to proceed with ΔS^* values of -20 to -30 e.u.[10] Of course, solvent electrostriction is not the only thing that contributes to the entropy of activation. If stringent stereochemical requirements exist in the transition state, then its formation is accompanied by a decrease in entropy. This may be more than sufficient to compensate for the positive entropy effect due to solvation. The results at hand are not numerous but do fit such an explanation. For example, the entropy of activation for the exchange of radiochloride ion with $[Pt(NH_3)_3Cl]^+$ is positive and that for the reaction of bromide ion with $[Au(dien)Cl]^{2+}$ is less negative than for the same reaction of $[Pt(dien)Cl]^+$. This suggests that solvation effects are more important for the first two complexes than for the last. Such is the case because $[Pt(NH_3)_3Cl]^+$ is smaller and $[Au(dien)Cl]^{2+}$ has a larger charge relative to $[Pt(dien)Cl]^+$. It is also in accord with the negative ΔS^* values found for the nonionic *trans*-$[Pt(P(C_2H_5)_3)_2X_2]$ systems, where solvation effects are small.

The k_1 path, as mentioned previously, is less important in the reactions of these Au(III) complexes than is the k_2 path, but the converse is true for Pt(II). In order to try to explain this difference between Au(III) and Pt(II), it would be desirable to compare the activation parameters of the k_1 paths. Unfortunately, k_1 is so small relative to $k_2[Br^-]$ for the reaction of $[Au(dien)Cl]^{2+}$ with Br^- that values of ΔH_1^* and ΔS_1^* were not obtained. For the $[Pt(dien)Cl]^+$–Br^- reaction, the activation parameters are given in Table VI. These data are consistent with the mechanistic path *via* the solvent route proposed by Gray and Olcott for $[Pt(dien)X]^+$ type complexes.[11] These workers suggested that the principal intermediate in the first-order path of Pt(II) reactions is an aquo complex formed by an S$_N$2 reaction with the solvent water. For Au(III) such an aquo intermediate would be expected to be a strong acid and would not exist in aqueous solutions in significant quantities except under extremely acid conditions. Over the pH range in which our experiments were carried out, the principal hydrolyzed species was undoubtedly a hydroxo complex, $[Au(dien)OH]^{2+}$ at the lower pH range and $[Au(dien\text{-}H)OH]^+$ in the pH 7 region. The question then arises as to what is the first-order path intermediate in the reaction of Au(III) complexes. As noted in the Results section, $[Au(dien)OH]^{2+}$ was generated *in situ* and allowed to react with bromide ion under the same conditions of acidity and bromide ion concentration at which the $[Au(dien)Cl]^{2+}$–Br^- reaction was carried out. A reaction occurred in which $[Au(dien)Br]^{2+}$ was formed too fast to measure with our stopped-flow system. This indicates that $[Au(dien)OH]^{2+}$ (or a species that is formed therefrom under these experimental conditions) is labile enough to serve as the first-order path intermediate.

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[11] H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

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The Kinetics of Some Related Electron-Transfer Reactions[1]

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The kinetics of the oxidation of a number of substituted tris(1,10-phenanthroline) complexes of iron(II) by cobalt(III) in perchloric acid have been investigated by the use of a flow technique. The results are compared with other oxidation–reduction reactions involving the iron(II)–phenanthroline complexes. The oxidation of $Fe(dipy)_3^{2+}$, $Fe(dipy)_2(CN)_2$, $Fe(dipy)(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, and the corresponding phenanthroline complexes by cerium(IV) in sulfuric acid has also been investigated. It was found that the oxidation of the mixed-ligand complexes proceeds more rapidly than the oxidation of the complexes containing identical ligands. Other oxidation–reduction reactions studied include the oxidation of $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ by Ce(IV) and $IrCl_6^{2-}$, as well as the $Mo(CN)_8^{3-}$–$W(CN)_8^{4-}$, $Mo(CN)_8^{3-}$–$Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$–$W(CN)_8^{4-}$ reactions. The results are discussed in the light of the Marcus theory of electron-transfer reactions.

