The Structure of a Conformationally Strained Macrocyclic Copper(II) Complex with Dimethyl 1-Thia-4,7-diaza-4,7-cyclononanediacetate

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Abstract. Chloro(dimethyl 1-thia-4,7-diaza-4,7cyclononanediacetate)copper(II) perchlorate, [Cu- $(C_{12}H_{22}N_2O_4S)Cl]ClO_4$, $M_r = 488.83$, monoclinic, $P_{2_1, a} = 13.808$ (2), b = 8.195 (2), c = 8.702 (2) Å, β = 104.68 (2)°, V = 952.5 (7) Å³, Z = 2, $D_x = 1.70$ g cm⁻³, λ (Mo K α) = 0.71073 Å, $\mu = 15.8$ cm⁻¹, F(000) = 502, T = 294 K, R = 0.043 for 1757 observed reflections. The Cu ion has a Jahn-Teller distorted octahedral coordination geometry: the Cu ion is bound strongly to the two N atoms [Cu-N(7)]2.010 (5), Cu-N(4) 2.051 (4) Å], the Cl ion [Cu-Cl(1) 2.241 (2) Å] and one of the ester O atoms [Cu-O(17) 2.058 (4) Å], but is only weakly bound to the S atom [Cu-S(1) 2.635(2) Å] and to the carbonyl O atom [Cu—O(12) 2.554 (4) Å] trans to S(1). The nine-membered macrocyclic ring adopts a rather strained conformation to accommodate the geometric and donor-atom preference of the copper(II) ion.

Introduction. During the course of studies of the coordination chemistry of mixed donor atom medium-ring macrocyclic ligands, the 1-thia-4,7-diazacyclononane derivative (1) was prepared. This ligand with five potential donors was complexed with copper(II) ions and the structure of the copper complex determined. Although there have been many structural determinations of transition-metal complexes with 9-N₃, 9-S₃ and 9-N₂S ligands, none has been reported for functionalized derivatives of the 9-N₂S ring system (Boeyens & Dobson, 1987). In the reported structures with 9-ring macrocyclic ligands, the macrocyclic ring tends to adopt preferentially a low-energy [333] conformation (Dale, 1974; Boeyens & Dobson, 1987).

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Experimental. The ligand was prepared by cyclization of ethylene glycol ditosylate with N,N'-thiodiethylene bis(toluenesulfonamide) in dimethylformamide in the presence of caesium carbonate, followed detosylation bv (HBr/AcOH/PhOH). alkylation (ClCH₂CO₂H/LiOH) and esterification (MeOH/H⁺). Blue monoclinic crystals of the title complex were grown by slow evaporation of a methanol solution containing LiCl. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a leastsquares treatment of the setting angles of 25 reflections in the range $8 < \theta < 20^{\circ}$. Crystal dimensions



Fig. 1. ORTEP diagram (Johnson, 1976) with the atomnumbering scheme and torsional angles (°) for the ninemembered ring. Non-H-atom ellipsoids are at the 50% probability level.

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Table	l. Fractio	nal coord	dinates d	and	isotropic	thermal
ра	arameters	with the	ir e.s.d.'.	s in	parenthe	ses

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

	x	у	Z	$B_{eq}^{*}(\text{Å}^2)$
Cu(1)	0.17385 (5)	0.225	-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 1 3 8 (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)

* $B_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + b^2B_{22} + b^2B_{22} + b^2B_{23} + b^2B_{23}$ $bc(\cos\alpha)B_{23}].$

 \dagger The y coordinate was fixed at 0.25 to define the origin.

 $0.15 \times 0.16 \times 0.56$ 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, $\omega - 2\theta$ scans; ω scan width (0.60 + $0.35 \tan\theta^{\circ}$. graphite-monochromatized Μο Κα 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; $R_{int} = 0.026$. Data were corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0.816, 0.759), Gaussian integration, grid $8 \times 10 \times 10$. The systematic absences (0k0 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-

