

1999

## Cubane Tetrameric Complexes of Copper(I) Chloride and Bromide with Triphenyl Phosphite

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### Recommended Citation

Pike, Robert D.; Starnes, William H. Jr.; and Carpenter, Gene B., Cubane Tetrameric Complexes of Copper(I) Chloride and Bromide with Triphenyl Phosphite (1999). *Acta Crystallographica Section C*, C55, 162-165. <https://doi.org/10.1107/S0108270198012451>

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*Acta Cryst.* (1999). **C55**, 162–165

## Cubane tetrameric complexes of copper(I) chloride and bromide with triphenyl phosphite

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(Received 2 February 1998; accepted 28 September 1998)

### Abstract

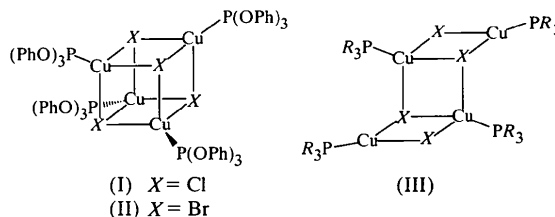
The crystal structures of tetra- $\mu_3$ -chloro-tetrakis[(triphenyl phosphite-*P*)copper(I)], [Cu<sub>4</sub>Cl<sub>4</sub>(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>P)<sub>4</sub>], and tetra- $\mu_3$ -bromo-tetrakis[(triphenyl phosphite-*P*)copper(I)], [Cu<sub>4</sub>Br<sub>4</sub>(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>P)<sub>4</sub>], are described. Both have distorted 'cubane' Cu<sub>4</sub>X<sub>4</sub> cores. Distortion of the cubane structure is reflected in X—Cu—X angles > 90° and Cu—X—Cu angles < 90°, and is more pronounced in the bromide complex.

### Comment

We have demonstrated recently that Cu<sup>I</sup>-halide-phosphite complexes can induce crosslinking in thermally degrading poly(vinyl chloride) (PVC; Pike *et al.*, 1997). This crosslinking appears to be the result of the reduc-

tive coupling of allylic chloride sites, caused by low-valent Cu centers. Given this activity, Cu<sup>I</sup>-phosphite complexes may be of importance as smoke-suppressant additives for PVC. During the course of our study, we prepared a number of complexes with the stoichiometry [CuXL]<sub>n</sub>, where X is a halide and L is a phosphite ligand. Although such complexes have long been known (Nishizawa, 1961), no X-ray structural information is available for these species.

We were readily able to prepare crystals of [Cu<sub>4</sub>Cl<sub>4</sub>(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>P)<sub>4</sub>], (I), and [Cu<sub>4</sub>Br<sub>4</sub>(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>P)<sub>4</sub>], (II). However, the iodide complex, which has a 1:2 Cu:I ratio (Nishizawa, 1961), was not readily crystallizable. Both (I) and (II) proved to be composed of a 'cubane' Cu<sub>4</sub>X<sub>4</sub> core, in which each halide bridges three metal atoms and each metal atom is coordinated to a phosphite and three halide ligands. This arrangement is very well known for complexes of Cu<sup>I</sup> and Ag<sup>I</sup> halides. The cubane core structure has previously been observed for many phosphine complexes, including [MXL]<sub>4</sub> (M = Cu or Ag, X = Cl, Br or I, and L = PPh<sub>3</sub> or PEt<sub>3</sub>; Churchill & Kalra, 1974a,c; Churchill, DeBoer & Mendak, 1975; Churchill & DeBoer, 1975; Churchill *et al.*, 1976; Teo & Calabrese, 1976a,b,c; Barron *et al.*, 1984; Dyason *et al.*, 1985), [CuI(PMePh<sub>2</sub>)<sub>4</sub>] (Churchill & Rotella, 1977), and [CuBr(P<sup>t</sup>Bu)<sub>3</sub>]<sub>4</sub> (Goel & Beauchamp, 1983). An alternative arrangement of the Cu<sub>4</sub>X<sub>4</sub> core, described as a step cluster, (III), is less common and is found for polymorphs of [CuX(PPh<sub>3</sub>)<sub>4</sub>] (X = Br or I; Churchill & Kalra, 1974b; Churchill, DeBoer & Donovan, 1975) and [AgI(PPh<sub>3</sub>)<sub>4</sub>] (Teo & Calabrese, 1976c). The trimesitylphosphine ligand proved sufficiently bulky to produce [CuBr(PMeS<sub>3</sub>)] as a monomer with two-coordinate Cu<sup>I</sup> (Alyea *et al.*, 1985).



