Appendix: Energy Levels for the d Electrons of an Octahedral Cluster

It is quite instructive for the interpretation of all-electron results to compute the d-electron energy levels of an octahedral complex analytically within the extended Hückel framework. One starts by introducing local coordinate systems at each vertex of the octahedron with the z axis directed toward the center of the cluster,[27,28] a very convenient choice. Due to the very localized nature of the involved atomic orbitals it is a very good approximation to neglect overlap between next-nearest neighbors, i.e. atoms at diagonally opposite vertices. In a first step, one expresses the overlap between d orbitals at neighboring sites in two-center contributions of type σ, π, and δ (see Table IX). Then symmetry-adapted linear combinations of atomic orbitals are formed for the various irreducible representations (see Table I). In Table X, the resulting energy levels are listed as functions of the overlap parameters S_1–S_9 in units of the effective atomic ionization energy $\mathrm{IE_{eff}}$(Au 5d).

Using the nonrelativistic DVM level spectrum for the cluster $\mathrm{Au_6}^{2+}$, one may deduce the four parameters of the model, S_σ, S_π, S_δ, and $\mathrm{IE_{eff}}$(Au 5d) from levels a_{2g}, a_{2u}, e_u, and t_{1g}, which would not be affected if Au 6s orbitals were included in the EH model. The resulting overlap values are displayed in Table II. The corresponding full EH d level spectrum for $\mathrm{Au_6}^{2+}$ is shown in Figure 2.

Explicit EH-type calculations on octahedral transition metal clusters have been performed previously.[27,28] In ref 28, some corrections to the expressions published of ref 27 have been given. However, the formulas of ref 28 are incomplete in so far as they neglect interactions between orbitals of the same irreducible representation, but of different local character, e.g. those corresponding to overlaps of type S_6–S_9 (see Table IX). These interactions are larger than those between orbitals located at opposite vertices, which were included in ref 28 but have been neglected here. These additional interactions were necessary for matching the spectrum from the all-electron DV results described above.

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(27) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1974**, 133.
(28) Cotton, F. A.; Haas, T. E. *Inorg. Chem.* **1964**, *3*, 10.

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Kinetics and Mechanism of the Complex Formation of the Chlorite Ion and Iron(III) in Aqueous Solution

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On the basis of rapid-scan spectrophotometric and one-wavelength stopped-flow experiments, the formation of the $\mathrm{FeClO_2}^{2+}$ complex was confirmed in the iron(III)–chlorite ion system. The complex formation is associated with the appearance of a new charge-transfer band in the visible spectral region. The stability constant of $\mathrm{FeClO_2}^{2+}$ was calculated from the final absorbance value of stopped-flow traces recorded at 510 nm. $\log K = 1.14 \pm 0.02$ and $\epsilon_{510} = 636 \pm 10\ \mathrm{M^{-1}\ cm^{-1}}$ ($I = 1.0$ M ($\mathrm{NaClO_4}$), 25 °C). It was demonstrated that the complex formation is kinetically coupled with catalytic decomposition of $\mathrm{ClO_2}^-$. The proposed mechanism for the ligand substitution reaction includes the reactions of Fe^{3+} and $\mathrm{Fe(OH)}^{2+}$ and also a generalized pathway for the chlorite ion decomposition. The rate constant for the $\mathrm{Fe}^{3+} + \mathrm{ClO_2}^- = \mathrm{FeClO_2}^{2+}$ step, $269 \pm 55\ \mathrm{M^{-1}\ s^{-1}}$, is consistent with an associative interchange mechanism predicted by previous kinetic data for complex formation reactions of Fe(III).

Introduction

Oxidation–reduction reactions of chlorite ion have been the subject of extensive kinetic studies in recent years. In the oxidation of metal ions, complex formation with chlorite ion or chlorous acid is generally considered one of the key reaction steps in the detailed mechanisms.[1-3] Although chlorito complexes are of kinetic importance in these systems, the properties of chlorite ion as a ligand are virtually unknown.

