Table I. Transitions and Rotational Constants for $PF_2C_2H_3$[a]

transition	ν(obsd), MHz	$\Delta\nu$, MHz[b]	transition	ν(obsd), MHz	$\Delta\nu$, MHz
3_{13}-4_{14}	20 905.99	−0.05	5_{15}-6_{16}	31 162.40	−0.05
3_{03}-4_{04}	21 613.91	0.24	5_{05}-6_{06}	31 695.21	0.11
3_{12}-4_{13}	23 106.43	0.18	5_{14}-6_{15}	34 323.77	−0.07
4_{14}-5_{15}	26 053.57	0.04	6_{06}-7_{07}	36 625.43	−0.06
4_{04}-5_{05}	26 708.71	0.18	6_{16}-7_{17}	36 235.64	−0.15
4_{13}-5_{14}	28 763.08	0.02	6_{15}-7_{16}	39 757.63	−0.20

[a] A = 7158.3 (10) MHz, B = 3041.28 (2) MHz, C = 2486.57 (1).
[b] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd, rigid rotor assumption})$.

the values in Table I by less than the estimated uncertainties.

The vibrational satellites appeared to be successively higher excited states of a single vibrational mode. Relative intensity measurements of the $v = 0$, $v = 1$, and $v = 2$ states gave a vibrational energy level spacing of 110 ± 30 cm^{-1}. The low-lying mode is probably the A″ torsion about the P–C bond.[2,6]

Dipole Moment. Second-order Stark coefficients (frequency shift vs. electric field) were measured for five transitions. They are given in Table S4 (available as supplementary material). These were used to determine the values of μ_a, μ_b, and μ_c by the standard procedure.[7] Four possible combinations of nonzero dipole components were tried in the analysis. Fits assuming $(\mu_a,\mu_c) \neq 0$ or $(\mu_a,\mu_b,\mu_c) \neq 0$ gave somewhat better agreement to the observed Stark coefficients than fits assuming $(\mu_a) \neq 0$ or $(\mu_a,\mu_b) \neq 0$. All four fits indicated that $|\mu_a| = 2.42$ D while $|\mu_b|$ and $|\mu_c|$ were estimated to be ≤0.090 D. In essence, these latter components were too small to be reliably estimated from the data. If μ_b is set to zero as required by symmetry for I or II, the result was $|\mu_a| = 2.42$ (3) D, $|\mu_c| = 0.08$ (5) D, and a total molecular dipole moment of 2.42 (3) D. This interpretation is preferred for reasons given below.

Analysis and Discussion

The presence of a plane of symmetry containing the phosphorus and vinyl group is indicated from several considerations. (1) Since $I_a + I_b - I_c = 33.53\ \mu\text{Å}^2$, totally planar configurations are ruled out. Moreover, $I_a + I_c - I_b = 2\sum m_i b_i^2 = 53.832\ \mu\text{Å}^2$ is similar to that in other PF_2X species such as PF_2H (54.99 $\mu\text{Å}^2$)[8] and PF_2CN (54.00 $\mu\text{Å}^2$).[6] This indicates that only the out of plane F···F interatomic distance contributes to $I_a + I_c - I_b$. (2) The observed values of μ_b and $\mu_c \simeq 0$ make some low-symmetry forms unlikely such as a conformation with C_1 symmetry which occurs in going from I to II by rotating the vinyl group about the P–C bond. As the vinyl moiety is rotated, one or both of these components must become sizeable due to the reorientation of the principal axes, even if the vinyl fragment has a low group moment. On the other hand, rough estimates of the components from assumed bond dipoles for a C_s conformation predict $\mu_a > \mu_c$ and $\mu_b = 0$ for either I or II. (3) The moments of inertia agree reasonably well with calculated values for I with assumption of plausible internal parameters. Conformer II and C_1 conformations do not appear to fit these moments unless unreasonable values for the internal coordinates are assumed.