The *a priori* calculation of the rates of electron-transfer reactions requires a knowledge of such properties of the reactants and products as interatomic distances, force constants, etc.[2] Unfortunately, many of these quantities are not known at the present time for most electron-transfer reactions of interest. However, Marcus has shown that these parameters tend to cancel when reactions involving a series of related systems are compared.[3] Thus, to a very good approximation, it is not necessary to know the values of

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

[3] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

these parameters when making such comparisons. Marcus has derived the expression

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \qquad (1)$$

where

$$\log f = (\log K_{12})^2 / 4 \log (k_1 k_2 / Z^2)$$

which relates k_{12}, the rate constant for an electron-transfer reaction accompanied by a net chemical change, to k_1 and k_2, the rate constants for the corresponding electron-exchange reactions, and K_{12}, the equilibrium constant for the electron-transfer reaction. Z is the collision frequency of two uncharged molecules in solution (10^{11} l. mole^{-1} sec.$^{-1}$). The above equation is applicable to outer-sphere electron-transfer reactions when the various work terms cancel or are negligible.

Equation 1 is satisfied by a number of systems.[4–6] An important exception is the iron(II)–cobalt(III) reaction, which proceeds much more slowly than predicted. It was therefore of interest to study some other reactions involving cobalt(III) in order to determine whether their rates, too, were anomalous. We have also studied the oxidation of $Fe(dipy)_3^{2+}$, $Fe(dipy)_2(CN)_2$, $Fe(dipy)(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, and the corresponding phenanthroline complexes by cerium(IV), as well as a number of other oxidation–reduction reactions involving a variety of systems. The results are discussed in the light of the Marcus theory.

Experimental

The phenanthroline, phenanthroline–cyanide, and dipyridine–cyanide complexes of iron(II) were prepared as described elsewhere.[5–7] Cobalt(III) was prepared by electrooxidation of cobalt(II) perchlorate solutions. Potassium octacyanomolybdate(IV) and potassium octacyanotungstate(IV) were prepared according to published procedures.[8,9] We are grateful to Dr. M. H. Ford-Smith for a gift of the latter compound. Potassium octacyanomolybdate(V) was prepared by electrooxidation of the lower oxidation state. Ammonium hexachloroiridate(IV) (A. D. Mackay, Inc.), ceric sulfate (G. Frederick Smith Chemical Co.), potassium hexacyanoferrate(II) (Baker and Adamson), potassium hexacyanoferrate(III) (Mallinckrodt Chemical Works), sulfuric acid (Baker and Adamson), and perchloric acid (Baker Chemical Co.) were used without further purification.

The reactions were studied at 25.0° by the use of the flow apparatus which has been described previously.[5] The reactant concentrations were between 10^{-3} and 10^{-6} M, depending on the rates of the reactions. In the case of the slower reactions the reactant concentrations were independently varied by more than a factor of ten, while in the very fast reactions only a two-fold variation in reactant concentrations was possible. With the exception of the reactions involving cobalt(III), which were studied in 3 M perchloric acid, all the reactions were studied in 0.5 M sulfuric acid.

Results and Discussion

The reactions were found to be first order with respect to each of the reactants. Values of the second-order rate constants for the oxidation of various substituted iron(II)–phenanthroline complexes by cobalt(III) in 3 M perchloric acid are presented in Table I together with the formal oxidation potentials of the complexes.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF IRON(II)–PHENANTHROLINE COMPLEXES BY COBALT(III) IN 3 M PERCHLORIC ACID AT 25.0°

Ligand	$E°$, v.[a]	$k_{12} \times 10^{-3}$, M^{-1} sec.$^{-1}$
5-Methyl-1,10-phenanthroline	1.02	15.0
1,10-Phenanthroline	1.06	14.0
5-Chloro-1,10-phenanthroline	1.12	5.02
5-Nitro-1,10-phenanthroline	1.25	1.49

[a] G. F. Smith and W. M. Banick, Jr., *Talanta*, **2**, 348 (1959).

