The six-membered chelate rings have slightly different conformations. While the ligand involved in the Cu—N bridge is planar within 0·028 (4) Å, the ring involved in plane-to-plane coupling adopts a half-chair conformation with a dihedral angle along the O···O vector of 171·6 (3)°; Cu is displaced from the ligand planes by 0·067 (1) and 0·228 (1) Å respectively. A half-chair conformation is also observed in the Cu-(CNpaac)$_2$ complex with a 0·5 Å metal displacement and a 158·3° angle of fold. The average chelate 'bite' distance is 2·768 (3) Å. Bond lengths and angles in the ligands are normal (see Table 3). We note that the C—CN bonds [av. 1·436 (4) Å] are longer than the in-ring C—C bonds [av. 1·416 (4) Å].

The intrinsic *mmm* (D_{2h}) point symmetry of the Cu(CNacac)$_2$ molecule is entirely lost in the crystal as only one of the CN groups is involved in an intermolecular coordination. The C(4')—N(7')···Cu^{iii} angle is 115·7 (2)° compared to 149·8 (9)° in Cu(CNpaac)$_2$. The N atom of the second cyano group is distant from Cu; its closest intermolecular contact is N(7)···C(3^{iii}) 3·493 (5) Å.

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Structure of Dicopper Tetramethylammonium Pentachloride

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Abstract. Cu$_2$[N(CH$_3$)$_4$]Cl$_5$, $M_r = 378·56$, monoclinic, $P2_1/c$, $a = 6·073$ (1), $b = 19·58$ (1), $c = 10·62$ (1) Å, $\beta = 99·46$ (5)°, $V = 1245·1$ (4) Å^3, $Z = 4$, $D_x = 2·02$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 44·67$ cm^{-1}, $F(000) = 744$, $T = 293$ K, $wR = 0·0329$ for 3450 reflections. The building block of this compound consists of a linear array of four edge-sharing square pyramids (approximate C_{4v} symmetry) with each alternate pyramid upside down. These building blocks are edge-sharing *via* the apical Cl$^-$ ions so as to form sheets. The sheets are held together by the large tetramethylammonium (TMA) ions.

Introduction. The research by our group is focused in part on the structural and magnetic properties of ternary halides in the system $AX—BX_2$ in which $A = $ Rb$^+$, Cs$^+$ or (CH$_3$)$_4$N$^+$, $B = $ Cu^{2+} and $X = $ Cl$^-$. The most thoroughly investigated structure class in this system is the hexagonal perovskite ABX_3 (2L). The cooperative Jahn–Teller effects in the Cu^{2+} and Cr^{2+} compounds were the main field of interest (Crama & Maaskant, 1983; Maaskant & Haije, 1986).

We previously reported (Haije, Dobbelaar & Maaskant, 1986) the crystal structure of a new compound in the same ternary system: TMPCu$_2$Cl$_5$ (TMP = tetramethylphosphonium). This compound has a similar composition to TMACu$_2$Cl$_5$ (TMA = tetramethylammonium) which was first synthesized by Weenk (1976) who only determined the lattice parameters. The present investigation was undertaken to prove the similarity between the two compounds, which, however, does not appear to exist after all.

Experimental. Single crystals were grown from an aqueous solution, acidified with concentrated hydrochloric acid, containing TMACl and CuCl$_2$ in the ratio

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = 8\pi^2 U_{eq}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Cu(1)	0.69075 (5)	0.03408 (1)	0.91994 (3)	2.227 (6)
Cu(2)	0.13075 (5)	0.10085 (2)	0.80668 (3)	2.139 (4)
Cl(1)	0.3922 (1)	0.05326 (3)	0.70652 (6)	2.64 (1)
Cl(2)	0.8610 (1)	0.13664 (3)	0.91939 (7)	3.23 (1)
Cl(3)	0.1981 (1)	0.20645 (3)	0.74818 (7)	3.63 (2)
Cl(4)	0.9646 (1)	−0.00683 (3)	0.81731 (6)	2.58 (1)
Cl(5)	0.4353 (1)	0.07417 (3)	0.04037 (5)	2.62 (4)
N	0.6493 (3)	0.1537 (1)	0.4288 (2)	2.62 (4)
C(1)	0.4296 (5)	0.1215 (2)	0.3800 (3)	3.49 (7)
C(2)	0.6195 (6)	0.2068 (2)	0.5253 (3)	4.12 (8)
C(3)	0.7393 (6)	0.1862 (2)	0.3202 (3)	4.27 (8)
C(4)	0.8091 (6)	0.1002 (2)	0.4894 (3)	4.01 (8)