The synthesis and redox properties of $\mathrm{Co(NH_3)_5ClO_2}^{2+}$ were discussed by Thompson in detail.[4] However, no kinetic or equilibrium data are available for the formation of this inert chlorito complex. Until recently, the only labile metal complex of $\mathrm{ClO_2}^-$ was that with the uranyl ion reported by Gordon and Kern.[5] This species was detected in the oxidation of uranium(IV) by chlorine(III), and a rough estimate was given for its stability constant.

Earlier, we reported the formation of $\mathrm{CuClO_2}^+$ in aqueous solutions containing Cu^{2+} and $\mathrm{ClO_2}^-$.[6] A relatively weak complex, $\mathrm{CuClO_2}^+$ is characterized by an intense absorbance band in the near-UV–visible spectral region ($\lambda_{max} = 387$ nm, $\epsilon_{max} = 1990 \pm 120\ \mathrm{M^{-1}\ cm^{-1}}$). It has a stability constant $K = 1.04 \pm 0.07\ \mathrm{M^{-1}}$, conveniently determined by using stopped-flow–rapid-scan spectrophotometry. This technique was applied in order to avoid spectral interference from the copper(II)-catalyzed decomposition of the chlorite ion. On the basis of these results, the formation of chlorito complexes is expected to be common in any reaction system containing a transition-metal ion and the chlorite ion.

Proper characterization of the coordination chemistry of the chlorite ion requires additional equilibrium and kinetic data for its various complex formation reactions. The iron(III)–$\mathrm{ClO_2}^-$ system appears to be one of the best choices for further studies. First of all, +3 is the most stable oxidation state of iron in aqueous solution.[7] Accordingly, no redox reaction between the metal ion and $\mathrm{ClO_2}^-$, which could compete with the complex formation, is expected in this system. Also, Fe^{3+} tends to form more stable complexes than Cu^{2+}.[8] In principle, the complex formation can be monitored by using more preferable experimental conditions, i.e. lower concentration levels, than in the Cu^{2+}–chlorite ion system. The interference from side reactions is presumably decreased by

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(1) Ondrus, M. G.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 985.
(2) Buchacek, R.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 2154.
(3) Cornelius, R. D.; Gordon, G. *Inorg. Chem.* **1976**, *15*, 1002.
(4) Thompson, R. C. *Inorg. Chem.* **1979**, *18*, 2379.
(5) Gordon, G.; Kern, D. M. H. *Inorg. Chem.* **1964**, *3*, 1055.
(6) Fábián, I.; Gordon, G. *Inorg. Chem.*, in press.
(7) Nelson, S. M. In *Comprehensive Coordination Chemistry*, 1st ed.; Wilkinson, G., Gillard, G., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 4, pp 217-276 and references therein.
(8) (a) Sillén, L. G.; Martell, A. E. *Stability Constants*; Chemical Society: London, 1964; Suppl. No. 1, 1971. (b) *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*; IUPAC Chemical Data Series No. 21; Högfeldt, E., Ed.; Pergamon: Oxford, U.K., 1982.

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decreasing the concentration of the reactants.

Besides these advantages, certain experimental difficulties also have to be anticipated. Iron(III) readily hydrolyzes even in acidic solution. Above pH 2.5, poorly defined polynuclear hydroxo complexes are formed, and at higher concentration levels of Fe^{3+}, precipitation of hydroxo species may occur.[8] In order to avoid these reactions, the experiments have to be performed in acidic solution. However, increasing the acid concentration increases the rate of the chlorite ion decomposition considerably[9] and decreases the rate of the complex formation. Furthermore, the complex is formed at lower concentration levels, increasing the uncertainty of the evaluation of the relevant kinetic and equilibrium data.

Catalytic decomposition of the chlorite ion also may compete with the complex formation. According to previous reports, iron(III) catalyzes the decomposition of the chlorite ion.[10,11] In general, chlorine dioxide is one of the products in the decomposition reactions. The contribution of chlorine dioxide to the observed spectra may be dominant, making it impossible to detect the formation of the iron complex. As a consequence, the optimum conditions for the experiments are very likely limited to a relatively narrow concentration and pH range.

