(ii) l'existence d'une zone hydrophile externe importante est confirmée;

(iii) la légère variation de la cage complexante s'explique par la variation du type d'hydratation, mais l'organisation cristalline n'induit pas d'autre modification intramoléculaire significative.

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Références

BARRANS, Y., ALLÉAUME, M. & DAVID, L. (1980). Acta Cryst. B36, 936–938.
DUAX, W. L., SMITH, G. D. & STRONG, P. D. (1980). J. Am. Chem. Soc. 102, 6725–6729.

HANEY, M. E. & HOEHN, E. E. (1967). Antimicrob. Agents Chemother. pp. 349–352.
International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
LUTZ, W. K., WINKLER, F. K. & DUNITZ, J. D. (1971). Helv. Chim. Acta, 54, 1103–1108.
PINKERTON, M. & STEINRAUF, L. K. (1970). J. Mol. Biol. 49, 533–546.
PULLMAN, A. (1974). Mol. Quantum Pharmacol. pp. 401–411.
SANDEAUX, R., SETA, P., JÉMINET, G., ALLÉAUME, M. & GAVACH, C. (1978). Biochim. Biophys. Acta, 511(3), 499–509.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.
WARD, D. L., WEI, K. T., HOOGERHEIDE, J. G. & POPOV, A. I. (1978). Acta Cryst. B34, 110–115.

Structures of N,N'-Propylenebis[(2-hydroxy-1-naphthyl)methaniminato]nickel(II) and N,N'-Propylenebis[(2-hydroxy-1-naphthyl)methaniminato]copper(II)– 0·5-Dimethyl Sulphoxide

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Abstract

$C_{25}H_{20}N_2NiO_2$, [NiL], $M_r = 438.9$, is orthorhombic, space group $Cmc2_1$, with $a = 30.78$ (1), $b = 8.498$ (6), $c = 7.76$ (1) Å, $U = 2030.2$ Å^3, $Z = 4$. $C_{25}H_{20}CuN_2O_2.0.5C_2H_6OS$, [CuL.0.5Me$_2$SO], $M_r = 482.8$, is monoclinic, space group $C2/c$, with $a = 23.416$ (11), $b = 9.24$ (1), $c = 20.194$ (11) Å, $\beta = 102.1$ (1)°, $U = 4272.7$ Å^3, $Z = 8$. 722 above-background diffractometer-measured reflections have been refined to $R = 0.058$ for [NiL] and 1276 to 0.075 for [CuL.0.5Me$_2$SO]. In both structures the metal coordination sphere is square planar. In [NiL] the molecule has crystallographically imposed m symmetry with Ni—O 1.866 (6) and Ni—N 1.871 (8) Å. The two parts of the molecule are folded so as to form an angle of 37.0 (1)° between the two metallocycle planes. In [CuL] the bond lengths are Cu—O 1.904 (11), 1.917 (10) and Cu—N 1.989 (12), 1.971 (13) Å. The two metallocycles intersect at 6.1 (1)°. The trimethylene group is slightly disordered. The solvent Me$_2$SO group is also disordered over two possible

orientations around the twofold axis. It seems likely that this variation in the conformation of the two molecules as indicated by the different folds is due to packing effects.

Introduction

The crystal structure of the 1:1 molecular complex of nickel and N,N'-ethylenebis[(2-hydroxy-1-naphthyl)-methanimine] and a comparison of its characteristics with the corresponding salicylideneimine complex have
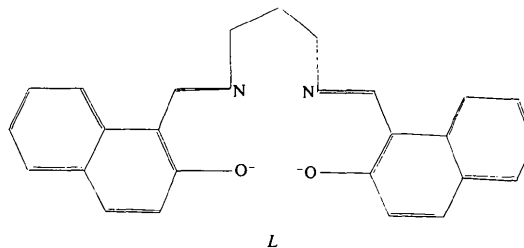
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been reported previously (Akhtar, 1981). As an extension to this work the ligand, N,N'-propylene-bis[(2-hydroxy-1-naphthyl)methanimine], L, has been prepared and the structures of the complexes of nickel and copper with the ligand are discussed in the present paper.

