In (II) the C=O bonds are slightly longer while the OC—N bonds are slightly shorter than the corresponding bonds in (I). These differences are due to the increased contribution of resonance form (*B*) for (II).

It is interesting to note that the coordination numbers of these two Cu^{II} complexes are different. This difference in coordination number agrees with the tendency toward decreased coordination in the axial positions of six-coordinate metal complexes which contain strong in-plane fields (Busch, 1978). The deprotonated-amide nitrogen is a stronger donor than the amide oxygen. After the Cu—O to Cu—N bond rearrangements at the two amide sites, the in-plane ligand field increases, and the extent of axial addition decreases (Liang & Chung, 1980).

Some of the N···O and O···O distances are sufficiently short to indicate hydrogen bonding and are summarized in Table 4. Packing diagrams are shown in Fig. 3.

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References

Busch, D. H. (1978). *Acc. Chem. Res.* pp. 392–400.

Chao, M. S. & Chung, C. S. (1981). *J. Chem. Soc. Dalton Trans.* pp. 683–686.

Chen, J. Y. (1982). MS Thesis, Institute of Chemistry, National Tsing Hua Univ.

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

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

Liang, B. F. & Chung, C. S. (1980). *Inorg. Chem.* **19**, 572–574.

Pavkovic, S. F. & Brown, J. N. (1982). *Acta Cryst.* B**38**, 274–276.

Wei, L. W., Chao, M. S. & Chung, C. S. (1979). *J. Chin. Chem. Soc.* (*Taipei*), **26**, 145–151.

Acta Cryst. (1984). C**40**, 1135–1137

Structure of [2,2′-(1,4,10,13-Tetraoxa-7,16-diaza-7,16-cyclooctadecylene)dipropionato]-copper(II), [Cu($C_{18}H_{32}N_2O_8$)]

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Dedicated to Professor J. D. Dunitz (*ETH, Zürich*) *on the occasion of his* 60*th birthday*

Abstract. $M_r = 467{\cdot}99$, monoclinic, $P2_1/c$, $a = 7{\cdot}032\,(5)$, $b = 15{\cdot}533\,(2)$, $c = 9{\cdot}836\,(2)$ Å, $\beta = 113{\cdot}46\,(4)°$, $V = 985{\cdot}5\,(8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}586\,(1)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 11{\cdot}23$ cm^{-1}, $F(000) = 494$, $T = 293$ K, final $R = 0{\cdot}034$ for 1431 observed reflections. The molecule is centrosymmetric (C_i) with the Cu atom at the centre of symmetry. The Cu atom is coordinated to atoms N(1), C(13) and O(7) and to their symmetry-related equivalents, forming an irregular octahedron with one elongated and skewed [by 11·58 (7)°] diagonal.

Introduction. The title compound (αPRCU) (Koliński & Mroziński, 1983) is an α-propionic acid analogue of 1,4,10,13-tetraoxa-7,16-diaza-7,16-cyclooctadecanediacetatocopper(II) complexes (ACCU, ACCU.$CuCl_2$) investigated recently by X-ray diffraction methods (Uechi, Ueda, Tazaki, Takagi & Ueno, 1982; Gluziński, Krajewski, Urbańczyk-Lipkowska, Bleidelis & Mishnyov, 1982; Gluziński, Krajewski, Urbańczyk-Lipkowska, Andreetti & Bocelli, 1984). The ligands of the above type are interesting because they seem to have a particular selectivity for Cu^{II} ions (Uechi *et al.*, 1982). The present X-ray diffraction investigation was undertaken in order to compare the structure of αPRCU with the already known structures of the complexes cited.

Experimental. Black crystal (0·28 × 0·18 × 0·12 mm) from reaction mixture. D_m not determined. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, $\omega/2\theta$ scan, $2\theta_{max} = 55°$, $hkl_{max} = 8, 19, 12$. Stability controlled with two reflections. 1935 unique reflections collected, 1431 with $I > 2\sigma_I$ regarded as observed. Cell constants

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refined against 25 reflections. Lorentz–polarization correction, no absorption correction. Space group $P2_1/c$ (from absences). Structure solved by heavy-atom method: Cu placed at (0,0,0) ($Z = 2$). Positional parameters for all non-H atoms of the asymmetric unit obtained from F_o Fourier syntheses; refinement with anisotropic temperature factors by the full-matrix least-squares method (*SHELX76*, Sheldrick, 1976) (scattering factors from *International Tables for X-ray Crystallography*, 1974). Final refinement (*XRAY70* system, Stewart, Kundell & Baldwin, 1970) with all H-atom parameters invariant (coordinates calculated geometrically, isotropic temperature factors set as B_{eq} of the adjacent atom + 1 Å^2). Final $R = 0{\cdot}034$ (unit weights). $\Delta/\sigma < 0{\cdot}01$. Max. electron density on final ΔF maps $< 0{\cdot}2$ e Å^{-3}. No correction for secondary extinction. Computations performed using CYBER-76 and CYBER-73 computers.

