molecular packing stress. The largest effect is shown by the methoxycarbonyl group. The Mn(1)–C(23)–O(6) angles are 111·8 (7) and 116·6 (7)° so that the difference of 4·8° is experimentally significant. This tilt of the methoxycarbonyl group is accompanied by a rotation of the group about the metal atom which is shown by the C(21)–Mn(1)–C(23) angles of 178·3 and 174·9°. The torsion angle of the methoxycarbonyl group to the metal atom changes by 9·9° between the two molecules. The phenyl to phosphorus torsion angles change by 10·7, 9·3, and 8·6° between the two molecules.

The shortest intermolecular nonbonded distances relative to expected van der Waals values are several C···H contacts, the shortest being 2·77 Å, and several O···H contacts, the shortest being 2·53 Å. The molecular packing thus appears to be of normal van der Waals type, but influenced by Coulombic attraction favoring short distances between hydrogen (which is expected to carry a positive net charge) and carbon and oxygen (expected to carry negative net charges).

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Structure of the Barium Salt of a Cu^{2+} Complex with a Tetraaza Macrocyclic Tetraacetate

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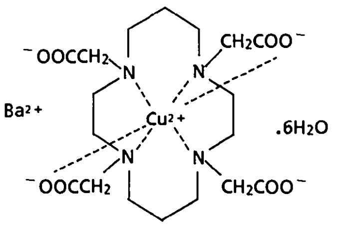
Abstract. Barium (1,4,8,11-tetraazacyclotetradecane-*N,N′,N″,N‴*-tetraacetato)cuprate hexahydrate, $Ba[Cu(C_{18}H_{28}N_4O_8)].6H_2O$, $M_r = 737{\cdot}40$, triclinic, $P\bar{1}$, $a = 8{\cdot}928\,(3)$, $b = 10{\cdot}893\,(4)$, $c = 15{\cdot}889\,(2)$ Å, $\alpha = 91{\cdot}98\,(2)$, $\beta = 101{\cdot}96\,(1)$, $\gamma = 117{\cdot}28\,(3)°$, $V = 1328{\cdot}5$ Å^3, $D_m = 1{\cdot}83$, $D_x = 1{\cdot}843$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}21$ mm^{-1}, $F(000) = 738$, $T = 298$ K, $R = 0{\cdot}055$ for 3755 reflections with $I \geq 2\sigma(I)$. In the unit cell two crystallographically different complex anions are situated with their Cu^{2+} atoms on two different inversion centres of the triclinic cell. The geometry for both units is a distorted octahedron with four amino nitrogens in a plane and two apical acetate oxygen donors. The Cu atom is situated exactly in the N_4 plane of the macrocycle, which takes the *trans*-III configuration.

Introduction. The coordination behaviour of tetrafunctionalized macrocyclic ligands with transition-metal ions has been described previously (Riesen, Zehnder & Kaden, 1985, 1986). So the structures of the binuclear Cu^{2+} complexes with dota (dota = 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetic acid) and teta (teta = 1,4,8,11-tetraazacyclotetradecane-*N,N′,N″,N‴*-tetraacetic acid) as well as that of the mononuclear Cu^{2+} complex with dota have been described. The mononuclear complex of teta was crystallized as a complex anion, $Ba[Cu(teta)].6H_2O$, and its structure was determined.



Experimental. Blue crystals of $Ba[Cu(teta)].6H_2O$ were prepared according to the literature procedure (Riesen *et al.*, 1986). An Enraf–Nonius CAD-4 diffractometer controlled by a Digital MicroVAX computer was used for measurements. The Mo $K\alpha$ radiation was monochromated by graphite. Cell parameters were taken on a crystal of size 0·1 × 0·1 × 0·2 mm from least-squares

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Table 1. *Fractional atomic coordinates and* U_{eq} (Å^2) *values*

$U_{\rm eq} = \frac{1}{3}\sum_i U_{ii}(\times 10^{-2})$ Å^2.

