

Fig. 1. Molecular structure of [Co{(-)-spartein}(NCS)<sub>2</sub>] with 50% probability thermal ellipsoids for those atoms for which anisotropic vibration parameters were refined.

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## Structure of Bis(methylenedithio)tetrathiafulvalene Dicyanoargentate(I)

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**Abstract.** [C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>][Ag(CN)<sub>2</sub>], *M<sub>r</sub>* = 516.54, orthorhombic, *Pmnm*, *a* = 8.794 (3), *b* = 20.333 (7), *c* = 4.247 (2) Å, *V* = 759.27 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.261 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, *F*(000) = 506, μ(Mo *Kα*) = 23.63 cm<sup>-1</sup>, 614 observed room-temperature reflections, *R* = 0.023. The charge-transfer salt consists of C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> cations (hereafter MT) and ribbons of infinite [Ag(CN)<sub>2</sub>] anions with both the MT molecule and the Ag atoms on inversion centers. Ribbon distances are 2.103 (5) Å Ag—C, 3.305 (5) Å Ag—N, and 1.021 (7) Å C—N bonds; MT intramolecular distances are 1.407 (8) and 1.354 (5) Å C=C, 1.723 (3), 1.728 (2), 1.745 (3) and 1.816 (2) Å C—S and 2.942 (1), 2.972 (1), 3.075 (1) and 3.220 (1) Å S—S separations, typical of expected values for singly charged ions; near-neighbor contacts between ions involve 3.340 (1) Å Ag—S and 3.649 (1) to 3.678 (1) Å S—S separations.

**Introduction.** Various charge-transfer salts derived from bis(alkyldithio)tetrathiafulvalene have been shown to attain metallic and superconducting states at low temperature (Williams, Beno, Wang, Leung,

Enge, Geiser & Carlson, 1985). This is believed to result from the interstack interactions between the organic salt ions and has motivated the preparation of various salts to characterize better the structural properties responsible for such conductivity. Because of the highly symmetrical structure of MT, such interstack interactions might be strongly affected. This note reports on the structural details of MT·Ag(CN)<sub>2</sub>.

**Experimental.** Single crystals of MT·Ag(CN)<sub>2</sub> were obtained by electrochemical oxidation at a platinum electrode in a 1 mM [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][Ag(CN)<sub>2</sub>] solution with that of a corresponding dilute solution (1.3 mM) of MT in chlorobenzene using a current density of 0.4 A cm<sup>-2</sup>. Only the single form crystallized in contrast to the observed various forms and hydrates found for the ethylene analog of bis(methylenedithio)tetrathiafulvalene (Kurmo, Pritchard, Talham, Day, Stringer & Howard, 1990).

Tiny black needle-shaped crystals were obtained which proved to be of orthorhombic symmetry using precession photography. Systematic absences for

reflections of the type  $h0l$  for  $h+l$  odd and of the type  $hk0$  for  $h+k$  odd determine the space group to be  $Pm\bar{3}n$  or  $P2_1n$ . Lattice constants were determined using the 24 strong reflections between  $25$  and  $30^\circ 2\theta$  preselected to cover the entire diffracting sphere as  $a = 8.794$  (3),  $b = 20.333$  (7) and  $c = 4.247$  (2) Å. The data crystal selected was in size  $0.04 \times 0.08 \times 0.12$  mm and mounted along the longest direction. Intensity data to  $2\theta$  limit of  $50^\circ$  were measured for two quadrants ( $\pm 11, 25, 6$ ) for 1643 reflections on a Nicolet automated diffractometer using monochromatized  $\text{Mo } K\alpha$  radiation and a scintillation counter. Scan range was  $1.0^\circ$  below  $2\theta$  ( $K\alpha_1$ ) to  $1.0^\circ$  above  $2\theta$  ( $K\alpha_2$ ) with scan speed varying from  $0.5$  to  $29^\circ \text{ min}^{-1}$  depending on the intensity. Three standard reflections ( $0\bar{2}0, \bar{1}03, \bar{1}04$ ) were monitored every 100 reflections and showed no sign of crystal deterioration with time (values ranged  $\pm 5\%$  from mean values). The data were corrected for Lorentz and polarization effects. Absorption corrections were not necessary for the intensity measurements because of the small crystal size with  $\mu(\text{Mo } K\alpha) = 23.63 \text{ cm}^{-1}$ .

