Inorganica Chimica Acta, 30 (1978) L305–L307

Reaction of Tris(dicyclohexyldithiophosphinato)iron(III) with Silver Nitrate

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Received June 22, 1978

During an investigation of possible methods of syntheses of bisdithiophosphinatoiron(III) complexes [1], $[Fe(R_2PS_2)_2X]$, an attempt was made to prepare the X = NO_3 or NO cases by reaction of the tris complex, $[Fe(R_2PS_2)_3]$, with silver nitrate. In the analogous reaction with tris-dithiocarbamatoiron(III) complexes, $[Fe(R_2NCS_2)_3]$, the nitrosyl complex $[Fe(R_2NCS_2)_2NO]$ readily formed [2]. The reaction of tris (dicyclohexyldithiophosphinato)iron(III), $[Fe(c\text{-}Hx_2PS_2)_3]$, with silver nitrate, however, gave an unexpected product. The results are of sufficient interest to warrant this communication.

Experimental

A solution of 1.0 g of $[Fe(c\text{-}Hx_2PS_2)_3]$ [1] in about 200 ml of CS_2 was treated with 0.39 g powdered $AgNO_3$ and the mixture stirred for about 10 min at room temperature. The initially deep green solution gradually changed to deep purple-violet. The mixture was filtered to remove unreacted $AgNO_3$, and the filtrate evaporated to dryness. The residue was dried at room temperature under vacuum. The deep purple compound significantly lightened in color and gradually decomposed upon attempted recrystallization from petroleum ether. Also, use of CH_2Cl_2 in place of CS_2 in the preparation, or long stirring times, even with CS_2 as solvent, resulted in significant decomposition with consequent lightening of the initial purple color, and formation of a brown precipitate. Two different samples of unrecrystallized deep violet complex were prepared and investigated. *Anal.* Sample 1: Calc'd for $[Fe(c\text{-}Hx_2PS_2)_3]\cdot 0.8\,AgNO_3$: C, 44.30; H, 6.82; N, 1.15; P, 9.52; S, 19.71; Ag, 8.84. Found: C, 44.83; H, 7.02; N, 1.30; P, 9.65; S, 17.99; Ag, 9.03.

Sample 2: Calc'd for $[Fe(c\text{-}Hx_2PS_2)_3]\cdot 0.7\,AgNO_3$: C, 45.65; H, 7.02; N, 0.93; P, 9.81; S, 20.31; Ag, 7.18. Found: C, 45.64; H, 7.02; N, 0.91; P, 9.59; S, 21.07; Ag, 9.17.

Sample recrystallized once from petroleum ether: Found C, 43.89; H, 7.52; N, 0.40; S, 17.82.

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, and visible and ultraviolet spectra, on a Cary 14 spectrophotometer. Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. Calibration was made with sodium nitroprusside and ^{57}Fe foil. The data were computer fitted to a least-squares approximation assuming Lorentzian line shapes. A Calcomp plotter was used to plot data. Magnetic moments were measured on solid samples at two field strengths: 7.096 kOe and 5.974 kOe. The necessary diamagnetic corrections were made.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Results

The purple compound was soluble in petroleum ether, cyclohexane, carbon disulfide and carbon tetrachloride to give rather unstable purple solutions, and in methylene chloride to give a green solution, the visible spectrum of which showed the presence of the tris complex, $[Fe(c\text{-}Hx_2PS_2)_3]$. A freshly prepared solution in CCl_4, measured from 1200–260 nm, had peaks (with approximate ϵ values) at 287 (5400), 358 (6900), ~430 (2700, shoulder) and 535 nm (3700).

Because of the difficulty in obtaining a pure compound, a Yoe-Jones molar ratio investigation [3] of the stoichiometry of the $[Fe(c\text{-}Hx_2PS_2)_3] + AgNO_3$ reaction was performed. Plots of absorbance *vs.* molar ratio of tris complex to $AgNO_3$ at several wavelengths in CS_2 solution were constructed. All indicated conclusively a 1:1 stoichiometry. A representative plot is shown in Fig. 1.

Corrected room temperature magnetic moments were: sample 1, 4.18 B.M.; sample 2, 4.71 B.M. These may be compared with that of the pure tris complex, 5.9 B.M., and of the halobis complexes, $[Fe(c\text{-}Hx_2PS_2)_2X]$, X = Cl, Br, I, 5.5–5.9 B.M. [1]. The presence of $AgNO_3$ caused a striking reduction in the magnetic moment from the high spin value.

Infrared spectra were superimposable in the 300–4000 cm^{-1} region for both samples. There were two additional peaks not present in the tris complex: 1250 cm^{-1} (sharp, strong) and 1525 cm^{-1} (sharp, very strong). Both decreased greatly in intensity upon recrystallization.

