Inorganica Chimica Acta, 13 (1975) 105–108

Halobis(dicyclohexyldithiophosphinato)iron(III) Complexes

R. Y. SALEH[1] and D. K. STRAUB*
Department of Chemistry University of Pittsburgh Pittsburgh, Pa. 15260, U.S.A.
Received May 7, 1974

Chloro, bromo and iodobis(dicyclohexyldithiophosphinato)iron(III) complexes have been synthesized. These compounds have magnetic moments of 5.5–5.9 B.M. at 298° K in methylene chloride solution and have Mössbauer isomer shifts of +0.63 ±0.02 mm/sec and quadrupole splittings of ~0.48 mm/sec.

Introduction

The halobis(N,N-disubstituted dithiocarbamato)iron (III) complexes contain iron(III) in an unusual spin quartet ground state[2,3]. Other five-coordinated iron (III) complexes of similar, somewhat distorted square pyramidal geometry, such as the chlorobis(β-diketonato)iron(III) complexes[4,5] or the hemin halides,[6] contain the more common high spin iron(III). It appears that the quartet state depends both upon the dithiocarbamate ligand and the geometry. Whether similar complexes with other bidentate sulfur ligands will shown unusual magnetic properties is not known. In order to answer this question, we have investigated the closely related halobis(dicyclohexyldithiophosphinato) iron(III) complexes and wish to report the syntheses and some physical properties of these compounds in this paper.

Experimental

All starting materials and solvents were reagent grade. Tris(dicyclohexyldithiophosphinato)iron(III) was prepared by mixing aqueous solutions of ferric chloride and ammonium dicyclohexyldithiocarbamate (Aldrich Chem. Co.) in a 1:3 molar ratio and recrystallizing the precipitate from methylene chloride–ethanol mixtures. *Anal.* Calcd. for [Fe(c-$Hx_2PS_2)_3$]: C, 53.79; H, 3.76; S, 23.93. Found: C, 54.02; H, 3.77; S, 23.74).

Preparation of Chlorobis(dicyclohexyldithiophosphinato)iron(III)

This complex was prepared by mixing ammonium dicyclohexyldithiophosphinate in methylene chloride with anhydrous ferric chloride in a 2:1 molar ratio. The resulting reddish-brown mixture was stirred, filtered and evaporated to dryness under vacuum. The dark brown residue was recrystallized several times from hot cyclohexane and dried over refluxing acetone under vacuum for three days. *Anal.* Calcd. for [Fe (c-$Hx_2PS_2)_2Cl] + \frac{1}{6}C_6H_{12}$: C, 47.96; H, 7.24; S, 20.48; Cl, 5.66. Found: C, 47.94; H, 7.18; S, 20.51; Cl, 5.64.

The chlorobis complex was also prepared by the following procedure: Chlorine gas was bubbled for about 20 seconds through a solution of 3 grams of the tris complex in 150 ml of methylene chloride. The deep green color characteristic of the tris complex changed to reddish-brown. This solution was evaporated to dryness under vacuum and the resulting dark brown residue was recrystallized in a similar manner to that described above. *Anal.* Calcd. for [Fe(c-$Hx_2PS_2)_2Cl$]: C, 46.94; H, 7.22; S, 20.88; Cl, 5.77. Found: C, 46.98; H, 7.16; S, 20.71; Cl, 5.88.

The chlorobis complex prepared in this way had identical infrared, electronic and Mössbauer spectra to the chlorobis complex prepared from ferric chloride.

Preparation of Bromobis(dicyclohexyldithiophosphinato)iron(III)

This complex was prepared and purified using the same procedure and conditions, followed in the chlorobis derivative case in which anhydrous ferric chloride was used, but using anhydrous ferric bromide. *Anal.* Calcd. for [Fe(c-$Hx_2PS_2)_2Br] + \frac{1}{6}C_6H_{12}$: C, 44.64; H, 6.89; S, 19.07; Br, 11.88. Found: C, 44.36; H, 6.73; S, 19.32; Br, 12.04.

