak})_2]^{2+}$ react with the adjacent primary amine groups to form the diamine-diimine macrocyclic ligand cation, $[\text{Ni}(\text{Me}_6[14]\text{trans-diene})]^{2+}$ [1,2].

The reaction of $[\text{Ni}(\text{en})_3]^{2+}$ with acetone ultimately forms the macrocycle cations $[\text{Ni}(\text{Me}_6[14]\text{cis-diene})]^{2+}$ and $[\text{Ni}(\text{Me}_6[14]\text{trans-diene})]^{2+}$ [5], though $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]^{2+}$, then $[\text{Ni}(\text{en}_2\text{-aib})]^{2+}$, can be isolated from early stages of the reaction [3]. $[\text{Ni}(\text{en}_2)(\text{NCS})_2]$ reacts with acetone to form $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})(\text{NCS})_2]$. Both $[\text{Ni}(\text{en})_3]\text{ZnCl}_4$ and $[\text{Ni}(\text{en})_2]\text{ZnCl}_4$ react with acetone to form $[\text{Ni}(\text{en-}\beta\text{aib})]\text{ZnCl}_4$ [3].

1.2. Reactions of (1,2-ethanediamine)copper(II) compounds with acetone

The reaction of $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ with acetone forms $[\text{Cu}(\text{en}_2\text{-}\beta\text{aib-}\beta\text{ak})](\text{ClO}_4)_2$ see Fig. 1 [2], structurally characterized as an acetonitrile solvate [6]. The kinetics of the base catalysed reaction of this to form $[\text{Cu}(\text{Me}_6[14]\text{trans-diene})]^{2+}$ have been reported [6]. It appears that copper(II) stabilizes by coordination of only one β -amino ketone group of initially formed $[\text{Cu}(\text{en-}\beta\text{ak})_2]^{2+}$, the other forming a $\beta\text{-aib}$ link, so the product has a pentadentate ligand with one coordinated β -amino ketone group and an β -amine-imine bridge.

Continued reaction of $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ with acetone ultimately forms $[\text{Cu}(\text{Me}_6[14]\text{trans-diene})]^{2+}$ [1,7]. Reaction of $[\text{Cu}(\text{en})_3](\text{ClO}_4)_2$ with acetone ultimately forms $[\text{Cu}(\text{Me}_6[14]\text{trans-diene})]^{2+}$ and $[\text{Cu}(\text{Me}_6[14]\text{cis-diene})]^{2+}$ [2].

1.3. Reactions of 1,3-propanediamine compounds of nickel(II) and copper(II) with acetone

Both $[\text{Ni}(\text{tmd})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{tmd})_2](\text{ClO}_4)_2$ react rapidly with acetone to form sparingly soluble bis(N-isopropylidene imine) compounds $[\text{M}(\text{tmd-im})_2](\text{ClO}_4)_2$ [8]. The structure of $[\text{Cu}(\text{tmd-im})_2(\text{OCIO}_3)]\text{ClO}_4$ has been reported [9]. Reaction continues slowly to form the macrocyclic ligand compounds $[\text{Ni}(\text{Me}_6[16]\text{trans-diene})](\text{ClO}_4)_2$ for nickel(II) [10,11]

and [Cu(Me₆[16]*trans*-diene)](ClO₄)₂ and [Cu(Me₆[16]*cis*-diene)](ClO₄)₂ for copper(II) [12], together with dark, tarry polymeric material.

Rapid reactions of [Ni(tmd)₂L₂] with acetone forms sparingly soluble yellow [Ni(tmd-im)₂]Br₂ and blue Ni(tmd-im)₂(NCS)₂ and more soluble blue [Ni(tmd-im)₂]Cl₂ and [Ni(tmd-im)₂](ONO₂)₂ [8]. The reaction for the nitrate continues to form a yellow product which was formulated as [Ni(tmd₂-βaib-im)(ONO₂)]NO₃ [8].

