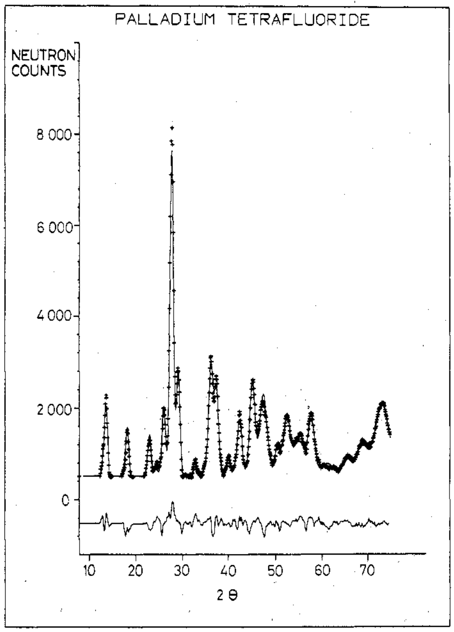

Figure 1. Powder pattern for PdF_4 obtained on the *D*2 diffractometer (λ 1.060 Å): +, observed intensities; –, calculated intensities. The difference curve is shown below.

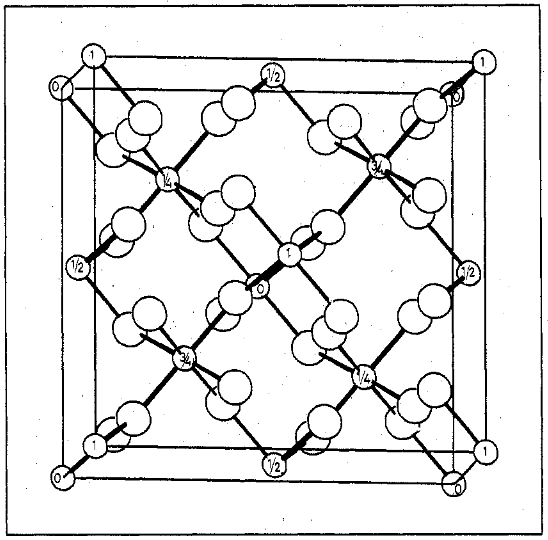

Figure 2. Unit cell of PdF_4 projected on the *a*–*b* plane (viewed obliquely): Pd, small circles marked with the fractional *z* coordinate along *c*; F, large circles.

Table II. Bond Lengths (Å) and Angles (deg) for PdF_4 and IrF_4

	Bond Lengths		
Pd-F(bridging)	1.91 (1), 2.00 (5)	Ir-F(bridging)	1.90, 1.89
Pd-F(nonbridging)	1.94 (5)	Ir-F(nonbridging)	2.08
	Bond Angles		
Ir-F-Ir (bridge)	147		
Pd-F-Pd (bridge)	134.0 (2.4)		
F(bridging)-Pd-F(bridging)	91.4 (1.5), 89.8 (1.5), 89.8 (1.5), 91.5 (1.5), 88.6 (2.8),		
F(bridging)-Pd-F(terminal)	88.8 (1.5), 89.8 (1.6), 89.8 (1.6), 88.9 (1.6), 92.7 (0.4), 92.7 (0.4)		
F(terminal)-Pd-F(terminal)	85.9 (2.8)		

the PdF_6 octahedra are approximately regular. The differences observed in bond lengths and bond angles within the PdF_6 octahedron are generally less than twice the calculated errors (see Table II). In addition, the observed Pd–F–Pd bridging angle of 134 ± 2.4° agrees well with that required (135°) for ideal hexagonal close packing of octahedra. We are not therefore able to distinguish between the Pd–F(bridging) bond lengths and the Pd–F(nonbridging) distances although we might expect the nonbridging bond to be shorter. In AuF_3[9] for example the fluorine bridges have a bond length of 2.04 Å compared to 1.91 Å for the terminal fluorine ligands, although in this low-spin d^8 compound there is a gross distortion of the AuF_6 octahedra toward square planar leaving two longer Au–F distances at 2.69 Å.

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Registry No. PdF_4, 13709-55-2.

