Structure of a Thiolate-Bridged Polymeric Copper(I) Compound, *catena*-(2,9-Dimethyl-1,10-phenanthroline)-μ-(thiophenolato)-copper(I)

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Abstract. $[Cu(C_6H_5S)(C_{14}H_{12}N_2)]$, $M_r = 380.97$, monoclinic, $P2_1$, $a = 10.047$ (1), $b = 15.797$ (2), $c = 10.581$ (1) Å, $\beta = 90.78$ (1)°, $V = 1679.2$ Å^3, $Z = 4$, D_m $(CCl_4/C_5H_{12}) = 1.50$, $D_x = 1.51$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu = 14.2$ cm^{-1}, $F(000) = 784$, $T = 293$ (1) K, $R = 0.026$, $wR = 0.026$ for 2709 observed reflections. The title compound, $[Cu(Me_2\text{-}phen)(C_6H_5S)]_n$, exists as chains of $[Cu(Me_2phen)]^+$ units linked by thiophenolate S atoms. Large bridging angles at thiolate S atoms $[Cu(1)—S—Cu(2)(av.) = 134\ (1)°]$ preclude any Cu—Cu bonding $[Cu\cdots Cu = 4.246\ (1), 4.284\ (1)$ Å] along the chain. The Cu^I atoms exhibit highly distorted tetrahedral coordination, with the largest deviations from tetrahedral stereochemistry involving the N—Cu—N and S—Cu—S angles $[N—Cu—N(av.) = 78.0(2), S—Cu—S(av.) = 126\ (3)°]$.

Introduction. The structural chemistry of systems containing thiolate (RS^-) ligands and copper(I) is surprisingly rich. Thiophenolato complexes of Cu^I, for example, exhibit a variety of structural types, ranging from simple mononuclear species such as $Cu(SR)_2^-$ $(SR^- = 2,3,5,6\text{-tetramethylbenzenethiolate};$ Koch, Fikar, Millar & O'Sullivan, 1984) and $Cu(SPh)_3^{2-}$ (SPh$^-$ = thiophenolate; Coucouvanis, Murphy & Kanodia, 1980; Garner, Nicholson & Clegg, 1984) to clusters exhibiting a variety of structures (Dance, Scudder & Fitzpatrick, 1985).

The presence of other ligands with high affinities for Cu^I further complicates the synthetic and structural picture for copper(I) thiolates. Triphenylphosphine, for example, reacts with polymeric insoluble CuSPh, and both dinuclear (Dance, Guerney, Rae & Scudder, 1983) and tetranuclear (Dance, Scudder & Fitzpatrick, 1985) mixed-ligand products have been obtained.

With the nitrogenous base 1,10-phenanthroline (phen) and *o*-tolylthiolate (S-*o*-tol) ligands, a neutral dinuclear unit also resulted (Chadha, Kumar & Tuck, 1987). In research designed to explore the structural possibilities for thiolate coordination to

Cu^I atoms, we reacted $[Cu(CH_3CN)_4]^+$ with 2,9-dimethyl-1,10-phenanthroline (Me$_2$phen) and the thiophenolate (SPh$^-$) anion. Instead of the expected polynuclear molecular unit, an extended polymeric chain was formed, the structure of which is the subject of this report. A preliminary report has been published (Reibenspies, Anderson, Laird & Brito, 1983).

Experimental. $[Cu(CH_3CN)_4]ClO_4$ prepared by literature methods (Hemmerich & Sigwart, 1963). 2,9-Dimethyl-1,10-phenanthroline (Me$_2$phen), thiophenol (HSPh) purchased from Aldrich Chemical Co., used without further purification. Potassium thiophenolate [K(SPh)] prepared by reaction of KOH and HSPh in ethanol, followed by evaporation of solvent under reduced pressure.

The title compound, $C_{20}H_{17}CuN_2S$, was synthesized as follows. 0.65 g (3.1 mmol) of Me$_2$phen, 0.36 g (1.1 mmol) of $[Cu(CH_3CN)_4](ClO_4)$ dissolved in 30 ml degassed CH$_3$CN under Ar in a Schlenk flask. 2.5 ml freshly prepared 0.39 M K(SPh) solution (absolute ethanol) diluted by addition to 40 ml degassed CH$_3$CN, placed in constant-rate addition funnel, added (several hours) to solution containing Me$_2$phen and copper(I). Small dark-red crystals formed on standing at room temperature.

