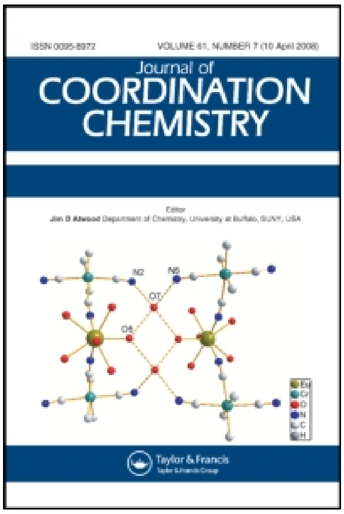

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CHIRAL METAL COMPLEXES. 46*. THE STRUCTURE OF {6*S*,14*S*-(4*R*,12*R*-DIMETHYL)-1,5,9,13-TETRAAZATRICYCLO-[12,2,1,1^{6,9}]OCTADECANE}PERCHLORATO-COPPER(II) PERCHLORATE

Robert J. Lancashire[a]; Paul D. Newman[b]; Frederick S. Stephens[c]; Robert S. Vagg[c]; Peter A. Williams[d]
[a] Department of Chemistry, University of the West Indies, Mona, Kingston, Jamaica [b] School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff, Wales, U.K. [c] School of Chemistry, Macquarie University, NSW, Australia [d] Department of Chemistry, University of Western Sydney, Kingswood, NSW, Australia

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NOTE

CHIRAL METAL COMPLEXES. 46*. THE STRUCTURE OF {6*S*,14*S*-(4*R*,12*R*-DIMETHYL)-1,5,9,13-TETRAAZATRICYCLO-[12,2,1,$1^{6,9}$]OCTADECANE}PERCHLORATO-COPPER(II) PERCHLORATE

ROBERT J. LANCASHIRE

Department of Chemistry, University of the West Indies, Mona, Kingston, Jamaica

PAUL D. NEWMAN

School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, Wales, U.K.

FREDERICK S. STEPHENS, ROBERT S. VAGG**

School of Chemistry, Macquarie University, NSW 2109, Australia

and PETER A. WILLIAMS**

Department of Chemistry, University of Western Sydney, Nepean, P.O. Box 10, Kingswood, NSW 2747, Australia

(Received August 30, 1994)

The crystal and molecular structure of {6*S*,14*S*-(4*R*,12*R*-dimethyl)-1,5,9,13-tetraazatricyclo[12,2,1,$1^{6,9}$]-octadecane}perchloratocopper(II) perchlorate, [Cu(*S*-mac5)ClO_4]ClO_4 has been determined by X-ray analysis. Crystal data: $C_{16}H_{32}N_4O_8Cl_8Cl_2Cu$ is monoclinic, space group $P2_1$, a = 11.340(3), b = 13.713(2), c = 15.002(1) Å, β = 97.13(1)°, Z = 4. The structure was refined by full-matrix least-squares procedures to R = 0.056 for 3494 non-zero ($I > 2\sigma(I)$) reflections and with η = 1.03(11) confirming the configurations at the chiral centres. The two independent cations are structurally equivalent with the N_4 macrocycle coordinating to the copper atom in a square-planar arrangement with Cu-N_{sec} of 1.988(6) and Cu-N_{tert} of 2.019(5) Å, and a square-based pyramidal geometry is completed by an oxygen atom of a perchlorate ion, Cu-O 2.63(1) Å. Folding of the non-chelate five-membered rings produces a conformation such that one face of the complex ion is more available for axial coordination of unidentate ligands.

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

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*Part 45 is reference 2.
**Authors for correspondence.

INTRODUCTION

In pursuance of our studies on the stereochemical features of $Me_2[14]$ane-N_4 ligands[1,2] we report here the crystal structure of {6*S*,14*S*-(4*R*12*R*-dimethyl)-1,5,9,13-tetraazatricyclo-$[12,2,1,1^{6,9}]$-octadecane}perchloratocopper(II) perchlorate, [Cu(*S*-mac5)ClO_4]ClO_4, which has ethyl 'straps' appended in the 6,8- and 13,1-positions of the [14]ane-N_4 macrocycle.

EXPERIMENTAL

The complex was synthesised by a previously reported method.[1]

Crystal Data

$C_{16}H_{32}N_4O_8Cl_2Cu$; M_r = 542.90; monoclinic; a = 11.340(3), b = 13.713(2), c = 15.002(1) Å, β = 97.13(1)°; U = 2314.8 Å^3; Z = 4; D_c = 1.558 g cm^{-3}; F(000) = 1132; μ(Mo-α) = 12.61 cm^{-1}; space group P+ + + + + + +2_1 (No. 4).