In contrast to several previously reported [MXL]<sub>4</sub> series, the triphenylphosphite chloride, (I), and bromide, (II), complexes of Cu<sup>I</sup> were not isomorphous. Complex (I) crystallized in the monoclinic space group *P2<sub>1</sub>/n* (*Z* = 4) and complex (II) in the trigonal space group *R $\bar{3}$*  (*Z* = 6). For complex (II), the atoms Br1, Cu1 and P1 are located on the threefold axis, and only one third of the molecule is independent. As has been observed previously, the cubane core becomes increasingly distorted as the size of the halide ligand increases. Thus, complex (I) shows only slight distortion from cubane geometry; Cl—Cu—Cl bond angles average 94 (3)°, and Cu—Cl—Cu angles average 85 (2)°. Complex (II)

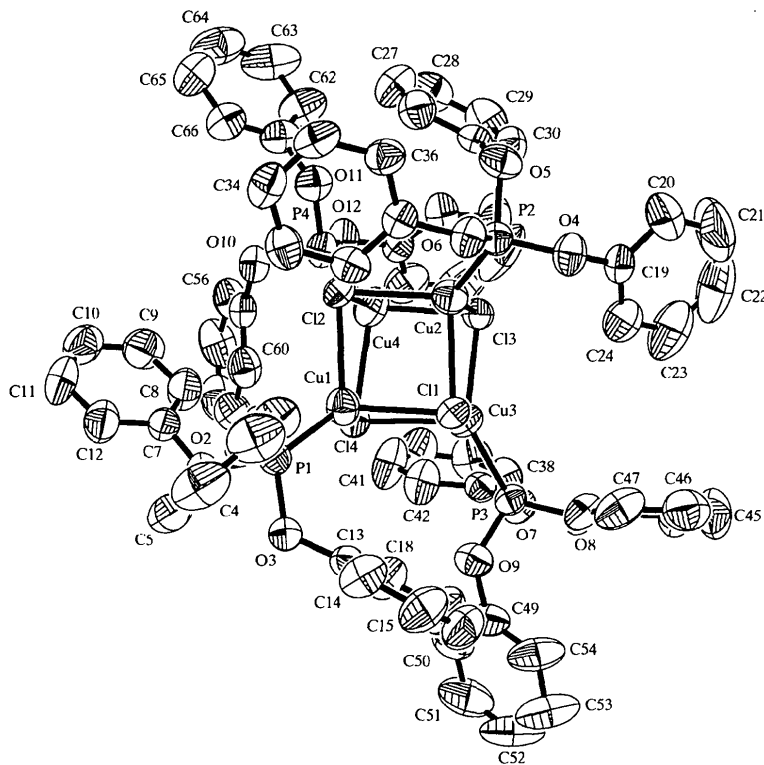


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

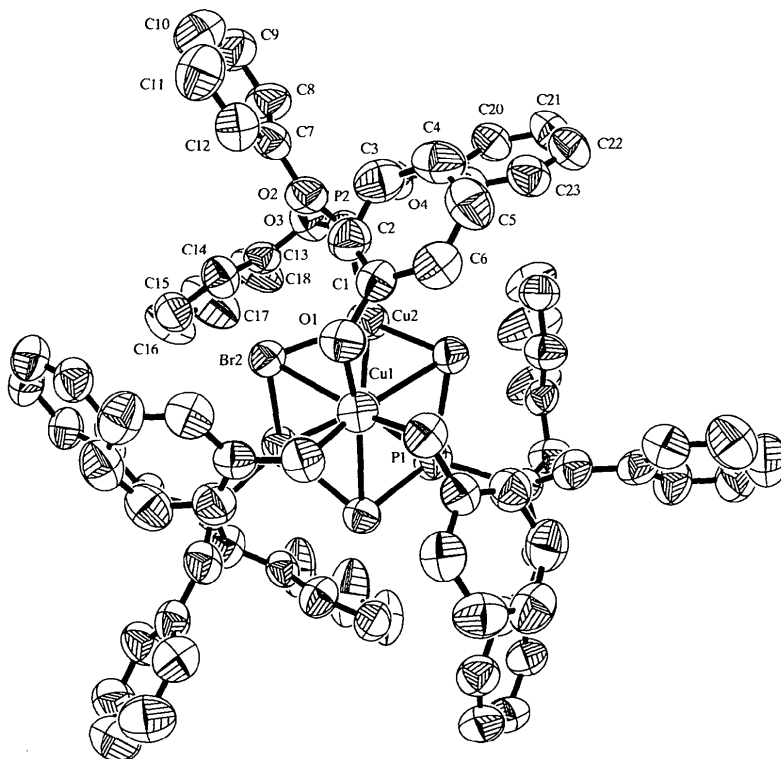


Fig. 2. The molecular structure of (II), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

shows two separate distortions in the cubane core. One of these involves compression around the Br sites and expansion around the Cu sites, which has been noted in similar complexes. In addition, there is significant compression of the cube perpendicular to the three-fold crystallographic axis. This results in slight expansion of the angles around Cu1 and Br1, which lie on the axis. The Br—Cu1—Br angles are 101.87 (3)° and the other Br—Cu—Br angles average 97 (4)°. Similarly, Cu—Br1—Cu is 83.71 (3)° and the other Cu—Br—Cu angles average 80 (3)°.