A number of oxidation–reduction reactions involving the iron(II)–phenanthroline complexes have now been studied. The results are summarized in Table II which also includes parameters calculated from eq. 1. It should be noted that the effect of acidity on the slopes and intercepts is small. Thus the slopes pertaining to the oxidation of ferrous ions by various substituted iron(III)–phenanthroline complexes in 0.5 M sulfuric and 0.5 M perchloric acids are the same within experimental error, while the intercepts vary by about 0.5 kcal. mole^{-1}.[4] Similarly, the slopes and intercepts for the oxidation of various substituted iron(II)–phenanthroline complexes by manganese(III) are the same in 1 and 3 M perchloric acid. The effect of acid on the individual reaction rates is also small. For example, the rate of the $Fe(phen)_3^{3+}$–Fe^{2+} reaction increases by about 20% as the acidity is decreased from 0.50 to 0.05 M perchloric acid.[10] The effect of acidity on the Ce(IV)–$Fe(phen)_3^{2+}$ reaction is also small.[5]

The observed slopes are seen to be in good agreement with the calculated values, and the rates of the Co(III)–$Fe(phen)_3^{2+}$ reactions, in particular, show the expected dependence on $\Delta G_{12}°$. It should be noted that the slope of ΔG_{12}^* *vs.* $\Delta G_{12}°$ for the Co(III)–$Fe(phen)_3^{2+}$ reactions is only 0.27, illustrating the importance of the f factor when the free energy changes become very large. On the other hand, the intercepts for all the reactions are smaller than predicted by eq. 1, and the disagreement is largest in the case of the Co(III)–$Fe(phen)_3^{2+}$ reactions. Marcus has suggested that this disagreement could arise from the noncancellation of the nonelectrostatic contributions to the work required to bring the various pairs of reactants together.[3] However, it is still necessary to invoke an additional factor to account for the fact that the Co(III)–$Fe(phen)_3^{2+}$ reactions proceed about 10^{-4} times as fast as the other three systems considered in Table II. In this connection it is worth recalling that the Co(III)–Fe^{2+} reaction also proceeds about 10^5 times more slowly than predicted.[5] The factor responsible for the slowness of the reactions involving the cobalt-

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(4) M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961).

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(10) N. Sutin and B. M. Gordon, *ibid.*, **83**, 70 (1961).

TABLE II

SLOPES AND INTERCEPTS OF PLOTS OF ($\Delta G_{12}^* + 0.50RT \ln f$) *vs.* $\Delta G_{12}°$ FOR OXIDATION–REDUCTION REACTIONS INVOLVING SUBSTITUTED IRON(II)–PHENANTHROLINE COMPLEXES AT 25.0°

Reaction	Slope[d]		Intercept,[d] kcal. mole^{-1}		Medium
	Obsd.	Calcd.	Obsd.	Calcd.	
$Fe(phen)_3^{3+}$–Fe^{2+}[a]	0.56	0.50	14.8	13.0	0.5 *M* H_2SO_4
Ce(IV)–$Fe(phen)_3^{2+}$[b]	0.48	0.50	14.8	13.0	0.5 *M* H_2SO_4
Mn(III)–$Fe(phen)_3^{2+}$[c]	0.49	0.50	17.6	15.8	1 and 3 *M* $HClO_4$
Co(III)–$Fe(phen)_3^{2+}$	0.51	0.50	19.5	12.9	3 *M* $HClO_4$

[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] The exchange rate constants used are: Fe^{2+}–Fe^{3+}, 4.0 M^{-1} sec.$^{-1}$ [J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952)]; Ce(III)–Ce(IV), 4.4 M^{-1} sec.$^{-1}$ [P. B. Sigler and B. J. Masters, *J. Am. Chem. Soc.*, **79**, 6353 (1957)]; Mn(II)–Mn(III), 3 × 10^{-4} M^{-1} sec.$^{-1}$ [ref. 6]; Co(II)–Co(III), 7 M^{-1} sec.$^{-1}$ [N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 3826 (1960)]; $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$, 1 × 10^6 M^{-1} sec.$^{-1}$ The Mn(II)–Mn(III) rate constant is an indirect estimate and only a lower limit of 1 × 10^5 M^{-1} sec.$^{-1}$ has been established for the rate constant for the $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ exchange reaction [M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963)].

