to preclude the formation of $[Ni(mepic)_3](ClO_4)_2$.[45] Thus the phenyl substituents of 6PAP must contribute significantly to steric interactions within its complexes, even precluding the formation of $M(6PAP)_3{}^{2+}$. The formation of $[Ni(6PAP)_2](ClO_4)_2$ (square planar), rather than the octahedral analog of $[Ni(mepic)_2(H_2O)_2](ClO_4)_2$,[45] also appears to be due to steric crowding at the axial positions by the phenyl groups.

The compound $Ni(6PAP)Cl_2$ is insoluble, with a reflectance spectrum (Table IV) and a magnetic moment (3.12 BM) indicative of an octahedral configuration, presumably achieved in a chloro-bridged polymeric structure, with 6PAP as a bidentate ligand. Corresponding five-membered chelate complexes $NiLX_2$ are paramagnetic for L = *o*-(dimethylamino)phenylenediphenylphosphine[11a] (mixed PN donor sites, Figure 3, VIII) and for L = 2,2'-bipyridine[40b] (two equivalent N donor sites), but for L = *cis*-1,2-bis(diphenylphosphino)ethylene[3a] or 1,2-bis(diphenylphosphino)ethane[3c] (two equivalent P donor sites in both cases) the complexes are diamagnetic and planar. Thus the P–N donor set is akin to an N–N rather than a P–P combination in these five-membered chelate systems.

The blue compound $[Co(6PAP)_2](ClO_4)_2 \cdot 5H_2O$ has a magnetic moment and a reflectance spectrum characteristic of tetrahedral Co(II),[21] the preferred structure for four-coordinate cobalt and one in which the interaction of the two 6-methyl groups of the chelating ligands is minimized. The complex $Co(6PAP)Cl_2$ (deep green),

(45) S. Utsuno, *J. Inorg. Nucl. Chem.*, **32**, 1631 (1970).

a nonelectrolyte in nitromethane, has similar magnetic and electronic absorption properties and hence a structure very similar to that of $[Co(6PAP)_2](ClO_4)_2$. In the spectrum, however, corresponding transitions appear at slightly lower energies, in keeping with a lowering of the field strength on replacing the chelating donor set P–N (*i.e.*, 6PAP) by two chloro groups. Unlike $Co(4PAP)Cl_2$, the 6PAP analog is monomeric in solution, implying chelation by 6PAP across two apices of the tetrahedron.

Other Complexes.—The complexes obtained with 4PAP or 6PAP and Pd(II), Hg(II), and Ag(I), indicate the affinity of the phosphinoaminopyridine type of ligand for "soft," as well as "hard," metal ion acceptors. An interesting comparison with *N,N*-dimethyl-*N'*-diphenylphosphinohydrazine (DPH) shows that, where $Pd(DPH)_2Cl_2$ is readily formed,[23c] the corresponding analogs with 4PAP and 6PAP are not obtained. It appears likely that the complexes Pd(4- or 6-PAP)Cl₂ contain relatively stable five-membered ring systems, whereas the strained, four-membered chelate ring system of $Pd(DPH)Cl_2$ is readily converted to $Pd(DPH)_2Cl_2$, containing monodentate ligands, by reaction with a second mole of DPH. Structural studies on these systems are in progress.

Contribution from the Department of Chemistry,
Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Transition Metal Complexes of 1,10-Phenanthroline and 2,2'-Bipyridine

By L. H. BERKA,*[1] R. R. GAGNE, G. E. PHILIPPON, and C. E. WHEELER

Four unique groups of powder pattern have been obtained corresponding to $[M(bipy)_2X_2]Y \cdot nH_2O$, $[M(phen)_2(H_2O)_2]Y_3 \cdot nH_2O$, and $[M(phen)_2X_2]Y \cdot nH_2O$ (two sets), with phen = 1,10-phenanthroline; bipy = 2,2'-bipyridine; M = Co, Cr, Rh, and Ir; X = Cl and Br; Y = Cl, Br, and NO_3; and *n* variable. The cations of all these compounds are formulated as the cis isomers, with the latter two groups corresponding to two crystal forms. *cis*-$[Ir(phen)_2Cl_2]Cl \cdot 3H_2O$, crystal form A, and *cis*-$[Ir(phen)_2Cl_2]Cl \cdot 2H_2O$, crystal form B, have been prepared in this work and the facile conversion of the A to the B form by rapid recrystallization has been demonstrated. Previous evidence for the nonexistence of trans cations and existence of polymorphism in these systems is augmented and confirmed.

