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Dinuclear Nickel(II) and Zinc(II) Complexes of 2,6-[N,N′-bis(2-hydroxyphenylmethyl)-N,N′-bis(2-pyridylmethyl)aminomethyl]-4-methylphenol

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The symmetric 'end-off' compartmental proligand 2,6-[N,N′-bis(2-hydroxy-phenylmethyl)-N,N′-bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (H_3L) has been used to generate homodinuclear nickel(II) and zinc(II) complexes. The crystal structures of the complexes reveal that the di-nickel(II) complex is donor asymmetric and the di-zinc(II) complex is coordination number asymmetric. In both complexes non-coordinated acetic acid molecules are tightly hydrogen-bonded to the pendant phenols of the ligand generating a double acid salt of the type $[CH_3COO\cdots H\cdots L\cdots H\cdots OOCCH_3]^{3-}$ in the dinickel complex and a single acid salt of the type $[CH_3COO\cdots H\cdots L]^{3-}$ in the dizinc complex. In both cases the ligand periphery has been extended to provide a supraligand in which the donor potential of the original ligand has been enhanced.

Keywords: Crystal structure; Di-zinc(II) complex; Di-nickel(II) complex; Heptadentate ligand

1. INTRODUCTION

It has been noted that the metal ions present at transition metal-derived bimetallobiosites can be found in chemically distinct environments and these have been classified by Satcher *et al.* [1] into four distinct groupings; (a) *symmetric* — in which an identical number of donor atoms of the same type are bound to each metal atom in similar geometries, (b) *donor atom asymmetric* — in which different types of donor atom coordinate to each metal atom, (c) *geometry asymmetric* — in which there are inequivalent geometric arrangements of the donor atoms about each metal atom and (d) *coordination number asymmetric* — in which an unequal number of donor atoms is coordinated to each metal atom. A combination of different types of asymmetry may also occur at a dinuclear center. To a first approximation the nature of the donor atom may be restricted to simply O, N, S *etc.*, but a more precise definition would also specify the functional grouping associated with each donor atom hence differentiating, for example, between, the oxygen atoms present in water and carboxylates, or the sulfur atoms present in thiolates and thioethers.

A similar behavior pattern has also been found in dinuclear metal complexes derived

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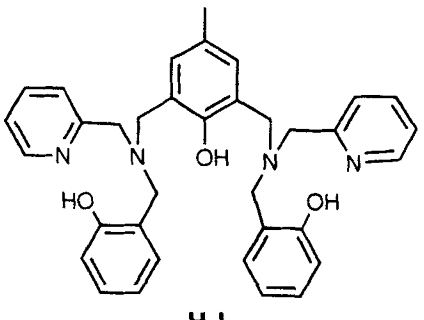
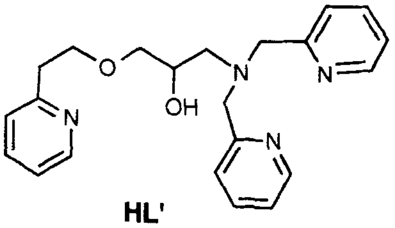
*Corresponding author. Tel.: +44-114-222 9333, Fax: +44-114-273 8673, e-mail: d.fenton@sheffield.ac.uk from dinucleating ligands and which serve as synthetic analogues for dinuclear biosites. The asymmetry can occur whether a symmetric or non-symmetric dinucleating ligand is used in the synthetic procedure [2, 3].

Herein we report the synthesis and crystal structures of a donor asymmetric di-nickel(II) complex and a coordination number asymmetric di-zinc(II) complex derived from the symmetric 'end-off' compartmental proligand 2,6-[N,N'-bis-(2-hydroxyphenylmethyl)-N,N'-bis(2-pyridylmethyl)-amino-methyl]-4-methylphenol (H_3L). This heptadentate proligand has previously been used to generate model di-iron(III) compounds for the oxidised uteroferrin-phosphate complex [4].



