

Structural Relationships among Solvates of Copper Halides. The Structure of Catena-di- μ -iodo-acetonitrile-copper(I) at 200 K

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This investigation is part of a systematic study on structural relationships in solid solvates of Cu(I), Ag(I) and Au(I). The formation of solvates of the type $M_mL_nX_m$, where M is the metal, L the solvent molecule and X a monovalent anion, implies a competition between the solvent molecule and the anion for the coordination sites around M. The solvents selected are aprotic and anoxic ones with nitrogen^{1,2} and sulfur³⁻⁵ as donor atoms. For each solvent, anions with various donor properties are used, from very poor donors, *e.g.* ClO_4^- ,^{1,2} to good ones *e.g.* I^- .^{3,5} This paper reports the structure of $[\text{Cu}(\text{AN})\text{I}]_\infty$ (AN=acetonitrile). When this work was completed the structure of the title compound, determined at room temperature, was reported by Jasinski *et al.*⁶ In the present study, however, a different method of preparation was used, the data refer to 200 K, and another space group was chosen.

$[\text{Cu}(\text{AN})\text{I}]_\infty$ was prepared by treating a copper foil with a solution of I_2 in acetonitrile. After a few hours colourless crystals were formed on the metal. A single crystal with the dimensions $0.28 \times 0.11 \times 0.12$ mm was used for data collection on a CAD4 diffractometer employing monochromatized $\text{MoK}\alpha$ -radiation ($\lambda = 0.7107$ Å). Since the dry crystals lose acetonitrile at room temperature all data were collected at 200 K with the aid of a $\text{N}_2(\text{g})$ -stream device. Laue class and systematic extinctions are consistent with the space groups $P2_1nb$ and $Pmnb$. Unit cell dimensions were obtained from 49 θ -values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$; $a = 4.2827(4)$, $b = 8.765(1)$, $c = 13.520(3)$ Å; $Z = 4$. The intensities of 759 reflections in one octant of the reflection sphere ($3.0 \leq \theta \leq 28.0$) were measured with ω -2 θ scan ($\Delta\omega = 0.9 + 0.5 \tan \theta$). The ratio $\sigma_c(I)/I$ requested in a scan was 0.028 ($\sigma_c(I)$ is based on

Table 1. Atomic coordinates and isotropic thermal parameters with estimated standard deviations. U_{iso} is calculated from the average of the anisotropic temperature factors.

	x	y	z	$U_{\text{iso}}/\text{Å}^2$
Cu	0.2500(0)	0.0904(3)	0.0519(2)	0.0418(8)
I	0.7500(0)	-0.0306(1)	0.1392(1)	0.0327(5)
N	0.2500(0)	0.315(2)	0.079(1)	0.036(4)
C(1)	0.2500(0)	0.442(2)	0.100(2)	0.034(5)
C(2)	0.2500(0)	0.606(2)	0.130(2)	0.045(7)

Table 2. Selected interatomic distances (Å) and angles (°) with estimated standard deviations. (') $\frac{1}{2} + x, -y, -z$.

Cu-I	2.665(2)	I-Cu-I	106.9(1)
Cu-I'	2.637(3)	I-Cu-I'	110.8(1)
Cu-N	2.00(2)	I-Cu-N	108.2(3)
N-C(1)	1.15(2)	I'-Cu-N	111.8(5)
C(1)-C(2)	1.49(3)	Cu-I-Cu'	69.2(1)
		Cu-N-C(1)	176(2)
		N-C(1)-C(2)	179(2)

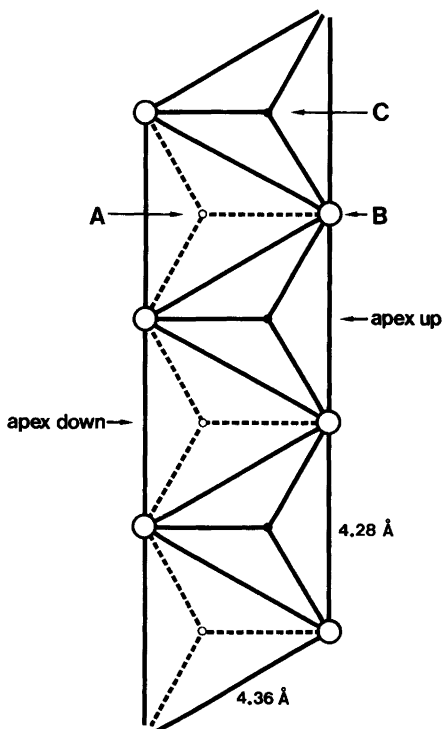


Fig. 1. Schematic view of "the cubic close-packed chain" along the a -axis. Layers A and C consist of N atoms and layer B of I atoms.

