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Splitting of principal quartets: Cl, 930, 920, 910 Hz; Br, 960, 940, 930 Hz; I, 900, 930, 920 Hz.[18,20]] In the step structure, the two crystallographically independent phosphorus atoms are bonded to three- and four-coordinate copper, respectively. Nevertheless, the splittings for each of the observed quartets are of the same order of magnitude and are, in fact, very similar to those observed for the cubane isomers: Br, (1650, 1930, 2000 Hz; 1440, 1820, 2080 Hz); I, (1350, 1740, 1850 Hz; 1410, 1750, 1820 Hz). These results suggest that the coordination number of the bonded copper atom is not a major factor in determining the magnitude of the quadrupolar splitting of the phosphorus resonance signal. In this context, it is of interest to note the similarity of the Cu–P bond lengths observed for each of these four structures: Cl (cubane), 2.193 (2), 2.192 (2) Å; Br (cubane), 2.209 (3), 2.206 (3) Å; Br (step), 2.194 (4), 2.207 (3) Å; I (step), 2.228 (5), 2.242 (4) Å.

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Registry No. $[CuClPPh_3]_4$ (cubane), 50409-58-0; $[CuBrPPh_3]_4$ (cubane), 92011-27-3; $[CuBrPPh_3]_4$ (step), 50576-71-1; $[CuIPPh_3]_4$ (step), 53432-64-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(19) Healy, P. C.; Klich, H. L.; Pakawatchai, C.; Patrick, V. A.; White, A. H., unpublished data.
(20) Barron, P. F.; Dyason, J. C.; Healy, P. C., unpublished data.

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Lewis Base Adducts of Group 1B Metal(I) Compounds. 9. Synthesis and Crystal Structures of Adducts of Copper(I) Thiocyanate with Substituted Pyridine Bases

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The crystal structures of the title compounds, Cu(SCN)L, L = 2-methylpyridine (**1**), 2,6-dimethylpyridine (**2**), and Cu(SCN)L_2, L = 2-, 3-, and 4-methylpyridine (**3**–**5**, respectively), 2,4-dimethylpyridine (**6**), quinoline (**7**), have been established by single-crystal X-ray diffraction at 295 K and refined by full-matrix least squares to residuals of 0.026, 0.039, 0.048, 0.032, 0.054, 0.058, and 0.029 for 1164, 1339, 1499, 1731, 903, 1748 and 468 independent "observed" reflections, respectively. Crystals of **1** are triclinic, $P\bar{1}$, with $a = 9.452$ (3) Å, $b = 8.077$ (3) Å, $c = 5.779$ (1) Å, $\alpha = 104.33$ (2)°, $\beta = 96.64$ (2)°, $\gamma = 100.83$ (3)°, and $Z = 2$; the structure is a polymer consisting of pairs of CuL(SCN)CuL(SCN) strands linked by centrosymmetric four-membered Cu_2S_2 and eight-membered $Cu(SCN)_2Cu$ rings. Crystals of **2** are monoclinic, $P2_1/c$, with $a = 7.721$ (2) Å, $b = 7.753$ (2) Å, $c = 16.113$ (4) Å, $\beta = 90.67$ (2)°, and $Z = 4$; the structure is a single-stranded polymer—CuL(SCN)CuL(SCN). Crystals of **3** are orthorhombic, $Fdd2$, with $a = 43.68$ (1) Å, $b = 16.402$ (4) Å, $c = 8.064$ (3) Å, and $Z = 16$. Crystals of **4** are monoclinic, $P2_1/n$, with $a = 17.68$ (1) Å, $b = 5.874$ (4) Å, $c = 14.367$ (8) Å, $\beta = 112.91$ (4)°, and $Z = 4$. Crystals of **5** are monoclinic, $P2_1$, with $a = 14.59$ (2) Å, $b = 5.823$ (6) Å, $c = 8.953$ (10) Å, $\beta = 106.44$ (10)°, and $Z = 2$. Crystals of **6** are monoclinic, $P2_1/c$, with $a = 28.93$ (3) Å, $b = 5.867$ (4) Å, $c = 20.19$ (3) Å, $\beta = 112.70$ (8)°, and $Z = 8$. Crystals of **7** are orthorhombic, $P2_12_12_1$, with $a = 16.219$ (4) Å, $b = 12.838$ (3) Å, $c = 8.032$ (2) Å, and $Z = 4$. In spite of the diverse crystal symmetries found for **3**–**7**, all contain single-stranded $CuL_2(SCN)CuL_2(SCN)CuL_2$ polymers, with different conformational types. All complexes were synthesized by reaction of copper(I) thiocyanate with the parent base, with or without the presence of acetonitrile as solvent.

Introduction

In an earlier report,[2] in our series of studies on the nature of adducts formed by the crystallization of group 1B metal(I) halides/pseudohalides from, or in the presence of, nitrogen bases, we have described the isolation and structure determination of the 1:1 adducts of silver(I) thiocyanate with 2- and 3-methylpyridine and 2,6-dimethylpyridine and the 1:2 adduct with quinoline; in all cases recrystallization was carried out from the pure base. Following this study with pyridine bases variously substituted in the 2- and 6-positions, we now turn to consider a similar array of derivatives obtained by the recrystallization of copper(I) thiocyanate from such bases or in the presence of acetonitrile as solvent. With use of 2-, 3-, and 4-methylpyridine, 2,4-dimethylpyridine, and quinoline, crystalline derivatives have been obtained from solutions of copper(I) thiocyanate in the pure base at room temperature, all being found to have 1:2 stoichiometry. With 2-methylpyridine in the presence of acetonitrile as solvent, a 1:1 adduct has also been obtained; a 1:1 adduct has also been obtained by the recrystallization of copper(I) thiocyanate from 2,6-dimethylpyridine. Structure determinations using single-crystal X-ray diffraction techniques have in all cases been carried out on material sealed in capillaries, since the base in complexes of this type is readily lost on exposure to the atmosphere. Abbreviations used are as follows: py, pyridine; quin, quinoline.

Crystallography

Following an initial photographic examination to establish approximate cell dimensions, probable space group (ultimately justified by solution), and the extent of available data, unique data sets were measured within a predetermined $2\theta_{max}$ limit with Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with graphite-monochromated radiation sources ($\lambda_{Mo} = 0.710\,6_9$ Å) in conventional $2\theta/\theta$ scan mode at 295 K. N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after solution of the structure by vector methods. Unless stated otherwise, analytical absorption corrections were applied. Non-hydrogen-atom thermal parameters were refined with an an-

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(1) (a) Griffith University. (b) University of Western Australia.
(2) Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 229.