Experimental

The compounds were prepared (Kar, 1979) by refluxing an equimolar mixture of the respective metal nitrate and ligand L in a 1:1 water–alcohol mixture. The compound (1), [NiL], was recrystallized from acetone at room temperature as purple elongated hexagonal prisms. The compound (2), [CuL.0·5Me$_2$SO], was recrystallized from Me$_2$SO as dark-green-brown needles on slow evaporation at room temperature over a period of 12 weeks. Both crystals were placed in Lindemann-glass tubes along their needle axis and after preliminary examination by precession photographs the crystals were transferred to a Stoe STADI-2 diffractometer equipped with a graphite monochromator. Precise determination of lattice constants was carried out from the accurate setting angles of a number of axial reflections. Data were taken via ω scans of width $(2 \cdot 0 + 0 \cdot 5 \sin \mu/\tan \theta)°$. The scan speed was $0 \cdot 01°$ s^{-1} and the background was measured at the ends of the scan for 30 s. One standard reflection per layer was measured after every 20 reflections but no deterioration was observed. Data collection and refinement details are given in Table 1.

Structure determination

The positions of the metal atoms were located from Patterson maps and those of the other non-H atoms of the molecule were obtained from Fourier maps and

Table 1. *Additional experimental data*

	(1) [NiL]	(2) [CuL.0·5Me$_2$SO]
μ(cm^{-1})	6·83	7·60
d_m (g cm^{-3})	1·43	1·48
d_c (g cm^{-3})	1·43	1·50
λ (Å)	0·7107	0·7107
$F(000)$	912	1000
Crystal size (mm)	1·0 × 0·1 × 0·25	0·8 × 0·2 × 0·05
Rotation axis	c	b
2θ maximum (°)	50	45
No. of data	2009	2993
Criterion for data inclusion	$>2\sigma(I)$	$>1 \cdot 5\sigma(I)$
No. of data in refinement	722	1276
No. of parameters	139	281
R	0·058	0·075
R_w	0·062	0·080

Table 2. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$ *for* (1) *with e.s.d.'s in parentheses*

For all atoms, $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
Ni	0	731 (2)	0	65 (1)
O(1)	−400 (2)	2322 (7)	474 (9)	69 (7)
N(1)	−448 (3)	−693 (9)	−475 (11)	76 (9)
C(1)	−999 (3)	1302 (11)	−1164 (12)	67 (9)
C(2)	−787 (3)	2490 (10)	−125 (20)	86 (11)
C(3)	−1011 (3)	3942 (10)	245 (21)	87 (11)
C(4)	−1420 (3)	4228 (11)	−449 (16)	94 (14)
C(5)	−1627 (3)	3096 (13)	−1566 (14)	83 (11)
C(6)	−2035 (4)	3408 (14)	−2310 (19)	104 (15)
C(7)	−2240 (4)	2344 (16)	−3414 (21)	100 (16)
C(8)	−2031 (4)	939 (15)	−3740 (18)	87 (15)
C(9)	−1632 (3)	574 (13)	−3034 (15)	77 (11)
C(10)	−1417 (3)	1622 (12)	−1912 (13)	77 (10)
C(11)	−827 (3)	−278 (12)	−1101 (15)	75 (11)
C(12)	−400 (4)	−2418 (12)	−188 (25)	94 (16)
C(13)	0	−2914 (18)	695 (24)	93 (12)

Table 3. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$ *for* (2) *with e.s.d.'s in parentheses*

U_{eq} defined in Table 2.