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Tetrachlorophosphonium Oxotetrachlorochromate(V)

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The reaction between chromium(VI) dioxide dichloride and phosphorus pentachloride has been reported several times this century.[1-5] At high temperature[4,6] or in the presence of a reducing agent,[2,3,5] the product has been identified as tetrachlorophosphonium tetrachlorochromate(III), $(PCl_4)[CrCl_4]$. At room temperature,[1,3] the product was described as an adduct of chromium(VI) dioxide dichloride, $CrO_2Cl_2{\cdot}PCl_5$. As part of our investigations into the chemistry of chromium(V),[7,8] we have reinvestigated this system, as the formation of a chromium(VI) adduct did not appear to be in accord with chemical experience (reports of the existence of $CrO_2Cl_2(py)$,[9] $CrO_2Cl_2(py)_2$,[9] and $CrO_2Cl_2(bpy)$[10] (py = pyridine; bpy = 2,2′-bipyridine) have recently been shown to be erroneous[11]). We find that the product of the reaction between CrO_2Cl_2 and PCl_5, at room temperature, in both polar and nonpolar solvents, is the novel complex tetrachlorophosphonium oxotetrachlorochromate(V), $(PCl_4)[CrOCl_4]$, and report some of its spectroscopic properties. We also discuss the nature of $(PCl_4)[CrCl_4]$.

Results and Discussion

The reaction between chromium(VI) dioxide dichloride and phosphorus pentachloride, in both phosphorus oxide trichloride and carbon tetrachloride, yields a solid (red-brown microcrystals or orange-brown powder, respectively) of empirical formula Cl_8CrOP, and not Cl_7CrO_2P as previously reported.[1,3] The products from both solvents had similar infrared and electronic spectra, were extremely air sensitive, and were

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Table I. Infrared Spectra of Tetrachlorophosphonium Salts (Units of cm^{-1})[c]

$(PCl_4)^+$ [a]	$(PCl_4)[CrOCl_4]$ [b]	Assignment
1308 vvw	1309 vw	$2\nu_3(PCl_4)^+$
1266 vw	1261 w	?
1223 w	1207 vvw	?
1111 vvw	1095 w	$\nu_3 + \nu_1(PCl_4)^+$
	1017 s	$\nu(Cr{=}O)$
839 w		$\nu_3 + \nu_2(PCl_4)^+$
707 vw	698 vw	$\nu_1 + \nu_4(PCl_4)^+$
658 vs	652 vs	$\nu_3(PCl_4)^+$
	587 w	?
430 sh, vw	448 vw	?
	401 vs	$\nu(Cr-Cl)$
	348 w	$\nu(Cr-Cl)$

[a] As assigned from the spectrum of $(PCl_4)[AlCl_4]$: G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963). [b] Compound prepared in CCl_4. [c] Key: w = weak, s = strong, sh = shoulder, v = very.

Table II. Electronic Reflectance Spectra of Tetrachlorophosphonium Salts (Units of cm^{-1} × 10^3)

	$^2B_2 \rightarrow {}^2E$		
	ν_1 [$d_{xy} \rightarrow d_{xz,yz}$]	ν_2 [Cr–O (π) → Cr–O (σ^*)]	Charge-transfer transitions[d]
$(PCl_4)[CrOCl_4]$[a]	13.5	18.1	22.9 sh, 24.3 br, 32.4 br, 36.9 br, 45.1

	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Charge-transfer transitions[d]	*Dq*	*B*
$(PCl_4)[CrCl_4]$[b]	12.8	17.55	32.7 br, sh, 37.5, 45.1	1.28	0.462
$(PCl_4)[CrCl_4]$[c]	12.3	17.60	32.2 br, sh, 37.1, 45.5	1.23	0.544

[a] Prepared in CCl_4. [b] Prepared by Groeneveld's method.[2] [c] Prepared by Weber's method.[6] [d] Key: br = broad, sh = shoulder.

vigorously hydrolyzed in water to give a yellow solution. The infrared spectrum confirmed the presence of the $(PCl_4)^+$ cation (see Table I), and the complex was accordingly formulated as $(PCl_4)[CrOCl_4]$. The values of $\nu(Cr{=}O)$ at 1017 cm^{-1} and $\nu_{as}(CrCl_4)$ at 401 cm^{-1} confirm the presence of the C_{4v} monomeric $[CrOCl_4]^-$ anion (cf. for established $[CrOCl_4]^-$ complexes, $\nu(Cr{=}O)$ = 1015–1025 cm^{-1}, $\nu_{as}(CrCl_4)$ = 395–410 cm^{-1} [7,8]), which has recently been characterized by X-ray crystallography in the complex $(Ph_4As)[CrOCl_4]$.[12,13] X-ray powder photographs of $(PCl_4)[CrOCl_4]$ and $(PCl_4)[VOCl_4]$[14] reveal them to be isostructural, and their infrared spectra show the expected close similarity. (N.B. For $(PCl_4)[VOCl_4]$,[14] $\nu(V{=}O)$ = 1015 cm^{-1} and $\nu_{as}(VCl_4)$ = 370 cm^{-1}.)