Data for the complex were collected at 298 K on an Enraf-Nonius FAST area detector diffractometer using documented procedures.[3] Unit cell parameters were determined from reflections in the range 1.5 <θ<25.0° *via* the REFINE procedure of MADNES software.[4] Intensities for 12203 reflections in the range 2.4 <θ<30.0° with indices h-14 to 14, k-11 to 19, l-20 to 19 were measured. These generate a unique data set of 7088 reflections of which 3494 have $I< 2\sigma(I)$ (R_{int} = 0.016) 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. Difference maps indicated disorder in one of the non-coordinated perchlorate ions; the occupancies of the oxygen atoms were assigned such that the atoms had approximately the same isotropic thermal parameters. In these and subsequent maps there was no evidence for the methyl hydrogen atoms and hence the positions for the other hydrogen atoms were calculated assuming C,N-H to be 1.0 Å and the appropriate geometry of the atom to which they are bonded. Final refinement was carried out with anisotropic thermal paramters for all non-hydrogen atoms of the macrocylic ligand, the copper and chlorine atoms and oxygen atoms O(1a) and O(2a). The weight for each reflection was unity. Refinement was terminated when the shift in any parameter was <0.1σ. The final values for R and $R'\{= (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}\}$ were 0.056 and 0.074, respectively, and with η = 1.03(11) confirming the configurations of the chiral centres. A final difference map showed no unusual features with density maxima < |0.7| e Å^{-3}.

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

The two independent complex cations are structurally similar and stereo-views[6] of them together with the atom labelling scheme are shown in Figure 1. Final atomic

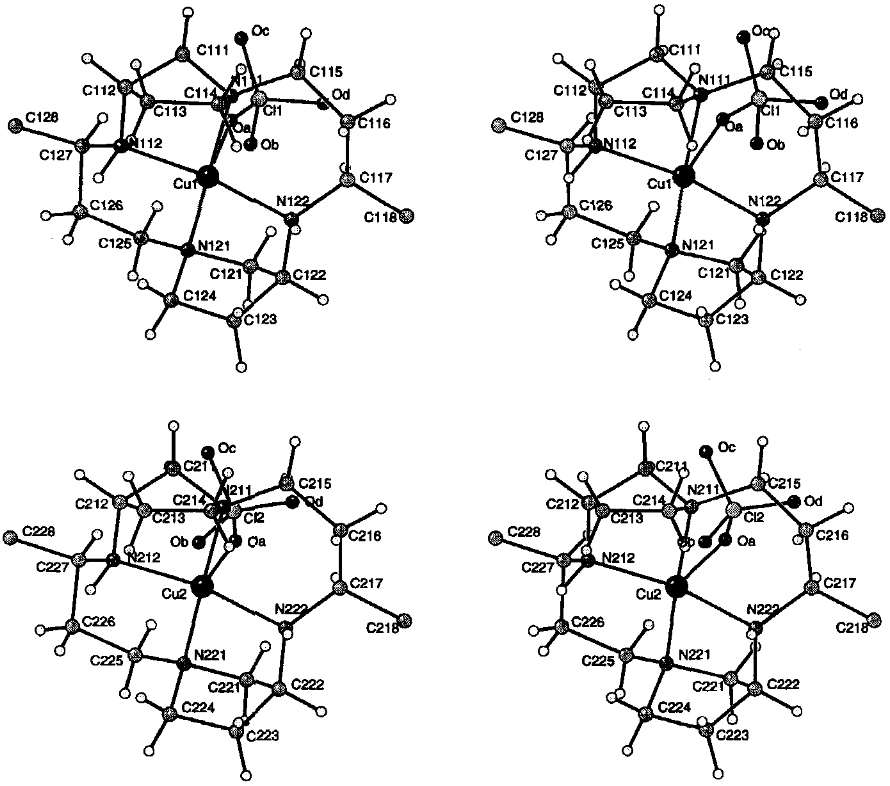

Figure 1 Stereo-views of the two independent complex cations showing the atom labelling.

coordinates for the non-hydrogen atoms and a list of selected bond lengths and angles are given in Tables 1 and 2, respectively.