	x	y	z	U_{eq} (Å^2)
Cu	2241 (1)	901 (2)	359 (1)	62 (2)
O(1)	2994 (5)	114 (14)	717 (5)	77 (15)
O(2)	2384 (4)	1748 (13)	1245 (5)	68 (14)
N(1)	2200 (5)	−205 (14)	−494 (6)	51 (15)
N(2)	1509 (5)	2007 (16)	96 (6)	70 (17)
C(1)	3157 (7)	−1400 (17)	−185 (8)	56 (20)
C(2)	3321 (7)	−742 (22)	447 (8)	59 (22)
C(3)	3902 (7)	−1015 (20)	810 (8)	63 (22)
C(4)	4285 (7)	−1819 (20)	566 (8)	64 (22)
C(5)	4113 (7)	−2583 (21)	−47 (8)	80 (23)
C(6)	4499 (7)	−3510 (19)	−298 (9)	92 (22)
C(7)	4327 (9)	−4203 (22)	−885 (9)	108 (26)
C(8)	3758 (9)	−4077 (25)	−1245 (9)	94 (27)
C(9)	3368 (9)	−3186 (18)	−1045 (8)	81 (23)
C(10)	3543 (7)	−2419 (18)	−437 (8)	77 (21)
C(11)	2593 (7)	−1082 (17)	−629 (8)	70 (20)
C(12)	1567 (6)	3265 (18)	1178 (8)	56 (19)
C(13)	2088 (6)	2678 (18)	1509 (7)	62 (19)
C(14)	2335 (7)	3159 (21)	2182 (8)	64 (22)
C(15)	2079 (7)	4153 (20)	2513 (8)	59 (21)
C(16)	1536 (7)	4751 (17)	2193 (8)	60 (20)
C(17)	1262 (7)	5753 (18)	2547 (8)	78 (21)
C(18)	729 (7)	6358 (20)	2258 (9)	87 (23)
C(19)	461 (7)	5881 (24)	1596 (10)	98 (26)
C(20)	724 (6)	4929 (19)	1254 (8)	67 (20)
C(21)	1275 (6)	4349 (18)	1519 (7)	63 (19)
C(22)	1315 (7)	2923 (20)	488 (8)	66 (21)
C(23)	1137 (8)	1812 (28)	−576 (9)	101 (30)
C(24a)	1406 (10)	1337 (27)	−1121 (12)	58 (7)*
C(24b)	1128 (19)	637 (52)	−867 (24)	58 (7)*
C(25)	1680 (7)	−58 (20)	−1074 (8)	67 (22)
S(1)	−81 (4)	987 (12)	2210 (4)	87 (3)*
O(26)	0	−327 (29)	2500	151 (9)*
C(27)	591 (9)	1974 (26)	2466 (10)	118 (8)*

* Isotropic value.

refined by full-matrix least squares. The H atoms were generated in trigonal or tetrahedral positions and an overall isotropic thermal parameter was refined. A difference Fourier map for (2) showed Me_2SO group disordered around the twofold axis. The S(1) and O(26) atoms were given occupancy factors of 0·5, the latter being on the twofold axis along **b**. The S(1) atom could be connected to two methyl groups related to each other by the twofold axis. The central trimethylene C atom in (2), C(24), had unrealistic thermal parameters and its bonding geometry was unsatisfactory. A difference Fourier synthesis without this atom revealed a peak elongated in a direction perpendicular to the ring plane. Therefore two positions C(24a) and C(24b) were refined with occupancy factors of x and $1 - x$ respectively. x refined to 0·64 (2). All the other non-H atoms except Me_2SO and C(24a) and C(24b) were refined anisotropically and there was an improvement in the bonding geometry of disordered C(24). An attempt to locate the H atoms of the methyl groups of Me_2SO was unsuccessful and these were not included in the final refinement. The weighting scheme used was $w = 1/[\sigma^2(F) + xF^2]$ where $x = 0·005$ and $0·002$ respectively in (1) and (2). $\sigma(F)$ was obtained from counting statistics. The final difference Fourier maps showed no important features and in the final cycles of refinement no shift was greater than $0·1\sigma$. Final R values were 0·058 and 0·075 respectively. Calculations were carried out using *SHELX* 76 (Sheldrick, 1976) at the University of Manchester Regional Computer Centre. Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Atomic parameters are given in Tables 2 and 3, bond lengths and angles in Table 4 and least-squares planes in Table 5.*

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36526 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Distances* (Å) *and angles* (°)

Geometry of the coordination sphere in (1)

Ni—O(1)	1·866 (6)	Ni—N(1)	1·871 (8)
O(1)—Ni—N(1)	91·2 (3)	N(1)—Ni—N(1^i)	94·9 (3)
O(1)—Ni—O(1^i)	82·6 (3)	O(1)—Ni—N(1^i)	173·7 (3)

Geometry of the coordination sphere in (2)

Cu—O(1)	1·904 (11)	Cu—N(1)	1·989 (12)
Cu—O(2)	1·917 (10)	Cu—N(2)	1·971 (13)
O(1)—Cu—O(2)	80·5 (4)	O(1)—Cu—N(2)	169·9 (5)
O(1)—Cu—N(1)	90·3 (5)	O(2)—Cu—N(2)	90·7 (5)
O(2)—Cu—N(1)	170·4 (4)	N(1)—Cu—N(2)	98·7 (5)

Table 4 (*cont.*)

Ligand dimensions in (1)

