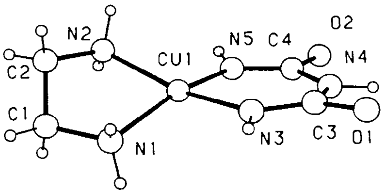

Fig. 1. Perspective view of one of the two crystallographically independent complex molecules.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···A	D···A	H···A	D–H···A
N(1)–H(N1)···O(12^{i})	3·036 (4)	2·22 (5)	156 (5)
N(1)–H′(N1)···O(11^{ii})	2·971 (4)	2·21 (5)	146 (4)
N(2)–H(N2)···O(12)	2·944 (4)	2·06 (5)	174 (4)
N(4)–H(N4)···O(1^{iii})	2·889 (4)	2·07 (4)	175 (4)
N(11)–H′(N11)···O(2^{iv})	2·874 (4)	2·08 (5)	159 (4)
N(12)–H(N12)···O(1^{v})	2·868 (4)	2·03 (5)	155 (4)
N(12)–H′(N12)···O(2^{vi})	2·989 (3)	2·23 (4)	151 (4)
N(13)–H(N13)···O(2^{iv})	2·993 (4)	2·26 (5)	139 (4)
N(14)–H(N14)···O(11^{vii})	2·905 (4)	2·19 (4)	165 (4)

Symmetry code

(i)	$1-x, 1-y, 1-z$	(ii)	$x, y, 1+z$
(iii)	$-x, -y, 1-z$	(iv)	$1-x, -y, -z$
(v)	$1-x, -y, 1-z$	(vi)	$1+x, y, z$
(vii)	$1-x, 1-y, -z$		

are very similar in the two molecules. Both Cu atoms have a tetrahedrally distorted planar coordination but the degree of distortion differs in the two molecules. The N atoms of ethylenediamine and the N atoms of the amide groups of the biuret ligand coordinate to Cu(1) in a pseudotetrahedral manner, with a dihedral angle of 25·6 (2)° between the N(1),Cu(1),N(2) and N(3),Cu(1),N(5) planes. The geometry around Cu(2) is much closer to planar, the dihedral angle between the N(11),Cu(2),N(12) and N(13),Cu(2),N(15) planes being only 12·6 (3)°.

The bond lengths and angles of the biuret ligand are essentially the same as those found for dipotassium bis[biuretato(2–)-N^1,N^5]cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961) and dipotassium di-μ-hydroxo-bis{[biuretato(2–)-N^1,N^5]copper(II)} tetrahydrate (Birker & Beurskens, 1974). The biuret residues are not planar. Each residue is slightly bent about the line joining Cu to the terminal N atom of the six-membered ring; and the two halves of each ligand are twisted in opposite directions around the bonds N(4)–C(3) [N(14)–C(13)] and N(4)–C(4) [N(14)–C(14)]. As a result of this twisting the angles between the N(3),C(3),O(1),N(4) and N(5),C(4),O(2),N(4) planes and between the N(13),C(13),O(11),N(14) and N(15),C(14),O(12),N(14) planes are 7·7 (7) and 5·9 (6)°, respectively.

The diamine ligands are in a *gauche* conformation. The packing is mainly determined by intermolecular N–H···O hydrogen bonds involving the diamine N atoms and the O atoms of the biuret ligand. The parameters of the hydrogen bonds are listed in Table 3.

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Tris(ethylenediamine)cobalt(III) Dihydrogen Tetrahydrofurantetracarboxylate Trihydrogen Tetrahydrofurantetracarboxylate Hydrate (1:1:1:2½)

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Abstract. $(C_2H_8N_2)_3Co^{3+}.C_8H_7O_9^-.C_8H_6O_9^{2-}.2\frac{1}{2}H_2O$, triclinic, $P\bar{1}$, a = 11·822 (2), b = 13·100 (2), c = 11·461 (2) Å, α = 68·81 (4), β = 79·72 (3), γ = 77·30 (3)°, V = 1605 Å^3, D_c = 1·58 Mg m^{-3}, Z = 2. Final R = 0·070 for 2460 observed reflexions. Both anions are of the *trans,cis,trans* isomer with very similar geometry. The anions are linked to the N protons of the cation and to the water molecules by an extensive three-dimensional network of hydrogen bonds.

