

Structure of Tri(²H)aqua(*N*-methyliminodiacetato)nickel(II) (²H)Monohydrate, [Ni(C₅H₇NO₄)(D₂O)₃].D₂O

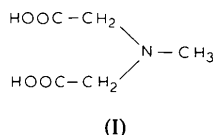
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(Received 12 September 1984; accepted 21 November 1984)

Abstract. $M_r = 283.9$, orthorhombic, $P2_12_12_1$, $a = 7.592$ (1), $b = 10.060$ (1), $c = 13.477$ (1) Å, $V = 1029.3$ (2) Å³, $Z = 4$, $D_m = 1.83$ (1), $D_x = 1.83$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 19.1$ cm⁻¹, $F(000) = 576$, $T = 298$ K, $R = 0.0167$ for 1340 unique observed reflections. *N*-Methyliminodiacetate coordinates in a tridentate, *facial* arrangement to the nickel atom with three water molecules completing the near-octahedral coordination sphere. A fourth water molecule outside the coordination sphere is contained in the asymmetric unit. The two five-membered rings formed by the organic ligand are unsymmetrical.

Introduction. Structural studies of metal complexes containing iminodiacetic acid (ida) or *N*-alkyl-substituted analogs such as *N*-methyliminodiacetic acid (mida) (I) have shown several coordination geometries.



The most commonly observed type of ligation is tridentate binding with a *facial* orientation of the ida ligand. This coordination geometry has been observed in bis(ligand) complexes (Corradi, Palmieri, Nardelli, Pellinghelli & Vidoni Tani, 1973; Kramarenko, Polynova, Porai-Koshits, Chalyi & Mitrofanova, 1973; Mammano, Templeton & Zalkin, 1977; Mootz & Wunderlich, 1980*a,b,c*), and in 1:1 metal:ligand complexes with either strongly donating ligands [e.g. 2,2'-bipyridine (Nardin, Randaccio, Bonomo & Rizzarelli, 1980)], or weakly donating ligands [e.g. H₂O (Podder, Dattagupta & Saha, 1979; Sinkha, Kramarenko, Polynova, Porai-Koshits & Mitrofanova, 1975)] completing the coordination sphere. A *meridional* conformation of the ida ligand has been observed only in solution with NMR techniques (Legg & Cooke,

1966). An alternate ligand coordination geometry, in which there is no nitrogen coordination and bridging between two metal centers *via* carboxylate binding, has been observed in some lanthanoid and actinoid complexes (Albertsson & Oskarsson, 1968, 1974; Bombieri, Forsellini, Tomat, Magon & Graziani, 1974; Oskarsson, 1971).

As part of our mechanistic studies of ligand exchange, it was desirable to establish the coordination geometry of the 1:1 nickel:mida complex. Deuterated water was used in the complex preparation for subsequent NMR water-exchange studies.

Experimental. Crystals obtained by slow evaporation of a D₂O solution of nickel(II) perchlorate and mida (1:1 molar ratio) neutralized with NaOD; green, irregular fragment of crystal, $\sim 0.5 \times 0.5 \times 0.6$ mm; D_m measured by flotation in CCl₄/CH₃I; Enraf-Nonius CAD-4 diffractometer equipped with an oriented graphite monochromator, ω - 2θ scan mode; 24 reflections of $\theta = 12.1$ to 14.4° used to measure lattice parameters; empirical absorption correction based on ψ scans, $t_{\min} = 0.88$, $t_{\max} = 1.00$; $(\sin\theta)/\lambda_{\max} = 0.5384$ Å⁻¹; $+h(0$ to $8)$, $+k(0$ to $10)$, $\pm l(-14$ to $14)$; three intensity standard reflections (513, 327, 154) measured every 2 h showed no loss in intensity; 1565 reflections measured, 1350 unique reflections, ten unobserved reflections [$I < 3\sigma(I)$], 1340 reflections used in refinement; standard Patterson and Fourier solution techniques; full-matrix least-squares refinement on F ; all hydrogen atoms located by difference Fourier syntheses and refined; 197 parameters refined (including secondary-extinction coefficient); $R = 0.0167$, $wR = 0.0224$, $S = 1.76$, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$, $p = 0.02$; alternate absolute configuration rejected by least-squares refinement of the enantiomeric structure which gave a substantial increase in R ; max. least-squares shift of any parameter = 0.31σ ; max. height = 0.351 e Å⁻³ in final difference Fourier synthesis; secondary-extinction coefficient = 3.24×10^{-6} ; scattering factors, f' , and f'' from *International Tables for X-ray Crystallography* (1974); all computer programs used from *Structure Determination Package User's Guide* (1982).

