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Crystal and Molecular Structure of Tetrameric Copper(I) Iodide–Piperidine, a Complex with a Tetrahedral Cu_4I_4 Core

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The tetrameric complex between copper(I) iodide and piperidine $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$ crystallizes in the centrosymmetric tetragonal space group $P4_2/n$ (No. 86) with $a = 14.7715$ (2) Å, $c = 7.6073$ (2) Å, and $Z = 2$. The x-ray intensity data were measured with an Enraf-Nonius CAD-4 diffractometer complete to $\theta_{\text{max}} = 30^\circ$ (Mo $K\alpha$ radiation). The structure was solved by the 3-dimensional Patterson function and refined by full-matrix least-squares methods to $R = 0.042$ and $R_w = 0.047$ for 1159 independent reflections. The tetrameric molecules are centered on sites of $\bar{4}$ (S_4) symmetry. The compound consists of a tetrahedral Cu_4 cluster with short Cu–Cu distances (2.630 (2) and 2.671 (2) Å) surrounded by a concentric and opposed larger I_4 tetrahedron. The piperidine rings are connected to the clusters by coordination of nitrogen to copper. Adjacent molecules form chains which are probably linked together by means of weak hydrogen bonding between the hydrogen atom attached to nitrogen and an iodide ion in a neighboring cluster.

Introduction

The detailed x-ray crystal structure determination of the tetrameric complex between copper iodide and piperidine, $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$, was undertaken as part of a study of the phenomena of "fluorescence thermochromism",^{1–3} i.e., changing of fluorescence color from room temperature to liquid nitrogen temperature. The necessary precondition for the possibility of "fluorescence thermochromism" in complexes of copper iodide with organic ligands is the presence of an electron-donating bond from a ligand to copper. Unexpectedly the complex with piperidine does not show the phenomena of "fluorescence thermochromism" whereas most of the analogous complexes with other nitrogen bases do.² This unexpected physical property led to the following working hypothesis: A tetrameric complex between copper iodide and nitrogen bases does not show a marked phenomenon of "fluorescence thermochromism" if the point symmetry of its cluster molecule

is at least of fourfold order, i.e., if the Cu–N bond lengths involved are equal by symmetry.⁴ The results of the structure determination are given below and are discussed.

Experimental Section

The compound $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$ was prepared as described in literature.⁵ Suitable crystals for structure determination were obtained by recrystallization from acetonitrile under vacuum. The crystals were transparent, pale yellow needles with a prismatic habit of well-formed $\{100\}$ and $\{110\}$ faces. The measured angles between $\{100\}$ and $\{110\}$ were 45° within the accuracy of the goniometer suggesting a tetragonal crystal system. A needle of rectangular cross section (dominated by the $\{110\}$ form) of 0.064×0.105 mm² was cut to a length of 0.159 mm to give a suitable sample for x-ray diffraction data collection.

The photographic study, using a Cu $K\alpha$ oscillation around the needle axis ($=c$ axis) and Mo $K\alpha$ $hk0$, $hk1$, and hhl precession, revealed $4/m$ (C_{4h}) Laue symmetry for the diffraction pattern and showed the following conditions limiting possible reflections (1) $(hk0)$ $h + k =$

$2n$ and (2) (001) $l = 2n$. The only possible space group is $P4_2/n$ (C_{4h}^4 , No. 86).

The crystal was centered on a CAD-4 diffractometer⁶ and had an arbitrary orientation. For 16 reflections (several forms of (224) $\theta = 11.46^\circ$, (16,0,0) $\theta = 22.60^\circ$, (338) $\theta = 22.75^\circ$, (10,14,0) $\theta = 24.40^\circ$, (668) $\theta = 25.16^\circ$, and (0,18,0) $\theta = 25.61^\circ$) the 2θ , ω , and κ settings of the Mo $K\alpha_1$ peaks (λ 0.709 26 Å) were determined. Orientation and cell parameters were least-squares refined. Resulting cell parameters were $a = 14.7715$ (2) and $c = 7.6073$ (2) Å. The volume of the unit cell is 1659.9 Å³; the measured density by means of the flotation method is 2.204 g cm⁻³ and yielded $Z = 8$ (for mol wt 275.595) to be compared with the calculated density of 2.216 g cm⁻³. In space group $P4_2/n$ therefore a tetrameric molecule (4 times the given molecular weight) is required to lie on an equivalent position of $\bar{4}$ (S_4) equipoint symmetry.

