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Dimethylaminodifluorophosphine Complexes of Cobalt(II) Halides

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It has been demonstrated that the ligand dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, will form coordination compounds with metal carbonyls such as $Ni(CO)_4$ and $Mo(CO)_6$ by displacement of carbon monoxide.[1] It has also been reported that the ligand will form complexes with CuCl.[2] In these complexes phosphorus rather than nitrogen appears to act as the bonding site. No complexes containing paramagnetic ions and $(CH_3)_2NPF_2$ have been reported. In this study the interactions of cobalt(II) halides with $(CH_3)_2NPF_2$ have been investigated. Data which will be presented suggest that the complex formed between CoX_2 (X = Br, I) and $(CH_3)_2NPF_2$ is five-coordinate and it is of low spin, both in solution and as a solid. Solid $CoCl_2$ displayed such slight solubility in liquid $(CH_3)_2NPF_2$ that no attempt was made to study the chloride complex. No evidence for the interaction of solid CoF_2 with liquid $(CH_3)_2NPF_2$ was obtained.

Experimental Section

Because the compounds employed in the reactions are sensitive to traces of moisture or oxygen, the reactions were carried out using standard high-vacuum techniques. Solid materials were handled in an atmosphere of dry nitrogen using a drybox.

Dimethylaminodifluorophosphine was prepared from dimethylaminodichlorophosphine.[3] The identity of the ligand was established by comparison of its infrared spectrum with a previously reported spectrum[1] and by a vapor pressure of 93.7 mm at 0° (lit.[1] pressure 93.4 mm).

Anhydrous cobalt(II) fluoride, chloride, and iodide were used as obtained from Alfa Inorganics (Beverly, Mass.). Anhydrous cobalt(II) bromide was used as obtained from Research Inorganic Chemical (Sun Valley, Calif.). Methylene chloride was dried over calcium hydride and distilled prior to use. Elemental analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tenn.

A Perkin-Elmer 237B spectrophotometer was employed to obtain ir spectra. The solid materials were examined as Nujol and Fluorolube mulls between sodium chloride plates. For volatile materials a gas cell with a 7.5-cm path length and KBr windows was used. Solution and mull electronic spectra were obtained by the use of a Cary 14 spectrophotometer. Solutions which were examined contained the complex plus excess ligand in methylene chloride while the reference solution contained an equivalent amount of ligand but no metal salt. Mull spectra were obtained using Nujol mulls between quartz plates.[4]

Magnetic susceptibility measurements of solids were made by the use of the Gouy method. Standards used for instrument and tube calibration were water and $HgCo(NCS)_4$. The susceptibilities of the halide ions and the ligands was calculated using Pascal's constants.[5] Temperature-dependence measurements were normally made on two samples and at two field strengths: about 2.3 and 3.6 kG. The results obtained agree within ±0.15 BM.

Solution magnetic moments were obtained by use of the Evans method, which has been modified by Herlocker and Drago.[6] The results obtained agree within ±0.06 BM. The solvent employed was $(CH_3)_2NPF_2$.

Dibromotris(dimethylaminodifluorophosphine)cobalt(II).—In a typical reaction a 1.80-g (8.3-mmol) sample of anhydrous cobalt(II) bromide was transferred to a tared 50-ml flask which was equipped with a standard taper joint and a magnetic stirrer. The flask was evacuated and a 6.90-g (61.1-mmol) sample of $(CH_3)_2NPF_2$ was condensed into the flask at −196°. The mixture was warmed to 23° and the resulting dark green solution was stirred by means of the magnetic stirrer for 3 days. At the end of this time the mixture was opened to the vacuum pumping system for about 0.5 hr. The unreacted $(CH_3)_2NPF_2$ (3.90 g; 34.5 mmol) was collected in a −196° trap. In a number of separate experiments it was found that the $(CH_3)_2NPF_2$:$CoBr_2$ mole ratio of the dark green solid which remained in the reaction flask ranged from 2.98 to 3.18. The complex has a dissociation pressure at 23° of about 5 mm. It requires several days for reaction between $CoBr_2$ and $(CH_3)_2NPF_2$ to reach equilibrium. To avoid dissociation of the complex $CoBr_2[(CH_3)_2NPF_2]_3$ it was stored in an atmosphere of excess $(CH_3)_2NPF_2$.

