References

Antberg, M. & Dahlenburg, L. (1986). *Inorg. Chim. Acta*, **111**, 73–76.

Cotton, F. A., Hunter, D. L. & Frenz, B. A. (1975). *Inorg. Chim. Acta*, **15**, 155–160.

Gregory, U. A., Ibekwe, S. D., Kilbourn, B. T. & Russell, D. R. (1971). *J. Chem. Soc. A*, pp. 1118–1125.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Keller, E. (1981). *SCHAKAL. Ein FORTRAN-Programm für die graphische Darstellung von Molekülmodellen.* Univ. of Freiburg.

Pietsch, B. & Dahlenburg, L. (1986). *Acta Cryst.* C**42**, 995–997.

Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1986). C**42**, 999–1001

Structure of Aqua[(1*SR*,4*RS*,8*SR*,11*RS*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) Perchlorate Monohydrate

By Tsong-Jen Lee, Tseng-Yuh Lee, Ching-You Hong, Der-Thing Wu and Chung-Sun Chung

National Tsing Hua University, Hsinchu, Taiwan 300

(*Received* 9 *January* 1986; *accepted* 21 *February* 1986)

Abstract. $[Cu(C_{14}H_{32}N_4)(H_2O)](ClO_4)_2.H_2O$, $M_r = 554{\cdot}91$, monoclinic, $P2_1/c$, $a = 9{\cdot}784\,(3)$, $b = 14{\cdot}081\,(3)$, $c = 16{\cdot}958\,(5)$ Å, $\beta = 91{\cdot}26\,(3)°$, $U = 2335{\cdot}85$ Å^3, $Z = 4$, $D_x = 1{\cdot}5785$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}258$ mm^{-1}, $F(000) = 1166{\cdot}0$, $T = 296\,(4)$ K, $R(F) = 0{\cdot}060$ for 2240 observed reflections $[I > 3\sigma(I)]$. The coordination geometry about the Cu^{II} atom is a buckled square-based pyramid. This complex has the (1*SR*,4*RS*,8*SR*,11*RS*) configuration at the chiral N centers, with the four attached methyl groups on the same side of the macrocyclic plane. The two six-membered chelate rings exhibit a chair form, and the two five-membered rings take distorted eclipsed forms.

Introduction. Preparations of divalent transition-metal complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) have been reported by Barefield & Wagner (1973). An X-ray structure determination of $[Ni(tmc)N_3]ClO_4$ prepared by combining the Ni^{II} ion with the free ligand has shown that the macrocyclic ligand is coordinated in a planar fashion with all four methyl groups on the same side of the metal–nitrogen plane. In this work, the crystal structure of $[Cu(tmc)H_2O](ClO_4)_2.H_2O$ obtained by direct interaction of the Cu^{II} ion with tmc is reported.

Experimental. The tmc was prepared according to a previously described procedure (Barefield & Wagner, 1973). Aqueous solutions of $Cu(ClO_4)_2.6H_2O$ (1·8 g in 20 ml) and tmc (1·25 g in 30 ml) were mixed and the mixture was filtered. The blue solution was evaporated under a gentle stream of air to give dark-blue crystals. The single crystals used in the X-ray analysis were obtained by recrystallization from an aqueous solution at room temperature, and were sealed in a capillary tube containing some moisture. The crystals thus grown are plate-like and blue and deteriorate gradually on exposure to the air.

Experimental data and structure solution parameters together with standard refinement procedures are listed in Table 1.