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Discussion. Atomic positions and isotropic thermal parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2.*

As can be seen from Fig. 1, the mida ligand is coordinated in the *facial* arrangement. The major deviation from octahedral coordination occurs with the nitrogen atom which is bent back towards the chelating acetate groups. The O(6)–Ni–N bond angle is 164.59 (5)°, while all of the other metal–ligand bond angles deviate less than 5° from ideal octahedral coordination. This bending is not related to internal crowding caused by the *N*-methyl group [distances H(5)–H(9), H(5)–H(8) and H(5)–O(5) are 2.62, 2.90 and 2.87 Å, respectively]. The same bending is seen in the bis(*ida*) species (Mammano *et al.*, 1977).

The two five-membered rings formed by the mida ligand are unsymmetrical. The ring involving O(3) is essentially planar, while the ring involving O(1) is puckered by up to 0.3 Å from the least-squares plane. The ligand distortion has been attributed to H(2)–H(3) steric interaction (Mammano *et al.*, 1977) which in this case is through a distance of 2.61 Å.

Intermolecular hydrogen bonding appears to be more important than internal *cis* or *trans* influences in determining nickel–oxygen bond distances. The Ni–O(1) distance is 0.079 Å longer than the Ni–O(3) distance because of an intermolecular hydrogen bond of O(1) to H(12). Similarly, the Ni–O(5) bond distance is about 0.075 Å longer than the Ni–O(6) and Ni–O(7) bond distances due to intermolecular hydrogen bonding

of O(5) to H(14) and not necessarily to their respective *cis* or *trans* orientations relative to the nitrogen. The molecular orientation within the unit cell is shown in Fig. 2.

Table 1. *Atomic fractional coordinates and isotropic thermal parameters*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> (Å ²)
Ni	0.06642 (3)	0.03571 (2)	0.14862 (1)	1.243 (4)
O(1)	0.1181 (2)	0.1691 (1)	0.26297 (9)	1.82 (2)
O(2)	0.2210 (2)	0.1777 (1)	0.4168 (1)	2.83 (3)
O(3)	0.2493 (2)	0.1162 (1)	0.06013 (9)	1.99 (2)
O(4)	0.5346 (2)	0.1526 (1)	0.0450 (1)	2.94 (3)
O(5)	0.0091 (2)	−0.1089 (1)	0.03940 (9)	1.99 (2)
O(6)	−0.1065 (2)	0.1675 (1)	0.08803 (9)	1.99 (2)
O(7)	−0.1237 (2)	−0.0576 (1)	0.23011 (9)	2.13 (3)
O(8)	−0.2157 (2)	0.0194 (2)	0.4146 (1)	5.02 (4)
N	0.2874 (2)	−0.0547 (1)	0.2170 (1)	1.46 (3)
C(1)	0.2695 (2)	−0.0209 (2)	0.3233 (1)	1.98 (3)
C(2)	0.1997 (3)	0.1200 (2)	0.3357 (1)	1.86 (3)
C(3)	0.4446 (2)	0.0098 (2)	0.1741 (2)	2.46 (4)
C(4)	0.4059 (2)	0.0994 (2)	0.0863 (1)	1.76 (3)
C(5)	0.3009 (3)	−0.2004 (2)	0.2047 (2)	2.28 (4)
H(1)	0.195 (2)	−0.076 (2)	0.353 (1)	1.6 (4)*
H(2)	0.369 (3)	−0.030 (2)	0.361 (2)	2.8 (4)*
H(3)	0.504 (3)	0.064 (2)	0.224 (2)	4.2 (6)*
H(4)	0.528 (3)	−0.050 (2)	0.159 (2)	3.0 (5)*
H(5)	0.316 (2)	−0.218 (2)	0.134 (2)	2.2 (4)*
H(6)	0.398 (2)	−0.227 (2)	0.238 (2)	2.5 (4)*
H(7)	0.190 (3)	−0.245 (2)	0.227 (2)	2.6 (4)*
H(8)	−0.036 (2)	−0.169 (2)	0.059 (1)	2.1 (4)*
H(9)	0.102 (3)	−0.132 (3)	−0.005 (2)	6.6 (8)*
H(10)	−0.212 (3)	0.151 (2)	0.078 (1)	2.6 (4)*
H(11)	−0.064 (3)	0.215 (2)	0.048 (2)	2.6 (4)*
H(12)	−0.131 (3)	−0.151 (2)	0.239 (2)	3.6 (5)*
H(13)	−0.154 (2)	−0.035 (2)	0.272 (1)	1.9 (4)*
H(14)	−0.306 (3)	0.028 (2)	0.434 (2)	5.6 (6)*
H(15)	−0.154 (3)	−0.024 (3)	0.448 (2)	6.5 (7)*

