

Table 1. Fractional coordinates and isotropic thermal parameters with their e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}^*(\text{\AA}^2)$
Cu(1)	0-17385 (5)	0-25†	-0-02073 (8)	2-43 (1)
Cl(1)	0-1514 (1)	0-5201 (2)	-0-0514 (2)	4-12 (4)
S(1)	0-1100 (1)	0-2223 (2)	0-2389 (2)	3-28 (3)
C(2)	0-2310 (5)	0-2819 (10)	0-3684 (8)	4-0 (2)
C(3)	0-3045 (5)	0-3503 (10)	0-2806 (8)	3-8 (2)
N(4)	0-3115 (3)	0-2582 (8)	0-1388 (5)	2-8 (1)
C(5)	0-3433 (5)	0-0858 (9)	0-1806 (8)	3-4 (1)
C(6)	0-2923 (5)	-0-0376 (9)	0-0571 (8)	3-4 (1)
N(7)	0-1854 (3)	0-0054 (7)	-0-0168 (5)	2-4 (1)
C(8)	0-1150 (5)	-0-0657 (8)	0-0710 (8)	3-1 (1)
C(9)	0-1224 (5)	-0-0012 (10)	0-2337 (8)	3-7 (2)
C(10)	0-3836 (6)	0-3427 (11)	0-0668 (9)	4-2 (2)
C(11)	0-3770 (5)	0-2846 (9)	-0-0982 (8)	3-6 (2)
O(12)	0-3010 (3)	0-2343 (8)	-0-1883 (5)	3-8 (1)
O(13)	0-4640 (3)	0-3011 (8)	-0-1342 (5)	4-6 (1)
C(14)	0-4655 (6)	0-2566 (16)	-0-2966 (9)	5-8 (2)
C(15)	0-1532 (5)	-0-0483 (9)	-0-1846 (7)	3-1 (1)
C(16)	0-0723 (5)	0-0644 (8)	-0-2707 (7)	2-8 (1)
O(17)	0-0591 (3)	0-1998 (6)	-0-2175 (5)	3-2 (1)
O(18)	0-0201 (4)	0-0080 (7)	-0-4040 (5)	3-6 (1)
C(19)	-0-0624 (6)	0-1139 (11)	-0-4929 (10)	4-8 (2)
Cl(2)	0-6502 (1)	0-2494 (3)	0-4212 (2)	4-57 (4)
O(21)	0-7045 (7)	0-2200 (14)	0-5821 (11)	11-1 (3)
O(22)	0-5555 (5)	0-2312 (27)	0-4115 (9)	18-4 (6)
O(23)	0-6778 (13)	0-4070 (17)	0-4077 (14)	17-7 (5)
O(24)	0-6817 (10)	0-1704 (23)	0-3202 (13)	12-9 (5)

* $B_{\text{eq}} = \frac{1}{3}[a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

† The *y* coordinate was fixed at 0-25 to define the origin.

0-15 × 0-16 × 0-56 mm; intensities of reflections with indices *h* -17 to 17, *k* 0 to 10, *l* 0 to 11, with $2 < 2\theta < 54^\circ$ measured, ω -2 θ scans; ω scan width (0-60 + 0-35 tan θ)°, graphite-monochromatized Mo *K* α radiation. Intensities of three reflections were measured every two hours and showed no evidence of crystal decay. 2430 reflections were measured, 2228 were unique and 1757 with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement; $R_{\text{int}} = 0-026$. Data were corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0-816, 0-759), Gaussian integration, grid 8 × 10 × 10. The systematic absences (0*k*0 absent if $k = 2n + 1$) allow the space group to be either $P2_1$ or $P2_1/m$. With $Z = 2$, the latter would require the molecule to have either mirror or inversion symmetry, and as this was unlikely, $P2_1$ was chosen and confirmed by the analysis. The coordinates of the Cu atom were determined from an analysis of the three-dimensional Patterson function and the coordinates of the remaining non-H atoms found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage of the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final rounds of calculations the H atoms were positioned on geo-

Table 2. Bond distances (Å) and bond angles (°) with their e.s.d.'s in parentheses