In the present study, the stability constant and rate constants for the formation of the $FeClO_2^{2+}$ complex were determined from stopped-flow (SF) and stopped-flow–rapid-scan spectrophotometric (SF–RS) studies. Further, a detailed mechanism for the complex ion formation is proposed. The rate constants in this mechanism follow the general trends of previously published kinetic data for ligand substitution reactions of iron(III).

Experimental Section

Chemicals. Reagent grade chemicals and deionized triply distilled water were used in all experiments. Commercially available sodium chlorite (OLIN; approximately 80% purity) was recrystallized as described earlier.[6,12] According to standard iodometric analysis, the purity of the final product was better than 99.7%. Furthermore, no chloride ion could be detected in the purified $NaClO_2$.

An iron(III) stock solution was prepared by dissolving $Fe(ClO_4)_3\cdot xH_2O$ (Aldrich; low chloride; $[Cl^-] < 0.005\%$) in perchloric acid solution. Another stock solution was prepared by dissolving iron (Mallinckrodt Chemical Works; low magnesium and manganese) in concentrated sulfuric acid (Fisher Scientific), oxidizing iron(II) with H_2O_2 (VWR Scientific), and removing the excess hydrogen peroxide by boiling the solution. At elevated temperatures and in the presence of iron(III), H_2O_2 rapidly decomposes. The acidity of the solution was reduced with an appropriate amount of $BaCO_3$ (Fisher Scientific). The excess sulfate ion was precipitated by dosing with equivalent amounts of $Ba(ClO_4)_2$ solution. The $Ba(ClO_4)_2$ solution was prepared by dissolving $BaCO_3$ in perchloric acid (Fisher Scientific).

The iron(III) content of the stock solutions was determined by either a standard iodometric method or complexometric titration with EDTA solution using Variamin B as indicator.[13] The acidity was determined by passing aliquots of the stock solution through a Dowex 50-X12 (J. T. Baker Chemicals) cation-exchange column in the acid form. The eluents were titrated with standardized NaOH solution (Fisher Scientific). Parallel experiments with the two iron(III) stock solutions gave indistinguishable results.

Sodium perchlorate, prepared from Na_2CO_3 and $HClO_4$, was used to adjust the ionic strength to 1.0 M. In all experiments, the temperature was set to 25.0 ± 0.05 °C.

Instrumentation. The pH of the samples was measured with a Radiometer GK2401B combination glass electrode attached to a Radiometer PHM64 pH meter. The electrode was calibrated such that the pH-meter reading directly gave the hydrogen ion concentration ($-\log [H^+]$). pH measurements were made only in the preliminary experiments, where the pH occasionally was higher than 2.5. In more acidic solutions, the hydrogen ion concentration was calculated from the concentration of the components and the relevant equilibrium data.

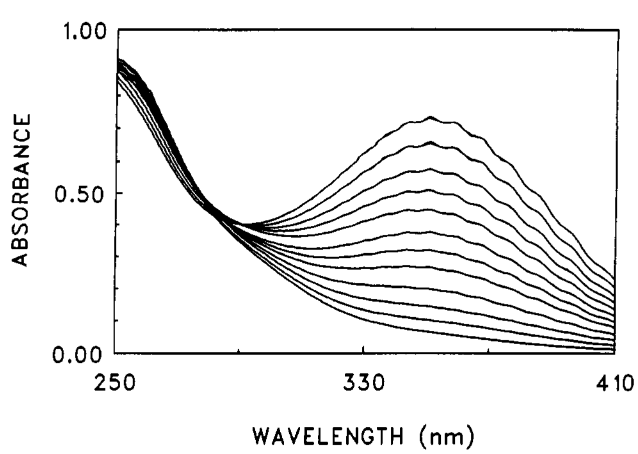

Figure 1. SF–RS spectra, recorded in a 2-mm cell, for the Fe^{3+}–chlorite ion system. $C_{ClO_2^-} = 9.90 \times 10^{-3}$ M, $C_{Fe^{3+}} = 1.10 \times 10^{-3}$ M, and pH = 2.33. Scan rate: 190 nm/20 ms for the first seven spectra and 190 nm/200 ms for the last five spectra. In the order of increasing absorbance, the absorbance values at 360 nm were measured 54.7, 214.7, 454.7, 894.7, 1554.7, 2214.7, 3094.7, 4547, 6747, 11 147, 19 947, and 33 147 ms after mixing the reactants.