H_3L



HL'

2. RESULTS AND DISCUSSION

The proligand was synthesized by modification of the method of Krebs *et al.* [4]. The complexes were then prepared by reaction of the proligand with the corresponding metal(II) acetate in acetonitrile. Crystals of each complex were removed from the mother liquor and the X-ray crystal structures determined.

2.1. $[Ni_2L(OAc)(OH_2)(CH_3COOH)]\cdot CH_3CO_2H\cdot CH_3CN$ (1)

The reaction of H_3L with nickel(II) acetate in acetonitrile gave a homodinuclear complex which was shown *via* the crystal structure to be donor atom asymmetric in the solid state. The molecular structure of (1) is given in Figure 1 together with bond lengths and angles at the metal centers. Both nickel(II) atoms were found to be hexa-coordinate with $[N_2O_4]$ coordination environments and distorted octahedral coordination geometries. The asymmetry arises from the definition of the donor sets. Both Ni atoms are coordinated by a bridging phenolato-O atom, a pyridinyl-N atom, a pendant phenolato-O atom, an articular-N atom from the pendant arm, and a bridging acetato-O atom. Ni(1) is further coordinated by the O atom of a monodentate acetic acid molecule whereas Ni(2) is further coordinated by the O atom of a water of solvation. Both the *syn–syn* acetato bridge [Ni(1)-O(4), 2.02 Å; Ni(2)-O(5), 2.04 Å; O(1)-Ni(1)-O(4), 90.8°, O(1)-Ni(2)-O(5), 89.0°] and the phenolato bridge [Ni(1)-O(1), 2.06 Å; Ni(2)-O(1), 2.04 Å] are close to symmetric. The Ni···Ni separation is 3.643 Å with a supporting Ni(1)-O(1)-Ni(2) angle of 125.5°. The Ni-O distances lie in the range 2.07–2.10 Å with the Ni-N distances in the range 2.08–2.12 Å.

The nickel ions in the asymmetric cation of (1) are bridged by an acetate anion and there are two further acetic acid molecules present in the complex based on the electrostatic charge count and assuming deprotonation of the phenols in the ligand. One of the acetic acid molecules coordinates to Ni(1) in a monodentate mode. There is a precedence for this type of behavior in the asymmetric dinuclear complex of proligand HL', $[Ni_2L'(C_6H_5COO)_2(CH_3COOH)]ClO_4\cdot C_4H_{10}O$, [5] in which complex the C-O bond lengths of the monodentate coordinated neutral acetic acid differ, having values of 1.212 (coordinated O) and 1.326 Å (non-coordinated O), suggesting the presence of a coordinated carbonyl

