Crystal Structure of Tetrabutylammonium Dicyanocuprate(I), $[N(C_4H_9)_4][Cu(CN)_2]$

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Tetrabutylammonium dicyanocuprate(I) is of potential interest for preparative purposes.[1] Higher order mixed organocuprates(I) like $(C_4H_9)_2Cu(CN)Li_2$ have been found[2] to be useful reagents in organic synthesis, butyl but not cyanide being transferred in reactions with organic halides.

The dicyanocuprate(I) ion has a polymeric structure in both the potassium[3] and the sodium[4] compounds. Since the tetrabutylammonium dihalocuprates(I), X=Cl, Br, I, contain discrete monomeric[5] or dimeric[6] anions it was conceivable that tetrabutylammonium dicyanocuprate(I) might also crystallize with discrete anions.

Crystals of $[N(C_4H_9)_4][Cu(CN)_2]$, M_r=358.1, are triclinic, $P\bar{1}$, with a=13.731(13), b=14.680(10), c=12.659(8)Å, α=113.88(5), β=92.52(6), γ=65.04(6)° at 168 K, Z=4, D_c=1.14 g cm^{-3}, μ(Mo$K\alpha$)=10.9 cm^{-1}. The compound was prepared as described previously[1] and recrystallized from acetone yielding colourless prisms. As mentioned previously,[1] tetrabutylammonium dicyanocuprate(I) decomposes readily to give a compound with a higher melting point. Despite the low temperature (168 K) used in the investigation and a protective covering of epoxy resin, the crystals disintegrated within a few days. Several attempts were therefore made to collect a reasonably complete set of intensities.

Intensities from a crystal, 0.16×0.08×0.29 mm, were measured at 168 K for $2\theta \leq 45°$ with a Syntex $P2_1$ diffractometer using graphite-monochromated Mo$K\alpha$ radiation and the ω-scan mode with a scan rate of 1.0–8.0° min^{-1}. A 19-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[7] was used to calculate the intensities.[8] Of the 5472 independent reflections measured, 2635 had $I>3.0\ \sigma(I)$ and were considered to be observed. Correction was made for Lorentz and polarization effects but not for absorption. The unit-cell parameters at 168 K were determined by least squares from diffractometer setting angles for 13 reflections.

The structure was determined from Patterson and successive electron density maps.[9] Solution in $P\bar{1}$ necessitated statistical distribution of the carbon and nitrogen atoms of two of the bridging cyanide groups [CN(1) and CN(2)] over centres of symmetry. Moreover, the butyl chains of one of the two cations in the asymmetric unit [C(17)–C(32)]were poorly defined. Attempts were therefore made to remove the centre of symmetry but these did not reduce R. Intensity statistics[10] were, moreover, consistent with the presence of a centre of symmetry. It thus seemed unlikely that it would be possible to distinguish between alternative ordered models in $P1$ and the disordered model in $P\bar{1}$. Refinement was therefore continued on the basis of the disordered model in $P\bar{1}$, mean scattering factors $(f_C+f_N)/2$ being used for the atoms of all three cyanide bridges, *i.e.* CN(1)–CN(4), since trends in distances favouring designation of CN(3) as carbon and CN(4) as nitrogen were not substantiated by an improved fit to the data. It was not, however, possible to resolve the carbon atoms of the second cation into partially occupied sites. Block-diagonal least-squares refinement of positional and isotropic thermal parameters yielded R=0.130. Inclusion of anisotropic thermal parameters for all atoms (397 parameters; 2635 reflections) led to R=0.081 but also to unrealistically high thermal parameters for some of the carbon atoms of the second cation, indicating compensation for unresolved disorder. Refinement based on partial data sets obtained from other crystals gave essentially the same model. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[11] and F_o values were weighted[12] according to $w=(31.0+F_o+0.009F_o^2)^{-1}$. A final difference map showed a maximum electron density of 1.2 e Å^{-3}. No attempt was made to include hydrogen atoms in the calculations.

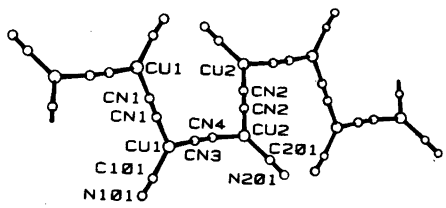

Fig. 1. Part of the $[Cu(CN)_2]^-$ chain showing the atomic numbering. The atoms have been drawn[14] as arbitrary spheres of radius 0.2 Å for copper(I) and 0.15 Å for all other atoms.

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) with estimated standard deviations in parentheses. $B_{eq} = (8\pi^2/3)(U_{11}a^{*2}a^2 + \cdots + U_{23}b^*c^*bc\cos\alpha)$, the anisotropic temperature factor being defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + U_{23}b^*c^*kl)]$.