Discussion. The fractional coordinates of the non-H atoms with their B_{eq} values are listed in Table 1.† Table 2 gives the bond lengths and angles of the molecule as well as the geometry of the Cu coordination sphere. Fig. 1 shows the projection of the complexed molecule with the labelling of the atoms.

As for ACCU (Uechi *et al.*, 1982; Gluziński *et al.*, 1982), point group C_i can be assigned to the αPRCU molecule with the Cu placed at the centre. As regards the bond lengths and angles in αPRCU the earlier observations of unusual elongations of some N—C bonds in the ligand are confirmed (Gluziński *et al.*, 1984). The other bond lengths and angles do not reveal any peculiarities.

The conformation of the diaza-18-crown-6 ring in αPRCU is very similar to that in ACCU. The sequence of torsion-angle types is the same as in ACCU [$(\text{-}g^*\text{-}g\text{-}a\text{-}a\text{-}g\text{-}g^*\text{-}a\text{-}g\text{-}a^*\text{-})_2$] (*g*: *gauche*; *a*: *anti*; *: deformed angle). It seems, therefore, that the introduction of a methyl group at the acetate α-C atom has no significant influence on the ligand conformation (the differences between the corresponding torsion angles in αPRCU and ACCU are within a range of 5°).

The Cu atom is coordinated to N(1), C(13) and O(7) atoms and to their symmetry equivalents forming an irregular octahedron. The base plane of the octahedron [N(1), C(13), N(1′) and C(13′)] approximates a square; the O(7)—Cu—O(7′) line forms an angle with the normal of that plane of 11·58 (7)°. Thus, the skewing of the elongated octahedron diagonal in the present case is greater than in the case of ACCU [7·3 (2)°].

Table 1. *Fractional atomic coordinates* ($\times 10^4$) (*e.s.d.'s in parentheses*)

	x	*y*	*z*	B_{eq}*(Å^2)
Cu	0	0	0	1·57 (3)
N(1)	524 (4)	827 (2)	−1437 (3)	1·88 (9)
C(2)	1464 (5)	414 (2)	−2396 (4)	2·19 (13)
C(3)	529 (6)	−440 (2)	−3064 (4)	2·46 (11)
O(4)	−1538 (4)	−334 (2)	−4166 (3)	2·70 (7)
C(5)	−2828 (6)	−1067 (2)	−4339 (4)	2·76 (11)
C(6)	−4004 (6)	−1037 (3)	−3356 (4)	3·09 (12)
O(7)	−2608 (4)	−1079 (2)	−1857 (3)	2·86 (9)
C(8)	−3585 (5)	−1271 (3)	−863 (4)	2·57 (12)
C(9)	−1916 (5)	−1540 (2)	571 (4)	2·27 (12)
C(10)	−1576 (5)	1195 (2)	−2360 (4)	2·04 (11)
C(11)	−2795 (5)	1287 (2)	−1375 (4)	2·07 (11)
C(12)	−1589 (6)	2006 (3)	−3231 (5)	3·01 (14)
O(13)	−2337 (4)	736 (2)	−313 (3)	2·42 (10)
O(14)	−4175 (4)	1825 (2)	−1685 (3)	3·14 (13)

* Calculated from the anisotropic thermal parameters (deposited) as $B_{eq} = 8\pi^2(U_1U_2U_3)^{1/3}$ where U_i are the eigenvalues of the U_{ij} matrix.

Table 2. *Bonding and* Cu *coordination distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(2)	1·494 (6)	C(8)—C(9)	1·491 (5)
C(2)—C(3)	1·510 (5)	C(9)—N(1′)	1·499 (4)
C(3)—O(4)	1·435 (4)	N(1)—C(10)	1·504 (4)
O(4)—C(5)	1·424 (5)	C(10)—C(11)	1·535 (6)
C(5)—C(6)	1·502 (7)	C(10)—C(12)	1·522 (6)
C(6)—O(7)	1·411 (4)	C(11)—O(13)	1·288 (4)
O(7)—C(8)	1·432 (6)	C(11)—O(14)	1·223 (4)
C(2)—N(1)—C(9′)	108·9 (3)	O(7)—C(8)—C(9)	107·1 (3)
C(2)—N(1)—C(10)	110·9 (3)	C(8)—C(9)—N(1′)	114·9 (3)
C(9′)—N(1)—C(10)	108·9 (2)	N(1)—C(10)—C(11)	108·4 (3)
N(1)—C(2)—C(3)	115·2 (3)	N(1)—C(10)—C(12)	116·0 (3)
C(2)—C(3)—O(4)	111·3 (3)	C(11)—C(10)—C(12)	113·5 (3)
C(3)—O(4)—C(5)	113·9 (3)	C(10)—C(11)—O(13)	115·3 (3)
O(4)—C(5)—C(6)	112·7 (3)	C(10)—C(11)—O(14)	119·6 (3)
C(5)—C(6)—O(7)	109·8 (3)	O(13)—C(11)—O(14)	125·0 (4)
C(6)—O(7)—C(8)	113·5 (3)	C(11)—O(13)—Cu	116·5 (3)
Cu—N(1)	2·050 (3)	Cu—O(13)	1·924 (3)
Cu—O(7)	2·615 (3)		
N(1)—Cu—O(7)	100·9 (1)	O(7)—Cu—O(13)	87·3 (1)
N(1)—Cu—O(13)	83·9 (1)		

Primed atoms are generated by inversion at (0,0,0).