1.4. Reactions of nickel(II) compounds of 1,2-ethanediamine and 1,3-propanediamine with acetone

Reaction of an equimolar mixture of [Ni(en)₃](ClO₄)₂ and [Ni(tmd)₃](ClO₄)₂ with acetone over a period of days at ambient temperatures forms as the major product the macrocyclic ligand compound [(5,7,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadec-4,12-diene)nickel(II)] perchlorate, [Ni(Me₆[15]*trans*-diene)](ClO₄)₂ [14,15].

2. Results

2.1. [(2,8,8,10-Tetramethyl-3,7,11-triazatridec-2,10-diene-13-amino)nickel(II)] perchlorate, [Ni(entmd-βaib-im)](ClO₄)₂

Reaction of [Ni(en)(tmd)](ClO₄)₂ with acetone initially forms sparingly soluble yellow [Ni(tmd-im)₂](ClO₄)₂. Continued reaction forms an orange coloured compound, which is stable in aqueous solution, though the ligand is slowly hydrolysed in boiling water. This product has bands in the IR characteristic of amine (ν(NH, NH₂): 3306, 3252, 3202; δ(NH₂): 1593 and imine functions: ν(C=N): 1667, 1651 cm⁻¹), and analysis supports formulation as [Ni(entmd-βaib-im)](ClO₄)₂, with en and tmd residues linked by the six-membered β-amine-imine bridge formed from two acetone molecules, and with an N-isopropylidene imine group. Several structures are possible, depending on the orientation of the amine-imine bridge and the location of the N-isopropylidene imine function. Crystallographic structure determination showed the product to be 7*RS*-[(2,8,8,10-tetramethyl-3,7,11-triazatridec-2,10-diene-13-amino)nickel(II)] perchlorate, [Ni(entmd-βaib-im)](ClO₄)₂.

The asymmetric unit contains one square-planar nickel(II) cation with the tetradentate ligand 2,8,8,10-trimethyl-3,7,11-triazatridec-2,10-diene-13-amine, with primary (N4) and secondary (N7 with *R* chirality) amine and two *trans* imine (N3 and N11) donor groups with two perchlorate ions. The cation is shown in Fig. 2 and selected dimensions in Table 1.

110

111 **Fig. 2.** The cation of $[\text{Ni}(\text{entmd-}\beta\text{aib-im})](\text{ClO}_4)_2$, drawn [15] with displacement
 112 ellipsoids at the 50% confidence level, with H-N atoms shown as circles with arbitrary radius.

113 The N_4 group is tetrahedrally twisted ($\pm 0.124(1)$ Å, with displacements (Å) of atoms
 114 from the $\text{Ni1}, \text{N3}, \text{N7}, \text{N11}$ best plane: Ni1 , $-0.059(2)$; N3 , $0.123(2)$; N7 , $-0.122(2)$; N11 ,
 115 $0.124(2)$; N14 , $-0.125(2)$, C21 , $-1.95(5)$; C5 , $2.064(4)$.; C82 , $-2.252(5)$.

116 The three chelate rings present are asymmetrical, and best described as:
 117 $\text{N1} \cdots \text{Ni1} \cdots \text{N3}$, gauche; $\text{N3} \cdots \text{Ni1} \cdots \text{N7}$, twist and $\text{N7} \cdots \text{Ni1} \cdots \text{N11}$, steeply folded boat.
 118 Displacements (Å) of atoms from their respective NiN_2 chelate planes are: plane $\text{Ni1}, \text{N3}, \text{N7}$;
 119 C4 , $1.201(5)$; C5 , $2.052(5)$; C6 , $1.333(5)$; plane $\text{Ni1}, \text{N7}, \text{N11}$; C8 , $-0.797(6)$; C81 , $-0.782(8)$; C82 , -
 120 $2.27(5)$; C9 , $-0.211(6)$; C10 , $-0.037(5)$; C101 , $0.140(7)$; plane $\text{Ni1}, \text{N11}, \text{N14}$; C12 , $0.264(5)$;
 121 C13 , $0.758(5)$.