Atom	x	y	z	B_{eq}
Cu(1)	0.1749(1)	0.0112(1)	0.0563(2)	4.09(4)
Cu(2)	0.1491(1)	0.3091(1)	0.4485(1)	3.95(4)
C(101)	0.3047(10)	–0.1164(11)	–0.0449(12)	4.6(4)
N(101)	0.3732(10)	–0.1930(11)	–0.1100(12)	6.6(4)
C(201)	0.2532(10)	0.2626(9)	0.5460(10)	3.5(3)
N(201)	0.3158(9)	0.2308(8)	0.5981(11)	5.2(3)
CN(1)	0.0414(8)	0.0031(10)	0.0121(12)	5.0(4)
CN(2)	0.0371(10)	0.4569(9)	0.4891(10)	4.9(4)
CN(3)	0.1584(10)	0.1374(10)	0.1983(12)	5.0(4)
CN(4)	0.1500(9)	0.2064(9)	0.2892(11)	4.5(3)
N(1)	0.4699(9)	0.0593(8)	0.7809(9)	4.3(3)
C(1)	0.5307(10)	0.0439(9)	0.6720(10)	3.5(3)
C(2)	0.6428(11)	0.0377(13)	0.6860(15)	6.1(5)
C(3)	0.6880(11)	0.0346(11)	0.5741(14)	5.3(4)
C(4)	0.8098(17)	0.0050(19)	0.5695(19)	9.8(8)
C(5)	0.5317(11)	–0.0325(9)	0.8197(12)	4.4(4)
C(6)	0.5558(11)	–0.1519(9)	0.7245(12)	4.3(4)
C(7)	0.6182(11)	–0.2330(9)	0.7783(12)	4.3(4)
C(8)	0.6490(14)	–0.3542(11)	0.6864(17)	6.9(5)
C(9)	0.4548(13)	0.1649(10)	0.8893(12)	5.8(4)
C(10)	0.3883(18)	0.2714(12)	0.8683(14)	8.7(6)
C(11)	0.3803(18)	0.3725(13)	0.9813(18)	10.0(7)
C(12)	0.4726(16)	0.3860(14)	1.0004(30)	14.1(10)
C(13)	0.3589(11)	0.0649(12)	0.7473(13)	5.0(4)
C(14)	0.2788(14)	0.0861(14)	0.8482(17)	7.6(6)
C(15)	0.1751(14)	0.0755(14)	0.7943(21)	9.1(7)
C(16)	0.1085(16)	0.1766(17)	0.7668(22)	10.1(8)
N(2)	0.8084(8)	0.3799(8)	0.2147(9)	3.8(3)
C(17)	0.7086(20)	0.4790(20)	0.2850(24)	17.9(10)
C(18)	0.6199(14)	0.4982(13)	0.3323(22)	9.5(7)
C(19)	0.5158(18)	0.6024(23)	0.3751(19)	12.1(10)
C(20)	0.4258(21)	0.6351(26)	0.4275(33)	17.1(14)
C(21)	0.7954(15)	0.3298(31)	0.0922(15)	17.2(12)
C(22)	0.8479(18)	0.2782(22)	–0.0026(16)	13.2(9)
C(23)	0.8251(12)	0.2184(12)	–0.1210(12)	5.5(5)
C(24)	0.7739(18)	0.2927(17)	–0.1834(21)	10.1(8)
C(25)	0.8407(16)	0.3015(13)	0.2658(19)	9.7(6)
C(26)	0.8504(18)	0.2993(22)	0.3580(24)	17.2(11)
C(27)	0.8921(14)	0.2030(14)	0.3931(16)	7.8(6)
C(28)	0.9087(17)	0.2449(20)	0.5179(21)	10.4(9)
C(29)	0.8899(14)	0.4217(21)	0.2174(16)	13.3(9)
C(30)	0.9279(14)	0.4597(24)	0.1769(17)	13.5(9)
C(31)	0.9951(16)	0.5087(17)	0.1909(20)	9.4(7)
C(32)	1.0894(21)	0.4728(34)	0.1506(32)	18.5(16)

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1 and interatomic distances and angles within the anion in Table 2. Structure factors, anisotropic thermal parameters and distances and angles within the tetrabutylammonium ions may be obtained from the authors.

As in the potassium [3] and sodium [4] compounds, the dicyanocuprate(I) ion forms a polymeric chain in which each copper(I) atom is coordi-

Table 2. Interatomic distances (Å) and angles (°) within the $[Cu(CN)_2]^-$ ion. Estimated standard deviations are given in parentheses.