Introduction

The cis–trans isomeric configurations of complexes of the type $[M(NN)_2X_2]Yy$, where NN = 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy), have been assigned by various methods, including, color,[2,3] solu-

bility,[3] acid adduct formation,[4] and infrared,[5,6] visible-ultraviolet,[7] and nuclear magnetic resonance[8,9] spec-

(1) To whom correspondence should be addressed.

(2) P. Pfeiffer and B. Werdelmann, *Z. Anorg. Allg. Chem.*, **263**, 31 (1950).

(3) B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.*, **26**, 47 (1964).

(4) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1640 (1964).

(5) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).

(6) W. R. McWhinnie, *ibid.*, **26**, 15 (1964).

(7) R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1951 (1965).

(8) J. D. Miller and R. H. Prince, *ibid.*, A, 520 (1969).

(9) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, **8**, 2517 (1969).

troscopy. Unfortunately, all of these techniques require a pair of complexes, believed to be isomers, to yield worthwhile information. In several cases compounds which were used to "prove" the validity of a given method have been shown by others to be invalid specimens. For example, "*trans*-[Co(bipy)₂Cl₂]Cl" in ref 6 has been shown[10] to be a mixture of the cis and tris cations with CoCl₄²⁻ and Cl⁻ anions. We have found[11] that *trans*-[Co(phen)₂Cl₂]Cl·2HCl in ref 2 is instead [Co(phen)₃]₂[CoCl₄]₃·2HCl and the adduct in ref 8 interpreted to contain the same trans cation by nmr is instead *cis*-[Co(phen)₂Cl₂][Co(phen)₃]-[CoCl₄]₂·3H₂O. As a result there has been considerable confusion about and discussion[12] of the configuration of several such compounds.

The compound *cis*-[Co(phen)₂Cl₂]Cl·3H₂O is the only one of this type for which the structure has been assigned by single-crystal X-ray analysis.[13] In these laboratories we had prepared two iridium compounds with stoichiometry [Ir(phen)₂Cl₂]Cl·nH₂O, with one of these materials having a powder pattern virtually identical with that of *cis*-[Co(phen)₂Cl₂]Cl·3H₂O and the other having a powder pattern virtually identical with that published[14] for [Ir(phen)₂Cl]Cl·3H₂O. To elucidate the structures of these two Ir compounds further we compared these powder patterns to those of several other analogous compounds given previously in the literature. Our results below show that compounds of the type [M(phen)₂X₂]Y·nH₂O give two unique groups of patterns. While one might assume that these two groups correspond to cis cations in one group and trans cations in the other, we present further support for the recent suggestion and evidence[15] of polymorphism in this system.

Experimental Section

Materials.—These were commercially obtained reagent grade chemicals and used without further purification.

Apparatus and Analyses.—X-Ray powder patterns were obtained using nickel-filtered copper radiation and a Philips, Debye–Scherrer 11.459-cm powder camera. *d*-Spacing calculations are based on Cu K$\bar{\alpha}$ with λ 1.5418 Å. An internal standard was not used in obtaining our powder patterns. Infrared spectra were taken in the region 4000–625 cm⁻¹ with a Perkin-Elmer 257 instrument as KBr pellets and in the region 4000–300 cm⁻¹ with a Perkin-Elmer 521 instrument (courtesy of A. J. Maeland) as mulls between CsBr plates. Solution conductivities were measured using a Yellow Springs Instrument Bridge, Model 31. Elemental analyses were performed by Baron Consulting Co., Orange, Conn.

Preparation of Cobalt Compounds.—The following compounds were prepared without difficulty by known methods: *cis*-[Co(phen)₂Cl₂]Cl·3H₂O,[16] *cis*-[Co(phen)₂Br₂]Br·3H₂O,[17] *cis*-[Co(bipy)₂Cl₂]Cl·3H₂O,[18] *cis*-[Co(bipy)₂Br₂]Br,[18] and *cis*-[Co(phen)₂(H₂O)₂](NO₃)₃·2H₂O.[16] *cis*-[Co(phen)₂Cl₂]NO₃·3H₂O

was obtained by addition of a concentrated solution of ammonium nitrate to a concentrated solution of the chloride salt in ethanol until precipitation was complete. The product was isolated, washed with water, ethanol, and ether, and air dried.

