

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<sub>4</sub>-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 rings, the occurrence of adjacent Al atoms in AlPO<sub>4</sub>-14A allows the presence of 5-rings.

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## Structure of Di- $\mu$ -bromo-bis- $\mu$ -{1-[2-(dimethylamino)phenyl]-2-(4-methylphenyl)-1-propenyl-*N,C*}-tetracopper(I)

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**Abstract.** [Cu<sub>4</sub>Br<sub>2</sub>(C<sub>18</sub>H<sub>20</sub>N)<sub>2</sub>], *M<sub>r</sub>* = 914.72, tetragonal, *I* $\bar{4}$ c2, *a* = 20.430 (8), *c* = 17.52 (1) Å, *V* = 7313 (6) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.662 g cm<sup>-3</sup>, *Mo K $\alpha$* ,  $\lambda$  = 0.71069 Å,  $\mu$  = 44.9 cm<sup>-1</sup>, *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<sub>4</sub> core. The Br-bridged edges are 2.507 (3) Å and significantly longer than the propenyl-bridged edges

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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 crystal 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 capillary under nitrogen. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo K $\alpha$  radiation. Cell constants from angular settings of 16 reflections with  $19 < 2\theta < 20^\circ$ . Intensity data for 2260 reflections collected in half an octant of the reflection sphere;  $0 \leq h \leq 26$ ,  $0 \leq k \leq 26$ ,  $0 \leq l \leq 22$ , with  $h \leq k$ ;  $1.4 < \theta < 27.5^\circ$ ;  $\omega/2\theta$  scan mode; scan width  $\Delta\omega = (1.0 + 0.35 \tan\theta)^\circ$ . The intensities of two reference reflections (202 and 020) were checked every half hour and showed a linear decrease of 10% over a period of 48 h of X-ray exposure time. Data were corrected for this decay, Lorentz–polarization effects and absorption (DIFABS; Walker & Stuart, 1983) (corrections in the range 0.287 to 1.211), resulting in a set of 860 unique observed reflections with  $I > \sigma(I)$ . The systematic absences  $hkl: h+k+l = 2n+1$  and  $0kl: k,l = 2n+1$  are compatible with the space groups  $I\bar{4}c2$ ,  $I4cm$  and  $I4/mcm$ . The correct space group ( $I\bar{4}c2$ ) 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 weighted blocked full-matrix refinement (on  $F$ ) riding on their carrier atom. All non-H atoms refined with anisotropic thermal parameters, H atoms refined with separate overall isotropic thermal parameters for CH and CH<sub>3</sub> groups respectively. Convergence with 200 parameters at  $R = 0.0572$ ,  $wR = 0.0645$ ,  $w = 0.95 / [\sigma^2(F_o) + 0.002064 |F_o|^2]$ ,  $S = 1.041$ ,  $(\Delta/\sigma)_{\max} = 0.231$ , max. and min. residual densities 0.49 and  $-0.59 \text{ e \AA}^{-3}$  near heavy atoms. The alternative polarity of the structure was rejected, based on the resulting higher  $R$  values ( $R = 0.0640$ ;  $wR = 0.0745$ ) obtained