* Atoms refined with isotropic thermal parameters.

Table 2. *Selected bond lengths (Å), angles (°) and intermolecular bonds to hydrogen up to 2.30 Å*

Ni–O(3)	2.002 (1)	Ni–C(5)	1.478 (2)
Ni–O(6)	2.037 (1)	C(2)–C(1)	1.523 (2)
Ni–O(7)	2.042 (1)	C(2)–O(1)	1.261 (2)
Ni–O(1)	2.081 (1)	C(2)–O(2)	1.248 (2)
Ni–O(5)	2.115 (1)	C(4)–C(3)	1.516 (2)
Ni–N	2.120 (1)	C(4)–O(3)	1.252 (2)
N–C(1)	1.478 (2)	C(4)–O(4)	1.245 (2)
N–C(3)	1.476 (2)		
O(1)–Ni–N	78.79 (5)	Ni–N–C(3)	106.32 (10)
O(3)–Ni–N	83.31 (5)	Ni–N–C(5)	115.56 (12)
O(5)–Ni–O(7)	84.99 (6)	C(1)–N–C(3)	110.64 (15)
O(3)–Ni–O(6)	86.84 (5)	C(1)–N–C(5)	110.06 (15)
O(1)–Ni–O(6)	89.92 (5)	C(3)–N–C(5)	109.63 (15)
O(3)–Ni–O(5)	90.37 (5)	N–C(1)–C(2)	110.65 (14)
O(1)–Ni–O(7)	91.79 (6)	C(1)–C(2)–O(1)	116.79 (14)
O(5)–Ni–O(6)	92.08 (5)	C(1)–C(2)–O(2)	118.98 (14)
O(1)–Ni–O(3)	92.84 (5)	O(1)–C(2)–O(2)	124.19 (14)
O(6)–Ni–O(7)	93.40 (6)	N–C(3)–C(4)	114.23 (15)
O(7)–Ni–N	97.37 (5)	C(3)–C(4)–O(3)	118.97 (15)
O(5)–Ni–N	99.80 (5)	C(3)–C(4)–O(4)	116.92 (15)
O(6)–Ni–N	164.59 (5)	O(3)–C(4)–O(4)	124.11 (15)
O(3)–Ni–O(7)	175.36 (6)	Ni–O(1)–C(2)	114.57 (10)
O(1)–Ni–O(5)	176.30 (5)	Ni–O(3)–C(4)	115.87 (10)
Ni–N–C(1)	104.47 (10)		
O(1)–H(12) ^b	1.82 (3)	O(4)–H(15) ^b	2.05 (4)
O(2)–H(8) ^b	2.110 (24)	O(5)–H(14) ^b	2.25 (3)
O(2)–H(9) ^b	1.77 (3)	O(8)–H(13)	2.049 (22)
O(4)–H(11) ^b	1.976 (24)		

Symmetry code: (i) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \bar{y}, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; (iv) $\frac{1}{2} + \bar{x}, \bar{y}, \frac{1}{2} + z$.