	x	y	z	$U_{\rm eq}$
Cu(1)	1·0	0·0	1·0	1·80 (6)
O(1)	0·9369 (7)	0·1794 (5)	0·9721 (3)	2·24
O(2)	0·9959 (8)	0·3813 (6)	1·0436 (4)	3·20
C(1)	1·0003 (9)	0·2689 (7)	1·0410 (5)	1·88
C(2)	1·0890 (11)	0·2427 (8)	1·1248 (5)	2·79
N(1)	1·0696 (8)	0·0983 (6)	1·1229 (4)	2·17
C(3)	0·9239 (10)	0·0112 (8)	1·1620 (5)	2·80
C(4)	0·7512 (11)	−0·0284 (9)	1·0983 (5)	3·11
N(2)	0·7372 (8)	−0·1153 (7)	1·0182 (4)	2·40
C(5)	0·6090 (10)	−0·1124 (8)	0·9427 (5)	2·93
C(6)	0·6058 (10)	−0·1782 (8)	0·8557 (5)	2·67
C(7)	0·7684 (10)	−0·1033 (9)	0·8231 (5)	2·89
C(8)	0·6937 (10)	−0·2591 (8)	1·0361 (5)	2·53
C(9)	0·5345 (10)	−0·3415 (8)	1·0733 (5)	2·68
O(3)	0·4059 (7)	−0·3194 (6)	1·0542 (4)	3·66
O(4)	0·5421 (9)	−0·4297 (7)	1·1181 (5)	3·92
Cu(2)	0·5	0·0	0·5	2·44
O(5)	0·6319 (7)	0·0737 (6)	0·6445 (4)	3·26
O(6)	0·5659 (8)	0·1121 (6)	0·7687 (4)	3·57
C(10)	0·5249 (10)	0·0690 (8)	0·6883 (5)	2·54
C(11)	0·3314 (11)	−0·0007 (10)	0·6413 (5)	3·40
N(3)	0·2968 (9)	−0·0120 (7)	0·5455 (4)	3·20
C(12)	0·2791 (11)	0·1120 (9)	0·5178 (6)	3·86
C(13)	0·4563 (12)	0·2399 (9)	0·5376 (6)	3·98
N(4)	0·5676 (9)	0·2143 (7)	0·4880 (4)	2·90
C(14)	0·7528 (12)	0·3076 (9)	0·5302 (6)	3·21
C(15)	0·8754 (12)	0·2773 (10)	0·4876 (6)	3·66
C(16)	0·8723 (11)	0·1399 (10)	0·4972 (6)	3·43
C(17)	0·5201 (12)	0·2355 (8)	0·3953 (5)	3·13
C(18)	0·5563 (14)	0·3856 (10)	0·3804 (6)	4·22
O(7)	0·7080 (10)	0·4676 (8)	0·3752 (6)	6·69
O(8)	0·4360 (11)	0·4133 (9)	0·3696 (7)	4·38
Ba	0·8474 (1)	0·3547 (1)	0·8630 (1)	2·18
O*W*(1)	1·2116 (8)	0·5165 (7)	0·8841 (4)	3·96
O*W*(2)	0·9538 (9)	0·2331 (7)	0·7525 (4)	4·33
O*W*(3)	0·6365 (12)	0·4419 (9)	0·7574 (5)	6·73
O*W*(4)	0·0848 (11)	0·2519 (10)	0·3477 (6)	7·14
O*W*(5)	0·2314 (13)	0·2919 (8)	0·6865 (6)	6·54
O*W*(6)	0·8866 (15)	0·3923 (13)	0·2748 (7)	11·23