Anal. Calcd for $C_6H_{18}CoF_6Br_2N_3P_3$: C, 12.93; H, 3.23; N, 7.54; Br, 28.70. Found: C, 12.65; H, 3.13; N, 7.59; Br, 28.59.

Although the absorbance spectra were not recorded, it was noticed that the green solution of $CoBr_2[(CH_3)_2NPF_2]_3$ in excess $(CH_3)_2NPF_2$ turned blue when a small amount of 1,2-dimethoxyethane, tetrahydrofuran, acetone, triethylamine, trimethylamine, or dioxane was added. The color change suggests than any of these neutral molecules are better ligands toward $CoBr_2$ than $(CH_3)_2NPF_2$ or alternatively that they allow formation of CoX_4^{2-} ions. The addition of dimethyl sulfoxide to a green solution of $CoBr_2$ in $(CH_3)_2NPF_2$ resulted in an almost colorless solution, again indicating that some sort of reaction, presumably displacement, occurs. The green solution turned pink when absolute ethanol was added. A solution of CoI_2 in $(CH_3)_2NPF_2$ underwent similar ligand-displacement reactions. Other workers[7] have observed that dissociative processes occur with five-coordinate cobalt(II) complexes which contain phosphine ligands and they made use of excess phosphine ligand to stabilize these complexes in solutions. We find that $CoBr_2$ and CoI_2 can be kept in a solution of methylene chloride and $(CH_3)_2NPF_2$ if the mole ratio of $(CH_3)_2NPF_2$ to cobaltous halide is greater than 4:1.

Because of the limited solubility of the $CoBr_2$ complex in organic solvent, the value of the molecular weight was obtained by determining the vapor pressure lowering of $(CH_3)_2NPF_2$ when $CoBr_2$ is dissolved in it. A mercury differential monometer of a type previously described was employed.[8]

Molecular weight determinations were made on solutions containing 10.9 and 10.7% by weight of $CoBr_2$ in excess $(CH_3)_2NPF_2$. If the two sets of data are averaged and the complex is assumed to be pure $CoBr_2[(CH_3)_2NPF_2]_3$, the calculated molecular weight is 630 ± 100 (theory 558).

Diiodotris(dimethylaminodifluorophosphine)cobalt(II).—In a typical experiment, a 2.50-g (7.98-mmol) sample of brown, anhydrous cobalt(II) iodide was transferred in a dry inert atmosphere to a tared 50-cm³ reaction tube which was equipped with a stopcock, standard taper joints, and a magnetic stirrer. The tube was evacuated and a 5.10-g (45.1-mmol) sample of CH_3NPF_2 was condensed in the bulb at −196°. The mixture was warmed to 23° and stirred for 3 hr. At the end of this time, the reaction tube was sealed by means of the stopcock and transferred to a dry bag. The bag was evacuated and filled with dry nitrogen several times. The reaction mixture was filtered in the inert atmosphere to remove solid, uncomplexed CoI_2. The filtrate which contained excess ligand, methylene chloride, and complex

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was transferred to a 50-ml round-bottom flask and the excess ligand and methylene chloride were removed by distillation *in vacuo*. The dark brown solid complex which was obtained was dried *in vacuo* for about 1 hr. Formation of a small nonstoichiometric amount of PF_3[9] when CoI_2 is allowed to react with $(CH_3)_2NPF_2$ prevented molecular weight determinations on the CoI_2 complex by the method used to determine the molecular weight of $CoBr_2[(CH_3)_2NPF_2]_3$. Dissociation of the complexes, similar to that discussed for $CoBr_2[(CH_3)_2NPF_2]_3$, prevented molecular weight determinations in other solvents. However, the esr spectrum of this complex shows the hyperfine interaction of one unpaired electron with a single ^{59}Co ($I = {}^7/_2$) nucleus which strongly suggests the complex is monomeric. The esr spectra of these and related complexes will be the subject of a future publication.