(II)-cobalt(III) couple would presumably have to become more important as the asymmetry or standard free energy changes of the reactions increased, since it is implicit in the above comparisons that the rate constant for the Co^{2+}-Co^{3+} electron exchange reaction is normal.

TABLE III

Reaction	k_{12} obsd., M^{-1} sec.$^{-1}$	k_{12} calcd.,[a] M^{-1} sec.$^{-1}$
Ce(IV)–$W(CN)_8^{4-}$	$>10^8$	6,1 × 10^8
Ce(IV)–$Fe(CN)_6^{4-}$	1.9 × 10^6	6.0 × 10^6
Ce(IV)–$Mo(CN)_8^{4-}$	1.4 × 10^7	1.3 × 10^7
$IrCl_6^{2-}$–$W(CN)_8^{4-}$	6.1 × 10^7	8.1 × 10^7
$IrCl_6^{2-}$–$Fe(CN)_6^{4-}$	3.8 × 10^5	5.7 × 10^5
$IrCl_6^{2-}$–$Mo(CN)_8^{4-}$	1.9 × 10^6	1.0 × 10^6
$Mo(CN)_8^{3-}$–$W(CN)_8^{4-}$	5.0 × 10^6	1.7 × 10^7
$Mo(CN)_8^{3-}$–$Fe(CN)_6^{4-}$	3.0 × 10^4	2.7 × 10^4
$Fe(CN)_6^{3-}$–$W(CN)_8^{4-}$	4.3 × 10^4	5.1 × 10^4

[a] The following oxidation potentials and exchange rate constants, respectively, were used to calculate the rate constants for the cross reactions: Ce(III)–Ce(IV), 1.44 v., 4.4 M^{-1} sec.$^{-1}$; $IrCl_6^{2-}$–$IrCl_6^{3-}$, 0.93 v., 2 × 10^5 M^{-1} sec.$^{-1}$; $Mo(CN)_8^{3-}$–$Mo(CN)_8^{4-}$, 0.80 v., 3 × 10^4 M^{-1} sec.$^{-1}$; $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$, 0.68 v., 3 × 10^2 M^{-1} sec.$^{-1}$; $W(CN)_8^{3-}$–$W(CN)_8^{4-}$, 0.54 v., 7 × 10^4 M^{-1} sec.$^{-1}$ Only lower limits of 2 × 10^3 and 4 × 10^4 M^{-1} sec.$^{-1}$ have been established for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ and $W(CN)_8^{3-}$–$W(CN)_8^{4-}$ exchanges, respectively [E. N. Sloth and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 1440 (1955), and ref. 9]. The other exchange reactions were studied under the following conditions: Ce(III)–Ce(IV) exchange in 0.4 *M* sulfuric acid, $Mo(CN)_8^{3-}$–$Mo(CN)_8^{4-}$ exchange in the absence of added electrolyte [R. J. Campion, unpublished observations] and the $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ exchange in 0.01 *M* potassium hydroxide [C. F. Deck and A. C. Wahl, *J. Am. Chem. Soc.*, **76**, 4054 (1954)].

In Table III some observed rate constants are compared with values calculated from eq. 1. The agreement of the observed and calculated rate constants is encouraging, particularly since the equilibrium constants for the reactions vary by a factor of 10^{13}. It should be noted, however, that the $IrCl_6^{2-}$–$IrCl_6^{3-}$ and $W(CN)_8^{3-}$–$W(CN)_8^{4-}$ exchange-rate constants are fitted values (which are consistent with the observed values provided separation-induced exchange is absent) and that the $Mo(CN)_8^{3-}$–$Mo(CN)_8^{4-}$ and $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ exchange-rate constants were measured in media which are somewhat different from those used for studying the cross reactions.

