09.4-19 X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS ON THE ORIENTATIONAL DISORDER OF THE COMPLEX CATIONS AND ANIONS IN THE HIGH TEMPERATURE PHASES OF COBALTOCENIUM PERCHLORATE AND TETRA-FLUOROBORATE. By H.J. Berthold and H.-G. Bäthge, Institut für Anorganische Chemie der Universität Hannover, Federal Republic of Germany.

Cobaltocenium perchlorate and tetrafluoroborate undergo phase transitions to high temperature phases at 376 K and 415 K respectively. The cubic high temperature phases (CsCl-lattice) contain one formula unit in the unit cell. The lattice constants are 660 pm (393 K) in the perchlorate and 663 pm (420 K) in the tetra-

The Cobaltocenium cations $Co(C_5H_5)^+$ occupy 3 orientations statistically in such a way that their fivefold axes lie parallel to the cubic crystal axes.

The tetrahedral anions Clo_{4}^{-} or BF_{4}^{-} take 6 orientations statistically such that one of the threefold axes each time points to a face centre of the cube. The 3 oxygen or fluorine atoms which do not lie on the preferentially oriented threefold axes, show additional disorder within their plane perpendicular to the threefold axis.

Structure factor calculations have proved that the observed intensity data are best fitted by assuming the C,H and O or F atoms to be distributed on the surface of a sphere and describing their contributions to the structure factors by means of spherical Bessel functions and cubic harmonics.

09.4–20 X-RAY CRYSTALLOGRAPHIC STUDIES OF THREE-CO-ORDINATED SILVER(I) COMPLEXES OF 2,11-BIS(DI-T-BUTYLPHOS-PHINOMETHYL)BENZO[c]PHENANTHRENE.

By M.Camalli, <u>F.Caruso</u>, Istituto di Strutturistica Chimica "G. Giacomello", CNR - C.P.10, 00016 Monterotondo Stazione, Italy; and L.M.Venanzi, Laboratorium für Anorganische Chemie, ETH-Zentrum CH-8092 Zurich, Switzerland.

Although the bidentate ligand $\widetilde{\text{PP}}=2,11-\text{bis}(\text{diphenylphos}$ phinomethyl)benzo[c]phenanthrene was designed to span trans position in square planar complexes (N.J.De Stefano, D.K.Johnson, R.M.Lane and L.M.Venanzi, Helv.Chim.Acta (1976) 59, 2674), it is able to form three-coordinated complexes with silver(I), $Ag(\widetilde{PP})X$, where the third ligand is an anion. For the Ib group (Cu,Ag,Au) crystallographic studies on chloride complexes have shown that the metal atoms are three-coordinated with P-M-P angles of 132, 141 and 176°, respectively, suggesting that PP is capable of accomodating a variety of microgeometric arrangements. In these structures the widening of the P-M-P angle is accompanied by an increase of the ionic character of the M-Cl bond (M.Barrow, H.B.Burgi, D.K.Johnson and L.M.Venanzi, J.Am.Chem.Soc. (1976) <u>98</u>, 2356). For the complexes Ag(\widetilde{PP})X with X=BF₄,NO₃,Cl,I,³¹P-NMR studies have shown that changes in the values of ${}^{1}J({}^{107}Ag{}^{-31}P)$ correlate with the capability of the anion, X, to coordinate to the metal (D.K.Johnson, P.S.Pregosin, L.M.Venanzi Helv.Chim. Acta (1976) 59,2691). Moreover for X=ClO₄, NO₃,Cl₃Sn,Cl the Ag-P bond distances and the P-Ag-P angles correlate with ¹J(¹⁰⁷Ag-³¹P)(M.Barrow, H.B.Burgi, M.Camalli, F.Caruso, E.Fischer, L.M.Venanzi, L.Zambonelli, Inorg.Chem.

(1983) <u>22</u>, 2356). Unfortunately these three X ligands are not enough different to produce very marked changes in structural parameters. Thus a study of the series Ag(t- \widetilde{PP})X, with t- \widetilde{PP} =2,11-bis(di-t-butylphosphinomethyl)-benzo[c]phenanthrene was undertaken to extend these correlations and to investigate possible steric effects on the coordination of the anion. Three complexes of this series, X=Br, C1,ClO_A are presented here.