Inspection of the preliminary moments of inertia which were predicted for I or II from an initial set of assumed internal parameters illustrates the basis for the assignment of the observed spectra to I. This model[9] predicted rotational constants of 6250, 3510, and 3020 MHz for II and 7300, 3010, and 2484 MHz for I. The discrepancies from the observed values of 13–18% for II cannot readily be corrected without some large and implausible changes in the initial structural parameters. However, it is a straightforward procedure to modestly alter these preliminary parameters and arrive at a reasonable structure for conformer I which agrees with the experimental moments of inertia. Such a structure will not be unique since only three equations are available which are functions of the 12 internal structural parameters. One solution has values for the vinyl moiety similar to other monosubstituted alkenes[10] and is consistent with the following parameters involving the PF_2 moiety: d(PF) = 1.577 Å, d(PC) = 1.805 Å, ∠FPF = 97.9°, ∠FPC = 98.0°, ∠PCC = 120.5°.[11] There is good reason to believe from comparison with other species that the true structure is within 0.02 Å and 3° of these values. For example, d(PF) and ∠FPF are usually between 1.567–1.591 Å and 95–99° in PF_2–R compounds.[6] This range of PF_2 parameters would be consistent with a range for d(PC) between 1.78–1.82 Å. This is somewhat shorter than in $P(CH_3)_3$ (1.843 (3) Å),[13] but it is similar to the value in PF_2CN (1.815 (5) Å)[6] and the estimated value for PF_2CH_3 (1.82 (2) Å).[3]

The possibility of II being present in low concentrations in the gas phase cannot be completely eliminated. Its spectrum, if present at all, is certainly less intense. This lower intensity would imply that II is higher in energy since its spectrum should be comparable in intensity to I apart from this Boltzmann factor.

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Registry No. $PF_2C_2H_3$, 51130-03-1.

Supplementary Material Available: Table S1, complete set of assigned frequencies for the ground state, Table S2, assigned frequencies for excited vibrational states, Table S3, rotational constants for the ground and excited states, and Table S4, Stark coefficients (6 pages). Ordering information is given on any current masthead page.

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(6) P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 1917 (1972).

(7) G. D. Fong, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1978; *Diss. Abstr. Int. B*, **39**, 4907 (1979).

(8) R. L. Kuczkowski, *J. Am. Chem. Soc.*, **90**, 1705 (1968).

(9) This model consisted of d(CH) = 1.09 Å, d(CC) = 1.33 Å, d(PC) = 1.84 Å, d(PF) = 1.54 Å, ∠HCH = 109°, ∠HCC = 125°, ∠HCP = 110°, ∠FPF = 99°, and ∠FPC = 99.7°.

(10) This model consists of d(CH) = 1.078 Å, d(CC) = 1.337 Å, ∠CCH_t = 119.8°, ∠CCH_c = 122.0°, and ∠CCH_g = 121.6°, where H_t, H_c, and H_g refer to cis, trans, or geminal to the phosphorus.

(11) Values close to these (within 0.006 Å and 0.6°) were also obtained by a fitting procedure called the method of predicate observables. In this procedure, the rotational constants and plausible structural parameters (with an uncertainty range) are treated as weighted data points to be fit by least squares. The details are described elsewhere.[7,12]

(12) L. S. Bartell, D. Romanesko, and T. C. Wong, *Mol. Struct. Diff. Methods*, **3**, Chapter 4 (1975).

(13) P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049 (1971).

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Oxidative Cleavage of Ditartrate-Bridged Binuclear Chromium(III) Complexes. A Stereochemical Correlation

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Gillard and Price have reported the oxidative cleavage by permanganate of vicinal diols in bridging tartrate groups in two diastereomers of the monotartrate-bridged complex μ-(d-tartrato(4−))-tetrakis(ethylenediamine)dicobalt(III), $[Co_2(tart)(en)_4]^{2+}$, to give (oxalato)bis(ethylenediamine)cobalt(III), $[Co(en)_2(ox)]^+$, enriched in one or the other enantiomer.[1] We report here a similar stereochemical correlation for the dibridged tartrate complexes of chromium(III) $[H_2Cr_2(tart)_2L_2]$ and $[HCr_2(tart)_2L_2]^-$ (L = 2,2′-bipyridyl or 1,10-phenanthroline) (**1**). Unlike the monobridged cobalt

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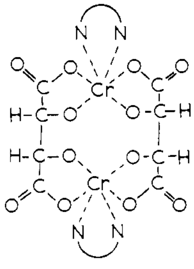
(1) Gillard, R. D.; Price, M. G. *J. Chem. Soc. D* **1969**, 67.