Intensity data up to a maximum θ of 30° of an octant of reciprocal space was measured using a coupled ω ($g \times \theta$) scan⁷ with optimum $g = 2/3$ and $\Delta\omega = a + b \tan \theta$ ($a = 0.5^\circ$, $b = 0.347^\circ$). The detector aperture perpendicular to the plane of diffraction was determined to be 2 mm and within the plane of diffraction to be variable with $\Delta 2\theta = a' + b' \tan \theta$ ($a' = 2.5^\circ$, $b' = 2.11^\circ$) at 173 mm from the crystal. Reflections were prescanned (speed = $1/3 \times 20.1166^\circ \text{ min}^{-1}$), and those which showed an intensity, I , with $\sigma(I) < 0.6I$ were then measured with the scan speed successively reduced so that, for the final scan, one of two conditions should be fulfilled: $\sigma(I) \approx 0.014I$, or time limit = 150 s. The intensities of three standard reflections were measured every 2 h during x-ray exposure time of the sample, in order to monitor decomposition and check misalignment of the crystal. Within the measuring time of 60 h the decomposition was linear and isotropic, but surprisingly made a sudden jump at 42 h and became faster (mean decay until 42 h 4.6%, from 42 h until 42.5 h 4.2%, and from 42.5 h until 60 h 10.0%).

Data reduction was carried out using the Program DARED.⁸ The standard deviation of the intensity, $\sigma(I)$, was calculated from

$$\sigma(I_{\text{net}}) = [I_{\text{total}} + 4(B_{\text{low}} + B_{\text{high}}) + (pI_{\text{net}})^2]^{1/2}$$

with a value of $p = 0.04$. Corrections for linear decomposition (as described above) and for absorption were calculated (linear absorption coefficient $\mu = 64.4 \text{ cm}^{-1}$; transmission factors from 0.687 to 0.755). Any negative I was reset to zero. A total of 1969 independent reflections were available for the following analysis.

Solution and Refinement of the Structure

Programs used in the structural part of this work were as follows: FOUR (a modified version of the Fourier synthesis program of the Oak Ridge system), SBLQ (a much modified version of SFLSQ, by C. T. Prewitt, for structure factor calculations and least squares), ORFFE (calculation of distances, angles, and thermal parameters, with standard deviations based upon inverted least-squares matrix, by W. R. Busing, K. O. Martin, and H. A. Levy), ORABS (calculation of absorption correction for crystals limited by planes, by D. J. Wehe, W. R. Busing, and H. A. Levy), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and CALCA (calculation of atomic positions, by G. J. Kruger and J. M. Stewart).

Scattering factors for uncharged atoms in the range to $(\sin \theta)/\lambda = 0.65 \text{ \AA}^{-1}$ were taken from an approximation with seven coefficients for exponential representation.⁹ The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Reliability factors used are defined as

$$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$R_w = \{ \Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2 \}^{1/2}$$

The iodine and the copper positions were found by interpreting the three-dimensional Patterson function based upon 1106 reflections ($\theta < 20.8^\circ$ and $F_o > 4\sigma(F_o)$). Using the same data set along with unit weights ($w = 1.0$) for an initial least-squares refinement of positional and isotropic thermal parameters for iodine and copper led to convergence after three cycles ($R = 0.133$). Changing to anisotropic thermal parameters, convergence was attained by two additional cycles ($R = 0.113$). At this stage a difference Fourier synthesis revealed the position of all nonhydrogen atoms. Refining two cycles including isotropic and three cycles with anisotropic thermal parameters for the carbon and nitrogen atoms with all 1969 reflections ($\theta < 30^\circ$,

Table I. Crystal Data for $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4$

Crystal system: tetragonal	Space group: $P4_2/n$ (C_{4h}^4 ; No. 86)
$a = 14.7715$ (2) Å	$Z = 2$ (tetramers)
$c = 7.6073$ (2) Å	Density (obsd) = 2.204 (5) g cm ⁻³
$V = 1659.9$ Å ³	Density (calcd) = 2.216 g cm ⁻³
Mol wt = 4×275.60	Absorption coeff, $\mu = 64.4 \text{ cm}^{-1}$

Table II. Final Atomic Coordinates for $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4$ ^a

