

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK]

The Inner-Sphere Activated Complex for the Electron Exchange of Iron(II) and the Monochloro Complex of Iron(III)¹

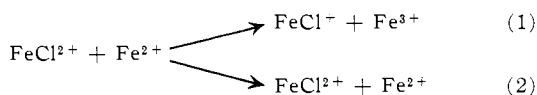
BY R. J. CAMPION, T. J. CONOCCHIOLI, AND N. SUTIN

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The kinetics of the iron(II)-catalyzed dissociation of FeCl^{2+} have been studied by the use of a flow technique. The rate constant for the dissociation is given by $k_d = k_1 + k_2/(\text{H}^+) + k_3(\text{Fe}^{2+})$, where $k_1 = 1.1 \pm 0.2 \text{ sec.}^{-1}$, $k_2 = 3.4 \pm 0.6 \text{ M sec.}^{-1}$, and $k_3 = 12.1 \pm 1.6 \text{ M}^{-1} \text{ sec.}^{-1}$ at 25.0° and ionic strength 3.0 M . The kinetics of the iron(II)-iron(III) electron exchange in the presence of chloride ions were studied using a radioactive tracer method. The rate constant for the electron exchange between FeCl^{2-} and Fe^{2+} was found to be $57.6 \pm 2 \text{ M}^{-1} \text{ sec.}^{-1}$ at 25.0° and ionic strength 3.0 M . The results suggest that the electron exchange between FeCl^{2+} and Fe^{2+} proceeds mainly by a chloride-bridged inner-sphere activated complex.

Introduction

The iron(II)-iron(III) electron exchange is catalyzed by a number of anions.²⁻⁸ This catalysis is generally ascribed to reactions between iron(II) and complexes of iron(III) with the added anions. The exchange reactions may proceed *via* electron-transfer or atom-transfer mechanisms, and indirect evidence for both types of mechanisms has been advanced.⁸⁻¹⁰ In the case of the exchange between iron(II) and the monochloro complex of iron(III), the electron-transfer and atom-transfer mechanisms may be represented as



where reactions 1 and 2 involve transfer of an electron and a chlorine atom, respectively.

In the course of recent studies of the oxidation of Fe^{2+} by Co^{3+} in the presence of chloride ions,¹¹ it was observed that the rate of dissociation of the FeCl^{2+} produced in the reaction depended upon the ferrous ion concentrations of the solutions. Because of the implication that this observation has for the mechanism of the chloride-catalyzed iron(II)-iron(III) exchange, we have made a more detailed study of the effect of Fe^{2+} on the rate of dissociation of FeCl^{2+} . Comparisons of the rates of the iron(II)-catalyzed dissociation of FeCl^{2+} and the chloride-catalyzed iron(II)-iron(III) electron exchange suggest strongly that the electron exchange between Fe^{2+} and FeCl^{2+} proceeds mainly *via* a chloride-bridged inner-sphere activated complex.

Experimental

The iron(III) perchlorate was obtained from the G. Frederick Smith Chemical Co. and was purified by recrystallization from perchloric acid. Solutions of iron(II) perchlorate were prepared by electroreduction of perchloric acid solutions of iron(III).

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(3) J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953).

(4) R. A. Horne, *J. Phys. Chem.*, **64**, 1512 (1960).

(5) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1326 (1957).

(6) D. Bunn, F. S. Dainton, and S. Duckworth, *ibid.*, **57**, 1131 (1961).

(7) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961).

(8) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(9) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(10) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961).

(11) T. J. Conocchioli, G. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

The labeled iron(III) perchlorate used in the exchange studies was prepared according to the procedure of Hudis and Wahl.³ A solution of iron(III) in 8 M hydrochloric acid containing the Fe^{59} tracer was extracted into isopropyl ether and back-extracted into water. Concentrated perchloric acid was added to the aqueous phase, which was heated until fumes were evolved. The fuming procedure was repeated until a negative test for chloride was obtained. The perchloric acid (70%) and the hydrochloric acid (37.8%) were obtained from the J. T. Baker Chemical Co. Solutions of magnesium, cobalt(II), nickel(II), and manganese(II) perchlorate were prepared by neutralizing magnesium oxide (Baker analyzed reagent), cobalt carbonate (Baker and Adamson), nickel carbonate, and manganese carbonate (Baker analyzed reagent), respectively, with perchloric acid.