The distribution of intensities suggested that the structure was centrosymmetric; hence, the symmetry equivalent sets were averaged ( $R = 0.018$ ). Of 686 unique observed reflections, 614 were greater than  $3\sigma$ . The structure was determined by Fourier methods with the H positions obtained from a difference synthesis and all atoms except H eventually refined using anisotropic thermal parameters. Weights of the form  $1/[\sigma^2(F) + gF^2]$  were used where the standard deviations,  $\sigma^2(F)$ , were calculated from counting statistics. Least-squares refinement was carried out on  $F$  with the 62 parameters (max.  $\Delta/\sigma = 0.002$ ) yielding  $R = 0.023$  and  $wR = 0.021$  for all 686 reflections. A final difference Fourier synthesis indicates the largest peak to be  $0.5 \text{ e } \text{Å}^{-3}$  located at the center of the MT ion (center of C—C bond). Atomic coordinates are given in Table 1.\* Atomic scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were carried out with the updated Nicolet *SHELX76* software (Sheldrick, 1976).

**Discussion.** The  $\text{MT}^+$  and  $\text{Ag}(\text{CN})_2^-$  ions both lie at inversion centers on mirror planes. Thus the MT group is defined by two S and three C atoms as indicated in Fig. 1 on which the corresponding intramolecular bond lengths and angles are given. These

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54915 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0531]

Table 1. Final least-squares positional parameters and equivalent isotropic thermal parameters

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
Ag	0	0	0	0.0449 (2)
S(1)	0.16724 (6)	0.43394 (3)	0.2908 (2)	0.0292 (2)
S(2)	0.16898 (7)	0.30612 (3)	-0.0961 (2)	0.0296 (2)
C(1)	0	0.4712 (2)	0.4082 (10)	0.026 (1)
C(2)	0.0769 (3)	0.37010 (11)	0.1005 (7)	0.024 (1)
C(3)	0	0.2550 (2)	-0.0771 (13)	0.034 (1)
C(4)	0	0.0802 (2)	0.3130 (12)	0.036 (1)
N	0	0.1186 (2)	0.4677 (13)	0.057 (2)
H(1)	0	0.225 (2)	-0.26 (1)	0.05 (1)
H(2)	0	0.231 (2)	0.13 (1)	0.06 (2)

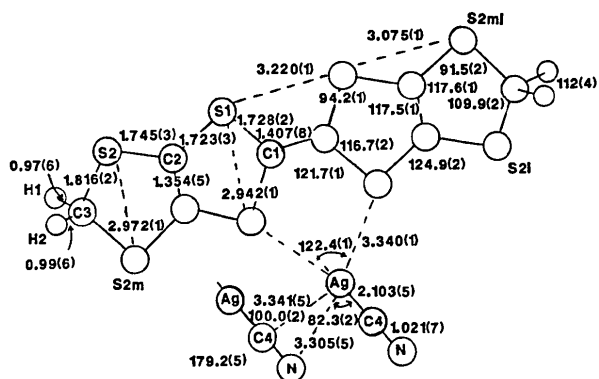


Fig. 1. Bond lengths (Å) and angles ( $^\circ$ ) in  $\text{MT-AG}(\text{CN})_2$ . Both the cation and the anion are located on inversion centers and mirrors as indicated by labeling on S2.

separations are consistent with other published structure results as well as with extended Hückel molecular orbital calculations (Kato, Kobayashi, Mori, Kobayashi & Sasaki, 1985) for such donor molecules/ions. As one changes the formal charge on such donor ions, small differences in the bond lengths are expected, with the C—C bond becoming longer while the C—S bond becomes shorter. This is because the character of the highest occupied molecular orbital is bonding on C—C bonds and antibonding on C—S bonds. Thus, 1.407 (8) and 1.354 (5) Å C=C bonds may be compared with 1.33 and 1.31 Å, respectively, and 1.728 (2) and 1.723 (3) Å C—S bonds with 1.76 and 1.75 Å, respectively, for the neutral donor values (Kato, Kobayashi, Sasaki & Kobayashi, 1984; hereafter KKSK, 1984).

