Refinement

Refinement on F^2
$R(F) = 0.0245$
$wR(F^2) = 0.0565$
$S = 1.086$
1085 reflections
133 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 14.2616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.006$ e Å^{-3}
$\Delta\rho_{\min} = -0.511$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.016 (10)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Au1	0	0	0.00000 (3)	0.0405 (2)
I1	0	0	0.19338 (7)	0.0546 (4)
I2	0.20575 (5)	−0.01867 (5)	0.29369 (8)	0.0644 (3)
P1	−0.00432 (15)	0.10561 (14)	−0.0223 (2)	0.0388 (6)
N1	−0.0748 (7)	0.1819 (7)	0.0010 (8)	0.070 (3)
N2	0.0562 (6)	0.2524 (5)	−0.0183 (7)	0.051 (2)
N3	−0.0221 (5)	0.1919 (5)	−0.1461 (6)	0.042 (2)
C1	0.0721 (8)	0.1955 (6)	0.0049 (8)	0.057 (3)
C2	−0.0757 (8)	0.1153 (8)	0.0286 (8)	0.063 (4)
C3	−0.0164 (6)	0.1244 (5)	−0.1376 (7)	0.043 (3)
C4	−0.0087 (11)	0.2445 (9)	0.0285 (10)	0.076 (4)
C5	0.0470 (7)	0.2573 (7)	−0.1116 (8)	0.050 (3)
C6	−0.0850 (7)	0.1848 (7)	−0.0909 (9)	0.058 (3)
C7	−0.0357 (8)	0.2038 (8)	−0.2389 (8)	0.064 (4)
C8	0.0159 (13)	0.2102 (11)	−0.3047 (12)	0.108 (7)
O1	0.2787 (8)	0.0154 (8)	0.5091 (10)	0.120 (5)

Table 2. *Selected geometric parameters (Å, °)*

Au1—P1	2.334 (3)	N2—C5	1.43 (2)
Au1···I1	2.9129 (12)	N2—C1	1.46 (2)
P1—C2	1.813 (14)	N2—C4	1.49 (2)
P1—C3	1.831 (10)	N3—C7	1.477 (15)
P1—C1	1.845 (12)	N3—C3	1.514 (13)
N1—C6	1.41 (2)	N3—C6	1.525 (14)
N1—C4	1.44 (2)	N3—C5	1.53 (2)
N1—C2	1.48 (2)	C7—C8	1.44 (3)
P1^{i}—Au1—P1	117.97 (3)	C3—P1—C1	97.5 (5)
P1—Au1···I1	98.27 (7)	C2—P1—Au1	119.6 (4)
C2—P1—C3	99.0 (5)	C3—P1—Au1	115.4 (3)
C2—P1—C1	98.4 (6)	C1—P1—Au1	122.3 (5)

Symmetry code: (i) $-y, x - y, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

Support from the National Science Foundation (CHE 9300107) and the Robert A. Welch Foundation is gratefully acknowledged.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1997). C**53**, 197-200

μ-Chloro-1:2*κ*^{2}*Cl*-trichloro-2*κ*^{3}*Cl*-(2,4-dimethyl-5,8-diazadec-4-ene-2,10-diamine-1*κ*^{4}*N*,*N′*,*N″*,*N‴*)copper(II)zinc(II)

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(*Received 9 July 1996; accepted 21 October 1996*)

Abstract

The title compound, $[\mathrm{Cu(C_{10}H_{24}N_4)(\mu\text{-}Cl)ZnCl_3}]$, is formed by the reaction of equimolar amounts of 3-azapentane-1,5-diamine, copper(II) chloride and zinc(II) chloride with excess 4-amino-4-methylpentan-2-one in methanol. The copper(II) ion is in a square-pyramidal coordination, with the tetradentate triamine mono-imine ligand in the basal plane (the mean Cu—N distance is 2.005 Å) and a Cl atom of a tetrachlorozincate ion axially coordinated, with a Cu—Cl distance of 2.6630 (7), a Cl—Zn distance of 2.3107 (7) Å and a Cu—Cl—Zn angle of 113.14 (2)°. The chloro-bridged