O(1)—C(2)	1·285 (13)	C(4)—C(5)	1·444 (15)
N(1)—C(11)	1·312 (13)	C(5)—C(6)	1·409 (15)
N(1)—C(12)	1·490 (13)	C(5)—C(10)	1·434 (14)
C(1)—C(2)	1·448 (16)	C(6)—C(7)	1·396 (18)
C(1)—C(10)	1·437 (13)	C(7)—C(8)	1·380 (17)
C(1)—C(11)	1·444 (15)	C(8)—C(9)	1·380 (17)
C(2)—C(3)	1·443 (13)	C(9)—C(10)	1·411 (15)
C(3)—C(4)	1·389 (15)	C(12)—C(13)	1·472 (17)
Ni—O(1)—C(2)	128·3 (6)	C(4)—C(5)—C(10)	119·7 (9)
Ni—N(1)—C(11)	123·7 (7)	C(6)—C(5)—C(10)	119·3 (10)
Ni—N(1)—C(12)	122·3 (7)	C(5)—C(6)—C(7)	122·2 (10)
C(11)—N(1)—C(12)	114·0 (9)	C(6)—C(7)—C(8)	117·6 (11)
C(2)—C(1)—C(10)	119·8 (8)	C(7)—C(8)—C(9)	122·4 (11)
C(2)—C(1)—C(11)	117·6 (8)	C(8)—C(9)—C(10)	121·3 (10)
C(10)—C(1)—C(11)	121·2 (9)	C(1)—C(10)—C(5)	119·5 (9)
O(1)—C(2)—C(1)	122·8 (8)	C(1)—C(10)—C(9)	123·3 (9)
O(1)—C(2)—C(3)	117·8 (10)	C(5)—C(10)—C(9)	117·2 (9)
C(1)—C(2)—C(3)	119·4 (9)	N(1)—C(11)—C(1)	126·0 (9)
C(2)—C(3)—C(4)	120·4 (11)	N(1)—C(12)—C(13)	115·7 (10)
C(3)—C(4)—C(5)	121·0 (9)	C(12^i)—C(13)—C(12)	113·7 (12)
C(4)—C(5)—C(6)	121·0 (10)		

Ligand dimensions in (2)

O(1)—C(2)	1·297 (19)	C(9)—C(10)	1·403 (21)
O(2)—C(13)	1·286 (16)	C(12)—C(13)	1·374 (19)
N(1)—C(11)	1·298 (17)	C(12)—C(21)	1·465 (21)
N(1)—C(25)	1·509 (17)	C(12)—C(22)	1·429 (19)
N(2)—C(22)	1·303 (19)	C(13)—C(14)	1·431 (20)
N(2)—C(23)	1·462 (20)	C(14)—C(15)	1·348 (21)
C(1)—C(2)	1·394 (20)	C(15)—C(16)	1·412 (19)
C(1)—C(10)	1·467 (21)	C(16)—C(17)	1·405 (20)
C(1)—C(11)	1·461 (20)	C(16)—C(21)	1·420 (19)
C(2)—C(3)	1·428 (20)	C(17)—C(18)	1·381 (20)
C(3)—C(4)	1·336 (21)	C(18)—C(19)	1·423 (22)
C(4)—C(5)	1·408 (21)	C(19)—C(20)	1·343 (22)
C(5)—C(6)	1·415 (21)	C(20)—C(21)	1·397 (19)
C(5)—C(10)	1·408 (19)	C(23)—C(24a)	1·446 (29)
C(6)—C(7)	1·332 (22)	C(23)—C(24b)	1·232 (46)
C(7)—C(8)	1·383 (21)	C(24a)—C(25)	1·434 (28)
C(8)—C(9)	1·352 (23)	C(24b)—C(25)	1·58 (4)
Cu—O(1)—C(2)	130·9 (10)	N(1)—C(11)—C(1)	126·0 (14)
Cu—O(2)—C(13)	131·0 (9)	C(13)—C(12)—C(21)	119·7 (13)
Cu—N(1)—C(11)	126·4 (10)	C(13)—C(12)—C(22)	122·0 (15)
Cu—N(1)—C(25)	120·8 (10)	C(21)—C(12)—C(22)	118·1 (14)
C(11)—N(1)—C(25)	112·8 (12)	O(2)—C(13)—C(12)	124·2 (14)
Cu—N(2)—C(22)	124·5 (10)	O(2)—C(13)—C(14)	117·1 (13)
Cu—N(2)—C(23)	120·1 (12)	C(12)—C(13)—C(14)	118·7 (14)
C(22)—N(2)—C(23)	115·4 (14)	C(13)—C(14)—C(15)	123·3 (14)
C(2)—C(1)—C(10)	121·7 (15)	C(14)—C(15)—C(16)	119·4 (14)
C(2)—C(1)—C(11)	120·9 (16)	C(15)—C(16)—C(17)	119·3 (15)
C(10)—C(1)—C(11)	117·4 (14)	C(15)—C(16)—C(21)	120·1 (15)
O(1)—C(2)—C(1)	125·3 (15)	C(17)—C(16)—C(21)	120·6 (14)
O(1)—C(2)—C(3)	118·4 (14)	C(16)—C(17)—C(18)	121·3 (15)
C(1)—C(2)—C(3)	116·3 (17)	C(17)—C(18)—C(19)	117·0 (15)
C(2)—C(3)—C(4)	123·4 (15)	C(18)—C(19)—C(20)	121·8 (14)
C(3)—C(4)—C(5)	120·8 (15)	C(19)—C(20)—C(21)	122·6 (15)
C(4)—C(5)—C(6)	122·1 (16)	C(12)—C(21)—C(16)	118·7 (13)
C(4)—C(5)—C(10)	120·1 (15)	C(12)—C(21)—C(20)	124·6 (14)
C(6)—C(5)—C(10)	117·8 (16)	C(16)—C(21)—C(20)	116·5 (14)
C(5)—C(6)—C(7)	120·8 (17)	N(2)—C(22)—C(12)	127·6 (15)
C(6)—C(7)—C(8)	120·4 (16)	N(2)—C(23)—C(24a)	118·4 (16)
C(7)—C(8)—C(9)	122·0 (18)	N(2)—C(23)—C(24b)	119·9 (26)
C(8)—C(9)—C(10)	118·5 (18)	C(23)—C(24a)—C(25)	118·9 (20)
C(1)—C(10)—C(5)	117·1 (15)	C(23)—C(24b)—C(25)	124 (3)
C(1)—C(10)—C(9)	122·6 (16)	N(1)—C(25)—C(24a)	114·1 (15)
C(5)—C(10)—C(9)	120·3 (16)	N(1)—C(25)—C(24b)	113·8 (19)