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses

	x	y	z	$U_{eq}(\text{\AA}^2)^*$
Br	0.8287 (1)	0.2062 (1)	0.0699 (2)	0.096 (1)
Cu(1)	0.7354 (1)	0.1445 (1)	0.0937 (1)	0.0577 (8)
Cu(2)	0.7372 (1)	0.2372 (1)	0	0.092 (1)
Cu(3)	0.6465 (1)	0.1465 (1)	0	0.0553 (8)
N	0.7612 (8)	0.068 (1)	0.172 (1)	0.087 (6)
C(1)	0.744 (1)	0.088 (1)	0.247 (1)	0.10 (1)
C(2)	0.830 (1)	0.052 (1)	0.167 (2)	0.12 (1)
C(3)	0.719 (1)	0.013 (1)	0.143 (1)	0.070 (8)
C(4)	0.732 (1)	-0.050 (1)	0.148 (1)	0.10 (1)
C(5)	0.689 (1)	-0.096 (1)	0.123 (2)	0.10 (1)
C(6)	0.633 (1)	-0.078 (1)	0.093 (1)	0.10 (1)
C(7)	0.616 (1)	-0.013 (1)	0.087 (1)	0.08 (1)
C(8)	0.662 (1)	0.0331 (9)	0.1117 (9)	0.049 (6)
C(9)	0.6458 (9)	0.1062 (9)	0.104 (1)	0.053 (6)
C(10)	0.5937 (9)	0.1349 (9)	0.134 (1)	0.050 (6)
C(11)	0.542 (1)	0.1009 (9)	0.182 (1)	0.08 (1)
C(12)	0.5825 (9)	0.203 (1)	0.125 (1)	0.057 (6)
C(13)	0.626 (1)	0.251 (1)	0.152 (1)	0.08 (1)
C(14)	0.611 (1)	0.317 (1)	0.140 (2)	0.11 (1)
C(15)	0.556 (1)	0.341 (1)	0.103 (2)	0.10 (1)
C(16)	0.545 (2)	0.417 (1)	0.089 (2)	0.21 (2)
C(17)	0.518 (1)	0.292 (1)	0.073 (1)	0.08 (1)
C(18)	0.5289 (9)	0.228 (1)	0.086 (2)	0.09 (1)

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

by refinement with negative anomalous-dispersion factors ( $-if''$ ). Final values of the refined parameters are given in Table 1.\* Scattering factors from Cromer & Mann (1968); anomalous-dispersion factors from Cromer & Liberman (1970). Calculations performed with SHELX76 (Sheldrick, 1976) and the EUCLID package (geometry calculations and illustrations) (Spek, 1982) on the CDC Cyber-855 of the University of Utrecht.

**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<sub>4</sub> 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

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43665 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

a planar six-nuclear Cu<sup>I</sup> core (Cecconi, 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 Cu<sup>I</sup> is 2.4597 Å (*International Tables for X-ray Crystallography*, 1968). The geometry of the central Cu<sub>4</sub> 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 forming the edges of the rhombus are 2.48 (3) Å in the present Br complex and 2.46 (2) Å in the corresponding dimethylaminophenyl complex. The Cu core in the present Cu—Br complex is a strongly distorted planar square; the diagonal non-bonding 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 Cu<sub>4</sub> 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 Cu<sub>4</sub> plane and the tolyl group which is 33.5 (9)°.

The propenyl ligands are bonded to the Cu<sub>4</sub> 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 (2) and 2.15 (2) Å respectively [averages are 2.06 (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 Cu<sub>4</sub> plane. The angle between the least-squares plane through the C(3)—C(8) phenyl ring and the Cu<sub>4</sub> plane is 38.0 (7)°.

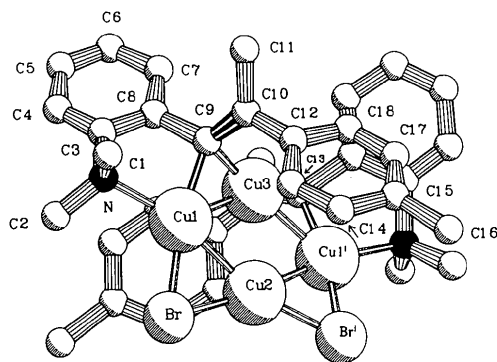


Fig. 1. PLUTO (EUCLID version) drawing of the title compound with the adopted numbering scheme. H atoms are omitted for clarity. The crystallographic twofold axis runs through Cu(2) and Cu(3).

