three H atoms are disordered over the four possible positions, and that this disorder precluded recognition on the final difference Fourier synthesis.

**Concluding remarks.** The complexity of the AlPO$_4$-14A structure testifies to the remarkable stereochemical properties of the aluminophosphates synthesized in the presence of organic species. Particularly important is the presence of three adjacent Al atoms (Figs. 2 and 3) which makes it impossible to convert the structure into a 4-connected framework by removal of the hydroxyl and encapsulated organic species. It is quite certain that the occurrence of Al in four-, five- and six-coordination, and the change of charge balance when hydroxyl bridges between two Al atoms, results in a new range of geometrical possibilities for viable structures additional to those for the zeolites which are restricted to four-coordinated Al. Whereas all tetrahedrally coordinated aluminophosphates have alternating Al and P with consequent even-numbered tings, the occurrence of adjacent Al atoms in AlPO$_4$-14A allows the presence of 5-rings.

We thank S. T. Wilson and E. M. Flanigen (Union Carbide Corporation) for synthesis and supply of the specimen, N. Weber for technical help, NSF for grant CHE 84-05167 and for general support from the Materials Research Laboratory supported by NSFDMR-8519460.

**References**


**Structure of Di-μ-bromo-bis-μ-1-[2-(dimethylamino)phenyl]-2-(4-methylphenyl)-1-propenyl-N,C]-tetracopper(I)**

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**Abstract.** [Cu$_4$Br$_2$(C$_{15}$H$_{20}$N)$_2$], $M_r$=914.72, tetragonal, $I4_1c2$, $a=20.430$ (8), $c=17.52$ (1) Å, $V=7313$ (6) Å$^3$, $Z=8$, $D_x=1.662$ g cm$^{-3}$, Mo Kα, $\lambda=0.71069$ Å, $\mu=44.9$ cm$^{-1}$, $F(000)=3648$, $T=295$ K, $R=0.0572$ for 860 observed reflections with $I > \sigma(I)$. The molecule has twofold crystallographic axial symmetry and consists of a central rhombus-type core of Cu atoms to which the propenyl and Br groups are bound in a bridging fashion. The two propenyl and the two Br groups each occupy adjoining edges of the Cu$_4$ core. The Br-bridged edges are 2.507 (3) Å and significantly longer than the propenyl-bridged edges.
which are 2.449(3) Å. The shortest non-bridged Cu–Cu distance is 2.621 (3) Å. The bridging Cu–Br distances of 2.323 (3) Å are rather short.

Introduction. The title compound was synthesized as part of a study of vinylcopper compounds (ten Hoedt, 1979; ten Hoedt, van Koten & Noltes, 1979). Vinylcopper compounds have found wide application as reagents for the stereo- and regioselective introduction of vinyl groups in organic substrates (Westmijze, Kleijn, Meijer & Vermeer, 1977). The present structure determination was carried out to provide the structural information to be used for the understanding of the underlying reaction mechanism. The two Br atoms may be substituted by dimethylaminophenyl groups with retention of the tetranuclear structure. The molecular structure of the latter compound has been reported previously (Noltes, ten Hoedt, van Koten, Spek & Schoone, 1982).

Experimental. Crystals used for X-ray diffraction work were obtained by slowly distilling pentane in a saturated solution of the title compound in toluene. Block-shaped crystal 0.25 × 0.25 × 0.30 mm, sealed in glass capillaries under nitrogen. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo Kα radiation. Cell constants were obtained by slowly distilling pentane in a saturated solution of the title compound in toluene. Block-shaped crystal 0.25 x 0.25 x 0.30 mm, sealed in glass capillaries under nitrogen. Enraf-Nonius CAD-4F diffractometer, Zr-filtered Mo Kα radiation. Cell constants were obtained through the structure determination process. Structure solved with Patterson (SHELX84; Sheldrick, 1984) and Fourier methods. H atoms introduced on calculated positions [C–H = 0.98 Å] and included in anisotropic thermal parameters with their e.s.d.'s in Table 1.*

The correct space group (I4c2) was determined during the structure determination process. Structure solved with Patterson (SHELX84; Sheldrick, 1984) and Fourier methods. H atoms introduced on calculated positions [C–H = 0.98 Å] and included in anisotropic thermal parameters with their e.s.d.'s in Table 1.*