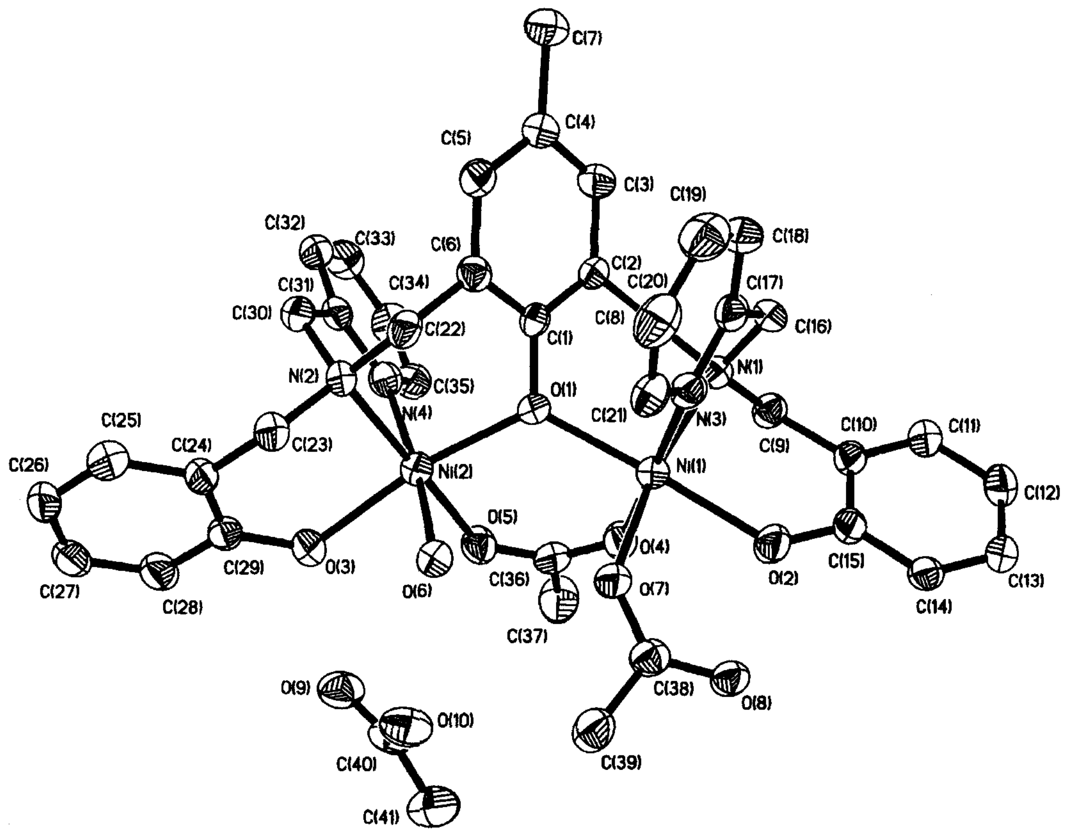


FIGURE 1 ORTEP drawing of the molecular structure of $[\mathbf{Ni_2L(OAc)(OH_2)(CH_3COOH)}]\cdot\mathbf{CH_3CO_2H\cdot CH_3CN}$ **(1)** – the acetonitrile of solvation is omitted for clarity – showing the crystallographic labeling. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bonds and angles at the metal atoms, Ni(1)-O(1), 2.055(2); Ni(1)-O(2), 2.102(3); Ni(1)-O(4), 2.017(3); Ni(1)-O(7), 2.098(3); Ni(1)-N(1), 2.102(3); Ni(1)-N(3), 2.083(3); Ni(2)-O(1), 2.043(2); Ni(2)-O(3), 2.073(2); Ni(2)-O(5), 2.036(3); Ni(2)-O(6), 2.088(2); Ni(2)-N(2), 2.120(3); Ni(2)-N(3), 2.085(3); Ni(1)-Ni(2), 3.6433(7) Å: O(4)-Ni(1)-N(3), 176.13(11); O(1)-Ni(1)-O(2), 177.15(11); O(7)-Ni(1)-N(1), 166.41(11); O(4)-Ni(1)-O(7), 93.54(10); O(7)-Ni(1)-N(3), 90.13(11); O(4)-Ni(1)-N(1), 95.36(11); N(3)-Ni(1)-N(1), 81.26(12); O(5)-Ni(2)-N(2), 173.79(11); O(1)-Ni(2)-O(3), 170.35(10); O(6)-Ni(2)-N(4), 171.82(12); O(5)-Ni(2)-O(1), 88.97(10); O(5)-Ni(2)-O(3), 87.41(10); O(1)-Ni(2)-N(2), 93.41(10); O(3)-Ni(2)-N(2), 91.10(11); Ni(1)-O(1)-Ni(2), 125.51(11)°.

group. It is likely that in complex (**1**) the monodentate acetic acid based on C(38) is coordinated through its carbonyl function although the bond lengths do not prove this, C(38)-O(7) 1.28 and C(39)-O(8) 1.27 Å. However, in (**1**) there is also an extremely close contact between O(8), presumed to be the -OH function of the acetic acid, and O(2) from the deprotonated pendant phenol of 2.44 Å suggesting that there is a very strong hydrogen-bonding interaction between them and that bidentate nature of the combined interaction leads to a delocalised acetate anion. This situation is reminiscent of the very strong hydrogen-bonding found in acid salts derived from carboxylic acids and related species [6, 7] — *e.g.*, in $KH(CH_3COO)_2$ the hydrogen bond length is 2.44 Å [8] — and leads to the suggestion that in complex (**1**) a related event has occurred.

