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N-meso-C-meso-(5,6,12,13-Tetramethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene)-nickel(II) Diperchlorate

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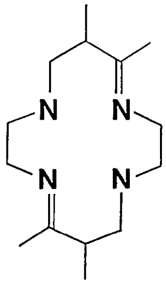
Abstract. $C_{14}H_{28}Cl_2N_4NiO_8$ (isomer *b*), $M_r = 510{\cdot}0$, monoclinic, $a = 7{\cdot}423\,(1)$, $b = 8{\cdot}100\,(2)$, $c = 18{\cdot}196\,(3)$ Å, $\beta = 98{\cdot}11\,(1)^\circ$, $V = 1083$ Å^3, $D_m = 1{\cdot}57\,(1)$, $Z = 2$, $D_c = 1{\cdot}56$ Mg m^{-3}, $F(000) = 532$; Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo $K\alpha$) = 0·8 mm^{-1}. Systematic absences $0k0$, $k = 2n + 1$; and $h0l$, $l = 2n + 1$ determine space group $P2_1/c$ uniquely. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0{\cdot}039$ for 2276 observed reflexions. The crystals contain centrosymmetric *N-meso-C-meso*-$[NiL]^{2+}$ cations and perchlorate anions; the Ni atom has square-planar coordination and the N—H bonds [at N(1) and N(8)] are *cis* to the nearest axial methyl groups [at C(13) and C(6) respectively]. Principal bond lengths are Ni—N(H) 1·926 (2), Ni—N(imine) 1·926 (2), N=C 1·282 (3), N—C(mean) 1·482 (5), C—C(mean) 1·508 (8) and Cl—O(mean) 1·425 (5) Å.

Introduction. Three Ni^{II} complexes of the ligand 5,6,12,13-tetramethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene [*L*, shown in (I)] have been prepared as perchlorate salts and labelled 'isomers (*a*), (*b*) and (*c*)' by Hay, Piplani & Jeragh (1977). In addition to the two chiral carbon centres in the ligand, the metal complexes contain two chiral nitrogen centres; there is, therefore, the possibility of 10 stereoisomers. The present paper reports the structure and stereochemistry of the orange-red isomer (*b*) and Ni^{II} complex $[NiL][ClO_4]_2$.



(I)

Material prepared by Hay, Piplani & Jeragh (1977) was recrystallized from a methanol–ethanol mixture; a crystal *ca* 0·08 × 0·37 × 0·39 mm was chosen for the X-ray analysis. Preliminary cell data were obtained from precession and Weissenberg photographs; accurate unit-cell data were obtained from a least-squares refinement of diffractometer setting angles of 12 strong general-order reflexions. Intensity data were collected to θ(Mo $K\alpha$) ≤ 25° on a Hilger & Watts Y290 computer-controlled diffractometer using graphite-monochromatized Mo $K\alpha$ radiation in a manner similar to that described previously (Roberts & Ferguson, 1977). 3370 independent intensity maxima were collected and corrected for Lorentz, polarization and absorption effects, and the 2276 reflexions with $I > 3\sigma(I)$ were considered 'observed' and used throughout the solution and refinement of the structure. All calculations were carried out with our local modification of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). (A local version of *DATCO* 5 was used for data handling.)

The Ni atom is constrained to lie at the origin of the cell from space-group considerations; the coordinates of the one independent Cl atom were obtained from a three-dimensional sharpened Patterson function and the positions of the remaining non-hydrogen atoms in the structure were readily found by application of the heavy-atom method. Four cycles of full-matrix least-squares refinement were then carried out allowing for anisotropic thermal motion of these atoms, and with a weighting scheme $w^{1/2} = 1/[\sigma^2(F) + pF^2]^{1/2}$, where the final parameter p was 5×10^{-4}. At this point a difference Fourier synthesis revealed electron-density maxima in chemically reasonable positions for all of the H atoms; there were no other significant features. Convergence was achieved in two further full-matrix cycles in which allowance was made for H atom contributions (with C—H and N—H 0·96 Å and an

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overall isotropic U value of 0·063 Å^2), but their parameters were not refined. The scattering factors of Cromer & Mann (1968) for the neutral species and of Stewart, Davidson & Simpson (1965) for H atoms were used throughout the refinement and anomalous-dispersion corrections (Cromer, 1965) were included for the Ni atom. The final value of $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0·039; that of $R' = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$ was 0·052. The estimated standard deviation of an observation of unit weight was 4·7. Atomic coordinates and standard deviations are listed in Table 1 and interatomic distances and angles computed from these are in Table 2.* An *ORTEP* (Johnson, 1971) view of the cation with the numbering scheme is in Fig. 1. Fig. 2 is a stereo pair showing the crystal structure.