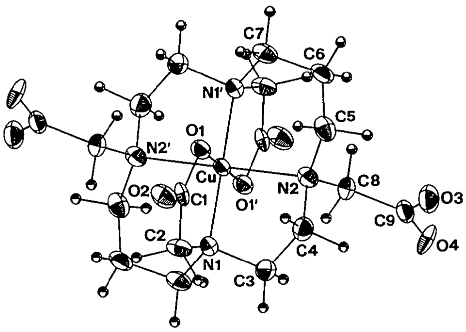

Fig. 1. *ORTEP* plot (Johnson, 1971) of the anion with atom-numbering scheme.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu(1)–N(1)	2·023 (6)	Cu(2)–N(3)	2·041 (7)
Cu(1)–N(2)	2·184 (6)	Cu(2)–N(4)	2·153 (6)
Cu(1)–O(1)	2·302 (5)	Cu(2)–O(5)	2·278 (6)
O(1)–C(1)	1·278 (8)	O(5)–C(10)	1·278 (10)
O(2)–C(1)	1·243 (8)	O(6)–C(10)	1·261 (9)
C(1)–C(2)	1·509 (10)	C(10)–C(11)	1·530 (11)
C(2)–N(1)	1·500 (9)	C(11)–N(3)	1·478 (10)
N(1)–C(3)	1·490 (9)	N(3)–C(12)	1·501 (10)
C(3)–C(4)	1·517 (11)	C(12)–C(13)	1·512 (12)
C(4)–N(2)	1·508 (10)	C(13)–N(4)	1·501 (11)
N(2)–C(5)	1·488 (9)	N(4)–C(14)	1·473 (10)
C(5)–C(6)	1·524 (11)	C(14)–C(15)	1·545 (14)
C(6)–C(7)	1·516 (11)	C(15)–C(16)	1·498 (14)
C(7)–N(1′)	1·497 (10)	C(16)–N(3)	1·505 (11)
N(2)–C(8)	1·485 (9)	N(4)–C(17)	1·502 (10)
C(8)–C(9)	1·546 (10)	C(17)–C(18)	1·552 (12)
C(9)–O(3)	1·257 (10)	C(18)–O(7)	1·257 (12)
C(9)–O(4)	1·233 (10)	C(18)–O(8)	1·244 (13)
Ba–O(1)	2·888 (5)	Ba–O*W*(1)	2·836 (6)
Ba–O(2)	2·844 (5)	Ba–O*W*(2)	2·725 (6)
Ba–O(6)	2·761 (5)	Ba–O*W*(3)	2·775 (8)
Ba–O(3′)	2·732 (6)		
Ba–O(2′)	2·754 (5)		
O(1)–Cu(1)–N(1)	80·5 (2)	O(5)–Cu(2)–N(3)	79·7 (2)
O(1)–Cu(1)–N(2)	86·6 (2)	O(5)–Cu(2)–N(4)	87·2 (2)
N(1)–Cu(1)–N(2)	86·7 (2)	N(3)–Cu(2)–N(4)	87·2 (3)

Primed atoms are related by a centre of symmetry.

procedure on 25 strong reflections in the 2θ range 12–28°. 4666 reflections ($2 \leq \theta \leq 25°$) were measured in the range $-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $0 \leq l \leq 18$ by $\omega/2\theta$ scan technique. No significant variation in the intensities of four standards ($\bar{2}0\bar{4}$; $\bar{3}\bar{1}1$; $01\bar{4}$; $\bar{1}\bar{2}0$) monitored every 3600 s was observed. The raw data set was corrected for polarization effects, but no corrections for absorption were made. Positional parameters of the metal ions were determined by a three-dimensional Patterson map (*SHELX*76; Sheldrick, 1976). The remaining atoms were localized by subsequent difference Fourier maps. Anisotropic thermal parameters for all non-H atoms and isotropic H atoms in calculated positions were refined to $R = 0{\cdot}0550$ using 3755 reflections in a full-matrix refinement on F with 346 parameters. $wR = 0{\cdot}0607$; $w = 0{\cdot}679/[\sigma^2(F) + 5{\cdot}82 \times 10^{-3}F^2]$. The maximum ratio of least-squares shift to e.s.d. was 0·04, and the largest positive peak on the ΔF map was 2·43, the largest negative peak −1·39 e Å^{-3}. Scattering factors for C, H, N, O are given in *SHELX*76 (Sheldrick, 1976), and those for Ba^{2+} and Cu^{2+} are from Cromer & Mann (1968). Atomic parameters are given in Table 1, selected bond lengths and angles in Table 2 and the numbering scheme is shown in Fig. 1.*

Discussion. The asymmetric unit of Ba[Cu(teta)].6H_2O consists of two half molecules with Cu^{2+} [Cu(1) and Cu(2)] on two different inversion centres of the triclinic cell. The distances and angles in both molecules are very similar to each other. The structure of Cu(1)(teta)$^{2-}$, shown in Fig. 1, indicates that the Cu ion has a distorted octahedral geometry and that the macrocycle is in the *trans*-III configuration according to the nomenclature of Bosnich, Poon & Tobe (1965). Owing to the symmetry the four nitrogens and the metal ion are in a plane. Whereas the Cu(1)—N(1) (2·02) and Cu(2)—N(3) (2·04 Å) distances are quite