Data-collection crystal $[0.14\ (100 \rightarrow \overline{1}00) \times 0.27$ $(010 \rightarrow 0\overline{1}0) \times 0.16$ mm $(001 \rightarrow 00\overline{1})]$ obtained by vapor diffusion of HSPh into CH$_3$CN solution containing 1:3:1 molar mixture of Cu^I, Me$_2$phen and triethylamine. Nicolet $R3m$ diffractometer, cell constants from least-squares fitting of angles for 22 reflections $[2\theta(av.) = 19.66°]$. Data collected for $3.5 \leq 2\theta \leq 50°$, $-13 \leq h \leq 13$, $0 \leq k \leq 20$, $0 \leq l \leq 14$, $\theta/2\theta$ scans. Control reflections $(05\overline{1}, \overline{1}81, 206)$ monitored every 100 reflections, no significant variation. Lorentz and polarization corrections, no absorption or extinction corrections; of 3277 measured reflections, 2709 observed $[F_o > 5\sigma(F_o)]$ used in calculations.

Structure solved by direct methods (*RANT*); block-cascade (max. 103 parameters/cycle), weighted $\{w = [\sigma^2(F) + gF^2]^{-1}, g = 8 \times 10^{-5}$ (refined)$\}$ least-

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* [Cu(Me₂phen)(SPh)]ₙ

E.s.d.'s in the least-significant digits are given in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	1·05570 (4)	0·60050	0·39987 (4)	0·0353 (1)
Cu(2)	0·91982 (4)	0·85420 (4)	0·43196 (4)	0·0357 (1)
S(1)	0·92114 (9)	0·70887 (6)	0·46816 (9)	0·0361 (1)
S(2)	1·0225 (1)	0·45550 (6)	0·41827 (9)	0·0352 (3)
N(1)	1·1440 (4)	0·6324 (2)	0·2222 (3)	0·042 (1)
N(2)	1·2563 (3)	0·6190 (2)	0·4517 (3)	0·035 (1)
N(3)	0·7564 (3)	0·8897 (2)	0·3105 (3)	0·034 (1)
N(4)	1·0143 (3)	0·8669 (2)	0·2557 (3)	0·032 (1)
C(1)	0·8505 (3)	0·6832 (2)	0·6159 (3)	0·033 (1)
C(2)	0·7992 (4)	0·7452 (3)	0·6935 (4)	0·041 (1)
C(3)	0·7333 (4)	0·7229 (3)	0·8032 (4)	0·048 (1)
C(4)	0·7204 (4)	0·6405 (3)	0·8390 (4)	0·043 (1)
C(5)	0·7757 (4)	0·5788 (2)	0·7648 (4)	0·044 (1)
C(6)	0·8406 (3)	0·5989 (3)	0·6543 (3)	0·039 (1)
C(7)	0·8658 (4)	0·4272 (2)	0·3523 (3)	0·034 (1)
C(8)	0·7703 (4)	0·4872 (3)	0·3198 (4)	0·047 (1)
C(9)	0·6504 (4)	0·4645 (3)	0·2661 (5)	0·062 (2)
C(10)	0·6201 (4)	0·3813 (3)	0·2422 (4)	0·052 (2)
C(11)	0·7137 (4)	0·3202 (3)	0·2751 (4)	0·046 (1)
C(12)	0·8348 (4)	0·3421 (3)	0·3296 (3)	0·041 (1)
C(13)	1·0855 (6)	0·6420 (3)	0·1089 (4)	0·061 (2)
C(14)	1·1613 (8)	0·6599 (3)	0·0019 (5)	0·084 (3)
C(15)	1·2927 (8)	0·6703 (4)	0·0104 (5)	0·091 (3)
C(16)	1·3583 (6)	0·6650 (3)	0·1282 (5)	0·069 (2)
C(17)	1·4961 (7)	0·6840 (4)	0·1502 (7)	0·091 (3)
C(18)	1·5517 (6)	0·6810 (3)	0·2671 (7)	0·087 (3)
C(19)	1·4740 (4)	0·6565 (3)	0·3740 (5)	0·059 (2)
C(20)	1·5238 (5)	0·6511 (3)	0·4965 (7)	0·079 (2)
C(21)	1·4425 (5)	0·6317 (3)	0·5917 (5)	0·066 (2)
C(22)	1·3073 (4)	0·6160 (2)	0·5683 (4)	0·044 (1)
C(23)	1·3368 (4)	0·6384 (2)	0·3552 (4)	0·040 (1)
C(24)	1·2778 (4)	0·6440 (3)	0·2312 (4)	0·043 (1)
C(25)	0·9395 (5)	0·6338 (4)	0·1025 (5)	0·088 (2)
C(26)	1·2110 (4)	0·5975 (3)	0·6697 (3)	0·051 (1)
C(27)	0·6301 (4)	0·9068 (3)	0·3408 (4)	0·044 (1)
C(28)	0·5370 (4)	0·9355 (3)	0·2486 (5)	0·056 (2)
C(29)	0·5730 (4)	0·9440 (3)	0·1268 (4)	0·059 (2)
C(30)	0·7034 (4)	0·9262 (3)	0·0906 (4)	0·047 (1)
C(31)	0·7518 (5)	0·9358 (3)	−0·0351 (4)	0·057 (2)
C(32)	0·8797 (5)	0·9217 (3)	−0·0630 (4)	0·056 (2)
C(33)	0·9741 (4)	0·8984 (3)	0·0340 (4)	0·044 (1)
C(34)	1·1098 (5)	0·8861 (3)	0·0121 (4)	0·053 (2)
C(35)	1·1939 (4)	0·8646 (3)	0·1104 (4)	0·049 (1)
C(36)	1·1428 (4)	0·8563 (3)	0·2326 (3)	0·037 (1)
C(37)	0·9305 (4)	0·8870 (2)	0·1576 (4)	0·037 (1)
C(38)	0·7929 (4)	0·9004 (2)	0·1871 (4)	0·037 (1)
C(39)	0·5929 (4)	0·8967 (3)	0·4752 (4)	0·056 (2)
C(40)	1·2290 (4)	0·8383 (3)	0·3442 (4)	0·045 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* [Cu(Me₂phen)(SPh)]ₙ