122 The six atoms of each of the imine functions are relatively co-planar, with mean
 123 displacement of atoms C2 , N3 , Ni1 , C4 , C1 and C21 from their best plane of $0.027(2)$ Å, with
 124 this plane inclined at $68.5(1)^\circ$ to the N_4 donor-atom best plane. Analogous values for the C10 ,
 125 N11 , Ni1 , C12 , C9 and C101 imine group are $\pm 0.027(3)$, $0.023(2)$ Å and $10.9(2)^\circ$.

126 Both sides of the NiN_4 plane are shielded, with the axially oriented $(\text{C62})\text{H}_3$ and
 127 $(\text{C121})\text{H}_3$ methyl groups on one side and the $(\text{C9})\text{H}_2$ methylene group of the boat
 128 conformation $\text{N7} \cdots \text{Ni1} \cdots \text{N11}$ chelate ring on the other side with $\text{Ni1} \cdots \text{C9} = 3.295(3)$ Å.

The cation is similar to $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]^{2+}$ [3], except that the β -amine imine bridge is relatively reversed, so the imine donor groups are *cis* for $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]^{2+}$, *trans* for $[\text{Ni}(\text{entmd-}\beta\text{aib-im})]^{2+}$. The $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]^{2+}$ cation is less twisted (mean displacements from the N3,N7,N11,N14 plane $\pm 0.065(5)$ Å) with Ni 0.054(5) Å from this plane.

Table 1. Selected dimensions (Å, °) for $\text{Ni}(\text{entmd-}\beta\text{aib-im})(\text{ClO}_4)_2$

Atoms	Dimension/Å	Atoms	Dimension/°
Ni1-N1	1.914(3)	N1-Ni1-N3	84.9(1)
Ni1-N3	1.909(3) (im)	N1-Ni1-N7	176.1(1)
Ni1-N7	1.915(3)	N1-Ni1-N11	94.0(1)
Ni1-N11	1.914(3) (im)	N3-Ni1-N7	95.5(1)
N3-C4	1.279(4)	N3-Ni1-N11	168.9(1)
N11-C12	1.277(5)	N7-Ni1-N11	86.4(1)

2.2. 5*RS*,8*RS*-[(14-Amino-4,4,9,9,11-pentamethyl-5,8,12-triazatetradec-11-ene-2-one)copper(II)] perchlorate·0.33 water, $[\text{Cu}(\text{entmd-}\beta\text{aib-}\beta\text{ak})](\text{ClO}_4)_2 \cdot 0.33\text{H}_2\text{O}$

Equimolar proportions of $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ and $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2$ were reacted with acetone and methanol, as for the nickel(II) compound. A precipitate of $\text{Cu}(\text{tmd-im})_2(\text{ClO}_4)_2$ formed and slowly redissolved. Evaporation of the resulting solution produced a blue oil. One preparation left standing under ethanol for a prolonged period deposited blue crystals, for which the structure was determined.

Fig. 3. The cation of $[\text{Cu}(\text{entmd-}\beta\text{aib-}\beta\text{ak})](\text{ClO}_4)_2 \cdot 0.33\text{H}_2\text{O}$, drawn [15] as for Fig. 2, but with displacement ellipsoids at 30% probability.

The asymmetric unit contains a Cu(II) cation with a pentadentate ligand with a coordinated primary amine (N16), two secondary amine (N5 and N8, both with *R* chirality), an imine (N12) nitrogen and a ketone oxygen (O2) donor atoms, with two perchlorate ions. A persistent residual peak was assigned as water oxygen O1 with refined s.o.f. of 0.32(3) which was fixed at 0.333 for the final refinement. The hydrogen atoms of the water were located from difference syntheses in positions appropriate for hydrogen bonding. The cation is shown in in Fig. 3 and selected dimensions in Table 2.