Anal. Calcd for $C_6H_{18}CoF_6I_2N_3P_3$: C, 11.04; H, 2.76; I, 38.93; N, 6.44. Found: C, 11.03; H, 2.76; I, 39.88; N, 5.88.

The Systems $CoCl_2$–$(CH_3)_2NPF_2$ and CoF_2–$(CH_3)_2NPF_2$.—A reaction system identical with the one described for the system Br_2–$(CH_3)_2NPF_2$ was employed. No evidence, on the basis of absorption of ligand, was obtained for any interactions of ligand and $CoCl_2$ or CoF_2.

Results and Discussion

The infrared spectrum of $CoI_2[(CH_3)_2NPF_2]_3$ mulled in Fluorolube has been obtained in the region 4000–2000 cm^{-1}. As can be seen from Figure 1, the absorptions in the 3000–2700-cm^{-1} region are virtually identical in the complex and in the uncomplexed ligand. Previous work[1,2,10,11] strongly suggests that the retention of the absorption band at about 2800 cm^{-1} is indicative of an uncoordinated nitrogen. If this is the case, phosphorus rather than nitrogen may act as the bonding site; however, it is possible that some of the nitrogen atoms in the systems are complexed. Shifts in infrared absorptions upon complexation, which are attributed to phosphorus–fluorine stretching modes, add additional support for bonding through phosphorus rather than nitrogen. Specifically, the P–F symmetric stretch in uncomplexed $(CH_3)_2NPF_2$ has been assigned to bands at 770 cm^{-1}.[12] In solid $CoI_2[(CH_3)_2NPF_2]_3$ the P–F symmetric stretch appears at 812 cm^{-1} and in $CoBr_2[(CH_3)_2NPF_2]_3$ at 805 cm^{-1}. The shift of the P–F stretching mode to higher wave numbers has also been observed in the B_4H_8 adduct of $(CH_3)_2NPF_2$, which is known to contain a B–P rather than a B–N bond, and has been attributed to a significant shortening of the P–F bond.[13]

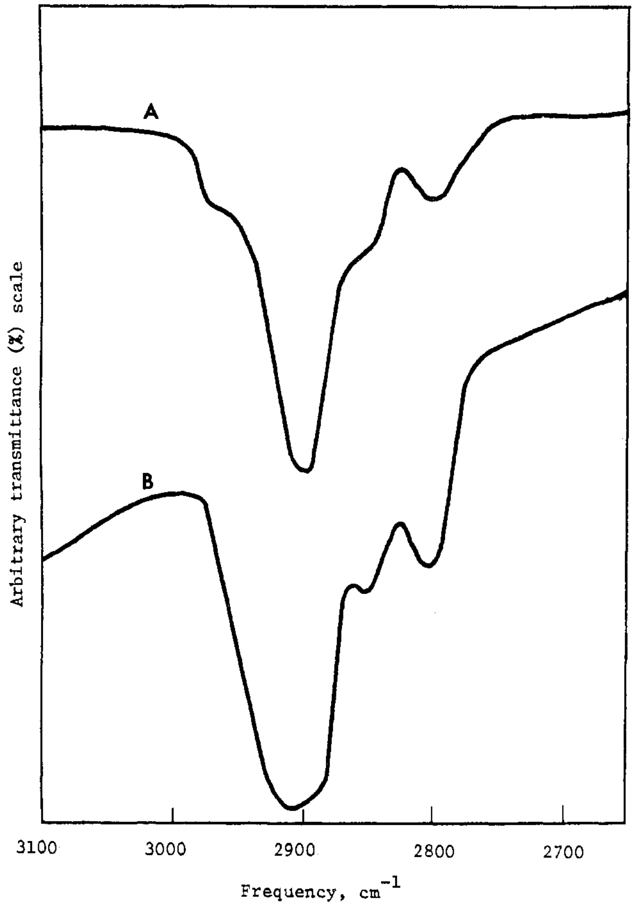

Figure 1.—Infrared spectra: (A) $(CH_3)_2NPF_2$, neat, gas phase (10 mm pressure); (B) $CoBr_2[(CH_3)_2NPF_2]_3$, Fluorolube mull.