Cu(1)	Cl(1)	2-241 (2)	N(7)	C(15)	1-482 (7)		
Cu(1)	S(1)	2-635 (2)	C(8)	C(9)	1-489 (10)		
Cu(1)	N(4)	2-051 (4)	C(10)	C(11)	1-494 (9)		
Cu(1)	N(7)	2-010 (5)	C(11)	O(12)	1-211 (7)		
Cu(1)	O(12)	2-554 (4)	C(11)	O(13)	1-323 (7)		
Cu(1)	O(17)	2-058 (4)	O(13)	C(14)	1-465 (9)		
S(1)	C(2)	1-829 (7)	C(15)	C(16)	1-495 (9)		
S(1)	C(9)	1-841 (8)	C(16)	O(17)	1-234 (7)		
C(2)	C(3)	1-523 (10)	C(16)	O(18)	1-287 (7)		
C(3)	N(4)	1-471 (8)	O(18)	C(19)	1-484 (9)		
N(4)	C(5)	1-496 (9)	Cl(2)	O(21)	1-431 (9)		
N(4)	C(10)	1-476 (9)	Cl(2)	O(22)	1-297 (7)		
C(5)	C(6)	1-513 (9)	Cl(2)	O(23)	1-360 (14)		
C(6)	N(7)	1-495 (7)	Cl(2)	O(24)	1-255 (11)		
N(7)	C(8)	1-498 (8)					
Cl(1)	Cu(1)	S(1)	96-94 (7)	C(5)	C(6)	N(7)	112-3 (5)
Cl(1)	Cu(1)	N(4)	97-2 (2)	Cu(1)	N(7)	C(6)	107-9 (4)
Cl(1)	Cu(1)	N(7)	174-0 (1)	Cu(1)	N(7)	C(8)	109-7 (4)
Cl(1)	Cu(1)	O(12)	94-4 (2)	Cu(1)	N(7)	C(15)	106-1 (4)
Cl(1)	Cu(1)	O(17)	92-5 (1)	C(6)	N(7)	C(8)	112-7 (5)
S(1)	Cu(1)	N(4)	82-9 (1)	C(6)	N(7)	C(15)	111-7 (5)
S(1)	Cu(1)	N(7)	86-6 (1)	C(8)	N(7)	C(15)	108-4 (5)
S(1)	Cu(1)	O(12)	155-9 (1)	N(7)	C(8)	C(9)	116-7 (5)
S(1)	Cu(1)	O(17)	110-0 (1)	S(1)	C(9)	C(8)	113-1 (5)
N(4)	Cu(1)	N(7)	88-0 (2)	N(4)	C(10)	C(11)	112-0 (5)
N(4)	Cu(1)	O(12)	74-6 (2)	C(10)	C(11)	O(12)	124-2 (6)
N(4)	Cu(1)	O(17)	162-8 (2)	C(10)	C(11)	O(13)	110-9 (6)
N(7)	Cu(1)	O(12)	84-1 (2)	O(12)	C(11)	O(13)	124-8 (6)
N(7)	Cu(1)	O(17)	81-7 (2)	Cu(1)	O(12)	C(11)	102-8 (4)
O(12)	Cu(1)	O(17)	90-6 (2)	C(11)	O(13)	C(14)	116-0 (5)
Cu(1)	S(1)	C(2)	93-1 (2)	N(7)	C(15)	C(16)	108-0 (5)
Cu(1)	S(1)	C(9)	90-6 (2)	C(15)	C(16)	O(17)	122-0 (5)
C(2)	S(1)	C(9)	101-8 (3)	C(15)	C(16)	O(18)	114-0 (5)
S(1)	C(2)	C(3)	114-2 (5)	O(17)	C(16)	O(18)	124-0 (6)
C(2)	C(3)	N(4)	115-2 (6)	Cu(1)	O(17)	C(16)	109-6 (4)
Cu(1)	N(4)	C(3)	109-7 (4)	C(16)	O(18)	C(19)	116-1 (5)
Cu(1)	N(4)	C(5)	107-4 (4)	O(21)	Cl(2)	O(22)	108-3 (6)
Cu(1)	N(4)	C(10)	109-7 (4)	O(21)	Cl(2)	O(23)	99-0 (7)
C(3)	N(4)	C(5)	111-0 (5)	C(11)	Cl(2)	O(24)	114-1 (1)
C(3)	N(4)	C(10)	108-1 (6)	O(22)	Cl(2)	O(23)	114-1 (1)
C(5)	N(4)	C(10)	111-0 (5)	O(22)	Cl(2)	O(24)	115-1 (1)
N(4)	C(5)	C(6)	113-8 (5)	O(23)	Cl(2)	O(24)	106-1 (1)