Second-order rate constants for the oxidation of $Fe(CN)_6^{4-}$, $Fe(phen)(CN)_4^{2-}$, $Fe(phen)_2(CN)_2$, $Fe(phen)_3^{2+}$, and the corresponding dipyridine complexes by cerium(IV) in 0.50 *M* sulfuric acid at 25.0° are presented in Table IV. It will be seen that the complexes containing both cyanide and phenanthroline or dipyridine groups react faster than the other iron(II) complexes. This behavior can be rationalized in terms of eq. 1. The equilibrium constants for the oxidation-reduction reactions tend to decrease as the cyanides are replaced by phenanthroline (or dipyridine) groups. On the other hand, the $Fe(CN)_6^{4-}$-$Fe(CN)_6^{3-}$ electron-exchange reaction is much slower than the $Fe(phen)_3^{3+}$-$Fe(phen)_3^{2+}$ exchange reaction, and it is quite likely that the exchange-rate constants increase monotonically in the series. In terms of this interpretation the relatively rapid reactions involving the mixed-ligand complexes reflect the best compromise of exchange-rate and equilibrium constants.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF IRON(II) COMPLEXES BY CERIUM(IV) IN 0.5 *M* SULFURIC ACID AT 25.0°

Complex	$E°$, v.[a-c]	$k_{12} \times 10^{-6}$, M^{-1} sec.$^{-1}$
$Fe(phen)_3^{2+}$	1.07	0.142[d]
$Fe(phen)_2(CN)_2$	0.79	7.11
$Fe(phen)(CN)_4^{2-}$	0.65	8.88
$Fe(dipy)_3^{2+}$	1.05	0.196
$Fe(dipy)_2(CN)_2$	0.81	8.40
$Fe(dipy)(CN)_4^{2-}$	0.67	12.5
$Fe(CN)_6^{4-}$	0.69	1.90

[a] P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959). [b] A. A. Schilt, *Anal. Chim. Acta*, **26**, 134 (1962). [c] J. Jordan and C. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962). [d] Reference 5.

Exchange reactions between ions of like charge are usually catalyzed by oppositely charged ions. For example, the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ and MnO_4^{2-}–MnO_4^- exchanges are catalyzed by positively charged ions. In the course of the studies described above we noticed that the rates of the $Fe(CN)_6^{4-}$–$Mo(CN)_8^{3-}$ and $Fe(CN)_6^{4-}$–$Fe(dipy)(CN)_4^-$ reactions decreased as the acidities of the solutions were increased. The direction of this effect is opposite to that which might be expected on the basis of simple electrostatic or ionic strength considerations. The lowering of the rates probably arises from the increase in the formal oxidation potential of the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ couple with acidity. This increase causes a corresponding decrease in the standard free energy changes for the reactions, thereby lowering their rates.

By and large the results satisfy the Marcus relation reasonably well. If additional studies show that eq. 1 is indeed satisfied by a large variety of systems then any departure from eq. 1, as has been found, for example, in the case of the reactions involving cobalt(III), may well be taken as evidence of a more complex mechanism. Further studies are necessary to determine whether this complexity arises from an inner-sphere mechanism, electronic factors, or some other complicating feature.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts

The Crystal and Molecular Structure of Tris(phenyldiethylphosphine)nonachlorotrirhenium(III)[1a]

By F. A. COTTON[1b] and JOEL T. MAGUE[1c]