Solvent dimensions in (2)

S(1)—O(26)	1·344 (23)	S(1)—C(27^{ii})	1·732 (10)
S(1)—C(27)	1·797 (23)		
O(26)—S(1)—C(27)	107·4 (9)	C(27)—S(1)—C(27^{ii})	105·3 (9)
O(26)—S(1)—C(27^{ii})	110·9 (6)		

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

Table 5. *Results of least-squares-plane calculations in*
(1) *and* (2)

Deviations of atoms from the planes are given in Å. Atoms not
contributing to the planes are marked with an asterisk.

Plane 1

Compound (1)

Ni* 0·02 (1), O(1) 0·00, N(1) 0·00, O(1¹) 0·00, N(1¹) 0·00,
C(12)* 0·62 (1), C(13)* 1·39 (1)

Compound (2)

Cu* −0·02 (1), O(1) 0·07 (1), O(2) −0·07 (1), N(1) −0·05 (1),
N(2) 0·05 (1), C(23)* 0·06 (1), C(25)* −0·08 (1),
C(24a)* 0·58 (2), C(24b)* −0·50 (2)

Plane 2

Compound (1)

Ni −0·23 (1), O(1) 0·15 (1), N(1) 0·19 (1), C(1) −0·20 (1),
C(2) 0·07 (1), C(11) 0·02 (1)

Compound (2)

(a) Cu 0·00 (1), O(1) −0·02 (1), N(1) 0·01 (1), C(1) −0·01 (1),
C(2) 0·03 (1), C(11) −0·01 (1)

(b) Cu 0·00 (1), O(2) 0·00 (1), N(2) −0·01 (1), C(12) −0·01 (1),
C(13) 0·01 (1), C(22) 0·01 (1)

Plane 3

Compound (1)

C(1) 0·03 (1), C(2) −0·04 (1), C(3) −0·01 (1), C(4) 0·02 (1),
C(5) 0·01 (1), C(6) 0·01 (1), C(7) −0·02 (1), C(8) −0·01 (1),
C(9) −0·01 (1), C(10) 0·03 (1)

Compound (2)

(a) C(1) 0·07 (1), C(2) −0·02 (1), C(3) −0·06 (1), C(4) 0·03 (1),
C(5) 0·01 (1), C(6) 0·01 (1), C(7) 0·02 (1), C(8) −0·04 (1),
C(9) −0·02 (1), C(10) 0·01 (1)