Preparation of Iodobis(dicyclohexyldithiophosphinato)iron(III)

Concentrated aqueous hydriodic acid was added slowly and with continuous stirring to a solution of 4 grams of [Fe(c-$Hx_2PS_2)_3$] in 300 ml methylene chloride until the original green color had completely changed to violet. The filtered solution was evaporated to dryness under vacuum. The brownish black residue was recrystallized several times from hot cyclohexane and dried over refluxing acetone vacuum for several days. *Anal.* Calcd. for [Fe(c-$Hx_2PS_2)_2I$]: C, 40.86;

H, 6.29; S, 18.18; I, 17.99. Found: C, 40.99; H, 6.27; S, 17.72; I, 17.10

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, visible and ultraviolet spectra, on a Cary 14 spectrophotometer, and nuclear magnetic resonance spectra, on a Varian A-60 instrument. Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. A source of ^{57}Co diffused in chromium kept at room temperature was used. Calibration with sodium nitroprusside was carried out before and after each run. Frequent checks on linearity were also made with ^{57}Fe foil. The data were computer-fitted to a least-squares approximation assuming Lorentzian line shapes of equal width. A Calcomp plotter was used to plot data.

Elemental analyses were performed by Chemalytics, Arizona.

Results

Electronic Spectra

Visible and ultraviolet spectra were measured on methylene chloride solutions. Peak maxima and absorption coefficients are given in Table I. Visible spectra of the three halides and the tris complex, for comparison, are shown in Figure 1.

Infrared Spectra

Infrared spectra were taken on Nujol mulls. Positions and relative intensities of the peaks occurring in the 1400–625 cm^{-1} regions of the spectra are given in Table II. This region includes the characteristic cyclohexyl, P–C(780–620 cm^{-1}) and P–S(<860 cm^{-1}) frequencies. The three halides showed very similar spectra.

Magnetic Moments

Magnetic susceptibilities were measured on methylene chloride solutions at 36° C by the nmr method[7] with tetramethylsilane as standard. Diamagnetic corrections were calculated from Pascal's constants. Data are given in Table III and represent averages of 4–6 different determinations which agreed to within ± 0.05 B.M. of each other.

TABLE I. Electronic Spectral Data in the Region 650–220 nm.[a]

Compound	*Peaks, λ_{max}, nm(ε,M^{-1}cm^{-1})*
[Fe(c-Hx$_2$PS$_2$)$_2$Cl]	588(1800), 515(2200), 438(3100), 369(5500), 319(4500), 285, 239
[Fe(c-Hx$_2$PS$_2$)$_2$Br]	568(2600), 463(3300), 371(6000), 321, 253
[Fe(c-Hx$_2$PS$_2$)$_2$I]	588(3000), 519(3400), 413(4300), 342(6500), 285, 257

[a] Spectra measured on methylene chloride solutions.

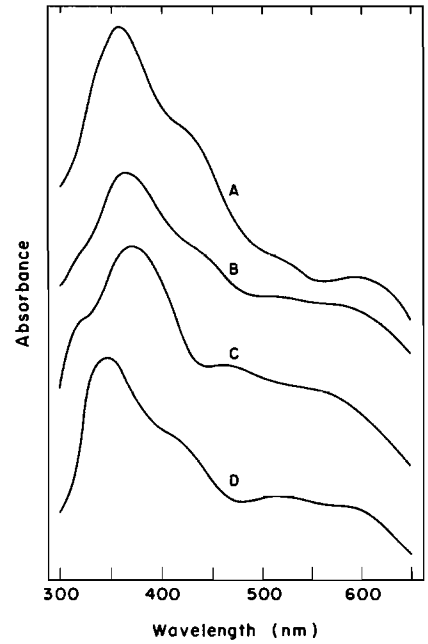

Figure 1. Visible spectra of A) [Fe(c-Hx$_2$PS$_2$)$_3$], B) [Fe(c-Hx$_2$PS$_2$)$_2$Cl], C) [Fe(c-Hx$_2$PS$_2$)$_2$Br and D) [Fe(c-Hx$_2$PS$_2$)$_2$I] in methylene chloride solution.

TABLE II. Infrared Data in the Region 1400–625 cm^{-1}.[a]

[Fe(c-Hx$_2$PS$_2$)$_2$Cl]
1338vs, 1292s, 1285s, 1262s, 1190m, 1175vs, 1110w, 1075w, 1070w, 1042m, 995w, 917w, 880w, 842m, 813m, 745s

[Fe(c-Hx$_2$PS$_2$)$_2$Br]
1340vs, 1295s, 1285s, 1260s, 1190s, 1172vs, 1107s, 1075s, 1068s, 1042s, 995m, 915m, 900m, 880m, 842m, 813m, 782w, 740s

[Fe(c-Hx$_2$PS$_2$)$_2$I]
1340vs, 1295vs, 1282sh, 1260s, 1190s, 1173vs, 1105m, 1075m, 1070s, 1040s, 995m, 913w, 881m, 846m, 814m, 742s

[a] Spectra taken on Nujol mulls. Key: v, very; s, strong; m, medium; w, weak; sh, shoulder. All values are in cm^{-1}.