Preparation of Chromium Compounds. *cis*-[Cr(phen)₂Cl₂]-Cl·1.5H₂O, **Crystal Form B.**—This compound was prepared several times by the literature method.[2] The dull green color of the complex was not uniform in these preparations and seemed to be a mixture of compounds. This latter conclusion was drawn from a visual qualitative comparison of the powder pattern films of the green product with those of the two pure forms of *cis*-[Ir(phen)₂Cl₂]Cl·nH₂O described below. Using this as a criterion a pure form was isolated on occasion and gave the *d* values listed in Table IV. Recrystallization from water yielded a brown material which had identical *d* values. The pure form was also obtained by a method similar to that used for the corresponding bipy complex below. Anhydrous chromic chloride (1.5 g) and phen (5.4 g in 50 ml of ethanol) were mixed and heated to boiling after the addition of a trace of zinc dust. The resulting deep brown solution was boiled for 10 min and dark brown crystals resulted on cooling. These crystals were isolated and recrystallized from water. *Anal.* Calcd for C₂₄H₁₉Cl₃-CrN₄O₁.₅: C, 52.81; H, 3.51; Cl, 19.49; N, 10.27. Found: C, 53.17; H, 3.59; Cl, 19.26; N, 10.31. An aqueous solution (10⁻³ M) of the material gave a conductance of 115 ohm⁻¹ cm² mol⁻¹.

cis-[Cr(bipy)₂Cl₂]Cl·2H₂O.—This compound was prepared several times by the published procedure[19] with analogous results. *Anal.* Calcd for C₂₀H₂₀Cl₃CrN₄O₂: C, 47.40; H, 3.98; Cl, 20.99; N, 11.06. Found: C, 47.77; H, 4.16; Cl, 19.41; N, 11.06.

cis-[Cr(phen)₂(H₂O)₂](NO₃)₃·1.5H₂O.—This compound was prepared by published methods.[20] *Anal.* Calcd for C₂₄H₂₃-CrN₇O₁₂.₅: C, 43.58; H, 3.50; N, 14.82. Found (product reported as the cis isomer in ref 20a): C, 43.90; H, 3.48; N, 14.78; Λ = 522 ohm⁻¹ cm² mol⁻¹. Found (product reported as the trans isomer in ref 20b): C, 43.07; H, 3.55; N, 14.56; Λ = 517 ohm⁻¹ cm² mol⁻¹.

Preparation of Iridium Compounds. *cis*-[Ir(phen)₂Cl₂]Cl·3H₂O, **Crystal Form A.**—Ammonium hexachloroiridate(IV) (2.69 g) and phen (6.7 g) were ground together, sealed in a test tube, and heated at 190° for 19 hr. The cooled tube was crushed and boiled in 80 ml of water for 10 min; the resulting red solution was filtered hot, evaporated with heat to 20 ml, and cooled overnight. The residue was extracted twice more with 50 ml of water and once with 40 ml of methanol in a similar manner. These latter extracts were combined and likewise evaporated to 20 ml and cooled overnight. The two resulting yellow products were combined, isolated, washed with cold water, methanol, and ether, and air dried; yield, 3.6 g, 83%. *Anal.* Calcd for C₂₄H₂₂Cl₃IrN₄O₃: C, 40.43; H, 3.11; Cl, 14.92; N, 7.86. Found: C, 39.74; H, 2.88; Cl, 14.90; N, 7.64; Λ = 105 ohm⁻¹ cm² mol⁻¹.