Atom	x	y	z
I	0.27260 (3)	0.40308 (4)	0.04540 (8)
Cu	0.26406 (7)	0.33791 (7)	0.37601 (15)
N	0.2791 (4)	0.4477 (4)	0.5388 (9)
C(2)	0.2052 (7)	0.5153 (6)	0.5171 (17)
C(3)	0.2115 (7)	0.5941 (6)	0.6436 (17)
C(4)	0.3053 (7)	0.6398 (6)	0.6281 (15)
C(5)	0.3785 (7)	0.5705 (6)	0.6501 (16)
C(6)	0.3684 (7)	0.4921 (6)	0.5280 (15)
H(1)	0.2728	0.4181	0.6607
H(2a)	0.2077	0.5402	0.3900
H(2b)	0.1436	0.4834	0.5324
H(3a)	0.1607	0.6397	0.6182
H(3b)	0.2035	0.5703	0.7694
H(4a)	0.3104	0.6681	0.5023
H(4b)	0.3110	0.6906	0.7169
H(5a)	0.4407	0.6001	0.6302
H(5b)	0.3766	0.5472	0.7780
H(6a)	0.3768	0.5139	0.4011
H(6b)	0.4170	0.4441	0.5545

^a The numbering of piperidine atoms begins at N, the connecting member of the ring; from that, H(1) is attached to N, etc. Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number; they are derived from the inverse of the final least-squares matrix. The parameters of the hydrogen atoms were not subject to refinement.

$F_o > \sigma(F_o)$, and $w = \sigma^{-2}(F_o)$) led to convergence with $R = 0.104$ and $R_w = 0.057$.

The hydrogen positions calculated for tetrahedral coordination (C-H = 1.02 Å) only roughly fit the peak positions of a subsequent difference Fourier synthesis and therefore were not made subject to refinement, but they were introduced with $B(\text{H}) = B(\text{C})$ for structure factor computations.

The restriction on F_o with respect to $\sigma(F_o)$ was raised, but reflections were omitted when (a) they were only prescan measured and (b) their low- and high-angle background counts were grossly different, i.e., when the following condition was met:

$$0.25(B_{\text{low}} - B_{\text{high}})^2 > 5(B_{\text{low}} + B_{\text{high}})$$

After two refinement cycles, convergence was obtained with $R = 0.042$ and $R_w = 0.047$. The largest final parameter shifts were less than $1/30\sigma$, and the "error of fit", defined by $\{ \sum w(|F_o| - |F_c|)^2 / (m - n) \}^{1/2}$, was 1.557 ($m = 1159$ reflections, $n = 73$ parameters). A table of observed and calculated structure factor amplitudes is available. [See paragraph at the end of this article.] Crystal data are presented in Table I, atomic coordinates are given in Table II, anisotropic thermal parameters are collected in Table III, and bond lengths, contacts, and angles are displayed in Table IV.

Discussion

The unit cell contains two tetrameric molecules, $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4$, each of which is centered on a site of crystallographic $\bar{4}$ (S_4) symmetry at $[1/4, 1/4, 1/4]$ and $[3/4, 3/4, 3/4]$, i.e., Wyckoff position a of space group No. 86 with origin fixed at $\bar{1}$. The tetrameric molecules (4 times the asymmetric unit) are separated from each other by van der Waals distances (see section "C—H...H—C contacts" of Table IV) and are possibly connected by hydrogen bonding between an iodide ion and a hydrogen attached to nitrogen in an adjacent molecule along the c axis (see section "hydrogen bond" of Table IV and discussion below).

The geometry of the tetrameric molecule is shown in Figure 1 and could be best described to be built up by an inner tetrahedral Cu_4 cluster surrounded by a concentric and opposed larger I_4 tetrahedron with each I attached to three copper