TABLE III. Solution Magnetic Moments at 36° C.

Complex	$10^{-6}\chi_D$[a], cgsu	$10^{-6}\chi_M$[b], cgsu	μ_{eff}[c], B.M.
[Fe(c-Hx$_2$PS$_2$)$_2$Cl]	–406	13750	5.85
[Fe(c-Hx$_2$PS$_2$)$_2$Br]	–420	13190	5.66
[Fe(c-Hx$_2$PS$_2$)$_2$I]	–436	12270	5.53

[a] Diamagnetic correction. [b] Corrected value. [c] Estimated error limits: ± 0.10 B.M.

TABLE IV. Mössbauer Data at 25° C.

Complex	δ,[a] mm/sec	Δ,[b] mm/sec	Γ,[c] mm/sec	Number of Baseline Counts
$[Fe(c\text{-}Hx_2PS_2)_2Cl]$.	+0.61	0.49	0.20	1.12×10^6
$[Fe(c\text{-}Hx_2PS_2)_2Br]$	+0.62	0.48	0.15	3.46×10^5
$[Fe(c\text{-}Hx_2PS_2)_2I]$	+0.65	0.48	0.16	5.37×10^5

[a] Isomer shift relative to sodium nitroprusside. [b] Quadrupole splitting; sign not determined. [c] Half width at half maximum. For $[Fe(c\text{-}Hx_2PS_2)_3]$, $\delta = 0.75$ mm/sec and $\Delta = 0.35$ mm/sec at 25° C. Error limits: +0.03 mm/sec for both δ and Δ.

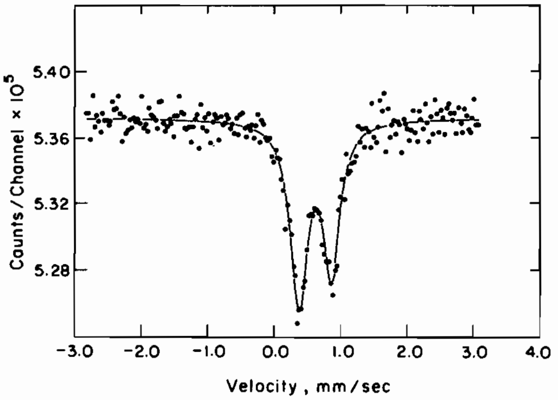

Figure 2. Mössbauer spectrum of $[Fe(c\text{-}Hx_2PS_2)_2I]$ at 298° K.

Mössbauer Data

The Mössbauer spectra at room temperature showed quadrupolar doublets with somewhat smaller splitting than in tris(dicyclohexyldithiophosphinato)iron(III), $[Fe(c\text{-}Hx_2PS_2)_3]$. The spectra were very similar to one another; the spectrum of $[Fe(c\text{-}Hx_2PS_2)_2I]$ is shown in Figure 2. Mössbauer data are given in Table IV. The asymmetry in the peaks might be due to relaxation and/or Goldanskii–Karyagin effects.

Discussion

As is the case with the dithiocarbamates,[3] halobis (dithiophosphinato)iron(III) complexes could be obtained from the reaction of a trisdithiophosphinate with halogen or hydrohalic acid or from the reaction of the dithiophosphinate anion with anhydrous iron(III) chloride or bromide in a 2:1 molar ratio. For the sake of convenience, the quantitative work on these bis complexes was done on the dicyclohexyldithiophosphinate derivative. Qualitative investigations indicated that tris(diphenyldithiophosphinato)iron(III) behaved entirely analogously, and that the halobis complexes were also formed from the reaction of the tris complex with mercuric chloride, alkylmercuric chloride or methyl iodide.

These $[Fe(c\text{-}Hx_2PS_2)_2X]$ complexes were rather different from the corresponding dithiocarbamates, $[Fe(R_2NCS_2)_2X]$, especially in regard to their magnetic and Mössbauer behavior. The halobisdithiocarbamates exist in an almost pure spin quartet ground state[2,3] and have moments of ~3.9 B.M. The halobisdicyclohexyldithiophosphinates have magnetic moments in solution only slightly lower than the purely high spin trisdicyclohexyldithiophosphinate. The decrease from the 5.9 B.M. expected for monomeric iron(III) could indicate some intermolecular association in solution, or a mixed spin state. Mixed spin states have been commonly invoked for other iron(III) complexes with sulfur-containing ligands, *e.g.* $[Fe(R_2NCS_2)_3]$[8] and $[Fe(Sdik)_3]$[9], where "Sdik" indicates a monothio-β-diketone anion.