Table 1. *Experimental data and structure-refinement parameters*

Crystal size (mm)	0·3 × 0·3 × 0·35
Diffractometer and data-collection technique used	ω–2θ scan, four-circle diffractometer (Nonius CAD-4) with graphite monochromator
Scan width (2θ)	$2\,(0{\cdot}7 + 0{\cdot}35\tan\theta)°$
Number and θ range used for measuring lattice parameters	25 reflections with $11 < 2\theta < 20°$
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Transmission factor	0·632
Max. $(\sin\theta)/\lambda$ in intensity measurement	0·5947 Å^{-1}
Range of *hkl*	0,0,−23 to 5,19,23
Standard reflections and intensity variation	$0\bar{8}0$, $\bar{4}49$, $53\bar{5}$; < 4%
Number of reflections measured	5741
Number of unique reflections	2240 $[I > 3\sigma(I)]$
Method used to solve the structure	Patterson and Fourier methods
Max. height in final difference Fourier synthesis	0·39 e Å^{-3}
Parameters refined, nonhydrogen atoms	Coordinates, occupancies and anisotropic temperature factors (281 parameters)
hydrogen atoms	Coordinates and isotropic temperature factor (144 parameters)
Quantity minimized	$\sum w(\Delta F)^2$; $w = 1/\sigma_F^2$
Atomic scattering factors, f' and f''	*International Tables for X-ray Crystallography* (1974)
Number of reflections per parameter	6
$R(F)$ and wR	0·060 and 0·058
S	2·769
R_{int}	0·032
Average, max. Δ/σ	0·58, 0·96
Programs used	*THUCP* (Hsieh & Lee, 1985); *XTAL*83 (Stewart, Hall, Alden, Olthof-Hazekamp, Doherty, Pagoaga & Norden, 1983); *ORTEP*II (Johnson, 1976)
Computer	CDC Cyber-840 and IBM PC-XT

0108-2701/86/080999-03$01.50

Table 2. *Atomic positional and thermal parameters of non-hydrogen atoms*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j b_{ij}$, where the $\mathbf{a}_i$'s are the length vectors in direct space.

	x	y	z	$B_{eq}(Å^2)$
Cu(1)	0·2123 (1)	0·8154 (1)	0·7946 (1)	2·4
Cl(1)	0·2721 (2)	1·3912 (1)	0·9841 (1)	4·2 (1)
Cl(2)	0·2427 (2)	0·5443 (1)	0·6156 (1)	4·3 (1)
O(11)	0·2635 (8)	1·3040 (4)	0·9474 (4)	9·6 (5)
O(12)	0·3534 (10)	1·4462 (6)	0·9479 (8)	19·4 (10)
O(13)	0·3079 (9)	1·3764 (6)	1·0627 (4)	11·8 (6)
O(14)	0·1463 (7)	1·4356 (5)	0·9848 (4)	7·9 (5)
O(21)	0·2411 (8)	0·5721 (7)	0·6935 (3)	10·4 (6)
O(22)	0·1027 (9)	0·5418 (6)	0·5893 (4)	10·9 (6)
O(23)	0·3065 (9)	0·6077 (6)	0·5715 (4)	11·8 (6)
O(24)	0·2819 (8)	0·4525 (6)	0·6149 (6)	12·7 (7)
O(*W*1)	0·1784 (7)	0·9619 (4)	0·8636 (3)	6·3 (4)
O(*W*2)	0·3561 (8)	1·1029 (5)	0·9137 (5)	10·7 (6)
N(1)	0·3794 (7)	0·7517 (4)	0·8455 (3)	3·7 (4)
N(2)	0·1026 (6)	0·7415 (4)	0·8784 (3)	3·0 (4)
N(3)	0·0467 (6)	0·8248 (4)	0·7146 (3)	3·3 (4)
N(4)	0·3250 (6)	0·8855 (4)	0·7093 (3)	3·4 (3)
C(1)	0·3281 (9)	0·6684 (5)	0·8875 (4)	4·1 (5)
C(2)	0·2110 (11)	0·6968 (6)	0·9328 (4)	6·7 (6)
C(3)	0·0241 (9)	0·6613 (5)	0·8409 (4)	4·9 (5)
C(4)	−0·0905 (9)	0·6980 (6)	0·7844 (5)	5·4 (6)
C(5)	−0·0349 (9)	0·7353 (6)	0·7070 (4)	5·0 (6)
C(6)	0·1159 (9)	0·8395 (6)	0·6392 (4)	5·3 (5)
C(7)	0·2159 (10)	0·9150 (6)	0·6467 (4)	4·9 (6)
C(8)	0·4244 (9)	0·8207 (6)	0·6740 (4)	5·1 (6)
C(9)	0·5348 (9)	0·7868 (6)	0·7302 (5)	5·2 (6)
C(10)	0·4868 (8)	0·7146 (5)	0·7872 (5)	4·2 (5)
C(11)	0·4550 (9)	0·8172 (6)	0·9031 (5)	5·3 (5)
C(12)	0·0110 (10)	0·7995 (6)	0·9285 (4)	6·0 (6)
C(13)	−0·0404 (9)	0·9075 (6)	0·7308 (5)	5·1 (6)
C(14)	0·4000 (10)	0·9723 (5)	0·7391 (5)	6·5 (6)