$VOCl_3$ has been shown to react with PCl_5 to form the complex $(PCl_4)[VCl_5]$,[14] which has recently been shown to contain the five-coordinate $[VCl_5]^-$ anion with a C_{2v} structure based upon a distorted trigonal bipyramid,[15] as predicted by spectroscopic measurements[14] and crystal field calculations,[16] and not the C_{4v} structure based upon a square pyramid predicted by angular overlap calculations.[17] The mechanism of formation of $(PCl_4)[VCl_5]$ and $(PCl_4)[CrOCl_4]$ by oxygen abstraction is formally analogous:

$$VOCl_3 + 2PCl_5 \xrightarrow[POCl_3]{\text{reflux}} (PCl_4)[VCl_5] + POCl_3 + {}^1/_2Cl_2$$

$$CrO_2Cl_2 + 2PCl_5 \xrightarrow[POCl_3]{20\ ^\circ C} (PCl_4)[CrOCl_4] + POCl_3 + {}^1/_2Cl_2$$

$$CrO_2Cl_2 + 3PCl_5 \xrightarrow{140\ ^\circ C} (PCl_4)[CrCl_4] + 2POCl_3 + {}^3/_2Cl_2$$

The electronic spectrum of $(PCl_4)[CrOCl_4]$ (see Table II) shows values of $\nu_1[d_{xy} \rightarrow d_{xz,yz}]$ and $\nu_2[Cr\text{–}O(\pi) \rightarrow Cr\text{–}O(\sigma^*)]$ in good agreement with those reported previously for other oxotetrachlorochromates(V),[8,12] and the magnetic moment (μ_{eff} = 1.91 μ_B at 20 °C) is characteristic of chromium(V) complexes.[7,8]

$(PCl_4)[CrCl_4]$ has been the subject of a recent controversy. Machin et al.[4] prepared this complex by the method of Weber[6] and concluded that it probably contained the tetrahedral $[CrCl_4]^-$ anion, on the basis of magnetochemical measurements. Dawson and Smith[5] prepared it by the method of Groeneveld[2] and suggested that the complex contained an essentially octahedral $(CrCl_6)$ chromophore in the form of a polymeric anion, on the basis of its electronic spectrum. We find, however, that samples of $(PCl_4)[CrCl_4]$ prepared by the method of Groeneveld[2] are appreciably contaminated with phosphorus oxide trichloride (clearly detectable in their infrared spectra) which cannot be removed, even by prolonged continuous evacuation at 150 °C. Indeed, examination of the published analytical data[2] indicates a 7% contamination with $POCl_3$, and the electronic spectra of our samples prepared by this method yield a similar value of *Dq* (1280 cm^{-1}) to that reported by Dawson and Smith.[5]

Samples of $(PCl_4)[CrCl_4]$ prepared by the method of Weber[6] are appreciably purer, as evidenced by analytical and infrared data. Their electronic spectra yield a value of *Dq* = 1230 cm^{-1}, which compares well with typical literature values of *Dq* for $[CrCl_6]^{3-}$ (e.g., 1266,[18] 1233,[8] and 1245[8] cm^{-1}). The higher values obtained for samples prepared by Groeneveld's method[2] by Dawson and Smith[5] are clearly due to the presence of phosphorus oxide trichloride in the coordination sphere of the metal. Nevertheless, the electronic spectral measurements still favor the conclusion that $(PCl_4)[CrCl_4]$ contains a polymeric six-coordinate anion. This is further supported by infrared spectral measurements. Samples of $(PCl_4)[CrCl_4]$ prepared by Weber's method show a broad band at ca. 320 cm^{-1} (with a shoulder at ca. 360 cm^{-1}), due to $\nu(Cr-Cl)$. This is to be compared with ν_3 for $[CrCl_6]^{3-}$, which occurs at 315 cm^{-1}.[19] Finally, it is interesting to note that a recent x-ray structural determination upon $K[CrF_4]$[20] revealed that it contained novel columnar anions, $[CrF_4^-]_\infty$, in which all the chromium atoms are six-coordinate.