The kinetics of the dissociation of FeCl^{2+} were studied using the apparatus and techniques described previously.¹²⁻¹⁴ Solutions containing iron(III), chloride, and perchloric acid were mixed with perchloric acid solutions containing either magnesium, cobalt(II), nickel(II), manganese(II), or iron(II) perchlorate and the disappearance of FeCl^{2+} followed at $336 \text{ m}\mu$. Some runs were also made in which the iron(III) and chloride were put in different solutions, and the formation of FeCl^{2-} was followed. The same rate constants were obtained as in the dissociation measurements. The iron(II)-iron(III) electron exchange was followed using a modification of the procedure described by Silverman and Dodson.² The exchange reaction was quenched by adding aliquots to a solution containing 2,2'-dipyridine and potassium acetate. The dipyridine complexed the ferrous ion, and in addition potassium perchlorate precipitated. This precipitation reduced the perchlorate concentration to a level sufficiently low for the sparingly soluble perchlorate salt of ferrous dipyridine to remain in solution. Iron(III) carrier was added and ferric hydroxide precipitated with ammonia. The precipitate was filtered off and the specific activity of the ferrous dipyridine complex in the filtrate determined by measuring the Fe^{59} activity with a scintillation counter and determining the concentration of the complex spectrophotometrically at $520 \text{ m}\mu$.

The kinetics of the dissociation of FeCl^{2-} and the iron(II)-iron(III) electron exchange were studied at 25.0° and an ionic strength of 3.0 M .

Results and Discussion

The Iron(II)-Catalyzed Dissociation of FeCl^{2+} .—The dissociation of FeCl^{2+} was studied in the presence of Co^{2+} , Mg^{2+} , Ni^{2+} , Mn^{2+} , and Fe^{2+} ions. The chloride concentration was varied from 5.1×10^{-4} to $5.1 \times 10^{-3} \text{ M}$ and the iron(III) concentration from 5.2×10^{-4} to $5.2 \times 10^{-3} \text{ M}$. Since the degree of complex formation is relatively small, the concentrations of uncomplexed iron(III) and chloride remained essentially constant during a particular run. The rate of dissociation was found to be first order with respect to FeCl^{2+} and independent of the iron(III) and chloride concentrations of the solutions. Values of the rate constants for the dissociation, calculated from the half-times for the reactions, are presented in Table I.

(12) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(13) D. Seewald and N. Sutin, *ibid.*, **2**, 643 (1963).

(14) G. H. Nancollas and N. Sutin, *ibid.*, **3**, 360 (1964).

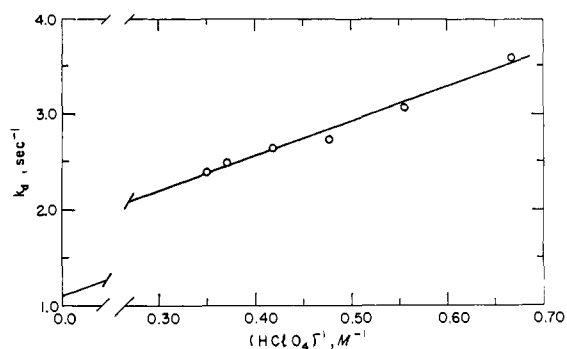


Fig. 1.—Plot of k_d vs. $(\text{HClO}_4)^{-1}$ at 25.0° and ionic strength $3.0 M$.

It will be seen that Co^{2+} , Mg^{2+} , Ni^{2+} , and Mn^{2+} all have the same relatively small effect on the rate of dissociation of FeCl^{2+} , whereas Fe^{2+} has a much larger effect. The dissociation in the absence of Fe^{2+} will be considered first. The increase in the rate of dissociation with increasing Co^{2+} , Mg^{2+} , Ni^{2+} , and Mn^{2+} concentrations can be interpreted in terms of the deas-

TABLE I

THE EFFECT OF DIVALENT CATIONS ON THE RATE OF DISSOCIATION OF FeCl^{2+} AT 25.0° AND IONIC STRENGTH $3.0 M$

(HClO_4) , M	$(\text{M}^{2+})^a$, M	k_d , sec.^{-1}				
		Mg^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}	Fe^{2+}
2.85	0.05	2.39	2.35	2.37	2.45	3.15
2.70	0.10	2.57	2.48	2.44	2.48	3.63
2.40	0.20	2.66	2.51	2.65	2.73	5.06
2.10	0.30	2.73	6.50
1.80	0.40	2.92	3.08	3.18	3.07	7.53
1.50	0.50	3.44	3.47	3.57	3.94	9.12

^a (M^{2+}) is the concentration of the divalent cation during the reaction.