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 C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>Cu<sub>4</sub>N<sub>2</sub>; bond lengths (Å), bond angles (°) and relevant torsion angles

Br—Cu(1)	2.323 (3)	C(6)—C(7)	1.38 (3)
Br—Cu(2)	2.323 (3)	C(7)—C(8)	1.40 (3)
Cu(1)—Cu(2)	2.507 (3)	C(8)—C(9)	1.54 (3)
Cu(1)—N	2.15 (2)	C(9)—C(10)	1.32 (3)
Cu(1)—C(9)	2.00 (2)	C(10)—C(11)	1.52 (3)
Cu(1)—Cu(3)	2.449 (3)	C(10)—C(12)	1.42 (3)
Cu(3)—C(9)	2.00 (2)	C(12)—C(13)	1.41 (3)
N—C(1)	1.42 (3)	C(12)—C(18)	1.38 (3)
N—C(2)	1.45 (3)	C(13)—C(14)	1.40 (3)
N—C(3)	1.50 (3)	C(14)—C(15)	1.39 (3)
C(3)—C(4)	1.32 (3)	C(15)—C(16)	1.59 (3)
C(3)—C(8)	1.35 (3)	C(15)—C(17)	1.37 (3)
C(4)—C(5)	1.36 (3)	C(17)—C(18)	1.35 (3)
C(5)—C(6)	1.31 (3)		
Cu(1)—Br—Cu(2)	65.31 (9)	C(4)—C(3)—C(8)	120 (2)
Br—Cu(1)—Cu(2)	57.34 (9)	C(3)—C(4)—C(5)	122 (2)
Br—Cu(1)—Cu(3)	118.6 (1)	C(4)—C(5)—C(6)	120 (2)
Br—Cu(1)—N	108.0 (5)	C(5)—C(6)—C(7)	121 (2)
Br—Cu(1)—C(9)	168.5 (5)	C(6)—C(7)—C(8)	117 (2)
Cu(2)—Cu(1)—Cu(3)	63.84 (8)	C(3)—C(8)—C(7)	120 (2)
Cu(2)—Cu(1)—N	164.9 (5)	C(3)—C(8)—C(9)	121 (2)
Cu(2)—Cu(1)—C(9)	111.6 (5)	C(7)—C(8)—C(9)	119.2 (2)
Cu(3)—Cu(1)—N	128.5 (5)	Cu(1)—C(9)—Cu(3)	75.5 (6)
Cu(3)—Cu(1)—C(9)	52.2 (5)	Cu(1)—C(9)—C(8)	101 (1)
N—Cu(1)—C(9)	83.2 (7)	Cu(1)—C(9)—C(10)	127 (1)
Br—Cu(2)—Cu(1)	57.35 (8)	Cu(3)—C(9)—C(8)	119 (1)
Br—Cu—Br <sup>i</sup>	135.8 (1)	Cu(3)—C(9)—C(10)	101 (1)
Br—Cu(2)—Cu(1')	161.7 (1)	C(8)—C(9)—C(10)	125 (2)
Cu(1)—Cu(2)—Cu(1')	114.0 (1)	C(9)—C(10)—C(11)	125 (2)
Cu(1)—Cu(3)—C(9)	52.2 (5)	C(9)—C(10)—C(12)	121 (2)
Cu(1)—Cu(3)—Cu(1')	118.3 (1)	C(11)—C(10)—C(12)	113 (2)
Cu(1)—Cu(3)—C(9')	156.4 (5)	C(10)—C(12)—C(13)	123 (2)
C(9)—Cu(3)—C(9')	145.5 (8)	C(10)—C(12)—C(18)	123 (2)
Cu(1)—N—C(1)	109 (1)	C(13)—C(12)—C(18)	114 (2)
Cu(1)—N—C(2)	111 (2)	C(12)—C(13)—C(14)	119 (2)
Cu(1)—N—C(3)	101 (1)	C(13)—C(14)—C(15)	126 (2)
C(1)—N—C(2)	111 (2)	C(14)—C(15)—C(16)	122 (2)
C(1)—N—C(3)	113 (2)	C(14)—C(15)—C(17)	112 (2)
C(2)—N—C(3)	112 (2)	C(16)—C(15)—C(17)	125 (2)
N—C(3)—C(4)	126 (2)	C(15)—C(17)—C(18)	123 (2)
N—C(3)—C(8)	114 (2)	C(12)—C(18)—C(17)	125 (2)
C(9)—Cu(1)—N—C(3)	38 (1)	C(3)—C(8)—C(9)—Cu(1)	29 (2)
Cu(1)—N—C(3)—C(8)	-31 (2)	C(3)—C(8)—C(9)—C(10)	-122 (2)
C(1)—N—C(3)—C(8)	85 (2)	C(8)—C(9)—Cu(1)—N	-35 (1)
C(2)—N—C(3)—C(8)	-150 (2)	C(8)—C(9)—C(10)—C(12)	179 (2)
N—C(3)—C(8)—C(9)	3 (2)	C(9)—C(10)—C(12)—C(13)	-61 (3)