Table 2. *Relevant bond distances (Å) and angles (°)*

Cu(1)–Cl(1)	2.6855 (7)	Cu(2)–Cl(2)	2.2918 (6)
Cu(1)–Cl(2)	2.2586 (6)	Cu(2)–Cl(4)	2.3476 (6)
Cu(1)–Cl(4)	2.2784 (6)	Cu(2)–Cl(5)	2.8880 (6)
Cu(1)–Cl(5)	2.3046 (5)	N–C(1)	1.489 (3)
Cu(1)–Cl(5′)	2.3151 (5)	N–C(2)	1.492 (3)
Cu(2)–Cl(1)	2.2528 (6)	N–C(3)	1.497 (3)
Cu(2)–Cl(3)	2.2158 (6)	N–C(4)	1.499 (4)

Cl(1)–Cu(2)–Cl(3)	94.39 (2)	Cl(1)–Cu(1)–Cl(2)	96.86 (2)
Cl(1)–Cu(2)–Cl(2)	173.12 (2)	Cl(1)–Cu(1)–Cl(4)	95.19 (2)
Cl(1)–Cu(2)–Cl(4)	89.62 (2)	Cl(1)–Cu(1)–Cl(5)	89.87 (2)
Cl(1)–Cu(2)–Cl(5)	85.94 (2)	Cl(1)–Cu(1)–Cl(5′)	94.82 (2)
Cl(3)–Cu(2)–Cl(2)	92.41 (2)	Cl(1)–Cu(1)–Cl(4)	177.49 (2)
Cl(3)–Cu(2)–Cl(5)	106.73 (2)	Cl(2)–Cu(1)–Cl(5)	92.81 (2)

1:2. The solution yielded three types of crystal, reddish brown (TMACuCl₃), yellow (TMA₂CuCl₄) and dark green, which were separated by hand. The green modification appeared to have the same unit-cell dimensions as given by Weenk (1976) for the TMA-Cu₂Cl₅ compound.

Dark-green oblique crystals, 0·6 × 0·4 × 0·4 mm, Enraf–Nonius four-circle diffractometer, graphite-monochromated Mo *K*α radiation, 24 reflections (−16·47 < θ < 16·45°) used for determination of unit-cell dimensions, from systematic absences *h0l* *l* = 2*n*, 0*k*0 *k* = 2*n* it was concluded that the space group is *P*2₁/*c*. 5824 reflections were measured (2 < θ < 35°), of which 5608 were independent, *R*ᵢₙₜ = 0·0324, 3456 observed and 2152 non-significant [for observed reflections: *I* > 2σ(*I*)], *h* 0 to 9, *k* 0 to 31, *l* −17 to 16, three standard reflections (363̄, 206, 008̄), decay scattering power 8·97%, observed reflections were corrected for this variation; e.s.d. of standard reflections 1·9%. Lp correction, absorption correction (de Graaff, 1973), min. and max. transmission 0·373 and 0·562 respectively, scattering factors from *International Tables for X-ray Crystallography* (1974) with correction for real and imaginary parts of anomalous dispersion. Function minimized during the least-squares refinement $\sum w(|F_{obs}| - |F_{calc}|)^2$, $w = 1/\sigma(F)^2$, σ(*F*) e.s.d. calculated from counting statistics

and by taking into account the above-mentioned corrections. For all calculations, computer programs were written or modified by Rutten-Keulemans and de Graaff and used on the Leiden University IBM 3081 computer. The determination of the crystal structure was started by solving a Patterson map for the heavy atoms. Subsequent Fourier syntheses were used to find all non-H atoms. Refinement of all Cu, Cl, C and N positions and anisotropic thermal parameters resulted in *wR* = 5·97%. Including the H atoms on calculated positions lowered *wR* to 3·74%. The calculated moduli of some of the strongest reflections were still much larger than the observed values, making correction for extinction (Zachariasen, 1969) necessary; final *wR* is 3·29% (*R* = 2·8%, *S* = 1·2). The ratio of the maximum least-squares shift to e.s.d. is smaller than 0·07 (isotropic *B* of H atom). The maximum and minimum heights in the final difference Fourier synthesis are 0·46 and 0·28 e Å⁻³ respectively (statistical height: 0·20 e Å⁻³).