Intensely green and brown solutions are obtained from the addition of anhydrous $CoBr_2$ and CoI_2, respectively, to excess $(CH_3)_2NPF_2$. These solutions do not conduct electricity. The nonconductance of these solutions reduces the possibility of ionic species.

Magnetic susceptibility measurements obtained from the solid complexes and from the complexes in solution are presented in Table I. The magnetic moments of these Co(II) five-coordinate complexes fall in the range 2.0–2.5 BM. These values are higher than those reported for low-spin, octahedral Co(II) complexes and lower than for low-spin, planar Co(II) complexes. The results reported in Table I are consistent with an $S = {}^1/_2$ ground state. The small discrepancy between the magnetic moments determined by different methods may indicate small amounts of high-spin impurity in these compounds.

TABLE I
MAGNETIC MOMENTS OF $CoX_2[(CH_3)_2NPF_2]_3$

Phase	Method	Temp, °K	μ_{eff}, BM
	$CoBr_2[(CH_3)_2NPF_2]_3$		
Solid	Guoy	293	2.27
		195	2.29
Soln in CH_2Cl_2	Evans	308	2.00
		265	1.98
		238	2.00
		217	1.99
	$CoI_2[(CH_3)_2NPF_2]_3$		
Solid	Guoy	297	2.42
		195	2.30
Soln in CH_2Cl_2	Evans	309	2.46
		263	2.49
		233	2.47
		206	2.45

Visible and uv results are presented in Table II and Figure 2. The fact that the uv–visible spectra of both solid $CoI_2[(CH_3)_2NPF_2]_3$ and $CoBr_2[(CH_3)_2NPF_2]_3$ are almost identical with the solution spectra suggests that the structures of the solids are unchanged when dissolved in excess ligand. All observed transitions and intensities of the CoX_2L_3 complexes (where X = Br, I; L = $(CH_3)_2NPF_2$) are consistent with a low-spin five-

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[9] Small amounts of PF_3 (less than 5%) were identified by infrared data. The PF_3 was evolved at the very start of the reaction. The evolution of PF_3 stopped before more than 20 mm pressure of PF_3 developed.

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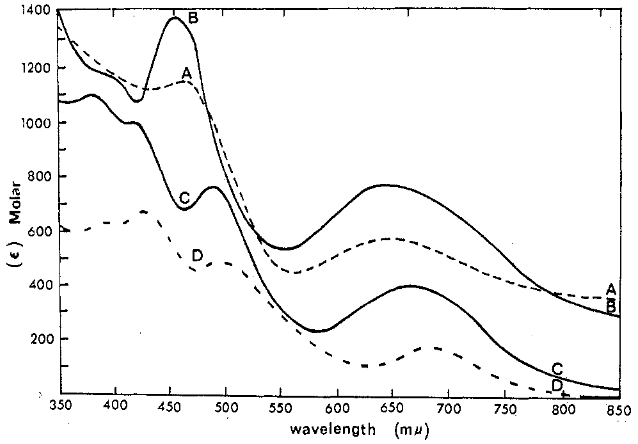

Figure 2.—Absorption spectra of $CoX_2[(CH_3)_2NPF_2]_3$ complexes: (A) $CoBr_2[(CH_3)_2NPF_2]_3$, mull, absorbance in arbitrary units; (B) $CoBr_2[(CH_3)_2NPF_2]_3$, solution in CH_2Cl_2 with excess $(CH_3)_2NPF_2$; (C) $CoI_2[(CH_3)_2NPF_2]_3$, solution in CH_2Cl_2 with excess $(CH_3)_2NPF_2$; (D) $CoI_2[(CH_3)_2NPF_2]_3$, mull, absorbance in arbitrary units.

