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

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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–

oxy–bis(trifluoromethyl)phosphorus material.[1] Repeating the process, we now have noticed that free mercury is a product, suggesting that an over-all reaction such as

$$2(CF_3)_3P + 4HgO \longrightarrow 2Hg + Hg(CF_3)_2 + Hg[O_2P(CF_3)_2]_2$$

might account for much of the nonvolatile product.

For a test of this interpretation, we performed the $(CF_3)_3P$–HgO reaction in a sealed tube containing gold foil (40 hr at 100°), finding that the gain in weight of the foil was only 21% of the expected amount of free mercury; however, in view of the probable formation of mercurous oxide in a process always requiring a goodly excess of HgO, a larger yield of metallic mercury might have been too much to expect.

For more direct evidence of the formation of a mercury phosphinate, the ether-soluble part of the nonvolatile product was extracted in the absence of air, and, after removal of the ether *in vacuo*, the white solid product was treated with CH_3I (5 hr, 100°) in a sealed tube cooled at the top for reflux action. After removal of the surplus CH_3I through a U trap *in vacuo* at $-60°$, the volatile product proved to be a pure sample of the methyl phosphinate; the yield was 75%, on the basis that the weighed extract was pure mercuric phosphinate, reacting as

$$Hg[O_2P(CF_3)_2]_2 + 2CH_3I \longrightarrow HgI_2 + 2CH_3O_2P(CF_3)_2$$

This methyl ester was identified by comparison of its volatility, molecular weight, infrared spectrum, and nmr spectra with those of samples of the same ester made by three independent methods.

Alternate Syntheses of the Ester.—One of the alternate syntheses of $CH_3O_2P(CF_3)_2$ was by methanolysis of $(CF_3)_2POCl$, which was made by previously reported methods.[2,3] However, this methanolysis was far from a simple process, for the presumed initial step

$$CH_3OH + (CF_3)_2POCl \longrightarrow CH_3O_2P(CF_3)_2 + HCl$$

was slow enough to require heating (60°), and the HCl reacted either with the desired ester or with methanol, accounting for larger yields of CH_3Cl and $(CF_3)_2POOH$ (nmr identified) than the observed 26% yield of $CH_3O_2P(CF_3)_2$.

The second method—methanolysis of $(CF_3)_2PCl_3$—gave an even smaller yield of the ester, along with the expected HCl and $(CH_3)_2O$; the product CH_3Cl was not separated from the latter. Virtually no yield of the ester was obtained from the cleavage of $(CH_3)_2O$ by $(CF_3)_2PCl_3$, for the reaction required temperatures around 155° and led to unintelligible decompositions: along with a 70% yield of CH_3Cl there was a comparable amount of noncondensable gases, suggesting the decomposition products of dimethyl ether, namely, H_2, CO, and CH_4.[4]

The third alternative synthesis was by passage of the phosphinite ester $CH_3OP(CF_3)_2$,[2] as a vapor at minimal pressure, over HgO, spread out in a glass helix at 100°. The passage was repeated until 80% of the sample had been converted, giving a 45% yield of the desired ester. A minor by-product had the volatility and infrared spectrum of the Arbuzov-rearrangement product $CH_3(CF_3)_2PO$.[2]

Proof of Formula.—A highly purified sample of the ester was subjected to vapor-tension measurements: 2.72 mm at $-15.2°$, 7.98 mm at 0.00°, 25.3 mm at 18.75°, and 74.5 mm at 39.60°, all exactly matched by calculations from the equation $\log P = 7.8550 + 1.75 \log T - 0.00745T - (2508/T)$ ($t_{760} = 102.1°$; Trouton constant = 21.00 eu). With such evidence of purity, the vapor-phase molecular weight results (216–218 for various samples; calcd, 216.0) left little doubt of the formula $CH_3O_2P(CF_3)_2$. Further confirmation came from basic hydrolysis at 25°: the 0.057-mmol sample yielded 0.057 mmol of HCF_3, quite in accord with the expectation of conversion to the anion of the phosphonic acid $CF_3PO(OH)_2$.[5]