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complexes, which are often obtained as impure glasses,[2] these dibridged chromium compounds are well characterized, and most diastereomers can be obtained optically pure.[3]

Experimental Section

CD spectra were determined on a Cary Model 60 spectrophotometer equipped with a CD accessory. Sodium bis(oxalato(2−))(2,2′-bipyridyl)chromate(III) dihydrate, $Na[Cr(ox)_2(bpy)]\cdot 2H_2O$, and potassium bis(oxalato(2−))(1,10-phenanthroline)chromate(III), $K[Cr(ox)_2(phen)]$, were prepared by a slightly modified literature method (the barium salt intermediates were eliminated).[4] We have reported the syntheses and characterization of the dibridged chromium(III) tartrate complexes elsewhere.[3] All compounds prepared gave satisfactory elemental analyses.

Oxidation of $[H_2Cr_2(tart)_2(bpy)_2]$ in Acidic Solution. Cold (5 °C) solutions of $[H_2Cr_2(d\text{-tart})_2(bpy)_2]\cdot 3.5H_2O$ (2.22 g, 2.86 mmol) or $[H_2Cr_2(ms\text{-tart})_2(bpy)_2]\cdot 3H_2O$ (2.20 g, 2.87 mmol) in 40 mL of water and of sodium permanganate trihydrate (1.4 g, 7 mmol) in 20 mL of water to which perchloric acid (4.5 mL of 70% $HClO_4$, 50 mmol) had been added were mixed with vigorous stirring. After being allowed to react for 1 h, while continuing to be stirred at 5 °C, the mixture was filtered, and an aliquot was checked for the presence of MnO_4^- with KI and CCl_4 with negative results. After the addition of 10 g of anhydrous sodium perchlorate, the filtrate was reduced in volume to ca. 35 mL and an equal volume of 95% ethanol was added. Upon standing at 5 °C overnight, the solution deposited deep red needle-shaped crystals, which were filtered off and recrystallized from water and ethanol. Analysis and comparison with material prepared by another method[4] showed the product to be $Na[Cr(ox)_2(bpy)]\cdot 2H_2O$.

Oxidation of $[H_2Cr_2(tart)_2(phen)_2]$ in Acidic Solution. Solutions of $[H_2Cr_2(d\text{-tart})_2(phen)_2]\cdot 3.5H_2O$ and $[H_2Cr_2(ms\text{-tart})_2(phen)_2]\cdot 3H_2O$ were allowed to react with sodium permanganate trihydrate with procedures and conditions similar to those described above. The solutions were filtered (MnO_4^- was found to be absent), 8-g portions of sodium perchlorate were added, and the mixtures were allowed to sit overnight at 5 °C, during which time red-pink plates were deposited. Diaquo(oxalato(2−))(1,10-phenanthroline)chromium(III) perchlorate was filtered off and recrystallized from hot acetone. Anal. Calcd for $[Cr(C_2O_4)(H_2O)_2(C_{12}H_8N_2)]ClO_4$: Cr, 11.4; C, 36.90; H, 2.65; N, 6.15; ClO_4^-, 21.8; $C_2O_4^{2-}$, 19.3. Found: Cr, 11.1; C, 37.02; H, 2.73; N, 6.16; ClO_4^-, 22.4; $C_2O_4^{2-}$, 19.1. Ion-exchange chromatography showed the presence of only two detectable complexes in the remaining solution—unreacted tartrate starting material and additional $[Cr(H_2O)_2(ox)(phen)]^+$. Titration of the diaquo complex with sodium hydroxide solution to give the aquohydroxo species permitted the determination of an equivalent weight of 456 for the perchlorate salt. This value is in good agreement with the theoretical value of 455. From the solutions made basic with NaOH, red-brown, slightly soluble aquohydroxo(oxalato(2−))(1,10-phenanthroline)chromium(III)precipitated. Anal. Calcd for $[Cr(H_2O)(OH)(C_2O_4)(C_{12}H_8N_2)]$: Cr, 14.6; C, 47.33; H, 3.12; N, 7.89. Found: Cr, 14.1; C, 46.67; H, 3.12; N, 7.57.