Experimental Section

Starting Materials, Physical Methods, and Analyses. Starting materials (e.g., BDH or Fisons) were used without further purification, unless otherwise stated. Carbon tetrachloride was dried (CaH_2) and distilled prior to use. Phosphorus oxide trichloride was fractionally distilled from phosphorus pentoxide. Physical measurements were made as previously described.[8] Analyses were performed by the Butterworth Microanalytical Consultancy, Ltd., or by the Alfred Bernhardt Mikroanalytisches Laboratorium.

All preparations and manipulations were performed under dry nitrogen or in vacuo.

Preparation of Tetrachlorophosphonium Oxotetrachlorochromate(V). (i) In $POCl_3$. A solution of phosphorus pentachloride (2 g) in phosphorus oxide trichloride (10 cm^3) was added slowly to a solution of chromium(VI) dioxide dichloride (0.8 cm^3) in phosphorus oxide trichloride (5 cm^3). The reaction mixture was allowed to stand at room temperature for 30 min. The red-brown microcrystalline product was filtered off in vacuo, washed with phosphorus oxide trichloride (10 cm^3), and dried in vacuo. Anal. Calcd for Cl_8CrOP: Cl, 74.13; Cr, 13.59; P, 8.10. Found: Cl, 73.9; Cr, 13.8; P, 8.2.

(ii) In CCl_4. A solution of phosphorus pentachloride (1.04 g) in carbon tetrachloride (80 cm^3) was added slowly to a solution of chromium(VI) dioxide dichloride (0.5 cm^3) in carbon tetrachloride (50 cm^3). The resultant red solution was allowed to stand at room temperature for 30 min, as an orange-brown suspension formed. The mixture was then stored at -20 °C for 24 h. The orange-brown powder was filtered off in vacuo at room temperature, washed with carbon tetrachloride (10 cm^3), and dried in vacuo. Anal. Calcd for Cl_8CrOP: Cl, 74.13; Cr, 13.59; P, 8.10. Found: Cl, 73.9; Cr, 13.5; P, 8.0.

Preparation of Tetrachlorophosphonium Tetrachlorochromate(III). **(i) Weber's Method.**[6] Phosphorus pentachloride (2.5 g) was heated with chromium(VI) dioxide dichloride (0.25 cm^3) in a vacuum-sealed Carius tube at 140 °C for 4 h. The resultant blue-purple powder was dried in vacuo. Anal. Calcd for Cl_8CrP: Cl, 77.37; Cr, 14.18; P, 8.45. Found: Cl, 77.0; Cr, 14.0; P, 8.58.

(ii) Groeneveld's Method.[2] Phosphorus trichloride (4.8 cm^3) was added slowly to a solution of chromium(VI) dioxide dichloride (3 cm^3) in phosphorus oxide trichloride (75 cm^3). A solution of phosphorus pentachloride (7.5 g) in phosphorus oxide trichloride (30 cm^3) was then added to the purple solution, and the resultant violet powder was filtered off in vacuo, washed with phosphorus oxide trichloride (75 cm^3), and dried in vacuo. Anal. Calcd for Cl_8CrP: Cr, 14.18; P, 8.45. Calcd for [Cl_8CrP + 7% $POCl_3$]: Cr, 13.78; P, 8.78. Found by Groeneveld:[2] Cr, 13.7; P, 8.7.

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Registry No. $(PCl_4)[CrOCl_4]$, 65045-58-1; $(PCl_4)[CrCl_4]$, 13859-46-6; PCl_5, 10026-13-8; CrO_2Cl_2, 7791-14-2.

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The Pfeiffer Effect with a Dissymmetric Metal Complex as an Environment Substance

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In our previous paper,[1] it was reported that the chiral equilibrium between Δ- and Λ-tris(acetylacetonato)cobaltate(II) (abbreviated as Δ- and Λ-$[Co(acac)_3]^-$) is displaced in favor of the former enantiomer upon the addition of Λ-tris(1,10-phenanthroline)cobalt(III) (abbreviated as Λ-$[Co(phen)_3]^{3+}$) in aqueous solutions. This system is, we believe, the first Pfeiffer-active system[2] in which a dissymmetric metal complex serves as a chiral environment substance. We present here another Pfeiffer-active system with Λ-$[Co(phen)_3]^{3+}$ as an environment substance.

