though the greater flexibility of the chain might make this less constricting. It might also be possible, in the presence of a guest molecule, for the bridge to buckle and rotate upwards, increasing its height at the cost of some conformational strain.

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Structure of a Binuclear Nickel(II) Complex of a Pyridine-Containing Tetraaza Macrocycle, Including a Tetradentate Oxalato Bridge, $[(L)Ni(\mu\text{-}ox)Ni(L)](ClO_4)_2$*

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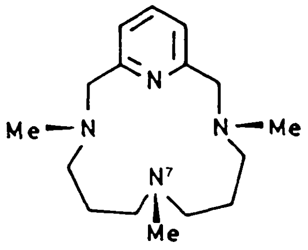
Abstract. (μ-Oxalato)bis(3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene)-dinickel(II) diperchlorate, $[Ni_2(C_2O_4)(C_{16}H_{28}N_4)_2](ClO_4)_2$, $M_r = 957{\cdot}1$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}394$ (2), $b = 20{\cdot}270$ (9), $c = 12{\cdot}410$ (3) Å, $\beta = 101{\cdot}22$ (2)°, $U = 2{\cdot}071$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}53$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = 11·09 cm^{-1}, $T = 290$ K, $F(000) = 1004$, $R = 0{\cdot}066$ for 1978 unique observed $[I/\sigma(I) \geq 3{\cdot}0]$ reflections. The tetradentate tetraaza macrocycle adopts a folded conformation, to produce a *cis*-pseudooctahedral geometry at each Ni atom, with the tetradentate bridging oxalate (two five-membered chelate rings) linking the two Ni atoms [Ni—O 2·124 (6) and 2·069 (5) Å; Ni—N(pyridine) 1·989 (7), Ni—N(Me) 2·157 (7), 2·187 (7) and 2·200 (7) Å].

Introduction. We have previously reported the synthesis of the pyridine-containing tetraaza macrocycle (L) and its metal complexes of formula $[M(L)][ClO_4]_2$ (M = Ni,Cu,Zn), $[Ni(L)X][ClO_4]_n$ ($n = 1$, X = Cl, NCS, NO$_2$; $n = 2$, X = dimethyl sulfoxide) and $[(L)Ni(\mu\text{-}ox)Ni(L)][ClO_4]_2$. Three isomers of the diamagnetic square-planar $[Ni(L)][ClO_4]_2$ were observed by ^{13}C NMR in nitromethane solution, and the structure of one of them (the asymmetric isomer) was established by X-ray crystallography. The paramagnetic five-coordinate nickel(II) complexes were found to have square-pyramidal geometries, as shown by crystal structures with X = Cl and dimethyl sulfoxide; X is coordinated in the basal plane in a *trans* position to the pyridine N atom, and with N^7 at the apex (Alcock, Moore & Omar, 1987). The six-coordinate oxalato complex was assigned a folded *cis* structure, based on an elemental analysis, spectroscopic data, and by comparison with related structures. An X-ray structural investigation was undertaken to establish the structure unequivocally, and to determine the mode of coordination of the bridging oxalate group.



(L)

Experimental. The complex $[(L)Ni(\mu\text{-}ox)Ni(L)][ClO_4]_2$ was prepared as described previously (Alcock, Moore & Omar, 1987). The fast-atom bombardment

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* L = 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene; ox = oxalate ion.

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Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2×10^3)

	x	y	z	U_{eq}*
Ni	1139·1 (12)	942·9 (5)	487·9 (8)	31 (1)
Cl	4924 (4)	1358 (1)	9070 (2)	69 (1)
O(11)	5981 (31)	1029 (7)	8699 (19)	336 (18)
O(12)	3381 (20)	1225 (9)	8821 (15)	267 (11)
O(13)	5145 (20)	1485 (12)	10065 (9)	302 (14)
O(14)	5020 (20)	1965 (6)	8567 (15)	231 (10)
O(1)	−940 (7)	713 (3)	4433 (4)	39 (2)
O(2)	−1813 (7)	−45 (3)	5491 (4)	41 (2)
C(1)	−773 (9)	191 (4)	4973 (6)	30 (3)
N(1)	3378 (8)	960 (3)	3158 (5)	40 (2)
N(2)	2132 (10)	1602 (4)	5125 (5)	49 (3)
N(3)	88 (8)	1791 (4)	3220 (5)	44 (3)
N(4)	−283 (9)	636 (4)	2163 (5)	49 (3)
C(2)	3830 (12)	1536 (4)	2519 (8)	54 (4)
C(3)	4728 (11)	830 (5)	4110 (8)	62 (4)
C(4)	5080 (12)	1379 (6)	4955 (9)	68 (4)
C(5)	3884 (15)	1429 (7)	5666 (9)	86 (5)
C(6)	1198 (16)	1592 (7)	5976 (8)	88 (6)
C(7)	2116 (15)	2270 (5)	4653 (8)	72 (5)
C(8)	535 (15)	2335 (5)	3771 (8)	64 (4)
C(9)	−290 (17)	2921 (5)	3488 (9)	82 (5)
C(10)	−1615 (15)	2909 (6)	2642 (11)	86 (5)
C(11)	−2087 (14)	2346 (7)	2092 (11)	84 (5)
C(12)	−1187 (12)	1778 (5)	2413 (9)	64 (4)
C(13)	−1677 (14)	1093 (6)	2004 (10)	87 (5)
C(14)	−993 (20)	−19 (6)	2080 (10)	110 (6)
C(15)	555 (14)	794 (6)	1273 (7)	76 (5)
C(16)	2170 (14)	410 (6)	1338 (8)	79 (5)
C(17)	3299 (12)	364 (5)	2432 (8)	60 (4)