The Mössbauer isomer shifts for $[Fe(c\text{-}Hx_2PS_2)_2X]$ complexes, +0.63 ± 0.03 mm/sec, were very close to the values for $[Fe(R_2NCS_2)_3]$[10], $[Fe(R_2NCS_2)_2X]$[11], $[Fe(R_2PS_2)_3]$[12], and $[Fe((RO)_2PS_2)_3]$[13] complexes. However, the quadrupole splittings, Δ, were very much smaller than those of $[Fe(R_2NCS_2)_2X]$, or the lower spin $[Fe(R_2NCS_2)_3]$ cases.

These small splittings, ~0.48 mm/sec, reflected the high spin nature of $[Fe(c\text{-}Hx_2PS_2)_2X]$, since the closer the approach to the spherically symmetric S-state iron(III) ion, the lower the expected splitting. For other high spin, tetragonal pyramidal five coordinated iron(III) complexes, Δ values at 298° K are 0.6–0.9 mm/sec for the hemin halides[14] and 0.9–1.0 mm/sec for chlorobis(diketonato)iron(III) complexes.[4,5]

There was little dependence of Δ on the halide X unlike the significant dependence found for the hemin halides[15,16] and the halobisdithiocarbamates.[11]

The P=S stretching band in the infrared is extremely variable both in intensity and position, and depends greatly upon the other groups attached to the phosphorus. A quoted range is 860–535 cm^{-1}; for P–S the range is 620–500 cm^{-1}.[17] The peak at 740–745 cm^{-1} in the halobisdicyclohexyldithiophosphinate spectra may be the $P\overset{\cdots}{—}S$ stretch, but this range seems very high for what is generally assumed to be nearly a single P–S bond. The $P\overset{\cdots}{—}S$ stretch might occur below 650 cm^{-1} for these complexes.

The electronic spectra of $[Fe(c\text{-}Hx_2PS_2)_3]$ and $[Fe(c\text{-}Hx_2PS_2)_2X]$ were very similar and resembled somewhat the spectra of the halobisdithiocarbamates. The peaks are due to charge transfer transitions which precluded the making of definite assignments.

Acknowledgement

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

References

1 Taken in part from the Ph.D. dissertation of R.Y. Saleh, University of Pittsburgh, 1974.
2 H.H. Wickman, A.M. Trozzolo, H.J. Williams, G.W. Hull and F.R. Merritt, *Phys. Rev., 155,* 563 (1966).
3 H.H. Wickman and A.M. Trozzolo, *Inorg. Chem., 7,* 63 (1968).
4 M. Cox, B.W. Fitzsimmons, A.W. Smith, L.F. Larkworthy and K.A. Rogers, *Chem. Commun.,* 183 (1969).
5 M. Cox, B.W. Fitzsimmons, A.W. Smith, L.F. Larkworthy and K.A. Rogers, *J. Chem. Soc. A,* 2158 (1971).
6 C. Maricondi, W. Swift and D.K. Straub, *J. Am. Chem. Soc., 91,* 5205 (1969).
7 D.F. Evans, *J. Chem. Soc.,* 2003 (1959).
8 R.L. Martin and A.H. White, *Trans. Metal Chem., 4,* 113 (1968).
9 M. Cox, J. Darken, B.W. Fitzsimmons, A.W. Smith, L.F. Larkworthy and K.A. Rogers, *Chem. Commun.* 105 (1970).
10 L.M. Epstein and D.K. Straub, *Inorg. Chem., 8,* 784 (1969).
11 L.M. Epstein and D.K. Straub, *ibid, 8,* 560 (1969).
12 P.M. Valov, S.V. Larionov, D.F. Kaplin and Yu.E. Razmakhnin, *Siberian Chem. J., 3,* 285 (1967).
13 L. Korecz, K. Burger and C.K. Jorgensen, *Helv. Chim. Acta, 51,* 211 (1968).
14 T.H. Moss, A.J. Bearden and W.S. Caughey, *J. Chem. Phys. 51,* 2624 (1969).
15 C. Maricondi, D.K. Straub and L.M. Epstein, *J. Am. Chem. Soc., 94,* 4157 (1972).
16 M.A. Torréns, D.K. Straub and L.M. Epstein, *ibid, 94,* 4162 (1972).
17 D.E.C. Corbridge, *Topics Phosphorus Chem., 6,* 235 (1969).