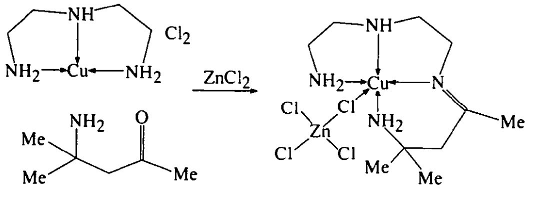
Acta Crystallographica Section C
ISSN 0108-2701 © 1997

copper–zinc units are linked by a network of N—H···Cl and C—H···Cl hydrogen bonds, together with a weak Cu···Cl interaction, *trans* with respect to the first, of 3.9362 (7) Å, forming layers parallel to the $x0z$ plane of the unit cell.

Comment

Compounds with amine–imine ligands have been prepared by reaction of 4-amino-4-methylpentan-2-one (diacetonamine) with amine compounds of copper(II) (Morgan, Martin & Curtis, 1979) or nickel(II) (Morgan & Curtis, 1980). Structures have been determined for the tetradentate ligand compounds $[Cu(pnda)](ClO_4)_2$ (Gladkikh & Curtis, 1997) and $[Ni(pnda)][ZnCl_4]$ (Gladkikh, Curtis & Heath, 1997) (pnda is 2,4,6,9,11-pentamethyl-5,8-diazadodeca-4,8-diene-2,11-diamine), formed from propane-1,2-diamine compounds, and the pentadentate ligand compound $[Cu(triena)](ClO_4)_2$ (triena is 2,4-dimethyl-5,8,11-triazatridec-3-ene-2,13-diamine), formed from 3,6-diazaoctane-1,8-diamine (triethylenetetramine) copper(II) perchlorate (Gladkikh & Curtis, 1997). Structures have been reported for compounds with a related bidentate ligand, 2-amino-4-imino-2-methylpentane, formed by the reaction of copper(II) or nickel(II) ammine compounds with ammonia in acetone (Hanic & Serator, 1964; Hanic & Machajdik, 1969; Hanic, Pavelcik & Gyepesova, 1972; Domiano, Musatti & Pelizzi, 1975).

The structure is now reported for the title compound, $[(diena)Cu\text{–}Cl\text{–}ZnCl_3]$ {or $[Cu(diena)][ZnCl_4]$ if the axial interaction between copper(II) and the tetrachlorozincate ion is disregarded}, (I). This is formed by reaction of the β-amino ketone with 3-azapentane-1,5-diamine (diethylenetriamine), copper(II) chloride and zinc(II) chloride (see scheme below).



(I)

The chloro-bridged unit of $[(diena)Cu\text{–}Cl\text{–}ZnCl_3]$ is shown in Fig. 1. The C4—N5 distance of 1.276 (3) Å and the angles about these atoms confirm the presence of the C4—N5 imine function in the ligand.

The copper(II) ion is in a flattened square pyramidal coordination involving the triamine mono-imine ligand diena, with the Cl1 atom of the $[ZnCl_4]^{2-}$ ion coordinated axially [Cu—Cl1 2.6630 (7) Å]. The Cu—N distances for the primary amine [Cu—N1 1.986 (2) and Cu—N11 2.028 (2) Å] and secondary amine [Cu—N8 2.010 (2) Å] N atoms are typical of those for amine donors (Fawcett *et al.*, 1980). The Cu—N distance for the imine N5 atom [1.995 (2) Å] is, as usual, slightly shorter (Gladkikh & Curtis, 1997; Gladkikh, Curtis & Turnbull, 1997; Gladkikh, Curtis & Heath, 1997).

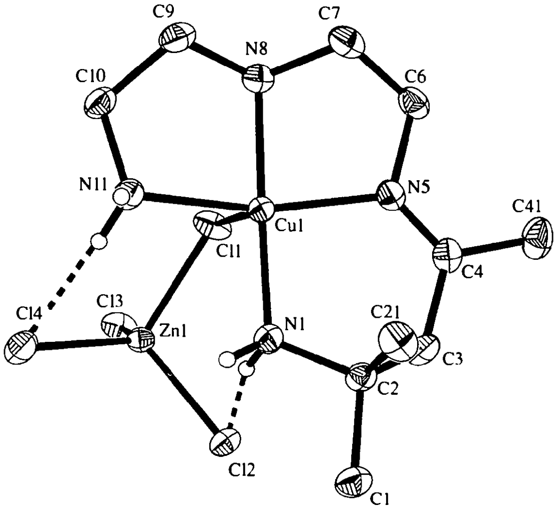


Fig. 1. The structure of the copper(II)–zinc(II) unit showing the hydrogen bonds, with displacement ellipsoids shown at the 50% probability level. H atoms bonded to C atoms are not shown.