## Experimental

The title complexes were prepared as previously described (Nishizawa, 1961) and were crystallized from toluene solutions layered with hexanes in a 3 mm (inside diameter) tube. Very large crystals resulted, which required cutting prior to X-ray analysis.

### Compound (I)

#### Crystal data

|  |   |
|--|---|
| [Cu <sub>4</sub> Cl <sub>4</sub> (C <sub>18</sub> H <sub>15</sub> O <sub>3</sub> P) <sub>4</sub> ] | Mo K $\alpha$ radiation                   |
| $M_r = 1637.15$  | $\lambda = 0.71073 \text{ \AA}$           |
| Monoclinic   | Cell parameters from 8192 reflections     |
| $P2_1/n$   | $\theta = 1.9\text{--}28.0^\circ$         |
| $a = 14.6643 (2) \text{ \AA}$  | $\mu = 1.467 \text{ mm}^{-1}$             |
| $b = 22.6409 (3) \text{ \AA}$  | $T = 298 (2) \text{ K}$                   |
| $c = 22.6645 (1) \text{ \AA}$  | Irregular block                           |
| $\beta = 107.434 (1)^\circ$  | $0.54 \times 0.24 \times 0.22 \text{ mm}$ |
| $V = 7179.2 (1) \text{ \AA}^3$   | Colorless                                 |
| $Z = 4$  |   |
| $D_x = 1.515 \text{ Mg m}^{-3}$  |   |
| $D_m$ not measured   |   |

#### Data collection

|  |  |
|--|--|
| Siemens P4 CCD diffractometer  | 7760 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans   | $R_{\text{int}} = 0.073$               |
| Absorption correction: empirical (SADABS; Blessing, 1995; Sheldrick, 1996) | $\theta_{\text{max}} = 25.03^\circ$    |
| $T_{\text{min}} = 0.483, T_{\text{max}} = 0.724$                           | $h = -17 \rightarrow 9$                |
| 56 312 measured reflections  | $k = -26 \rightarrow 24$               |
| 12 671 independent reflections   | $l = -23 \rightarrow 26$               |
|  | Intensity decay: $-0.6\%$              |

