

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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 TETRAFLUOROBORATE. By H.J. Berthold and H.-G. Bätghe, 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 tetrafluoroborate.

The Cobaltocenium cations $\text{Co}(\text{C}_5\text{H}_5)_2^+$ 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-COORDINATED SILVER(I) COMPLEXES OF 2,11-BIS(DI-T-BUTYLPHOSPHINOMETHYL)BENZO[C]PHENANTHRENE.

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Although the bidentate ligand $\tilde{\text{P}}\tilde{\text{P}}=2,11$ -bis(diphenylphosphinomethyl)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), $\text{Ag}(\tilde{\text{P}}\tilde{\text{P}})\text{X}$, 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 accommodating 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) **98**, 2356). For the complexes

$\text{Ag}(\tilde{\text{P}}\tilde{\text{P}})\text{X}$ with $\text{X}=\text{BF}_4^-, \text{NO}_3^-, \text{Cl}^-, \text{I}^-$, ^{31}P -NMR studies have shown that changes in the values of $^1\text{J}({}^{107}\text{Ag}-{}^{31}\text{P})$ 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 $\text{X}=\text{ClO}_4^-, \text{NO}_3^-, \text{Cl}_3\text{Sn}, \text{Cl}$ the Ag-P bond distances and the P-Ag-P angles correlate with $^1\text{J}({}^{107}\text{Ag}-{}^{31}\text{P})$ (M. Barrow, H.B. Burgi, M. Camalli, F. Caruso, E. Fischer, L.M. Venanzi, L. Zambonelli, *Inorg. Chem.*

(1983) **22**, 2356). Unfortunately these three X ligands are not enough different to produce very marked changes in structural parameters. Thus a study of the series $\text{Ag}(\text{t-}\tilde{\text{P}}\tilde{\text{P}})\text{X}$, with $\text{t-}\tilde{\text{P}}\tilde{\text{P}}=2,11$ -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, $\text{X}=\text{Br}, \text{Cl}, \text{ClO}_4^-$ are presented here.

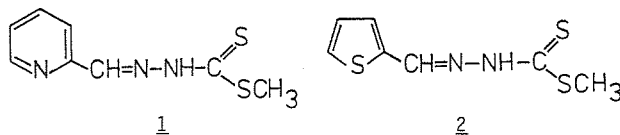
Compound	$\text{Ag}(\text{t-}\tilde{\text{P}}\tilde{\text{P}})\text{Br}$	$\text{Ag}(\text{t-}\tilde{\text{P}}\tilde{\text{P}})\text{Cl}$	$\text{Ag}(\text{t-}\tilde{\text{P}}\tilde{\text{P}})\text{ClO}_4$
Formula	$\text{C}_{36}\text{H}_{50}\text{AgP}_2\text{Br}$	$\text{C}_{36}\text{H}_{50}\text{AgP}_2\text{Cl}$	$\text{C}_{36}\text{H}_{50}\text{AgP}_2\text{ClO}_4$
Sp. group	$\text{P2}_1/\text{n}$	$\text{P2}_1/\text{n}$	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.
$V(\text{Å}^3)$	3759(2)	3735.7(18)	8028.3(29)
Selected structural parameters			
$\text{P1AgP2}(\text{°})$	141.6(2)	142.6(1)	161.5(1)
$\text{Ag-P1}(\text{Å})$	2.463(4)	2.457(2)	2.394(2)
$\text{Ag-P2}(\text{Å})$	2.433(5)	2.427(2)	2.393(2)
$\text{Ag-Y}(\text{Å})(\text{a})$	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 $\tilde{\text{P}}\tilde{\text{P}}$ ligand.

09.4-21 STRUCTURAL STUDIES OF IRON(II) AND COBALT(II) COMPLEXES WITH TRIDENTATE SCHIFF BASES HAVING N,S DONOR SYSTEMS. By P. Nienaber 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).

The free dithiocarbazic acid is very unstable, but the ester derivatives react with carbonyl groups of certain bifunctional aldehydes or ketones such as pyridine-2-aldehyde and thiophene-2-aldehyde to stable tridentate ligands. The crystal structures of products formed by the reaction of S-methyl- β -N-(2-pyridyl)methylenedithiocarbazate (NNSH, 1) or the thiophene analogue (SNSH, 2) with



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.

$[\text{Fe}(\text{NNS})_2]$ is monoclinic ($\text{P2}_1/\text{n}$, $a = 14.264(3)$, $b = 10.236(2)$, $c = 26.545(5)$ Å, $\beta = 92.07(2)^\circ$), with two independent, structurally almost identical molecular complex units in the asymmetric unit. The iron atom in the $[\text{Fe}(\text{NNS})_2]$ complex is octahedrally coordinated by four nitrogen and two thio-sulfur atoms, so that five-mem-