There is also a very short contact between O(9), presumed to be the OH function of the non-coordinated acetic acid based on C(40), and O(3) from the deprotonated phenol of 2.48 Å; this is supplemented by a distance of 2.72 Å between the water O(6) and the second O of the acetate at C(40), O(10). This suggests that this acetic acid molecule bridges the two sites and

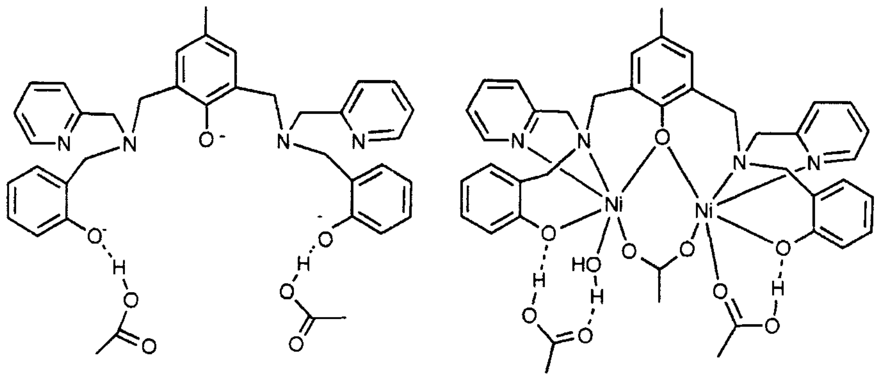


FIGURE 2 Schematic representations of the extended ligand (double acid salt) and the di-nickel(II) complex.

