should be able to distinguish between the square pyramid and the trigonal bipyramid since the latter would not give an axially symmetric g tensor. Of course, line widths might prevent sorting out of g_x and g_y for small distortion of the molecular structure away from square pyramidal toward trigonal bipyramidal. Since the unpaired electron is still in a nonbonding d_{xy} orbital in both geometries, A_0 values probably should not be sensitive to the structure.[13] Finally, the anomalous position of the visible absorption maxima for VO(acen) and VO(tfen) might be evidence for a difference in geometry. A detailed discussion of this point must await a determination of the molecular structure of the complexes. An X-ray crystallographic study of these complexes is now in progress.[14]

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Electron-Transfer Rate Studies of Metal Complexes of Ethylenediaminetetraacetate and *trans*-1,2-Diaminocyclohexanetetraacetate

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Rate studies of only a relatively small number of redox reactions which are unambiguously outer sphere have been investigated. This is unfortunate since this is an area where the theoretical approach has been most fruitful.[1] Although a large number of metal ions form complexes with the EDTA-type ligand,[2] only the very slow isotopic exchange between Co(EDTA)$^{2-}$ and Co(EDTA)$^{-}$ ions[3,4] and between Co(PDTA)$^{2-}$ and Co(PDTA)$^{-}$ ions[4] has been measured. A lower limit of about 10^2 M^{-1} sec^{-1} at 20° can be estimated for the second-order rate constant for the Fe(EDTA)$^{2-}$–Fe(EDTA)$^{-}$ isotopic exchange.[3,5] We have now investigated the kinetics of a number of redox reactions involving these types of complexes (Table I).

Experimental Section

Materials.—The disodium salt of EDTA (Fischer) and the free acid CyDTA (City Chemical Corp.) were used without further purification. Cr(II) solutions were prepared by dissolving Cr pellets (United Mineral and Chemical Corp.) in deaerated dilute H_2SO_4. H[Cr(EDTA)]$\cdot H_2O$,[6] K[Mn(EDTA)]$\cdot 2.5H_2O$,[7] K[Mn(CyDTA)]$\cdot 2.5H_2O$,[8] and K[Co(EDTA)]$\cdot 3H_2O$[9] were prepared by known methods. Solutions containing Fe(EDTA)$^-$ and Fe(CyDTA)$^-$ were prepared by aerial oxidation of the corresponding iron(II) complex. The same spectra and results were obtained as using a solution of NH_4[Fe(EDTA)]$\cdot H_2O$. Other materials used were reagent grade.

Spectra.—The spectra of the air-sensitive species Cr(EDTA)$^{2-}$, Cr(CyDTA)$^{2-}$, Fe(EDTA)$^{2-}$, and Fe(CyDTA)$^{2-}$ have not previously been reported. They were measured by passing deaerated solutions of these ions through a flow-through cell until thoroughly flushed, closing stopcocks at either end of the cell, and fitting into a specially adapted holder which could be placed in the cell compartment of a Cary 14 spectrophotometer. The absence of iron and chromium tervalent metal complex (<5%) was shown by the relatively low absorption at 260 and 400 mμ, respectively.

Kinetic Experiments.—The EDTA or CyDTA complexes of Cr(II), Mn(II), Fe(II), and Co(II) were prepared *in situ* by adding a slight excess of ligand to a buffered solution of the metal ion.[10] Their reactions with solutions containing weighed amounts of the tervalent metal complexes were studied spectrally with a glass–Lucite stopped-flow apparatus or a Cary 14 spectrophotometer. All experiments involving Cr or Fe complexes were carried out in an N_2 atmosphere, but because of the extreme sensitivity of Cr^{II}-EDTA to O_2,[11] it was found more satisfactory to form this complex immediately prior to the redox reaction by mixing Cr_{aq}^{2+} in one syringe with M(III) complex, ligand, and lutidine buffer in the other syringe.

Reaction 1 was followed at 305 mμ where the chromium(III) complexes ($2–5 \times 10^{-3}$ M) have little absorption and the absorption coefficients of Cr(EDTA)$^{2-}$ and Cr(CyDTA)$^{2-}$ (4×10^{-4} M) are 90 and 290, respectively. Similar results were obtained when the small absorbance increase at 540 mμ was followed ($\epsilon_{Cr^{III}(EDTA)}$ - 200,[2,6,12] $\epsilon_{Cr^{III}(CyDTA)}$ - 240[13]).

Reaction 2 was monitored at 490 mμ where the manganese(II) complex (2×10^{-2}–10^{-1} M) has a very small absorption compared with Mn(EDTA)$^-$ and Mn(CyDTA)$^-$ (2×10^{-4}–10^{-3} M) with ϵ_M's of 444[8] and 330,[9] respectively.