(b) C(12) 0·02 (1), C(13) −0·02 (1), C(14) −0·02 (1),
C(15) 0·00 (1), C(16) 0·02 (1), C(17) 0·00 (1), C(18) 0·00 (1),
C(19) −0·03 (1), C(20) −0·01 (1), C(21) 0·05 (1)

Angles between metallocycle planes

In (1) angle between plane 2 and the symmetry-related plane is
37·0 (1)°

In (2) angle between plane (2a) and (2b) is 6·1 (1)°

larger than the comparable distances of 1·829 Å (mean
Ni—O) and 1·859 Å (mean Ni—N) in N,N'-
ethylenebis(salicylideneiminato)nickel (Shkol'nikova,
Yumal, Shugam & Voblikova, 1970) and 1·849 (2) Å
(mean Ni—O) and 1·840 (2) Å (mean Ni—N) for
N,N'-ethylenebis[(2-hydroxy-1-naphthyl)methanimina-
to]nickel(II) (Akhtar, 1981), though unlike the
latter structure the Ni—N length in the present case is
larger than the Ni—O distance. The Ni—N distance in
(1) is of the same order as reported for the other
diamagnetic Ni^{II} complexes [Cambridge Crystallo-
graphic Data Centre (1981) files]. In (2) the Cu—O
distances of 1·904 (11) and 1·917 (10) Å are similar to
values found in analogous structures. The Cu—N
distances of 1·989 (12) and 1·971 (13) Å are longer
than the Cu—O distances and a similar difference was
noted in the structure of bis(N-methylsalicylidene-
iminato)copper (Lingafelter, Simmons, Morosin,
Scheringer & Freiburg, 1961). The slight increase in
metal to nitrogen bond lengths in (1) and (2) may be
attributed to the steric hindrance of the bulkier
trimethylene group between the N atoms.

There are some major differences between tne con-
formations of the two molecules. These are observed
in the metal coordination sphere, the six-membered
rings and in the fold between the two halves of the
molecule. In (1) the four donor atoms are perforce
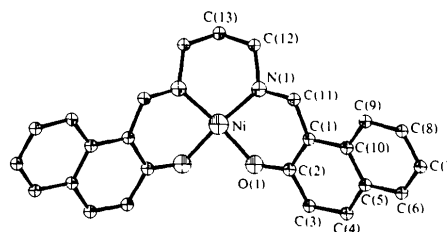planar with the Ni atom 0·02 (1) Å above the basal

Fig. 1. The structure of (1).

Discussion

Both structures contain discrete molecules. The struc-
tures of (1) and (2) are shown in Figs. 1 and 2
respectively together with the atomic-numbering
scheme. In both structures the molecules have the *cis*
form as imposed by the geometry of the tetradentate
ligand and the coordination of the metal atom is square
planar. In (1) the two parts of the molecule are related
by the mirror plane passing through Ni and C(13). The
angle subtended at the metal atom in the metallocycle
[*i.e.* N(1)—Ni—O(1)] is 91·2 (3)° and in the tri-
methylene bridging moiety [*i.e.* angle N(1)—Ni—N(1¹)]
is 94·9 (3)°. Corresponding angles in (2) are 90·3 (5),
90·7 (5) and 98·7 (5)°. The two bond lengths Ni—O
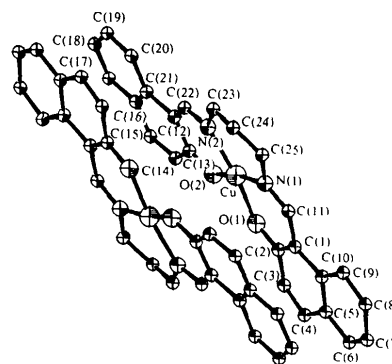1·866 (6) and Ni—N 1·871 (8) Å are both slightly

Fig. 2. The structure of (2). The two molecules are weakly
associated across a centre of symmetry.