Cu(1)–C(101)	1.94(1)	Cu(2)–C(201)	1.93(1)
C(101)–N(101)	1.12(2)	C(201)–N(201)	1.12(2)
Cu(1)–CN(1)	1.93(1)	Cu(2)–CN(2)	1.92(1)
CN(1)–CN(1)	1.20(2)	CN(2)–CN(2)	1.17(2)
Cu(1)–CN(3)	1.92(1)	Cu(2)–CN(4)	1.96(1)
CN(3)–CN(4)	1.16(2)		
C(101)–Cu(1)–CN(1)	113.8(5)	C(201)–Cu(2)–CN(2)	126.0(5)
C(101)–Cu(1)–CN(3)	130.7(5)	C(201)–Cu(2)–CN(4)	122.4(5)
CN(1)–Cu(1)–CN(3)	115.3(5)	CN(2)–Cu(2)–CN(4)	111.6(5)
Cu(1)–C(101)–N(101)	173(1)	Cu(2)–C(201)–N(201)	177(1)
Cu(1)–CN(1)–CN(1)	178(2)	Cu(2)–CN(2)–CN(2)	174(1)
Cu(1)–CN(3)–CN(4)	173(1)	Cu(2)–CN(4)–CN(3)	173(1)

nated by a terminal cyanide group and bridged to neighbouring copper(I) atoms by two other cyanide ligands (Fig. 1). Both copper atoms are surrounded by an approximately trigonal–planar arrangement of ligands, Cu(1) and Cu(2) lying 0.05(1) and 0.02(1) Å, respectively, from the planes defined by the three ligand atoms. These two planes are inclined at an angle of 43° so that in this respect the polymeric $[Cu(CN)_2]^-$ chain in $[N(C_4H_9)_4][Cu(CN)_2]$ is intermediate between the approximately planar chain in $Na[Cu(CN)_2]\cdot 2H_2O$[4] and that spiralling along a two-fold screw axis in $K[Cu(CN)_2]$.[3]

By analogy with $Na[Cu(CN)_2]\cdot 2H_2O$[4] and $K[Cu(CN)_2]$[3] it would seem likely that Cu(1) and Cu(2) are each coordinated by one nitrogen and two carbon atoms. Bond distances and angles are in good general agreement with those in the potassium and sodium compounds,[3,4] but a detailed comparison of the coordination geometry with those of the ordered dicyanocuprates(I) is not pertinent. The Cu(I)–CN distances in $[N(C_4H_9)_4][Cu(CN)_2]$ are, however, in good agreement with those in $Cu_3(NH_3)_3(CN)_4$[13] which crystallizes with disordered cyanide bridges.

The packing of tetrabutylammonium ions and $[Cu(CN)_2]^-$ chains is illustrated[14] in Fig. 2. Whereas bond distances and angles within cation (1) show no unusual features, there are some abnormally short C–C distances (≈1.2 Å) and large C–C–C angles (≈140°) within cation (2). These are undoubtedly artefacts of the inability to resolve this cation into proper sites. The closest distances of approach between cations and the $[Cu(CN)_2]^-$ chains are C(10)···N(201)=3.40(2) Å for cation (1) and C(22)···CN(1)=3.70(3) Å, C(21)···N(101)=

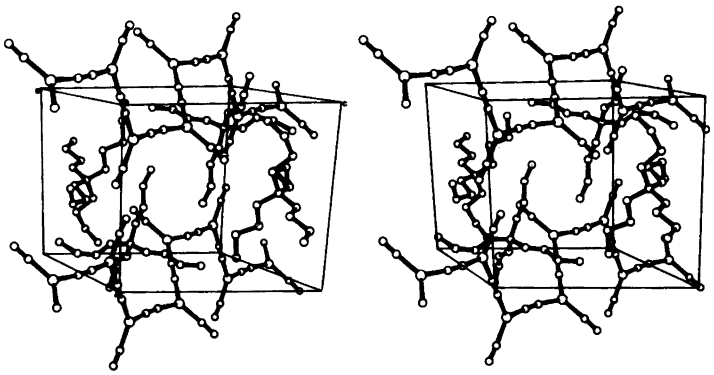

Fig. 2. Stereoscopic view of the unit cell of $[N(C_4H_9)_4][Cu(CN)_2]$. The atoms are depicted as spheres of radius 0.2 Å for copper(I) and 0.15 Å for all other atoms.

3.71(3) Å and C(29)···CN(2)=3.70(2) Å for cation (2).

It would thus seem that whereas the tetrabutylammonium cation stabilizes monomeric or dimeric configurations in the solid state for the dihalocuprates(I), *i.e.* $[CuCl_2]^-$, $[CuBr_2]^-$ and $[Cu_2I_4]^{2-}$, it is not sufficient to prevent the polymerization of $[Cu(CN)_2]^-$.

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