component in the bonding between C(10) and Ru(1) and Ru(3) involving the t_{2g} set of orbitals on the metals. The Ru—Ru distances within the Ru$_3$ triangle are all shorter, the unbridged Ru(2)—Ru(3) edge by ca 0·11 Å, than the average distance of 2·854 (4) Å for the Ru—Ru edges in Ru$_3$(CO)$_{12}$ (Churchill, Hollander & Hutchinson, 1977). While the metal–metal edge-lengthening influence of a bridging hydride is well established (Churchill, DeBoer & Rotella, 1976), it seems that the $\mu_3-\eta^2$-CC(CH$_3$)C$_6$H$_5$ ligand exerts an edge-shortening influence which counterbalances the effect of the hydrides on the Ru(1)—Ru(2) and Ru(1)—Ru(3) edges and causes the considerable shortening of the Ru(2)—Ru(3) edge.

If the $\mu_3-\eta^2$-CC(CH$_3$)C$_6$H$_5$ ligand is considered to donate formally four electrons to cluster bonding, then the cluster as a whole has a 48 electron count, consistent with the presence of three formal metal–metal bonds.

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Structure of Bis(3-cyano-2,4-pentanedionato)copper(II)

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Abstract. [Cu(C$_6$H$_6$NO$_2$)$_2$], $M_r = 311\cdot78$, monoclinic, $P2_1/n$, $a = 10\cdot005$ (1), $b = 12\cdot149$ (1), $c = 11\cdot246$ (1) Å, $\beta = 96\cdot748$ (4)°, $V = 1357\cdot5$ (4) Å^3, $Z = 4$, $D_x = 1\cdot525$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 16\cdot2$ cm^{-1}, $F(000) = 636$, $T = 293$ K, $R = 0\cdot033$ for 2046 observed reflections with $I > 3\sigma(I)$. The Cu(CNacac)$_2$ (CNacacH = 3-cyano-2,4-pentanedione) chelate molecules occupy general positions and are associated in infinite zigzag chains parallel to **b**. The CuO$_4$N coordination polyhedron is a distorted square pyramid, with Cu—O distances 1·912 (2)– 1·928 (2) Å and with Cu shifted from the O$_4$ plane towards the apical N atom by 0·114 (1) Å. The CNacac ligands are planar with normal geometry, but are structurally non-equivalent: one coordinates to Cu *via* the cyano group with Cu···N = 2·468 (3) Å, whilst the other takes part in a plane-to-plane coupling with a centrosymmetrically equivalent molecule (distance between ligand planes 3·056 Å).

Introduction. In a preceding paper we have shown that the dipropyl ester of 1-cyano-2,4-propylphosphonic acid (CNpaacH) forms chelate bridges in the structure of Cu(CNpaac)$_2$ (Macicek, Angelova, Petrov & Kirilov, 1988). Spectroscopic investigations of CNpaacH indicated a similarity of its coordination properties to those of β-diketonates (Petrov, 1972a). The analogy between O=P—C(CN)—C=O and O=C—C(CN)— C=O fragments focused attention on the simplest cyano-β-diketone derivative – 3-cyano-2,4-pentanedione (CNacacH). The latter, and its metal complexes, are well characterized by various techniques other than crystallographic methods.

The IR and UV spectra of CNacacH (Wierzchowski & Shugar, 1965) indicated that in different solutions the molecule exists exclusively as the *cis*-enol form and that the anion is symmetric with complete charge delocalization. The cyano group was found to cause an electron density rearrangement (due to its large

