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X-ray Molecular Structure of the Orange Isomer of (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) Perchlorate, $[Cu(C_{16}H_{32}N_4)](ClO_4)_2^*$

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Abstract. $M_r = 542{\cdot}92$, monoclinic, $P2_1/c$, $a = 10{\cdot}331\,(5)$, $b = 10{\cdot}641\,(5)$, $c = 11{\cdot}050\,(6)$ Å, $\beta = 111{\cdot}96\,(4)°$, $U = 1126{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}60$, $D_m = 1{\cdot}61$ Mg m^{-3} (by flotation in CCl_4–hexane), μ(Mo $K\alpha$) = 1·297 mm^{-1}, $F(000) = 566$, room temperature. Final $R = 0{\cdot}05$ for 1468 observed reflections. The complex cations are centrosymmetric. The Cu atom and four N atoms are coplanar. Two *gem*-dimethyl groups are on the opposite side of the amine hydrogens relative to the macrocyclic plane.

Introduction. Macrocyclic complexes provide stimulating examples for studying the conformational properties of the molecules, owing to the possible stable arrangements which the ligand can adopt around the metal ion (Dei, 1979). The complex (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) exists in two isomeric forms. These two isomeric crystals were isolated under slow evaporation of the solution of the compound, [Cu(*trans*-[14]diene)]$(ClO_4)_2$ (Palmer, Papaconstantinou & Endicott, 1969). One is translucent, deep red and rhomboid-like and the other is translucent, orange in color and plate-like. The former crystal is much larger than the latter, as they are crystallized simultaneously from the solution. The structure of the red crystal has been reported (Lu, Lee, Liang & Chung, 1981).

Experimental. Syntex four-circle $P\bar{1}$ diffractometer, Nb-filtered Mo $K\alpha$, unit-cell parameters from 15 reflections with $12° < 2\theta < 25°$, data collected by ω–2θ scans, scan range $2{\cdot}0° + 0{\cdot}7° \tan\theta$ (starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$), scan rate 4° min^{-1}; intensities of two strong reflections ($\bar{1}12$ and $\bar{2}12$) monitored every 100 reflections showed deviations of less than 3% during the course of data collection; time-decay correction omitted, 4450 reflections measured, 1468 independent reflections found with $I > 3\sigma(I)$ after correction for Lorentz–polarization (seven unobserved reflections), maximum $(\sin\theta)/\lambda = 0{\cdot}638$ Å^{-1} ($0 \le h \le 14$, $0 \le k \le 12$, $-14 \le l \le 14$). The orange crystal was roughly ground into a sphere of 0·3 mm diameter ($\mu R = 0{\cdot}195$) and an absorption correction was made by interpolating the values listed in *International Tables for X-ray Crystallography* (1967). Heavy-atom method, full-matrix least-squares refinement of coordinates and anisotropic temperature factors of nonhydrogen atoms, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F)$ with $\sigma_F = [k/2\sqrt{(\mathrm{Lp})}] \times \{[\sigma^2(I)_{\mathrm{counting}} + (0{\cdot}01I)^2]/I\}^{1/2}$ and Lp, I, k the Lorentz–polarization factor, reflection intensity and scale factor respectively. To locate the positions of H atoms in the methyl groups, one of the highest peaks around the C atom in each methyl group was fixed and the other two H-atom positions were calculated on a tetrahedral basis. The C—H and N—H bond distances and the angles C—C—H and Cu—N—H were adjusted to 0·95 Å and 109°28′, respectively. Isotropic temperature factors of the H atoms assigned according to the relative peak heights in the difference map and calculated F_c based on Table 1; $R = 0{\cdot}050$, $R_w = 0{\cdot}059$, $(\Delta/\sigma)_{\mathrm{ave}} = 0{\cdot}2$, $(\Delta/\sigma)_{\max} = 0{\cdot}4$, final $\Delta\rho$ excursions $\le 0{\cdot}26$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1968), those for Cu and Cl corrected for anomalous dispersion.

Discussion. Fig. 1 [prepared with *ORTEP* (Johnson, 1976)] shows the molecular structure for the orange crystal and the displacements of atoms from the CuN_4 plane. A side view is shown in Fig. 2.† The isotropic temperature factor for H atoms on the figures has been assigned the value of 1 Å^2. The atomic coordinates and thermal factors are given in Table 1, bond lengths and angles in Table 2. Fig. 3 shows a stereoview of the packing.

Referred to the crystal axes, the equation of the equally weighted least-squares plane formed by the Cu

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† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38890 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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atom and four N atoms is $2{\cdot}152x-10{\cdot}057y-1{\cdot}720z=0$ (in Å).