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Table I. Non-Hydrogen Atom Coordinates for 1

atom	*x*	*y*	*z*
Cu	0.34679 (5)	0.00994 (5)	0.37844 (6)
thiocyanate			
N	0.3266 (3)	−0.0892 (3)	1.0354 (4)
C	0.3438 (3)	−0.1421 (3)	0.8385 (5)
S	0.37094 (9)	−0.21879 (10)	0.55735 (12)
py ligand			
N(1)	0.2701 (2)	0.1930 (3)	0.5972 (4)
C(2)	0.1449 (3)	0.2413 (4)	0.5394 (5)
C(3)	0.1014 (4)	0.3713 (5)	0.7009 (8)
C(4)	0.1830 (4)	0.4525 (5)	0.9236 (8)
C(5)	0.3092 (4)	0.4023 (5)	0.9859 (6)
C(6)	0.3483 (3)	0.2734 (4)	0.8204 (5)
C(21)	0.0565 (4)	0.1453 (7)	0.2935 (8)

Table II. Non-Hydrogen Atom Coordinates for 2

atom	*x*	*y*	*z*
Cu	0.21013 (6)	0.11883 (6)	0.17978 (3)
thiocyanate			
N	−0.0808 (5)	0.5262 (4)	0.2298 (2)
C	0.0084 (5)	0.4583 (5)	0.1843 (3)
S	0.1413 (2)	0.3669 (1)	0.11730 (7)
py ligand			
N(1)	0.4033 (4)	−0.0172 (4)	0.1315 (2)
C(2)	0.3683 (5)	−0.1462 (5)	0.0772 (2)
C(21)	0.1824 (6)	−0.1701 (6)	0.0525 (3)
C(3)	0.4992 (6)	−0.2512 (5)	0.0479 (2)
C(4)	0.6665 (6)	−0.2274 (6)	0.0750 (3)
C(5)	0.7029 (5)	−0.0947 (6)	0.1293 (3)
C(6)	0.5681 (5)	0.0088 (5)	0.1560 (2)
C(61)	0.5995 (6)	0.1556 (7)	0.2147 (3)

isotropic form, with $(x, y, z, U_{iso})_H$ estimated and constrained at idealized values. Residuals at convergence, R, R', are quoted on $|F|$, reflection weights being $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$. Neutral complex scattering factors were used.[3] Computation was with the X-RAY 76 program system[4] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Atom numberings for the present ligand systems are given in the figures.

Specific Crystal Data. Complex 1: Cu(2-Mepy)(SCN) ≡ $C_7H_7CuN_2S$, $Mr = 214.8$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.452$ (3) Å, $b = 8.077$ (3) Å, $c = 5.779$ (1) Å, $\alpha = 104.33$ (2)°, $\beta = 96.64$ (2)°, $\gamma = 100.83$ (3)°, $V = 413.7$ (2) Å^3. $D_{calcd}(Z = 2) = 1.82$ g cm^{-3}, $F(000) = 216$, $\mu_{Mo} = 26.7$ cm^{-1}, specimen 0.40 × 0.10 × 0.06 mm, $A^*_{min} = 1.16$, $A^*_{max} = 1.32$, $2\theta_{max} = 50°$, $N = 1643$, $N_o = 1164$, $R = 0.026$, $R' = 0.034$.

Complex 2: Cu(2,6-Me$_2$py)(SCN) ≡ $C_8H_9CuN_2S$, $M_r = 228.8$, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 7.721$ (2) Å, $b = 7.753$ (2) Å, $c = 16.113$ (4) Å, $\beta = 90.67$ (2)°, $V = 964.5$ (4) Å^3, $D_{calcd}(Z = 4) = 1.58$ g cm^{-3}, $F(000) = 464$, $\mu_{Mo} = 24.9$ cm^{-1}, specimen 0.55 × 0.20 × 0.13 mm, $A^*_{min} = 1.45$, $A^*_{max} = 1.55$, $2\theta_{max} = 50°$, $N = 1830$, $N_o = 1339$, $R = 0.039$, $R' = 0.049$.

Complex 3: Cu(2-Mepy)$_2$(SCN) ≡ $C_{13}H_{14}CuN_3S$, $M_r = 307.9$, orthorhombic, space group $Fdd2$ (C_{2v}^{19}, No. 43), $a = 43.68$ (1) Å, $b = 16.402$ (4) Å, $c = 8.064$ (3) Å, $V = 5777$ (2) Å^3, $D_{calcd}(Z = 16) = 1.42$ g cm^{-3}, $F(000) = 2528$, $\mu_{Mo} = 15.8$ cm^{-1}, specimen irregular ~0.2 mm (no absorption correction), $2\theta_{max} = 60°$, $N = 2195$, $N_o = 1499$, $R = 0.048$, $R' = 0.053$ (preferred chirality).

Complex 4: Cu(3-Mepy)$_2$(SCN) ≡ $C_{13}H_{14}CuN_3S$, $M_r = 307.9$, monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, No. 14), $a = 17.68$ (1) Å, $b = 5.874$ (4) Å, $c = 14.367$(8) Å, $\beta = 112.91$ (4)°, $V = 1374$ (1) Å^3, $D_{calcd}(Z = 4) = 1.49$ g cm^{-3}, $F(000) = 632$, $\mu_{Mo} = 16.2$ cm^{-1}, specimen 0.50 × 0.20 × 0.10 mm, $A^*_{min} = 1.16$, $A^*_{max} = 1.41$, $2\theta_{max} = 45°$, $N = 2161$, $N_o = 1731$, $R = 0.032$, $R' = 0.045$.

Complex 5: Cu(4-Mepy)$_2$(SCN) ≡ $C_{13}H_{14}CuN_3S$, $M_r = 307.9$, monoclinic, space group $P2_1$ (C_2^2, No. 4), $a = 14.59$ (2) Å, $b = 5.823$ (6) Å, $c = 8.953$ (10) Å, $\beta = 106.44$ (10)°, $V = 700$ (1) Å^3, $D_{calcd}(Z = 2) = 1.46$ g cm^{-3}, $F(000) = 316$, $\mu_{Mo} = 16.2$ cm^{-1}, specimen 0.30

Table III. Non-Hydrogen Atom Coordinates for 3–5

	3			4			5		
atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.04524 (1)	0.19580 (4)	0[a]	0.24477 (3)	0.04843 (7)	−0.00658 (3)	0.2207 (1)	0[a]	−0.0119 (2)
thiocyanate									
N	−0.0081 (1)	0.2929 (4)	0.3645 (8)	0.2082 (2)	−0.6338 (5)	−0.0247 (2)	0.2370 (7)	−0.6817 (19)	0.0590 (13)
C	0.0148 (1)	0.2948 (3)	0.2961 (8)	0.1794 (2)	−0.4568 (5)	−0.0399 (2)	0.2479 (7)	−0.4974 (32)	0.1196 (13)
S	0.04844 (3)	0.29948 (10)	0.2002 (3)	0.13413 (5)	−0.20459 (15)	−0.06293 (7)	0.2646 (3)	−0.2533 (6)	0.2122 (4)
ligand a									
N(1)	0.0824 (1)	0.2046 (3)	−0.1527 (7)	0.3134 (2)	−0.0084 (4)	0.1457 (2)	0.0855 (6)	−0.084 (2)	−0.154 (1)
C(2)	0.1119 (2)	0.1858 (4)	−0.1119 (10)	0.3689 (2)	0.1448 (5)	0.2011 (2)	0.0394 (9)	0.045 (3)	−0.273 (2)
C(3)	0.1344 (2)	0.1832 (6)	−0.2302 (13)	0.4144 (2)	0.1257 (6)	0.3037 (2)	−0.0511 (8)	−0.004 (3)	−0.376 (1)
C(4)	0.1276 (2)	0.2014 (8)	−0.3913 (14)	0.3391 (2)	−0.0616 (6)	0.3517 (2)	−0.0959 (9)	−0.200 (2)	−0.357 (1)
C(5)	0.0986 (2)	0.2206 (6)	−0.4329 (11)	0.3423 (2)	−0.2188 (6)	0.2970 (3)	−0.0477 (8)	−0.338 (2)	−0.230 (2)
C(6)	0.0767 (1)	0.2216 (5)	−0.3114 (10)	0.3006 (2)	−0.1896 (6)	0.1952 (2)	0.0414 (9)	−0.282 (2)	−0.132 (1)
C(*n*1)	0.1183 (2)	0.1681 (6)	0.0646 (11)	0.4767 (2)	0.3030 (7)	0.3605 (3)	−0.1951 (9)	−0.263 (3)	−0.463 (1)
ligand b									
N(1)	0.0440 (1)	0.0841 (3)	0.1303 (7)	0.3179 (2)	−0.0053 (5)	−0.0880 (2)	0.3189 (7)	−0.067 (2)	−0.141 (1)
C(2)	0.0422 (2)	0.0128 (4)	0.0466 (8)	0.3785 (2)	0.1384 (6)	−0.0803 (2)	0.3945 (8)	0.056 (2)	−0.129 (1)
C(3)	0.0389 (2)	−0.0600 (4)	0.1312 (12)	0.4291 (2)	0.1199 (6)	−0.1328 (2)	0.4673 (7)	0.002 (3)	−0.196 (1)
C(4)	0.0386 (2)	−0.0616 (4)	0.2979 (11)	0.4130 (2)	−0.0592 (7)	−0.1997 (3)	0.4639 (8)	−0.195 (2)	−0.282 (1)
C(5)	0.0404 (2)	0.0108 (5)	0.3864 (9)	0.3517 (2)	−0.2088 (7)	−0.2096 (3)	0.3849 (9)	−0.331 (2)	−0.297 (2)
C(6)	0.0430 (1)	0.0817 (4)	0.2943 (9)	0.3052 (2)	−0.1781 (6)	−0.1533 (2)	0.3147 (9)	−0.272 (2)	−0.225 (2)
C(*n*1)	0.0440 (2)	0.0170 (4)	−0.1358 (12)	0.4967 (3)	0.2891 (8)	−0.1188 (3)	0.5412 (9)	−0.264 (3)	−0.356 (2)