The same product was prepared using ammonium hexachloroiridate(III), though mixtures of forms A and B sometimes resulted as determined by qualitative visual inspection of powder pattern films of the products and those of the pure forms.

cis-[Ir(phen)₂Cl₂]Cl·2H₂O, **Crystal Form B.**—This compound was prepared by two routes. The first is the fusion process. (NH₄)₂IrCl₆ (0.6 g) and phen (1.5 g) were ground together, sealed in a test tube, and heated at 195° for 19 hr. The cooled tube was crushed and added to 20 ml of hot water. The mixture was stirred briefly, the extract filtered off, and the filtrate cooled. The resulting yellow solid was filtered off, washed twice with acetone, and air dried; yield, 0.5 g, 53%. *Anal.* Calcd for C₂₄H₂₀Cl₃IrN₄O₂: C, 41.48; H, 2.90; Cl, 15.30; N, 8.06. Found: C, 41.17; H, 2.85; Cl, 15.70; N, 8.24; Λ = 113 ohm⁻¹ cm² mol⁻¹. A reflux process was the second type of preparation used. Phen (0.6 g) was dissolved in 40 ml of hot

(10) F. Aprile, M. Lederer, and F. Maspero, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, **36**, 70 (1964).

(11) L. H. Berka and R. R. Gagne, *Inorg. Chem.*, **9**, 1278 (1970).

(12) J. V. Rund, *ibid.*, **7**, 24 (1968).

(13) A. V. Ablov, A. Yu Kon, and T. I. Malinovskii, *Dokl. Akad. Nauk SSSR*, **167**, 1051 (1966).

(14) R. D. Gillard and B. T. Heaton, *J. Chem. Soc. A*, 451 (1969).

(15) J. G. Gibson and E. D. McKenzie, *ibid., A*, 2637 (1969).

(16) A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).

(17) A. V. Ablov and D. M. Palade, *ibid.*, **6**, 306 (1961).

(18) A. A. Vlcek, *Inorg. Chem.*, **6**, 1425 (1967).

(19) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(20) (a) R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, **15**, 62 (1961); (b) R. G. Inskeep and M. Benson, *J. Inorg. Nucl. Chem.*, **20**, 290 (1961).

TABLE I
d Spacings (Å) for Complexes of the Type cis-[M(bipy)$_2$X$_2$]Y·nH$_2$O

M	Co	Co	Cr	Ir [a]	Ir [b]	Ir [b]	Rh [b]	Rh [b]
X	Cl	Br	Cl	Cl	Cl	Br	Cl	Br
Y	Cl	Br	Cl	Cl	Cl	Br	Cl	Br
n	3	0	2	1	2	3	2	2
	12.74 vs	12.81 vs	12.99 vs	12.80 vs	12.9 vs	12.9 vs	12.9 vs	12.9 vs
	8.84 vs	8.95 vs	8.94 vs	8.90 vs	9.02 vs	9.02 vs	8.93 vs	8.93 vs
	6.90 vs	7.00 vs	6.91 vs	6.91 vs	6.96 m	7.07 m		7.07 m
						6.80 w	6.85 m	
	6.51 vw	6.49 vw	6.56 vw	6.50 m	6.55 w	6.51 w	6.51 w	
	5.96 s	6.07 s	5.97 s	5.91 s	5.90 s	6.23 s	6.06 w	6.15 w
						6.02 w		
	5.80 s	5.75 s	5.79 s	5.75 s	5.78 s	5.78 s	5.82 s	5.78 s
	5.54 w		5.57 w	5.54 w				
	5.25 w	5.29 m	5.29 w	5.27 m	5.32 m	5.37 m	5.24 m	5.27 m
	4.65 m	4.80 m	4.69 m	4.95 w	4.98 m	4.98 m	4.93 m	
	4.48 vw	4.51 vw	4.40 vw	4.67 s	4.50 w	4.79 m	4.79 w	
	4.18 w	4.23 w	4.23 m	4.22 m	4.23 m	4.27 m	4.23 m	4.26 m
				4.08 w	4.11 w	4.11 w		
	3.92 vs	3.94 vs	3.95 vs	3.94 s	3.93 s	4.00 s	3.91 s	3.93 s
	3.76 s	3.80 vs	3.79 vs	3.79 s	3.78 s	3.86 s	3.78 s	3.83 s

[a] Prepared by reflux procedure, this work.   [b] Data from ref 14.

water containing 2 drops of 10 *N* HCl. To this solution was added a solution containing (NH$_4$)$_3$IrCl$_6$ (0.5 g) in 20 ml of hot water. The solution turned rapidly from dark brown to orange and then slowly to yellow as it was refluxed for a two-week period. The solution was then filtered hot and the filtrate was cooled overnight. The resulting yellow crystals were filtered and washed with ice water and acetone and air dried; yield, 0.3 g. Found: C, 41.26; H, 2.84; Cl, 15.03; N, 8.13.