counting statistics) and the maximum recording time was 150 s. The variations in three standard reflections were less than 2%. I and $\sigma_c(I)$ were corrected for Lorentz, polarisation and absorption effects ($\mu=104.3 \text{ cm}^{-1}$, transmission factors 0.265–0.394). Only the 597 reflections with $I > 3\sigma_c(I)$ were used in the calculations. The structure was solved by vector and Fourier difference methods. Since intensity statistics gave no conclusive evidence regarding the choice of space group, $P2_1nb$ was chosen arbitrarily. The resulting positional parameters from the least-squares refinement were, however, close to those for a centrosymmetric structure. A refinement in $Pmnb$ converged as smoothly as in $P2_1nb$ and to practically the same R -value, 0.0577 versus 0.0571. Therefore $Pmnb$ was chosen. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = [(\sigma_c^2/4|F_o|)^2 + (0.11|F_o|)^2 + 1.5]^{-1}$. Scattering factors with correction for anomalous dispersion were taken from Ref. 7. Tables of $|F_o|$, $\sigma_c(|F_o|)$ and $|F_c|$ are available on request from the authors. Final positional and thermal parameters are given in Table 1, and selected distances and angles in Table 2. The computer programs used are those compiled and amended by Lundgren.⁸

The positional coordinates obtained in this study are not significantly different from those obtained by Jasinski *et al.*⁶ Each Cu(I) coordinates three I atoms and one AN molecule tetrahedrally. These tetrahedra share edges so that chains running along a are formed (Fig. 1). The linear AN molecule is situated in the yz -plane perpendicular to the elongation of the chain. Between the chains only van der Waals interactions exist. The structure within a chain is closely related to the zinc blende structure adopted by CuI(s).⁹ Each I atom is surrounded by four other I atoms at a distance which is about the same as in CuI(s).⁹ If the I atoms are regarded as belonging to a close-packed layer B, then the nitrogens at the apices pointing down and up (Fig. 1), occupies close-packed positions in layers A and C, respectively. A very important difference between the two structures is, however, that only half of the tetrahedral voids are occupied in CuI, while every tetrahedral void is occupied in $[\text{Cu}(\text{AN})\text{I}]_\infty$. This results in a much shorter Cu–Cu distance in the latter compound (Table 3). Among the isostructural halide compounds $[\text{Cu}(\text{AN})\text{X}]_\infty$, X=Cl,¹⁰ Br,¹¹ I, only

Table 3. Geometric parameters (Å) for CuX, [Cu(AN)X] $_{\infty}$ and [Cu(AN)] $_{4}$ C $_{20}$ H $_{24}$ O $_{6}$; X=Cl, Br or I. CuX has the zinc blende structure, [Cu(AN)X] $_{\infty}$ the "close-packed" chain structure, and [Cu(AN)] $_{4}$ C $_{20}$ H $_{24}$ O $_{6}$ the stella-quadrangula structure. T=center of gravity for a tetrahedral void.

	CuCl	[Cu(AN)Cl] $_{\infty}$	CuBr	[Cu(AN)Br] $_{\infty}$	CuI	[Cu(AN)I] $_{\infty}$	[Cu(AN)] $_{4}$ C $_{20}$ H $_{24}$ O $_{6}$
X-X	3.830	3.81	4.024	4.02	4.279	4.324	4.458
Cu-Cu	3.830	3.04	4.024	3.05	4.279	3.010	2.770
T-T	2.708	—	2.845	—	3.026	—	—
Cu-X	2.345	2.41	2.464	2.51	2.620	2.656	2.692
Cu-N	—	2.00	—	2.00	—	2.00	2.00

$[\text{Cu}(\text{AN})\text{I}]_{\infty}$ has the short Cu–Cu distance expected from the distance between the tetrahedral voids (Table 3). Cu(I) is probably too large to fit into voids formed by close-packed Cl or Br. To achieve van der Waals contact between the halide atoms in these cases Cu(I) is moved out from the halide plane. The average Cu–N distance in $[\text{Cu}(\text{AN})\text{X}]_{\infty}$, 2.00(2) Å, is about the same as observed in $\text{Cu}(\text{AN})_4\text{ClO}_4$, 1.99(2) Å.¹² The Cu–N distance in acetonitrile solvates is thus not sensitive to the nature of the other donor atoms.

Solid halide nitrogen base adducts of the composition CuLX form two types of structures; the chain structure reported here $[\text{CuLX}]_{\infty}$ ($\text{L}=\text{C}_5\text{H}_5\text{CN}$,¹³ $\text{CH}_3(\text{CH})_2\text{CN}$,¹⁴ $\text{C}_5\text{H}_5\text{N}$ ^{15,16}) and a tetrameric structure $[\text{CuLX}]_4$ ($\text{L}=\text{C}_5\text{H}_5\text{N}$,¹⁷ $\text{C}_5\text{H}_{11}\text{N}$ ¹⁸). As has been discussed elsewhere, the tetrameric structure has two limiting forms, viz. the cubane and the stella-quadrangula.³ To judge from the fact that $\text{Cu}(\text{C}_5\text{H}_5\text{N})\text{I}$ crystallizes as a chain at 60 °C and as a stella-quadrangula below 0 °C,^{16,17} the difference in energy between these structures must be small. It is therefore not surprising that it is possible to prepare an AN solvate of CuI which has the stella-quadrangula structure, as is the case with $[\text{Cu}(\text{AN})\text{I}]_4$ dibenzo-18-crown-6.⁶ In this structure the crown ether is situated outside the coordination sphere of Cu(I).

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