The terminal primary amine nitrogen atom N16, with a large a.d.p. was split into components N16a and N16b, with refined complementary s.o.f.s of 0.41(3), 0.59(3). The geometry about Cu1, including site N16b, is best considered as square pyramidal, with O2 axial, with the basal square of N5, N8, N12 and N16b tetrahedrally twisted ($\pm 0.28(1)$ Å), with Cu1 0.14(1) Å from this plane). The four basal Cu-N distances range from 1.98(1) – 2.06(1) Å and the O-Cu-N angles from 85.2(7) – 104.6(6)°. The geometry including site N16a is better considered as trigonal bipyramidal, with O2, N8, N1b equatorial and N5 and N12 axial (N5-Cu1-N12 = 171°) and O2-Cu1-N8 = 104; O2-Cu1-N16a = 129 and N8-Cu1-N16a = 125°. Displacements of atoms from selected best planes (Å) are: plane Cu1, O2, N5; C1, -0.35(3); C2, -0.09(2); C3, 0.08(3); C4, 0.73(3); C41, 0.70(3); C42, 2.18(2); plane Cu1, N5, N8; C6, 0.16(4); C7, -0.54; plane Cu1, N8, N12; C9, -0.88(3); C91, -0.86(4); C92, -2.31(3); plane C10, -0.31(4); C11, -0.20(3); C111, -0.31(4); plane Cu1, N12, N16A; C13, 1.27(3); C14, 1.16(4); C15, 0.90(3); N16B, 1.03(2); plane Cu1, N12, N16B; C13, 0.81(3); C14, -0.06(4); C15, -0.57(4); N16A, -1.15(3); plane N5, N8, N16B; N5, 0.29(1); N8, -0.30(1); N12, 0.29(1); O2, 2.39(2); N16A, -1.38(3). The six atoms of the imine group are close to coplanar (rms deviation from their best plane for atoms N12, C11, Cu1, C13, C10 and C111 = 0.06(1) Å).

The cation is similar to $[\text{Cu}(\text{en}_2\text{-}\beta\text{aib-}\beta\text{ak})]^{2+}$ [6], except that the β -amine imine bridge is relatively reversed. This cation has a more regular square-pyramidal structure, with the ketone oxygen atom coordinated in the basal plane with Cu-O = 2.048(7) Å and with the terminal primary amine group axial, with Cu-N = 2.157(8) Å.

Table 2. Selected dimensions (Å, °) for $[\text{Cu}(\text{entmd-}\beta\text{aib-}\beta\text{ak})](\text{ClO}_4)_2 \cdot 0.33\text{H}_2\text{O}$.

Atoms	Dimension/Å, °	Atoms	Dimension/°
Cu1-O2	2.25(2)	O2-Cu1-N16a	130.3(7)
Cu1-N5	2.05(1)	O2-Cu1-N16b	100.4(9)
Cu1-N8	2.02(1)	N5-Cu1-N8	86.0(4)

Cu1-N12	1.98(1)	N5-Cu1-N12	170.9(8)
Cu1-N16a	2.29(3)	N5-Cu1-N16a	100.9(8)
Cu1-N16b	2.03(2)	N5-Cu1-N16b	96.1(6)
C2-O2	1.24(2)	N8-Cu1-N12	93.4(4)
C11-N12	1.28(2)	N8-Cu1-N16a	124.7(9)
O2-Cu1-N5	84.3(7)	N8-Cu1-N16b	154.6(9)
O2-Cu1-N8	104.9(5)	N12-Cu1-N16a	87.0(7)
O2-Cu1-N12	86.9(5)	N12-Cu1-N16b	89.4(6)