Comparing the results between the red (RED) and orange (ORG) isomeric crystals we found the following significant results: (1) The two imine methyl groups are *trans* to one another in the ring and oriented in an equatorial manner for the orange crystal, while they are on the same side of the CuN_4 plane for RED. (2) Both H(1) and H(2) are on the same side (*cis*) of the CuN_4 plane for RED, whereas H(2) [labeled as H(1′) in Figs. 1 and 2 of this paper] is above and H(1) below the macrocyclic plane (*trans*) for ORG. (3) For both isomers, the two perchlorate ions are located on opposite sides of the macrocyclic plane. (4) For ORG, the two *gem*-dimethyl groups are on opposite sides of the macrocyclic plane and each is opposite the H atom

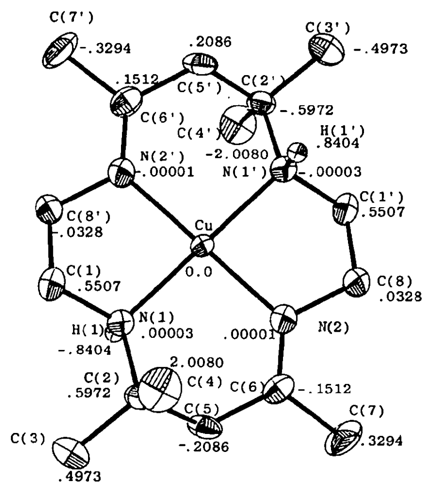

Fig. 1. Molecular structure, showing displacements of atoms from the CuN_4 plane (Å) (the atomic positions below the CuN_4 plane are indicated by negative signs). The center-related atoms are shown with primes.

Table 1. *Atomic positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j B_{ij}.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cu	0	0	0	2·01 (5)
Cl	2434 (2)	3327 (2)	1479 (2)	3·53 (13)
O(1)	1425 (9)	2634 (9)	434 (8)	6·61 (58)
O(2)	2119 (11)	3216 (8)	2630 (8)	6·51 (63)
O(3)	3781 (9)	2802 (9)	1704 (11)	7·37 (71)
O(4)	2432 (11)	4617 (7)	1133 (9)	6·43 (66)
N(1)	1384 (6)	−439 (6)	−837 (5)	2·11 (26)
N(2)	1403 (6)	8 (6)	1799 (5)	2·62 (26)
C(1)	545 (8)	−1024 (9)	−2103 (7)	3·04 (41)
C(2)	2633 (6)	−1153 (6)	22 (7)	2·18 (33)
C(3)	3642 (10)	−1399 (11)	−729 (11)	3·85 (61)
C(4)	2218 (12)	−2395 (8)	445 (10)	3·49 (55)
C(5)	3398 (7)	−317 (7)	1182 (8)	2·52 (25)
C(6)	2723 (7)	−64 (8)	2154 (6)	2·61 (31)
C(7)	3727 (10)	133 (14)	3526 (8)	4·33 (49)
C(8)	739 (9)	279 (9)	2746 (7)	3·29 (41)

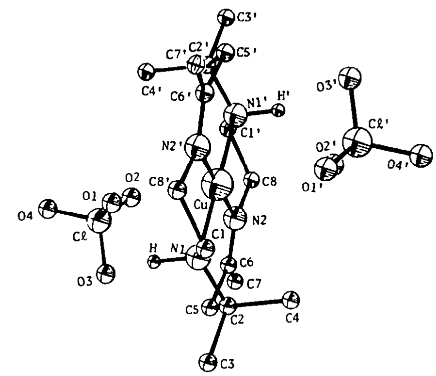

Fig. 2. Side view.

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1′), N(2′) and C(8′) indicate the center-related atoms and O(2)* indicates the screw-related O(2).

Cu(1)–N(1)	2·027 (7)	C(6)–N(2)	1·273 (9)
Cu(1)–N(2)	1·974 (5)	C(6)–C(5)	1·508 (12)
Cu(1)–N(1′)	2·027 (7)	C(6)–C(7)	1·497 (9)
Cu(1)–N(2′)	1·974 (5)	C(8)–N(2)	1·478 (12)
C(1)–N(1)	1·480 (9)	Cl(1)–O(1)	1·436 (8)
C(2)–N(1)	1·492 (8)	Cl(1)–O(2)	1·431 (11)
C(2)–C(3)	1·578 (15)	Cl(1)–O(3)	1·432 (9)
C(2)–C(4)	1·516 (12)	Cl(1)–O(4)	1·424 (8)
C(2)–C(5)	1·517 (10)	N(1)···O(2)*	3·162 (11)

C(8′)–C(1)–N(1)	109·3 (4)	C(7)–C(6)–N(2)	124·1 (8)
C(1)–N(1)–Cu(1)	105·3 (5)	C(6)–N(2)–Cu(1)	127·5 (5)
C(1)–N(1)–C(2)	116·7 (6)	Cu(1)–N(2)–C(8)	110·7 (4)
Cu(1)–N(1)–C(2)	114·6 (5)	C(6)–N(2)–C(8)	121·4 (5)
N(1)–C(2)–C(3)	109·5 (7)	N(2)–C(8)–C(1′)	109·6 (6)
N(1)–C(2)–C(5)	107·0 (5)	O(1)–Cl(1)–O(2)	109·6 (6)
N(1)–C(2)–C(4)	111·3 (6)	O(2)–Cl(1)–O(3)	110·0 (6)
C(3)–C(2)–C(4)	109·6 (8)	O(3)–Cl(1)–O(1)	107·8 (6)
C(4)–C(2)–C(5)	111·6 (7)	O(4)–Cl(1)–O(1)	110·6 (6)
C(2)–C(5)–C(6)	118·2 (6)	O(4)–Cl(1)–O(2)	109·9 (5)
C(5)–C(6)–C(7)	114·6 (7)	O(4)–Cl(1)–O(3)	109·0 (6)
C(5)–C(6)–N(2)	121·3 (6)	N(1)–H(1)···O(2)*	157 (3)