metrical grounds (C—H 0-95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 5-0 Å². The final cycle of refinement on *F* included 234 variable parameters, $R = 0-043$, $wR = 0-054$, goodness-of-fit 1-37, $w = 1/[\sigma^2(F_o) + 0-040(F_o)^2]$. Max. shift/e.s.d. = 0-11; extreme values in final difference map $\pm 0-95 e \text{ \AA}^{-3}$ adjacent to the markedly anisotropic perchlorate counterion. As the copper complex of (1) is chiral, refinement calculations were performed with the opposite hand. The model corresponding to the absolute stereochemistry indicated had *R* factors that were lower than that of the enantiomer ($R = 0-053$, $wR = 0-065$). The coordinates and molecular diagram refer to this absolute stereochemistry. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983). Atomic coordinates and details of molecular geometry are given in

Tables 1 and 2.* Fig. 1, prepared using ORTEPII (Johnson, 1976), shows details of the cation structure and copper coordination.

Discussion. The copper coordination geometry is distorted octahedral with longer bonds to the axial O(12) and S(1) atoms. The macrocyclic ring adopts a rather strained [333] conformation (Dale, 1973, 1974; Boeyens & Dobson, 1987) as evidenced in the 'non-ideal' torsional angles about C(6) (Fig. 1). The alternative [234] conformation is energetically less stable by about 12–20 kJ mol⁻¹ (Dobson, 1986) but may be preferred by those metal ions which do not accept facial symmetrical coordination – such as Cu^{II} and Pt^{II}. Related macrocyclic Cu^{II} complexes with the unfunctionalized nine-membered N₂S ligand have been reported (Dobson, 1986; Boeyens, Dobson & Hancock, 1985) in both of which the macrocycle adopts a [234] conformation. This [234] con-

formation is common for mixed-donor nine-membered macrocyclic ligands that may interact asymmetrically with metal ions that cannot accept symmetrical facial coordination.

We thank SERC and Celltech Ltd for support and NSERC for continuing support *via* operating grants.

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* Lists of structure factors, thermal parameters, calculated H-atom coordinates and all torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51978 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1989). **C45**, 1500–1503

Structures of *trans*-Cyanobis(dimethylglyoximato)pyridinecobalt(III) Hemihydrate and *trans*-Cyclohexylbis(dimethylglyoximato)(1,5,6-trimethylbenzimidazole)cobalt(III)

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(Received 5 December 1988; accepted 13 February 1989)

Abstract. (I) [Co(CN)(C₄H₇N₂O₂)₂(C₅H₅N)].0.5H₂O, *M_r* = 403.3, monoclinic, *P*2₁/*m*, *a* = 7.564 (1), *b* = 13.950 (1), *c* = 8.653 (1) Å, β = 98.20 (1)°, *V* = 903.7 (3) Å³, *Z* = 2, *D_x* = 1.48 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 9.2 cm⁻¹, *F*(000) = 418, *T* = 295 (1) K, *R* = 0.027 for 1815 unique observed

reflections. (II) [Co(C₆H₁₁)(C₄H₇N₂O₂)₂(C₁₀H₁₂N₂)], *M_r* = 532.5, monoclinic, *P*2₁/*n*, *a* = 17.133 (2), *b* = 8.566 (1), *c* = 19.369 (3) Å, β = 115.36 (3)°, *V* = 2568.6 (9) Å³, *Z* = 4, *D_x* = 1.37 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 7.0 cm⁻¹, *F*(000) = 1128, *T* = 295 (1) K, *R* = 0.044 for 3290 unique observed reflections. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—N distances of 1.995 (2) and 1.937 (2) Å in

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