In each cation the copper atom is five-coordinate with a distorted square-based pyramidal geometry. This distortion is manifest in a tetrahedral twist of *ca.* 22° in the N_4 plane; the copper atom lies 0.092 Å towards the apex with deviations of 0.24 and −0.24 Å for N_{tert} and N_{sec}, respectively. This means, with respect to the square-based pyramid, that the N_{tert}-Cu-N_{tert} angle is 188.8(4)°. The Cu-N_{sec} and Cu-N_{tert} distances of 1.988(6) and 2.019(5)Å, respectively, are significantly shorter than corresponding distances found in structural analogues.[1,2] The apical positions are occupied by oxygen atoms of perchlorate ions with Cu-O lengths of 2.63(1) Å, which are considerably longer than both that of 2.44 Å found in the related eicosane structure, $[Cu(S\text{-mac7})ClO_4]^+$,[1] and of 2.508 Å reported by Orpen *et al.*[7]

As with the previously reported structures, $[Cu(S\text{-mac7})ClO_4]^+$[1] and $[Cu(S\text{-mac6})Cl]^+$,[2] the conformations of the five-membered chelate rings are δ and the six-membered chelate rings adopt chair conformations. The other two

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

	Occ#	*x/a*	*y/b*	*z/c*	B*
Cul		233.3(11)	2500	2425.8(8)	2.7
N111		767(9)	1610(9)	1512(7)	3.2
N112		-1400(8)	2309(9)	1738(6)	3.3
N121		-328(10)	3204(10)	3453(7)	3.4
N122		1839(9)	3098(9)	2841(7)	3.2
C111		-247(14)	954(12)	1309(10)	4.0
C112		-1190(12)	1705(12)	963(9)	3.8
C113		-565(13)	2304(14)	322(8)	4.9
C114		767(13)	2189(12)	658(8)	4.4
C115		1938(13)	1092(10)	1815(9)	3.5
C116		2950(12)	1800(13)	2156(9)	3.8
C117		2821(12)	2362(13)	3009(8)	3.9
C118		4030(12)	2833(12)	3353(10)	4.4
C121		757(12)	3169(14)	4124(9)	4.0
C122		1584(13)	3724(13)	3623(10)	4.2
C123		844(16)	4630(12)	3238(12)	4.9
C124		-463(16)	4246(13)	3201(11)	4.7
C125		-1384(11)	2769(13)	3811(8)	4.4
C126		-2435(11)	2667(14)	3071(9)	4.2
C127		-2315(13)	1931(15)	2331(10)	4.7
C128		-3562(13)	1804(17)	1722(13)	6.3
Cu2		4362.0(11)	2506.6(19)	7497.2(8)	2.8
N211		3408(10)	1824(10)	6477(7)	3.6
N212		5777(10)	1941(10)	7002(8)	3.9
N221		5288(10)	3361(9)	8395(7)	3.2
N222		3017(9)	2690(9)	8252(6)	3.2
C211		4225(16)	1836(14)	5775(9)	5.2
C212		5272(15)	1330(14)	6253(11)	5.1
C213		4608(17)	439(14)	6610(14)	5.8
C214		3385(14)	766(11)	6687(11)	4.0
C215		2236(14)	2274(14)	6199(9)	5.4
C216		1462(12)	2399(17)	6979(10)	4.6
C217		1894(12)	3102(13)	7728(11)	4.2
C218		853(15)	3207(16)	8323(12)	6.4
C221		4363(14)	4037(12)	8657(9)	3.9
C222		3586(13)	3298(12)	9019(9)	4.2
C223		4450(14)	2714(13)	9636(8)	4.5
C224		5636(13)	2775(11)	9221(9)	4.2
C225		6310(13)	3883(11)	8043(10)	4.0
C226		7177(13)	3198(14)	7667(11)	4.5
C227		6654(13)	2714(13)	6769(10)	4.8
C228		7725(17)	2245(15)	6361(16)	8.5
C11		594(4)	222(4)	4082(3)	4.8
O1a		286(15)	921(11)	3408(8)	7.2
O1b		152(16)	565(16)	4895(13)	10.9(5)
O1c		329(20)	-729(20)	3861(15)	13.3(7)
O1d		1824(27)	23(27)	4308(20)	18.4(9)
C12		4034(4)	4887(4)	5941(2)	4.9
O2a		3987(14)	4125(13)	6549(9)	7.9
O2b	0.9	4866(21)	5548(20)	6215(16)	12.5(7)
O2c	0.9	3450(23)	4741(21)	5122(16)	12.5(6)
O2d	0.8	4498(26)	4479(24)	5170(19)	13.1(8)
O2e	0.4	3517(51)	5757(53)	6198(40)	13.5(17)
C13		7279(4)	17(4)	8975(2)	5.2
O3a		7471(16)	769(17)	8392(13)	11.0(5)