The Mössbauer spectrum at 298 °K showed an unsymmetrical, unresolved doublet with an isomer shift of 0.75 mm/sec (relative to nitroprusside) and a

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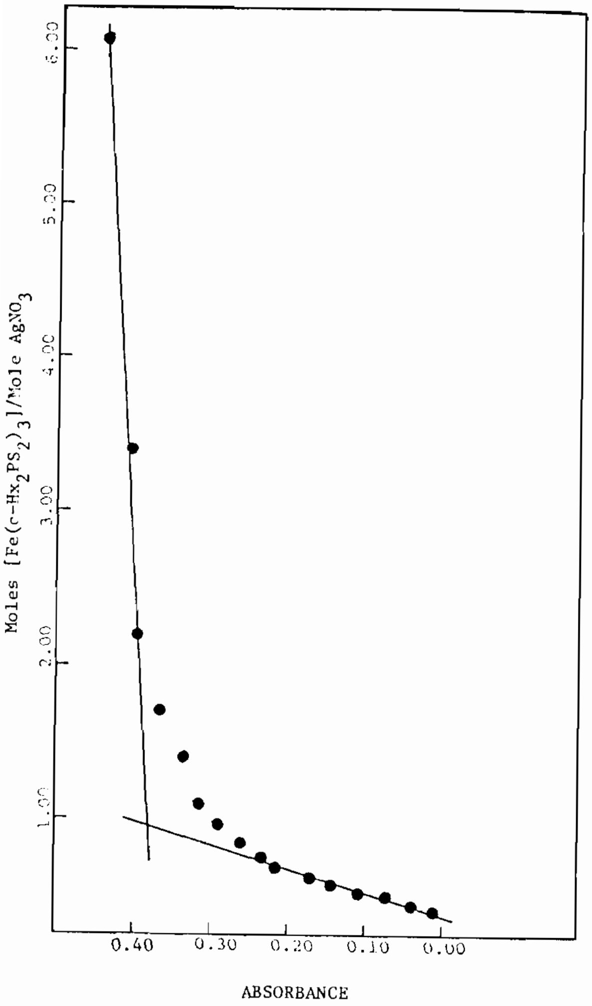


Figure 1. Yoe–Jones plot for the [Fe(c-$Hx_2PS_2)_3$]-$AgNO_3$ complex in carbon disulfide solution. Wavelength, 600 nm.

quadrupole splitting, 0.33 mm/sec. The spectrum is shown in Fig. 2.

Discussion

Because the unstable deep purple 1:1 adduct, formed between [Fe(c-$Hx_2PS_2)_3$] and $AgNO_3$ in non-reactive solvents, must be prepared heterogeneously, the pure 1:1 adduct is difficult to obtain as a solid. However, careful examination of two samples, [Fe(c-$Hx_2PS_2)_3$]$\cdot$0.8 $AgNO_3$ and [Fe(c-$Hx_2PS_2)_3$]$\cdot$ 0.7 $AgNO_3$, leads to the following conclusions concerning the structure of the adduct.

1) The compound is non-ionic since it is soluble in solvents such as petroleum ether, cyclohexane, CS_2 and CCl_4. It appears to at least partly dissociate, however, in CH_2Cl_2.

2) The 1250 and 1525 cm^{-1} are clearly ν_1 and ν_4, respectively, *coordinated* nitrate [4] (the ν_2 band of coordinated nitrate cannot be unambiguously determined since there is overlap with dithiophosphinate peaks in the expected region, 970–1030 cm^{-1}). In the ionic nitrate cases, $AgNO_3$ [4] and R_2SAgNO_3 [5], peaks occur at 1362, 801 cm^{-1}, and 1370, 819 cm^{-1}, respectively.

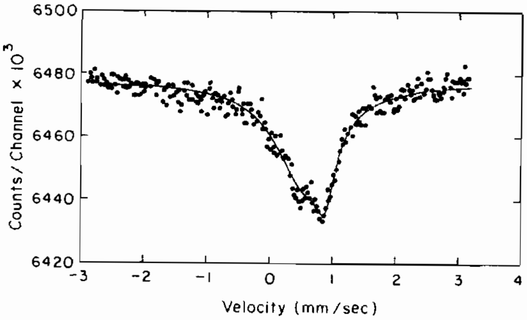
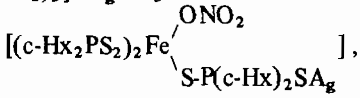


Figure 2. Mössbauer spectrum of [Fe(c$Hx_2PS_2)_3$]$\cdot$0.8 Ag-NO_3 at 298 °K.

3) The magnetic moment at 298 °K is strongly dependent upon the molar ratio of $AgNO_3$ to tris complex. The isolated solid nearest to stoichiometry (the 0.8 $AgNO_3$ product) has a magnetic moment of 4.18 B.M., so the stoichiometric adduct probably should have a moment $\leqslant$4 B.M.

4) The Mössbauer data strongly suggest that the adduct is an iron(III) complex. The small splitting rules out a spin-quartet state, since all other cases of known iron(III) complexes in pure quartet states have quadrupole splittings of 2 mm/sec or greater [6]. A thermal mixture of low spin–high spin states is common for many ferric complexes with bidentate sulfur ligands (*e.g.*, the trisdithiocarbamates [7].

The most plausible structure for [Fe(c-Hx_2-$PS_2)_3$]$\cdot A_gNO_3$ based on these considerations is



$[(c\text{-}Hx_2PS_2)_2Fe\begin{smallmatrix}/ONO_2\\ \\ \backslash S\text{-}P(c\text{-}Hx)_2SA_g\end{smallmatrix}]$, with two bidentate and one bridging dithiophosphinate ligands (the iron could also be 7-coordinate, with bidentate nitrate). Models indicate that such a structure is sterically possible.

Acknowledgement

We wish to thank the National Science Foundation University Science Development Program, Grant No. GU-3184, for support of this research.

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