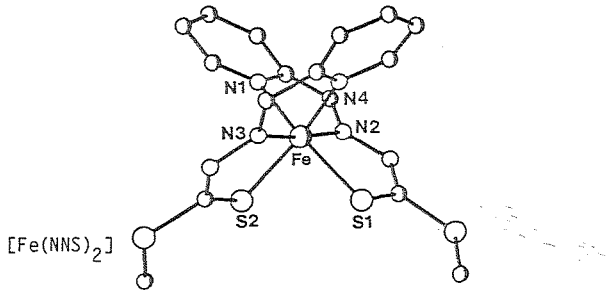
bered chelate rings are formed. The symmetry of the complex is close to C_2. Within both independent molecules



the distances from iron to the pyridine nitrogen atoms (Fe-N1 1.978 Å, Fe-N4 2.002 Å) are significantly longer than to the Schiff base nitrogens (Fe-N2 1.880 Å, Fe-N3 1.850 Å). Due to the influence of the dithiocarbazate delocalized electron system in conjugation with the aromatic rings the latter values are smaller by about 0.06 Å as compared to other iron complexes with N,S donor ligands. This stabilizing effect is also reflected in the rather uniform bond lengths in the ligand backbone. The arrangement of the molecules in the crystal structure is determined by a pairwise parallel packing of the planar ligand systems. Very similar coordination and bonding properties are observed in the analogous complexes $[Co(NNS)_2]$, $[Fe(SNS)_2]$ and $[Co(SNS)_2]$, the complete crystal structures of which will also be reported in detail.

In spite of their composition which in the empirical formulation as $[Ph_4P]_2[Mn_2(tdt)_2]\cdot 4MeOH$ implies the presence of dimeric anions as well, crystals obtained from the reaction of Mn(III) with tdt^{2-} in methanolic solution on addition of Ph_4PBr were analysed by X-ray diffraction to contain the monomeric anions $[Mn(tdt)_2]^-$(I) and $[Mn(tdt)_2MeOH]^-$ (II) simultaneously (see Figure; crystal data [T = -130 °C]: triclinic, $P\bar{1}$, a = 10.001(4), b = 19.447(8), c = 19.814(8) Å, α = 99.64(3), β = 90.01(3), γ = 104.12(3)°, Z = 2).
Due to significant superstructure effects (distribution of $\langle E^2 \rangle$ by parity groups: eee 2.502, eeo 1.098, eoe 0.198, eoo 0.171, oee 0.172, oeo 0.199, ooe 1.138, ooo 2.473) as a consequence of extended pseudosymmetries between crystallographically non-equivalent anions and cations the initial steps of the structure solution process were performed in the space group $F\bar{1}$ by Patterson methods. The resulting partial structure consisting of superimposed square-planar MS_4 units was expanded by symmetry reduction and completed in the space group $C\bar{1}$ by successive Fourier and least-squares refinement procedures. Finally the structural model was transformed to the primitive lattice of the superstructure and successfully refined in the space group $P\bar{1}$ to R = 0.040.
In both $[Mn(tdt)_2]^-$ (I) and $[Mn(tdt)_2MeOH]^-$ (II) the tdt^{2-} groups are related by pseudo inversion centers resulting in common planes for all except the methyl hydrogen atoms. In the case of I the position of the manganese atom coincides perfectly well with the pseudo center. The anion II derives from I by an additional $methanol^-$ ligand whose oxygen atom not only expands the coordination sphere of manganese towards a square pyramid but is also responsible for the observed deviation of the metal atom from the plane defined by the tdt^{2-} substituents. From comparison of the mean Mn-S distances in I (2.281 Å) and in II (2.310 Å) the expected dependence from the coordination number is obvious.

09.4–22 SIMULTANEOUS STABILIZATION OF SQUARE-PLANAR $[Mn(tdt)_2]^-$ AND SQUARE-PYRAMIDAL $[Mn(tdt)_2MeOH]^-$ ANIONS (tdt^{2-}= TOLUENE-3,4-DITHIOLATE) BY LATTICE EFFECTS IN THE PSEUDO-CENTERED STRUCTURE OF $[Ph_4P]_2[Mn(tdt)_2][Mn(tdt)_2MeOH]\cdot 3MeOH$. By G. Henkel, K. Greiwe and B. Krebs, Anorganisch-Chemisches Institut der Universität Münster, Corrensstr. 36, D-4400 Münster, Fed. Rep. of Germany.

The chemistry of trivalent iron and manganese ions towards 1,2-dithiolates in organic solvents is characterized by the formation of thiolato-bridged penta-coordinated dimers. They have been shown to define stable crystals with quaternary ammonium or phosphonium counterions (see G. Henkel, W. Tremel, U. Kuhlmann, B. Krebs, "Abstracts of papers", XXI ICCC, Toulouse, 1980, p. 351; T. Costa, J.R. Dorfman, K.S. Hagen, R.H. Holm, Inorg. Chem. (1983), 22, 4091, and references cited therein).

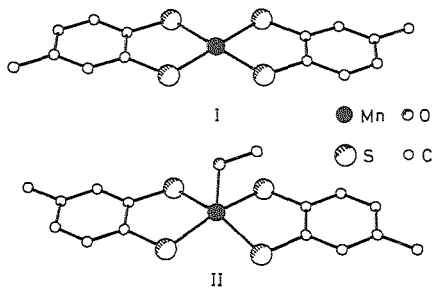


Figure: Structures of $[Mn(tdt)_2]^-$ (I) and $[Mn(tdt)_2MeOH]^-$ (II) in crystals of $[Ph_4P]_2[Mn(tdt)_2][Mn(tdt)_2MeOH]\cdot 3MeOH$

09.4–23 BONDING PROPERTIES AND COORDINATION ABILITY OF THE SELENOCYANATE LIGANDS IN COPPER COMPLEXES. By J. Garaj and V. Vrabel, Dpt. of Analytical Chemistry, Slovak University of Technology, Janska 1, 880 37 Bratislava, Czechoslovakia.

Seven crystal structures of copper(I)-copper(II) and copper(II) selenocyanate complexes: $Cu_3(en)_2(SeCN)(CN)_3.H_2O$, $Cu_9(en)_6(SeCN)_6(CN)_6$, $Cu_3(en)_2(SeCN)_2(CN)_2.H_2O$, $[Cu(en)_2(NO_3)]SeCN$, $Cu(en)_2(SeCN)_2$, $[Cu(den)_2](NCSe)_2$ and $[Cu(amp)_2](SeCN)_2$ have been described, where en, den and amp are the N-containing ligands.

The crystallochemical conclusions could be summarized as follows:

1. Copper(II) atoms are coordinated by two molecules of N-containing ligands. Cu(II) atoms are stabilized by a planare Cu(II)-N_4 chromophore.

2. The selenocyanate groups act as anionic ligands in all copper(II) complexes and lie far from the metal atoms.

3. The selenocyanate groups have a great bonding variability in copper complexes. All of the next six theoretically possible ways of bonding the SeCN group have been found in the above given complexes:

$SeCN^-$,	M – NCSe,	M – SeCN
M – NCSe,	M – Se – M,	M – SeCN – M
M	C N	M

4. The bridging function of the selenocanate groups is present in all copper(I)-copper(II) mixed valency complexes.