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Cu	0.64795 (4)	0.38510 (3)	0.38163 (3)	2.711 (6)
O(1)	0.7034 (2)	0.4412 (2)	0.5391 (2)	2.97 (4)
O(1')	0.5770 (2)	0.3263 (2)	0.2295 (2)	3.51 (4)
O(2)	0.5682 (2)	0.5238 (2)	0.3287 (2)	3.15 (4)
O(2')	0.7025 (2)	0.2422 (2)	0.4423 (2)	3.49 (4)
N(7)	0.6565 (4)	0.8216 (2)	0.5944 (3)	5.68 (8)
N(7')	0.6343 (3)	−0.0558 (2)	0.1798 (2)	4.01 (6)
C(1)	0.6997 (3)	0.5399 (2)	0.5744 (3)	2.83 (6)
C(1')	0.5783 (3)	0.2273 (3)	0.1949 (3)	3.05 (6)
C(2)	0.5767 (3)	0.6141 (2)	0.3840 (3)	3.02 (6)
C(2')	0.6948 (3)	0.1518 (2)	0.3869 (3)	3.25 (6)
C(3)	0.6421 (3)	0.6272 (2)	0.5019 (3)	2.92 (6)
C(3')	0.6348 (3)	0.1399 (2)	0.2673 (3)	2.85 (6)
C(4)	0.6491 (3)	0.7361 (3)	0.5534 (3)	3.76 (7)
C(4')	0.6315 (3)	0.0317 (3)	0.2175 (3)	3.15 (6)
C(5)	0.7589 (4)	0.5612 (3)	0.7007 (3)	4.19 (7)
C(5')	0.5146 (4)	0.2059 (3)	0.0696 (3)	4.71 (8)
C(6)	0.5106 (4)	0.7112 (3)	0.3185 (3)	4.43 (8)
C(6')	0.7530 (5)	0.0525 (3)	0.4538 (3)	6.2 (1)

inductive effect) leading to an increased negative charge at N and a decrease at O. As a consequence copper CNacac chelates form weaker coordination bonds in solution (Tanaka, Shono & Shinra, 1969). Fackler (1962) attributed the observed splitting of the CN-stretching band in (KBr disc) IR spectra of several metal(II) and -(III) complexes to solid-state inter-actions on the cyano group. Simultaneous coordi-nation of the three functional groups present in the CNacac ligand have been reported by Thompson, Barrett, Lefelhoez & Lock (1973) in the case of trichloro(CNacac) complexes of Sn^{IV} and Ti^{IV}. Further, Lock & Thompson (1980) spectroscopically confirmed the trifunctional bridge-bonding of CNacac in some Zr^{IV} complexes. They also reported a splitting of the CN-stretching frequency, ascribed to the presence of both coordinated and non-coordinated cyano groups, and assigned the band at av. 2222 cm^{-1} to non-coordinated CN, while the band at av. 2254 cm^{-1} was related to the coordinated group.

Contrary to Lock & Thompson's (1980) con-clusions the CN-stretching band of crystalline Cu(CNpaac)$_2$, with both cyano groups participating in intermolecular bonding, appears at 2195 cm^{-1} (Petrov, 1972b). Well resolved bands at 2210 and 2195 cm^{-1} were observed for the title compound (cf. 2196 cm^{-1}; Fackler, 1962). The present structure analysis examines the copper coordination by the CNacac ligand.

Experimental. Complex prepared from a mixture of aqueous solutions of Cu(CH$_3$COO)$_2$ and CNacacH synthesized according to Fackler (1962). Dark-blue crystals obtained by evaporation of an absolute ethanolic solution at room temperature; a specimen with approximate dimensions 0.20 × 0.12 × 0.25 mm was investigated. D_m not determined. Enraf–Nonius

CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); $\omega/2\theta$ scan: speed 2 to 10° min^{-1}, width = 1.0° + 0.34°tanθ. Cell constants by least squares for 25 reflections with $18 < \theta < 20°$. 4328 reflections measured with $(\sin\theta)/\lambda < 0.703$ Å^{-1} (h: 0 to 14, k: 0 to 17, l: −15 to 15). Three standard reflections monitored every 2.0 h, intensity variation $< 0.1\%$. No decay correction. Lorentz and polarization correction; empirical absorption correction by *DIFABS* (Walker & Stuart, 1983), correction factors from 0.854 to 1.181. 2143 reflections considered unobserved $[I < 3\sigma(I)]$. Structure solved by heavy-atom method and refined by full-matrix least squares on 2046 F's. H atoms located from difference Fourier map and refined isotropically. Final $R = 0.033$, $wR = 0.037$ and $S = 1.17$; weights defined as $w = 4F_o^2/[\sigma(F_o)^2]^2$. Max. $(\Delta/\sigma) = 0.095$; max. residual density within ±0.26 e Å^{-3} in the vicinity of the heavy atom. No correction for secondary extinction. Atomic scattering factors and anomalous-dispersion coefficients as quoted in *SDP/PDP V3.0* software package (Enraf–Nonius, 1985) operating on a PDP11/44 computer.