Discussion. Our analysis establishes that crystals of the orange-red isomer (*b*) [Ni*L*][ClO$_4$]$_2$ contain centrosymmetric cations (II and Fig. 1); this immediately requires them to have the *N-meso-C-meso* configuration. The N–H bonds at N(1) and N(1′) are shown to be *cis* to the nearest (axial) methyl groups [at C(6′) and C(6) respectively] and the *trans*-diimine stereochemistry assigned by Hay, Piplani & Jeragh (1977) for ligand (I) is independently confirmed. The conformations of the five- and six-membered rings in the cation are very similar to those found in the related macrocylic cation *trans*-diisothiocyanato-*N*-*rac*-(5,12-dimethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene)cobalt(III) (Restivo, Horney & Ferguson, 1976). The

Table 1. *Atomic positional parameters* (×10^5 *for* Cl, ×10^4 *for* O, N *and* C, ×10^3 *for* H) *in* [Ni*L*][ClO$_4$]$_2$ (*form b*) *with estimated standard deviations in parentheses*

	x	y	z
Ni	0	0	0
Cl	16074 (9)	16643 (8)	38421 (3)
O(1)	192 (4)	2020 (5)	3260 (1)
O(2)	3028 (4)	744 (3)	3579 (1)
O(3)	2333 (4)	3158 (3)	4175 (2)
O(4)	855 (4)	741 (3)	4400 (1)
N(1)	701 (3)	−1871 (2)	−548 (1)
N(4)	2072 (3)	−534 (3)	722 (1)
C(2)	2681 (4)	−2087 (3)	−335 (2)
C(3)	3033 (4)	−2021 (3)	494 (2)
C(5)	2655 (4)	136 (4)	1349 (1)
C(6)	1835 (4)	1706 (4)	1592 (1)
C(7)	−198 (4)	1818 (4)	1365 (1)
C(15)	4211 (5)	−534 (6)	1875 (2)
C(16)	2894 (5)	3192 (4)	1344 (2)
H(11)	5	−282	−35
H(21)	335	−118	−55
H(22)	307	−318	−52
H(31)	256	−304	71
H(32)	437	−192	67
H(61)	210	178	215
H(71)	−79	83	156
H(72)	−66	284	158
H(151)	452	23	231
H(152)	526	−63	160
H(153)	390	−165	206
H(161)	420	312	157
H(162)	283	319	79
H(163)	235	424	150

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* [Ni*L*][ClO$_4$]$_2$ (*form b*)

Standard deviations are in parentheses.

(*a*) The cation

Ni–N(1)	1·926 (2)	Ni–N(4)	1·926 (2)
N(1)–C(2)	1·477 (3)	C(5)–C(6)	1·503 (4)
N(1)–C(7$^{\text{I}}$)	1·481 (3)	C(5)–C(15)	1·494 (5)
C(2)–C(3)	1·496 (4)	C(6)–C(7)	1·509 (4)
C(3)–N(4)	1·489 (4)	C(6)–C(16)	1·540 (5)
N(4)–C(5)	1·282 (3)		
N(1)–Ni–N(4)	85·92 (9)	N(4)–Ni–N(1$^{\text{I}}$)	94·08 (9)
Ni–N(1)–C(2)	106·8 (2)	Ni–N(4)–C(5)	130·5 (2)
Ni–N(1)–C(7$^{\text{I}}$)	116·6 (2)	N(4)–C(5)–C(6)	121·3 (2)
C(2)–N(1)–C(7$^{\text{I}}$)	111·6 (2)	N(4)–C(5)–C(15)	123·4 (3)
N(1)–C(2)–C(3)	106·7 (2)	C(15)–C(5)–C(6)	115·3 (3)
C(2)–C(3)–N(4)	106·7 (2)	C(5)–C(6)–C(7)	113·7 (2)
C(3)–N(4)–Ni	111·1 (2)	C(5)–C(6)–C(16)	109·3 (3)
C(3)–N(4)–C(5)	118·3 (2)	C(16)–C(6)–C(7)	113·9 (3)
		C(6)–C(7)–N(1$^{\text{I}}$)	112·1 (2)

(*b*) The anion

Cl–O(1)	1·412 (3)	Cl–O(3)	1·424 (3)
Cl–O(2)	1·428 (3)	Cl–O(4)	1·435 (3)
O(1)–Cl–O(2)	111·2 (2)	O(2)–Cl–O(3)	109·5 (2)
O(1)–Cl–O(3)	110·0 (2)	O(2)–Cl–O(4)	110·1 (1)
O(1)–Cl–O(4)	108·3 (2)	O(3)–Cl–O(4)	107·6 (2)

