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Fe(II) and Cr(III) Complexes of 1,2-Bis(diphenylphosphino)ethane

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Complexes of Fe(II) and Cr(III) with 1,2-bis(diphenylphosphino)ethane (dpe) have been prepared and characterized. The Cr(III) species all have the general formulation $Cr(dpe)_{1.5}X_3$ *and are proposed to be binuclear with a bridging dpe. Two types of Fe(II) complexes were obtained,* $Fe(dpe)X_2$ *(X = Cl^- and Br^-) and diamagnetic* $Fe(dpe)_2(NCS)_2$.

The complexes have been characterized by infrared, electronic and Mössbauer spectra and by magnetic measurements.

Introduction

Complexes of 1,2-bis(diphenylphosphine)ethane (hereafter, dpe) with a wide variety of metal ions have been studied extensively.[2,3] Complexes of dpe with second and third row transition metals appear to be more common than those with first row transition metals. Within the 3*d* series, complexes in which the metal exhibits an unusually low oxidation state predominate.[2,3] In particular there appear to be no reports of well characterized complexes of dpe with the common ions Fe(II) and Cr(III). We wish to report here the preparation and characterization of three complexes of dpe with Fe(II) and four with Cr(III).

Experimental

$Fe(dpe)Cl_2$

Iron(II) chloride tetrahydrate (0.8 g) was dissolved in 50 ml of ethanol and added to 1.5 g of dpe dissolved in 150 ml of 1:1 acetone:ethanol. The light green precipitate which resulted was filtered, washed with acetone and vacuum dried. The compound was air stable when dry.

$Fe(dpe)Br_2 \cdot H_2O$

Iron(II) bromide (0.8 g) which had been dissolved in 50 ml of methanol and allowed to stand 24 hours over iron filings was mixed with 1.5 g of dpe in 100 ml of acetone. A yellow precipitate resulted which was filtered, washed with acetone and vacuum dried.

$Fe(dpe)_2(NCS)_2$

Barium thiocyanate was added to an equal molar amount of iron(II) sulfate in methanol. The $BaSO_4$ which formed was removed by filtration. The filtrate was added dropwise to an excess of dpe in methanol. The solution was refluxed for two hours and a light blue precipitate formed. The solution was filtered, the solid washed with methanol and vacuum dried.

$Cr(dpe)_{1.5}X_3 \cdot 2H_2O$ (X = Cl^- and Br^-)

Two mmol of the appropriate hydrated Cr(III) halide dissolved in 50 ml of isopropyl alcohol was added dropwise to 4 mmol of dpe dissolved in 100 ml of the alcohol. After approximately two hours a precipitate began to form. The solid was removed by filtration, washed with ethanol and vacuum dried.

$Cr(dpe)_{1.5}I_3 \cdot 4H_2O$ and $Cr(dpe)_{1.5}(NCS)_3$

Hydrated Cr(III) perchlorate (2 mmol) was dissolved in 50 ml of isopropyl alcohol and added dropwise to 4 mmol of dpe in 100 ml of alcohol. Three mmol of NaI or NaNCS was dissolved in 30 ml of alcohol and added to the solution which was refluxed for several hours. The resulting solid was filtered, washed and dried as above.

Analytical data for all of the compounds are given in Table I.

Physical Measurements

Infrared spectra were obtained using a Perkin–Elmer 521 grating spectrophotometer in Nujol and hexachlorobutadiene mulls. Mössbauer spectra were obtained using a constant acceleration spectrometer as previously described.[4] Electronic spectra were obtained in Kel-F mulls pressed between silica plates using a Cary Model 14 spectrophotometer. Magnetic data were obtained on a Faraday balance which has been described previously.[5] All microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

TABLE I. Analytical Data for Fe(II) and Cr(III) Complexes.

Compound	Analyses[a]				
	C	H	N	P	Metal
$Fe(dpe)Cl_2$	59.5(60.2)	4.6(4.4)	–	–	10.6(10.9)
$Fe(dpe)Br_2 \cdot H_2O$	49.4(48.6)	4.2(4.0)	–	–	8.8(8.7)
$Fe(dpe)_2(NCS)_2$	66.9(67.2)	5.0(5.0)	2.9(2.9)	–	–
$Cr(dpe)_{1.5}Cl_3 \cdot 2H_2O$	59.1(59.1)	5.1(4.8)	–	11.7(12.0)	6.6(6.4)
$Cr(dpe)_{1.5}Br_3 \cdot 2H_2O$	50.6(50.3)	4.4(4.2)	–	10.0(10.2)	5.6(5.7)
$Cr(dpe)_{1.5}I_3 \cdot 4H_2O$	42.5(41.4)	4.0(3.3)	–	8.4(8.4)	4.7(4.7)
$Cr(dpe)_{1.5}(NCS)_3$	60.6(61.1)	4.5(4.4)	5.2(5.2)	11.4(11.4)	6.4(5.8)

[a] Calculated (found).