Table III. Anisotropic Thermal Parameters for $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4^a$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$\langle U_1 \rangle$	$\langle U_2 \rangle$	$\langle U_3 \rangle$
I	522 (4)	474 (3)	417 (3)	9 (3)	28 (3)	122 (3)	0.179 (1)	0.227 (1)	0.241 (1)
Cu	555 (6)	357 (5)	408 (6)	-18 (5)	-21 (5)	-77 (5)	0.173 (2)	0.215 (2)	0.236 (1)
N	48 (4)	35 (3)	45 (4)	-3 (3)	-2 (4)	-8 (3)	0.17 (1)	0.22 (1)	0.22 (1)
C(2)	62 (6)	48 (5)	100 (9)	10 (4)	-26 (6)	-17 (6)	0.21 (2)	0.22 (2)	0.35 (2)
C(3)	73 (6)	42 (5)	89 (8)	6 (4)	2 (7)	-18 (5)	0.19 (2)	0.27 (1)	0.31 (1)
C(4)	88 (7)	37 (5)	69 (6)	-8 (5)	1 (6)	-10 (5)	0.18 (2)	0.27 (1)	0.30 (1)
C(5)	68 (6)	46 (5)	76 (7)	-20 (4)	3 (6)	-18 (5)	0.17 (2)	0.26 (2)	0.30 (1)
C(6)	60 (5)	41 (5)	81 (7)	-6 (4)	16 (6)	-18 (5)	0.18 (2)	0.23 (2)	0.31 (1)

^a The values of U_{ij} for I and Cu are to be multiplied by 10^{-4} ; the rest by 10^{-3} ; the thermal parameters U_{ij} have units of \AA^2 and enter the expression for F_o in the form $\exp \{-2\pi^2(U_{11}h^2a^{*2} + \dots + U_{23}klb^*c^*)\}$. The values $\langle U_i \rangle$ are the root-mean-square amplitudes of vibration (in \AA) along the principal axes of the atomic ellipsoids. For orientations, see Figure 1.

Table IV. Bond Lengths (\AA) and Angles (deg) for $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4^a$

		The Cu_4I_4 Core			
Cu-Cu ²	$2.671 (2) \times 4^b$	Cu ² -Cu-Cu ³	60.51 (3)	I-Cu-I ²	112.00 (4)
Cu-Cu ³	$2.630 (2) \times 2$	Cu ² -Cu-Cu ⁴	58.99 (6)	I-Cu-I ⁴	112.84 (4)
I...I ²	$4.4877 (15) \times 4$	Cu ³ -Cu-Cu ⁴	60.50 (3)	I ² -Cu-I ⁴	115.42 (5)
I...I ³	$4.571 (2) \times 2$	I ² -I ³	59.38 (1)	Cu-I-Cu ²	59.46 (5)
Cu-I	2.6959 (17)	I ² -I ⁴	61.24 (3)	Cu-I-Cu ⁴	59.13 (4)
Cu-I ²	2.6906 (14)	I ³ -I ⁴	58.38 (3)	Cu ² -I-Cu ⁴	58.20 (5)
Cu-I ⁴	2.7173 (15)				
		Copper and the Piperidine Ring			
Cu-N	2.052 (7)	Cu-N-C(2)	112.6 (6)	I-Cu-N	106.0 (2)
		Cu-N-C(6)	114.5 (6)	I ² -Cu-N	105.2 (2)
				I ³ -Cu-N	104.2 (2)
		Torsion			
N-C(2)	1.489 (13)	-54.2 (1.3)	C(2)-N-C(6)	110.5 (0.7)	
N-C(6)	1.476 (12)	52.8 (1.3)	N-C(2)-C(3)	113.6 (1.0)	
C(2)-C(3)	1.513 (17)	55.1 (1.3)	N-C(6)-C(5)	113.6 (0.9)	
C(6)-C(5)	1.493 (16)	-54.5 (1.4)	C(2)-C(3)-C(4)	110.1 (1.0)	
C(3)-C(4)	1.545 (16)	-53.4 (1.4)	C(6)-C(5)-C(4)	112.9 (1.0)	
C(5)-C(4)	1.499 (16)	53.6 (1.4)	C(3)-C(4)-C(5)	109.9 (0.8)	
		Intramolecular Separations, the Hydrogen Bond			
N...I	3.812 (7)			N...I[z + 1]	3.911 (7)
N...I ²	3.786 (7)	H(1)...I ²	3.74	H(1)...I[z + 1]	2.94
N...I ⁴	3.788 (7)	H(1)...I ⁴	3.78	Cu-N-I[z + 1]	117.3 (3)
C(2)...I ²	3.96 (1)	H(2b)...I ²	3.24	H(1)-N-I[z + 1]	15.9
C(6)...I ⁴	3.98 (1)	H(6b)...I ⁴	3.30	H(1)-I[z + 1]-N	5.5
		C-H...H-C Contacts (intermolecular, less than 3 \AA only)			
H(4a)...H(3b) ⁶ [z - 1]	2.55	C(4)...C(3) ⁶ [z - 1]	4.11 (2)		
H(4b)...H(2a) ⁶	2.58	C(4)...C(2) ⁶	4.09 (2)		
H(4b)...H(4a) ⁶	2.82	C(4)...C(4) ⁶	4.59 (1)		
H(5a)...H(2a) ⁶	2.55	C(5)...C(2) ⁶	3.77 (2)		
H(5b)...H(2a) ⁶	2.80				
H(5a)...H(6b) ⁷	2.61	C(5)...C(6) ⁷	4.09 (2)		
H(4b)...H(3a) ³ [y + 1]	2.65	C(4)...C(3) ³ [y + 1]	3.94 (2)		
H(4b)...H(4b) ³ [y + 1]	2.52	C(4)...C(4) ³ [y + 1]	3.34 (2)		