[a] Defines origin.

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(3) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Brimingham, England, 1974; Vol. 4.

(4) Stewart, J. M., Ed. "The X-RAY System-Version of March, 1976", Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

Table IV. Non-Hydrogen Atom Coordinates for 6

	ligand a			ligand b		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Polymer 1						
Cu	0.39125 (5)	0.4959 (3)	0.28328 (8)			
thiocyanate						
N	0.3751 (3)	−0.1946 (15)	0.2433 (4)			
C	0.3674 (4)	−0.0165 (20)	0.2177 (5)			
S	0.3544 (1)	0.2441 (6)	0.1844 (2)			
ligand						
N(1)	0.3488 (3)	0.4768 (15)	0.3483 (4)	0.4669 (3)	0.4179 (15)	0.3311 (4)
C(2)	0.3531 (4)	0.3085 (18)	0.3937 (5)	0.4994 (4)	0.5338 (19)	0.3869 (5)
C(21)	0.3939 (4)	0.1297 (20)	0.4081 (5)	0.4779 (4)	0.7248 (23)	0.4151 (6)
C(3)	0.3202 (4)	0.2803 (19)	0.4294 (5)	0.5492 (4)	0.4777 (20)	0.4177 (5)
C(4)	0.2825 (4)	0.4374 (18)	0.4181 (5)	0.5690 (4)	0.2949 (19)	0.3939 (5)
C(41)	0.2460 (4)	0.4096 (25)	0.4539 (6)	0.6246 (4)	0.2366 (23)	0.4290 (6)
C(5)	0.2786 (4)	0.6164 (20)	0.3711 (5)	0.5351 (4)	0.1805 (20)	0.3353 (5)
C(6)	0.3118 (4)	0.6272 (18)	0.3376 (5)	0.4855 (4)	0.2469 (20)	0.3061 (5)
Polymer 2						
Cu	0.11787 (5)	0.1091 (2)	0.24123 (8)			
thiocyanate						
N	0.1282 (3)	−0.5796 (16)	0.2769 (4)			
C	0.1341 (4)	−0.3984 (19)	0.3021 (5)			
S	0.1421 (1)	−0.1450 (5)	0.3401 (2)			
ligand						
N(1)	0.0420 (3)	0.0308 (15)	0.1780 (4)	0.1544 (3)	−0.0242 (15)	0.1781 (4)
C(2)	0.0156 (4)	0.1385 (20)	0.1167 (5)	0.2016 (3)	0.0199 (19)	0.1871 (5)
C(21)	0.0425 (5)	0.3251 (23)	0.0918 (6)	0.2287 (4)	0.2110 (22)	0.2350 (6)
C(3)	−0.0338 (4)	0.0828 (21)	0.0736 (6)	0.2257 (3)	−0.1093 (20)	0.1510 (5)
C(4)	−0.0588 (4)	−0.0889 (20)	0.0932 (5)	0.2013 (4)	−0.2857 (20)	0.1061 (6)
C(41)	−0.1119 (4)	−0.1504 (22)	0.0499 (6)	0.2280 (5)	−0.4315 (23)	0.0695 (6)
C(5)	−0.0319 (4)	−0.1943 (20)	0.1572 (6)	0.1531 (4)	−0.3305 (20)	0.0989 (6)
C(6)	0.0170 (4)	−0.1338 (21)	0.1969 (5)	0.1308 (4)	−0.1948 (19)	0.1349 (6)

Table V. Non-Hydrogen Atom Coordinates for 7

	ligand a			ligand b		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.1901 (1)	0.1583 (1)	0.0911 (2)			
thiocyanate						
N	0.2423 (8)	−0.0705 (9)	−0.2553 (16)			
C	0.1984 (10)	−0.0134 (11)	−0.1922 (18)			
S	0.1256 (2)	0.0636 (3)	−0.1125 (5)			
quinoline						
N(1)	0.0975 (6)	0.2205 (6)	0.244 (1)	0.2776 (6)	0.2762 (6)	0.041 (1)
C(2)	0.0953 (6)	0.1946 (8)	0.401 (2)	0.3237 (8)	0.3035 (9)	0.169 (1)
C(3)	0.0349 (8)	0.2279 (11)	0.508 (2)	0.3847 (8)	0.3784 (9)	0.160 (2)
C(4)	−0.0253 (8)	0.2916 (9)	0.458 (2)	0.3984 (8)	0.4323 (10)	0.016 (2)
C(5)	−0.0265 (7)	0.3230 (9)	0.286 (2)	0.3503 (7)	0.4087 (8)	−0.127 (2)
C(6)	−0.0879 (8)	0.3882 (9)	0.224 (2)	0.3614 (9)	0.4592 (10)	−0.282 (2)
C(7)	−0.0827 (8)	0.4163 (9)	0.057 (2)	0.3081 (9)	0.4368 (10)	−0.403 (2)
C(8)	−0.0209 (8)	0.3817 (9)	−0.048 (2)	0.2499 (8)	0.3553 (10)	−0.396 (2)
C(9)	0.0374 (7)	0.3182 (9)	0.015 (2)	0.2400 (8)	0.3060 (8)	−0.248 (2)
C(10)	0.0383 (8)	0.2823 (8)	0.187 (1)	0.2892 (6)	0.3279 (8)	−0.107 (2)

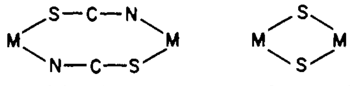
× 0.06 × 0.04 mm, $A^*_{\min} = 1.06$, $A^*_{\max} = 1.11$, $2\theta_{\max} = 50°$, $N = 1418$, $N_o = 903$, $R = 0.054$, $R' = 0.061$ (preferred chirality).

Complex 6: $(Cu(2,4\text{-}Me_2py)_2(SCN))_2 \equiv C_{30}H_{36}Cu_2N_6S_2$, $M_r = 671.9$, monoclinic, space group $P2_1/c$, $a = 28.93$ (3) Å, $b = 5.867$ (4) Å, $c = 20.19$ (3) Å, $\beta = 112.70$ (8)°, $V = 3162$ (5) Å^3, $D_{calcd}(Z = 8) = 1.41$ g cm^{-3}, $F(000) = 1392$, $\mu_{Mo} = 15.5$ cm^{-1}, specimen 0.07 × 0.60 × 0.10 mm, $A^*_{\min} = 1.11$, $A^*_{\max} = 1.19$, $2\theta_{\max} = 40°$, $N = 2924$, $N_o = 1748$, $R = 0.058$ $R' = 0.048$.