E.s.d.'s in the least-significant digits are given in parentheses.

Cu(1)—S(1)	2·304 (1)	Cu(1)—S(2)	2·323 (1)
Cu(1)—N(1)	2·150 (3)	Cu(1)—N(2)	2·102 (3)
Cu(2)—S(1)	2·328 (1)	Cu(2)—N(3)	2·146 (3)
Cu(2)—N(4)	2·114 (3)	Cu(2)—S(2')	2·320 (1)
S(1)—C(1)	1·773 (4)	S(2)—C(7)	1·771 (4)
N(1)—C(13)	1·336 (5)	N(1)—C(24)	1·359 (6)
N(2)—C(22)	1·331 (5)	N(2)—C(23)	1·347 (5)
N(3)—C(27)	1·341 (5)	N(3)—C(38)	1·372 (5)
N(4)—C(36)	1·328 (5)	N(4)—C(37)	1·365 (5)

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S(1)—Cu(1)—S(2)	128·4 (1)	S(1)—Cu(1)—N(1)	110·5 (1)
S(1)—Cu(1)—N(2)	112·3 (1)	S(2)—Cu(1)—N(1)	111·5 (1)
S(2)—Cu(1)—N(2)	104·7 (1)	N(1)—Cu(1)—N(2)	77·9 (1)
S(1)—Cu(2)—S(2')	124·6 (1)	S(1)—Cu(2)—N(3)	111·0 (1)
S(1)—Cu(2)—N(4)	103·7 (1)	N(3)—Cu(2)—N(4)	78·2 (1)
S(2')—Cu(2)—N(3)	114·3 (1)	S(2')—Cu(2)—N(4)	115·2 (1)
Cu(1)—S(1)—Cu(2)	133·1 (1)	Cu(1)—S(1)—C(1)	110·5 (1)
Cu(2)—S(1)—C(1)	111·7 (1)	Cu(1)—S(2)—C(7)	110·1 (1)
Cu(1)—S(2)—Cu(2')	134·6 (1)	Cu(2')—S(2)—C(7)	107·9 (1)
Cu(1)—N(1)—C(13)	129·0 (3)	Cu(1)—N(1)—C(24)	112·9 (2)
C(13)—N(1)—C(24)	118·1 (4)	Cu(1)—N(2)—C(22)	126·4 (2)
Cu(1)—N(2)—C(23)	114·7 (2)	C(22)—N(2)—C(23)	118·9 (3)
Cu(2)—N(3)—C(27)	128·9 (3)	Cu(2)—N(3)—C(38)	113·0 (2)
C(27)—N(3)—C(38)	118·0 (3)	Cu(2)—N(4)—C(36)	126·8 (2)
Cu(2)—N(4)—C(37)	114·4 (2)	C(36)—N(4)—C(37)	118·8 (3)
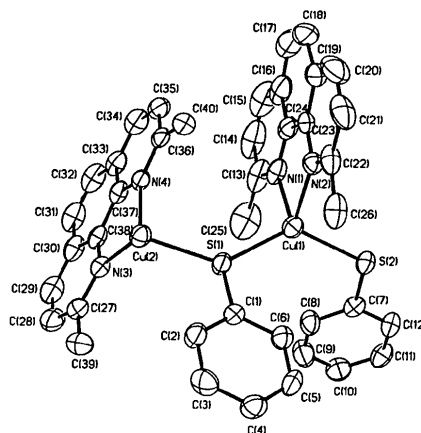
Fig. 1. A thermal ellipsoid plot (50% probability) depicting the arrangement and numbering scheme for the atoms of the asymmetric unit of [Cu(Me₂phen)(SPh)]ₙ.