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51124 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

normal, the bonds Cu(1)—N(2) (2·18) and Cu(2)—N(4) (2·15 Å) are somewhat elongated. The strongest distortion due to the Jahn–Teller effect leads to axial bond lengths Cu(1)—O(1) of 2·30 and Cu(2)—O(5) of 2·28 Å, respectively. This fact is in contrast to the structure of an analogous C-substituted Cu^{2+} complex (Moi, Yanuck, Deshpande, Hope, Denardo & Meares, 1987), in which the metal ion is situated in the N_2O_2 plane and the two amino nitrogens with the noncoordinated COOH groups are in axial positions with bond lengths of 2·37, 2·43 Å. Interesting also is the comparison with the structure of a Ni^{2+} complex with the related ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N,N'*-diacetic acid (Xu Ji-De, Ni Shi-Sheng & Lin Yu-Juan, 1986) for which a *cis*-octahedral structure was found. Finally the Cu^{2+} complex of the analogous 12-membered macrocycle dota also gives a *cis*-octahedral structure with two elongated Cu—N bonds (Riesen *et al.*, 1986). All these results show that these macrocyclic amino carboxylic acids, having so many donor atoms, can coordinate metal ions in so many different ways that a prediction is practically impossible.

In our compound the Ba^{2+} cation is surrounded by eight O atoms, of which five are carboxylates and three water molecules. A total of six crystal water molecules could be localized in the crystal.

It is interesting to note that another form of the same compound also exists. The blue-green crystals have been partially studied by X-ray diffraction and the unit-cell parameters were $a = 8·619 (1)$, $b = 10·578 (1)$, $c = 16·787 (2)$ Å, $\alpha = 99·89 (2)$, $\beta = 97·73 (2)$, $\gamma = 110·90 (1)°$. The structure is very similar to the one discussed above with two Cu ions on special positions and Ba^{2+} in a common site. Instead of six a total of seven water molecules were found. Further work on this form is not intended.

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Complexes of Strontium and Barium Dimethylpropanoates with Dicyclohexano-18-crown-6(*A*) Ether

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Abstract. (1): Bis(2,2-dimethylpropanoato)strontium-*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacosane monohydrate, $[Sr(C_{20}H_{36}O_6)(C_5H_9O_2)_2].H_2O$, $M_r = 680·39$, triclinic, $P\bar{1}$, $a = 14·528 (2)$, $b = 13·966 (2)$, $c = 9·0403 (9)$ Å, $\alpha = 95·967 (8)$, $\beta = 103·035 (6)$, $\gamma = 87·75 (8)°$, $V = 1777·1 (7)$ Å^3, $Z = 2$, $D_x = 1·27$, $D_m = 1·28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 15·2$ cm^{-1}, $F(000) = 724$, $T = 293$ K, $R(F) = 0·071$ for 1992 reflections ($F_o > 3\sigma$). (2): 2,2-Dimethylpropanoato(diaqua)barium-*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacosane 2,2-dimethylpropanoate hydrate, $[Ba(C_{20}H_{36}O_6)(C_5H_9O_2)(H_2O)_2][C_5H_9O_2].H_2O$, $M_r = 766·13$, triclinic, $P\bar{1}$, $a = 12·716 (2)$, $b = 14·231 (2)$, $c = 12·024 (4)$ Å, $\alpha = 94·18 (1)$, $\beta = 96·82 (1)$, $\gamma = 116·72 (1)°$, $V = 1910 (2)$ Å^3, $Z = 2$, $D_x = 1·33$, $D_m = 1·38$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 10·1$ cm^{-1}, $F(000) = 800$, $T = 291$ K, $R(F) = 0·025$ for 4136 reflections ($F_o > \sigma$). The Sr^{2+} ion in (1) is coordinated by all six O atoms of the crown ether and by two bidentate dimethylpropanoate ions (dmp), and the resulting complex molecules are linked by H_2O molecules through H bonding. Complex (2) crystallizes as ion pairs, $[Ba(dmp).(H_2O)_2.DC18C6]^+$ and $(dmp)^-$, separated by H_2O molecules to which they are H bonded.

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