Oxidation of $[Cr(ox)_2(bpy)]^-$ in Acidic Solution. Cold (5 °C) solutions of sodium permanganate trihydrate (0.314 g, 1.58 mmol) in 25 mL of water to which perchloric acid had been added (1.5 mL of 70% $HClO_4$, 17 mmol) and $Na[Cr(ox)_2(bpy)]$ (1.67 g, 4.09 mmol) in 80 mL of water were mixed and stirred for 9 h at 5 °C. Only starting material could be isolated (by precipitation as the barium salt) from aliquots removed during this time. After being allowed to warm to room temperature, the reaction mixture was stirred for an additional 19 h. Again, only starting material could be isolated from aliquots. Any remaining permanganate was reduced with sodium bisulfite, and aliquots were passed down cation-and anion-exchange columns. Only two species were detected on the columns—starting material and chromate (CrO_4^{2-}). There was no evidence for an aquo species. Approximately 42% of the starting material was recovered. The remainder was apparently oxidized to chromate.

Oxidation of $[Cr(ox)_2(phen)]^-$ in Acidic Solution. Cold (5 °C) solutions of potassium permanganate (0.184 g, 0.93 mmol) in 25 mL of water containing perchloric acid (4.4 mL of 70% $HClO_4$, 49 mmol) and $K[Cr(ox)_2(phen)]$ (1.01 g, 2.27 mmol) in 25 mL of water were mixed and allowed to react for 0.5 h. The mixture was then filtered (MnO_4^- was determined to be absent) and refrigerated overnight, during which time pink crystals formed. The product was recrystallized from acetone/water and was determined to be $[Cr(ox)(H_2O)_2(phen)]ClO_4$ by elemental analysis. The IR spectrum was identical with that of the material obtained from oxidation of $[H_2Cr_2(tart)_2(phen)_2]$.

Oxidation of $Na[HCr_2(d\text{-tart})_2(bpy)_2]$ for CD studies. For preparation of the monosodium salt of the tartrate complex, an equimolar amount of 0.14 M sodium hydroxide solution was added to $[H_2Cr_2(d\text{-tart})_2(bpy)_2]\cdot 3.5H_2O$ (0.50 g, 0.65 mmol) in 100 mL of water. To this solution wad added a solution of sodium permanganate trihydrate (0.507 g, 2.56 mmol) in 30 mL of water, and the reaction mixture was stirred for 20 min. To quench the reaction and reduce MnO_2 to Mn^{2+}, we added sodium bisulfite (1.27 g, 12.2 mmol) along with sodium perchlorate monohydrate (67.4 g, 480 mmol) to give an ionic strength of 1.00 ± 0.04 M when the solution was diluted to 500 mL in a volumetric flask. The first CD spectrum was recorded 15 min after quenching the reaction, and six subsequent spectra were recorded at 25-min intervals thereafter, while the solution temperature was maintained at 23 ± 2 °C. A final spectrum was recorded after 21 h. A plot of log $(\Delta\epsilon - \Delta\epsilon^\infty)$, where $\Delta\epsilon$ is the extinction coefficient difference for left and right circularly polarized light, as a function of time was linear over 3 half-lives. The final solution pH was 6.0.

Oxidation of $Na[HCr_2(d\text{-tart})_2(phen)_2]$ and $(CD^+)_{589}$-$Na[HCr_2(ms\text{-tart})_2(bpy)_2]$ for CD studies. These compounds were oxidized and CD spectra collected in manner analogous to that described above. Again the log $(\Delta\epsilon - \Delta\epsilon^\infty)$ vs. t plots were linear. The solution pH values were 6.1 and 7.0 for the phenanthroline and bipyridyl complexes, respectively.

Results and Discussion

Permanganate oxidation of binuclear chromium(III) ditartrate-bridged complexes containing either 2,2′-bipyridyl or 1,10-phenanthroline as the additional ligands results in cleavage of the tartrate ligands to give bis(oxalato) compounds. When 1,10-phenanthroline is present, further oxidation occurs to give diaquo(oxalato)(1,10-phenanthroline)chromate(III). That the bis(oxalato) compound is present as an intermediate in the oxidation of the 1,10-phenanthroline-containing complexes is evidenced by the following observations. First, when large excesses of $[H_2Cr_2(tart)_2(phen)_2]$ are oxidized, small amounts of $[Cr(ox)_2(phen)]^-$ can be isolated. Second, $K[Cr(ox)_2(phen)]$ prepared by an alternative method[4] is readily oxidized to the diaquo complex under the conditions employed for oxidation of the tartrates. This latter observation contrasts with the failure of $[Cr(ox)_2(bpy)]^-$ to give a diaquo product upon reaction with permanganate. To the best of our knowledge the syntheses of $[Cr(ox)(H_2O)_2(phen)]^+$ and (by proton abstraction) $[Cr(ox)(H_2O)(OH)(phen)]$ have not been previously reported.