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ni–O(1)	2·124 (6)	Ni–N(1)	2·157 (7)
Ni–N(2)	2·187 (7)	Ni–N(3)	1·989 (7)
Ni–N(4)	2·200 (7)	Ni–O(2)	2·069 (5)
O(1)–C(1)	1·245 (9)	O(2)–C(1)	1·275 (10)
C(1)–C(1a)	1·503 (15)		

O(1)–Ni–N(1)	167·9 (2)	O(1)–Ni–N(2)	92·9 (3)
N(1)–Ni–N(2)	91·9 (3)	O(1)–Ni–N(3)	88·8 (3)
N(1)–Ni–N(3)	103·1 (3)	N(2)–Ni–N(3)	79·1 (3)
O(1)–Ni–N(4)	87·0 (3)	N(1)–Ni–N(4)	92·6 (3)
N(2)–Ni–N(4)	158·2 (3)	N(3)–Ni–N(4)	79·1 (3)
O(1)–Ni–O(2)	78·9 (2)	N(1)–Ni–O(2)	89·4 (2)
N(2)–Ni–O(2a)	99·4 (2)	N(3)–Ni–O(2a)	167·5 (3)
O(11)–Cl–O(12)	122·7 (13)	O(11)–Cl–O(13)	119·4 (13)
O(12)–Cl–O(13)	103·2 (12)	O(11)–Cl–O(14)	101·4 (12)
O(12)–Cl–O(14)	102·7 (11)	O(13)–Cl–O(14)	104·7 (13)
O(1)–C(1)–O(2)	125·1 (7)	O(1)–C(1)–C(1′)	117·9 (9)
O(2)–C(1)–C(1′)	117·0 (8)		

(f.a.b.) mass spectrum shows peaks at m/z 860 (0·54), 859 (0·78), 858 (1·0), 857 (0·44) and 856 (0·94) {calc. for $[(L)_2Ni_2(ox)(HClO_4)]^+$ m/z 860 (0·53), 859 (0·43), 858 (1·0), 857 (0·35) and 856 (0·84)}, and at m/z 759 (0·72), 758 (0·49), 757 (0·84) and 756 (1·0) {calc. for $[(L)_2Ni_2(ox)]^+$ m/z 759 (0·37), 758 (0·87), 757 (0·42) and 756 (1·0)} (relative intensities of each cluster in parentheses). Crystals were obtained as blue needles by slow diffusion of ethanol (4 cm^3) into a nitromethane solution of the complex (2 cm^3). The crystals have a tendency to twin, but after some searching a small untwinned crystal was found. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range ± 1·1° (2θ) around the $K\alpha_1 - K\alpha_2$ angles, and scan speeds 3–29° min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0·25 of the scan time; hkl ranges: h 0–9; k 0–23; l −14 to 14. Three standard reflections were monitored every 200 reflections, and showed no significant changes during data collection. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 reflections with $16 < 2\theta < 20°$.