Complex 7: $Cu(quin)_2(SCN) \equiv C_{19}H_{14}CuN_3S$, $M_r = 380.0$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 16.219$ (4) Å, $b = 12.838$ (3) Å, $c = 8.032$ (2) Å, $V = 1672.4$ (7) Å^3, $D_{calcd}(Z = 4) = 1.51$ g cm^{-3}, $F(000) = 776$, $\mu_{Mo} = 16.2$ cm^{-1}, specimen 0.20 × 0.10 × 0.05 mm (no absorption correction), $2\theta_{\max} = 40°$, $N = 800$, $N_o = 468$, $R = 0.029$, $R' = 0.027$ (preferred chirality).

Discussion

Previous structural work on copper(I) thiocyanate systems is sparse. Copper(I) thiocyanate itself has recently been shown to exhibit polytypism and has been the subject of two recent studies.[5,6] The $[Cu_2(SCN)_3]_\infty^{\infty-}$ polyanion, as its pyridinium salt, has recently been determined,[7] while the complex $(NH_3)_3Cu^{II}Cu^{I}(SCN)_3$ has also been studied.[8] In the absence of competing ligands, common features of these structures (and, for that matter, many thiocyanate complexes generally) are the presence of eight- and four-membered cyclic units:



As ligand competition increases the MS_2M units are the first to be removed. By inference from other studies,[2] the eight-membered ring units are subsequently lost, leading to M–S–C–N–M single-stranded polymers, which, in turn, ultimately

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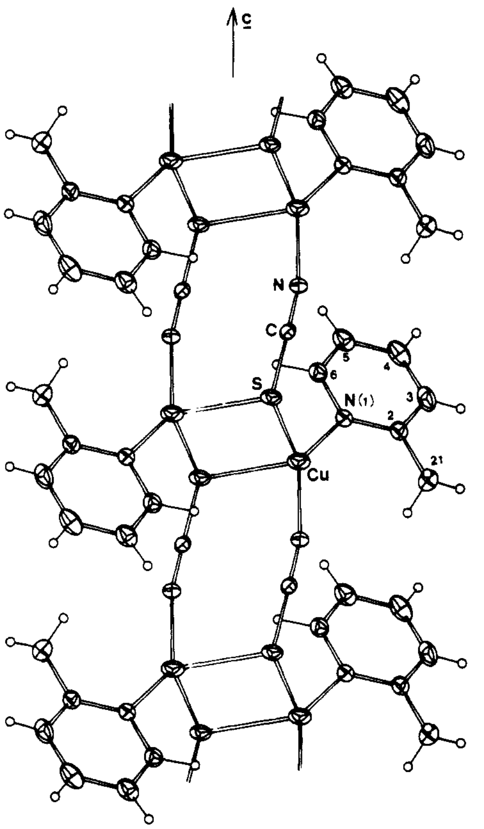

Figure 1. View of the polymer of **1** normal to *c*. Thermal ellipsoids (20% probability) are given for the non-hydrogen atoms, together with atom labeling. Hydrogen atoms have an arbitrary radius of 0.1 Å.

Table VI. Copper Atom Environments of **1-7**[a]

Complex 1

	$r_{\text{Cu-L}}$	N	N(1)	S′
S	2.363 (1)	106.31 (8)	110.46 (8)	106.30 (4)
N	1.918 (2)		136.3 (1)	96.53 (8)
N(1)	2.000 (3)			95.16 (7)
S′	2.806 (1)			

Complex 2

	$r_{\text{Cu-L}}$	N′	N(1)
S	2.232 (1)	122.9 (1)	117.1 (1)
N′	1.915 (4)		119.9 (1)
N(1)	1.993 (3)		

Complex 3

	$r_{\text{Cu-L}}$	N	N(a1)	N(b1)
S	2.349 (2)	111.3 (2)	108.4 (2)	106.7 (1)
N	1.966 (6)		108.4 (2)	109.7 (2)
N(a1)	2.043 (5)			112.5 (2)
N(b1)	2.113 (5)			

Complex 4

	$r_{\text{Cu-L}}$	N	N(a1)	N(b1)
S	2.336 (2)	111.8 (1)	109.3 (1)	109.2 (1)
N	1.959 (3)		108.7 (1)	108.3 (1)
N(a1)	2.074 (3)			109.5 (1)
N(b1)	2.078 (4)			

Complex 5

	$r_{\text{Cu-L}}$	N	N(a1)	N(b1)
S	2.366 (4)	111.0 (3)	109.1 (3)	104.3 (3)
N	1.94 (1)		115.0 (4)	107.7 (5)
N(a1)	2.06 (1)			109.1 (4)
N(b1)	2.08 (1)			

Complex 6

	$r_{\text{Cu-L}}$	N	N(a1)	N(b1)
		Cu(1)		
S	2.380 (4)	105.7 (3)	107.9 (2)	107.7 (3)
N′	1.969 (9)		101.6 (4)	115.8 (4)
N(a1)	2.118 (10)			117.4 (3)
N(b1)	2.074 (8)			
		Cu(2)		
S	2.371 (4)	109.0 (3)	105.8 (3)	102.9 (3)
N′	1.944 (9)		113.7 (3)	122.3 (4)
N(a1)	2.121 (8)			101.6 (3)
N(b1)	2.096 (10)			

Complex 7

	$r_{\text{Cu-L}}$	N	N(a1)	N(b1)
S	2.290 (4)	113.1 (4)	107.1 (3)	123.3 (2)
N	2.00 (1)		104.2 (4)	98.8 (4)
N(a1)	2.10 (1)			108.7 (3)
N(b1)	2.11 (1)			

[a] The first column in each matrix is the metal-ligand distance (Å). Other entries are the angles (deg) subtended at the copper by the relevant atoms at the head of each row and column. Transformations of the thiocyanate nitrogen atom in **2-7**: (2) $\bar{x}$, $y - {}^1/_2$, ${}^1/_2 - z$; (3) $\bar{x}$, ${}^1/_2 - y$, $z - {}^1/_2$; (4) x, $1 + y$, z; (5) x, $1 + y$, z; (6) x, $1 + y$, z; (7) ${}^1/_2 - x$, $\bar{y}$, $z - {}^1/_2$. For **1**, N is at x, y, $z - 1$ and S′ at $1 - x$, $\bar{y}$, $1 - z$.

become M-S-C-N or M-N-C-S with unidentate N- or S-thiocyanato species; these trends are paralleled by a diminution in the sulfur component of the coordination sphere of the metal. It might therefore be anticipated that such trends would be reflected in the compounds which form the basis of the present study and that, in addition, in the absence of strongly sterically hindered ligands, the predominant coordination number of the copper(I) atom should be 4.

In CuSCN,[5] the three Cu-S distances range from 2.344 (2) to 2.367 (2) Å, with Cu-N = 1.927 (6) Å. In $[Cu_2(SCN)_3]_\infty{}^{\infty-}$,[7] the three Cu-S distances are more diverse (2.319 (3)-2.448 (3) Å) about one copper atom, with Cu-N = 1.926 (9) Å, while about the other Cu-S = 2.430 (3), 2.493 (4) Å and Cu-N = 1.935 (9), 1.947 (10) Å. The environment of the Cu^I in $(NH_3)_3Cu^{II}Cu^I(SCN)_3$[8] is similar to that in the latter with two Cu-S distances at 2.376 (8), 2.470 (7) Å and Cu-N at 2.01 (3), 2.00 (2) Å.