No evidence has been found for the oxidation of either the nitrogen-containing ligands or (under most conditions employed) the chromium during the reactions. This contrasts with the oxidation of phenanthroline in Re(II) complexes by alkaline permanganate.[5] In no case is there any evidence for a monotartrate-bridged complex either as an intermediate or

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[2] Gillard, R. D.; Price, M. G. *J. Chem. Soc. A* **1969**, 1813.

[3] Robbins, G. L.; Tapscott, R. E. *Inorg. Chem.* **1975**, *15*, 154. This paper gives the wrong absolute configuration designations for tartrate enantiomers. The designations should be "$d = R,R$; $l = S,S$".

[4] Broomhead, J. A. *Aust. J. Chem.* **1962**, *15*, 228.

[5] Gillard, R. D.; Hill, R. E. E.; Maskill, R. *J. Chem. Soc. A* **1970**, 707.

Inorg. Chem. **1981**, *20*, 2345–2348

as a product. Both acidic and neutral pH conditions give essentially the same oxidation rates and the same products. To inhibit product racemization and to increase solubilities, we carried out oxidations where CD spectra were obtained near neutral pH. In basic solution, the tartrate complexes are destroyed by permanganate, giving chromate as one product.

The CD spectra (corrected for presence of unreacted optically active starting material) of the products of the oxidations of $[HCr_2(d\text{-tart})_2(bpy)_2]^-$ and $(CD^+)_{589}$-$[HCr_2(ms\text{-tart})_2(bpy)_2]^-$ have maxima and relative band intensities in agreement with those reported for $[Cr(ox)_2(bpy)]^-$.[6] The linear log plots obtained from the time dependence of these spectra show that the products of the *d*-tartrate and *ms*-tartrate complex oxidations racemize in first-order reactions with $t_{1/2}$ values of 48 and 46 min, respectively, at 23 °C. These values are reasonably close to that of 63 min at 25 °C calculated for the same conditions of pH and ionic strength from kinetic parameters for racemization of $[Cr(ox)_2(bpy)]^-$;[7] however, the values measured for our products are undoubtedly lowered, owing to catalysis by the Mn^{2+} ions present.[7] Comparisons of CD spectra for reactions and products in these oxidations permit chemical correlations of the absolute configuration of $[HCr(d\text{-tart})_2(bpy)_2]^-$ (which must be Δ at chromium)[3] with that of $(CD^-)_{513}$-$[Cr(ox)_2(bpy)]^-$ and of the absolute configuration of $(CD^+)_{589}$-$[HCr_2(ms\text{-tart})_2(bpy)_2]^-$ with that of $(CD^+)_{513}$-$[Cr(ox)_2(bpy)]^-$. These correlations are based on the not unreasonable assumption that oxidation occurs with (at least, primarily) retention of configuration at chromium, and they are in agreement with previous assignments[3] of opposite absolute configurations to $[HCr_2(d\text{-tart})_2(bpy)_2]^-$ and $(CD^+)_{589}$-$[HCr_2(ms\text{-tart})_2(bpy)_2]^-$ on the basis of CD spectra alone.

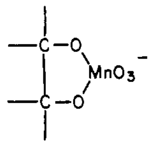
The optically active product formed in the permanganate oxidation of $[HCr_2(d\text{-tart})_2(phen)_2]^-$ exhibits a CD spectrum with a major negative band at 537 nm (differing from the value of 526 nm reported for $[Cr(ox)_2(phen)]^-$).[6] All of our results indicate that this product is primarily $[Cr(ox)(H_2O)_2(phen)]^+$, which must have a *cis* configuration in order for optical activity to occur. The time-dependent CD spectra show that this product loses optical activity in a first-order reaction at T = 23 °C, μ = 1.00 M, and pH 6.1 with $t_{1/2}$ = 41 min (in the presence of Mn^{2+}). This oxidation reaction shows that the chromium absolute configurations of $[HCr_2(d\text{-tart})_2(phen)_2]^-$ (which is Δ)[3] and $(CD^-)_{537}$-$[Cr(ox)(H_2O)_2(phen)]^+$ are the same.