(*c*) Inter-ion contacts < 3·5 Å

O(3)···Ni$^{\text{II}}$	2·866 (3)	O(4)···N(1$^{\text{IV}}$)	3·139 (3)
O(3)···N(4$^{\text{II}}$)	3·438 (4)	O(4)···H(11$^{\text{IV}}$)	2·50
O(4)···N(1$^{\text{III}}$)	3·181 (3)	O(3)···C(3$^{\text{V}}$)	3·410 (4)
O(4)···H(11$^{\text{III}}$)	2·26		

(*d*) Torsion angles (°)

Ni–N(4)–C(5)–C(6)	−7·6 (4)
N(4)–C(5)–C(6)–C(7)	37·0 (4)
C(5)–C(6)–C(7)–N(1$^{\text{I}}$)	−64·4 (3)
C(6)–C(7)–N(1$^{\text{I}}$)–Ni	60·5 (3)
C(7)–N(1$^{\text{I}}$)–Ni–N(4)	−28·0 (2)
N(1$^{\text{I}}$)–Ni–N(4)–C(5)	2·4 (2)
N(1)–Ni–N(4)–C(3)	−0·8 (2)
Ni–N(4)–C(3)–C(2)	27·5 (2)
N(4)–C(3)–C(2)–N(1)	−48·9 (3)
C(3)–C(2)–N(1)–Ni	48·1 (2)
C(2)–N(1)–Ni–N(4)	−26·5 (2)

Symmetry code

(I) $-x,-y,-z$

(II) $x,\frac{1}{2}-y,\frac{1}{2}+z$

(III) $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$

(IV) $x,-\frac{1}{2}-y,\frac{1}{2}+z$

(V) $1-x,\frac{1}{2}+y,\frac{1}{2}-z$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33847 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

five-membered rings are close to an envelope conformation with φ[C(3)—N(4)—Ni—N(1)] near to 0°; the six-membered rings are in a sofa conformation (Altona, Geise & Romers, 1968). As has been found previously (Bailey & Maxwell, 1972) the Ni—N(4)—C(5) angle [130·5 (2)°] is considerably enlarged from the normal 120° to accommodate the strain in forming the six-membered rings, and the Ni—N distances [both 1·926 (2) Å] show the same absence of differentiation between Ni—N(H) and Ni—N(imino) bonds; the other ligand bonds [*e.g.* C(sp^2)—N(imino) 1·282 (3) Å] are close to values normally observed in macrocyclic ring complexes (see, *e.g.*, Curtis, Swann & Waters, 1973).

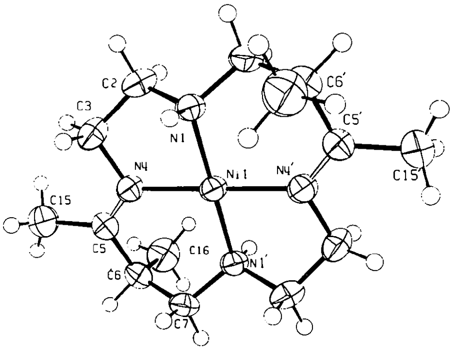


Fig. 1. An *ORTEP* drawing of the [Ni*L*]$^{2+}$ cation showing the atomic numbering and thermal ellipsoids at the 50% probability level; for clarity the H atoms have been included with arbitrary isotropic thermal parameters.

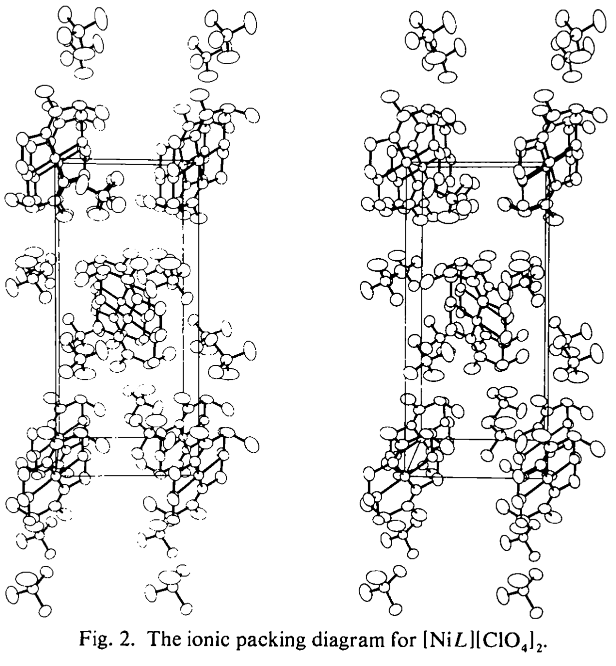
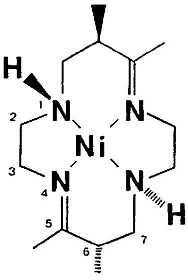
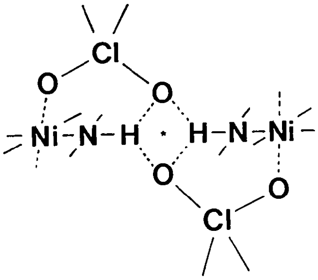


Fig. 2. The ionic packing diagram for [Ni*L*][ClO$_4$]$_2$.



