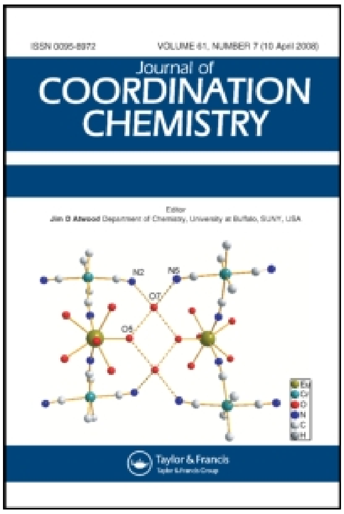

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CHIRAL METAL COMPLEXES. 45*. THE STRUCTURE OF CHLORO-{6*S*,15*S*-(4*R*,13*R*-DIMETHYL)-1,5,10,14 TETRAAZATRICYCLO-[13,3,1,$1^{6,10}$]EICOSANE}COPPER(II)

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NOTE

CHIRAL METAL COMPLEXES. 45*. THE STRUCTURE OF CHLORO-{6*S*,15*S*-(4*R*,13*R*-DIMETHYL)-1,5,10,14 TETRAAZATRICYCLO-[13,3,1,$1^{6,10}$]EICOSANE}COPPER(II)

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The crystal and molecular structure of chloro-{6*S*,15*S*-(4*R*,13*R*-dimethyl)-1,5,10.14-tetraazatricyclo[13,3,1,$1^{6,10}$]eicosane}copper(II)perchlorate, [Cu(*S*-mac6)Cl]ClO_4, has been determined by X-ray analysis. Crystal data: $C_{18}H_{36}N_4O_4Cl_2Cu$ is orthorhombic, space group $P2_12_12_1$, a = 11.915(2), b = 12.290(2), c = 15.705(6) Å Z = 4. The structure was refined by full-matrix least-squares procedures to $R = 0.040$ for 2477 unique non-zero ($I > 1.5\sigma(I)$) reflections and with η = 1.02(7) confirming the absolute configurations of the chiral centres. The N_4 macrocycle coordinates to the copper atom in a square-planar arrangement with Cu-N_{sec} of 2.005(5) and Cu-N_{tert} of 2.060(4) Å, and a square-based pyramidal geometry is completed by a chloride ion, Cu-Cl 2.711(2)Å. Folding of the non-chelate six-membered rings produces a conformation such that only one face of the complex ion is available for axial coordination of unidentate ligands.

KEYWORDS: X-ray analysis, Cu(II) complex, chiral macrocycle, steric crowding

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*Part 44 is R.R. Fenton, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta*, submitted for publication.

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INTRODUCTION

In continuance of our studies on the stereochemical features of $Me_{12}[14]ane\text{-}N_4$ ligands[1] we report here the crystal structure of chloro-{6*S*,15*S*-(4*R*,13*R*-dimethyl)-1,5,10,14-tetraazatricyclo [13,3,1,$1^{6,10}$]eicosane}copper(II) perchlorate,[Cu(*S*-mac6) Cl] ClO_4, in which propyl 'straps' are appended in the 6,8- and 13,1-positions of the [14]ane-N_4macrocycle.

EXPERIMENTAL

The complex was synthesized using a method described previously.[1]

Crystal Data

$C_{18}H_{36}N_4O_4Cl_2CU$; $M_r = 506.95$; orthorhombic; $a = 11.915(2)$, $b = 12.290(2)$, $c = 15.705(6)$ Å; $U = 2299.8$ Å^3; $Z = 4$; $D_c = 1.464$ g cm^{-3}; $F(000) = 1068$; μ(Mo-Kα) = 12.15 cm^{-1}; space group $P2_12_12_1$ (No. 19).

Data for the complex were collected at 298 K on an Enraf-Nonius FAST area detector diffractometer using documented procedures.[2] Unit cell parameters were determined from reflections in the range $1.5 < \theta < 25.0°$ *via* the REFINE procedure of MADNES software.[3] Intensities for 8839 reflections in the range $2.4 < \theta < 30.0°$ with indices *h*-16 to 15, *k* −15 to 15, *l* 0 to 20 were measured. These generate a unique data set of 5253 reflections of which 2477 have $I > 1.5\ \sigma(I)(R_{int} = 0.029)$ and these were used for the structure determination. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods. Approximate positions for hydrogen atoms were obtained from difference maps and their positions were optimised assuming C,N-H to be 1.0 Å. After isotropic refinement absorption corrections (max = 1.256, min = 0.874) were applied using the DIFFABS procedure.[4] Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and unit weight for each reflection. Refinement was terminated when the shift in any parameter was $<0.1\sigma$. The final values for R and R' $\{(= \Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}\}$ were 0.040 and 0.050, respectively, and with $\eta = 1.02(7)$ confirming the configurations of the chiral centres. A final difference map showed no unusual features with density maxima $<|1.4|$ e Å^{-3}.