There are several interesting features of the oxidations themselves that should be pointed out.

(a) There is an unexpectedly large difference in the reactivities of $[Cr(ox)_2(bpy)]^-$ and $[Cr(ox)_2(phen)]^-$ with permanganate. The former is exceedingly stable toward oxidation. Higher temperatures and longer times are required, and the only chromium-containing product detected under these conditions is chromate (CrO_4^{2-}). On the other hand, the 1,10-phenanthroline compound is rapidly oxidized to the dihydrate. This difference in reactivity may be due to steric effects (coordinated 2,2′-bipyridyl can twist);[8] however, molecular models fail to show any steric differences likely to significantly affect permanganate attack.

(b) The absence of any detectable monotartrate-bridged species in the tartrate complex oxidations is unexpected and indicates either that both diols are cleaved simultaneously or that a monobridged complex is significantly more susceptible to further oxidation.

(c) It is interesting that the *meso*-tartrate and *d*-tartrate complexes, despite their large differences in geometry,[3] react so similarly with permanganate. Of particular importance is the steric impossibility (shown by molecular models) for the *d*-tartrate complexes to form the cyclic manganese(VII) ester (**2**) given as a possible (though not necessarily likely) intermediate in glycol–permanganate reactions.[9] However, owing to the close approach of hydroxy oxygen atoms of different ligands in both the *meso*-tartrate and *d*-tartrate complexes,[3,10] simultaneous coordination of oxygen atoms on different bridging ligands by permanganate is possible. Formation of such an intermediate could allow simultaneous (or nearly so) bridge cleavage.



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Registry No. $H_2Cr_2(d\text{-tart})(bpy)_2$, 57172-74-4; $H_2Cr_2(ms\text{-tart})(bpy)_2$, 57172-56-2; $H_2Cr_2(d\text{-tart})_2(phen)_2$, 57129-82-5; $H_2Cr_2(ms\text{-tart})_2(phen)_2$, 57172-57-3; $[Cr(H_2O)_2(ox)(phen)]ClO_4$, 77257-28-4; $Cr(H_2O)(OH)(ox)(phen)$, 77270-02-1; $Na[Cr(ox)_2(bpy)]$, 77257-29-5; $K[Cr(ox)_2(phen)]$, 14516-02-0; $Na[HCr_2(d\text{-tart})_2(bpy)_2]$, 57129-83-6; $Na[HCr_2(d\text{-tart})_2(phen)_2]$, 57129-85-8; $(CD^+)_{589}$-$Na[HCr_2(ms\text{-tart})_2(bpy)_2]$, 57129-84-7; $(CD^-)_{537}$-$[Cr(ox)(H_2O)_2(phen)]^+$, 77287-03-7.

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(6) Kaizaki, S.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 988.

(7) Broomhead, J. A.; Kane-Maguire, N.; Lauder, I. *Inorg. Chem.* **1970**, *9*, 1243.

(8) McKenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 187.

(9) Stewart, R. *Org. Chem.* (*N. Y.*) **1965**, *5*, Chapter I.

(10) An X-ray structure determination on (±)-$Na[HCr_2(ms\text{-tart})_2(bpy)_2]\cdot 7H_2O$ shows a distance of 2.418 Å between hydroxyl oxygen atoms on separate bridges: Ortega, R. B. Ph.D. Dissertation, University of New Mexico, 1980.

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Heteronuclear Mixed-Valence Ions Containing Ruthenium and Ferrocene Centers

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and Henry Taube*

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The study of binuclear mixed-valence complexes has accelerated steadily since the first such diruthenium species was reported by Creutz and Taube in 1969.[1] Various metal centers have now been reported to form symmetrical homonuclear weakly coupled structures, of which the most common examples are those containing two ruthenium or two ferrocene nuclei.[2-4] Meyer and co-workers have also looked at the mixed-valence properties of unsymmetrical homonuclear diruthenium species of the type $[(NH_3)_5RuLRuCl(bpy)_2]^{4+}$ (L = pyz, 4,4′-bpy, BPE).[5] These unsymmetrical mixed-valence ions exhibited near-infrared intervalence-transfer (IT) bands

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