0567-7408/82/051588-04$01.00

Introduction. Tetrahydrofurantetracarboxylic acid, H_4TTA, is commercially available as a mixture of diastereoisomers (Aldrich). It has been suggested as a metal trap in detergent formulations (Konort, 1971; Yang, 1971) but no studies of its metal complexes have been reported either from solution studies or in the solid state. In principle, the manifold diastereoisomers of H_4TTA should form different complexes with metal ions and thus be separable if these complexes can be crystallized. Solutions of H_4TTA mixed with metal ions either refuse to crystallize or give immediate precipitates of fine powders. The first crystals to be obtained suitable for crystallography were those of the title compound.

Data were collected for levels (0–8)*kl* using a Stoe Stadi II diffractometer. The *SHELX* 76 (Sheldrick, 1976) program system was used for all calculations. The direct-methods routine *TANG* in space group $P1$ revealed two CoN_6 octahedra related by a centre of symmetry. Calculations were continued in space group $P\bar{1}$. All non-H atoms were revealed by difference syntheses alternated with least-squares refinement. The weakest planes were found to be very unreliable; the rejection limit was eventually set at $F_o < 5\sigma_F$, which left 2460 out of the original 5983 unique reflexions. The structure refined to $R = 0\cdot11$ with Co as the only anisotropic atom and to convergence at $R = 0\cdot070$ with all non-H atoms except O(63) anisotropic. H atoms for the ethylenediamine ligands and the tetrahydrofuran ring were included on calculated positions, the remaining H atoms were omitted. O(63) was interpreted as a water molecule ideally at the special position $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The very high isotropic thermal parameter $0\cdot244\,(20)$ Å^2 together with the refined site occupancy factor of $1\cdot00\,(3)$ shows that the true position of this water molecule is very ill-defined.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. Atomic coordinates are given in Table 1, with interatomic distances and angles in Table 2.

The crystals contain $H_3TTA^-(A)$ and $H_2TTA^{2-}(B)$ anions balancing the charge of the $Co(en)_3{}^{3+}$ cation. Fig. 1 and Table 3 show that both anions are of the *trans,cis,trans* isomer with the ring conformation very similar in both. The C(26), C(46) and C(29), C(49) carboxylate groups are aligned very similarly with respect to the tetrahydrofuran plane but the remaining carboxylate groups are twisted to different angles in the two anions, forming in the one case an internal hydrogen bond O(28)···O(37) but in the other an internal