(i) Indicates symmetry operation:  $y + \frac{1}{2}, x - \frac{1}{2}, -z$ .

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## Structure of Bis[(18-crown-6)ammonium]\* Aquadioxotetrathiocyanatouranate

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**Abstract.**  $[\text{NH}_4(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{UO}_2(\text{NCS})_4(\text{H}_2\text{O})]$ ,  $M_r = 1085.09$ , orthorhombic,  $Fdd2$ ,  $a = 29.927$  (3),  $b = 34.527$  (3),  $c = 8.724$  (1) Å,  $V = 9014.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.599$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 36.539$  cm<sup>-1</sup>,  $F(000) = 4352$ ,  $T = 293$  K,  $R = 0.042$  for 1877 observed reflections with  $F^2 > 3\sigma(F^2)$ . 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<sup>-</sup> ions and one water molecule. The NH<sub>4</sub><sup>+</sup> 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 struc-

tures. As part of these studies we report here the structure of the title compound.

**Experimental.** Yellow crystal (0.12 × 0.18 × 0.24 mm).  $D_m$  not determined. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Cell constants refined from 25 reflections ( $14 < \theta < 15^\circ$ ). Three standard reflections every 3600 s,  $2\theta_{\text{max}} = 60^\circ$ ,  $h = 0$  to 42,  $k = 0$  to 48,  $l = 0$  to 12. 3684 independent reflections but only 1877 with  $F^2 > 3\sigma(F^2)$  were used in the refinement. Variation of standard reflections  $12, \bar{1}\bar{2}, 4, \bar{6}\bar{4}\bar{6}$  and  $\bar{1}\bar{1}, \bar{1}\bar{7}, 3$ ,  $\pm 0.7\%$ . Data corrected for Lorentz–polarization but not absorption. Systematic absences,  $hkl: h+k, k+l, (h+l) = 2n+1$ ,  $Ok1: k+l = 4n\pm 1$ ,  $h0l: h+l = 4n\pm 1$ . Structure solved by Patterson method,  $\Delta F$  syntheses. No attempts were made to locate the H atoms. Full-matrix least-squares refinement with anisotropic temperature factors. 254 variables,  $(\Delta/\sigma)_{\text{max}} < 0.06$ ,  $R = 0.042$ ,  $wR = 0.047$  where  $w = 1$ ,  $F^2 > 3\sigma(F^2)$ ;  $w = 0$ ,  $F^2 < 3\sigma(F^2)$ . Correction for isotropic extinction, extinction coefficient =  $7.47 \times 10^{-8}$ . Max. value in final difference density map was  $1.976 \text{ e } \text{Å}^{-3}$  located near the U atom. Calculation performed on a PDP 11/44 computer

\* 18-Crown-6 = 1.4.7.10.13.16-hexaoxacyclooctadecane.