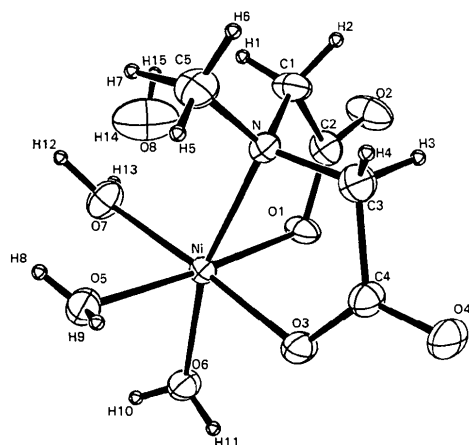


Fig. 1. View of the [Ni{NCH₃(CH₂COO)₂}(D₂O)₃].D₂O molecule showing the atom numbering and 50% vibrational ellipsoids. The hydrogen atoms are represented by spheres of arbitrary size.

* Lists of structure factors, anisotropic thermal parameters and internal hydrogen-bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39923 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

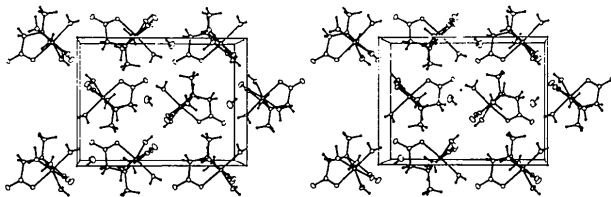


Fig. 2. Stereoscopic packing diagram for $[\text{Ni}\{\text{NCH}_3(\text{CH}_2\text{COO})_2\} \cdot (\text{D}_2\text{O})_3] \cdot \text{D}_2\text{O}$ along the a axis with the b axis vertical.

The orientation of the protons on the methyl group provides minimal overlap with the protons on nearby C(1) and C(3) methylene carbon atoms. The average internal hydrogen-bond distance for hydrogen atoms attached to carbon is 0.94 Å, and 0.81 Å for hydrogen atoms attached to oxygen.

The equipment used in this study was funded in part by the National Science Foundation, grant No. CHE79-007027. We are grateful to Diane C. Fisher, Frederick J. Hollander, D. H. Templeton and Kenneth N. Raymond for their assistance.

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Redetermination of the Structure of μ -Oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] at 122 K, $[\text{Fe}_2\text{O}(\text{C}_{44}\text{H}_{28}\text{N}_4)_2]$

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(Received 27 August 1984; accepted 19 November 1984)

Abstract. $M_r = 1353.2$, orthorhombic, $C2cb$ (C_{2v}^{17}), $a = 15.094$ (4), $b = 24.938$ (7), $c = 17.825$ (4) Å, $V = 6709.5$ Å³, $Z = 4$, crystallographically imposed C_2 molecular symmetry, $D_x = 1.34$ g cm⁻³, Mo $K\alpha$, $\lambda(K\alpha_1) = 0.7093$ Å, graphite monochromator, $\mu(\text{Mo } K\alpha) = 4.86$ cm⁻¹, $F(000) = 2802.4$, $T = 122$ K, $R(F^2) = 0.093$ for 11 416 unique observed reflections. Structural parameters derived from an extensive low-temperature data set are presented. The previously reported room-temperature structure [Hoffman, Collins, Day, Fleischer, Srivastava & Hoard (1972). *J. Am. Chem. Soc.* **94**, 3620–3626] is confirmed and improved.

Introduction. The structure of μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] was previously de-

termined (Fleischer & Srivastava, 1969; Hoffman *et al.*, 1972). Recent theoretical interest in this and other oxo-bridged molecules (Tatsumi, Hoffmann & Whangbo, 1980; Tatsumi & Hoffmann, 1981) prompted us to collect an extensive low-temperature data set for an experimental charge-density investigation. We were unable to produce a reasonable description of the valence electron density distribution from this study, but nonetheless we derived highly accurate structural parameters.

Experimental. The chosen aspect of space group C_{2v}^{17} was that of previous investigators (Fleischer & Srivastava, 1969) and is $C2cb$ (equivalent positions: $0,0,0; \frac{1}{2}, \frac{1}{2}, 0 + x, y, z; x, \bar{y}, \bar{z}; x, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z$). The origin has been fixed by x of Fe. Bounding faces of the