Results and Discussion

Cr(III) Complexes

The unusual analytical data for the Cr(III) complexes suggest a number of possible formulations. Among the possibilities are: (a) $[Cr(dpe)_3][CrX_6]$, (b) $[Cr(dpe)_2X_2][Cr(dpe)X_4]$, (c) $[(dpe)X_3Cr(dpe)CrX_3(dpe)]$. There are also the many additional possibilities which involve the insertion of water into the coordination sphere with the removal of X or the formation of monodentate dpe ligands. The possibility of species with bridging X groups also exists. Based on the available data which are presented in part in Table II, formulation (c) involving a bridging dpe appears to be most likely. Such structures involving dpe have been confirmed for Cu(I),[6,7] but there have been no reports of dpe bridges in Cr(III).

The reasons for this conclusion are as follows. The compounds are extremely insoluble in both polar and non-polar solvents to the extent that solution spectra and conductivity data could not be obtained. This property suggests that ionic species are unlikely except for those involving highly charged ions such as (a). Molecular models indicate extreme steric hindrance to formation of a *tris* dpe species and the electronic spectra show no evidence of a CrX_6^{3-} species. In the electronic spectra, the first spin-allowed band for the three halide complexes is broadened but shows no sign of splitting, suggesting that all chromium ions have the same environment. Furthermore, the dependence of the electronic spectra on the nature of the anion shows clearly that the anion is coordinated, and the order of energies for the first band, $NCS > Cl^- > Br^- > I^-$ is as expected. The magnetic moments are essentially temperature invariant, a fact which argues against bridging anions, especially for the chloride and bromide.[8]

Finally, the infrared spectra indicate that all of the phosphorus atoms are coordinated. Carty[9] has shown that a band at 1090 cm^{-1} in dpe shifts to higher energies and increases in intensity on coordination through the phosphorus. Based on this assumption the infrared spectra indicate that all of the phosphorus atoms are coordinated.

Assuming the binuclear structure involving a bridging dpe ligand is correct, there are two possible isomers, *facial* and *peripheral.* Both the electronic and infrared spectra suggest the *peripheral* structure. As previously mentioned, the first spin allowed band in the electronic spectra of the halides is broadened, particularly in the

TABLE II. Magnetic and Spectral Data.

Compound	Magnetic Moment (B.M.)[a]	Band Energy (cm^{-1})[b]
$Fe(dpe)Cl_2$	5.54	7800 (broad)
$Fe(dpe)Br_2 \cdot H_2O$	5.45	5000
$Fe(dpe)_2(NCS)_2$	diamagnetic	12,100; 12,900; 17,500; 21,700
$Cr(dpe)_{1.5}Cl_3 \cdot 2H_2O$	3.84	15,400; 19,000(sh); 20,400
$Cr(dpe)_{1.5}Br_3 \cdot 2H_2O$	3.91	14,700; 18,400; 19,600(sh)
$Cr(dpe)_{1.5}I_3 \cdot 4H_2O$	3.92	13,700; 19,500 (broad)
$Cr(dpe)_{1.5}(NCS)_3$	3.78	18,200(sh); 20,400; 23,500

[a] At room temperature. All compounds show a small linear decrease in moment down to 20° K. [b] At 80° K.

bromide and iodide, and in the thiocyanate there is a clear splitting. Such an effect is predicted for the *peripheral* structure.[10] Furthermore, the infrared spectra of the thiocyanate shows two bands in the C–N stretching region at 2060 cm^{-1} and a second with one-half the intensity at 2090 cm^{-1}. These results are compatible with the *peripheral* structure because the single thiocyanate which is *trans* to the π-acceptor phosphorus should have the higher C–N stretching frequency due to less d-electron density in the π^*orbitals. The energies of the C–N bands also suggest N-coordination for the thiocyanate ligands.[11]