Table 3. *Bond lengths* (Å) *and angles* (°)

Cu(1)–N(1)	2·041 (6)	N(1)–Cu(1)–N(2)	84·9 (2)
Cu(1)–N(2)	2·078 (5)	N(2)–Cu(1)–N(3)	94·1 (2)
Cu(1)–N(3)	2·095 (6)	N(3)–Cu(1)–N(4)	86·2 (2)
Cu(1)–N(4)	2·086 (5)	N(4)–Cu(1)–N(1)	94·0 (2)
Cu(1)–O(*W*1)	2·398 (5)	N(1)–C(1)–C(2)	108·6 (6)
N(1)–C(1)	1·466 (9)	C(1)–C(2)–N(2)	109·9 (6)
C(1)–C(2)	1·450 (13)	C(2)–N(2)–C(3)	106·8 (6)
C(2)–N(2)	1·526 (10)	N(2)–C(3)–C(4)	111·6 (6)
N(2)–C(3)	1·499 (10)	C(3)–C(4)–C(5)	112·3 (7)
C(3)–C(4)	1·549 (12)	C(4)–C(5)–N(3)	114·6 (6)
C(4)–C(5)	1·525 (11)	C(5)–N(3)–C(6)	107·3 (5)
C(5)–N(3)	1·497 (10)	N(3)–C(6)–C(7)	110·5 (6)
N(3)–C(6)	1·474 (9)	C(6)–C(7)–N(4)	108·5 (6)
C(6)–C(7)	1·449 (12)	N(4)–C(8)–C(9)	114·3 (6)
C(7)–N(4)	1·547 (10)	C(8)–C(9)–C(10)	113·4 (7)
N(4)–C(8)	1·470 (10)	C(9)–C(10)–N(1)	114·4 (6)
C(8)–C(9)	1·503 (12)	C(10)–N(1)–C(1)	106·5 (5)
C(9)–C(10)	1·485 (11)	Cu(1)–N(1)–C(10)	115·2 (4)
C(10)–N(1)	1·550 (10)	Cu(1)–N(1)–C(11)	112·2 (5)
N(1)–C(11)	1·523 (10)	Cu(1)–N(2)–C(12)	116·1 (4)
N(2)–C(12)	1·492 (10)	Cu(1)–N(3)–C(13)	111·8 (4)
N(3)–C(13)	1·472 (10)	Cu(1)–N(4)–C(14)	114·3 (5)
N(4)–C(14)	1·507 (10)	Cu(1)–N(4)–C(8)	110·7 (4)
Cl(1)–O(11)	1·378 (7)	O(11)–Cl(11)–O(12)	110·9 (5)
Cl(1)–O(12)	1·277 (11)	O(11)–Cl(1)–O(13)	108·2 (5)
Cl(1)–O(13)	1·387 (7)	O(11)–Cl(1)–O(14)	111·2 (5)
Cl(1)–O(14)	1·381 (7)	O(12)–Cl(1)–O(13)	114·0 (7)
Cl(2)–O(21)	1·378 (6)	O(12)–Cl(1)–O(14)	107·1 (5)
Cl(2)–O(22)	1·432 (9)	O(13)–Cl(1)–O(14)	105·4 (5)
Cl(2)–O(23)	1·329 (8)	O(21)–Cl(2)–O(22)	106·0 (5)
Cl(2)–O(24)	1·349 (8)	O(21)–Cl(2)–O(23)	111·4 (5)
O(*W*1)–Cu(1)–N(1)	106·9 (2)	O(21)–Cl(2)–O(24)	106·9 (6)
O(*W*1)–Cu(1)–N(2)	91·1 (2)	O(22)–Cl(2)–O(23)	107·4 (5)
O(*W*1)–Cu(1)–N(3)	98·6 (2)	O(22)–Cl(2)–O(24)	104·1 (5)
O(*W*1)–Cu(1)–N(4)	90·7 (2)	O(23)–Cl(2)–O(24)	120·1 (5)
N(1)–Cu(1)–N(3)	154·6 (2)	O(*W*1)–Cu(1)–O(21)	175·2 (2)
N(2)–Cu(1)–N(4)	178·1 (2)		