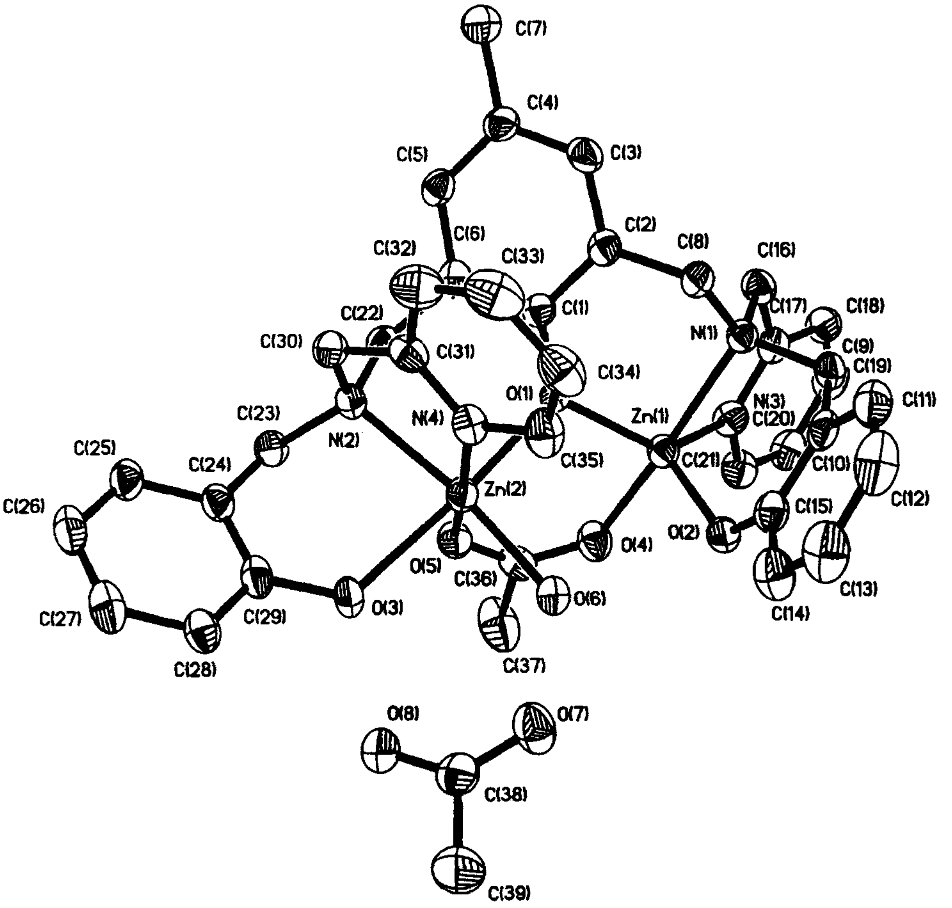


FIGURE 3 ORTEP drawing of the molecular structure of $[\mathbf{Zn_2L(OAc)(OH_2)}]\cdot\mathbf{CH_3CO_2H}$ (**2**) showing the crystallographic labeling. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level Selected bonds and angles at the metal atoms, Zn(1)-O(1), 1.975(2); Zn(1)-O(2), 1.957(2); Zn(1)-O(4), 2.052(3); Zn(1)-N(1), 2.205(3); Zn(1)-N(3), 2.114(3); Zn(2)-O(1), 2.133(2); Zn(2)-O(3), 2.310(2); Zn(2)-O(5), 2.021(2); Zn(2)-O(6), 2.041(3); Zn(2)-N(2), 2.180(3); Zn(2)-N(3), 2.089(3); Zn(1)-Zn(2), 3.4074(6) Å: O(2)-Zn(1)-O(1), 113.11(10); O(2)-Zn(1)-N(3), 116.34(11); O(1)-Zn(1)-N(3), 129.61(11); O(4)-Zn(1)-N(3), 91.02(11); O(2)-Zn(1)-N(1), 94.31(10); O(4)-Zn(1)-N(1), 167.50(10); O(6)-Zn(2)-N(2), 169.44(11); O(1)-Zn(2)-O(3), 175.42(9); O(5)-Zn(2)-N(4), 171.92(11); O(5)-Zn(2)-O(6), 90.48(10); O(5)-Zn(2)-N(2), 94.47(10); O(6)-Zn(2)-O(3), 86.30(9); O(3)-Zn(2)-N(2), 84.37(10); Zn(1)-O(1)-Zn(2), 112.02(10)°.

has its carbonyl at O(10). The C-O bond distances are C(40)-C(9), 1.28 and C(40)-C(10), 1.24 Å and so show some asymmetry in support of the above proposal.

As both acetic acids are tightly hydrogen bonded to the pendant phenols it can be proposed that a double acid salt of the type $[CH_3COO\cdots H\cdots L\cdots H\cdots OOCCH_3]^{3-}$, has been formed in which the ligand periphery has been extended to provide a supraligand in which the donor potential of the original ligand has been enhanced (Fig. 2).

2.2. $[Zn_2L(OAc)(OH_2)]\cdot CH_3CO_2H$ (2)

The reaction of H_3L with zinc(II) acetate in acetonitrile gave a homodinuclear complex which was shown *via* the crystal structure to be coordination number asymmetric in the solid state. The molecular structure of (**2**) is given in Figure 3. In contrast to the above the zinc complex showed only one acetic acid residue to be present and in this case the structure of the anion resembled a single acid salt of the type $[CH_3COO\cdots H\cdots L]^{3-}$ (Fig. 4).