^a For distances and angles involving hydrogen no esd's are given (see comment for Table II). The prime numbers indicate the equivalent atomic positions as used in Figure 3. ^b This distance occurs four times by symmetry.

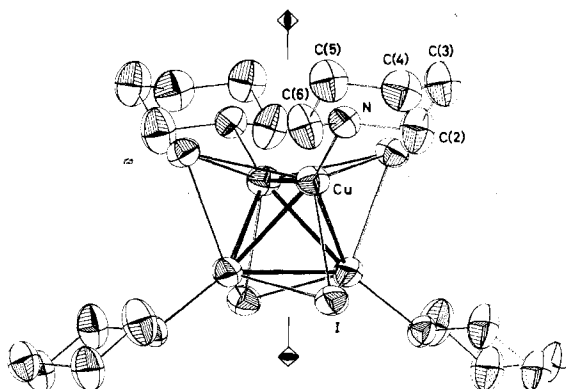


Figure 1. Tetrameric unit of $[\text{CuI} \cdot \text{C}_5\text{H}_{11}\text{N}]_4$ (ORTEP diagram, 50% probability ellipsoids) with $\bar{4}$ (S_4) crystallographic symmetry. The projection is perpendicular to the c axis at 57.6° from the a axis direction.

atoms and each piperidine ring bonded via nitrogen donating its lone pair to one copper atom. The Cu_4I_4 core only slightly deviates from its highest possible $43m$ (T_d) symmetry as originally found in the related cubic structure of $[\text{CuI} \cdot \text{As}(\text{C}_2\text{H}_5)_3]_4$.^{10,11} The Cu_4 cluster is rotated only by $0.68 (5)^\circ$ against the I_4 tetrahedron (around c -axis direction). The copper-copper distances, twice $2.630 (2) \text{\AA}$ and four times $2.671 (2) \text{\AA}$, are short (in metal: $\text{Cu}-\text{Cu} = 2.56 \text{\AA}$) and may be compared with $\text{Cu}-\text{Cu}$ lengths in other complexes with a tetrahedral Cu_4 core: $2.59 (3)$ – $2.71 (3) \text{\AA}$ in $[\text{CuI} \cdot \text{C}_4\text{H}_9\text{N}-\text{O}]_4$,¹² $2.618 (4)$ – $2.723 (4) \text{\AA}$ in $[\text{CuI} \cdot \text{C}_5\text{H}_5\text{N}]_4$,¹³ $2.658 (5)$ – $2.757 (5) \text{\AA}$ in $[\text{CuS}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4$,¹⁴ $2.783 (2) \text{\AA}$ in reinvestigated $[\text{CuI} \cdot \text{As}(\text{C}_2\text{H}_5)_3]_4$.¹⁵ In the class of complexes $[\text{CuX} \cdot \text{P}(\text{C}_2\text{H}_5)_3]_4$,^{15,16} the corresponding values are $2.927 (2) \text{\AA}$ for $\text{X} = \text{I}$, $3.184 (2) \text{\AA}$ for $\text{X} = \text{Br}$, and $3.211 (2) \text{\AA}$ for $\text{X} = \text{Cl}$. The iodine...iodine contacts, twice $4.571 (2) \text{\AA}$ and four times $4.488 (2) \text{\AA}$, are significantly longer than the van der Waals distance of $4.30 (\pm 0.10) \text{\AA}$ ¹⁷ and the values of 4.424