Infrared Spectra.—The two crystal forms of [Ir(phen)$_2$Cl$_2$]-Cl·nH$_2$O gave identical spectra in the 4000–300-cm^{-1} region, including two strong bonds at 308 and 333 cm^{-1}.

Crystal Form Conversion.—A sample of [Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O, crystal form A (0.7 g), was added to 5 ml of hot water; the mixture was swirled and filtered immediately by suction into a test tube placed in an ice–salt bath. The resulting crystals were isolated by filtration and air dried. The total time elapsed between addition to the water and isolation was 2 min or less, with formation of crystals noted after 45 sec. The recovered solid gave a powder pattern that was virtually identical with that of the analogous compound, crystal form B. Observed *d* spacings (Å): 14.49 (s), 11.24 (vs), 9.49 (s), 8.59 (vs), 7.49 (w),

TABLE II
d Spacings (Å) for Complexes of the Type cis-[M(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·nH$_2$O

M	Co	Cr [a]	Cr [b]	Ir [c]
n	2	1.5	1.5	3
	9.41 vs	9.21 vs	9.34 vs	9.39 vs
	8.72 vs	8.81 vs	8.78 vs	8.79 vs
	8.19 m	8.16 m	8.16 m	8.27 m
	7.06 m	7.12 s	7.06 m	7.11 s
	6.13 vs	6.18 vs	6.11 vs	6.08 vs
	5.64 w			5.45 w
	4.71 m	4.71 m	4.65 m	4.71 m
	4.20 vs	4.20 vs	4.19 vs	4.19 vs
	3.83 s	3.83 s	3.82 s	3.80 s
	3.47 w	3.47 w	3.47 w	3.47 w
	3.27 m	3.29 m	3.29 m	3.27 m
	3.16 w	3.17 w	3.17 w	
	2.93 w	2.94 w	2.93 w	2.93 w
	2.73 w	2.73 w	2.73 w	2.74 m
	2.55 w	2.50 m	2.55 w	2.55 w
	2.43 w	2.44 m	2.45 w	2.43 m

[a] Assigned cis in ref 20.   [b] Assigned trans in ref 20.   [c] Prepared in ref 21.

TABLE III
d Spacings (Å) for Complexes of the Type cis-[M(phen)$_2$X$_2$]Y·nH$_2$O, Crystal Form A

M	Co	Co	Co	Ir [a]
X	Cl	Cl	Br	Cl
Y	Cl	NO$_3$	Br	Cl
n	3	3	3	3
	10.17 w	10.24 w	10.17 w	10.24 w
	8.24 vs	8.27 vs	8.34 vs	8.31 vs
				7.87 s
	7.54 s	7.63 s	7.54 s	7.48 s
	6.76 s	6.76 s	6.84 s	6.74 s
	6.19 vw			6.13 vw
	5.91 w	5.97 w	5.97 w	5.87 w
	5.20 vw	5.20 vw	5.27 w	5.29 w
	5.04 w	4.98 w	5.04 w	5.10 w
	4.76 w	4.72 w	4.74 vw	4.87 w
	4.51 w	4.51 w	4.55 w	4.54 w
	3.94 m	3.93 m	3.98 w	3.95 m
	3.69 m	3.61 w	3.66 w	3.66 w
	3.35 vs	3.36 vs	3.39 vs	3.40 vs
	3.04 vw	2.99 vw	3.06 vw	3.03 vw
	2.84 vw	2.87 vw	2.82 vw	2.85 vw
		2.68 vw	2.63 vw	2.69 vw
	2.52 m	2.53 m	2.55 w	2.57 m
	2.42 w	2.42 w	2.44 w	2.45 w
	2.32 w	2.30 w	2.33 vw	2.29 vw

[a] Prepared by fusion procedure, this work.

6.70 (vs), 6.30 (w), 5.92 (s), 5.45 (s), 5.13 (w), 4.73 (w), 4.45 (s), 4.27 (m), 3.87 (w), 3.72 (w), 3.55 (s), 3.12 (m), 2.96 (w).

cis-[Ir(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·3H$_2$O.—The preparation of this compound is described elsewhere.[21]

cis-[Ir(bipy)$_2$Cl$_2$]Cl·nH$_2$O.—Compounds having this general formula gave identical powder patterns, whether prepared by fusion or reflux procedures analogous to those used for the Ir-phen compounds described above. *Anal.* Calcd for reflux product, C$_{20}$H$_{18}$Cl$_3$IrN$_4$O: C, 38.19; H, 2.88; Cl, 16.91; N, 8.91. Found: C, 38.42; H, 3.19; Cl, 16.87; N, 8.82.