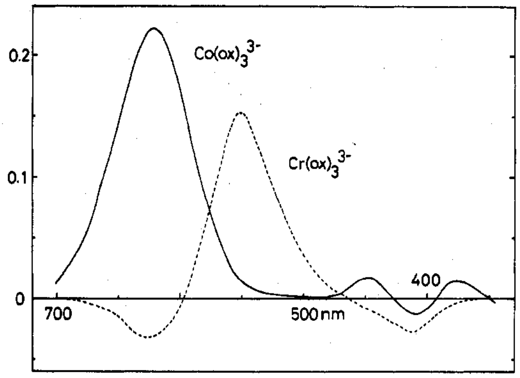

Figure 1. CD spectra for the $[Cr(ox)_3]^{3-}$ (4.39 mM)–Λ-$[Co(phen)_3]^{3+}$ (13.6 mM) and the $[Co(ox)_3]^{3-}$ (6.44 mM)–Λ-$[Co(phen)_3]^{3+}$ (10.2 mM) systems to each of which 10 mL of dioxane was added.

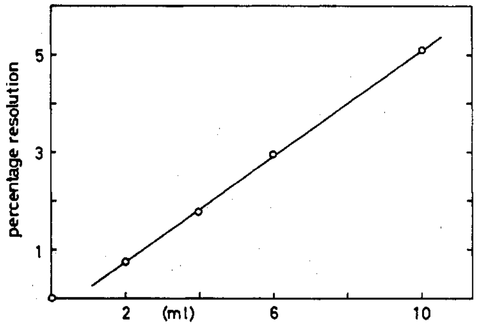

Figure 2. Influence of added dioxane on the percentage resolution for the $[Cr(ox)_3]^{3-}$ (4.39 mM)–Λ-$[Co(phen)_3]^{3+}$ (13.6 mM) system.

Experimental Section

Racemic $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ (ox = oxalate anion) were prepared by standard methods,[3] and Λ-$[Co(phen)_3](ClO_4)_3\cdot 3H_2O$ resolved by a usual method[4] was converted to the chloride form by treating with a Dowex 1X8 anion-exchange resin in Cl^- form. Sample solutions were prepared by mixing aqueous stock solutions of $K_3[Cr(ox)_3]$ or $K_3[Co(ox)_3]$ with those of Λ-$[Co(phen)_3]Cl_3$ in volumetric flasks (25 mL) to which varying amounts (up to 10 mL) of dioxane (reagent grade) were added. These solutions were kept standing in the dark for 1 day to attain the chiral equilibrium[5] and then were poured into a cation-exchange column (SP-Sephadex C-25 in Na^+ form) to remove Λ-$[Co(phen)_3]^{3+}$. During the ion-exchange process, the column was cooled with ice water to depress the racemization of $[Cr(ox)_3]^{3-}$ or $[Co(ox)_3]^{3-}$. Great care was taken to ensure that no precipitate was formed in the sample solutions as well as in the cation-exchange column, for Λ-$[Co(phen)_3]^{3+}$ precipitates preferentially with Λ-$[Cr(ox)_3]^{3-}$ or Λ-$[Co(ox)_3]^{3-}$ if a large amount of dioxane is added. The absorption (AB) and circular dichroism (CD) spectra were recorded for the effluents from the column as quickly as possible on a Shimadzu UV-200 and a Jasco J-40CS spectrometer, respectively.

Results and Discussion

The CD spectra (Figure 1) obtained for the $[Cr(ox)_3]^{3-}$ and $[Co(ox)_3]^{3-}$ systems clearly indicate that Λ enantiomer[6] is enriched in both systems when Λ-$[Co(phen)_3]^{3+}$ is employed as an environment, though Δ enantiomer is enriched in the $[Co(acac)_3]^-$–Λ-$[Co(phen)_3]^{3+}$ system.[1] This means that the Pfeiffer effect does not always work as a reliable means for the determination of the absolute configuration of labile metal complexes, as was pointed out earlier.[7]

By comparing the CD intensities at 552 nm,[6a] the percentage resolution was estimated and is plotted in Figure 2 as a function of the amount of added dioxane for the $[Cr(ox)_3]^{3-}$ system. It is seen that the addition of dioxane is quite favorable to this Pfeiffer system;[8] no optical activity is detected under our experimental conditions unless dioxane is added. Though it is not known at present why added dioxane enhances the Pfeiffer effect so greatly, an accompanying decrease in di-