The predominance of 1:2 adducts in the present study is in contrast to the adducts of AgSCN with similar nitrogen bases. The silver adducts were predominantly 1:1 derivatives, even from the neat base solution, and only the quinoline adduct existed as a 1:2 complex. However, the present results parallel those previously found in the crystallization of the corresponding metal(I) halides from nitrogen bases,[9-12] suggesting that the 1:2 compounds are readily obtainable generally for Cu(I), whereas they are much less accessible for silver(I).

Complex 1. The structure determination established the stoichiometry to be that of the 1:1 Cu(SCN):2-methylpyridine adduct. Figure 1 displays the structure, showing it to be a one-dimensional polymer along *c*, comprising a pair of -(LCu)(SCN)(LCu)(SCN)- strings, generated by the unit *c* translation and linked by inversion centers so that a system of alternating four-membered $-CuS_2Cu-$ and eight-membered $-Cu(SCN)_2Cu-$ rings of the type discussed above results. About the four-coordinate (2 S, 2 N) copper atom, distances are as expected above, but with one Cu-S distance very long (2.806 (1) Å); this distance is the Cu-S contact bridging the

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Table VII. Thiocyanate Geometries in 1-7

	dist/Å		angles/deg		
compd	C-N	C-S	Cu-S-C	S-C-N	C-N-Cu
1	1.154 (3)	1.657 (3)	103.8 (1)	179.1 (7)	166.7 (2)
2	1.141 (6)	1.657 (4)	102.7 (1)	177.8 (5)	170.4 (4)
3	1.143 (8)	1.661 (6)	103.5 (2)	178.4 (6)	171.5 (6)
4	1.141 (4)	1.655 (3)	103.1 (1)	177.8 (4)	173.4 (3)
5	1.18 (2)	1.61 (2)	100.3 (5)	177 (1)	172 (1)
6	1.15 (1), 1.16 (1)	1.65 (1), 1.65 (1)	105.9 (4), 103.4 (4)	176 (1), 178 (1)	176 (1), 176 (1)
7	1.14 (2)	1.67 (2)	105.4 (6)	173 (1)	168 (1)

Table VIII. Ligand Geometries in 1-5

	1	2	3	4	5
			Distances (Å)		
N-C(2)	1.346 (4)	1.354 (5)	1.364 (8), 1.354 (8)	1.341 (4), 1.334 (5)	1.29 (2), 1.30 (2)
N-C(6)	1.348 (3)	1.343 (5)	1.333 (9), 1.323 (9)	1.346 (5), 1.340 (5)	1.36 (2), 1.39 (2)
C(2)-C(3)	1.381 (5)	1.385 (6)	1.369 (11), 1.382 (10)	1.382 (4), 1.381 (6)	1.40 (2), 1.38 (2)
C(3)-C(4)	1.358 (5)	1.371 (7)	1.366 (15), 1.344 (13)	1.380 (5), 1.378 (5)	1.35 (2), 1.36 (2)
C(4)-C(5)	1.368 (6)	1.378 (7)	1.349 (12), 1.387 (11)	1.366 (5), 1.359 (6)	1.37 (2), 1.37 (2)
C(5)-C(6)	1.367 (5)	1.386 (6)	1.369 (11), 1.386 (11)	1.368 (5), 1.371 (6)	1.37 (2), 1.38 (2)
C(*n*)-C(*n*1)	1.502 (5)	1.497 (6), 1.499 (7)	1.480 (12), 1.475 (12)	1.505 (5), 1.507 (6)	1.52 (2), 1.50 (2)
			Angles (deg)		
Cu-N-C(2)	124.9 (2)	119.9 (3)	126.1 (5), 120.2 (4)	120.7 (2), 120.8 (2)	121.7 (9), 123.8 (9)
Cu-N-C(6)	117.9 (2)	121.1 (2)	116.4 (4), 121.6 (4)	122.3 (2), 122.5 (3)	121.9 (7), 120.2 (9)
C(2)-N-C(6)	117.2 (3)	118.8 (3)	117.1 (6), 118.1 (5)	116.8 (3), 116.6 (4)	116.3 (10), 115.2 (12)
N-C(2)-C(3)	120.9 (3)	120.9 (4)	121.0 (7), 120.4 (7)	124.4 (3), 125.1 (3)	124.7 (14), 125.7 (13)
C(2)-C(3)-C(4)	120.9 (4)	120.1 (4)	120.1 (7), 120.8 (7)	116.9 (3), 116.1 (4)	119.9 (13), 120.2 (13)
C(3)-C(4)-C(5)	118.6 (4)	119.1 (4)	119.4 (8), 119.8 (7)	119.6 (3), 120.4 (4)	115.8 (11), 116.0 (12)
C(4)-C(5)-C(6)	118.6 (3)	118.7 (4)	118.8 (8), 116.6 (7)	120.0 (4), 119.4 (4)	122.1 (12), 121.6 (12)
C(5)-C(6)-N	123.8 (3)	122.3 (4)	123.6 (6), 124.3 (6)	122.2 (3), 122.5 (3)	121.2 (11), 121.2 (12)
C(*n*1)-C(*n*)-N,C(*n* − 1)	116.3 (3)	116.5 (3), 116.4 (3)	117.1 (6), 117.0 (6)	121.4 (3), 121.6 (3)	122.8 (11), 122.7 (11)
C(*n* + 1)-C(*n*)-C(*n*1)	122.7 (3)	122.6 (4), 121.3 (4)	121.9 (7), 122.6 (6)	121.7 (3), 122.3 (4)	121.3 (12), 121.3 (12)

Table IX. Ligand Geometries in 6

	ligand			
	1/a	1/b	2/a	2/b
	Distances (Å)			
N-C(2)	1.32 (1)	1.34 (1)	1.34 (1)	1.33 (1)
N-C(6)	1.34 (1)	1.33 (2)	1.35 (2)	1.33 (1)
C(2)-C(3)	1.41 (2)	1.37 (1)	1.40 (1)	1.41 (2)
C(3)-C(4)	1.38 (2)	1.39 (2)	1.38 (2)	1.38 (2)
C(4)-C(5)	1.39 (2)	1.39 (1)	1.37 (1)	1.37 (2)
C(5)-C(6)	1.38 (2)	1.38 (1)	1.38 (1)	1.39 (2)
C(2)-C(21)	1.52 (2)	1.50 (2)	1.53 (2)	1.49 (2)
C(4)-C(41)	1.50 (2)	1.52 (2)	1.49 (1)	1.52 (2)
	Angles (deg)			
Cu-N-C(2)	123.3 (8)	123.4 (8)	122.9 (8)	125.1 (7)
Cu-N-C(6)	118.9 (7)	120.0 (6)	121.9 (6)	115.4 (8)
C(2)-N-C(6)	117.3 (10)	116.6 (8)	115.2 (8)	118.4 (10)
N-C(2)-C(3)	122.9 (10)	122.2 (11)	123.2 (11)	120.7 (9)
C(2)-C(3)-C(4)	119.0 (10)	122.1 (9)	120.9 (10)	121.0 (10)
C(3)-C(4)-C(5)	118.1 (11)	114.8 (9)	115.4 (9)	117.1 (12)
C(4)-C(5)-C(6)	118.8 (10)	120.2 (11)	120.9 (11)	119.5 (10)
C(5)-C(6)-C(1)	123.9 (10)	124.0 (9)	124.3 (9)	123.3 (10)
N-C(2)-C(21)	120.3 (11)	116.1 (9)	117.5 (9)	119.3 (10)
C(3)-C(2)-C(21)	116.7 (10)	121.7 (9)	119.2 (9)	119.9 (10)
C(3)-C(4)-C(41)	120.4 (10)	121.1 (9)	122.8 (9)	121.0 (11)
C(5)-C(4)-C(41)	121.5 (10)	124.0 (11)	121.7 (11)	121.9 (10)