ONNO plane. In (2), however, O(1) and N(2) are 0·07 (1) and 0·05 (1) Å above the plane while O(2) and N(1) are 0·07 (1) and 0·05 (1) Å below the plane so as to give a slight tetrahedral distortion. The C—O, C—N and C—C bond lengths are as expected in both molecules. A further difference between the two molecules is observed in the deviations of atoms from the metallocycle plane. The maximum deviation of an atom from the six-atom plane is −0·23 (1) Å for Ni in (1). In (2) this ring is far more planar, the maximum deviation being only 0·03 (1) Å. The average C—C distance in the naphthyl ring is 1·415 Å in (1) and 1·393 and 1·399 Å in (2). The sum of the valence angles at the N atoms is 360° in both structures, indicating planar configuration corresponding to sp^2 hybridization. The angles at the trimethylene C atoms are C(12) 115·7 (10) and C(13) 113·7 (12)° indicating a small deviation from regular tetrahedral configuration. The deviations of these C atoms in (1) from the NiN$_2$ plane are 0·62 (1) and 1·39 (1) Å respectively giving the expected chair conformation. In (2), on the other hand, the trimethylene C(24) is disordered and the two constituent positions C(24a) and C(24b) are 0·55 (1) and −0·54 (1) Å from the CuN$_2$ plane, while C(23) and C(25) are only 0·00 (1) and −0·06 (1) Å from the plane. The angles at the C atoms range between 113·8 (2) and 124·0 (3)° and bond lengths between 1·23 (4) and 1·58 (4) Å. The smallest and largest values involve the disordered C(24). The difference in this metallocycle ring conformation is related to the different angle of fold in the two molecules. This angle is defined as the angle between the two planes numbered (2) in Table 5 for each molecule and is 37·0 (1)° in [NiL] and 6·1 (1)° in [CuL]. These differences are due, we believe, to the variations in packing in the two structures.

The packing diagram for (1) is shown in Fig. 3 in the **b** projection. The structure is made up of molecules parallel to **c** which are stacked with each Ni atom almost directly above the other. The closest Ni···Ni approach is 4·07 (1) Å and there is an infinite Ni···Ni···Ni chain along **c**. The arrangement is similar to the chain in bis(dimethylglyoximato)nickel (Godycki & Rundle, 1953) and a copper chain in bis(N-methylsalicylideneiminato)copper (Lingafelter *et al.*, 1961) though the Ni···Ni distance in (1) is much
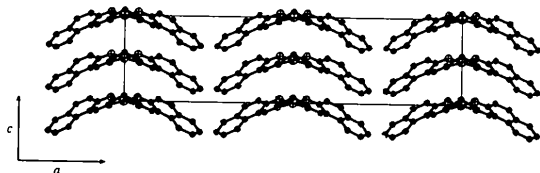
longer than the values 3·25 and 3·33 Å in these chains. The complex is diamagnetic and the metal···metal interaction is too weak to affect the magnetic properties of the compound. There are only six close contacts less than 3·75 Å between non-H atoms.*

The structure (2) is also monomeric but the molecules are associated as centrosymmetric pairs with a Cu···Cu distance of 3·613 (3) Å. The arrangement is in contrast to the dimeric structure of N,N'-ethyl-enebis(salicylideneiminato)copper (Hall & Waters, 1960) where the dimers are formed by fairly strong Cu—O bonds of 2·43 Å and each Cu atom is five-coordinate with a pyramidal arrangement of ligands. The metal–metal interaction in this compound is similar to those in dimeric N,N'-ethylenebis(sali-cylideneiminato)nickel (3·21 Å) (Shkol'nikova *et al.*, 1970) and N,N'-ethylenebis[(2-hydroxy-1-naphthyl)-methaniminato]nickel(II) (3·324 Å) (Akhtar, 1981). The direction of the Cu···Cu interaction in the dimer makes an angle of 81·6 (1)° with the coordination plane which is comparable to the values 75 and 76° in the aforementioned two nickel structures.

The two metallocycles in [CuL] are planar within experimental error. The angle between these planes is 6·1 (1)° and the effect of this distortion appears to permit the formation of the weak Cu···Cu interaction and at the same time to minimize interactions between separate molecules. This dimeric interaction, illustrated in Fig. 2, over a centre of symmetry is only possible with relatively planar molecules and this we believe to be the cause of the unexpected planar structure of (2) with its strained trimethylene bridge. The crystal packing of (2) as shown by the density of 1·50 *vs* 1·43 g cm^{-3} in (1) is much more efficient, no doubt helped by the Me$_2$SO. There are 33 interactions less than 3·70 Å in the unit cell.

The disordered Me$_2$SO group has dimensions (Table 4) which are comparable to the corresponding values in Me$_2$SO (Thomas, Shoemaker & Eriks, 1966). The S—O distance of 1·344 (23) Å is, however, considerably lower than 1·531 Å observed in Me$_2$SO and other structures in which it is a solvate. We presume the value observed here to be a consequence of the disorder and not significant. The Me$_2$SO molecules appear to perform space-filling functions only in this structure. No significant intermolecular contact exists and the packing of the molecules in (1) and (2) appears to be due to van der Waals interactions only.