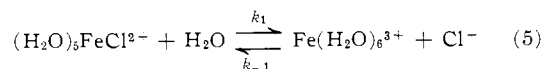
ing perchloric acid concentrations of the solutions since the measurements were made at a constant ionic strength. Thus it is evident from Fig. 1 that a linear relationship is obtained when the average value of k_d for a given concentration of the above cations is plotted against $(\text{HClO}_4)^{-1}$. The kinetic data in the absence of Fe^{2+} are thus consistent with the rate law

$$-\frac{d(\text{FeCl}^{2+})}{dt} = \left[k_1 + \frac{k_2}{(\text{H}^+)} \right] [(\text{FeCl}^{2+}) - (\text{FeCl}^{2+})_{\text{eq}}] \quad (3)$$

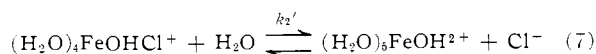
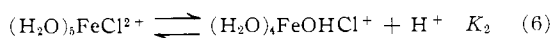
with

$$k_d = \frac{0.693}{t_{1/2}} = \left[k_1 + \frac{k_2}{(\text{H}^+)} \right] \quad (4)$$

where $t_{1/2}$ is the half-time for the dissociation of FeCl^{2+} , and k_1 and k_2 are the rate constants for the reactions



and



where $k_2 = K_2 k_2'$. The values of k_1 and k_2 calculated

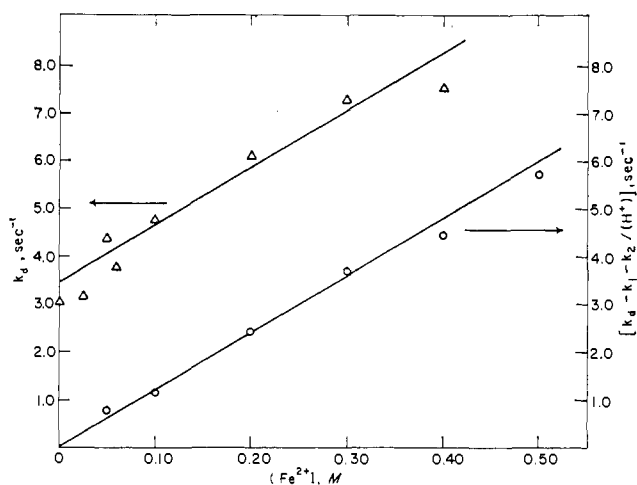


Fig. 2.—Plots of k_d and $[k_d - k_1 - k_2/(\text{H}^+)]$ vs. (Fe^{2+}) at 25.0° and ionic strength $3.0 M$.

from the intercept and slope of Fig. 1 are $1.1 \pm 0.2 \text{ sec.}^{-1}$ and $3.4 \pm 0.6 M \text{ sec.}^{-1}$, respectively, at 25.0° and ionic strength $3.0 M$. A similar two-term rate law has previously been found by Connick and Coppel¹⁵ for the dissociation of FeCl^{2+} in perchloric acid-sodium perchlorate media at an ionic strength of $1.0 M$. They found that k_1 and k_2 are $2.3 \pm 0.2 \text{ sec.}^{-1}$ and $4.5 \pm 0.5 M \text{ sec.}^{-1}$, respectively, at 25.0° and ionic strength $1.0 M$.

