Table I

Estimates of Equilibrium Constants at 23° and $\mu = 5.35\ M$ at Various Wavelengths

Wavelength, nm	$10^{-2}K_1$	$10^{-2}K_2{}^a$
400	1.8	3.5
420	1.4	1.6
440	1.1	2.6
460	1.9	1.1
470	2.1	2.2
480	2.0	1.8
500	1.7	0.8
520	1.5	2.2
540	1.1	1.2
Av	1.6 ± 0.1	1.9 ± 0.3

[a] The value $K_H = 0.90\ M$ has been assumed at $\mu = 5.35\ M$ and 23°.[6]

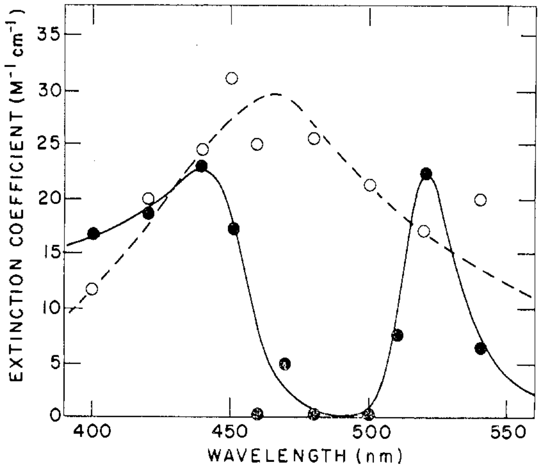

Figure 2.—Derived spectra of $MnF_{aq}{}^{2+}$ (○) and $Mn(OH)F_{aq}{}^{+}$ (●).

by chlorine[7a] and bromine.[7b] The rate-determining step in this reaction is[7] the first-order decomposition of the monooxalato complex

$$MnC_2O_4{}^+ \xrightarrow{k_1} Mn^{2+} + C_2O_4{}^- \qquad (IV)$$

The observed rate of reaction at constant acidity varies with the concentrations of added oxalic acid and chloride or fluoride ions, and the data of Taube[7] can now be rationalized by combining reactions I–III with

$$Mn^{3+} + H_2C_2O_4 \rightleftharpoons MnC_2O_4{}^+ + 2H^+ \quad (K_a) \qquad (V)$$

$$MnC_2O_4{}^+ + H_2C_2O_4 \rightleftharpoons Mn(C_2O_4)_2{}^- + 2H^+ \quad (K_b) \qquad (VI)$$

$$Mn^{3+} + Cl^- \rightleftharpoons MnCl^{2+} \quad (K_{Cl}) \qquad (VII)$$

$$MnC_2O_4{}^+ + HF \rightleftharpoons Mn(C_2O_4)F + H^+ \quad (K_{aF}) \qquad (VIII)$$

In the absence of added chloride or fluoride ion we have obtained the values of k_1, K_a, and K_b of 11.9 min^{-1}, $1.64 \times 10^5\ M$, and 45 M, respectively. Comparison of these estimates with those obtained by Taube[7b] in the absence of reaction I shows that the principal effect of its inclusion in the calculations is to increase the value of K_a. The kinetic data[7b] in the presence of up to a 10^5-fold excess of chloride only require the additional equilibrium VII, with $K_{Cl} = 13.5 \pm 0.5\ M^{-1}$ at $\mu = 2\ M$ and 25°. In the presence of added fluoride the data is accounted for by the additional equilibria II, III, and VIII with $(2K_1 + K_2K_H) = 1.1 \times 10^3\ M$ and $K_{aF} = 118$ at $\mu = 2\ M$ and 25°. Individual values of K_1 and K_2 cannot be obtained from the original[7b] kinetic data since the acidity was kept constant at 2.0 M. However, the present results for $\mu = 5.35\ M$ suggest that $K_1 \approx K_2$, whereupon we calculate $K_1 \approx K_2 \approx 370$ at $\mu = 2\ M$ and 25°. The stability constants for fluoride complexation thus appear to increase with decreasing total ionic strength. The value of the composite stability constant obtained from spectral measurements by Fackler and Chawla[2] is consistent with these estimates, since it was obtained at varying ionic strength and acidity.

The ratio $K_1/K_2 = K_H/K_{FH}$, where $K_{FH} = [Mn(OH)F^+][H^+]/[MnF^{2+}] \approx 1.1\ M$ at $\mu = 5.35\ M$ and 23°, shows that the presence of F^- results in little change in the acidity of the remaining water molecules of the inner sphere. This conclusion is consistent with the similarity of the spectra of $Mn_{aq}{}^{3+}$, $MnOH_{aq}{}^{2+}$, $MnCl_{aq}{}^{2+}$, and $MnF_{aq}{}^{2+}$ in both the visible and the uv regions.

The splitting of the visible spectrum of $Mn(OH)F_{aq}{}^+$ is presumably[8] due to splitting of the ^5E_g (and possibly $^5T_{2g}$) level by tetragonal distortion. It is not possible to assess the importance of *cis–trans* isomerism in this complex in the absence of data on other mixed-ligand complexes of this type. However, it should be noted that the high-spin[9] complex $Mn(CYDTA)OH^{2-}$ has a spectral maximum at 448 nm which moves to 510 nm on protonation.[10] Changes in the spectra of the aquo species in the presence of very large excesses of chloride,[3,11] where higher order chloro complexes are formed, suggest that cumulative effects of negative charge can indeed cause measurable spectral changes in mixed complexes of Mn(III).