Table 1 *Continued*

	x/a	*y/b*	*z/c*	B*
O3b	6930(17)	-758(17)	8525(14)	11.5(5)
O3c	6648(16)	385(16)	9663(13)	10.4(5)
O3d	8381(23)	-300(23)	9429(18)	16.1(8)
C14	2445(5)	-18(4)	9262(3)	6.0
O4a	1929(13)	757(15)	8747(11)	8.9(4)
O4b	2724(16)	-822(16)	8751(12)	10.3(5)
O4c	1682(18)	-407(19)	9845(15)	12.1(6)
O4d	3259(15)	291(15)	9962(12)	10.2(5)

#Only partial occupancies are indicated. *B_{eq} or B_{iso} with estimated standard deviations in parentheses.

five-membered rings, formed by the ethyl 'straps', are again folded to the same side of the N_4 plane. However, unlike the related structures containing six-[2] and seven-membered[1] rings in which only one face of the complex is available for axial coordination, folding and other steric effects in the present macrocycle make both faces less accessible, although with an obvious preference for one. A detailed discussion of the steric features of these macrocylic ligands will be reported elsewhere.

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

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

a) Distances (Å)	n = 1		n = 2	
	m = 1	m = 2	m = 1	m = 2
Cu(n)-O(na)	2.616(13)		2.642(15)	
Cu(n)-N(nm1)	1.986(11)	1.989(10)	1.995(11)	1.984(11)
Cu(n)-N(nm2)	2.022(10)	2.023(11)	2.006(10)	2.025(10)
N(nm1)-C(nm1)	1.46(2)	1.49(2)	1.47(2)	1.49(2)
N(nm1)-C(nm4)	1.51(2)	1.48(2)	1.49(2)	1.49(2)
N(nm1)-C(nm5)	1.52(2)	1.50(2)	1.48(2)	1.51(2)
N(nm2)-C(nm2)	1.47(2)	1.50(2)	1.46(2)	1.52(2)
N(nm2)-C(nm ± 17)	1.54(2)	1.51(2)	1.52(2)	1.50(2)
C(nm1)-C(nm2)	1.53(2)	1.48(2)	1.48(2)	1.49(2)
C(nm2)-C(nm3)	1.51(2)	1.57(2)	1.56(3)	1.49(2)
C(nm3)-C(nm4)	1.54(2)	1.57(2)	1.48(2)	1.55(2)
C(nm5)-C(nm6)	1.54(2)	1.53(2)	1.56(2)	1.52(2)
C(nm6)-C(nm7)	1.52(2)	1.52(2)	1.51(2)	1.55(2)
C(nm7)-C(nm8)	1.54(2)	1.59(2)	1.57(2)	1.56(2)
b) Angles (°)	n = 1		n = 2	
	m = 1	m = 2	m = 1	m = 2
N(n11)-Cu(n)-N(n21)	171.1(5)		171.4(5)	
N(n12)-Cu(n)-N(n22)	160.4(4)		161.4(5)	
N(n11)-Cu(n)-N(n22)	97.0(4)		96.5(4)	
N(n12)-Cu(n)-N(n21)	95.5(4)		95.7(5)	
N(nm1)-Cu(n)-N(nm2)	84.6(4)	85.8(4)	85.2(5)	85.3(4)
O(na)-Cu(n)-N(nm1)	83.8(4)	87.3(5)	86.8(5)	84.6(5)
O(na)-Cu(n)-N(nm2)	97.8(5)	101.8(5)	102.0(5)	95.6(5)

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

a) Proposed Hydrogen Bonding*			
N(112)....O(4b^{I})	3.01(2)	N(212)....O(3a)	3.10(2)
N(122)....O(3b^{II})	3.05(2)	N(222)....O(4a)	3.06(2)
b) Intermolecular Distances <3.4Å*			
C(126)....O(2e^{III})	*3.15(7)*	*C(212)....O(2d^{IV})*	*3.35(4)*
C(127)....O(2e^{III})	*3.17(6)*	C(124)....O(1b^{I})	3.36(3)
C(122)....O(2c)	*3.21(3)*	C(113)....O(4c^{I})	3.38(3)
C(213)....O(2d^{IV})	*3.25(4)*	C(123)....O(1b^{I})	3.40(3)

Those in italics involve disordered perchlorate oxygen atoms.

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

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

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 on request.

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