Discussion. Final fractional coordinates for the non-H atoms are given in Table 1.* The atom-numbering scheme is depicted in Fig. 1. Bond lengths and angles are summarized in Table 2. The structure is built up of infinite zigzag chains of Cu(CNacac)$_2$ chelate molecules linked by long Cu$\cdots$N^i coordination bonds (Fig. 2a). Two such chains run through every unit cell parallel to **b**. The shortest Cu$\cdots$Cu^{ii} distance is 5.0498 (5) Å.

The Cu atom occupies a general position in contrast to all Cu(Racac)$_2$ complexes studied so far (see Table 3). The Cu coordination sphere is a distorted tetrag-onal pyramid of four basal O atoms from two chelating ligands and a cyano N atom of an adjacent molecule at the apex. Cu is displaced from the O$_4$ plane by 0.114 (1) Å towards the N atom. The average Cu—O distance of 1.920 (2) Å is slightly longer than

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51571 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
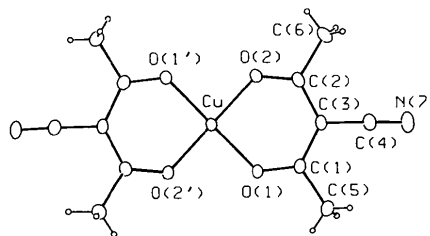

Fig. 1. Molecular structure and atom-labeling scheme for Cu(CNacac)$_2$ (30% thermal ellipsoids).

corresponding values in other Cu(Racac)₂ complexes (Table 3) but significantly shorter than the value of 1·953 (7) Å in Cu(CNpaac)₂ (Macicek *et al.*, 1988). The Cu···Nⁱ distance in Cu(CNacac)₂ [2·468 (3) Å] is also shorter than in Cu(CNpaac)₂ [2·516 (5) Å]. This can be ascribed to the different Cu coordination spheres: in Cu(CNpaac)₂ it is a tetragonally distorted

octahedron where both cyano groups occupy apical positions. In this structure the access to the sixth site of the metal coordination sphere is hindered by the plane-to-plane interaction of centrosymmetrically related molecules as illustrated in Fig. 2(b). The shortest nonbonding contacts are Cu···C(3ⁱⁱ) [3·324 (3) Å] and Cu···C(4ⁱⁱ) [3·471 (3) Å].

Table 2. *Bond distances (Å) and angles (°) with their e.s.d.'s*

Cu—O(1)	1·918 (2)	C(1)—C(5)	1·495 (4)
Cu—O(1')	1·912 (2)	C(1')—C(5')	1·501 (4)
Cu—O(2)	1·928 (2)	C(2)—C(6)	1·503 (4)
Cu—O(2')	1·921 (2)	C(2')—C(6')	1·503 (5)
Cu···N(7'ⁱ)	2·468 (3)		
		C(3)—C(4)	1·443 (4)
O(1)—C(1)	1·265 (3)	C(3')—C(4')	1·428 (4)
O(1')—C(1')	1·265 (3)		
O(2)—C(2)	1·259 (3)	N(7)—C(4)	1·136 (4)
O(2')—C(2')	1·261 (3)	N(7')—C(4')	1·146 (4)
C(1)—C(3)	1·418 (4)		
C(1')—C(3')	1·416 (4)		
C(2)—C(3)	1·417 (5)		
C(2')—C(3')	1·414 (4)		

O(1)—Cu—O(1')	174·75 (9)	O(1')—C(1')—C(3')	123·8 (3)
O(1)—Cu—O(2)	92·25 (8)	O(1')—C(1')—C(5')	115·8 (3)
O(1)—Cu—O(2')	87·33 (8)	C(3')—C(1')—C(5')	120·6 (3)
O(1')—Cu—O(2)	87·32 (9)		
O(1')—Cu—O(2')	92·33 (9)	O(2)—C(2)—C(3)	123·9 (3)
O(2)—Cu—O(2')	171·63 (8)	O(2)—C(2)—C(6)	116·2 (3)
O(1)—Cu—N(7')	89·20 (9)	C(3)—C(2)—C(6)	119·9 (3)
O(1')—Cu—N(7')	96·05 (9)	O(2')—C(2')—C(3')	123·6 (3)
O(2)—Cu—N(7')	90·37 (8)	O(2')—C(2')—C(6')	117·0 (3)
O(2')—Cu—N(7')	97·98 (9)	C(3')—C(2')—C(6')	119·3 (3)
Cu—O(1)—C(1)	127·7 (2)	C(1)—C(3)—C(2)	124·5 (2)
Cu—O(1')—C(1')	128·0 (2)	C(1)—C(3)—C(4)	117·2 (3)
Cu—O(2)—C(2)	127·4 (2)	C(2)—C(3)—C(4)	118·3 (3)
Cu—O(2')—C(2')	127·8 (2)	C(1')—C(3')—C(2')	124·5 (2)
		C(1')—C(3')—C(4')	118·4 (3)
O(1)—C(1)—C(3)	123·6 (3)	C(2')—C(3')—C(4')	117·1 (3)
O(1)—C(1)—C(5)	116·1 (3)		
C(3)—C(1)—C(5)	120·3 (3)	N(7)—C(4)—C(3)	179·1 (4)
		N(7')—C(4')—C(3')	177·1 (3)

