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

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Abstract
The crystal structures of tetra-μ3-chloro-tetrakis[(triphenyl phosphite-P)nickel(I)], [Cu3Cl4(C18H15O3P)4], and tetra-μ3-bromo-tetrakis[(triphenyl phosphite-P)-copper(I)], [Cu4Br4(C18H15O3P)4], are described. Both have distorted 'cubane' Cu4X4 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 Cu1-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-
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 parallel to the three-fold crystallographic axis. This results in slight expansion of the angles around CuI and BrI, which lie on the axis. The Br-CuI--Br angles are 101.87 (3)° and the other Br--Cu--Br angles average 97 (4)°. Similarly, CuI--BrI--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**

\[\text{[Cu}_4\text{Cl}_4(\text{C}_1\text{H}_8\text{O}_3\text{P})_4]\]

- Mr = 1637.15
- Monoclinic
- \(P2_1/n\)
- \(a = 14.6643 (2) \text{Å}\)
- \(b = 22.6409 (3) \text{Å}\)
- \(c = 22.6645 (1) \text{Å}\)
- \(\beta = 107.434 (1) {}^\circ\)
- \(V = 7179.2 (1) \text{Å}^3\)
- \(Z = 4\)
- \(D_r = 1.515 \text{ Mg m}^{-3}\)
- \(D_m\) not measured

**Data collection**

- Siemens P4 CCD diffractometer
- \(\omega\) and \(\phi\) scans
- Absorption correction: empirical (SADABS; Blessing, 1995; Sheldrick, 1996)
- \(T_{\text{min}} = 0.483, T_{\text{max}} = 0.724\)
- 56312 measured reflections
- 12671 independent reflections

**Refinement**

- Refinement on \(F^2\)
- \(R(F^2) = 0.049\)
- \(wR(F^2) = 0.111\)
- \(S = 1.013\)
- 12671 reflections
- 856 parameters
- H atoms riding
- \(w = 1/\sigma^2(F_C^2) + (0.0214P)^2\)
  \(wP = (F_C^2 + 2F_E^2)/3\)

**Data collection**

- Siemens P4 CCD diffractometer
- \(\omega\) and \(\phi\) scans
- Absorption correction: empirical (SADABS; Blessing, 1995; Sheldrick, 1996)
- \(T_{\text{min}} = 0.307, T_{\text{max}} = 0.507\)
- 18958 measured reflections
- 4304 independent reflections

**Refinement**

- Refinement on \(F^2\)
- \(R(F^2) = 0.048\)
- \(wR(F^2) = 0.147\)
- \(S = 1.131\)
- 4304 reflections
- 289 parameters
- H atoms riding
- \(w = 1/\sigma^2(F_C^2) + (0.0808P)^2 + 3.6171P\)
  \(wP = (F_C^2 + 2F_E^2)/3\)

**Selected bond lengths (Å) for (I)**

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1--P1</td>
<td>2.1482 (12)</td>
</tr>
<tr>
<td>Cu1--Cl4</td>
<td>2.3784 (12)</td>
</tr>
<tr>
<td>Cu1--ClI</td>
<td>2.3916 (11)</td>
</tr>
<tr>
<td>Cu1--Cl2</td>
<td>2.4268 (12)</td>
</tr>
<tr>
<td>Cu2--P2</td>
<td>2.1541 (12)</td>
</tr>
<tr>
<td>Cu2--Cl2</td>
<td>2.3915 (11)</td>
</tr>
<tr>
<td>Cu2--ClI</td>
<td>2.4453 (11)</td>
</tr>
<tr>
<td>Cu2--Cl3</td>
<td>2.4532 (12)</td>
</tr>
</tbody>
</table>

**Compound (II)**

**Crystal data**

\[\text{[Cu}_4\text{Br}_4(\text{C}_1\text{H}_8\text{O}_3\text{P})_4]\]

- Mr = 1814.96
- Trigonal
- \(R3\)
- \(a = 21.1645 (1) \text{Å}\)
- \(c = 28.9378 (1) \text{Å}\)
- \(V = 11225.66 (8) \text{Å}^3\)
- \(Z = 6\)
- \(D_r = 1.611 \text{ Mg m}^{-3}\)
- \(D_m\) not measured

**Data collection**

- Siemens P4 CCD diffractometer
- \(\omega\) and \(\phi\) scans
- Absorption correction: empirical (SADABS; Blessing, 1995; Sheldrick, 1996)
- \(T_{\text{min}} = 0.307, T_{\text{max}} = 0.507\)
- 3021 reflections with \(I > 2\sigma(I)\)
- 18958 measured reflections
- 4304 independent reflections

**Refinement**

- Refinement on \(F^2\)
- \(R(F^2) = 0.048\)
- \(wR(F^2) = 0.147\)
- \(S = 1.131\)
- 4304 reflections
- 289 parameters
- H atoms riding
- \(w = 1/\sigma^2(F_C^2) + (0.0808P)^2 + 3.6171P\)
  \(wP = (F_C^2 + 2F_E^2)/3\)

**Selected bond lengths (Å) for (II)**

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br1--Cu2</td>
<td>2.4904 (9)</td>
</tr>
<tr>
<td>Br1--Cu3</td>
<td>2.4940 (9)</td>
</tr>
<tr>
<td>Br1--Cu4</td>
<td>2.4903 (9)</td>
</tr>
<tr>
<td>Cu1--P1</td>
<td>2.145 (2)</td>
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<tr>
<td>Cu1--Br2</td>
<td>2.4910 (7)</td>
</tr>
<tr>
<td>Cu1--Br3</td>
<td>2.4911 (7)</td>
</tr>
</tbody>
</table>

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 e Å\(^{-3}\) 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: SAINT (Siemens, 1995); data reduction: SAINT and SADABS (Blessing, 1996; 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.

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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.

References

Abstract
The crystal structure determination of the title complex, [Cu2(C8H4F3O2S)n(C6H8N6)] or [Cu(TTA)2]2btrz, where TTA is 1,1,1-trifluoro-3-(2-thienyl)acetone and btrz is μ-[1,1′-(1,2-ethanediyl)bis(1H-1,2,4-triazole)], shows that the btrz ligand links two CuII 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., 1988) 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)2]2btrz, (I), where TTA is 1,1,1-trifluoro-3-(2-thienyl)acetone and btrz is μ-[1,1′-(1,2-ethanediyl)bis(1H-1,2,4-triazole)]. In (I), the flexible btrz ligand (Torres et al., 1988) links two CuII ions.

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