stretching region (3120–3525 cm^{-1}) is complicated and shows bands which may be attributed to uncoordinated and coordinated amine groups. The NH_2 deformation mode also consists of two strong bands (1623, 1559 cm^{-1}) indicating two types of amine groups. In general, the spectrum of the yellow isomer is more complicated than that for the pink isomer indicative of a less symmetric structure for the yellow isomer.

The difficulty in obtaining analytically pure samples of the yellow isomer may be attributed to the presence of the uncoordinated amine group. This polar group would have a distinct tendency to hydrogen bond to hydroxylic solvent molecules and also to coprecipitate excess ligand. In the hydrated form of the yellow isomer the water does not coordinate to the metal ion as shown by the magnetic moment of the hygroscopic complex which does not change significantly as it absorbs water from the atmosphere. The uncoordinated amine group is probably also responsible for the fact that the yellow isomer is unstable in aqueous solution, precipitating nickel hydroxide immediately. This accounts for the failure to observe this isomer when the preparative reactions are carried out in water.

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
REDSTONE RESEARCH LABORATORIES,
HUNTSVILLE, ALABAMA 35807

Complexes of the Group VI Metal Hexacarbonyls with the Difluorodithiophosphate and Difluorothiophosphate Anions

BY JOHN K. RUFF AND MAX LUSTIG

Received May 15, 1968

The interaction of the group VI metal hexacarbonyls with electron donors has been widely explored. This reaction has generally required thermal activation although in a few cases (where neutral ligands were employed) photolytic activation was found to be applicable. We wish to report the photolytic preparation of some new anionic derivatives of chromium, molybdenum, and tungsten hexacarbonyls involving both the difluorodithiophosphate anion and the difluorothiophosphate anion as ligands. Although a few neutral carbonyl complexes of organic dithiophosphates are known[1,2] no anionic derivatives have been prepared. Furthermore, the use of organic thiophosphates as ligands has been little explored,[3] and no known carbonyl derivatives have been reported. Therefore, it was of interest to determine if the recently reported difluorodithiophosphate[4,5] and difluorothiophosphate[6] anions would function as ligands.

The reaction between the metal hexacarbonyl and the complexing anion was carried out in methylene chloride solution using a twofold excess of the carbonyl. An immediate difference in the behavior of the two anions was noted. Reasonable yields were obtained with the difluorodithiophosphate anion only when the irradiation was carried to the point where 2 equiv of carbon monoxide was evolved, whereas, with the difluorothiophosphate anion, the reaction could be stopped after 1 equiv of carbon monoxide had been evolved. In fact, the addition of the difluorodithiophosphate anion to a solution of $Cr(CO)_5 \cdot THF$ (THF = tetrahydrofuran) in the absence of light produced only trace amounts of the product. In both cases the yield was much lower for the molybdenum derivatives than for the others.

The chemical analyses (see Table I) and the spectroscopic properties of the products (see Table II) suggest that the difluorodithiophosphate anion acts as a bidentate ligand, while the difluorothiophosphate anion acts as a monodentate ligand

$$M(CO)_6 + PF_2S_2^- \longrightarrow M(CO)_4PF_2S_2^- + 2CO$$

$$M(CO)_6 + PF_2OS^- \longrightarrow M(CO)_5PF_2OS^- + CO$$

where M = Cr, Mo, or W.

All of the products are yellow solids which are fairly stable in air in the solid state, although solutions are oxidized by atmospheric oxygen. The stability increases from the chromium to tungsten derivatives. The complexes formed with the difluorodithiophosphate anion appear to be more stable than the complexes obtained by treatment of the hexacarbonyls with the difluorothiophosphate anion. The analytical data for the materials prepared are summarized in Table I. The proton nmr spectra of the complexes showed the absence of hydridic hydrogen or paramagnetic impurities. The F^{19} nmr spectra are given in Table III. The small change in the P–F coupling constants in the free and complexed anion indicates that only a small change in the amount of s character in the P–F bond has occurred upon complexation.[7]

The infrared spectra of the complexes in the carbonyl stretching region are quite similar for all the metals employed regardless of whether the difluorodithiophosphate or difluorothiophosphate anions are employed as ligands. In general, four bands are observed (see Table II). To a first approximation this number of bands is anticipated for a molecule of the type $M(CO)_4L$, where L acts as a bidentate ligand bonded to the metal in a *cis* position (C_{2v} symmetry), whereas for a monosubstituted metal hexacarbonyl derivative, $M(CO)_5L$, only three bands are expected (C_{4v} symmetry). Thus, it would appear that both the $PS_2F_2^-$ and $POSF_2^-$ anions are acting as bidentate ligands. However, the infrared spectra in the P—O and P—S regions (see Table II) of the complexes containing the difluorothiophosphate anion as a ligand all exhibit an

---

(1) F. A. Hartman and A. Wojcicki, *Inorg. Nucl. Chem. Letters*, **2**, 303 (1966).