squares refinement (444 parameters, data/parameters = 6·1) on F; all non-H atoms refined anisotropically, H atoms in calculated positions [$U(\text{H}) = 1\cdot2U_{iso}(\text{C})$]. At convergence {mean $\Delta/\sigma = 0\cdot028$, max. $\Delta/\sigma = 0\cdot247$ [rotation of methyl group C(25) about C(13)—C(25) bond] over last five cycles}, $R = 0\cdot026$, $wR = 0\cdot026$, $S = 1\cdot37$, slope of normal probability plot = 1·19, max. $\Delta\rho = 0\cdot27$ [1·16 Å from Cu(2)], min. $\Delta\rho = -0\cdot19$ e Å^{-3}. Neutral-atom scattering factors, with anomalous-dispersion corrections, from *International Tables for X-ray Crystallography* (1974); software for diffractometer provided with Nicolet *R3m*; *SHELXTL* programs (Sheldrick, 1983) used for structure solution, refinement and plotting.

Discussion. The structure and numbering scheme within a single asymmetric unit of the title com-

pound, [Cu(Me₂phen)(SPh)]ₙ, are depicted in Fig. 1. Final atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are given in Table 1, while selected bond lengths and angles are listed in Table 2.*

Neutral polynuclear molecular units, such as the dinuclear [Cu(phen)(S-*o*-tol)]₂ (Chadha, Kumar & Tuck, 1987), are not found in the title compound, despite similar formulation. Instead, [Cu(Me₂-

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phen)]$^+$ units are linked by SPh$^-$ ions into long-chain thiolate-bridged metallopolymers in the solid state (see Fig. 2, which shows a portion of one such chain). The Cu_2S_2 elements of the chain (Fig. 1) are related by the action of the crystallographic twofold screw axis.

Similar long-chain polymers involving the $[Cu(Me_2phen)]^+$ unit have been found in $[Cu(Me_2-phen)(CN)]_n$ and $[Cu(Me_2phen)(NCS)]_n$ (Morpurgo, Dessy & Fares, 1984), in which the bridging between $[Cu(Me_2phen)]^+$ units is accomplished by ambidentate cyano and thoicyanato ligands, respectively. In both of those compounds, as well as in $[Cu(Me_2-phen)_2](ClO_4)$ (Dessy & Fares, 1978), the restricted 'bite' of the bidentate Me_2phen ligand manifests itself in small N—Cu—N angles, very similar to the values [N—Cu—N(av.) = 78·0 (2)°] observed here for $[Cu(Me_2phen)(SPh)]_n$.