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Cation				
Co(1)	−1641 (1)	1755 (1)	2558 (1)	22 (1)
N(1)	−949 (6)	2945 (6)	1231 (7)	36 (2)
C(2)	337 (8)	2764 (9)	1411 (11)	61 (4)
C(3)	462 (8)	2389 (8)	2765 (11)	53 (4)
N(4)	−247 (5)	1511 (6)	3408 (7)	32 (2)
N(5)	−965 (6)	726 (5)	1614 (6)	30 (2)
C(6)	−1496 (7)	−293 (6)	2178 (9)	30 (3)
C(7)	−1595 (7)	−560 (6)	3569 (9)	31 (3)
N(8)	−2204 (5)	466 (5)	3859 (6)	26 (2)
N(9)	−3084 (5)	2154 (5)	1743 (7)	30 (2)
C(10)	−3824 (10)	3097 (12)	2038 (15)	74 (6)
C(11)	−3645 (11)	3198 (13)	3154 (14)	95 (6)
N(12)	−2449 (6)	2717 (6)	3540 (7)	32 (2)
Anion *A*				
O(21)	−796 (4)	4863 (4)	−3715 (5)	27 (1)
C(22)	−1599 (6)	5486 (6)	−4605 (8)	28 (2)
C(23)	−2802 (6)	5574 (6)	−3849 (8)	27 (2)
C(24)	−2652 (6)	4418 (6)	−2831 (8)	31 (3)
C(25)	−1380 (7)	4202 (6)	−2567 (9)	38 (3)
C(26)	−1637 (8)	4921 (8)	−5558 (10)	40 (3)
O(27)	−2022 (6)	5539 (6)	−6596 (6)	57 (2)
O(28)	−1287 (5)	3899 (5)	−5281 (6)	44 (2)
C(29)	−2993 (6)	6531 (7)	−3297 (11)	32 (3)
O(30)	−2887 (6)	6348 (5)	−2217 (8)	49 (2)
O(31)	−3239 (5)	7484 (4)	−4119 (6)	43 (2)
C(32)	−3486 (8)	4225 (8)	−1657 (11)	59 (4)
O(33)	−4591 (5)	4635 (5)	−1843 (6)	56 (2)
O(34)	−3182 (7)	3680 (9)	−671 (8)	135 (4)
C(35)	−816 (7)	2990 (8)	−2245 (11)	37 (3)
O(36)	−645 (5)	2417 (5)	−1178 (7)	51 (2)
O(37)	−543 (5)	2623 (5)	−3212 (7)	49 (2)
Anion *B*				
O(41)	−3628 (4)	1388 (4)	5965 (5)	23 (1)
C(42)	−4685 (6)	947 (6)	6308 (8)	23 (2)
C(43)	−5157 (6)	1095 (5)	7583 (8)	26 (2)
C(44)	−4004 (6)	804 (6)	8160 (7)	22 (2)
C(45)	−3134 (5)	1307 (6)	7043 (7)	23 (2)
C(46)	−4513 (6)	−278 (6)	6424 (8)	27 (3)
O(47)	−5416 (4)	−673 (4)	6526 (6)	38 (2)
O(48)	−3481 (4)	−808 (4)	6388 (6)	33 (2)
C(49)	−5755 (8)	2291 (7)	7343 (9)	37 (3)
O(50)	−5246 (6)	3038 (5)	7143 (8)	66 (3)
O(51)	−6887 (5)	2393 (5)	7295 (6)	50 (2)
C(52)	−4005 (8)	1103 (7)	9328 (9)	37 (3)
O(53)	−2968 (5)	927 (6)	9704 (6)	54 (2)
O(54)	−4879 (5)	1407 (5)	9904 (6)	48 (2)
C(55)	−1888 (7)	635 (6)	7075 (9)	26 (3)
O(56)	−1320 (4)	582 (5)	6079 (6)	30 (2)
O(57)	−1537 (4)	198 (5)	8169 (6)	40 (2)
Water molecules				
O(61)	−6145 (6)	3553 (6)	9904 (7)	62 (2)
O(62)	8287 (8)	5203 (6)	1211 (8)	91 (4)
O(63)	5000	5000	5000	244 (19)*

* Isotropic atom.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36617 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Cation

Co(1)–N(1)	1·953 (7)	Co(1)–N(8)	1·959 (6)
Co(1)–N(4)	1·970 (8)	Co(1)–N(9)	1·969 (8)
Co(1)–N(5)	1·973 (8)	Co(1)–N(12)	1·969 (9)
N(1)–C(2)	1·527 (14)	C(7)–N(8)	1·499 (12)
C(2)–C(3)	1·472 (18)	N(9)–C(10)	1·459 (17)
C(3)–N(4)	1·470 (13)	C(10)–C(11)	1·389 (27)
N(5)–C(6)	1·483 (11)	C(11)–N(12)	1·491 (15)
C(6)–C(7)	1·491 (12)		
N(1)–Co(1)–N(8)	174·6 (3)	N(1)–Co(1)–N(4)	85·6 (3)
N(4)–Co(1)–N(9)	173·8 (4)	N(5)–Co(1)–N(8)	85·4 (3)
N(5)–Co(1)–N(12)	174·6 (3)	N(9)–Co(1)–N(12)	86·2 (3)