(2) R. L. Lambert and T. A. Manuel, *Inorg. Chem.*, **5**, 1287 (1966).

(3) W. Kuchen and H. Hertel, *Angew. Chem.*, **79**, 148 (1967).

(4) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 1272 (1967).

(5) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **6**, 2115 (1967).

(6) H. W. Roesky, *Chem. Ber.*, **100**, 950 (1967).

(7) E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 244 (1962).

TABLE I

ANALYTICAL DATA FOR THE COMPOUNDS PREPARED

Compound	Mp, °C	Yield, %	Analytical data Found, % C	H	N	F	CO	Calcd, % C	H	N	F	CO
$[(C_6H_5)_3P]_2NCr(CO)_4PF_2S_2^-$	115–117	52	57.3	3.58	1.88	4.7	13.0	57.5	3.59	1.68	4.6	13.4
$[(C_6H_5)_3P]_2NMo(CO)_4PF_2S_2^-$	92–93	19	54.9	3.40	1.58	4.2	12.8	54.7	3.91	1.59	4.3	12.7
$[(C_6H_5)_3P]_2NW(CO)_4PF_2S_2^-$	99–100	51	49.7	3.13	1.50	3.8	11.8	49.7	3.10	1.45	3.9	11.6
$(C_6H_5)_4AsCr(CO)_5POSF_2^-$	273–275[a]	72	50.0	2.86		5.7	21.0	50.3	2.89		5.5	20.2
$(C_6H_5)_4AsMo(CO)_5POSF_2^-$	282–285[b]	15	47.2	2.80		5.4	19.2	47.3	2.70		5.2	19.0
$(C_6H_5)_4AsW(CO)_5POSF_2^-$	298[c]	67	42.4	2.35		4.9	17.3	42.3	2.43		4.6	17.0

[a] Dec pt 135°. [b] Dec pt 125°. [c] Dec pt 130°.

TABLE II

INFRARED SPECTRA OF THE COMPLEXES PREPARED (cm^{-1})

Anion	Carbonyl freq	P=S	P=O
$Cr(CO)_4PF_2S_2^-$	2061 m, 1980 m, 1935 vs, 1876 s	711 m, 735 s	
$Mo(CO)_4PF_2S_2^-$	2072 m, 1981 m, 1938 vs, 1879 s	710 m, 737 w	
$W(CO)_4PF_2S_2^-$	2069 m, 1975 m, 1928 vs, 1868 s	710 m, 735 w	
$Cr(CO)_5PF_2OS^-$	2064 w, 1971 m, 1932 s, 1877 s	624 m	1274 m
$Mo(CO)_5PF_2OS^-$	2065 w, 1979 m, 1934 s, 1869 m	623 m	1272 m
$W(CO)_5PF_2OS^-$	2067 m, 1973 m, 1926 s, 1866 m	623 m	1274 m
$PF_2S_2^-$ [a]		720 m, 740 w	
$POSF_2^-$ [b]		648 m	1273 m

[a] See ref 5. [b] See ref 6.

TABLE III

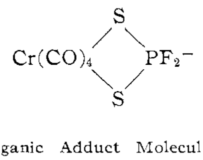
THE F^{19} NMR SPECTRA OF THE COMPLEXES PREPARED

Anion	Chem shift, ppm (*vs.* CCl_3F)	J_{PF}, cps
$Cr(CO)_4PF_2S_2^-$	12.3	1196
$Mo(CO)_4PF_2S_2^-$	12.5	1197
$W(CO)_4PF_2S_2^-$	13.6	1200
$Cr(CO)_5PF_2OS^-$	40.2	1128
$Mo(CO)_5PF_2OS^-$	39.8	1131
$W(CO)_5PF_2OS^-$	38.4	1136
$PF_2S_2^-$ [a]	2.4	1164
PF_2OS^- [b]	34.2	1098

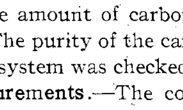
[a] See ref 5. [b] See ref 6.

increase in frequency of the P=O stretching mode and a decrease in frequency of the P=S stretching mode over that in the free ion. This strongly suggests that coordination is occurring only through the sulfur[8] and that the oxygen is free from interaction with a metal carbonyl moiety. On the other hand, both of the P=S stretching frequencies are slightly decreased in the complexes containing the difluorodithiophosphate anion as would be expected if this ion was acting as a bidentate ligand. The reason for the extra band in the CO stretching region is not known but may arise from the fact that the ligand is unsymmetrical and the anion actually has C_s symmetry instead of C_{4v}. This would lead to an increase in the number of bands expected.