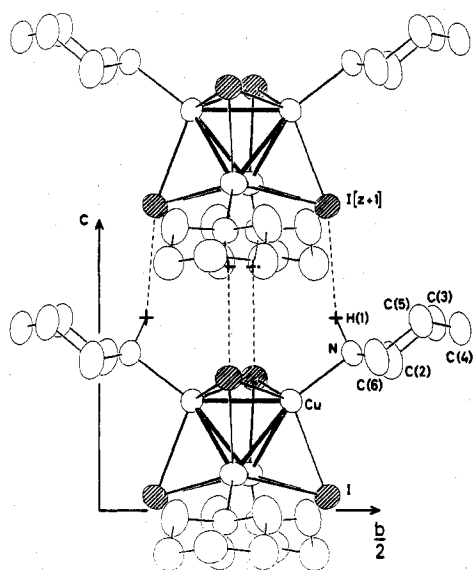


Figure 2. Hydrogen-bonded chain of tetrameric units of $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$ along the c -axis direction (ORTEP diagram, 50% probability ellipsoids). The projection is along the a axis.

(2) and 4.380 (1) Å found in the cubic structures of the arsine and the phosphine complexes,¹⁵ respectively. They are similar to the I...I contacts of 4.347 (4)–4.775 (8) Å and 4.429 (2)–4.576 (3) Å in the complexes with morpholine¹² and pyridine,¹³ respectively. The comparably large widening of the I...I separation in the above mentioned complexes containing nitrogen bases cannot be assumed to be dictated by iodine...iodine repulsions as suggested for the arsine and phosphine complexes.¹⁵ It may be caused by an intermolecular hydrogen bonded coordination of one iodine to one hydrogen attached to nitrogen in an adjacent molecule with a separation of $\text{N}\cdots\text{I}[z+1] = 3.911$ (7) Å to be discussed below.

Comparing the I...I contacts and the Cu—Cu distances within the Cu_4I_4 units considered above, it can be stated that the copper-copper lengths are inversely dependent on the iodine...iodine separations but are not noticeably influenced by the copper-iodine bonds discussed below.

The copper-iodine bond lengths are 2.691 (1), 2.696 (2), and 2.717 (2) Å indicating a nearly exact trigonal surrounding of the copper atom by three iodine ions and vice versa. One nitrogen of a piperidine ring at a distance of 2.052 (7) Å completes the coordination around copper with tetrahedral bond directions. ($\text{ICuI} = 112.00$ (4)–115.42 (5)° and $\text{ICuN} = 104.2$ (2)–106.0 (2)°). The copper-iodine bond distances found are within the range of 2.622–2.785 Å of the above considered complexes with copper iodide.^{12,13,15,16} This suggests that the copper-iodine bond length is almost a constant steric parameter for all these molecules under consideration.

The piperidine ring is chair-shaped as in the related structure of a tetrameric complex between silver iodide and piperidine, $[\text{AgI-C}_5\text{H}_{11}\text{N}]_4$.¹⁸ The tetrahedral coordination angles $\text{C}(2)\text{-N-C}(6) = 110.5$ (7)°, $\text{Cu-N-C}(2) = 112.6$ (6)°, and $\text{Cu-N-C}(6) = 114.5$ (6)° clearly indicate an axial position of the lone pair donated to copper. Another indication for an electron-donating bond between nitrogen and copper is that the distance between these two atoms, 2.052 (7) Å, is equal to the sum of their covalent radii, 2.05 Å. The ring distances and angles lie within the range of their expected values; the somewhat elongated $\text{C}(3)\text{-C}(4)$ distance of 1.545 (16) Å is probably caused by the higher thermal motion at the free end of the ring.