Hydrogen bonds

	O···O	∠O–H···O
O(*W*1)–H(*W*1)···O(*W*2)	2·760 (10) Å	134·9 (8)°
O(*W*2)–H(*W*2)···O(11)	3·032 (10)	151·9 (6)

Discussion. The atomic coordinates and temperature factors are listed in Table 2.* A perspective view of the molecule with the numbering scheme and the deviations of the atoms from the plane through N(1), N(2), N(3) and N(4) are shown in Fig. 1. The bond distances and angles are listed in Table 3. A stereoview of the molecule is shown in Fig. 2.

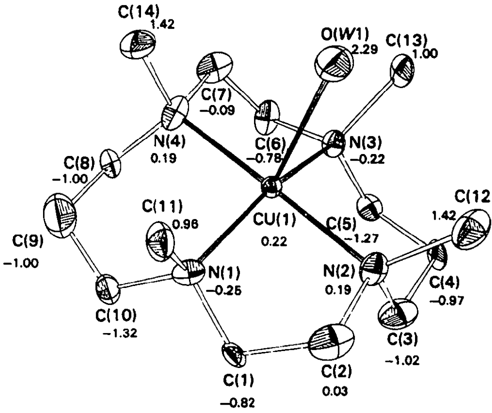

Fig. 1. Perspective view of $[Cu(C_{14}H_{32}N_4)(H_2O)]^{2+}$, showing the atom-numbering scheme and displacements (Å) of atoms from the least-squares plane of N(1), N(2), N(3) and N(4); e.s.d.'s are approximately 0·01 Å. Thermal ellipsoids are depicted at the 50% probability level.

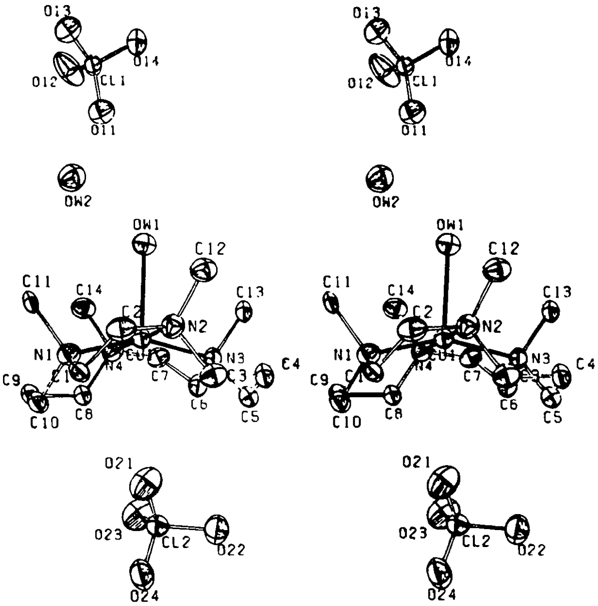

Fig. 2. Stereoview of the molecule, illustrating the shape of the ligand complex (*ORTEP*II, Johnson, 1976).

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42842 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This complex ion has approximate C_2 symmetry. The coordination geometry about the $\mathrm{Cu^{II}}$ ion is intermediate between the two limiting structures for five-coordinate complexes: a trigonal bipyramid and a square-based pyramid. This geometry may be referred to as a buckled square-based pyramid or a squashed trigonal bipyramid. The four donor N atoms of the macrocyclic ligand form a buckled plane, and the $\mathrm{Cu^{II}}$ ion is 0·220 (3) Å out of this buckled plane towards the aqua group. The perchlorate ions are not within bonding distance of the cation. The four methyl groups are on the same side of the metal–nitrogen buckled plane. The two six-membered chelate rings exhibit a chair form, and the two five-membered rings take distorted eclipsed forms. All bond angles and distances are normal.