(II)

In the crystal structure (Fig. 2), the Ni atom is weakly bonded [Ni···O 2·866 (2) Å] to two symmetry-related perchlorate O atoms which sit above and below the macrocycle plane. Each perchlorate group is further weakly linked to the cation by an N—H···O hydrogen bond [O(4)···H—N(1) 3·18 Å]. The same perchlorate oxygen, O(4), also forms a weak N—H···O hydrogen bond with the N—H group of a neighbouring cation [O(4)···H—N(1) 3·14 Å]. Thus, the cations are linked by pairs of bifurcated N—H···O hydrogen bonds as indicated in (III).



(III)

The structure of the Ni^{II} complex of isomer (*c*) has been established (Murray-Rust, 1977) as containing *N-rac-C-rac* cations and will be the subject of a later paper.

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Bis[1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-μ-(*N*-methyl-2-hydroxybenzylideneiminato)-μ-*O*]-dicopper(II). A Mixed-Ligand Binuclear Cu^{II} Complex

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Abstract. $C_{26}H_{18}Cu_2F_{12}N_2O_6$, monoclinic, $C2/c$, a = 23·414 (2), b = 7·727 (1), c = 16·430 (1) Å, β = 91·33 (1)°, Z = 4, D_m = 1·807, D_x = 1·809 Mg m^{-3}. The structure has a centre of symmetry. Each Cu atom has square-pyramidal coordination geometry. The bridging CuO_2Cu unit is nearly rectangular (Cu–O, 1·897, 2·450, Cu···Cu, 3·181 Å, Cu–O–Cu, 93·2°).

Introduction. Yokoi & Chikira (1975) reported that an equimolar mixture of bis(hexafluoroacetylacetonato)-copper(II), $Cu(hfa)_2$, and bis(*N*-salicylidenealkylaminato)copper(II), $Cu(R\mathrm{Sal})_2$, in toluene gives a new series of binuclear mixed-ligand chelates, $[Cu(R\mathrm{Sal})hfa]_2$, where the number of C atoms in the alkyl group (R) is from 0 to 5. The magnetic properties and electronic spectra of their crystals vary delicately with the alkyl group; particularly drastic changes are observed between the complex (1) where R is *tert*-butyl and the other members. In order to furnish a structural basis for these properties, we have determined the crystal structure of (1) and the complex (2) where R is methyl as a representative of the latter group (Shimanouchi, Sasada, Koyano & Yokoi, 1976). Since Sinn (1976) has published the structure of (1) as well as some related complexes $[Cu(R\mathrm{Sal})hfa]_2$ where R is C_6H_5, iso-C_3H_7 or C_2H_5, the present paper deals with only the structure of (2).

Crystals of (2) (green needles) are monoclinic, the space group being $C2/c$ from systematic absences (hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$).

Intensity data of 1816 independent reflexions were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation up to 2θ = 44° using a crystal, 0·40 × 0·30 × 0·30 mm in size. Of these, 1423 were considered as observed according to the criterion $|F_o| \geq 3\sigma(F_o)$. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied (μ = 1·62 mm^{-1} for Mo $K\alpha$ radiation).

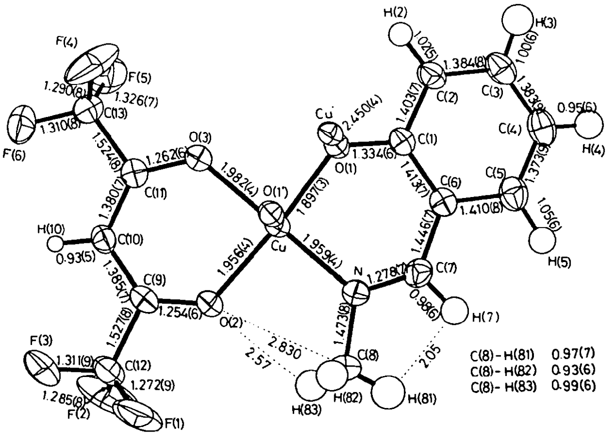

Fig. 1. Interatomic distances (Å), their e.s.d.'s (in parentheses) and thermal ellipsoids at the 30% probability level, viewed along the vector perpendicular to the least-squares plane of N, O(1), O(2), and O(3). Primed atoms, Cu′ and O(1′), are related to unprimed ones (at x,y,z) by a centre of symmetry at ($\frac{1}{4},\frac{1}{4}$,0). The other symmetry-related atoms in the molecule are omitted.

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