Potentiometric titrations were made with a Radiometer ABU93 Triburette autoburet station connected to a Radiometer VIT90 Video Titrator unit. A standard P101 platinum–K401 SCE electrode pair (Radiometer) was used for the iodometric titrations. Regular spectra were recorded on a Hewlett Packard 8450 UV/visible diode array spectrophotometer.

SF and SF–RS measurements were made with an Atago Bussan/Photal Otsuka Electronics RA-401 stopped-flow instrument equipped with an RA-451 data processor unit. With 2- and 10-mm cells, the dead time is estimated to be about 0.5 and 2 ms, respectively. SF traces were monitored with a Hamamatsu R374 photomultiplier. Each trace was taken as the average of at least five parallel runs. In SF–RS mode, the spectra were recorded with a 512-channel photodiode array (190-nm spectral range) by using an RA-415 rapid-scan attachment. With this configuration, the scan rate can be selected between 190 nm/2 ms and 190 nm/200 ms. According to our calibration, the reproducibility of the SF and SF–RS measurements is ±2%.

Results and Discussion

Preliminary Experiments. In the first set of experiments, solutions of chlorite ion and iron(III) were mixed by using the conventional batch method. The spectra, recorded approximately 15–20 s after mixing, proved the formation of chlorine dioxide in significant amounts. This indicates that iron(III) is a very efficient catalyst of the chlorite ion decomposition.

When the concentration of the reactants and the pH were systematically varied ($[ClO_2^-] = 0.005$–0.5 M; $[Fe^{3+}] = 5 \times 10^{-5}$–$0.002$ M; pH = 1.0–3.5), the rate of chlorine dioxide formation was altered. However, the spectral effect of this species was always overwhelming and no spectrophotometric evidence was found for the formation of a new species. This finding is in sharp contrast with the observations in the Cu^{2+}–ClO_2^- system.[6] In that case, reliable, though somewhat corrupted, spectral information could be obtained for the $CuClO_2^+$ complex by using a similar experimental arrangement.

As shown in Figure 1, chlorine dioxide was formed in the very early phase of the reaction. The increasing absorbance band around 360 nm, with the characteristic fine structure, is primarily attributed to ClO_2.[14] The 250–300-nm region of the same spectra is basically the composite of the individual spectra of iron(III) (Fe^{3+} and hydroxo complexes), $HClO_2/ClO_2^-$, and chlorine dioxide. It should be noted that, in the far-UV region (<250 nm), the absorbance sharply increases and exceeds the limitations of the applied experimental technique. These results indicate that reliable information cannot be obtained for the formation of the chlorito complex, even if it exists, from the UV spectral range.

Additional SF–RS measurements in the visible region were made at higher chlorite ion concentrations. The 380–460-nm

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(9) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1972; Vol. 15, pp 201–286.

(10) Launer, H. F.; Tomimatsu, Y. *J. Am. Chem. Soc.* **1954**, *76*, 2591.

(11) Schmitz, G.; Rooze, H. *Can. J. Chem.* **1985**, *63*, 975.

(12) Peintler, G.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954.

(13) Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd ed.; Longman: London, 1961; pp 372, 444.

(14) Kieffer, R. G.; Gordon, G. *Inorg. Chem.* **1968**, *7*, 235.