Despite the small N—Cu—N angles, the coordination geometry about copper(I) in $[Cu(Me_2-phen)(SPh)]_n$ is best described as tetrahedral, though significant distortions are clearly present. While S—Cu—N angles cluster about the ideal tetrahedral value [S—Cu—N(av.) = 110 (4)°], the S—Cu—S angles are much more open [S(1)—Cu(1)—S(2) = 128·4 (1)°, S(1)—Cu(2)—S(2') = 124·6 (1)°] than would be expected for tetrahedral coordination. These large S—Cu—S angles are not simply a consequence of the restricted bite of the Me_2phen ligand, since in $[Cu(Me_2phen)(CN)]_n$ and $[Cu(Me_2phen)-(NCS)]_n$ the interbridge angles at Cu^I were only 111·9 (5) and 103·7 (2)°, respectively. The S atoms do not appear to make significant contacts along the chain [S(1)···S(2) = 4·165 (1), S(1)···S(2') = 4·114 (1) Å], and thus repulsive S···S interactions are not likely to be the cause of the open S—Cu—S angles. Contacts between N and S atoms, which would be expected to close the S—Cu—S angles, are also not significant [e.g. S(1)···N(av.) = 3·63 (9) Å]. It is possible that the packing of the phenyl groups of the SPh$^-$ ligands and the fused aromatic rings of the Me_2phen ligands lead to the open S—Cu—S angles observed here, but specific causative interactions of this type are difficult to pinpoint.
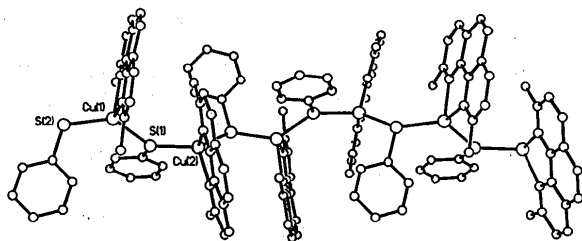

Fig. 2. A plot showing the extended polymeric nature of $[Cu(Me_2-phen)(SPh)]_n$. The linked contents of three asymmetric units are depicted; the 2_1 axis relates each pair of Cu^I atoms and associated ligands to the next.

In the dinuclear complex $[Cu(phen)(S-o-tol)]_2$, Cu—Cu bonding draws the Cu^I atoms close together [Cu···Cu = 2·613 (3) Å] and makes the Cu—S—Cu angles acute [Cu(1)—S—Cu(2) = 68·1 (1), 67·8 (1)°]. The absence of any such Cu···Cu bonding interactions in $[Cu(Me_2phen)(SPh)]_n$ [Cu···Cu = 4·246 (1), 4·284 (1) Å] allows the Cu—S—Cu angles at the S atom to be much more open [Cu(1)—S(1)—Cu(2) = 133·1 (1), Cu(1)—S(2)—Cu(2') = 134·6 (1)°].

Bond lengths between Cu^I and ligand atoms such as N and thiolate S are strongly dependent on all the usual factors – coordination number, coordination geometry, and the type(s) of other ligands present – and may also depend on the counterion. For example, Cu—S bond lengths in the trigonal planar anion $[Cu(SPh)_3]^{2-}$ range from 2·274 (4) to 2·335 (4) Å in the tetraphenylphosphonium salt (Coucouvanis, Murphy & Kanodia, 1980), but are distinctly shorter [2·239 (2) to 2·258 (2) Å] in the tetraethylammonium salt. The Cu—S distances in $[Cu(Me_2phen)(SPh)]_n$ fall within a narrow range [Cu—S(av.) = 2·32 (1) Å] at the upper end of the distribution of Cu—S distances seen in $[Cu(SPh)_3]^{2-}$, and are comparable in length to the Cu—S distances in $[Cu(phen)(S-o-tol)]_2$ [Cu—S = 2·304 (4) to 2·379 (5) Å].

The Cu—N distances in $[Cu(Me_2phen)(SPh)]_n$ [Cu—N(av.) = 2·13 (2) Å] are distinctly longer than those in $[Cu(Me_2phen)_2]^+$ [Cu—N = 2·053 (6) Å] and $[Cu(Me_2phen)(NCS)]_n$ [Cu—N(av.) = 2·077 (1) Å], but quite similar to the Cu—N distances in $[Cu(phen)(S-o-tol)]_2$ [Cu—N(av.) = 2·10 (3) Å] and $[Cu(Me_2phen)(CN)]_n$ [Cu—N(av.) = 2·126 (7) Å].