An increase of absorbance at 258 mμ accompanies reaction 3 where the absorption coefficients for Fe(EDTA)$^{2-}$, Fe(CyDTA)$^{2-}$, Fe(EDTA)$^{-}$,[14] and Fe(CyDTA)$^{-}$ are, respectively, 480, 530, 9.4×10^3, and 8.2×10^3. Reactions were carried out with excess Fe^{II}-EDTA complex ($3.5–7.0 \times 10^{-4}$ M) over Fe^{III}-CyDTA ($4–6 \times 10^{-5}$ M). All studies were at pH 4.5–6.5 using sodium acetate or lutidine buffers. In (1) and (3) the second-order redox reactions were followed by slower, easily separable spectral

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TABLE I

KINETIC DATA FOR REDOX REACTIONS INVOLVING METAL–EDTA AND SIMILAR TYPES OF COMPLEXES AT 25°

Reaction no.	Reductant	Oxidant	k, M^{-1} sec^{-1}	k_{calcd},[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1	$Cr(CyDTA)^{2-}$	$Cr(EDTA)^{-}$	3.0×10^3	...	5.0	−26
2	$Mn(EDTA)^{2-}$	$Mn(CyDTA)^{-}$	1.2	...	7.1[b]	−34
3	$Fe(EDTA)^{2-}$	$Fe(CyDTA)^{-}$	3.0×10^4	...	4.0	−25
4	$Co(EDTA)^{2-}$	$Co(EDTA)^{-}$	4.0×10^{-7} [c]	...	20.0[c]	−21[c]
5	$Cr(EDTA)^{2-}$	$Fe(EDTA)^{-}$	$\geqslant 10^6$	$\geqslant 10^9$	...	...
6	$Cr(EDTA)^{2-}$	$Co(EDTA)^{-}$	$\sim 3 \times 10^5$	$\sim 4 \times 10^7$	...	...
7	$Fe(EDTA)^{2-}$	$Mn(CyDTA)^{-}$	$\sim 4 \times 10^5$ [d]	6×10^6 [e]	...	...
8	$Co(EDTA)^{2-}$	$Mn(CyDTA)^{-}$	0.9	2.1	4.8	−42
9	$Fe(PDTA)^{2-}$	$Co(EDTA)^{-}$	13[f]	19	6.7[f]	−32[f]
10	$Fe(PDTA)^{2-}$	$Co(CyDTA)^{-}$	12[f]	18	...	...

[a] On the basis of eq 1 and 2. For the calculation of K_{12} the following redox potentials were used: $Mn(EDTA)^{2-,1-}$, −0.82 V, N. Tanaka, T. Shirakaski, and H. Ogina, *Bull. Chem. Soc. Japan*, **38**, 1515 (1965); $Mn(CyDTA)^{2-,1-}$, −0.81 V, ref 9; $Co(EDTA)^{2-,1-}$, −0.40 V, $Co(CyDTA)^{2-,1-}$, −0.37 V, R. G. Wilkins and R. Yelin, unpublished work; $Cr(EDTA)^{2-,1-}$, ~1.0 V, ref 2; $Fe(EDTA)^{2-,1-}$, −0.12 V, ref 2. The Cr^{-} and Fe-CyDTA potentials were assumed to be equal to those of the EDTA system. [b] From data at $I = 0.25\ M$. [c] Reference 4. [d] At 5.0° and $I = 0.05\ M$ to reduce rate. [e] From rate constant values at 5.0°. [f] B. Grossman and R. G. Wilkins, *J. Am. Chem. Soc.*, **89**, 4230 (1967), and unpublished work.

changes which could be shown by separate studies to arise from the reaction of the excess M(II) complexes with buffer.[15]

Results and Discussion

Inspection of the redox potential values (Table I) and examination of the spectra at the completion of the reaction showed that reactions 1–3 were complete with 10-fold excess of one of the reactants (the low absorbing used). The poor oscilloscope traces obtained with reactions 1 and 3, arising from small absorbance changes and short half-lives, meant that the second-order rate law could be demonstrated over a limited range of reactant concentrations only. In addition the rapidity of reactions 5–7 allowed only approximate rate constants to be obtained. These were assumed to be second order on the reasonable analogy with (1)–(3).