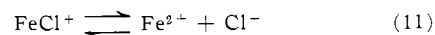
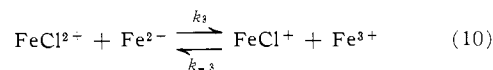
The rate of disappearance of FeCl^{2+} in the presence of Fe^{2+} is given by

$$-\frac{d(\text{FeCl}^{2+})}{dt} = \left[k_1 + \frac{k_2}{(\text{H}^+)} + k_3(\text{Fe}^{2+}) \right] \times [(\text{FeCl}^{2+}) - (\text{FeCl}^{2+})_{\text{eq}}] \quad (8)$$

with

$$k_d = \frac{0.693}{t_{1/2}} = \left[k_1 + \frac{k_2}{(\text{H}^+)} + k_3(\text{Fe}^{2+}) \right] \quad (9)$$

where k_3 is the rate constant for the reaction



In the lower curve of Fig. 2, values of $[k_d - k_1 - k_2/(\text{H}^+)]$ are plotted as a function of the iron(II) concentrations of the solutions. It will be seen that the data satisfy eq. 9 reasonably well. Additional measurements of the iron(II)-catalyzed dissociation of FeCl^{2+} were also made at constant acidity by using magnesium perchlorate to maintain constant ionic strength. These data are presented in Table II and are plotted as a function of the iron(II) concentrations of the solutions in the upper curve of Fig. 2. Good agreement with eq. 9 is again obtained. The value of k_3 calculated from the slopes of the lines in Fig. 2 is $12.1 \pm 1.6 M^{-1} \text{ sec.}^{-1}$ at 25.0° and ionic strength $3.0 M$.

(15) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

TABLE II

THE RATE OF DISSOCIATION OF FeCl^{2+} IN IRON(II) PERCHLORATE-MAGNESIUM PERCHLORATE-PERCHLORIC ACID^a

$(\text{Fe}^{2+}), M$	$t_{1/2}, \text{msec.}$	$k_d, \text{sec.}^{-1}$
0.025	219	3.16
0.050	159	4.36
0.060	185	3.75
0.10	146	4.76
0.20	113	6.10
0.30	95	7.29
0.40	92	7.53

^a Mixtures at 25.0° and ionic strength 3.0 M; $(\text{HClO}_4) = 1.80 M$.

The Chloride-Catalyzed Iron(II)-Iron(III) Exchange.—The dependence of the rate of the iron(II)-iron(III) exchange on the chloride concentrations of the solutions is presented in Table III. It will be seen that the rates

TABLE III

THE EFFECT OF CHLORIDE ON THE RATE OF THE IRON(II)-IRON(III) ELECTRON EXCHANGE^a

$[\text{Fe(II)}] \times 10^4, M$	$[\text{Fe(III)}] \times 10^4, M$	$(\text{Cl}^-) \times 10^2, M$	$t_{1/2}, \text{sec.}$	$k, M^{-1} \text{sec.}^{-1}$
3.00	1.00	...	65	26.7
6.00	2.00	...	33	26.3
1.50	0.50	...	128	27.1
1.50	0.50	2.04	108	32.0
1.50	0.50	4.32	90	38.5
3.00	1.00	4.32	45	38.5
2.00	1.00	4.32	58	39.8
1.50	0.50	6.50	77	45.0
1.50	0.50	8.65	70	49.5
1.50	0.50	10.2	65	53.3

^a At 25.0° and ionic strength 3.0 M; $(\text{HClO}_4) = 1.80 M$; $[\text{Mg}(\text{ClO}_4)_2] = 0.40 M$.

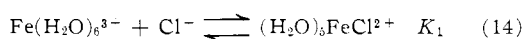
increase with increasing chloride concentration. The measurements can be interpreted in terms of the rate law^{2,7}

$$R = k_4(\text{Fe}^{2+})(\text{Fe}^{3+}) + k_5(\text{Fe}^{2+})(\text{FeOH}^{2+}) + k_6(\text{Fe}^{2+})(\text{FeCl}^{2+}) + k_7(\text{Fe}^{2+})(\text{FeCl}_2^+) \quad (12)$$

from which it follows that

$$\frac{k[1 + K_1(\text{Cl}^-) + K_1K_4(\text{Cl}^-)^2] - k_0}{(\text{Cl}^-)} = K_1k_6 + K_1K_4k_7(\text{Cl}^-) \quad (13)$$

where k is the over-all second-order rate constant in the presence of chloride ions, and k_0 is the rate constant in the absence of chloride ions, both at the same acidity. k_6 and k_7 are the rate constants for the electron exchange of Fe^{2+} with FeCl^{2+} and FeCl_2^+ , respectively, and K_1 and K_4 are the equilibrium constants for the reactions



and

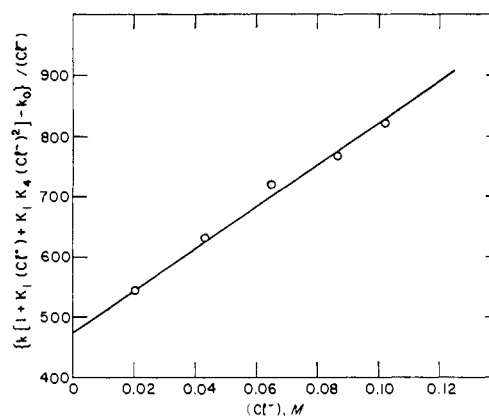
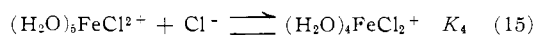