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Structures of Four- and Five-Carbon Alkyldiammonium Tetrachlorocuprate(II) and Tetrabromocuprate(II) Salts

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Abstract. 1,4-Butanediammonium tetrabromocuprate(II), $C_4H_{14}N_2^{2+}.CuBr_4^{2-}$, $M_r = 473$, monoclinic, $P2_1/a$, $a = 7.914$ (2), $b = 7.887$ (4), $c = 9.432$ (2) Å, $\beta = 102.83$ (2)°, $V = 574$ Å^3, $Z = 2$, $D_x = 2.74$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 157$ cm^{-1}, $T = 293$ K, $F(000) = 442$, 1259 unique reflections, of which 1192 with $F \geq 3\sigma(F)$ were refined to a final $R = 0.0439$ for the 3σ data set with empirical extinction corrections ($wR = 0.0541$). The following structures used reflections with $F \geq 6\sigma(F)$. 1,4-Butanediammonium tetrachlorocuprate(II), $C_4H_{14}N_2^{2+}.CuCl_4^{2-}$, $M_r = 296$, monoclinic, $P2_1/a$, $a = 7.588$ (1), $b = 7.599$ (1), $c = 9.268$ (1) Å, $\beta = 103.14$ (1)°, $V = 520$ Å^3, $Z = 2$, $D_x = 1.88$ g cm^{-3}, Mo $K\alpha$, $\mu = 31.7$ cm^{-1}, $F(000) = 298$, 1184 unique reflections, 786 of 805 for the 6σ data set after discarding twin overlaps were refined to a final $R = 0.0652$ ($wR = 0.0861$). 1,5-Pentanediammonium tetrabromocuprate(II), $C_5H_{16}N_2^{2+}.CuBr_4^{2-}$, $M_r = 487$, monoclinic, $P2_1/n$, $a = 8.142$ (3), $b = 7.560$ (2), $c = 21.736$ (10) Å, $\beta = 101.49$ (3)°, $V = 1311$ Å^3, $Z = 4$, $D_x = 2.47$ g cm^{-3}, Mo $K\alpha$, $\mu = 146$ cm^{-1}, $F(000) = 916$, 3527 unique reflections, 995 of 1030 for the 6σ data set were refined to a final $R = 0.0734$ ($wR = 0.0948$). 1,5-Pentanediammonium tetrachlorocuprate(II), $C_5H_{16}N_2^{2+}.CuCl_4^{2-}$, $M_r = 308$, monoclinic, $P2_1/n$, $a = 7.747$ (3), $b = 7.203$ (2), $c = 21.761$ (6) Å, $\beta = 102.12$ (2)°, $V = 1188$ Å^3, $Z = 4$, $D_x = 1.73$ g cm^{-3}, Mo $K\alpha$, $\mu = 27.5$ cm^{-1}, $F(000) = 628$, 2842 unique reflections, 501 of 530 for the 6σ data set were refined to a final $R = 0.0925$ ($wR = 0.1096$). Each Cu^{II} ion has two short and two long (semi-coordinate) bonds to halide ions forming sheets puckered from the *ab* plane plus two short bonds to halide ions axial to the sheets, completing a tetragonally elongated octahedral coordination. Adjacent sheets have axial halide ions in an eclipsed conformation. The diammonium ions provide links between sheets, hydrogen bonding to the halides. The C$_4$ salts have the two ends of the diammonium ions equivalent by symmetry with C$_4$ chains *trans* around the central bond and *gauche* for N *versus* C positioning around each terminal C—C bond. The hydrogen bonds include one to an axial halide, arranged *gauche* to the N—C—C alignment, and two to sheet halides, one *gauche* and one *trans* to the N—C—C alignment. The C$_5$ chains are *trans* at both of the C—C—C—C sites, one N—C—C—C site is *trans* and one *gauche*, and both N atoms have two hydrogen bonds to axial halides and one to a sheet halide. The C$_5$ chains have about a 90° different direction of approach at the two ends.

Introduction. The monoammonium alkylammonium salts of copper(II) tetrahalides, $(C_nH_{2n+1}NH_3)_2CuX_4$, form puckered antiferrodistortive layer perovskite structures with adjacent layers staggered which give strong ferromagnetic interactions in the copper-halogen sheet layer and weak magnetic interactions between layers (Willett, 1964; Steadman & Willett, 1970; Barendrecht & Shenk, 1970; de Jongh & van Amstel, 1971; de Jongh, van Amstel & Miedema, 1972; Drumheller, Dickey, Reckliss, Zaspel & Glass, 1972; Zaspel & Drumheller, 1977; Wong, Willett & Drumheller, 1981). The structures contain layers of square-planar CuX_4^{2-} anions. In each anion, two Cu—X bonds are involved in bridges to adjacent