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Contribution from the General Electric Research and Development Center, Schenectady, New York 12301

A High-Pressure Form of Palladium Disulfide

By Ronald A. Munson[1] and John S. Kasper

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An orthorhombic palladium disulfide (I) ($a = 5.46$, $b = 5.54$, $c = 7.53$ Å) may be prepared by heating palladium dichloride and excess sulfur at 450° in an evacuated quartz tube for 4 days.[2] The structure of the palladium disulfide so prepared[3,4] [space group $D_{2h}{}^{15}$ (Pbca)] is derived from the pyrite structure, which places the cation in a nearly perfect octahedral environment, by elongation of one of the fourfold octahedral axes.[5]

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[1] Bureau of Mines, Metallurgy Research Center, College Park, Md. 20740.

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TABLE I

SPACING, INDEXING, AND INTEGRATED INTENSITIES OF THE REFLECTIONS OF PALLADIUM DISULFIDE (II)[a]

d_{obs}	hkl	Intensity	d_{calc}
3.584	002	79	3.580
3.433	111	60	3.434
3.003	102	8	3.002
2.782	020	65	2.780
2.753	200		2.755
2.644	112	8	2.642
2.587	021	6	2.591
2.469	210	5	2.468
2.340	121	7	2.345
	211		2.334
2.195	022	60	2.195
2.186	202		2.183
2.046	122	40	2.040
2.034	113		2.038
	212		2.032
1.956	220	19	1.957
1.806	023	3	1.811
1.717	123	100	1.720
	222		1.717
	213		1.716
1.706	131		1.706
	104		1.702
1.693	311		1.694
1.64	302	4	1.634
	114		1.628
1.51	223	14	1.513
	024		1.505
	231		1.503
	204		1.501
	321		1.492
1.411	133	24	1.415
	232		1.413
	322		1.409
	313		1.408
1.292	042+	14	1.296
1.238	420+	6	1.234
1.167	422+	10	1.167

[a] Cu Kα, nickel-filtered radiation. *d* values were obtained with a Guinier camera and the intensities from a diffractometer tracing. There is evidence for the presence of some preferred orientation.

This type of Jahn–Teller distortion, which is frequently encountered in palladium compounds, removes the degeneracy of the dγ energy levels so that spin pairing in the lower dγ level results. As expected, PdS_2 (I) is spin-paired and a semiconductor.[6]

We have found that a second orthorhombic palladium disulfide (II) ($a = 5.51$, $b = 5.56$, $c = 7.16$ Å) may be prepared from an intimate mixture of the elements or directly from I by reaction for 5 min at 63 kbars and 1450° followed by quenching. This high-pressure form of PdS_2 has apparently been prepared elsewhere.[7] At 250–300° and 1 atm the conversion of II to I is accompanied by decomposition to PdS and sulfur. The pattern of the intensities of the X-ray reflections of II (Table I) suggests that the structure of II, like that of I, is derived from the pyrite structure by elongation of the *z* axis; however, the elongation in the case of II is not so great as in the case of I and is in fact intermediate between I and the ideal cubic pyrite configuration. The pycnometric density of II in acetone is 4.92 ± 0.10 g cm^{-3} which may be compared with the calculated density, $z = 4$, of 5.17 g cm^{-3}.

Both II and I exhibit weak temperature-independent paramagnetism. II is a better conductor (specific resistivity, $\rho_{II} \cong 0.5$ ohm cm at 25°) than I ($\rho_{I} \cong 100$ ohm cm) and although difficulty was encountered in making reproducible four probe electrical contacts, ρ_{II} appears to increase by a factor of 2 from liquid nitrogen to room temperature. Compound II does not suffer a superconducting transition above 1.45°K. The apparent presence of metallic-type conduction in II suggests that the delocalization of the electrons in the dγ levels stabilizes the shorter bond lengths along the *z* axis in the high-pressure form of palladium disulfide. The formation of two distinct pyrite phases of iridium disulfide[8] is accompanied by a change in stoichiometry from a sulfur to iridium mole ratio of approximately 3 to a mole ratio of nearly 2. This is not the case with palladium disulfide, for both I (37.6% by $BaSO_4$ precipitation[2]) and II (38.2 ± 0.5% S by thermogravimetric analysis) analyze very nearly as PdS_2 (37.5% S).

The preparation of II was carried out in the "belt" superpressure apparatus[9] using a cell constructed of sodium chloride with a graphite heater. The cell was calibrated at room temperature with the bismuth 25.5- and 27-kbar and the barium 58-kbar transformations. Temperature, uncorrected for pressure, was determined from a calibration of the high-pressure cell with a Pt—Pt–10% Rh thermocouple.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA,
LOS ANGELES, CALIFORNIA 90007

Further Knowledge of the Mercuric Oxide–Tris(trifluoromethyl)phosphine Reaction. Nuclear Magnetic Resonance Comparison of Four Bis(trifluoromethyl)phosphorus Compounds

BY ANTON B. BURG AND INDU B. MISHRA

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When the compound $Hg(CF_3)_2$ was made from $(CF_3)_3P$ and HgO at 100°, the nonvolatile by-product was empirically formulated as an uncertain mercury–