The infrared spectrum offers further confirmation, with all features as expected for $CH_3O_2P(CF_3)_2$. The frequencies (cm^{-1}) (recorded by the Beckman IR7 instrument, with CsI optics when needed) are listed with relative intensities in parentheses and assigned as follows: C—H stretching, 2976 (2.5) and 2875 (0.8); CH_3 deformations, 1463 (0.87) and 1293 (0.7); P=O stretching, 1332 (13); C—F stretching, 1211 sh (51), 1193 (82), and 1142 (13); C—O stretching, 1045 (36); P—OCH_3 stretching, 817 (3.8); CF_3 symmetric deformation, 765 (1.0); P=O bending (covering the asymmetric CF_3 deformation), 589 (35); P—CF_3 stretching, 508 (6.7); and an ambiguous band at 369 (1.3). A combination was observed at 1857 (0.47) and an overtone at 2378 (0.4).

Nmr Comparisons.—Still further confirmation of the ester was found in the resonance spectra of the three magnetic nuclei: the ^1H and ^{19}F spectra showed the expected doublets (with fine structure barely resolvable) and the ^{31}P spectrum showed a fully delineated septet of quartets. For comparison, the study included three other $(CF_3)_2P$ compounds, as given in Table I.

The proton spectra (with δ values marked negative for measurement downfield from tetramethylsilane) were recorded by the Varian A-60 instrument. The HA-100 instrument was used for ^{19}F at 94.1 Mc and for ^{31}P at 40.3 Mc; the δ values were measured from Cl_3CF or H_3PO_4, with the upfield direction taken as positive. The long-range coupling constants $J_{H\cdots F} = J_{F\cdots H}$ (near the limit of resolution) could be measured most surely from the clearly observed quartets of which the ^{19}F doublets consisted. From the proton side, two HA-100 runs were roughly confirmatory, with measurement possible among the middle three peaks of each

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[2] J. E. Griffiths and A. B. Burg, *ibid.*, **84**, 3446 (1962).

[3] A. B. Burg and A. J. Sarkis, *ibid.*, **87**, 238 (1965).

[4] This suggestion relates to an observation by the senior author (some 35 years ago at the University of Chicago) that the decomposition of gaseous $(CH_3O)_2BH$ (25°, 1 month) gave not only the expected $(CH_3O)_3B$ and B_2H_6 but also $(CH_3)_2O$, white solids, and an equimolar mixture of H_2, CO, and CH_4, known to be the usual thermal decomposition products of dimethyl ether.

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TABLE I

	$CH_3OP(O)$-$(CF_3)_2$	CH_3OP-$(CF_3)_2$	$CH_3P(O)$-$(CF_3)_2$	CH_3P-$(CF_3)_2$
$\delta(^1H)$, ppm	−3.72	−3.47	−1.80	−1.20
J_{HP}, cps	11.1	13.0	15.6	4.6
$J_{H\cdots F}$, cps	"0.5"	...	0.83	...
$\delta(^{19}F)$, ppm	73.3	66.2	72.4	66.9
J_{FP}, cps	120	85.4	99	75
$J_{F\cdots H}$, cps	0.37	0.46	0.78	...
$\delta(^{31}P)$, ppm	−2.5	−94.8	...	5.76
J_{PF}, cps	120	86	...	76
J_{PH}, cps	10.8	12.7	...	?

septet. The relation of these J values to variously placed oxygen is interesting, especially since such coupling could not be resolved for $CH_3P(CF_3)_2$.

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The Use of the (+)- or (−)-Tris(ethylenediamine)cobalt(III) Cation as a Resolving Agent for Some Complex Anions[1]

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The tris(oxalato) complexes of chromium(III) and cobalt(III) were first resolved by the use of strychnine salts.[4] Until recently Werner's method was probably the best way of obtaining the optical antipodes of these complexes; however, in 1956 Dwyer and Sargeson[5] demonstrated that the (+)-tris(1,10-phenanthroline)-nickel(II) cation could be utilized to resolve the tris(oxalato) complexes of Co(III), Cr(III), and Rh(III). The method of Dwyer and Sargeson avoids the difficulties of working with extremely toxic resolving agents.

This investigation was initiated to determine if the (+)- or (−)-tris(ethylenediamine)cobalt(III) cation could be utilized to resolve racemic complexes of ionic charge 3−. This cation can be prepared economically in quantity; the reagent has a good solubility in water thus avoiding the use of mixed solvents; and the diastereoisomer isomer formed is not of a "mixed type" and hence should have a lower water solubility than the double complex obtained by use of the tris(1,10-phenanthroline)nickel(II) ion.