The four N-donor atoms are close to coplanarity, with displacements from the best N_4 plane of 0.024 (2) (for N1), −0.025 (2) (N5), 0.028 (2) (N8) and −0.025 (2) Å (N11), with the Cu atom 0.1434 (2) Å from this plane. The *trans*-N—Cu—N angles are 173.25 (8) for N1—Cu—N8 and 165.43° for N5—Cu—N11.

The six-membered amine–imine chelate ring has a twist-boat conformation, with displacements from the relevant CuN_2 plane of 0.411 (2) (for C2), −0.463 (3) (C3) and −0.267 (2) Å (C4). The two five-membered chelate rings have asymmetric *gauche* conformations, with displacements from the relevant CuN_2 planes of 0.036 (3) (for C6), 0.654 (3) (C7), 0.411 (3) (C9) and −0.290 (3) Å (C10). The axially oriented C21 methyl group lies on the opposite side of the ligand ‘plane’ to the axially coordinated $[ZnCl_4]^{2-}$ ion, while the N8—H group lies on the same side as this ion.

The Zn—Cl1 distance to the bridging chloride [2.3107 (7) Å] is significantly longer than the other Zn—Cl distances [mean 2.2558 (7) Å], with the Zn—Cl1—Cu angle being 113.14 (2)°.

The structure of the title complex has similarities to that of a chloro-bridged tetraaza macrocycle complex of copper(II) which has an axially coordinated $[CuCl_4]^{2-}$ ion (Comba *et al.*, 1988). This has distances Cu(macrocycle)—Cl 2.507 (2) and Cu(tetrachloro)—Cl 2.266 (2) Å, and a Cu—Cl—Cu angle of 110.67 (9)°. Dinuclear chloro-bridged copper(II) tetraaza macrocycle ligand compounds with linear Cu—Cl—Cu units have been reported, with Cu—Cl distances of 2.501 (4) (Bauer, Robinson & Margerum, 1973) and 2.831 (1) Å (Gladkikh & Curtis, 1997).

The (diena)copper(II) and tetrachlorozincate(II) ions are linked by a Cu—Cl—Zn interaction (above) and also by N1—H1···Cl2 and N11—H11···Cl4 hydrogen bonds (the first and second interactions given in Table 2; Fig. 1). These units are linked into chains by the *n*-glide symmetry parallel to the *x*0*z* diagonal by N—H···Cl contacts (the fourth and fifth interactions in Table 2; Fig. 2). There is a very weak Cu···Cl3^{i} interaction of 3.936 (1) Å *trans* to the primary axial Cu—Cl interaction [symmetry code: (i) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$]. The third and sixth C—H···Cl and N—H···Cl contacts (Table 2) link these chains into sheets parallel to the *x*0*z* plane of the lattice. No specific interactions between the sheets were found.

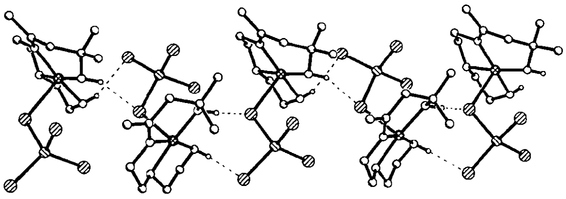


Fig. 2. The cation–anion chain parallel to the *x*0*z* diagonal, showing hydrogen bonds linking the chloro-bridged copper(II)–zinc(II) units shown in Fig. 1.

Experimental

Excess 4-amino-4-methylpentan-2-one (diacetonamine) was added to the blue gum resulting from the reaction of equimolar amounts of copper(II) chloride, zinc(II) chloride and 3-azapentane-1,5-diamine (diethylenetriamine) in methanol. Over a period of weeks, the gum dissolved and the purple product crystallized. The product was filtered off and recrystallized from hot methanol (Morgan, Martin & Curtis, 1979).