One zinc atom, Zn(1), is penta-coordinate with an $[N_2O_3]$ coordination environment derived from a bridging phenolato-O atom, a pyridinyl-N atom, a pendant phenolato-O atom, an articular-N atom from the pendant arm and a bridging ethanoato-O atom. The coordination geometry is distorted trigonal bipyramidal ($\tau = 0.63$, where τ is an index of the degree of trigonality within the structural continuum between square-pyramidal and trigonal-bipyramidal geometries) [9]. The second zinc atom, Zn(2), is hexa-coordinate with an $[N_2O_4]$ coordination environment derived from a bridging phenolato-O atom, a pyridinyl-N atom, a pendant phenolato-O atom, an articular-N atom from the pendant arm, a bridging ethanoato-O atom and the O atom of a water of solvation. The coordination geometry is distorted octahedral with the water-O atom and articular-N atom axial to each other. The *syn*–*syn* acetate bridge is close to symmetric [Zn(1)-O(4), 2.05 Å; Zn(2)-O(5), 2.02 Å; O(1)-Zn(1)-O(4), 93.0°; O(1)-Zn(2)-O(5), 89.6°] but the phenolato-bridge is non-symmetric [Zn(1)-O(1), 1.98 Å; Zn(2)-O(1), 2.13 Å] and the Zn(1)-O(1)-Zn(2) angle is 112.0°. The Zn(1)···Zn(2) separation is 3.407 Å, shorter than that observed for the Ni(1)···Ni(2) separation of 3.643 Å found in (**1**) and the supporting Zn(1)-O(1)-Zn(2) angle is 112.0°. The Zn-O distances lie in the range 1.96–2.31 Å with dissimilar pendant phenolato-O to Zn(II) interactions [Zn(1)-O(2), 1.96 Å; Zn(2)-O(3), 2.31 Å] and the Zn-N distances lie in the range 2.09–2.21 Å.

A molecule of acetic acid is hydrogen-bonded to the phenolato-O coordinated to Zn(2) [O(8)····O(3), 2.52 Å] and has C(38)-O(8), 1.26 Å and C(38)-O(7), 1.24 Å. In this instance a single acid salt of the type $[CH_3COO\cdots H\cdots L]^{3-}$ has been formed. The second O atom, O(7), is

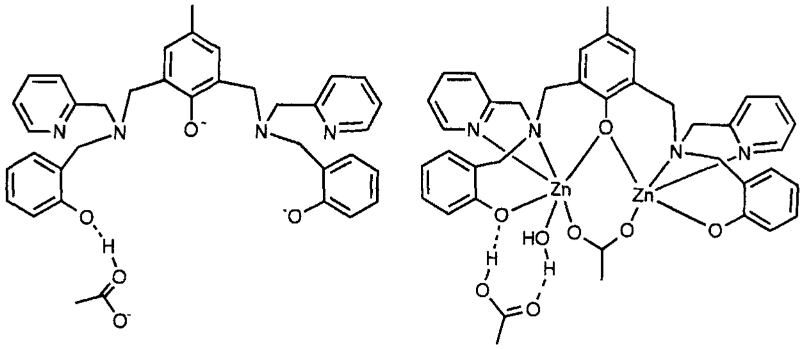


FIGURE 4 Schematic representations of the extended ligand (single acid salt) and the di-zinc(II) complex.

hydrogen-bonded to the coordinated water molecule [O(7)-O(6), 2.60 Å]. As in the case of complex (**1**) the bidentate nature of this interaction leads to a delocalised acetate anion.

3. EXPERIMENTAL

Elemental analyses were carried out by the University of Sheffield microanalytical service. Electrospray (E.S.) and positive ion fast atom bombardment (FAB) mass spectra were recorded using Micromass Platform and a Micromass ProSpec spectrometers respectively (the matrix used for FAB was 4-nitrobenzyl alcohol). 2,6-[N,N′-bis(2-hydroxyphenylmethyl)-N,N′-bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (H_3L) was prepared by modification of the method of Ref. [4].

3.1. The Metal Complexes

In both cases the ligand (H_3L) [4] was gently warmed in MeCN (10–15 cm^3) in the presence of two equivalents of NEt_3 until complete dissolution had occurred. Two equivalents of metal acetate was then added and the solution gentle refluxed for 1 hour. The solution was then allowed to cool to room temperature and left to crystallize; crystallization occurred within 7–10 days.