Table X. Ligand Non-Hydrogen Atom Geometries for 7

	ligand a	ligand b
	Distances (Å)	
N(1)-C(2)	1.30 (2)	1.32 (1)
N(1)-C(10)	1.33 (1)	1.37 (1)
C(2)-C(3)	1.37 (2)	1.38 (2)
C(3)-C(4)	1.34 (2)	1.36 (2)
C(4)-C(5)	1.43 (2)	1.42 (2)
C(5)-C(6)	1.39 (2)	1.42 (2)
C(5)-C(10)	1.42 (2)	1.44 (1)
C(6)-C(7)	1.39 (2)	1.33 (2)
C(7)-C(8)	1.38 (2)	1.41 (2)
C(8)-C(9)	1.35 (2)	1.36 (2)
C(9)-C(10)	1.46 (2)	1.41 (2)
	Angles (deg)	
Cu-N(1)-C(2)	119.3 (7)	114.8 (7)
Cu-N(1)-C(10)	122.8 (8)	127.2 (7)
C(2)-N(1)-C(10)	117.8 (10)	118.0 (9)
N(1)-C(2)-C(3)	123.2 (11)	123.1 (11)
C(2)-C(3)-C(4)	121.2 (12)	121.1 (12)
C(3)-C(4)-C(5)	118.4 (11)	119.0 (11)
C(4)-C(5)-C(6)	121.6 (11)	122.9 (11)
C(4)-C(5)-C(10)	115.1 (10)	116.4 (11)
C(6)-C(5)-C(10)	123.4 (11)	120.7 (11)
C(5)-C(6)-C(7)	117.3 (11)	117.5 (12)
C(6)-C(7)-C(8)	123.1 (11)	124.4 (13)
C(7)-C(8)-C(9)	118.4 (11)	117.3 (12)
C(8)-C(9)-C(10)	123.6 (11)	122.9 (11)
C(9)-C(10)-N(1)	121.5 (11)	121.2 (9)
C(9)-C(10)-C(5)	114.1 (10)	116.4 (11)
N(1)-C(10)-C(5)	124.3 (11)	122.4 (10)

copper atoms of the two strings making up the polymer.

The structure contrasts with that of the silver(I) analogue, in which a two-dimensional polymeric array is observed comprised solely of a repetition of the eight-membered ring motif with the base groups lying to either side of the plane.

Complex 2. The structure determination established the stoichiometry to be that of the 1:1 Cu(SCN):2,6-lutidine adduct. Figure 2 displays the structure, showing it to be a one-dimensional polymer along *b*, generated by the 2_1 screw operation. The copper atom is only three-coordinate and pseudo trigonal planar with an environment in which the three angles all lie close to 120° and whose sum is 359.9°. The individual distances do not differ greatly from their counterparts in **1**, a consequence of the fact that the additional cross-linking sulfur contact in **1** is long; nevertheless, in **1** the comparable angles are appreciably different and their sum is diminished to 353.1°. In **1** and **2** and subsequently also **3–7**, the copper–nitrogen (thiocyanate) distance is shorter than its copper–nitrogen (base) counterpart; although the difference

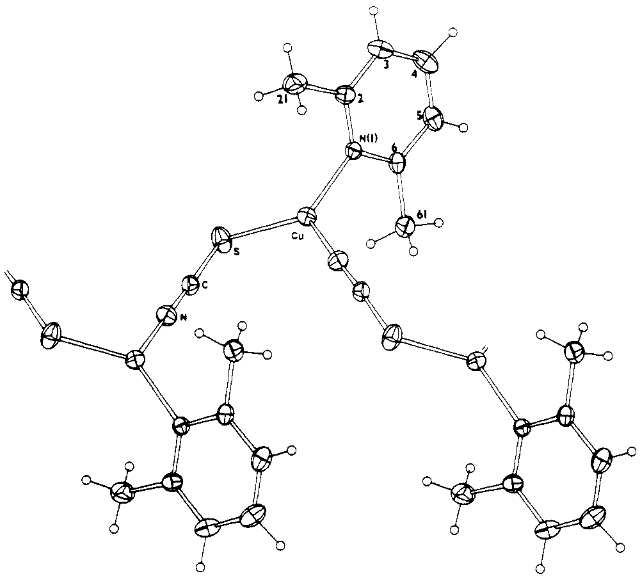
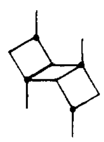


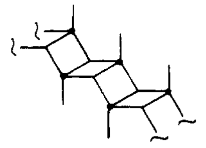
Figure 2. The polymer of **2** viewed normal to *b*.

between these is normally of the order of 0.1 Å, it can vary appreciably, as inspection of **3** will show.

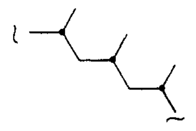
The nature of the polymer is of considerable interest. We have drawn attention elsewhere[11,13] in our studies of the MXL system (M = Cu, Ag(I); X = Cl, Br, I; L = nitrogen base ligand) to the fact that the quite common "stair polymer" type of structure, seemingly the nitrogen base counterpart of the "step" structure observed in the phosphine analogues, may be regarded as an artifact of a parent rock-salt lattice type. In situations where the base becomes very sterically hindered, we have shown[9] that the two strands of the stair polymer may be regarded as separating to give the "split stair polymer". In the present context it is expedient to regard the structure of **1** to correspond to that of an "expanded stair polymer" by virtue of the substitution of ambidentate thiocyanate groups for halide atoms. In the context of a strongly hindered base, as in **2**, we find, by analogy again, that the consequent structure could be described as a "split expanded stair polymer". Unlike the –(CuN)I(CuN)I(CuN)I system in, e.g., the 1:1 copper(I) iodide:collidine (2,4,6-trimethylpyridine)[13] or copper(I) iodide:acridine[9] adducts, however, which is planar, we find that a spiral results, in this case coupled with the crystallographic 2_1 screw operation. In a number of the 2:1 base:CuSCN adducts below, however, a planar (CuN)(SCN)(CuN)(SCN) chain may be observed. Where the bulk of the ligand is greater because of the presence of a 2-substituent (as in **2**), however, this becomes transformed into a spiral. In delineating these models, it is of interest to note the nature of the parent Cu(SCN) structure[5] and also those of derivative polymeric anions.[7] Whereas the above structures may be regarded as derivative of a rock-salt archetype, this archetype corresponds to the structure of the parent *silver* halides (X = Cl, Br (I)) but *not* the copper, which are more generally derivative of four-coordinate metal–ligand systems, corresponding to wurtzite/zinc blende arrays. The parent Cu(SCN)/$Cu_2(SCN)_3^-$, etc. arrays may be conveniently regarded



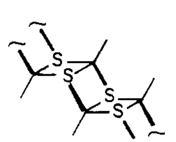
"step structure" (e.g. $[AgI(PPh_3)_4]$[14]



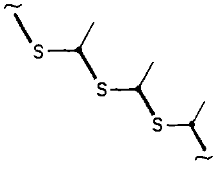
"stair polymer" (e.g. $[AgI(3\text{-mepy})]_\infty$[11])



"split stair polymer" (e.g. $[CuI(2,4,6\text{-Me}_3\text{py})]_\infty$[13], $[CuI(acridine)]_\infty$[9]