Discussion. The molecular structure with the adopted atom numbering is shown in Fig. 1; bond distances, angles and some torsion angles are listed in Table 2. The tetragonal unit cell contains eight discrete molecules which have twofold axial symmetry about a line through Cu(2) and Cu(3). The complex consists of a core of four Cu atoms in a planar rhombus-type configuration, with adjacent sides bridged by two crystallographically identical propenyl ligands and two Br atoms respectively. The Br atoms deviate 0.617 (7) Å out of the central Cu plane. Both Cu–Br bond distances are 2.323 (3) Å and thus rather short compared with the average Cu–Br distance of 2.40 (1) Å (range: 2.385 to 2.415 Å) in a complex with...
a planar six-nuclear CuI core (Ceccone, Ghilardi, Midollini & Orlandini, 1982). The present Cu–Br distance is similar to the non-bridging distance of 2.346 (2) Å reported for bromobis(triphenylphosphine)copper(I) (Davis, Belford & Paul, 1973). The Cu–Br bond distance for four-coordinated CuI is 2.4597 Å (International Tables for X-ray Crystallography, 1968). The geometry of the central Cu4 core is similar to the one found in the related complex where dimethylaminophenyl ligands were substituted for Br atoms (Noltes, ten Hoedt, van Koten, Spek & Schoone, 1982). The averages of the short Cu–Br distances forming the edges of the rhombus are 2.48 (3) Å and 2.507 (3) Å in the present Br complex and 2.46 (2) Å in the corresponding non-Br complex. The Cu core in the present Cu–Br complex is a strongly distorted planar square; the diagonal non-bonding Cu–Cu distances are 2.48 (3) Å and 2.46 (2) Å in the corresponding non-Br complex. The angles between the two phenyl rings of the propenyl ligand is 7 (1) ° in the present Br complex with corresponding values of 3 (2) and 50 (2) ° for the non-Br complex.

The central propenyl group [C(8),C(9),C(10),C(11),C(12)] is planar within 0.009 Å. The angles between this plane and the planes through the phenyl rings of the dimethylamino and tolyl groups are 58 (1) ° and 64 (1) ° respectively [51 (2), 48 (2) and 77 (2), 53 (2) ° in the corresponding non-Br complex]. The angle between the two phenyl rings of the propenyl ligand is 7 (1) ° in the present Br complex with corresponding values of 3 (2) and 50 (2) ° for the non-Br complex.

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Table 2. Data on the geometry of CuBr_C_{18}H_{20}N_{2}; bond lengths (Å), bond angles (°) and relevant torsion angles

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
<th>Torsion Angle (°)</th>
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</thead>
<tbody>
<tr>
<td>Cu(1)–Br–Cu(2)</td>
<td>2.323 (3)</td>
<td>Cu(6)–C(7)</td>
<td>1.38 (3)</td>
</tr>
<tr>
<td>Cu(1)–Cu(2)</td>
<td>2.323 (3)</td>
<td>Cu(7)–C(8)</td>
<td>1.40 (3)</td>
</tr>
<tr>
<td>Cu(1)–Cu(3)</td>
<td>2.507 (3)</td>
<td>Cu(8)–C(9)</td>
<td>1.54 (3)</td>
</tr>
<tr>
<td>Cu(1)–N</td>
<td>2.00 (2)</td>
<td>Cu(9)–C(10)</td>
<td>1.32 (3)</td>
</tr>
<tr>
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<td>2.00 (2)</td>
<td>Cu(10)–C(11)</td>
<td>1.52 (3)</td>
</tr>
<tr>
<td>Cu(1)–Cu(3)</td>
<td>2.449 (3)</td>
<td>Cu(11)–C(12)</td>
<td>1.42 (3)</td>
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<tr>
<td>Cu(3)–C(9)</td>
<td>2.15 (2)</td>
<td>Cu(12)–C(13)</td>
<td>1.41 (3)</td>
</tr>
<tr>
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<td>1.45 (3)</td>
<td>Cu(13)–C(14)</td>
<td>1.38 (3)</td>
</tr>
<tr>
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<td>1.45 (3)</td>
<td>Cu(14)–C(15)</td>
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<tr>
<td>N–C(3)</td>
<td>1.50 (3)</td>
<td>Cu(15)–C(16)</td>
<td>1.59 (3)</td>
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<td>Cu(16)–C(17)</td>
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<td>C(5)–C(6)</td>
<td>1.31 (3)</td>
<td>Cu(19)–C(20)</td>
<td>1.31 (3)</td>
</tr>
</tbody>
</table>