All reactions have been investigated in the pH region 4.5–6.5 where one species predominates for the bivalent and tervalent metal complexes. We have avoided the more acid region where the monoprotonated form appears and the alkaline pH where the monohydroxo species is formed.[2,8,11,12] It is clear from the bulky nature of the ligands and the inertness of one of the reactant partners that these rapid redox reactions will take place through an intact coordination sphere,[14] *i.e.*, that they are outer-sphere processes and amenable to theoretical treatment.[1] Reactions (1)–(3) have small values for $\Delta G°$ and simulate closely the EDTA (or CyDTA) isotopic exchange reaction. The observed free energy of activation $\Delta G^{\ddagger}_{\text{obsd}}$ for an outer-sphere isotope exchange reaction is considered made up of contributory terms (a) $\Delta G^{\ddagger}_{\text{t}}$, (b) $\Delta G^{\ddagger}_{\text{o}}$, and (c) $\Delta G^{\ddagger}_{\text{i}}$, respectively, the free energies required to (a) bring the reactants from infinity to the transition state, (b) reorganize the solvent molecules surrounding the reactants, and (c) reorganize the inner coordination shells of the reactants.[1] It is informative to compare the results for the EDTA exchanges with those of the only other extensively investigated systems of isotopic exchange, namely, the metal aquated ions. Except for the cobalt system, electron transfer involving the EDTA complexes is the faster. The $\sim 10^4$ higher value for the rate constants for the Mn- and Fe-EDTA redox systems compared to those of the aquo ions resides mainly in smaller values for the sum of the easily calculable[1] ($\Delta G^{\ddagger}_{\text{t}} + \Delta G^{\ddagger}_{\text{o}}$), which in turn simply arises from a larger separation and smaller product of charges with the EDTA complexes. On the other hand, the $\Delta G^{\ddagger}_{\text{i}}$ term for the Cr_{aq}^{2+}–Cr_{aq}^{3+} exchange (11.1 kcal mol^{-1}) is much higher than the value for the $Cr(EDTA)^{2-}$–$Cr(EDTA)^{-}$ exchange (4.2). One could imagine that a Jahn–Teller distortion would cause a much greater disparity in metal–ligand bond distances in the case of Cr_{aq}^{2+} and Cr_{aq}^{3+} (and hence necessitate greater readjustment to produce the transition state) than with the more rigid EDTA-type complexes. The small values of $\Delta G^{\ddagger}_{\text{i}}$ accompanying reactions 1–3 probably reflect only small changes in the structure of reactant, transition state, and product. The structures of the Mn and Fe complexes in solution are unknown but the Cr complexes likely have the structures $Cr(EDTA)H_2O^{2-}$ and $Cr(EDTA)H_2O^{-}$ in solution, with the EDTA acting as a quinquedentate ligand.[11,16] The structures of the cobalt complexes in solution are similar, $Co(EDTA)^{-}$ and $Co(EDTA)^{2-}$,[17] each containing hexacoordinate EDTA, and the apparent anomaly of a large value for $\Delta G^{\ddagger}_{\text{i}}$ for this system (17.4 kcal mol^{-1}) can be ascribed to spin-multiplicity restrictions,[3] residing in a high enthalpy term (Table I).

A value for the rate constant (k_{12}) of a reaction such as (7), Table I, can be calculated, knowing the isotopic exchange rate constant for reactions 3 (k_{11}) and 2 (k_{22}) and the equilibrium constant for reaction 7, $\log K_{12} = 16.9\Delta E°$. Marcus[18] has derived the appropriate relations I and II for outer-sphere redox re-

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad \text{(I)}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \qquad \text{(II)}$$

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[15] A table of detailed data has been deposited as Document No. NAPS-00096 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

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actions. Application of these expressions to the six "cross reactions" (5)–(10) in Table I which all involve similarly charged reactants (−1 and −2) shows quite good agreement between the calculated and experimentally determined rate constants. This is particularly so when one considers the approximate values of certain E_0 values and the large differences in k_{11} and k_{22} and the large values for K_{12} which exist in some cases.

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Preparation and Reactions of Tetracarbonyl-μ-bis(difluorodithiophosphato)-dirhodium(I)

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Several new rhodium compounds having the empirical formulas $Rh(CO)_2(S_2PF_2)$, $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$, $Rh(CO)[As(C_6H_5)_3](S_2PF_2)$, and $Rh(CO)[Sb(C_6H_5)_3](S_2PF_2)$ have been synthesized. The difluorodithiophosphate $PS_2F_2^-$ ligand[1,2] and its conjugate acid HPS_2F_2[1,3,4] are useful intermediates for the formation of compounds containing the $PS_2F_2^-$ group.[4,5] The chemistry of this ligand is, indeed, similar to that of the analogous dialkoxydithiophosphate ligands.[6]

Experimental Section

Materials.—Tetracarbonyl-μ-dichloro-dirhodium(I) was synthesized from $RhCl_3 \cdot 3H_2O$ (Alfa Inorganics, Inc.) and CO. The cesium salt of difluorodithiophosphate was prepared as described in the literature.[2] Triphenylphosphine, -arsine, and -stibine were obtained from commercial sources and used without further purification. Solvents were distilled from molecular sieves (Linde 5A) immediately before use.