#### Refinement

|   |  |
|---|--|
| Refinement on $F^2$                     | $(\Delta/\sigma)_{\text{max}} = 0.043$   |
| $R[F^2 > 2\sigma(F^2)] = 0.049$         | $\Delta\rho_{\text{max}} = 0.715 \text{ e \AA}^{-3}$                             |
| $wR(F^2) = 0.111$                       | $\Delta\rho_{\text{min}} = -0.619 \text{ e \AA}^{-3}$                            |
| $S = 1.013$                             | Extinction correction: none  |
| 12671 reflections                       | Scattering factors from <i>International Tables for Crystallography</i> (Vol. C) |
| 865 parameters                          |  |
| H atoms riding                          |  |
| $w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$ |  |
| where $P = (F_o^2 + 2F_c^2)/3$          |  |

Table 1. Selected bond lengths (Å) for (I)

|         |             |         |             |
|---------|-------------|---------|-------------|
| Cu1—P1  | 2.1482 (12) | Cu3—P3  | 2.1663 (12) |
| Cu1—Cl4 | 2.3784 (12) | Cu3—Cl3 | 2.3562 (11) |
| Cu1—Cl1 | 2.3916 (11) | Cu3—Cl1 | 2.4744 (11) |
| Cu1—Cl2 | 2.4268 (12) | Cu3—Cl4 | 2.4769 (11) |
| Cu2—P2  | 2.1541 (12) | Cu4—P4  | 2.1558 (13) |
| Cu2—Cl2 | 2.3915 (11) | Cu4—Cl3 | 2.3770 (11) |
| Cu2—Cl1 | 2.4453 (11) | Cu4—Cl2 | 2.4079 (12) |
| Cu2—Cl3 | 2.4532 (12) | Cu4—Cl4 | 2.5306 (12) |

### Compound (II)

#### Crystal data

|  |   |
|--|---|
| [Cu <sub>4</sub> Br <sub>4</sub> (C <sub>18</sub> H <sub>15</sub> O <sub>3</sub> P) <sub>4</sub> ] | Mo K $\alpha$ radiation                   |
| $M_r = 1814.96$  | $\lambda = 0.71073 \text{ \AA}$           |
| Trigonal   | Cell parameters from 8192 reflections     |
| $R\bar{3}$   | $\theta = 1.70\text{--}24.89^\circ$       |
| $a = 21.1645 (1) \text{ \AA}$  | $\mu = 3.400 \text{ mm}^{-1}$             |
| $c = 28.9378 (1) \text{ \AA}$  | $T = 298 (2) \text{ K}$                   |
| $V = 11225.66 (8) \text{ \AA}^3$   | Irregular block                           |
| $Z = 6$  | $0.33 \times 0.33 \times 0.20 \text{ mm}$ |
| $D_x = 1.611 \text{ Mg m}^{-3}$  | Colorless                                 |
| $D_m$ not measured   |   |

#### Data collection

|  |  |
|--|--|
| Siemens P4 CCD diffractometer  | 3021 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans   | $R_{\text{int}} = 0.043$               |
| Absorption correction: empirical (SADABS; Blessing, 1995; Sheldrick, 1996) | $\theta_{\text{max}} = 24.89^\circ$    |
| $T_{\text{min}} = 0.307, T_{\text{max}} = 0.507$                           | $h = -19 \rightarrow 24$               |
| 18 958 measured reflections  | $k = -24 \rightarrow 23$               |
| 4304 independent reflections   | $l = -22 \rightarrow 34$               |
|  | Intensity decay: $-0.1\%$              |

#### Refinement

|   |  |
|---|--|
| Refinement on $F^2$                               | $(\Delta/\sigma)_{\text{max}} = 0.058$   |
| $R[F^2 > 2\sigma(F^2)] = 0.048$                   | $\Delta\rho_{\text{max}} = 1.314 \text{ e \AA}^{-3}$                             |
| $wR(F^2) = 0.147$                                 | $\Delta\rho_{\text{min}} = -0.415 \text{ e \AA}^{-3}$                            |
| $S = 1.131$                                       | Extinction correction: none  |
| 4304 reflections                                  | Scattering factors from <i>International Tables for Crystallography</i> (Vol. C) |
| 289 parameters                                    |  |
| H atoms riding                                    |  |
| $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 3.6171P]$ |  |
| where $P = (F_o^2 + 2F_c^2)/3$                    |  |