(e.g. $[Cu(SCN)(2\ Mepy)]_\infty$)



"split expanded stair polymer" (a) planar (see text) and (b) spiral (e.g. $[Cu(SCN)(3\text{-Mepy})_2]_\infty$ (e.g. $[Cu(SCN)(2,6\text{-Me}_2py)]_\infty$)

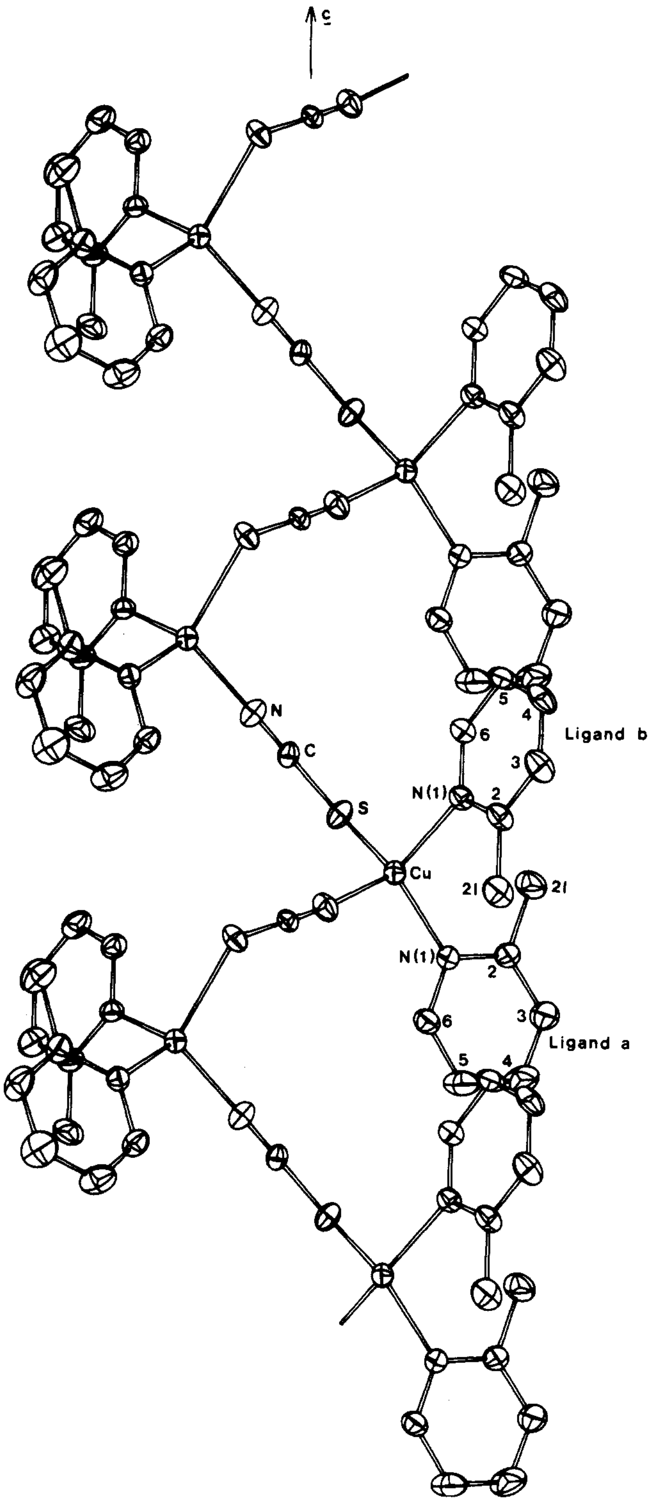


Figure 3. The polymer of **3** viewed along *b*.

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as expanded zinc blende/wurtzite.

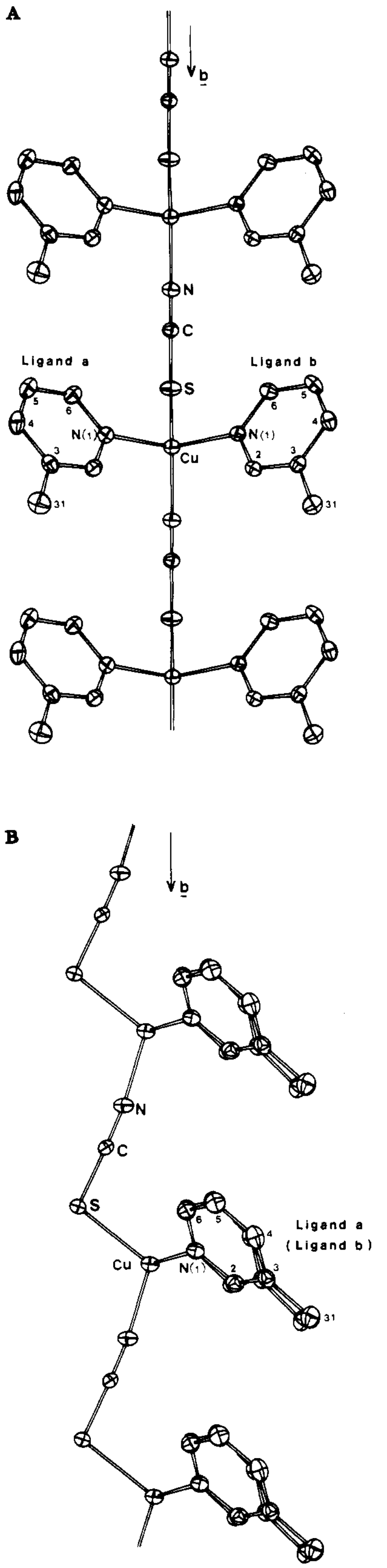

Figure 4. The polymer of **4** viewed normal to *b* and (A) along a line in the Cu/SCN/Cu plane and (B) normal to the Cu/SCN/Cu plane.

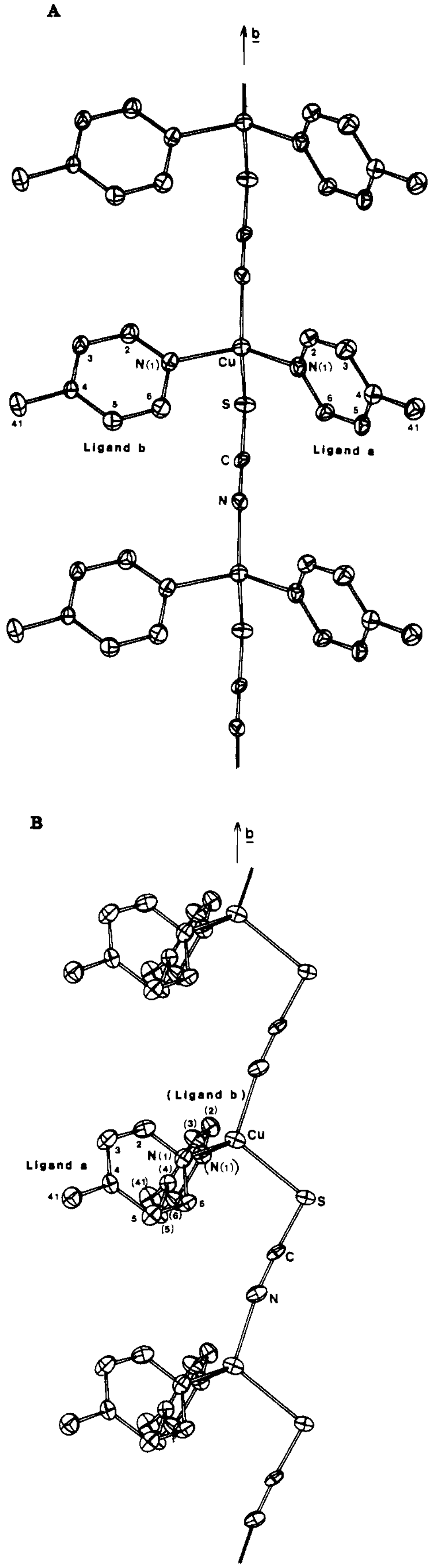

Figure 5. (A, B) The polymer of **5** projected similarly to Figure 4.