The equivalent conductivity of these complexes plotted as a function of concentration suggests that only 1:1 electrolytes are present in nitromethane solution.[9] Thus, bridged dimers can be eliminated. The structure of the complexes involving the difluorodithiophosphate anion probably contains four-membered rings, *e.g.*



while the complexes containing the difluorothiophosphate anions can probably be written as



Experimental Section

Materials.—The hexacarbonyls of the group VI metals were obtained from Alfa Inorganics, Inc. The bis(triphenylphosphine)-iminium salt of the difluorodithiophosphate anion and the tetraphenylarsonium salt of the difluorothiophosphate anion were prepared by literature methods.[5,6]

Preparation of $[(C_6H_5)_3P]_2NM(CO)_4PF_2S_2$.—The preparation of all three of the metal derivatives was carried out in an analogous manner. A mixture of 0.75 g of $[(C_6H_5)_3P]_2NPF_2S_2$ and 0.52 g of $Cr(CO)_6$ in 25 ml of THF was irradiated until 45 cm^3 of gas (at STP) was evolved. The mixture was evaporated to dryness under vacuum and the residue was extracted with 50 ml of ether. Pentane was added to the extract and a 0.82-g sample of product was obtained.

Preparation of $(C_6H_5)_4AsM(CO)_5POSF_2$.—All preparations were carried out in an analogous manner. For example, a mixture of 0.71 g of $Cr(CO)_6$ and 0.99 g of $(C_6H_5)_4AsPOSF_2$ in 50 ml of CH_2Cl_2 was irradiated until 67 cm^3 of gas (at STP) was evolved. The mixture was filtered and the solvent was removed under vacuum. The residue was dissolved in 20 ml of CH_2Cl_2, and 80 ml of ether was added. The mixture was filtered and pentane was added to the filtrate. A 1.08-g sample of product was obtained.

Analyses.—The amount of carbon monoxide present in the complexes was determined by decomposition of the complexes in a pyridine–iodine mixture at 120° for 4 hr. The amount of carbon monoxide formed was measured by means of a Toepler pump and a calibrated bulb system. Duplicate determinations were made on each complex. Also to ensure that the reaction was complete, each sample tube was reheated for an additional 4 hr after the initial removal of carbon monoxide. In no case was more than a trace amount of carbon monoxide found after the second heating. The purity of the carbon monoxide collected in the calibrated bulb system was checked by mass spectrometry.

Conductivity Measurements.—The conductivity of the salts $[(C_6H_5)_3P]_2NCr(CO)_4PF_2S_2$ and $(C_6H_5)_4AsCr(CO)_5POSF_2$ was obtained as a function of concentration in nitromethane solution using equipment previously described.[10] The specific conductivity of the nitromethane employed was 3.89×10^{-7}. For the salt $[(C_6H_5)_3P]_2NCr(CO)_4PF_2S_2$, the molar concentration and equivalent conductance (cm^2/ohm equiv) are: 5.020×10^{-3}, 73.2; 2.510×10^{-3}, 76.4; 1.255×10^{-3}, 79.1; 0.6175×10^{-3}, 80.5; and 0.318×10^{-3}, 82.8. For the salt $(C_6H_5)_4AsCr(CO)_5POSF_2$, the same values are: 5.887×10^{-3}, 74.2; 2.944×10^{-3}, 79.3; 1.472×10^{-3}, 81.7; 0.7360×10^{-3}, 86.4. This leads to a value at infinite dilution of 91.3 and 90.4, respectively. A plot of $\Lambda_\infty \Lambda_C$ *vs.* $\sqrt{C}$ gave slopes of 193 and 217, well within the range accepted for 1:1 electrolytes.

Infrared Spectra.—The infrared spectra of the new compounds

---

[8] I. Linquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1962.

[9] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

[10] J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963)

were obtained in the carbonyl region on methylene chloride solutions. The $P=O$ and $P=S$ regions of the spectrum were obtained on Nujol mulls. The spectra were recorded on a Perkin-Elmer 521 spectrometer which had been calibrated with indene and polystyrene.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DAAH01-67-C-0655.