Apparatus and General Procedure.—Infrared spectra of solid samples were measured on a Perkin-Elmer 521 spectrometer. The ^{19}F nmr spectra were obtained with a Varian Model V4310 spectrometer operating at 40 Mc using benzene as a solvent for the samples and fluorotrichloromethane as an internal standard. Solutions were placed in 5-mm o.d. tubes. Molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 301, in benzene solution.

Preparation of $[Rh(CO)_2(S_2PF_2)]_2$.—In a typical preparation, tetracarbonyl-μ-dichloro-dirhodium(I) (0.952 g, 2.45 mmol) dissolved in 100 ml of pentane was stirred with an excess af $CsPS_2F_2$ (1.34 g, 5.05 mmol). After 4 hr, the solvent was removed under reduced pressure (*ca.* 20 mm, between 0 and −10°). The residue was sublimed *in vacuo* onto a probe cooled to about −30°. The yield of the orange-red solid (mp 48°) was 0.640 g (44.6%). *Anal.* Calcd for $C_4F_4O_4P_2Rh_2S_4$: C, 8.22; F, 13.01; P, 10.62; mol wt, 584. Found: C, 8.20; F, 13.45; P, 9.2; mol wt, 590. The ^{19}F nmr spectrum showed a doublet ($J_{P-F} = 1312$ cps) at ϕ 3.4.

Preparation of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$.—Triphenylphosphine (0.314 g, 1.20 mmol) and $[Rh(CO)_2(S_2PF_2)]_2$, (0.350 g, 0.60 mmol) were weighed into a 50-ml flask. The flask was cooled to −196° and evacuated. Approximately 5 ml of benzene was distilled into the flask. Upon warming to room temperature, the solution changed from deep red to yellow and carbon monoxide was evolved. After 0.2 hr the solvent was removed and the residue was extracted with pentane until the extracts were colorless. The pentane solution was concentrated in a stream of nitrogen before cooling to 0°. Yellow crystals were collected and vacuum dried. The product weighed 0.510 g (81% of theory) and decomposed above 100°. *Anal.* Calcd for $C_{19}H_{15}F_2OP_2RhS_2$: C, 43.47; H, 2.87; mol wt, 526. Found: C, 43.50; H, 2.87; mol wt, 544. A doublet centered at ϕ 2.7 ($J_{P-F} =$ 1312 cps) was observed in the nmr spectrum.

When a benzene solution of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$ was allowed to interact with excess triphenylphosphine, no further evolution of carbon monoxide was observed even when the solution was heated to 60° for several hours.

Reaction of $[Rh(CO)_2(S_2PF_2)]_2$ with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$.—Using a procedure similar to that described for the preparation of $Rh(CO)[P(C_6H_5)_3](S_2PF_2)$, both $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ react with the parent dicarbonyl. Carbon monoxide, detected by mass spectral analysis, was again evolved. Brownish red solids were obtained upon removal of benzene and subsequent recrystallization from CH_2Cl_2–C_5H_{12} mixtures. The outcome of these reactions appears to be the same when excess arsine or stibine is used. *Anal.* Calcd for $C_{19}H_{15}AsF_2OPRhS_2$: C, 40.02; H, 2.65; F, 6.66; P, 5.44; mol wt, 570. Found: C, 40.00; H, 2.66; F, 6.4; P, 4.9; mol wt, 700. Calcd for $C_{19}H_{15}F_2OPRhSbS_2$: C, 36.98; H, 2.45; F, 6.16; P, 5.02; Sb, 19.74; mol wt, 617. Found: C, 36.65; H, 2.50; F, 6.2; P, 4.8; Sb, 19.6; mol wt, 2100.

Results and Discussion

The reaction of tetracarbonyl-μ-dichloro-dirhodium(I) with $CsPS_2F_2$ yields a volatile, orange solid of empirical formula $Rh(CO)_2(S_2PF_2)$. The fluorine magnetic resonance spectrum of the complex consists of a doublet caused by phosphorus–fluorine coupling centered at ϕ 3.4 ($J_{P-F} = 1312$ cps). Additional splitting due to ^{103}Rh was not observed. The position of the signal and the magnitude of the PF spin–spin coupling are consistent with a chelate attachment of the difluorodithiophosphato group.[4,5] Molecular weight measurements indicate that the complex is dimeric in benzene solution.

Examination of the infrared spectrum (Table I) of the complex provides further insight into the structure of the new dicarbonyl. Absorptions associated with the P–S stretch are observed at 692 and 670 cm^{-1} in Nujol whereas the related absorptions of $CsPS_2F_2$ occur at 735 and 710 cm^{-1}. The shift of the P–S stretch to lower wave number values in the complex implies coordination of the PS_2F_2 entity to rhodium through equivalent sulfur atoms. The positions of the four absorptions in the metal carbonyl region are characteristic of terminal carbonyl ligands. Moreover, the spectral features in this region are similar to those of [Rh-

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