3. Conclusions

These structures can be compared with those of analogous compounds formed by reaction of the bis(1,2-ethanediamine)metal(II) cations with acetone, which are similar except that the β aiB chelate ring is reversed. For $[\text{Ni}(\text{en}_2\text{-}\beta\text{aib-im})]^{2+}$ [3] the imine groups are *cis*, while for $[\text{Ni}(\text{entmd-}\beta\text{aib-im})]^{2+}$ they are *trans*. Similarly, for $[\text{Cu}(\text{en}_2\text{-}\beta\text{aib-ak})]^{2+}$ [6] the primary amine group is *trans* to the imine group, while for $[\text{Cu}(\text{entmd-}\beta\text{aib-}\beta\text{ak})]^{2+}$ these functions are *cis*.

Solutions containing nickel(II) or copper(II) and both 1,2-ethanediamine and 1,3-propanediamine will include cations with all possible combinations of ligands, though mixed-ligand species will be thermodynamically favoured. The reactions with acetone, forming imines and β -amino ketone functions, probably occur at different rates for the different amines, but scrambling of the ligands will be rapid for these labile systems. The studies here reported indicate that the mixed-ligand species are favoured overall for the condensation reactions with acetone for combinations of 1,2-ethanediamine and 1,3-propanediamine.

The structurally different products formed by reaction of the $[\text{M}(\text{en})_2]^{2+}$, $[\text{M}(\text{tmd})_2]^{2+}$ and $[\text{M}(\text{en})(\text{tmd})]^{2+}$ cations with acetone can be understood if the reactions for the mixed-ligand cation predominate and proceed by the sequence shown in Fig. 6. The amine groups of the coordinated en and tmd ligands both react with acetone to form labile en-im and tmd-im functions, but the further reaction of the tmd-im functions with acetone is slower, so the more rapid reaction of the en-im function to form the β -amino-ketone function determines the structure of the products. The β -amino ketone function could equally well be formed with mesityl oxide or diacetone alcohol as the reactant as these will be formed in acetone in the presence of labile amine complexes. Amine complexes, particularly of 1,3-propanediamine, catalyse the formation of diacetone alcohol, mesityl oxide and higher acetone polymers from acetone, so it is not clear what is the reactive species in this reaction. The formation of $[\text{Ni}(\text{tmd}_2\text{-}\beta\text{aib})]^{2+}$ by a slow reaction of $[\text{Ni}(\text{tmd})_3]^{2+}$ with diacetone alcohol has been reported [16].

199

Fig. 4. Showing the postulated sequence of reactions leading to the formation of $[Ni(entmd-\beta ak-im)]^{2+}$ and $[Cu(entmd-\beta aib-\beta ak)]^{2+}$.

4. Crystallography

The structures were solved and refined by using SHELXS-97 [177] and SHELXL-2014 [18,19]. H-C atoms are in calculated positions, refined by using the riding model with default parameters. Crystallographic details are in Table 3.

For $[Cu(entmd-\beta aib-\beta ak)](ClO_4)_2 \cdot 0.33H_2O$ the structure of the ligand and the geometry about the copper(II) ion is unambiguous, but many of the atoms of the ligand, particularly those of chelate rings $N5 \cdots Cu1 \cdots O2$ and $N8 \cdots Cu2 \cdots N12$, have large prolate a.d.p.s which mask differing conformations of the chelate rings associated with the two N16 sites. Attempts to model this by splitting the carbon atom sites were unsuccessful. The atoms of the perchlorate ion also have large a.d.p.s, indicative of disorder, but again this was not successfully modelled.

Table 3. Crystallography.