The  $\text{MT}^+$  monocation is in a chair configuration due to its site symmetry and may best be considered in three parts with least-squares planes through atoms composing these parts. The angle between the plane formed by S(1), C(1), and their inversion and mirror related atoms and the plane formed by S(1), C(2), S(2) and corresponding mirror related atoms, S(1m), S(2m) and C(2m), is  $1.1(2)^\circ$  while that between the latter plane and the methylene group,

S(2), C(3) and S(2m), is  $37.6(2)^\circ$ . Such angles between least-squares planes do not appear to show trends with respect to formal charge and are probably due to packing forces. (For example, see Nigrey, Duesler, Wang & Williams, 1987; Nigrey, Morosin, Kwak, Venturini, Schirber & Baughman, 1986; KSKS, 1984.)

Ribbons of  $[\text{Ag}(\text{CN})_2]_\infty$  are formed by direct 2.103 (5) Å bonds to two  $\text{CN}^-$  ions as well as by more distant interactions with neighboring  $\text{CN}^-$  groups at about 3.3 Å. From the angles formed (Fig. 1) the interaction appears to be to the C—N bond rather than to either the C or N of the group. The  $\text{Ag}(\text{CN})_2$  are essentially linear considering the estimated error of the angle. The nearest contacts normal to the ribbons involve Ag and S, with each Ag having four S(1) atoms at 3.340 (1) Å, significantly shorter than the 3.57 Å van der Waals sum; these S contacts and the bond to C(4) form C(4)—Ag—S(1) angles of 81.7 (1) and 98.3 (1)°.

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## Structure of Bis(*n*-butylammonium) Tetrachlorocadmate(II)

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**Abstract.**  $2\text{C}_4\text{H}_{12}\text{N}^+\cdot\text{CdCl}_4^{2-}$ ,  $M_r = 402.52$ , orthorhombic, *Abma*,  $Z = 4$ . At 295 K,  $a = 7.538$  (1),  $b = 7.416$  (3),  $c = 30.803$  (4) Å,  $V = 1722$  (1) Å<sup>3</sup>,  $D_x = 1.55$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.85$  mm<sup>-1</sup>,  $F(000) = 808$ ,  $R = 0.045$  for 1211 independent reflections with 46 refined parameters. This lamellar phase is similar to the  $\delta$  phase observed in parent compounds, with a tilting of the  $\text{CdCl}_6$  octahedra favouring one specific hydrogen bond to the ammonium end of the aliphatic chains. No simple model can convincingly explain the disorder affecting the chains, in contrast with the analogous manganese compound [Depmeier & Chapuis (1979). *Acta Cryst.* B35, 1081–1084]. The separation of successive aliphatic layers is probably too large for a modulated phase to occur. Phase transitions are observed around 200 K, at which temperature monocrystals are damaged.

**Introduction.** The family  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$  (hereafter *C<sub>n</sub>M*) has been the subject of many studies during the last 15 years. These compounds contain  $\text{MCl}_4$  layers alternating with packed aliphatic chains

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(Fig. 1). Interesting two-dimensional magnetic properties (Yamasaki, 1979) have been detected. These substances have also been used as models of biological membranes (Needham, Willett & Franzen, 1984). The large number of phase transitions observed in these materials has created a rich area of structural research (see *e.g.* Kind, 1980). Surprisingly, the case  $n = 3$  exhibited modulated phases, the metallic atoms being Mn (see Depmeier, 1986, for a review), Cd (Doudin & Chapuis, 1988) or Cu (Jahn, Knorr & Ihringer, 1989; Doudin & Chapuis, 1990). The study of the butylammonium compound was motivated by the search for a similar phase. Our results revealed the existence of a commensurate phase  $\delta$ , similar to the one observed for the propylammonium compounds at ambient temperature. A phase transition was observed at approximately 210 K. It was accompanied by a splitting of the Bragg peaks, thus making a study on monocrystals more tedious.

C4Mn also exhibits the same symmetry. Depmeier & Chapuis (1979) showed that the terminal methyl group takes a *gauche* conformation. This effect has