Anions	*A*	*B**
O(21)–C(22)	1·418 (10)	1·425 (9)
C(22)–C(23)	1·532 (11)	1·532 (13)
C(23)–C(24)	1·537 (10)	1·534 (12)
C(24)–C(25)	1·532 (12)	1·532 (10)
C(25)–O(21)	1·439 (10)	1·419 (11)
C(22)–C(26)	1·536 (18)	1·534 (12)
C(26)–O(27)	1·270 (12)	1·254 (11)
C(26)–O(28)	1·250 (12)	1·266 (9)
C(23)–C(29)	1·555 (16)	1·518 (12)
C(29)–O(30)	1·198 (16)	1·191 (14)
C(29)–O(31)	1·272 (10)	1·324 (12)
C(24)–C(32)	1·495 (14)	1·525 (15)
C(32)–O(33)	1·322 (12)	1·317 (13)
C(32)–O(34)	1·170 (15)	1·194 (11)
C(25)–C(35)	1·517 (12)	1·540 (10)
C(35)–O(36)	1·207 (13)	1·234 (12)
C(35)–O(37)	1·324 (16)	1·279 (12)
O(21)–C(22)–C(23)	106·2 (6)	104·2 (8)
C(22)–C(23)–C(24)	99·0 (6)	99·1 (6)
C(23)–C(24)–C(25)	104·1 (7)	103·8 (6)
C(24)–C(25)–O(21)	104·5 (7)	104·8 (6)
C(25)–O(21)–C(22)	110·9 (6)	111·3 (6)
O(21)–C(22)–C(26)	112·8 (7)	113·5 (6)
C(22)–C(23)–C(29)	110·6 (7)	108·2 (6)
C(23)–C(24)–C(32)	118·3 (7)	117·7 (7)
C(24)–C(25)–C(35)	113·3 (8)	114·7 (6)
O(27)–C(26)–O(28)	124·0 (12)	125·1 (8)
O(30)–C(29)–O(31)	126·0 (11)	125·5 (8)
O(33)–C(32)–O(34)	123·4 (10)	122·4 (11)
O(36)–C(35)–O(37)	123·6 (9)	126·3 (7)

* Molecule *B* has atoms C(20 + *n*).

hydrogen bond O(53)···O(57). The C–O bond lengths show that the protonated atoms are O(31), O(33), O(37), O(51) and O(53). The mean values are C–OH 1·312 (12), C–O 1·259 (12) and C=O 1·192 (12) Å.

The *trans,cis,trans* isomer is formally *meso* but optical activity is restored by the non-planar conformation of the ring. The great similarity of the two anions suggests that intramolecular steric factors are more important in establishing the detailed conformation than changes in packing or intermolecular hydrogen bonding. Intermolecular hydrogen bonding is very extensive. In addition to the possibilities shown in Figs. 1 and 2 the water molecules are connected to each

Table 3. *Stereochemistry of the tetrahydrofuran-tetracarboxylate anions*

	H_3TTA (*A*)	H_2TTA^{2-} (*B*)*
Angle between line and normal to plane of tetrahydrofuran ring (°)		
Line		
C(22)–C(26)	164·6 (8)	166·0 (9)
C(23)–C(29)	8·6 (9)	7·4 (8)
C(24)–C(32)	68·4 (8)	68·9 (9)
C(25)–C(35)	131·0 (8)	131·3 (9)
Angle between the normals to the planes of the carboxylate group and the tetrahydrofuran ring (°)		
Group		
C(26)	86·4 (11)	82·9 (11)
C(29)	85·6 (12)	85·2 (11)
C(32)	17·5 (11)	30·6 (11)
C(35)	70·7 (11)	40·1 (12)

* Molecule *B* has atoms C(20 + *n*).

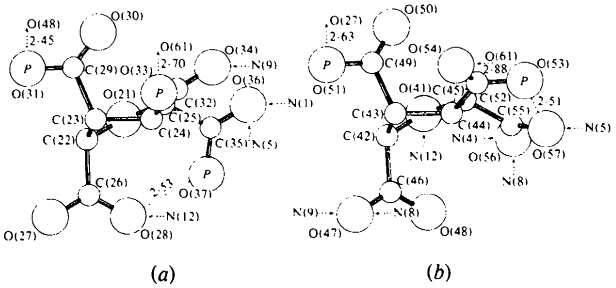

Fig. 1. (*a*) Anion *A* and (*b*) anion *B* viewed down the bisector of the angle O(23)···O(21)···C(24) or C(43)···O(41)···C(44). The protonated O atoms are marked *P*. Possible hydrogen bonds (Å) are shown schematically by dotted lines with arrows from the proton-carrying atoms. The internal hydrogen bonds are indicated by dashed lines. Hydrogen-bond lengths are given where these do not appear on Fig. 2.