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The compound of empirical formula $ReCl_3[(C_6H_5)(C_2H_5)_2P]$ has been shown to be a trimer having essentially the same structure as the $[Re_3Cl_{12}]^{3-}$ ion except that the three in-plane, nonbridging positions are filled by $(C_6H_5)(C_2H_5)_2P$, instead of by Cl^-. The Re_3Cl_9 portions of the two molecules are essentially identical in all their dimensions. The Re–P bonds are considerably longer than would be expected for normal single bonds, an effect which could be caused by crowding of the Cl atoms projecting above and below the Re_3 plane. The earlier suggestion that some compounds of empirical formula ReX_3L might have structures with clusters of three rhenium atoms, like that in the $[Re_3Cl_{12}]^{3-}$ ion, has thus been confirmed. The similar electronic spectra of the $[Re_3Cl_{12}]^{3-}$ and $[Re_3Cl_9(PR_3)_3]$ species are also reported.

Introduction

The recent discovery[2,3] of the existence of a cluster of three rhenium atoms strongly bonded to one another[4] in the compound of empirical formula $CsReCl_4$ has led to investigations of other complexes of trivalent rhenium.[5] Among the several studies completed or in progress in this laboratory is a single-crystal X-ray study of the structure of the compound with the empirical formula $ReCl_3[(C_6H_5)(C_2H_5)_2P]$. This is only one of several compounds of the stoichiometric type ReX_3L, where X = Cl, L = $(C_6H_5)_3P$[6,7]; X = Cl, L = C_5H_5N[6]; X = Cl, L = $P(C_6H_5)(C_2H_5)_2$[7]; and X = Br, L = $P(C_6H_5)(C_2H_5)_2$.[8] It was earlier suggested[3a] that some of these ReX_3L compounds might have trimeric formulas, $Re_3X_9L_3$, with structures derived from that of the $[Re_3Cl_{12}]^{3-}$ ion by replacement of the three in-plane, nonbridging Cl^- ions with the neutral ligands, L. The structural study reported here was carried out to test this suggestion and, as will be seen, shows it to be correct.

Experimental

The compound was prepared by the method of Chatt and Rowe.[7] Small, dark red crystals were obtained directly from the solution of $(C_2H_5)_2(C_6H_5)P$ and $ReCl_3$ in dimethylformamide by allowing the hot solution to cool slowly in a dewar vessel filled with hot water. *Anal.* Calcd.: C, 26.48; H, 3.38. Found: C, 26.2; H, 3.30. The density, determined by flotation in 1,2-dibromoethane, was 2.17 g. cm.$^{-3}$. The linear absorption coefficient for Cu Kα radiation is 224 cm.$^{-1}$.

Using precession and Weissenberg photographs, it was established that the crystals are cubic with $a = 20.53 \pm 0.02$ Å. The following systematic absences were observed: $hk0,\ h \neq 2n;\ 0kl,\ k \neq 2n;\ h0l,\ l \neq 2n$. These unequivocally establish that the space group is Pa3 (No. 205).[9a] Using the measured density and unit cell dimension, the number of $(C_2H_5)_2(C_6H_5)PReCl_3$ moieties per cell was calculated as 24.7, indicating, therefore, that the rhenium atoms lie on the 24 general positions for this space group, which in turn, means that they fall into eight groups of three, those in each group being related by a threefold axis.

The crystal used for collecting intensity data had the form of a rectangular plate with dimensions 0.10 × 0.15 × 0.15 mm. Intensity data were recorded photographically by the equi-inclination Weissenberg method using Cu Kα radiation. Approximately 1000 reflections were recorded using the $hk0$–$hk5$ layers. The relative intensities were estimated visually by comparison with an intensity wedge prepared from the same crystal. Absorption corrections were made using a general absorption correction program, GNABS, written for the IBM 7094 computer by Dr. C. Burnham and supplied through the courtesy of Professor M. J. Buerger of this Institute. Lorentz and polarization corrections were made in the usual way. Anomalous dispersion corrections have been neglected throughout.

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[1] (a) Supported by the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation; (c) National Science Foundation Predoctoral Fellow.

[2] W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[3] (a) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); (b) *Inorg. Chem.*, **2**, 1166 (1963).

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[5] J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

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[7] J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

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