Compound	$Ag(t-\widetilde{PP})Br$	Ag(t-PP)Cl	Ag(t-PP)Cl0 ₄	
Formula	C_H_AgP_2Br	C H AgP 2CI	C H AgP 2C10 4	
Sp. group	P2 ₁ /n	P2 ₁ /n	Pbca	
a(Å)	11.174(3)	11.163(3)	16.015(4)	
b(Å)	24.323(9)	24.382(7)	20.050(4)	
c(Å)	. 14.178(4)	14.094(4)	25.002(5)	
β(°)	102.69(2)	103.12(2)	90.	
V(Å ³)	3759(2)	3735.7(18)	8028.3(29)	
Selected structural parameters				
P1AgP2(°)	141.6(2)	142.6(1)	161.5(1)	
Ag-P1(Å)	2.463(4)	2.457(2)	2.394(2)	
Ag-P2(Å)	2.433(5)	2.427(2)	2.393(2)	
Ag-Y(Å)(a)	2.681(2)	2.569(2)	2.913(13)	
(a) Y is the anion's atom bonded to the silver atom.				

In the three compounds the metal atom has a distorted trigonal coordination; the metal is out of the plane determined by the donor atoms by 0.06, 0.06 and 0.07 Å for bromine, chlorine and perchlorate complexes respectively. These results will be discussed and compared with those of related complexes of the $\widetilde{\text{PP}}$ ligand.

09.4-21 STRUCTURAL STUDIES OF IRON(II) AND COBALT(II) COMPLEXES WITH TRIDENTATE SCHIFF BASES HAVING N,S DONOR SYSTEMS. By <u>P. Nienaber</u> and B. Krebs, Anorganisch-Chemisches Institut der Universität Münster, Corrensstr. 36, D-4400 Münster, Fed. Rep. of Germany

Dithiocarbazic acids, their derivatives (NRR'-NH-CSSR") and their metal complexes have been extensively studied because of their good antifungal activity against a number of fungal plant pathogens. Their practical use for different applications has been shown (A. Saxena et al., Inorg. Chim. Acta (1982) 63, 71; L. El-Sayed et al., Trans. Met. Chem. (1979) 4, 300).

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 $\rm Fe(II)$ and Co(II) salts are determined from single crystal X-ray data. The structural properties are correlated in detail with the results of IR, NMR, Mössbauer and mass spectroscopic studies.

 $[Fe(NNS)_2]$ is monoclinic $(P2_1/n, a = 14.264(3), b = 10.236(2), c = 26.545(5)$ Å, $\beta = 92.07(2)^{\circ}$, with two independent, structurally almost identical molecular complex units in the asymmetric unit. The iron atom in the $[Fe(NNS)_2]$ complex is octahedrally coordinated by four nitrogen and two thiolo-sulfur atoms, so that five-mem-

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bered chelate rings are formed. The symmetry of the complex is close to ${\rm C}_2.$ 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.

09.4-22 SIMULTANEOUS STABILIZATION OF SQUARE-PLANAR [Mn(tdt)2] AND SQUARE-PYRAMIDAL [Mn(tdt)2 MeOH] ANIONS (tdt²⁻= TOLUENE-3,4-DITHIOLATE) BY LATTICE EFFECTS IN THE PSEUDO-CENTERED STRUCTURE OF [Ph₄P]2[Mn(tdt)2][Mn(tdt)2-MeOH]·3MeOH. By <u>G. Henkel</u>, 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), <u>22</u>, 4091, and references cited therein).



Figure: Structures of [Mn(tdt)₂]⁻ (I) and [Mn(tdt)₂MeOH]⁻ (II) in crystals of [Ph₄P]₂ [Mn(tdt)₂][Mn(tdt)₂MeOH]·3MeOH

In spite of their composition which in the empirical formulation as $[\rm Ph_4P]_2[\rm Mn_2(tdt)_2]\cdot 4MeOH$ 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)_2 MeOH]_(II) simultaneously (see Figure; crystal data [T = -130 °C]: triclinic, PI, 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) $_0^0$, 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 FI by Patterson methods. The resulting partial structure consisting of superimposed "square-planar MS4 units was expanded by symmetry reduction and completed in the space group CI 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 PI to R = 0.040. In both [Mn(tdt)₂]⁻ (I) and [Mn(tdt)₂ MeOH]⁻ (II) the tdt²⁻ 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

In both $[m(tdt)_2]$ (1) and $[m(tdt)_2](tdt)_2$ (devid) (11) the tdt²⁻ 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 tdt²⁻ 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.

09.4-23 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: $Cu_3(en)_2(SeCN)(CN)_3$.H₂O, $Cu_9(en)_6(SeCN)_6(CN)_6$, $Cu_3(en)_2(SeCN)_2(CN)_2$.H₂O, [Cu(en)_2(NO₃)]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 ligends. 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)-N₄ 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 - NCȘe,	M - Se - M,	M - ŞeCN - M
M	U N	Ŵ

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