Final refinement calculations were carried out on a FACOM M350S computer using programs written by F.S.S. Neutral atom scattering factors, corrected for anomalous dispersion were taken from International Tables for X-ray Crystallography.[5]

DISCUSSION

A stereo-view[6] of the complex cation showing the atom labelling scheme is shown in Figure 1. Final atomic coordinates for the non-hydrogen atoms and a list of selected bond lengths and angles are given in Tables 1 and 2, respectively.

The N_4 macrocycle coordinates to copper atom in a square-planar arrangement with Cu-N_{sec} of 2.005(5) and Cu-N_{tert} of 2.060(4) Å, and a square-based pyramidal geometry is completed by a chloride ion, Cu-Cl 2.711(2) Å. That this latter distance

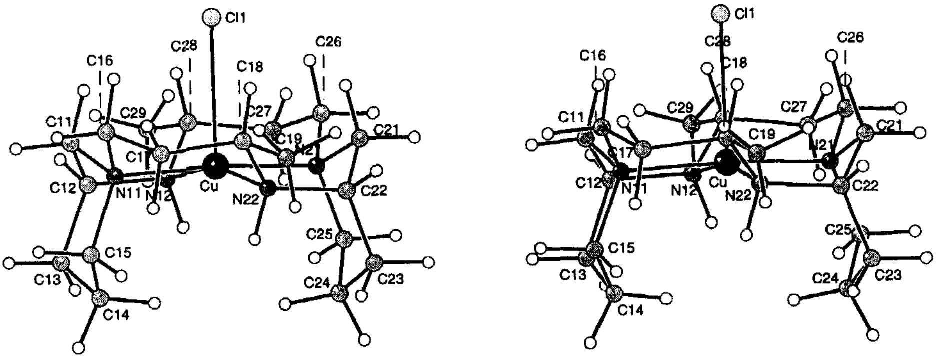

Figure 1 A stereo-view of the complex cation showing atom labelling.

is rather long is a consequence of steric effects generated by the hydrogen atoms attached to carbon atoms C(*n*1), C(*n*6) and C(*n*8). The copper atom lies 0.18 Å above the N_4 plane towards the apical chlorine atom; the deviations of the nitrogen atoms from this plane are 0.12 Å. for N_{sec} and -0.12 Å for N_{tert}.

Table 1 Final Atomic Coordinates (fractional 10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x/a	*y/b*	*z/c*	*Beq*
Cu	35.4(10)	4345.8(6)	8612.5(4)	3.0
Cl1	-64(3)	2148(1)	8480(1)	4.9
N11	1628(6)	4281(6)	9034(4)	3.6
N12	699(6)	4676(5)	7437(4)	3.1
N21	-1541(6)	4507(5)	8200(4)	3.5
N22	-615(6)	4503(5)	9829(4)	3.9
C11	2223(8)	3866(8)	8266(6)	4.6
C12	1947(8)	4629(7)	7539(5)	4.0
C13	2424(7)	5754(9)	7724(6)	4.3
C14	1964(8)	6179(7)	8561(6)	4.2
C15	2122(8)	5371(8)	9269(6)	4.4
C16	1785(9)	3474(8)	9753(5)	4.9
C17	1056(10)	3729(8)	10524(5)	5.2
C18	-220(10)	3660(7)	10421(5)	4.8
C19	-794(10)	3757(9)	11312(6)	6.8
C21	-2187(8)	4015(8)	8905(6)	4.8
C22	-1856(8)	4613(8)	9727(5)	4.4
C23	-2190(8)	5779(9)	9674(6)	5.2
C24	-1679(8)	6344(8)	8884(6)	4.6
C25	-1898(7)	5685(8)	8086(6)	4.2
C26	-1764(9)	3880(8)	7405(5)	4.8
C27	-1046(9)	4209(8)	6664(5)	4.6
C28	241(9)	3992(6)	6747(4)	3.7
C29	824(10)	4211(8)	5882(5)	6.0
Cl2	221(2)	-2807(2)	11324(1)	4.7
O2a	110(12)	-1666(6)	11323(6)	11.2
O2b	-684(10)	-3269(12)	11654(11)	18.0
O2c	1160(9)	-3017(12)	11747(7)	13.9
O2d	377(12)	-3158(9)	10491(6)	13.6