X-Ray Powder Patterns.—Measured *d* spacings for the compounds prepared in this study are given in Tables I–IV. Several of the dihalogeno compounds were dried in an oven at 120° for varying lengths of time and the resulting *d* spacings were identical with those values listed in the tables for the corresponding hydrated compounds.

(21) L. H. Berka and G. E. Philippon, *J. Inorg. Nucl. Chem.*, in press.

TABLE IV

d SPACINGS (Å) FOR COMPLEXES OF THE TYPE
cis-[M(phen)$_2$X$_2$]Y·nH$_2$O, CRYSTAL FORM B

	a	b	c	c	c	c
M Cr	Ir	Ir	Ir	Rh	Rh	Ir
X Cl	Cl	Cl	Cl	Cl	Br	Br
Y Cl	Cl	Cl	Cl	Cl	Br	Br
n 1.5	2	2	3	3	2	2
14.63 s	14.74 s	14.30 s	14.64 s	14.64 s	14.66 s	14.72 s
11.19 s	11.27 vs	11.21 vs	11.18 s	11.18 s	11.24 s	11.46 s
9.47 s	9.51 s	9.46 s	9.40 s	9.40 s	9.40 s	9.40 s
8.51 s	8.58 vs	8.55 s	8.50 s	8.42 s	8.50 s	8.83 s
7.38 w	7.50 w	7.41 vw	7.43 w	7.49 w	7.46 w	7.43 w
6.76 vs	6.69 vs	6.68 vs	6.75 vs	6.75 vs	6.75 vs	6.85 vs
6.31 w	6.32 w		6.27 w	6.27 w	6.27 w	6.19 w
5.94 m	5.93 s	5.91 s	5.94 s	5.94 s	5.94 s	5.94 s
5.51 s	5.44 m	5.44 m	5.47 m	5.47 m	5.47 m	5.53 m
	5.14 w	5.08 w	5.15 w	5.15 w	5.12 w	5.21 w
4.72 m	4.74 m	4.71 w	4.72 w	4.72 w	4.74 w	4.74 w
4.43 s	4.45 s	4.44 m	4.43 m	4.43 m	4.43 m	4.46 m
4.24 s	4.27 m	4.22 m	4.23 m	4.21 m	4.25 m	4.30 m
3.86 m	3.88 w	3.86 w	3.86 w	3.84 w	3.86 w	3.91 w
	3.73 w	3.71 w	3.69 w	3.72 w	3.72 w	3.72 w
3.56 s	3.57 s	3.54 s	3.54 s	3.54 s	3.54 s	3.56 s
3.15 s	3.14 m	3.14 s	3.14 s	3.14 s	3.16 s	3.18 s
2.94 w	2.96 w	2.95 w	2.95 w	2.93 w	2.93 w	2.88 w

[a] Prepared by fusion procedure, this work. [b] Prepared by reflux procedure, this work. [c] Data from ref 14.

Results

General Data.—The powder patterns of the compounds prepared in this study and those published in ref 14 fall into four distinct groups corresponding to [M(bipy)$_2$X$_2$]Y·nH$_2$O (Table I), [M(phen)$_2$(H$_2$O)$_2$]-Y$_3$·nH$_2$O (Table II), and [M(phen)$_2$X$_2$]Y·nH$_2$O (Tables III and IV). Within each group the effects of changes in the central metal atom, M, the unidentate ligand, X, the counterion, Y, and the amount of lattice water, n, on the d spacings are small and can be attributed to changes in the size of the ions involved. The similarity in relative intensities of lines within a given group indicates similar molecular packing in the crystal. The differences among the groups are significant.