Crystal data

[CuZnCl$_4$(C$_{10}$H$_{24}$N$_4$)]
M_r = 471.04
Monoclinic
$P2_1/n$
a = 9.828 (1) Å
b = 19.741 (2) Å
c = 10.259 (1) Å
β = 112.573 (2)°
V = 1838.0 (4) Å^3
Z = 4
D_x = 1.702 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7753 reflections
θ = 2.15–28.33°
μ = 3.038 mm^{-1}
T = 160 (2) K
Block
0.32 × 0.28 × 0.14 mm
Purple

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frames
Absorption correction: semi-empirical (*SHELXTL/PC*; Sheldrick, 1994)
$T_{\min}$ = 0.513, $T_{\max}$ = 0.654
11 318 measured reflections

4195 independent reflections
3747 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0309
$\theta_{\max}$ = 28.57°
$h = -12 \rightarrow 12$
$k = -26 \rightarrow 22$
$l = -12 \rightarrow 13$
Standard reflections: not relevant

Refinement

Refinement on F^2
$R(F)$ = 0.0283
$wR(F^2)$ = 0.0650
S = 1.129
4179 reflections
185 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 2.1665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = −0.014

$\Delta\rho_{\max}$ = 0.707 e Å^{-3}
$\Delta\rho_{\min}$ = −0.693 e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.00061 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1	1.986 (2)	C4—N5	1.276 (3)
Cu1—N5	1.995 (2)	Zn1—Cl3	2.2483 (7)
Cu1—N8	2.010 (2)	Zn1—Cl4	2.2556 (7)
Cu1—N11	2.028 (2)	Zn1—Cl2	2.2636 (7)
Cu1—Cl1	2.6630 (7)	Zn1—Cl1	2.3107 (7)
N1—Cu1—N5	95.39 (8)	N8—Cu1—Cl1	87.86 (6)
N1—Cu1—N8	173.25 (8)	N11—Cu1—Cl1	89.27 (6)
N5—Cu1—N8	83.69 (8)	C2—N1—Cu1	117.3 (1)
N1—Cu1—N11	94.93 (8)	C6—N5—Cu1	111.7 (2)
N5—Cu1—N11	165.43 (8)	C7—N8—Cu1	106.9 (2)
N8—Cu1—N11	84.85 (8)	C9—N8—Cu1	108.3 (2)
N1—Cu1—Cl1	98.88 (6)	C10—N11—Cu1	108.4 (1)
N5—Cu1—Cl1	99.26 (6)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*E*···Cl2	0.961 (2)	2.527 (1)	3.472 (2)	168.1 (1)
N11—H11*A*···Cl4	0.907 (2)	2.849 (1)	3.727 (2)	163.6 (1)
C3—H3*A*···Cl4^{i}	0.990 (4)	2.661 (3)	3.626 (3)	164.9 (3)
N1—H1*D*···Cl1^{ii}	0.954 (2)	2.497 (1)	3.376 (2)	153.3 (1)
N11—H11*B*···Cl3^{ii}	0.817 (2)	2.587 (1)	3.352 (2)	156.5 (1)
N8—H8···Cl4^{iii}	0.872 (2)	2.595 (1)	3.367 (2)	148.1 (1)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$.

The semi-empirical absorption correction was based on multiple measurements of a large number of symmetry-equivalent reflections (*SHELXTL/PC*; Sheldrick, 1994). The structure was solved by heavy-atom methods and refined with anisotropic parameters for non-H atoms (*SHELXTL/PC*). H(N) atoms were located from difference syntheses and H(C) atoms were placed in calculated positions. Parameters were refined in isotropic approximation with fixed displacement parameters.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local program (Clegg, 1996). Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *XPMA* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

The authors thank Professor William Clegg, Chemistry Department, University of Newcastle, England, for use of the diffractometer.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: TA1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C53, 200-202