Fig. 3.—Analysis of the chloride ion catalysis of the iron(II)-iron(III) exchange reaction at 25.0° and ionic strength 3.0 M; $(\text{HClO}_4) = 1.80 M$.

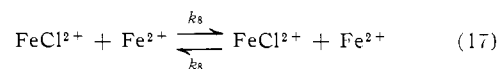
respectively. Hence k_6 and k_7 can be calculated from the intercepts and slopes of plots of the left-hand side of eq. 13 vs. chloride, provided K_1 and K_4 are known. According to Woods, *et al.*,¹⁶ K_1 is equal to $8.2 M^{-1}$ at 25.0° and ionic strength 3.0 M. The value of K_4 at this ionic strength is not known, but we shall assume that the value of K_1/K_4 does not vary much in the ionic strength range of 1.0 to 3.0 M. Consequently, we have used $K_4 = 2.7 M^{-1}$ at 25.0° and ionic strength 3.0 M.¹⁷ As is evident from Fig. 3, the data satisfy eq. 13 reasonably well. The values of k_6 and k_7 calculated from the slope and intercept are $57.6 \pm 2 M^{-1} \text{sec.}^{-1}$ and $159 \pm 10 M^{-1} \text{sec.}^{-1}$, respectively, at 25.0° and ionic strength 3.0 M. The above value of k_6 may be compared with the value of $31 M^{-1} \text{sec.}^{-1}$ at 25.0° and ionic strength 0.50 M.⁷

The formulation of the third term in the rate law for the exchange as $k_6(\text{FeCl}^{2+})(\text{Fe}^{2+})$ involves an assumption. Strictly speaking, this term is $K_1k_6(\text{Fe}^{3+})(\text{Fe}^{2+})(\text{Cl}^-)$, *i.e.*, it defines an exchange path which is first order in iron(II), iron(III), and chloride. However, it is very likely that the reactants in this exchange path are in fact FeCl^{2+} and Fe^{2+} (as well as FeCl^+ and Fe^{3+}), rather than Fe^{2+} , Fe^{3+} , and chloride. For example, recent studies of the chloride-catalyzed chromium(II)-iron(III) reaction have shown that the rate law for this reaction also contains a term $k(\text{Fe}^{3+})(\text{Fe}^{2+})(\text{Cl}^-)$ and that the FeCl^{2+} - Cr^{2+} path makes by far the biggest contribution to this term.¹⁸

Comparison of the Dissociation and Exchange Rate Studies.—The rate constant k_6 includes all the electron-exchange paths involving Fe^{2+} and FeCl^{2+} . It is thus equal to the sum of the rate constants for the electron transfer and the chlorine atom transfer paths and is given by

$$k_6 = (2k_3 + k_8) \quad (16)$$

where k_8 is the rate constant for the chlorine atom transfer path



(16) M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

(17) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

(18) G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964).

The coefficient 2 in eq. 16 is necessary because both the forward and reverse reactions of eq. 10 contribute to the observed electron transfer. Since the system is at equilibrium, the rates of these two reactions are equal. Consequently, the forward reaction of eq. 10 is only responsible for half the observed electron transfers.¹⁹ Substitution of $k_3 = 12.1 \pm 1.6 M^{-1} \text{ sec.}^{-1}$ and $k_6 = 57.6 \pm 2 M^{-1} \text{ sec.}^{-1}$ gives $k_8 = 33.4 \pm 2.6 M^{-1} \text{ sec.}^{-1}$ at 25.0° and ionic strength 3.0 *M*. A comparison of the magnitudes of these rate constants shows that the electron exchange between Fe^{2+} and FeCl^{2+} proceeds mainly by a chlorine atom transfer mechanism (provided, as seems reasonable, the third-order term involving Fe^{2+} , Fe^{3+} , and chloride may be neglected).