It would be expected that a change in isomeric configuration in the cation would lead to different powder patterns due to different packing of the cis and trans isomers, and, hence, the compounds within each group have the same configuration. The compound [Co(bipy)$_2$Cl$_2$]Cl·3H$_2$O in Table I was prepared by a route analogous to that for the known cis-[Co(phen)$_2$Cl$_2$]Cl·3H$_2$O. The compound [Co(phen)$_2$-(H$_2$O)$_2$](NO$_3$)$_3$·2H$_2$O in Table II was prepared by gentle treatment of this same cis Co compound, for which the powder pattern is given in Table III. Hence, by relating the compounds in Tables I–III to cis-[Co(phen)$_2$Cl$_2$]Cl·3H$_2$O, the cations in all these compounds are assigned the cis configuration.

The differences in powder patterns between the compounds in Tables III and IV are consistent with a trans configuration for the cations of the latter group. *However*, in view of the general inertness of Ir(III) systems and the facile and rapid conversion of our Ir fusion product in Table III to a new product having the powder pattern in Table IV, conversion to the trans configuration is ruled out. This conversion is readily acceptable in terms of a change in crystal habit, and, hence, we assign the cis configuration to

this fourth group as well. This assignment is supported by the equivalent infrared spectra obtained for the two crystal forms of [Ir(phen)$_2$Cl$_2$]Cl·nH$_2$O and the presence of two bands in the Ir–Cl stretching region at 308 and 333 cm^{-1}.

Specific Assignments. 1. cis-[Cr(bipy)$_2$Cl$_2$]Cl·2H$_2$O. —The trans assignment[22] by infrared spectroscopy[6] (*vide infra*) is not confirmed.

2. cis-[Cr(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$·1.5H$_2$O.—The original report[20] of two isomeric compounds having this formulation is not confirmed. Rather, the published procedures both give the same cis product.

3. cis-[Cr(phen)$_2$Cl$_2$]Cl·1.5H$_2$O, Crystal Form B.— The published preparative procedure for this compound[2] gives a green product consisting of a mixture of crystal forms A and B. The pure B form has been obtained by further work-up and another route as a brown compound.

4. cis-[Rh(bipy)$_2$Cl$_2$]Cl·2H$_2$O.—This compound was originally assigned the cis configuration on the basis of its infrared spectrum.[5] Later the trans assignment was made on the basis of acid adduct formation[4] and electronic spectrum.[7]

5. cis-[Rh(phen)$_2$Cl$_2$]Cl·3H$_2$O, Crystal Form B.— The original trans assignment using the electronic spectrum[7] is not confirmed.

6. Two Compounds Containing the cis-Ir(phen)$_2$Cl$_2$$^+$ **Cation.**—cis-[Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O, crystal form A, was prepared by a "large-scale" fusion of a mixture of (NH$_4$)$_2$IrCl$_6$ and phen, and cis-[Ir(phen)$_2$Cl$_2$]Cl·2H$_2$O, crystal form B, was prepared by either a "small-scale" fusion of (NH$_4$)$_2$IrCl$_6$ and phen or 2-week reflux of an aqueous mixture of (NH$_4$)$_3$IrCl$_6$ and phen. Form A is readily converted to form B by a very rapid recrystallization. Form B appears in ref 14.

7. cis-[Ir(bipy)$_2$Cl$_2$]Cl·nH$_2$O.—Both fusion and reflux reactions give only one crystal form.

Discussion

A comparison of powder patterns shows that our compounds cis-[M(phen)$_2$Cl$_2$]Cl·nH$_2$O, crystal forms A and B, correspond to the α and ϵ forms, respectively, given in ref 15 for identical or analogous Co and Cr compounds. In the latter reference it is not clear from the experimental details whether the authors followed preparative procedures given previously in the literature. Our compounds were made following published procedures whenever possible and exceptions are noted.

In the III oxidation state Ir compounds are known to be much more inert than analogous compounds of Co and Cr. Thus, our conversion of one form of [Ir(phen)$_2$Cl$_2$]Cl·nH$_2$O to another provides a more conclusive example in support of polymorphism than those given in ref 15.

The previous infrared criterion for assignment of configuration[5,6] was restricted to bipy complexes and consisted of a split in a band at about 755 cm^{-1} and complexity in the 700–800-cm^{-1} region of the spectrum

(22) W. A. Baker and M. G. Phillips, *Inorg. Chem.*, **5**, 1042 (1966).