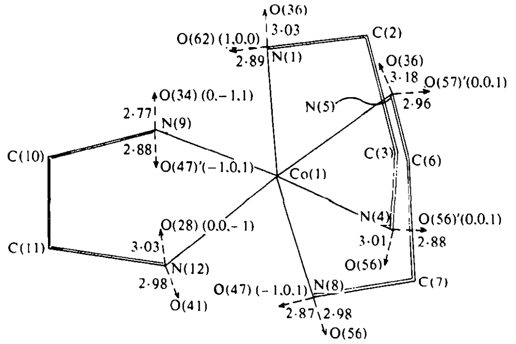

Fig. 2. The $Co(en)_3^{3+}$ cation viewed perpendicular to the plane N(5), N(8), N(9). Dashed lines are directed towards calculated amine hydrogen positions and show all possible hydrogen bonds less than 3·2 Å. Symmetry-related atoms are given as O(*ij*) at *x,y,z*, O(*ij*)' at –*x*,–*y*,–*z* with atoms in neighbouring cells shown by displacement coordinates (*x,y,z*).

other and to the anions to complete a three-dimensional array.

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Structure of Di-μ-chloro-bis[chloro(2-ethyl-2-hydroxymethyl-1,3-propanediol) copper(II)]

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Abstract. $[Cu(C_6H_{14}O_3)Cl_2]_2$, monoclinic, $P2_1/c$, a = 6·188 (2), b = 11·404 (2), c = 15·161 (4) Å, β = 109·60 (2)° (at 295 K), V = 1007·8 Å^3, Z = 4, M_r = 268·5, $F(000)$ = 548, D_c = 1·77 g cm^{-3}, λ(Mo K) = 0·7107 Å, μ = 27·4 cm^{-1}. Least-squares refinement based on 2456 reflections gave a conventional R value of 0·033. The complex crystallizes as discrete centrosymmetric dichloro-bridged dimers containing two five-coordinated Cu^{II} ions each bound by a bidentately coordinated triol molecule and three chloride ions. The dimers are held together by hydrogen bonds. Cu^{II} has coordination geometry intermediate between a trigonal bipyramid and a square pyramid. Cu—O bond lengths are 1·976 (1) and 1·991 (1) Å; the terminal Cu—Cl distance is 2·228 (1) Å and the bridging Cu—Cl distances are 2·271 (1) and 2·690 (1) Å. The six-membered chelate ring adopts the chair conformation.

Introduction. There has been considerable research activity recently on the coordination chemistry of weak neutral ligands (Poonia & Bajaj, 1979). Our principal interest is in coordination compounds with neutral polyol ligands. In this work we have prepared the $CuCl_2$ adduct of 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane, abbreviated here as tmp) in a molar ratio of 1:1.

The first trimethylolpropane complexes in which tmp acts as a neutral ligand were reported by Hein & Buckhardt (1957), who prepared $NiSO_4$ and $CoSO_4$ adducts of the ligand in a metal-to-ligand molar ratio of 1:2. They suggested that the ligand is coordinated to the metal ion by all three neutral alcoholic O atoms. Kilivnik, Lipatova & Veselovskii (1975) found that alkaline-earth-metal chlorides inhibit the reaction of isocyanates with tmp, probably as a result of reaction of these salts with tmp. They succeeded in synthesizing $MgCl_2$, $CaCl_2$. $SrCl_2$ and $Mg(ClO_4)_2$ adducts of tmp in a molar ratio of 1:2.

In order to obtain precise information about the coordination chemistry of trimethylolpropane we have synthesized $CuCl_2$ (tmp) and determined its structure.

The complex was prepared by the addition of 3·82 g (28·4 mmol) of ligand to a stirred solution of 1·829 g (13·6 mmol) of anhydrous copper(II) chloride in 70 cm^3 of tetrahydrofuran. 15 cm^3 hexane was added to the solution and the container stoppered and set aside at room temperature. Large green crystals were obtained after about one month and were filtered off and washed with ether.

The X-ray diffraction measurements were made on a crystal 0·2 × 0·2 × 0·4 mm, with a Syntex $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell parameters were calculated by least squares from the setting angles for 25 reflections. The intensities were recorded using the ω-scanning mode with a variable scan speed (3·0–29·3° min^{-1}), depending on the peak intensity of the reflection. 3093 intensities were measured for $2\theta \leq 55°$, and the 2456 reflections for which $I > 3\sigma(I)$ were used in the refinement. One check reflection was recorded after every 100 measurements. The net intensities were corrected for Lorentz and polarization effects; no absorption correction was made. The systematic absences were consistent with space group $P2_1/c$.

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