Compound	$[Ni(entmd-\beta aib-im)](ClO_4)_2^A$	$[Cu(entmd-\beta aib-\beta ak)](ClO_4)_2 \cdot 0.33(H_2O)^B$
Formula	$C_{14}H_{30}Cl_2N_4NiO_8$	$C_{17}H_{35.67}Cl_2CuN_4O_{9.33}$

Formula weight	512.03	579.92
Crystal system	monoclinic	orthorhombic
Space group, H. M. (Hall)	P 21/c (-P 2ybc)	P ca 21 (P2c -2ac)
$a/\text{\AA}$	11.4496(3)	18.371(2)
$b/\text{\AA}$	14.0168(4)	10.714(1),
$c/\text{\AA}$	13.3365(4)	12.858(3)
$\beta/^\circ$	95.988(2)	90
Volume/ $\text{\AA}^3$	2128.7(1)	2530.8(7)
Z	4	4
Cell determination (refl., $\theta_{\min}$, $\theta_{\max}/^\circ$)	2448, 3.34, 73.98	3293, 2.2, 27.5
Temperature/K	123(1)	160(2)
$\rho_{\text{calc}}/\text{g/cm}^3$	1.598	1.526
Crystal, size/mm		0.2 × 0.1 × 0.08
F(000)	1072	1218
Radiation	CuK $_{\alpha}$ (1.54184 Å)	MoK $_{\alpha}$ (0.71073 Å)
μ/mm^{-1}	4.067	1.131
$T_{\max}$, $T_{\min}$	1.000, 0.870	0.311, 0.277
Index range h	-13, 11	0, 23
Index range k	-16, 15	0, 13
Index range l	-15, 11	0, 16
θ range/ $^\circ$	3.88 - 65.50	2.20 - 25.00
Reflections number (avge. R equiv)	7780 (0.0401)	3040
Reflections unique	3664	3040
Reflections [$I > 2\sigma(I)$]	2888	1528
Reflections used	3664	2467

Parameters, restraints	276, 0	333, 20 ^C
Goodness of fit on F^2 [all data]	1.032	1.079
Final R indexes [$I > 2\sigma(I)$] R_1 , wR ,	0.0451, 0.0614	0.0792, 0.1392
Final R indexes [all data] R_1 , wR ,	0.1095, 0.1203,	0.1493, 0.1707
Flack parameter [20]		0.12(12)

214

215 ^A Diffractometer, Xcalibur, Ruby, Gemini. Data collection, cell refinement, data reduction and
216 absorption correction: CrysAlisPro, Agilent Technologies, Version 1.171.36.28.

217 ^B Diffractometer, Seimens SMART CCD, data collection and reduction, Seimens SMART
218 and SAINT. Absorption correction, SADABS.

219 ^C DFIX restraints on N-H and O-H bonds, SADI restraints on C15-N16a, C15-N16b, ISOR
220 restraints on N16a, N16b.

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225 **Appendix A. Supplementary data**

226 The supplementary crystallographic data for [(2,8,8,10-tetramethyl-3,7,11-triazatridec-
227 2,10-diene-13-amino)nickel(II)] perchlorate, CCDC 1481539 and [(14-amino-4,4,9,11,11-
228 pentamethyl-5,8,12-triazatetradec-11-ene-2-one)copper(II) perchlorate 0.33 water, CCDC
229 1481550 can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>,
230 or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ,
231 UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. The Supplementary
232 Material contains preparations of the compounds and details of hydrogen bonding.

233

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Figure 1

Figure 2

Figure 3

Figure 4

acetone

acetone

Table 1. Selected dimensions (Å, °) for Ni(entmd-βaib-im)](ClO₄)₂

Atoms	Dimension/Å	Atoms	Dimension/°
Ni1-N1	1.914(3)	N1-Ni1-N3	84.9(1)
Ni1-N3	1.909(3) (im)	N1-Ni1-N7	176.1(1)
Ni1-N7	1.915(3)	N1-Ni1-N11	94.0(1)
Ni1-N11	1.914(3) (im)	N3-Ni1-N7	95.5(1)
N3-C4	1.279(4)	N3-Ni1-N11	168.9(1)
N11-C12	1.277(5)	N7-Ni1-N11	86.4(1)

Table 2. Selected dimensions (Å, °) for [Cu(entmd-βaib-βak)](ClO₄)₂·0.33H₂O.