DIFLUOROPHOSPHINE OXIDE

being characteristic of *cis*-M(bipy)$_2$X$_2$$^+$ and a single band or lack of complexity being characteristic of the trans isomer. As shown in the Results, this criterion has given incorrect assignments. It is probable that the differences observed in this region result from specific crystal-packing effects. Solution infrared spectra of these compounds, which would eliminate these effects, cannot be obtained due to low solubilities in appropriate solvents.

The orginal cis assignment[3] of [Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O prepared by a fusion process was confirmed by optical resolution work.[23] However, Gillard and Heaton[14] were not able to effect resolution using the same resolving agent on their analogous product. The later compound is assigned the cis configuration on the basis of its published powder pattern (Table IV) and our analysis here. Apparently experimental difficulties account for the unsuccessful resolution.

The insensitivity of the powder patterns of bis-phen and bis-bipy complexes to M, X, Y, and *n* is probably due to the bulkiness of the bidentate nitrogen ligands. The principal groups controlling the crystal packing are the phen and bipy ligands and not the comparatively small halogen and nitrate ions or water. This empirical observation may be quite useful in assigning configurations to more complicated systems.

The work reported here points out the problems inherent in assigning structures to analogous systems. Techniques, such as infrared and visible–ultraviolet spectroscopy, may work well in one system (ethylenediamine) and not in another (bipy). Application of these methods, proven in simple systems, to complex molecules of biochemical interest must be done with caution.

(23) J. A. Broomhead and W. Grumley, *J. Inorg. Nucl. Chem.*, **29**, 2126 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

Fluorophosphine Ligands. VIII. The Chemistry of Difluorophosphine Oxide

BY LOUIS F. CENTOFANTI AND ROBERT W. PARRY*

F$_2$POPF$_2$ has been found to interact with amines and alcohols in a two-step process. The reaction with amines gives PF$_3$, PF$_2$NR$_2$, and NR$_2$H$_2$HFPO$_2$ and with alcohols gives PF$_3$, HFPO$_2$R, and HFPO$_2$R. The reaction of F$_2$POPF$_2$ with N$_2$F$_4$ gives N$_2$, PF$_5$, PF$_3$O, and colored products. PF$_2$HO has been found to react with amines to give PF$_3$ and NR$_{4-x}$H$_x$$^+$HFPO$_2$$^-$, with PF$_2$OR to give PFHO$_2R, PF_3$, and HFPO$_2$H, with PF$_2$N(CH$_3$)$_2$ to give PF$_3$, PF$_2$OPF$_2$, and N(CH$_3$)$_2$H$_2$$^+$HFPO$_2$$^-$, and with BF$_3$ to give a weakly bonded adduct PF$_2$HOBF$_3$. PF$_2$HOBF$_3$ is observed to decompose to BF$_3$ and HFPO$_2$HBF$_3$. No reaction is observed between B$_2$H$_6$ and PF$_2$HO. A mechanism for the various reactions is discussed and explained in terms of association found in PF$_2$HO.

Introduction

Difluorophosphine oxide was first observed by Treichel, Goodrich, and Pierce in the decomposition of HPF$_4$.[1] Charlton and Cavell[2] and Centofanti and Parry[3] were able to prepare the compound in significant enough quantity to characterize the molecule. Difluorophosphine oxide is rather unstable as a liquid and undergoes complete decomposition in about 2 hr.[3] It is believed[4] that this decomposition results from association found in the condensed phases. Investigation of the chemistry of PF$_2$HO has shown that PF$_2$HO is a very reactive molecule. The work is described herein.

Discussion

1. Reaction of HX (X = OR, NR$_2$, etc.) with F$_2$POPF.—It was thought that the reaction of F$_2$POPF$_2$ with various proton sources should result in the preparation of PF$_2$HO and PF$_2$X, by a reaction similar to that observed with HBr: PF$_2$OPF$_2$ + HBr → PF$_2$HO + PF$_2$Br. The general reaction would then be PF$_2$OPF$_2$ + HX → PF$_2$HO + PF$_2$X.

Two proton sources were studied. In both cases the results can be explained in terms of the general reaction given above, followed by a second reaction between PF$_2$HO and PF$_2$X.

(1) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).
(2) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).
(3) L. F. Centofanti and R. W. Parry, *ibid.*, **7**, 1005 (1968).
(4) L. F. Centofanti and R. W. Parry, *ibid.*, **9**, 744 (1970).