Correspondence

Proton Magnetic Resonance and Vibrational Spectra of Concentrated Aqueous Solutions of Aluminum(III) Nitrate. The Distinction between Intimate and Solvent-Separated Ion Pairs

Sir:

Recently much attention has been devoted to using the vibrational spectroscopy of concentrated aqueous solutions containing the nitrate ion as a probe to detect the formation of ion pairs.[1-8] The basis of the application is that if there occurs a "strong" specific association of a cation with the NO_3^- ion along the C_2 axis of the latter, the "site" symmetry of NO_3^- is lowered from D_{3h} to C_{2v} (or C_s). This lowering of the symmetry is usually manifested in the splitting of the band for the doubly degenerate stretching mode (ν_3) into two components in the ir and Raman spectra and in the appearance in the ir spectrum of the ν_1 band which is forbidden for the free NO_3^- ion.[1-8]

These effects have been observed for a variety of nitrates of the representative elements (*e.g.*, $Ca(NO_3)_2$ and $Al(NO_3)_3$[2-8]), and it is generally agreed that they are due to a specific association of NO_3^- with a cation. However, with the use of vibrational spectroscopy alone, it has not been possible to distinguish unequivocally whether NO_3^- in these "ion pairs" resides in the first or second hydration sphere of the cation, that is, to distinguish whether an intimate or solvent-separated ion pair is formed. By using proton magnetic resonance (pmr) spectroscopy we have been able to show that the primary hydration number of the Al(III) ion is 6 in concentrated aqueous aluminum nitrate solutions and from this result we infer that the Al^{3+}–NO_3^- ion pair, detected in vibrational spectroscopy, is a solvent-separated one.

A typical 60-MHz pmr spectrum of a concentrated aqueous solution of $Al(NO_3)_3$ at a low temperature is represented in Figure 1. From the dependence of the relative signal intensities upon the solution composition, the low-field resonance is assigned to water within and the high-field one to water outside the first hydration sphere of the Al(III) ion. The large area of the coordinated water signal relative to that of the "bulk" water permits the determination of the very precise hydration numbers listed in Table I which also includes signal line widths and relative chemical shifts. It is apparent that the hydration number of the Al(III) ion in the concentrated solutions of $Al(NO_3)_3$ is not significantly different from 6 and it exhibits no apparent trend with the temperature or composition of the solution. In the 100-MHz pmr spectra of solutions having the compositions listed in Table I, the bulk and coordinated water signals are well resolved at −14° and provide a hydration number for Al(III) of 6.01 ± 0.02.[9] The hydration number of 6 is consistent with the values obtained from: (a) isotope dilution studies of $Al(ClO_4)_3$ aqueous solutions;[10] (b) O^{17} nmr studies of $Al(ClO_4)_3$ aqueous solutions;[11] and (c) pmr studies of $AlCl_3$ aqueous solutions.[12]

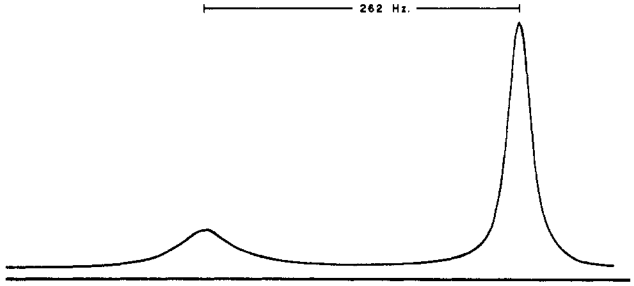


Figure 1. Pmr spectrum of a 2.1 *m* aqueous solution of $Al(NO_3)_3$ at −40°. The magnetic field increases from left to right.

Unless a coordination number of 7 for Al(III) is invoked, our pmr data demonstrate that only trace quantities of NO_3^- can reside in the primary hydration sphere of the Al(III) ion in concentrated aqueous nitrate solutions. Nonetheless, Raman and ir data indicate that significant quantities of NO_3^- ion are in some way associated to Al(III). Hester and Plane[2]

---

(1) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

(2) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(3) H. Lee and J. K. Wilmshurst, *Australian J. Chem.*, **17**, 943 (1964).

(4) R. E. Hester and R. A. Plane, *J. Chem. Phys.*, **40**, 411 (1964).

(5) R. E. Hester and R. A. Plane, *ibid.*, **45**, 4588 (1966).

(6) D. E. Irish and G. E. Walrafen, *ibid.*, **46**, 378 (1967), and references therein.

(7) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).

(8) R. E. Hester and K. Krishman, *J. Chem. Phys.*, **46**, 3405 (1967).

(9) A referee has expressed concern that the systems discussed here might be solids. It should be emphasized that they are *solutions*. At the temperatures listed in Table I, the solutions, though viscous, flow freely, do *not* exhibit a Tyndall effect, and do *not* deposit precipitates even when stored over powdered glass at −55° for 8 hr. In addition, the pmr signal shapes for solutions having the compositions listed in Table I are characteristic of those for liquids, not glasses or solids. When the solutions were cooled below the freezing point (< −65°), a copious amount of precipitate developed in the nmr tube and the pmr signals could be detected no longer with the high-resolution Varian A-60A spectrometer which was used.

(10) H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960).

(11) R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).

(12) R. E. Schuster and A. Fratiello, *ibid.*, **47**, 1554 (1967).