Atoms	Dimension/Å,°	Atoms	Dimension/°
Cu1-O2	2.25(2)	O2-Cu1-N16a	130.3(7)
Cu1-N5	2.05(1)	O2-Cu1-N16b	100.4(9)
Cu1-N8	2.02(1)	N5-Cu1-N8	86.0(4)
Cu1-N12	1.98(1)	N5-Cu1-N12	170.9(8)
Cu1-N16a	2.29(3)	N5-Cu1-N16a	100.9(8)
Cu1-N16b	2.03(2)	N5-Cu1-N16b	96.1(6)
C2-O2	1.24(2)	N8-Cu1-N12	93.4(4)
C11-N12	1.28(2)	N8-Cu1-N16a	124.7(9)
O2-Cu1-N5	84.3(7)	N8-Cu1-N16b	154.6(9)
O2-Cu1-N8	104.9(5)	N12-Cu1-N16a	87.0(7)
O2-Cu1-N12	86.9(5)	N12-Cu1-N16b	89.4(6)

Table 3. Crystallography.

Compound	[Ni(entmd-βaib-im)](ClO ₄) ₂ ^A	[Cu(entmd-βaib-βak)](ClO ₄) ₂ ·0.33(H ₂ O) ^B
Formula	C ₁₄ H ₃₀ Cl ₂ N ₄ NiO ₈	C ₁₇ H _{35.67} Cl ₂ CuN ₄ O _{9.33}
Formula weight	512.03	579.92
Crystal system	monoclinic	orthorhombic
Space group, H. M. (Hall)	P 21/c (-P 2ybc)	P ca 21 (P2c -2ac)
<i>a</i> /Å	11.4496(3)	18.371(2)
<i>b</i> /Å	14.0168(4)	10.714(1),
<i>c</i> /Å	13.3365(4)	12.858(3)
β/°	95.988(2)	90
Volume/Å ³	2128.7(1)	2530.8(7)
Z	4	4
Cell determination (refl., θ _{min} , θ _{max} /°)	2448, 3.34, 73.98	3293, 2.2, 27.5
Temperature/K	123(1)	160(2)
ρ _{calc} /g/cm ³	1.598	1.526
Crystal, size/mm		0.2 × 0.1 × 0.08
F(000)	1072	1218
Radiation	CuK _α (1.54184 Å)	MoK _α (0.71073 Å)
μ/mm ⁻¹	4.067	1.131
<i>T</i> _{max} , <i>T</i> _{min}	1.000, 0.870	0.311, 0.277
Index range <i>h</i>	-13, 11	0, 23
Index range <i>k</i>	-16, 15	0, 13
Index range <i>l</i>	-15, 11	0, 16
θ range/°	3.88 - 65.50	2.20 - 25.00
Reflections number (avge. <i>R</i> equiv)	7780 (0.0401)	3040
Reflections unique	3664	3040

Reflections [$I > 2\sigma(I)$]	2888	1528
Reflections used	3664	2467
Parameters, restraints	276, 0	333, 20 ^C
Goodness of fit on F^2 [all data]	1.032	1.079
Final R indexes [$I > 2\sigma(I)$] R_1 , wR ,	0.0451, 0.0614	0.0792, 0.1392
Final R indexes [all data] R_1 , wR ,	0.1095, 0.1203,	0.1493, 0.1707
Flack parameter [20]		0.12(12)

^A Diffractometer, Xcalibur, Ruby, Gemini. Data collection, cell refinement, data reduction and absorption correction: CrysAlisPro, Agilent Technologies, Version 1.171.36.28.

^B Diffractometer, Seimens SMART CCD, data collection and reduction, Seimens SMART and SAINT. Absorption correction, SADABS.

^C DFIX restraints on N-H and O-H bonds, SADI restraints on C15-N16a, C15-N16b, ISOR restraints on N16a, N16b.