Bis(piperazinium) Pentakis(trioxomolybdo)bis(ethylphosphonate) Dihydrate

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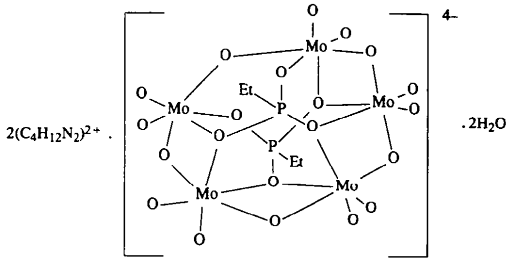
(Received 25 July 1996; accepted 27 September 1996)

Abstract

The title compound, bis(piperazine-1,4-diylium) bis(ethylphosphonato)-$1\kappa O,2:3\kappa^2O',4:5\kappa^2O''$;$1:2\kappa^2O$,$3:4\kappa^2O',5\kappa O''$-penta-$\mu$-oxo-$1:2\kappa^2O$;$1:5\kappa^2O$;$2:3\kappa^2O$;$3:4\kappa^2O$;$4:5\kappa^2O$-decaoxo-$1\kappa^2O,2\kappa^2O,3\kappa^2O,4\kappa^2O,5\kappa^2O$-pentamolybdenum(4−) dihydrate, $(C_4H_{12}N_2)_2[Mo_5O_{15}(C_2H_5O_3P)_2].2H_2O$, crystallizes as isolated five-unit rings of vertex- and edge-sharing distorted-octahedral MoO_6 groups, doubly capped by PC_2H_5 entities {as $[(C_2H_5)PO_3]^{2-}$ ethylphosphonate groups}, resulting in $[(MoO_3)_5\{(C_2H_5)PO_3\}_2]^{4-}$ {or $[Mo_5P_2O_{21}(C_2H_5)_2]^{4-}$} anions. Doubly protonated piperazinium cations and water molecules complete the structure. This phase shows reversible dehydration/rehydration without loss of structure.

Comment

We have recently reported the hydrothermal syntheses and structures of a family of novel layered alkali metal/ammonium molybdenum methylphosphonates (Harrison, Dussack & Jacobson, 1995), which are based on the hexagonal tungsten oxide (HTO) motif of vertex-sharing octahedra (Gérand, Nowogrocki, Guenot & Figlarz, 1979). We report here the preparation and characterization of $(C_4H_{12}N_2)_2[(MoO_3)_5\{(C_2H_5)PO_3\}_2].2H_2O$, (I), a molecular species prepared under similar conditions from closely related starting materials. It is related to similar clusters prepared earlier (Kwak, Pope & Scully, 1975; Stalick & Quicksall, 1976; Kortz & Pope, 1995).



(I)

The five crystallographically distinct Mo atoms in the pentamolybdodi(ethylphosphonate) cluster (Fig. 1) are all octahedrally coordinated by O atoms. All the Mo centers show the two short, two intermediate and two long Mo—O bond-distance distribution within the distorted MoO_6 unit which is characteristic of Mo^{VI}. Each MoO_6 center has two short ($d < 1.73$ Å) 'oxo' Mo═O bonds in a *cis* configuration [θ_{ave}(O═Mo═O) = 103.3°]. These short bonds are both *trans* with respect to a long ($d > 2.18$ Å) Mo—O link, and the two remaining Mo—O bonds are intermediate in length between these two extremes. All the Mo═O links are terminal bonds, not joined to any other atoms in the cluster [three of them (O6, O13 and O14) form hydrogen-bonding links to the piperazinium dications]. These five octahedral MoO_6 units are fused together into an isolated ring. There are four edge-sharing links (Mo1–Mo2, Mo2–Mo3, Mo4–Mo5 and Mo5–Mo1) and one vertex-sharing connection (Mo3–Mo4). Average Mo—O bond lengths and molybdenum bond-valence sum (BVS) values (Brese & O'Keeffe, 1991) are typical for Mo^{VI} (expected BVS = 6.00): d_{ave}(Mo1—O) = 1.985 (2) Å, BVS(Mo1) = 6.02; d_{ave}(Mo2—O) = 1.983 (2) Å, BVS(Mo2) = 6.02; d_{ave}(Mo3—O) = 1.977 (2) Å, BVS(Mo3) = 6.01; d_{ave}(Mo4—O) = 1.979 (2) Å, BVS(Mo4) = 6.02; d_{ave}(Mo5—O) = 1.972 (2) Å, BVS(Mo5) = 6.05.