The crystal structure possibly contains hydrogen bonds between iodine and hydrogen attached to nitrogen of an adjacent molecule along the c -axis direction, Figure 2. In-

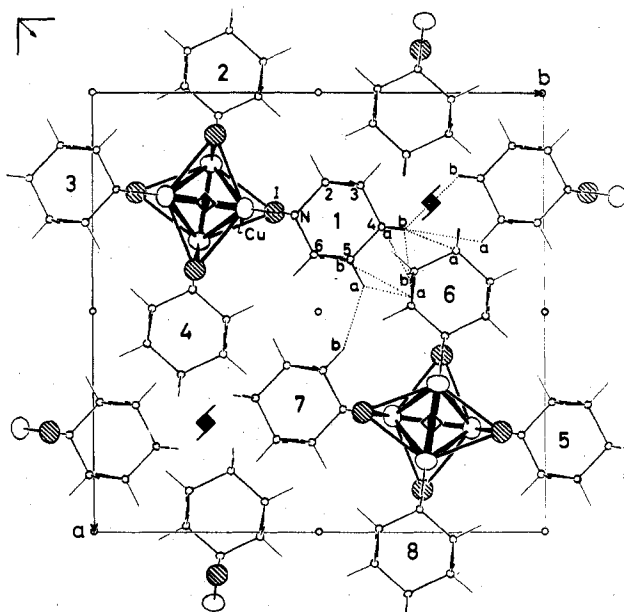


Figure 3. Intermolecular contacts of tetrameric units of $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$ (ORTEP diagram, 50% probability ellipsoids for I and Cu only). The projection is along c . The numbering of asymmetric units corresponds to the following equipoints: (1) x, y, z ; (2) $1/2 - y, x, 1/2 - z$; (3) $1/2 - x, 1/2 - y, z$; (4) $y, 1/2 - x, 1/2 - z$; (5) $1/2 + x, 1/2 + y, 1 - z$; (6) $1 - y, 1/2 + x, 1/2 + z$; (7) $1 - x, 1 - y, 1 - z$; (8) $1/2 + y, 1 - x, 1/2 + z$.

dications for the presence of hydrogen bonding are (1) the angles $\text{Cu-N-I}[z+1] = 117.3$ (3)°, $\text{I}[z+1]\text{-N-H}(1) = 15.9$ °, and $\text{N-I}[z+1]\text{-H}(1) = 5.5$ ° constraining the hydrogen to point toward the iodide ion, (2) the $\text{N}\cdots\text{I}[z+1]$ distance of 3.911 (7) Å being about 0.5 Å shorter than the corresponding van der Waals separation of 4.4 (± 0.10) Å¹⁷ (and comparable with the values of 3.92 (3) and 3.98 (3) Å in the similar built up complex containing morpholine¹²), and (3) the needle shape of the crystals indicating the c axis to be the direction of fastest growth, i.e., the buildup of intermolecular bonding in this direction gives the highest energy gain.

The hydrogen-bonded chains of tetrameric molecules are connected by normal van der Waals forces in directions mainly perpendicular to the c axis. Figure 3 shows these chains in a projection along c and Table IV summarizes the separations involved.

For the interpretation of "fluorescence thermochromism", structural determinations of the following compounds are in progress and will be published later: 3-picolinocopper(I) iodide, 3-ethylpyridinocopper(I) iodide, and pyridinocopper(I) bromide.

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Registry No. $[\text{CuI-C}_5\text{H}_{11}\text{N}]_4$, 65059-18-9.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Insertion Reaction of Carbon Monoxide into M-C Bonds. Synthesis and Structural Characterization of Cobalt(II) and Nickel(II) Acyl Complexes with Tri(tertiary arsines and phosphines)