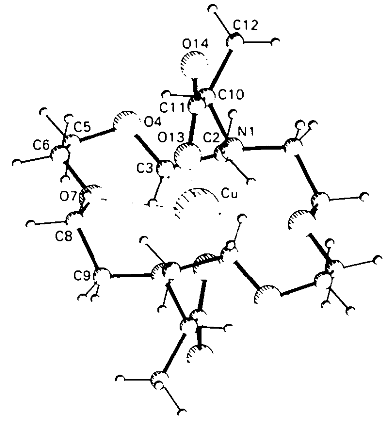

Fig. 1. Parallel projection of the complexed molecule with crystallographic labelling of the atoms. The orientation is that for optimal viewing.

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† Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39318 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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References

GLUZIŃSKI, P., KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z., ANDREETTI, G. D. & BOCELLI, G. (1984). *Acta Cryst.* C**40**, 778–781.

GLUZIŃSKI, P., KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z., BLEIDELIS, J. & MISHNYOV, A. (1982). *Cryst. Struct. Commun.* **11**, 1589–1592.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KOLIŃSKI, R. A. & MROZIŃSKI, J. (1983). *Polyhedron*, **2**, 1217–1220.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

UECHI, T., UEDA, I., TAZAKI, M., TAKAGI, M. & UENO, K. (1982). *Acta Cryst.* B**38**, 433–436.

Acta Cryst. (1984). C**40**, 1137–1139

Di(4,4′,5,5′-tetramethyl-2,2′-bi-1,3-diselenolyliden)ium Perrhenate, $C_{20}H_{24}Se_8^+.ReO_4^-$, $(TMTSF)_2ReO_4$. Detailed Superstructure at 120 K

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Abstract. $M_r = 1146{\cdot}3$, triclinic, space group $F\bar{1}$ ($P\bar{1}$ in conventional setting), $a = 14{\cdot}295\ (3)$, $b = 15{\cdot}419\ (2)$, $c = 26{\cdot}649\ (3)$ Å, $\alpha = 83{\cdot}96\ (1)$, $\beta = 88{\cdot}75\ (1)$, $\gamma = 69{\cdot}39\ (1)°$, $V = 5467\ (2)$ Å^3, $Z = 8$, $D_x = 2{\cdot}785$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 21{\cdot}21$ mm^{-1}, $F(000) = 4184$, $T = 120$ K, final $R = 0{\cdot}052$, $wR = 0{\cdot}070$, for 4042 observed reflections. Unlike the room-temperature structure the ReO_4^- anions are ordered and, in addition, the anions as well as the TMTSF molecules are displaced relative to their positions in the average structure previously reported. Bond distances and angles in TMTSF are the same as in the average structure. The ReO_4^- ion is an almost perfect tetrahedron.

Introduction. $(TMTSF)_2ReO_4$ belongs to a series of compounds $(TMTSF)_2X$ ($X = PF_6$, AsF_6, TaF_6, ClO_4, ReO_4, NO_3 *etc.*) which have been intensively studied in recent years because of their unusual physical properties (*e.g.* superconductivity of some members around 1 K). The structure of $(TMTSF)_2ReO_4$ at 295 and 120 K has previously been determined (Rindorf, Soling & Thorup, 1982). At 295 K ReO_4^- is situated at a site of inversion symmetry leading to orientational disorder of this anion. At 120 K a doubling of all three axial lengths is accompanied by an ordering of the ReO_4^- ions. The quality and size of the crystal used did not allow inclusion of the weaker superstructure reflections, *i.e.* only the average structure at 120 K was determined. Our data suggested no further distortion of the low-temperature phase, and the metal–insulator transition at 182 K in this material was described accordingly (Jacobsen, Pedersen, Mortensen, Rindorf, Thorup, Torrance & Bechgaard, 1982). Further measurements, however, indicated some additional displacements of Re atoms as well as TMTSF molecules below the phase transition (Moret, Pouget, Comes & Bechgaard, 1982; Guy, Boebinger, Marseglia, Friend & Bechgaard, 1983). An improved model for the metal–insulator transition has recently been proposed (Bruinsma & Emery, 1983), a model which also accounts for the transition in the analogous sulfur compound $(TMTTF)_2ReO_4$ taking place at approximately 160 K (Parkin, Mayerle & Engler, 1983).

Therefore, this redetermination using a better quality crystal now available in order to reveal the full superstructure at 120 K was initiated.

Experimental. Crystals of good quality prepared as described earlier (Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981) supplied by Dr K. Bechgaard. Crystal $0{\cdot}05 \times 0{\cdot}1 \times 0{\cdot}2$ mm. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections, $24 < \theta < 34°$.

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