3.2. $[Ni_2L(OAc)(OH_2)(CH_3COOH)]\cdot CH_3CO_2H\cdot CH_3CN$ (1)

H_3L (204 mg, 0.36 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (179 mg, 0.72 mmol) were used. The product yield was 250 mg (76%). *Anal.* Calc. for $C_{43}H_{49}N_5Ni_2O_{10}$: C, 56.55; H, 5.41; N, 7.67. Found: C, 56.70; H, 5.42; N, 8.06%. MS(ES): *m/z*: 673 (92%) $[Ni_2L]^+$.

3.3. $[Zn_2L(OAc)(OH_2)]\cdot CH_3CO_2H$ (2)

H_3L (347 mg·0.62 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (271 mg, 1.24 mmol) were used. The product yield was 450 mg (88%). *Anal.* Calc. for $C_{39}H_{42}N_4O_8Zn_2$: C, 56.74; H, 5.13; N, 6.79. Found: C, 56.55; H, 4.98; N, 7.14%. MS(FAB): *m/z*: 687 (100%) $[Zn_2L]^+$.

3.4. X-ray Crystallography

Data collected were measured at 150(2) K on a Bruker Smart CCD area detector with an Oxford Cryosystems low temperature system. Complex scattering factors were taken from the program package SHELXTLY as implemented on the Viglen Pentium computer [10].

3.5. $[Ni_2L(OAc)(OH_2)(CH_3COOH)]\cdot CH_3CO_2H\cdot CH_3CN$ (1)

M = 913.29. Crystallizes from acetonitrile as green blocks; crystal dimensions 0.14 × 0.12 × 0.11 mm. Monoclinic, $a = 47.623(5)$, $b = 12.4982(14)$, $c = 14.4604(16)$ Å, $\alpha = 90°$, $\beta = 95.492(2)°$, $\gamma = 90°$, $U = 8567.4(16)$ Å^3, Z = 8, $D_c = 1.416$ Mg/m^{-3}, space group C2/c, Mo-K$_\alpha$ radiation $\lambda = 0.71073$ Å, μ(Mo-K$_\alpha$) = 0.942 mm^{-1}, F(000) = 3824. Cell parameters were refined from the setting angles of 71 reflections (θ range 2.08 < 28.33°). Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 27596 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.8794 and 0.9035), 5238 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0543 (wR2 = 0.1126, for all 10196 data, 547 parameters, mean and maximum δ 0.000, 0.001) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.586 and 0.946 e.Å^{-3}. A weighting scheme w = $1/[\sigma^2(F_o^2) + (0.0516^*P)^2 + 0.00^*P]$ where $P = (Fo^2 + 2^*Fc^2)/3$ was used in the latter stages of refinement.

3.6. [$Zn_2L(OAc)(OH_2)$]·CH_3CO_2H (2)

M = 825.21. Crystallizes from acetonitrile as colorless blocks; crystal dimensions 0.23 × 0.14 × 0.05 mm. Monoclinic, $a = 9.8597(9)$, $b = 19.1637(17)$, $c = 19.5439(17)$ Å, $\alpha = 90°$ $\beta = 94.717(2)°$, $\gamma = 90°$, $U = 3680.3(6)$ Å^3, $Z = 4$, $D_c = 1.490$ Mg/m^{-3}, space group P2(1)/n, Mo-Kα radiation $\lambda = 0.71073$ Å), μ(Mo-K$_\alpha$) = 1.362 mm^{-1}, F(000) = 1712. Cell parameters were refined from the setting angles of 43 reflections (θ range 2.09 < 28.32°). Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 22650 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.7447 and 0.9350), 5021 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0559 (wR2 = 0.1090, for all 8662 data, 487 parameters, mean and maximum δ 0.000, 0.001)) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −1.1071 and 0.867 e.Å^{-3}. A weighting scheme w = $1/[\sigma^2(F_o^2) + (0.0505^*P)^2 + 0.00^*P]$ where $P = (Fo^2 + 2^*Fc^2)/3$ was used in the latter stages of refinement.

Acknowledgements

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