The chlorine atom transfer presumably occurs in a chloride-bridged, inner-sphere activated complex, while the electron transfer may occur in either an outer-sphere activated complex or in a water-bridged, inner-sphere activated complex. It is of interest that reaction *via* the chloride-bridged path is only about three

(19) J. Silverman, Ph.D. Thesis, Columbia University, New York, N. Y., 1951.

times as rapid as reaction *via* the outer-sphere or water-bridged paths. This small difference, and indeed the relatively small effect of chloride on the iron(II)–iron(III) exchange, contrasts markedly with its effect on the iron(II)–chromium(III) and chromium(II)–chromium(III) reactions. In the latter systems, chloride bridging increases the rates of the reactions by factors of 10^4 and more than 2×10^6 , respectively.¹⁸ Moreover, the chromium(II)-catalyzed dissociation of CrCl^{2+} is slower by a factor of more than 10^4 than the Cr^{2+} – CrCl^{2+} exchange.²⁰ The difference in the chloride effects cannot be ascribed to any difference in the mechanisms of the reactions since these studies show that it is very likely that the chloride-catalyzed iron(II)–iron(III) exchange, like the chloride-catalyzed chromium(II)–iron(III) and chromium(II)–chromium(III) reactions, proceeds *via* an inner-sphere activated complex.

Acknowledgment.—The authors wish to acknowledge helpful discussions with R. W. Dodson.

(20) H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027]

The Electronic Structures of Square-Planar Metal Complexes. V. Spectral Properties of the Maleonitriledithiolate Complexes of Nickel, Palladium, and Platinum

BY S. I. SHUPACK,^{1a} E. BILLIG, R. J. H. CLARK, RAYMOND WILLIAMS,^{1b} AND HARRY B. GRAY

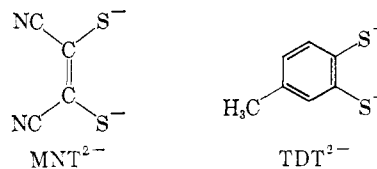
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The results of molecular orbital calculations of the square-planar nickel complexes of maleonitriledithiolate are reported. Electronic spectra of the nickel, palladium, and platinum complexes are assigned on the basis of the derived energy levels for the dinegative nickel complex. The observed bands are due to d–d, ligand-to-metal and metal-to-ligand charge transfer, and intraligand transitions. The spectral assignments are consistent with the known spectra of square-planar halides, cyanides, and simple derivatives of maleonitriledithiolate. The orbital parameter Δ_1 is reported for all the complexes, affording a comparison of the $x^2-y^2 \rightarrow xy$ splitting for several complexes containing a nickel-group central metal. Evidence is presented for the assignment of the highest filled orbital as $4a_g(x^2-y^2)$ in D_{2h} symmetry for the dinegative complexes of the nickel group.

Introduction

For several years we have been investigating the syntheses, electronic structures, and reaction mechanisms of square-planar metal complexes. Until very recently, the square-planar geometry was restricted to the diamagnetic, d^8 complexes of Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), and Au(III), except for a few paramagnetic ($S = 1/2$), square-planar Co(II) and Cu(II) complexes containing fairly complicated ligands. It is clear that one of the important problems in inorganic chemistry is the preparation and study of square-planar complexes containing as many different transition metals and with as many different ground states as possible. From such research we can hope to help determine the relative energies of the molecular orbitals in planar metal complexes, a problem for which many different solutions have been suggested in the past few years.^{2–11}

From the results of our initial theoretical work, we believe that one way to stabilize the square-planar geometry is to involve the metal d_{xz} , d_{yz} , and p_z valence orbitals in an extensive π -orbital network spanning the entire complex, thus allowing as much delocalization of charge as possible. Two ligands which have good donor atoms and also a considerably delocalized π -orbital system are the dianions of maleonitriledithiol (MNT²⁻) and toluene-3,4-dithiol (TDT²⁻), which are shown below. Whether or not for the reason given above,



(6) S. Kida, J. Fukita, K. Nakamoto, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 79 (1958).

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(1) (a) NIH Postdoctoral Fellow, 1963–1964; (b) NSF Graduate Fellow, 1963–1964.

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(3) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958); **29**, 1129 (1958).

(4) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **71**, 538 (1959).

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