Table 2 Selected Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

Distances (Å)			
	Cu-Cl(1) 2.711(2)		
		$n = 1$	$n = 2$
	Cu-N(n1)	2.012(7)	1.997(7)
	Cu-N(n2)	2.049(6)	2.071(6)
	N(n1)-C(n1)	1.490(10)	1.478(10)
	N(n1)-C(n5)	1.508(12)	1.519(12)
	N(n1)-C(n6)	1.514(10)	1.490(10)
	N(n2)-C(n2)	1.496(12)	1.494(11)
	N(*n*2)-C(*n*± *19*)	1.476(9)	1.469(10)
	C(n1)-C(n2)	1.513(12)	1.537(13)
	C(n2)-C(n3)	1.522(13)	1.490(14)
	C(n3)-C(n4)	1.517(12)	1.546(13)
	C(n4)-C(n5)	1.503(12)	1.515(12)
	C(n6)-C(n7)	1.523(13)	1.499(13)
	C(n7)-C(n8)	1.531(15)	1.562(14)
	C(n8)-C(n9)	1.563(12)	1.550(11)

Angles(°)			
N(11)-Cu-N(21)	176.5(3)	N(12)-Cu-N(22)	163.2(2)
N(11)-Cu-N(22)	93.0(3)	N(12)-Cu-N(21)	92.9(3)
N(11)-Cu-N(12)	86.6(3)	N(21)-Cu-N(22)	86.5(3)
N(11)-Cu-Cl(1)	91.6(2)	N(21)-Cu-Cl(1)	91.9(2)
N(12)-Cu-Cl(1)	98.3(2)	N(22)-Cu-Cl(1)	98.5(2)

The five-membered chelate rings have δ conformations and the six-membered rings adopt chair conformations. The other two six-membered rings, formed by the propyl 'straps', are folded down so as to effectively block the potential sixth site of the copper atom, a situation dictated by the chirality of the carbon atoms C(6) and C(15). This structural arrangement closely parallells that found in the related docosane complex[1] in which seven-membered rings are formed using butyl 'straps'. A full discussion of the structural and steric features of present and related coordinated ligands will appear elsewhere.

In the crystal, weak hydrogen bonds between the NH groups and the chloride ion and perchlorate oxygen atoms are evident and the details of these, together with the closest non-bonded contacts, are given in Table 3.

Table 3 Contact Distances (Å) with Estimated Standard Deviations in Parentheses.

a) Proposed Hydrogen Bonding*			
N(12)....Cl(1^{I})	3.446(6)	N(22)....O($2d^{II}$)	3.276(12)
b) Intermolecular Distances <3.5Å*			
C(11)....O($2c^{III}$)	3.239(16)	C(15)....O($2d^{II}$)	3.357(14)
C(12)....O($2c^{III}$)	3.250(16)	C(24)....O($2c^{IV}$)	3.440(14)
C(26)....O($2b^{V}$)	3.346(17)		

*Roman numeral superscripts refer to the following equivalent positions relative to x, y, z:

I -x, 1/2 + y, 3/2 - z
II x, 1 + y, z
III 1/2 - x, -y, z - 1/2
IV x -1/2, 1/2 - y, 2 - z
V -1/2 - x, -y, z - 1/2

SUPPLEMENTARY MATERIAL

Lists of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom coordinates and a comprehensive table of bond lengths and angles are available from the authors upon request.

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References

1. R. Edwards, P.D. Newman, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta,* **204,** 125 (1993).
2. A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J.Chem. Soc., Dalton Trans.,* 1855 (1991).
3. MADNES VERSION 11-SEP-1989, J.W. Pflugrath and A. Messerschmidt, Distributed by Enraf-Nonius, Delft (1989).
4. N.P.C. Walker and D. Stuart, *Acta Cryst.,* **A39**, 158 (1983).
5. *International Tables for X-ray Crystallography,*(Kynoch, Birmingham, UK, 1974), Vol. IV, pp. 72–79,149.
6. R.S. Vagg, *3D-MOL,* integrated microcomputer programs for molecular graphics Macquarie University (1993).