Cu(1) Cu(1) Cu(1) Cu(1) Cu(1) Cu(1) S(1) S(1) C(2) C(3) N(4) N(4) C(5) C(6)	Cl(1) S(1) N(4) N(7) O(12) O(17) C(2) C(9) C(3) N(4) C(5) C(10) C(6) N(7)	2:241 (2:635 (2:051 (2:054 (2:058 (1:829 (1:841 (1:523 (1:471 (1:496 (1:476 (1:513 (1:495 (2) 2) 4) 5) 5) 4) 4) 7) 8) 10) 8) 9) 9) 9) 9) 9) 7)	N(7) C(8) C(10) C(11) O(13) C(15) C(16) C(16) C(16) C(16) C(16) C(12) C(2) C(2) C(2)	C(15) C(9) C(11) O(12) O(13) C(14) C(16) O(17) O(18) C(19) O(21) O(22) O(23) O(24)	1-482 (1-489 (1-494 (1-211 (1-323 (1-465 (1-465 (1-234 (1-287 (1-287 (1-484 (1-297 (1-360 (1-255 (7) 10) 9) 7) 7) 9) 9) 9) 7) 7) 7) 9) 9) 7) 14) 11)
N(7) Cl(1) Cl(1) Cl(1)	C(8) Cu(1) Cu(1)	1·498 (S(1) N(4) N(7)	8) 96·94 (7) 97·2 (2) 174·0 (1)	C(5) Cu(1) Cu(1)	C(6) N(7) N(7)	N(7) C(6) C(8)	112·3 (5) 107·9 (4) 109·7 (4)
CI(1)	Cu(1) Cu(1)	O(12)	94·4 (2) 92·5 (1)	Cu(1) Cu(1)	N(7)	C(15)	109.7 (4) 106.1 (4) 112.7 (5)
S(1)	Cu(1) Cu(1)	N(4)	82·9 (1)	C(6)	N(7)	C(15)	111.7 (5)
S(1) S(1)	Cu(1) Cu(1)	O(12)	155.9 (1)	N(7)	C(8)	C(9)	116.7 (5)
S(1) N(4)	Cu(1) Cu(1)	O(17) N(7)	110·0 (1) 88·0 (2)	S(1) N(4)	C(9) C(10)	C(8)	113·1 (5) 112·0 (5)
N(4)	Cu(1)	O(12)	74·6 (2)	C(10)	C(10)	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)	0(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) S(1)	C(9)	90.0 (2)	C(15)	C(16)	O(17)	122.0 (5)
S(1)	C(2)	C(3)	101.8(3) 114.2(5)	0(17)	C(10)	0(18)	124.0 (5)
C(2)	C(3)	N(4)	1152(6)	$C_{\rm D}(1)$	O(17)	C(16)	109.6 (4)
$\tilde{Cu}(1)$	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)	O(21)	Cl(2)	O(24)	114 (1)
C(3)	N(4)	C(10)	108·1 (6)	O(22)	Cl(2)	O(23)	114 (1)
C(5)	N(4)	C(10)	111.0 (5)	O(22)	Cl(2)	O(24)	115 [,] (1)
N(4)	C(5)	C(6)	113.8 (5)	O(23)	Cl(2)	O(24)	106. (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 ± 0.95 e Å⁻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 'nonideal' 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] conformation is common for mixed-donor ninemembered macrocyclic ligands that may interact asymmetrically with metal ions that cannot accept symmetrical facial coordination.

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

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Abstract. (I) $[Co(CN)(C_4H_7N_2O_2)_2(C_5H_5N)].0.5H_2O$, $M_r = 403.3$, monoclinic, $P2_1/m$, a = 7.564 (1), b = 13.950 (1), c = 8.653 (1) Å, $\beta = 98.20$ (1)°, V = 903.7 (3) Å³, Z = 2, $D_x = 1.48$ g cm⁻³, λ (Mo K α) = 0.7107 Å, $\mu = 9.2$ cm⁻¹, F(000) = 418, T = 295 (1) K, R = 0.027 for 1815 unique observed

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reflections. (II) $[Co(C_6H_{11})(C_4H_7N_2O_2)_2(C_{10}H_{12}N_2)], M_r = 532.5$, monoclinic, $P2_1/n$, a = 17.133 (2), b = 8.566 (1), c = 19.369 (3) Å, $\beta = 115.36$ (3)°, V = 2568.6 (9) Å³, Z = 4, $D_x = 1.37$ g cm⁻³, λ (Mo Ka) = 0.7107 Å, $\mu = 7.0$ 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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^{*} 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.