Discussion. The positional parameters are given in Table 1.* Relevant bond lengths and angles are also tabulated (Table 2). The structure of this compound is clearly different from that found for the phosphonium analog discussed in the *Introduction* (Haije, Dobbelaar & Maaskant, 1986), which explains the difference in colour. The TMP compound is red

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*Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51579 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
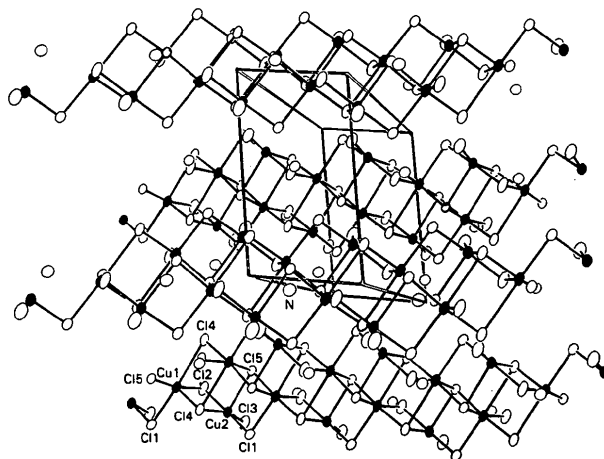

Fig. 1. Perspective view of the Cu–Cl network. The *ac* plane is parallel to the plane of the paper; the *b* axis is pointing out of this plane. The four-pyramid building block is easily recognized, as are the two distinct copper species (five- and six-coordinated). For clarity, the CH₃ groups of the TMA ions are left out of the drawing (N: non-bonded open ellipsoid).

whereas the TMA compound is green. In the TMA case the structure contains two definitely different Cu sites, one [Cu(2); coordinated to Cl(1), Cl(2), Cl(3), Cl(4) and Cl(5)] being square pyramidal (five coordinated) and the other [Cu(1); coordinated to Cl(1), Cl(2), two Cl(4) ions and two Cl(5) ions] effectively six coordinated although the site symmetry remains approximately C_{4v} as one of the apical Cl ions [Cl(4)] has a much larger bond length [3·2446 (7) Å]. The square-pyramidal environment of Cu is distorted via a pseudo-Jahn–Teller effect in the ground state of the C_{4v} complex as described for other compounds by Bacci (1979).

The Cu–Cl backbone consists of linear arrays of four edge-sharing pyramids coupled together so as to form sheets (Fig. 1) which are held together by the TMA ions.

From a magnetochemists' point of view it might be interesting to see whether this system behaves mag-

netically as weakly coupled linear tetramers of four coupled $S = \frac{1}{2}$ ions, since the unpaired electron is most likely confined to the $d_{x^2-y^2}$ orbital which is in the equatorial plane of the pyramid (the d_{z^2} orbital is pointing toward the apical Cl ions).

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Structures of *trans*- and *cis*-Dichloro(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-*O,O'*)-bis(triphenylphosphine)ruthenium(II)

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Abstract. (I) *trans*-[RuCl$_2$\{CF$_3$C(O)CHC(O)CF$_3$\}(PPh$_3$)$_2$], $M_r = 903·61$, monoclinic, $P2_1/n$, $a = 12·151$ (3), $b = 17·613$ (4), $c = 18·542$ (2) Å, $\beta = 103·92$ (1)°, $V = 3852$ (1) Å^3, $Z = 4$, $D_x = 1·56$ g cm^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 6·83$ cm^{-1}, $F(000) = 1820$, $T = 295$ K, $R = 0·039$, 4122 unique observed reflections. (II) *cis*-[RuCl$_2$\{CF$_3$C(O)CHC(O)CF$_3$\}(PPh$_3$)$_2$], $M_r = 903·61$, monoclinic, $P2_1/c$, $a = 9·977$ (1), $b = 16·544$ (2), $c = 23·205$ (3) Å, $\beta = 93·062$ (9)°, $V = 3825$ (1) Å^3, $Z = 4$, $D_x = 1·57$ g cm^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 6·88$ cm^{-1}, $F(000) = 1820$, $T = 295$ K, $R = 0·038$, 4516 unique observed reflections. The crystals were prepared from

dichlorotris(triphenylphosphine)ruthenium and 1,1,1,-5,5,5-hexafluoro-2,4-pentanedione in cold (I) and warm (II) benzene under aerobic conditions. The Ru atoms in both compounds are in octahedral coordination with two O atoms of the bidentate ligand, the P atoms of two PPh$_3$ groups and two Cl atoms. In (I), the Cl atoms are *trans* and the PPh$_3$ groups are *cis*, while in (II) these conformations are reversed.

Introduction. The ruthenium(II) and osmium(II) complexes [MCl$_2$(PPh$_3$)$_3$] undergo 'oxidative substitution' reactions with β-diketones in benzene solution under aerobic conditions to form the corresponding β-diketonates [MCl$_2$\{RC(O)CHC(O)R'\}(PPh$_3$)$_2$] ($R,R' = $ CH$_3$, CF$_3$, C$_2$H$_5$ or C$_6$H$_5$) one of which, [RuCl$_2$-

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