Complexes 3–7. In each case the structure determination establishes the stoichiometry to be that of the 1:2 Cu(SCN):pyridine base adduct. In each case, the structure is a single-stranded $-(CuL_2)(SCN)(CuL_2)(SCN)-$ polymer generated by a screw and/or unit translation element of the crystallographic symmetry. Figures 3–5 show the structures of **3**–**5** (**6** being similar to **4** and **5** and **7** isomorphous with its silver(I) analogue[2]) in projection normal to the generating axis. All thiocyanates are ambidentate, and the coordination sphere of each copper atom comprises a sulfur atom and a nitrogen atom from the thiocyanate, together with a pair of base nitrogen atoms. The coordination environment of each copper atom is spacious and, in contrast to the halide analogues,[9–11] the substituents on the pyridine appear to play little role in determining the structural details beyond considerations of crystal packing and polymer conformation, as discussed below. (In **7**, however, it is of interest to note that Cu–S is short (2.290 (4) Å), paralleled by increases in Cu–N(a,b1) to >2.1 Å. Although this may be a consequence of different electronic properties of the quinoline, S–Cu–N(b1) is unusually large and the influence of steric considerations cannot be totally discounted.) Cu–S–C is remarkably constant, with a range of 100.3 (5) (**4**)–105.4 (6)° (**5**). Thiocyanate geometries are as expected, as are those of the pyridine bases. Angular asymmetries at the coordinated nitrogen atoms are found in the cases of **1**, **3**, **6**, and **7**, where the base has a 2-substituent. The structure of **7** is isomorphous with that of its silver(I) analogue, the only 1:2 Ag(SCN):nitrogen base adduct thus far characterized. In the latter Ag–S is 2.495 (4) Å, with Ag–N(SCN) = 2.332 (5) Å and Ag–N(base) = 2.364 (3), 2.361 (3) Å. The metal–sulfur distance has increased by 0.20$_5$ Å on passing from copper(I) to silver(I), while the metal–nitrogen distances have increased by 0.33 Å in the case of the thiocyanate and 0.25 Å in the case of the base nitrogens, indicative of a strengthening of the metal–sulfur bond at the expense of the metal–nitrogen bonds (thiocyanate in particular). This is equivocably supported by the changes in angular geometry: S–Ag–N(thiocyanate, bases) = 119.6 (1), 109.2 (1), 122.3 (1)°; N(thiocyanate)–Ag–N(bases) = 95.9 (1) 98.3 (1)°; N(base–Ag–N(base = 108.0 (1)°. The Ag–S–C value is not significantly different from that in the copper(I) analogue, being 104.4 (1)°, but C–N–Ag, reflecting the increase in Ag–N(SCN), is greatly diminished, to 142.9 (4)°.

The role of the ligand in determining crystal packing and polymer conformation in **3**–**7** is of interest. All polymers are one-dimensional and may be considered as derivative of the "split-stair" polymer found in the 1:1 adduct of CuI with 2,4,6-collidine or acridine.[10] Consideration of the figures shows that in **3** (and **7**)[2] the generating element of the polymer is a 2_1 screw axis, so that the polymer takes on the aspect of a helix or "spiral" with copper atoms at every half-turn and the ligand planes lying quasi-parallel to the generating axis. We note that the base in each case has the common feature of the presence of a 2-substituent in the pyridine ring. By contrast, in **4** and **5**, where this substituent is absent, the polymer takes on a different aspect, having quasi-*m* symmetry in each case with a planar Cu–(SCN)Cu array (σ = 0.003 (**3**), 0.016 Å (**4**)) and the base nitrogen atoms disposed to either side (δN(1a,b): 1.68, −1.71 Å (**3**); −1.56, 1.80 Å (**4**)). The polymer axis in each case is parallel to monoclinic *b*. In the more symmetrical of these complexes, **4**, H(2) and H(6) of each ligand are comfortably disposed relative to the polymer plane (H(2a)···H(2b), N(1 − *y*) 3.220 (**3**), 3.284 Å (**4**); H(6a)···H(6b), C 2.767 (**3**), 2.825 Å (**4**)) a relationship that presumably becomes much more strained with the adoption of a 2-substituent, resulting in the helical conformation. It has been noted elsewhere[11] that the 1:1 adducts of CuCl and CuBr with pyridine result in the stair polymer lying in a $P2_1$ unit cell, while in the case of the iodide analogue the cell volume is doubled as the array passes to $P2_1/c$. It is of interest to note in the present system that a somewhat similar occurrence is found: in **5** the unit cell symmetry is $P2_1$, while in **4**, the cell volume is doubled on passing to $P2_1/c$. **6** is unique in having two similar but independent polymer strings packed pairwise in the structure, resulting in a further cell doubling. The two strands differ in the respect of substituent dispositions. In contradiction of the above tentative classification, **6**, although having a planar spine, also contains a base with a 2-substituent.

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Registry No. **1**, 63610-86-6; **2**, 63610-93-5; **3**, 92126-90-4; **4**, 92126-92-6; **5**, 92126-94-8; **6**, 92126-96-0; **7**, 92126-98-2.

Supplementary Material Available: Listings of structure factor amplitudes, non-hydrogen thermal and hydrogen positional and thermal parameters, and ligand geometries and planes and unit cell projections (61 pages). Ordering information is given on any current masthead page.

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Molecular and Crystal Structure of an Open Cyclamphosphorane Adduct: Cyclamphosphane–Bis(borane)

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The first X-ray structure determination of an "open tautomeric form" derivative of a tetracyclic tetraaminophosphorane, cyclamphosphane–bis(borane), $C_{10}H_{21}N_4P \cdot 2BH_3$ (**5**), is reported. **5** crystallized in the monoclinic space group $P2_1/c$ with a = 12.538 (1) Å, b = 9.835 (1) Å, c = 13.263 (1) Å, β = 114.19 (1)°, and Z = 4. The borane groups are coordinated to the P and N atoms, confirming the NMR data in solution, which pointed to the presence of only one of the two possible diastereoisomers; this has now been identified as **5′**, in which the P–B and N–B bonds are oriented trans to each other with respect to the molecule's mean plane. The P–B bond length (1.858 (5) Å) and N–B bond length (1.619 (6) Å) are in the usual ranges. There is no linear correlation between the sum ($\sum$N) of the bond angles around the three tertiary nitrogen atoms (N1, N2, and N3) and the three corresponding P–N bond lengths. A very short P–N2 bond (1.653 (4) Å) is found, in spite of the distinctly pyramidal geometry of the N2 atom ($\sum$N2 = 341.6 ± 3.0°). The five- and six-membered rings adopt the low-energy "envelope" and "chair" conformations, indicating the absence of noticeable constraints in the polycyclic structure. The results presented in this paper are expected to be relevant to most open tautomeric forms of the tetracyclic tetraaminophosphoranes, whether they are uncomplexed or act as mono- or bidentate ligands toward Lewis acids.

Cyclamphosphorane[2] is known to exist in solution as an equilibrium mixture of the closed phosphorane and the open phosphane tautomers, **1a** (80%) and **1b** (20%), respectively (in toluene). It has recently been shown that under the action