Table 2. Selected bond lengths (Å) for (II)

|                       |            |                       |            |
|-----------------------|------------|-----------------------|------------|
| Br1—Cu2 <sup>i</sup>  | 2.4904 (9) | Cu1—Br2 <sup>ii</sup> | 2.4911 (7) |
| Br1—Cu2               | 2.4904 (9) | Br2—Cu2 <sup>ii</sup> | 2.4465 (9) |
| Br1—Cu2 <sup>ii</sup> | 2.4903 (9) | Br2—Cu2               | 2.749 (1)  |
| Cu1—P1                | 2.145 (2)  | Cu2—P2                | 2.165 (2)  |
| Cu1—Br2 <sup>i</sup>  | 2.4910 (7) | Cu2—Br2 <sup>i</sup>  | 2.4465 (9) |
| Cu1—Br2               | 2.4911 (7) |                       |            |

Symmetry codes: (i)  $1 - x + y, 1 - x, z$ ; (ii)  $1 - y, x - y, z$ .

All H atoms were introduced in ideal positions (C—H 0.93 Å), riding on the C atom to which each is bonded; each was refined with an isotropic displacement factor 20% greater than that of the attached atom. All other atoms were refined with anisotropic displacement parameters. The final difference map for (II) showed a density peak of  $1.31 \text{ e \AA}^{-3}$  at a distance of

3.74 Å from H18A. This distance was only slightly less than that from three other H atoms in other molecules; furthermore, it was only 0.80 Å from an equivalent of itself.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE* and *SADABS* (Blessing, 1995; Sheldrick, 1996); program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97*.

We are indebted to the GenCorp Foundation for partial support of this research. The X-ray equipment was purchased with assistance from an instrumental grant from the National Science Foundation (CHE-8206423) and a grant from the National Institutes of Health (RR-06462).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1019). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 165–167

## $\mu$ -[1,1'-(1,2-Ethanediy)]bis(1H-1,2,4-triazole)-N<sup>4</sup>:N<sup>4'</sup>-bis{bis[1,1,1-trifluoro-3-(2-thenoyl)acetonato-O,O']copper(II)}

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(Received 6 April 1998; accepted 15 September 1998)

## Abstract

The crystal structure determination of the title complex, [Cu<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>F<sub>3</sub>O<sub>2</sub>S)<sub>4</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>6</sub>)] or [Cu(TTA)<sub>2</sub>]<sub>2</sub>btrz, where TTA is 1,1,1-trifluoro-3-(2-thenoyl)acetone and btrz is  $\mu$ -[1,1'-(1,2-ethanediy)]bis(1H-1,2,4-triazole)], shows that the btrz ligand links two Cu<sup>II</sup> ions, forming a binuclear complex. Each Cu atom is in a distorted square-pyramidal coordination environment.

## Comment

In the search for molecular-based materials with functions of catalysis, magnetism and clathration, polynuclear coordination complexes have recently been widely studied (Makoto *et al.*, 1994). Although many rigid bridging ligands, such as 4,4'-bipyridine (Fujita *et al.*, 1994), *trans*-1,2-bis(2-pyridyl)ethylene (Kitagawa *et al.*, 1991) and metalloporphyrins (Abrahams *et al.*, 1991), have been employed to build up these materials, relatively few flexible ligands have been exploited for this purpose. We report here the preparation and crystal structure of the binuclear copper(II) complex [Cu(TTA)<sub>2</sub>]<sub>2</sub>btrz, (I), where TTA is 1,1,1-trifluoro-3-(2-thenoyl)acetone and btrz is  $\mu$ -[1,1'-(1,2-ethanediy)]-bis(1H-1,2,4-triazole)]. In (I), the flexible btrz ligand (Torres *et al.*, 1988) links two Cu<sup>II</sup> ions.