The configuration of the four chiral N centers is 1*SR*,4*RS*,8*SR*,11*RS*, which is also found in the divalent Ni complex which is prepared by combining the metal salt with this ligand in aqueous solution (D'Aniello, Mocella, Wagner, Barefield & Paul, 1975). It is interesting to note that the four donor N atoms of this $\mathrm{Ni^{II}}$ complex, $[\mathrm{Ni(tmc)N_3}]^+$, form a perfect plane, while the four donor N atoms of $[\mathrm{Cu(tmc)H_2O}]^{2+}$ form a buckled plane. The reason for this difference is readily seen on viewing the angular overlap model for these complexes (Purcell & Kotz, 1979). This model indicates that the square-based pyramid is significantly more favored over the trigonal bipyramid for a d^8 complex than for a d^9 complex.

A water molecule is situated between the perchlorate ion and the coordinated aqua group. The hydrogen-bonding network listed in Table 3 stabilizes the crystal lattice. Hence the crystal state collapses as soon as it is dehydrated following exposure to air for a few hours.

The temperature factors of some perchlorate O atoms are larger than usual. These unusually large temperature factors may be due to the disordered orientation of the perchlorate ion and is manifested in the residual peaks around the perchlorate ions in the difference Fourier map.

We thank the National Science Council for financial support.

References

Barefield, E. K. & Wagner, F. (1973). *Inorg. Chem.* **12**, 2435–2439.

D'Aniello, M. J. Jr, Mocella, M. T., Wagner, F., Barefield, E. K. & Paul, I. C. (1975). *J. Am. Chem. Soc.* **97**, 192–194.

Hsieh, M.-Y. & Lee, T.-Y. (1985). Tsing Hua University crystal package, *THUCP*. Computer Center, National Tsing Hua University, Hsinchu, Taiwan 300.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 202. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Purcell, K. F. & Kotz, J. C. (1979). *Inorganic Chemistry*, p. 588. Philadelphia: Saunders.

Stewart, J. M., Hall, S. R., Alden, R. A., Olthof-Hazekamp, R., Doherty, R. M., Pagoaga, M. K. & Norden, T. M. (1983). *XTAL*83. A system of crystallographic programs. Univ. of Maryland, Computer Science Center, College Park, Maryland 20742.

Acta Cryst. (1986). C**42**, 1001–1004

Structure of [(1*RS*,4*RS*,7*RS*,8*SR*,11*SR*,14*SR*)-1,4,5,5,7,8,11,12,12,14-Decamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Perchlorate

By Tseng-Yuh Lee, Ming-Yei Hsieh, Tsong-Jen Lee,* Jy-Wann Chen and Chung-Sun Chung

National Tsing Hua University, Hsinchu, Taiwan 300

(*Received* 3 *December* 1985; *accepted* 10 *March* 1986)

Abstract. $[\mathrm{Ni(C_{20}H_{44}N_4)}](\mathrm{ClO_4})_2$, $M_r = 598{\cdot}21$, triclinic, $P\bar{1}$, $a = 8{\cdot}562\ (2)$, $b = 8{\cdot}898\ (3)$, $c = 10{\cdot}812\ (3)$ Å, $\alpha = 68{\cdot}72\ (3)$, $\beta = 59{\cdot}09\ (3)$, $\gamma = 79{\cdot}91\ (3)°$, $U = 658{\cdot}47\ (3)$ Å^3, $Z = 1$, $D_x = 1{\cdot}508$, $D_m = 1{\cdot}48$ Mg m^{-3} (by flotation in $\mathrm{CCl_4}$/hexane mixture), Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}9907$ mm^{-1}, $F(000) = 318{\cdot}6$, $T = 296\ (4)$ K, $R(F) = 0{\cdot}053$ for 1659 observed reflections $[I > 3\sigma(I)]$. The complex ion is centrosymmetric with respect to the $\mathrm{Ni^{II}}$ atom. The $\mathrm{Ni^{II}}$ and the four N donor atoms are coplanar. This complex has the (1*RS*,4*RS*,8*SR*,11*SR*) configuration at the chiral nitrogen centers. The ligand is in its most stable planar conformation with both six-membered chelate rings in a chair form and both five-membered rings in a *gauche* form.

---

* Author to whom correspondence should be addressed.

0108-2701/86/081001-04$01.50