Table II

Spectral Data for $CoX_2[(CH_3)_2NPF_2]_3$ Complexes

X	Solvent	λ (ε)[a]			
I	CH_2Cl_2[b]	26,109 (1100)	23,697 (1000)	20,408 (750)	14,881 (400)
I	Mull	25,773	23,202	19,960	14,706
Br	CH_2Cl_2[b]	25,510 sh (1170)	21,692 (1370)	[d]	15,625 (760)
Br	Mull	25,000 sh	21,739 sh		15,385

[a] Wavelength in cm^{-1}. [b] Excess $(CH_3)_2NPF_2$ added. [c] sh = shoulder. [d] This transition is not observed.

coordinate structure. Other five coordinate low-spin Co(II) complexes exhibit absorptions similar to those which are observed for $CoI_2[(CH_3)_2NPF_2]_3$ and $CoBr_2[(CH_3)_2NPF_2]_3$.[14-17] The true geometry of these pentacoordinate complexes probably is intermediate between trigonal-bipyramidal and square-pyramidal configurations.

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Laser Raman Spectrum of Tetrafluoronitrogen(V) Hexafluoroarsenate(V)

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The preparation[1-4] and the vibrational spectrum[5] of $NF_4^+AsF_6^-$ have previously been reported. It was shown that the NF_4^+ cation is tetrahedral.[1-5] Out of the four fundamental vibrations of NF_4^+, the A_1 and the E mode can be observed only in the Raman spectrum. At the time of the previous spectroscopic study,[5] only a very small amount of material and no laser Raman spectrometer were available to us. The observed infrared spectrum was of very good quality; however, owing to a low signal to noise ratio in the Raman spectrum, only tentative assignments could be made at that time for the A_1 and the E mode.

In this note, we wish to report the laser Raman spectrum of $NF_4^+AsF_6^-$ (see Figure 1, trace A). It is shown that ν_1 (A_1) and ν_2 (E) of NF_4^+ occur at 847 and 445 cm^{-1}, respectively. The value of 847 cm^{-1} for ν_1 (A_1) is close to those of 844 and 836 cm^{-1} deduced from the infrared-active[5] combination bands ($\nu_1 + \nu_4$) and ($\nu_1 + \nu_3$), respectively. The symmetry force constants computed with these revised Raman frequencies are $F_{11} = 8.03$ and $F_{22} = 0.74$ mdyn/Å. Adopting for the F_2 block the previously reported values,[5] the internal force constants of NF_4^+ can be calculated (see Table I). These force constants are not unique since in the F_2 block, three force constants had to be computed from two vibrational frequencies using the approximating method of Fadini.[6] For the isoelectronic species, CF_4 and BF_4^-, this method has yielded values close to those of the general valence force field and, hence, may also be a good approximation for NF_4^+. A detailed discussion of the trends observed within this isoelectronic series has previously been given.[5]

Table I

Force Constants of the Isoelectronic Series NF_4^+, CF_4, BF_4^- (mdyn/Å)

	NF_4^+	CF_4[a]	BF_4^-[a]
f_r	6.22	6.93	4.87
f_{rr}	0.60	0.77	0.62
$f_\alpha - f_{\alpha\alpha'}$	0.98	1.02	0.72
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.12	0.16	0.13
$f_{r\alpha} - f_{r\alpha'}$	0.77	0.57	0.43

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 69.

The sample used for the present investigation was prepared by the high pressure–temperature method.[4] However, contrary to previous reports,[4] the reaction product was not homogeneous. At the bottom of the Monel reactor, a white, loose solid had accumulated which, according to its elemental analysis, had the approximate composition (in mol %) 93.2 $NF_4^+AsF_6^-$, 5.8 $Ni(AsF_6)_2$, and 1.0 $Cu(AsF_6)_2$. Its vibrational spectrum is depicted by traces A in Figures 1 and 2 and shows the bands expected for the tetrahedral NF_4^+ and the approximately octahedral AsF_6^- ion. About an equal amount of solid product was uniformly distributed over the walls of the reactor. It was pale yellow and, according to its elemental analysis, showed a substantially increased Ni and Cu content. Furthermore, its infrared and Raman spectra (traces B in Figures 1 and 2) show that the bands which in traces A could not be accounted for in terms of octahedral AsF_6^- and tetrahedral NF_4^+ have strongly increased in relative intensity. Therefore, these additional bands must be at-

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