The geometry of the central Cu4 core is similar to the one found in the related complex where dimethylaminophenyl ligands were substituted for Br atoms (Noltes, ten Hoedt, van Koten, Spek & Schoone, 1982). The averages of the short Cu–Cu distances being 2.621 (3) and 4.204 (4) Å [2.930 (6) and 3.930 (6) Å in the Cu–dimethylaminophenyl complex]. This distortion may be ascribed to the different coordination of the Cu atoms which are bonded to two or three non-Cu atoms. The Cu4 group is sandwiched between the two symmetry-related tolyl groups, as may be seen from the short intramolecular Cu–C contacts, e.g. Cu(1)–C(13) 3.28 (2), Cu(2)–C(13) 3.51 (2), Cu(3)–C(18) 3.30 (2) Å, and by the angle between the Cu4 plane and the tolyl group which is 33.5 (9) °.

The propenyl ligands are bonded to the Cu4 core by the bridging C atom of the propenyl double bond and by the coordinating N atom of the dimethylamino moiety. The relevant Cu–C and Cu–N distances are 2.00 (8) and 2.30 (5) Å in the related dimethylaminophenyl complex. C(9) and N deviate -0.69 (2) and 0.30 (2) Å from the Cu4 plane. The angle between the least-squares plane through the C(3)–C(8) phenyl ring and the Cu4 plane is 38.0 (7) °.
The crystals were supplied by Dr R. W. M. ten Hoedt, Dr J. G. Noltes and Professor G. van Koten.
The X-ray data were collected by Dr A. J. M. Duijssen.

References


Structure of Bis[(18-crown-6)ammonium]* Aquadioxotetra(thiocyanato)turanate

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Abstract. [NH4(C12H24O6)]2[UB2(NCS)4(H2O)], M, = 1085.09, orthorhombic, Fdd2, a = 29.927(3), b = 34.527(3), c = 8.724(1) Å, V = 9014.5 Å3, Z = 8,

D = 1.599 g cm-3, λ(Mo Kα) = 0.71073 Å, μ = 36.539 cm-1, F(000) = 4352, T = 293 K, R = 0.042

for 1877 observed reflections with F2 > 3σ(F2). The uranyl group does not enter into the 18-crown-6 cavity, but presents the usual pentacoordination in the equatorial plane with four linear NCS- ions and one water molecule. The NH4 cation is anchored in the crown ether ring by hydrogen bonds and ion–dipolar interactions via oxygen atoms of the crown ether.

Introduction. Recently several systems for the extraction of uranium with crown ethers have been studied. It was reported that the extractability of uranium with crown ethers is different in various thiocyanate solutions (Jin & Xu, 1982). However, little is known about the structures and properties of these complexes. It is also of interest to know how uranium and crown ethers link up when some thiocyanates coexist. We synthesized some complexes and determined their structures. As part of these studies we report here the structure of the title compound.

Experimental. Yellow crystal (0.12 × 0.18 × 0.24 mm). D, not determined. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo Ka radiation. Cell constants refined from 25 reflections (14 < θ < 15°). Three standard reflections every 3600 s, 2θmax = 60°, h = 0 to 42, k = 0 to 48, l = 0 to 12. 3684 independent reflections but only 1877 with F2 > 3σ(F2) were used in the refinement. Variation of standard reflections 12, 1-2, 4, 3, 6 and 11, 17, 3, +0.7%. Data corrected for Lorentz–polarization but not absorption. Systematic absences, hkl: h+k, k+l, (h+l) = 2n+1, 0kl: k+l = 4n+1, 0h0: h+l = 4n+1. Structure solved by Patterson method, ΔF syntheses. No attempts were made to locate the H atoms. Full-matrix least-squares refinement with anisotropic temperature factors. 254 variables, (Δ/σ)max < 0.06, R = 0.042, wR = 0.047 where w = 1, F2 > 3σ(F2); w = 0, F2 < 3σ(F2). Correction for isotropic extinction, extinction coefficient = 7.47 x 10^-4. Max. value in final difference density map was 1.976 e Å^-3 located near the U atom. Calculation performed on a PDP 11/44 computer

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