Fig. 3. The unit cell of (1) in the **b** projection.

* See deposition footnote.

References

Akhtar, F. (1981). *Acta Cryst.* B37, 84–88.
Cambridge Crystallographic Data Centre (1981). February update. Univ. Chemical Laboratory, Lensfield Road, Cambridge, England. [*Molecular Structures and Dimensions*, Vols. 1–13. Dordrecht: Reidel.]
Godycki, L. E. & Rundle, R. E. (1953). *Acta Cryst.* 6, 487–495.
Hall, D. & Waters, T. N. (1960). *J. Chem. Soc.* pp. 2644–2648.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kar, S. (1979). MSc dissertation, Jahangirnagar Univ., Savar, Dacca, Bangladesh.
Lingafelter, E. C., Simmons, G. L., Morosin, B., Scheringer, C. & Freiburg, C. (1961). *Acta Cryst.* 14, 1222–1225.
Sheldrick, G. M. (1976). *SHELX 76*. A program for crystal structure determinations. Univ. of Cambridge, England.
Shkol'nikova, L. M., Yumal, E. M., Shugam, E. A. & Voblikova, V. A. (1970). *Zh. Strukt. Khim.* 11, 886–890.
Thomas, R., Shoemaker, C. B. & Eriks, K. (1966). *Acta Cryst.* 21, 12–20.

Structural Studies on Metal Complexes of Chiral Cyclen. III.
The Structure of Chloro[(2R,5S,8R,11S)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) Chloride Chloroform Solvate

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Abstract

$[Cu(C_{44}H_{60}N_4)Cl]Cl.2CHCl_3$ is triclinic, $P\bar{1}$, with $a = 14.297$ (13), $b = 14.542$ (18), $c = 12.960$ (9) Å, $\alpha = 99.81$ (8), $\beta = 108.33$ (7), $\gamma = 85.67$ (10)°, $U = 2520$ (4) Å^3, $Z = 2$, $D_m = 1.324$, $D_c = 1.342$ Mg m^{-3}. The structure was refined to a final R of 6.4% for 4646 independent reflections. The 12-membered tetramine ring is coordinated to Cu^{II} as a quadridentate ligand, and takes a rectangular form. The Cu^{II} atom forms an approximate trigonal bipyramid with five coordination. The observed Cu–Cl distance, 2.354 (3)Å, is shorter than those found in the cyclen complexes of Cu with a square-pyramidal conformation.

Introduction

This paper is part of a series of investigations on the metal complexes of chiral cyclens.* The cyclens can be divided into four geometrical isomers, *viz* C_4, C_i, C_1 and S_4, and all the molecular structures have been determined (Sakurai, Kobayashi, Tsuboyama &

Tsuboyama, 1978*a,b*; Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979; Sakurai, Hiramatsu, Tsuboyama & Tsuboyama, 1980; Sakurai, Watanabe, Tsuboyama & Tsuboyama, 1981). These molecules form metal complexes, and the C_4 isomer has square-pyramidal coordination (Sakurai, Kobayashi, Hasegawa, Tsuboyama & Tsuboyama, 1982). Electronic absorption, circular dichroism and ESR spectra reveal that the form of the complex with the S_4 isomer is considerably different from the other three (Tsuboyama *et al.*, 1981). This paper reports the structure of the complex with the S_4 isomer.

Experimental

The Cu^{II} complex was prepared by heating a mixture of $CuCl_2 . 2H_2O$ (1 mmol) in absolute ethanol (25 ml) and tbte-($RSRS$)-cyclen (1 mmol). The heating was continued until the solvent had evaporated. By repeated recrystallization from chloroform–ethyl acetate yellow-green plate crystals were obtained.

A crystal, 0.4 × 0.4 × 0.2 mm, sealed in a glass capillary with the solvent, was used for the X-ray study. Intensity data were measured on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \le 50°$, 4646 independent reflections with $F > 3\sigma(F)$

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* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbte-($RRRR$)-cyclen: (2R,5R,8R,11R)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-cyclen; C_4 isomer: tbte-($RRRR$)-cyclen; C_i isomer: tbte-($RRRS$)-cyclen; S_4 isomer: tbte-($RSRS$)-cyclen; C_i isomer: tbte-($RRSS$)-cyclen.