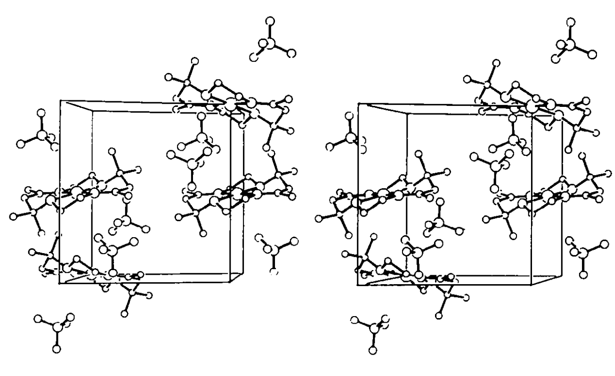

Fig. 3. Stereoview of the packing (viewed down the negative **c** direction).

of the neighboring N—H group; for RED they are on the same side of the CuN_4 plane and opposite the H atoms of the N—H groups. The equatorial geminal methyl groups lie away from the metal-ion center and their bond axes are parallel to each other. (5) The Cu atom and four N atoms are coplanar for ORG and coplanar within 0·05 Å for RED (the four N atoms form a slightly distorted rectangle). (6) With respect to the Cu atom, the bite angle of the six-membered ring is 94·8 (2)°, while that of the five membered ring is 85·2 (2)°. (7) For both isomers, the five-membered rings are *gauche* and the six-membered ring a twist-boat. (8) The double bonds between N(2)—C(6) and between N(4)—C(14) [labeled as N(2′)—C(6′) here]* are shorter than all the other single bonds for both crystals. (9) Both isomers of the diene involve a *trans* configuration of the imine groups and exhibit a certain symmetry: an approximate twofold (C_2) axis in the red molecule and an inversion center in the orange molecule. The temperature factors of the perchlorate ion are high as is usually observed for perchlorate crystals.

* N(2′) and C(6′) are the center-related atoms of N(2) and C(6) respectively.

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Structures of Three Polymeric Complexes [Silver(I) Nitrate]$_x$–1,4-Oxathiane, $(AgNO_3)_x.C_4H_8OS$ [x = 1 (I), 2 (II), 6 (III)]

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Abstract. (I) $M_r = 274·04$, monoclinic, $P2_1/c$, $a = 6·12$ (1), $b = 7·39$ (1), $c = 18·13$ (2) Å, $\beta = 97·0$ (3)°, $U = 813·7$ Å^3, $Z = 4$, $D_x = 2·24$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 21·4$ mm^{-1}, $F(000) = 536$, $T = 293$ K, final $R = 0·090$ for 886 unique reflexions. (II) $M_r = 443·91$, monoclinic, $P2_1/c$, $a = 12·065$ (2), $b = 6·259$ (3), $c = 13·527$ (2) Å, $\beta = 82·42$ (2)°, $U = 1012·6$ Å^3, $Z = 4$, $D_x = 2·91$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 3·8$ mm^{-1}, $F(000) = 1012$, $T = 293$ K, final $R = 0·060$ for 1821 observed reflexions. (III) $M_r = 1123·41$, triclinic, $P\bar{1}$, $a = 10·7347$ (9), $b = 13·1367$ (13), $c = 7·2488$ (3) Å, $\alpha = 91·556$ (5), $\beta = 92·668$ (5), $\gamma = 89·141$ (8)°, $U = 1020·6$ Å^3, $Z = 2$, $D_x = 3·65$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 5·4$ mm^{-1}, $F(000) = 1036$, $T = 293$ K, final $R = 0·057$ for 5308 observed reflexions. (I), (II) and (III) are polymeric lattice complexes in which Ag atoms are coordinated by the S atoms of 1,4-oxathiane at about 2·5 Å and by nitrate groups with 2·4 < Ag—O < 3·1 Å. In (II) and (III) the O atom of 1,4-oxathiane is also coordinated. The coordination numbers of the Ag atoms vary from six to ten, with irregular geometries. There are no strongly bonded polymeric fragments common throughout the series.

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Introduction. The crystal structures of the 1,4-oxathiane (tx) complexes of silver perchlorate, $AgClO_4$.tx and $AgClO_4$.2tx have been described recently (Barnes, Blyth & Paton, 1982). Walton (1966) reported the preparation and IR spectrum of $AgNO_3$.tx (I). In the present work two new complexes, $(AgNO_3)_2$.tx (II) and $(AgNO_3)_6$.tx (III) have been prepared and the crystal structures of (I), (II) and (III) have been determined.

Experimental. A sample of Walton's preparation of (I) was available. (II) and (III) were prepared together by

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