Reflections were processed using profile analysis to give 4025 unique reflections (R_{int} = 0·02); 1978 were considered observed $[I/\sigma(I) \geq 3·0]$ and used in refinement. Corrections were made for Lorentz, polarization and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors 0·89 and 0·92. Crystal dimensions were 0·27 × 0·075 × 0·13 mm. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicate space group $P2_1/c$. Ni and Cl were located by the Patterson interpretation section of *SHELXTL* (Sheldrick, 1983), and the light atoms were found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. H atoms were given fixed isotropic temperature factors, U = 0·07 Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on F by cascaded least-squares methods, refining 271 parameters. Largest positive and negative peaks on a difference Fourier synthesis were of height 0·9 and −0·8 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$, with g = 0·0017, was used, and found to be satisfactory by a weight analysis. Final R = 0·066, wR = 0·071, with maximum Δ/σ in the final cycle of 0·018. Computing was with *SHELXTL* (Sheldrick, 1983) on a Data General DG30. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2.[*]

Discussion. The X-ray determination has confirmed the suggested structure (Fig. 1), and shows that tetradentate oxalate ions bridge between two macrocycle/nickel(II) complexes. The geometry at each Ni is octahedral, with *cis*-oxygen atoms. This gives a

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[*] Lists of structure factors, anisotropic thermal parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44179 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

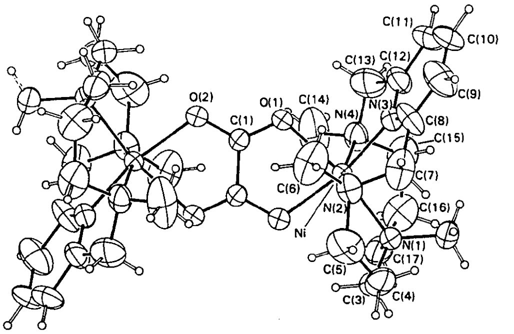

Fig. 1. View of the cation showing the atomic numbering. There is a centre of symmetry at the centre of the oxalate group.

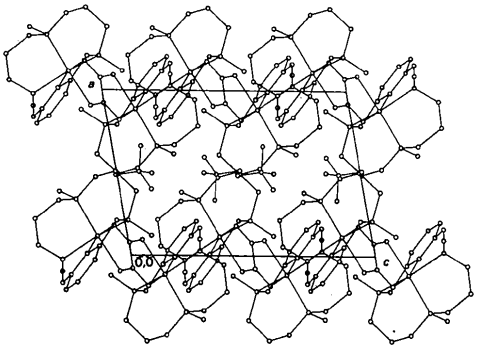

Fig. 2. Structure projected down **b**.

relatively unusual folded macrocycle; this ligand more often takes up the apex and three basal positions of a square pyramid (Alcock, Moore & Omar, 1987). Indeed, it is evident from the *trans* angle [N(2)—Ni—N(4)] of only 158·2 (3)° that the ligand is unable to accommodate the present geometry entirely satisfactorily. Another distortion arises from the 78·9° angle between the oxygen atoms, which is controlled by the bite of the oxalate ion. Ni—N and Ni—O distances are standard for high-spin Ni; as is normal, the Ni—N(3) (pyridine) distance is shorter than the others.

Tetradentate oxalate ions are rare, but not unknown (Davis, Einstein & Willis, 1982), and are generally planar, as here, forming five-membered chelate rings (rather than four-membered rings) with the metal ion.

In the crystal (Fig. 2), the cations are arranged in layers in the *bc* plane, with anions between the layers.

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Structure of μ-Oxo-bis[(2,3,7,8,12,13,17,18-octaethylporphyrinato)oxomolybdenum(V)] Diethanol Solvate

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Abstract. $[Mo_2(C_{36}H_{44}N_4)_2O_3].2C_2H_6O$, $M_r = 1397·6$, tetragonal, $P4/nnc$ (D^4_{4h}), $a = 13·796$ (5), $c = 17·021$ (6) Å, $V = 3239$ (3) Å^3, $Z = 2$, $D_x = 1·43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7093$ Å, $\mu = 4·3$ cm^{-1}, $F(000) = 1448·7$ (including anomalous dispersion), $T = 123$ K, $R(F^2) = 0·078$ for 1414 reflections. The Mo dimer has crystallographically imposed 422 symmetry with a linear O=Mo—O—Mo=O arrangement along a fourfold axis. The Mo=O and Mo—O bond lengths are 1·721 (6) and 1·951 (1) Å, respectively. The two porphyrin rings, interplanar distance 3·54 Å, are twisted by 22·3° with respect to one another. The ethanol solvent molecule lies on a fourfold axis and is disordered.

Introduction. Metal–metal bonded Mo^{II} porphyrin dimers have been prepared to study the rotational barrier about the Mo—Mo quadruple bonds (Collman & Woo, 1984). In an attempt to crystallize one of these dimers, $[Mo(oep)]_2$ (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato), we accidentally obtained the title compound, presumably as a result of air oxidation of the parent complex. Here we report its molecular structure and compare it with that of the corresponding tpp complex (tpp = 5,10,15,20-tetraphenylporphyrinato) (Johnson & Scheidt, 1978).

Experimental. Dark-blue crystals of the title compound were obtained accidentally by slow diffusion of pentane

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