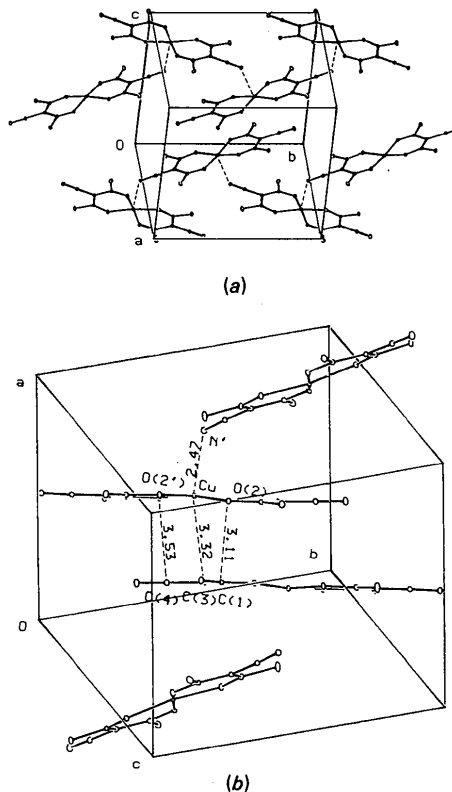Symmetry code: (i) ½−x, ½+y, ½−z; in the text: (ii) 1−x, 1−y, 1−z; (iii) ½−x, −½+y, ½−z.

Fig. 2. (*a*) Zigzag-chain arrangement of the molecules along the *b* axis. (*b*) Plane-to-plane coupling of centrosymmetrically related molecules with selected intermolecular distances (Å).

Table 3. *Selected geometry parameters of 3-substituted-2,4-pentanedione copper complexes, Cu(Racac)₂*

R	Cu—O (Å)	O—Cu—O (°)	O—C (Å)	C—C(3)_endo (Å)	C(3)—C_exo (Å)	Cu···X* (Å)	Reference
Hydrogen	1·912 (4)	93·2 (2)	1·264 (7)	1·371 (9)	—	3·059 (6)	(1)
	1·914 (4)		1·281 (7)	1·400 (8)			
Methyl	1·907 (4)	92·6 (2)	1·284 (7)	1·396 (9)	1·504 (9)	3·216 (7)	(2)
	1·908 (4)		1·285 (7)	1·422 (9)			
Allyl	1·904 (3)	91·76 (12)	1·271 (5)	1·407 (5)	1·518 (6)	3·18	(3)
	1·905 (3)		1·273 (5)	1·411 (5)			
Phenyl	1·902 (8)	91·4 (3)	1·248 (15)	1·438 (14)	1·488 (16)	3·5	(4)
	1·911 (7)		1·263 (14)	1·454 (12)			
Cyano	1·912 (2)	92·25 (8)	1·259 (3)	1·414 (4)	1·428 (2)	2·468 (3)	(5)
	1·918 (2)	92·33 (9)	1·261 (3)	1·416 (4)	1·443 (4)		
	1·921 (2)		1·265 (3)	1·417 (5)			
	1·928 (2)		1·265 (3)	1·418 (4)			

References: (1) Lebrun, Lyon & Kuska (1986); (2) Robertson & Truter (1967); (3) Aruffo, Anderson, Lingafelter & Schomaker (1983); (4) Carmichael, Steinrauf & Belford (1965); (5) this work.

* X = C for references (1)–(4), and N for reference (5).

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^{rii}) 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, β = 99·46 (5)°, V = 1245·1 (4) Å^3, Z = 4, D_x = 2·02 g cm^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 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