Experimental Section

Preparation of Complexes.—The (+)- or (−)-tris(ethylenediamine)cobalt(III) iodide was prepared according to standard methods.[6] Potassium (±)-tris(oxalato)cobaltate(III) trihydrate was prepared by literature methods.[7] Potassium (±)-tris(oxalato)chromate(III) trihydrate was prepared by the method given by Palmer.[8] Potassium (±)-tris(oxalato)rhodate(III) hydrate was prepared by the method of Werner,[9] starting with the water-soluble rhodium(III) chloride trihydrate.

Resolution of the (±)-Tris(oxalato)chromate(III) Ion.—A solution of 1.6 g (0.0025 mol) of (−)-tris(ethylenediamine)-cobalt(III) iodide in 40 ml of water at 15° was quickly added to a stirred solution of 2.2 g (0.005 mol) of potassium (±)-tris(oxalato)chromate(III) trihydrate in 40 ml of water at 15°. The reaction mixture was stirred for 1 min before the brownish tan precipitate of $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$ was collected by filtration. The filtration was carried out in such a fashion that the filtrate was run directly into about 400 ml of cold acetone. The precipitated $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$ was washed with acetone and air dried. The diastereoisomer was obtained in 95% yield (1.3 g). *Anal.* Calcd for $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$: C, 26.0; H, 4.3; N, 15.1. Found: C, 26.2; H, 4.4; N, 14.8.

The filtrate obtained from the collection of $[Co(en)_3][Cr(C_2O_4)_3]$ was stirred for 2–3 min to coagulate the precipitated $(+)$-$K_3[Cr(C_2O_4)_3]\cdot H_2O$. The precipitate was collected by filtration, washed with acetone, and air dried. The product was obtained in 44% yield (0.5 g). A 0.02% solution gave $[\alpha]_D$ +1550–1600°.

The following method was utilized to obtain the (−) form of the active anion in the form of the potassium salt from the diastereoisomer. The entire sample of the double complex was placed in a mortar in an ice bath and 5–10 ml of ice water was added along with 5–7 g of solid potassium iodide. This mixture was ground for 3–5 min at 5–10°. During the grinding the mixture turned brownish yellow owing to the precipitation of $(-)$-$[Co(en)_3]I_3$. The pasty reaction mixture was filtered and the blue-green filtrate was run directly into 100 ml of cold, stirred acetone. The acetone solution was stirred for 3 min to coagulate the precipitate before the product was collected by filtration. To remove the excess potassium iodide from the product, the collected material was crushed to a powder and slurried three times with 100-ml portions of 95% alcohol for 3 min each. The product was collected, washed with acetone, and air dried. This procedure gave 44% (0.5 g) of $(-)K_3[Cr(C_2O_4)_3]\cdot H_2O$. A 0.02% solution gave $[\alpha]_D$ −1680°.

Resolution of the (±)-Tris(oxalato)cobaltate(III) Ion.—The method was the same as that utilized for the resolution of the corresponding chromium(III) complex except that the initial water volumes were reduced to 20 ml each. This procedure gave the double complex in 98% yield (1.4 g) and the optical antipode obtained directly from the acetone solution after the removal of the diastereoisomer weighed 1.0 g (82%). The following specific rotations were found for the antipode obtained from the acetone solution: $[\alpha]_{5461}$ −1425° for a 0.04% solution and $[\alpha]_D$ −1750° for a 0.02% solution. This product was dissolved in water and reprecipitated by the addition of alcohol and the rotation was redetermined. This material gave $[\alpha]_D$ −1850°. Further recrystallization did not raise the angle of rotation.

The double complex $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$ had a very low solubility in water and prolonged grinding with solid potassium iodide in cold water was necessary to cleave this material. The $(+)_{5461}K_3[Co(C_2O_4)_3]$ was obtained in poor yield (30%) and in a low degree of optical purity, $[\alpha]_{5461}$ +1030° for a 0.04% solution and $[\alpha]_D$ +1200° for a 0.02% solution.

Resolution of the (±)-Tris(oxalato)rhodate(III) Ion.—The

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(2) National Science Foundation Research Participant.

(3) National Science Foundation Undergraduate Research Participant.

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