There are two additional pieces of information which are useful to derive from the electronic spectra. These are the ligand field strength and the nephelauxetic character of dpe. Although it was not possible to isolate $Cr(dpe)_3^{3+}$, an estimate of the ligand field strength of dpe can be obtained using the rule of average environment.[12] Using values of 13,700, 12,900 and 17,800 cm^{-1} for $10D_q$ for $CrCl_6^{3-}$, $CrBr_6^{3-}$ and $Cr(NCS)_6^{3-}$ respectively,[13,14] and 15,400, 14,700 and 18,300 cm^{-1} for the corresponding $10D_q$ values in $Cr(dpe)_{1.5}X_3$, one calculates $10D_q$ values for dpe of 17,100, 16,500 and 18,800 for an average of 17,500 cm^{-1}. These results suggest that the ligand field strength of dpe is similar to that of water.

From the data in Table II one can also get an estimate of the nephelauxetic effect of dpe. Because there is band splitting as a result of the low symmetry of the ligand field, precise band assignment and exact calculation of B is not possible. However, if one uses the simple assumption that the separation of the first two spin-allowed bands is 12B and makes extreme estimates of the magnitude of the difference in energy between the two bands, the largest B obtained is 440 cm^{-1} and most estimates of band positions give lower values. The second band in the iodide is not sufficiently well resolved to use for this calculation. One must therefore conclude that dpe is very high in the nephelauxetic series.

Fe(II) Complexes

Attempts to prepare dpe complexes with both Fe(II) and Fe(III) resulted in the formation of only three well characterized species, all of Fe(II). The compounds $Fe(dpe)Cl_2$ and $Fe(dpe)Br_2 \cdot H_2O$ are postulated to be tetrahedral or distorted tetrahedral species and the data support this conclusion. The magnetic moments and their temperature behavior are compatible with such a structure. The x-ray powder pattern of $Fe(dpe)Cl_2$ is identical with that of $Zn(dpe)Cl_2$ which has been reported, based on infrared studies, to be a distorted tetrahedron.[15] The electronic spectra of both show a single band in the near infrared region although the band in the chloride is very broad and may contain several unresolved components.

The value of 5000 cm^{-1} for the bromide is in agreement with the values found by Forster and Goodgame[16] for a series of complexes of general formula FeL_2Br_2. They found in each case a single band in the range 4600–5100 cm^{-1} although they concluded from the energies that the observed band was a result of a splitting of the ^5T state due to distortion from tetrahedral symmetry. Bertini and Mani[17] observed three bands in $Fe(Me_4pn)Br_2$ at 4600, 6400 and 7300 cm^{-1} which they interpreted in a similar fashion. The larger value (and the broader band) which we observe in the chloride is probably due to a larger field strength as well as greater distortion. Support for the large distortion in the chloride may be found in the Mössbauer spectrum.

The isomer shift relative to iron foil for the chloride is 0.64 (0.67) and the quadrupole splitting 2.53 (2.57) mm/sec at room temperature (80° K). A low value of the isomer shift for high spin Fe(II) is typical for species with low coordination number, although this value is much lower than that reported for most tetrahedral species.[18] The lack of temperature dependence of the quadrupole splitting is indicative of a large distortion from tetrahedral symmetry. This distortion is probably the explanation of the higher energy electronic band in the chloride, the bromide presumably being more regularly tetrahedral as a result of the larger anion size. Unfortunately we were unable to get good Mössbauer spectra for the bromide because of a high non-resonant absorption.

The compound $Fe(dpe)_2(NCS)_2$ is clearly best described as a six coordinate low spin species. Both the magnetic and Mössbauer data (isomer shift, 0.33, and quadrupole splitting, 0.35) confirm this assignment. The fact that the relatively weak field dpe can lead to spin pairing is probably a consequence of its high nephelauxetic character as discussed above. The electronic spectrum taken in mulls revealed several bands, but as no extinction coefficient could be obtained no assignment of the bands will be attempted. The infrared spectrum shows two peaks in the thiocyanate C–N region at 2100 and 2110 cm^{-1}. Bands at these energies suggest sulfur bonded groups, but a clear distinction cannot be made[11] on this band alone and the C–S stretch and bending modes were not identifiable due to the complexity of the spectrum. One expects N-bonding to Fe(II) although the π-accepting behavior of dpe may favor S-coordination. Molecular models indicate a *trans* configuration would be favored over the *cis* structure and the splitting of the band is probably due to crystal effects.

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