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Nickel(II) acyl complexes with the general formula $[\text{Ni}(\text{COR})(\text{L})]\text{BPh}_4$ ($\text{L} = \text{tris}(2\text{-diphenylarsinoethyl})\text{amine} (\text{nas}_3)$, $\text{tris}(2\text{-diphenylphosphinoethyl})\text{amine} (\text{np}_3)$; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5$) have been obtained by insertion reactions of carbon monoxide with alkyl compounds of the type $[\text{NiR}(\text{L})]\text{BPh}_4$. The structure of the $[\text{Ni}(\text{COCH}_3)(\text{np}_3)]\text{BPh}_4 \cdot 2.5\text{THF}$ derivative has been determined by an x-ray analysis using diffractometric data. The crystals are triclinic, space group $P\bar{1}$, with $a = 18.168$ (4) Å, $b = 17.537$ (4) Å, $c = 10.789$ (3) Å, $\alpha = 95.62$ (4)°, $\beta = 100.88$ (4)°, $\gamma = 85.80$ (4)°, and $Z = 2$. The structure was refined to a final conventional R factor of 0.094 over the 1208 independent reflections. The structure consists of $[\text{Ni}(\text{COCH}_3)(\text{np}_3)]^+$ cations, of tetraphenylborate anions, and of interposed tetrahydrofuran molecules. The chromophore is a distorted trigonal bipyramid with the acetyl group linked to the nickel in an axial position, the Ni-C distance being 1.97 (6) Å. Some intermediate products of the acyl compounds have also been isolated for the np_3 derivatives. The structure of the intermediate of the methyl derivative has been determined by three-dimensional x-ray data. The crystals are monoclinic, space group $P2_1/n$, with $a = 35.169$ (7) Å, $b = 17.347$ (4) Å, $c = 10.905$ (3) Å, $\beta = 95.15$ (4)°, and $Z = 4$. The structure was refined to a R factor of 0.102. The crystals consist of a solid solution of $[\text{Ni}(\text{CO})(\text{np}_3)]^+$ and $[\text{Ni}(\text{COCH}_3)(\text{np}_3)]^+$, in a ratio of ca. 1:1, of tetraphenylborate anions and of interposed tetrahydrofuran molecules. In these two species having distorted trigonal-bipyramidal geometries, the nickel atom is bonded to the four donor atoms of the ligand np_3 and to the carbon atom of either a carbonyl or an acetyl group, respectively. The results of this analysis allow an hypothesis to be put forward for the mechanism of the insertion of carbon monoxide. Some alkyl and aryl cobalt(I) and cobalt(II) complexes with tetradentate tripod ligands are also reported. The reactivity of these complexes toward carbon monoxide has been studied.

Introduction

Various examples of insertion of carbon monoxide into metal-carbon σ bonds have been reported,¹ but only in a few instances are the mechanisms of such reactions known. In this work we studied the action of carbon monoxide on alkyl complexes of nickel with poly(tertiary arsines and phosphines) with the aim of obtaining the corresponding acyl derivatives, which are, as yet, extremely rare.² In fact, the only acyl complexes of nickel obtained by insertion of carbon monoxide into the M-C bond presently known are square-planar complexes of the type $[\text{Ni}(\text{COCH}_3)\text{X}(\text{P}(\text{CH}_3)_3)_2]^3$ ($\text{X} = \text{Cl}, \text{Br}$).

Several five-coordinate alkyl complexes of the type $[\text{NiR}(\text{L})]\text{BPh}_4$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5$; $\text{L} = \text{tris}(2\text{-diphenylphosphinoethyl})\text{amine} (\text{np}_3)$, $\text{tris}(2\text{-diphenylarsinoethyl})\text{amine} (\text{nas}_3)$) have been described and characterized in a previous study.⁴ By the action of carbon monoxide on these alkyl complexes the corresponding acyl derivatives with the formula $[\text{Ni}(\text{COR})(\text{L})]\text{BPh}_4$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5$; $\text{L} = \text{np}_3, \text{nas}_3$) have been obtained, which have been characterized by the usual physical-chemical techniques. A complete x-ray structural analysis has been carried out on the acetyl

derivative with np_3 . For this ligand, intermediate products have also been isolated; x-ray analysis has revealed that for the methyl derivative the intermediate product is a solid solution of the carbonyl and acetyl compounds. By examination of these compounds we have tried to put forward a hypothesis about the mechanism of the insertion of carbon monoxide into the Ni-C σ bond in these pentacoordinate cationic complexes.

In a way analogous to that for the previously described nickel(II) complexes, cobalt(I) complexes of general formula $[\text{CoR}(\text{L})]$ ($\text{L} = \text{np}_3, \text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) and cobalt(II) of the type $[\text{CoR}(\text{np}_3)]\text{BPh}_4$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$) have been synthesized. By the action of carbon monoxide on the cobalt(II) methyl derivative a complex of formula $[\text{Co}(\text{COCH}_3)(\text{np}_3)]\text{BPh}_4$ has been obtained which is the first acyl cobalt(II) complex so far reported.⁵

Experimental Section

The solvents were dried by standard methods. All the reactions were performed under a nitrogen atmosphere. The alkyl complexes with the formula $[\text{NiR}(\text{L})]\text{BPh}_4$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5$; $\text{L} = \text{np}_3, \text{nas}_3, \text{pp}_3$) were prepared as previously described.⁴

Physical Measurements. Magnetic, conductometric, and spectrophotometric (both visible and infrared) measurements were carried