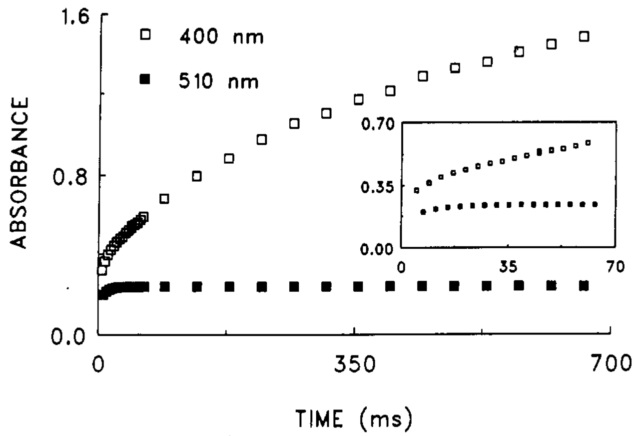

Figure 2. Kinetic profiles for the Fe^{3+}–chlorite ion system at 400 and 510 nm. The absorbance values, recorded in a 10-mm cell, were obtained from SF–RS measurements. $C_{ClO_2^-} = 9.98 \times 10^{-2}$ M, $C_{Fe^{3+}} = 8.81 \times 10^{-4}$ M, and pH = 2.02. Inset: Enlarged first portion of the same curves.

region of these spectra indicated the rapid formation of ClO_2 again. An unexpectedly high absorbance was observed in the 470–540-nm wavelength range. Under the applied conditions, this observation cannot be assigned to any known component (iron(III), chlorite ion, or chlorine dioxide) of this system. When only the absorptivities of these species are considered, no significant absorbance is expected above 450–460 nm.

The spectra also show considerably different kinetic patterns in the lower and the higher wavelength ranges. The difference is quite apparent if the absorbance vs time curves at 400 and 510 nm are compared (Figure 2). These results are consistent with the formation of the $FeClO_2^{2+}$ complex, a new species in this system.

A few SF–RS measurements were made in large excess of iron(III). In order to prevent the formation of hydroxo precipitates, the pH was never higher than ~1.3 for these experiments. The SF–RS spectra indicated fast ClO_2 formation, i.e. rapid depletion of the chlorite ion. Since the chlorite ion concentration was not constant during the complex formation, these conditions were not suitable for studying the formation kinetics of $FeClO_2^{2+}$.

Stability Constant of $FeClO_2^{2+}$. The complex formation was investigated by the SF method at 510 nm. Chlorite ion always was in large excess over Fe(III), and the pH did not exceed 2.10. The SF traces showed a fast, first-order process which is practically completed in under 10–15 ms. According to additional experiments at longer times, the final absorbance did not change in 400–500 ms. For the traces recorded in 40 or 50 ms, the first-order rate constants (k) and background-corrected final absorbances (A_∞) were calculated by using a nonlinear least-squares-fitting program.[15] The average deviation between the measured and calculated curves was less than 2%. The concentrations and the measured and calculated k and A_∞ values are listed in Table I.

Under the applied conditions, polynuclear hydroxo complexes of iron(III), $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$, are formed in negligible concentration.[16] Accordingly, the equilibria of this system can be approximated by considering the following reactions:

$$Fe^{3+} + ClO_2^- = FeClO_2^{2+} \tag{1}$$

$$K_1 = [FeClO_2^{2+}]/([Fe^{3+}][ClO_2^-])$$

$$H^+ + ClO_2^- = HClO_2 \tag{2}$$

$$K_p = [HClO_2]/([H^+][ClO_2^-])$$

$$Fe^{3+} = Fe(OH)^{2+} + H^+ \tag{3}$$

$$K_h = [Fe(OH)^{2+}][H^+]/[Fe^{3+}]$$

Table I. Stopped-Flow Results for the Formation of the $FeClO_2^{2+}$ Complex

pH	$10^2C_{ClO_2^-}$, M	$10^4C_{Fe^{3+}}$, M	A_∞ (±0.008)		k (±6.4%), s^{-1}	
			obs	calc[a]	obs	calc[b]
2.03	9.98	11.02	0.300	0.301	139	144
2.03	9.98	11.02	0.302	0.301	142	144
2.02	9.98	8.26	0.228	0.226	141	143
2.01	9.98	5.51	0.150	0.151	143	142
2.01	9.98	3.86	0.107	0.106	143	141
2.00	9.98	2.20	0.062	0.060	143	140
2.00	9.98	1.10	0.030	0.030	139	140
2.00	9.98	0.55	0.015	0.015	145	140
2.03	6.99	11.02	0.251	0.242	138	140
2.04	4.99	11.02	0.201	0.192	131	134
2.05	3.00	11.02	0.135	0.129	126	131
2.07	1.00	11.02	0.052	0.049	119	129
2.06	1.00	8.81	0.047	0.039	124	127
1.78	1.00	8.81	0.038	0.034		
1.52	1.00	8.81	0.026	0.026	63	73
2.03	4.99	8.81	0.155	0.153	142	133
1.77	4.99	8.81	0.137	0.137	103	97
1.51	4.99	8.81	0.126	0.117	85	77
2.02	9.98	8.81	0.245	0.241	145	143
1.76	9.98	8.81	0.216	0.220	109	105
1.51	9.98	8.81	0.178	0.184	76	83
2.01	19.95	8.81	0.342	0.337	179	166
1.76	19.95	8.81	0.307	0.315	138	122
1.51	19.95	8.81	0.263	0.277	99	94
2.01	29.92	8.81	0.398	0.389	196	190
1.75	29.92	8.81	0.362	0.369	146	139
1.50	29.92	8.81	0.316	0.333	107	105
2.01	39.91	8.81	0.435	0.421	215	214
1.75	39.91	8.81	0.401	0.403	159	156
1.50	39.91	8.81	0.353	0.370	116	117
2.00	49.88	8.81	0.463	0.443	213	238
1.75	49.88	8.81	0.429	0.427	162	173
1.50	49.88	8.81	0.383	0.397	118	128

[a] Calculated by using the program PSEQUAD.[17] [b] Calculated on the basis of eq 9.

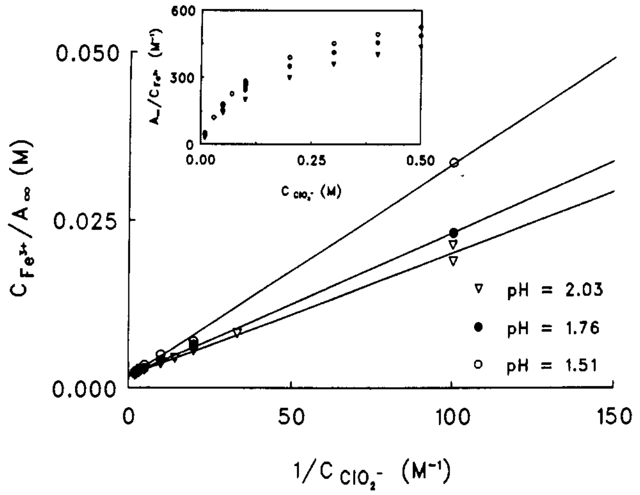

Figure 3. Plot, based on the final absorbances of the SF measurements at 510 nm, to test eq 4. Inset: Normalized final absorbance as a function of $C_{ClO_2^-}$ under the same circumstances.

By assuming that $FeClO_2^{2+}$ is the only absorbing species at 510 nm and taking into account that $C_{ClO_2^-} \gg C_{Fe^{3+}}$, we obtain

$$C_{Fe^{3+}}/A_\infty = 1/\epsilon + 1/(\epsilon K_1' C_{ClO_2^-}) \tag{4}$$

where

$$K_1' = K_1/\{(1 + K_h/[H^+])(1 + K_p[H^+])\}$$

As shown in Figure 3, the experimental data are in excellent agreement with eq 4. On the basis of these results, the formation of the $FeClO_2^{2+}$ complex appears to be consistent with the given interpretation.

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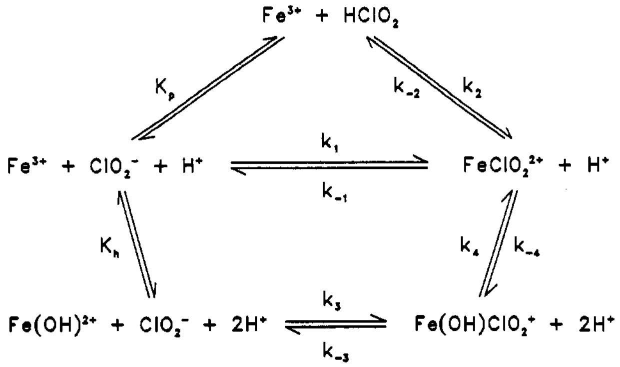
(15) Fábián, I. *NESSIE: A General Purpose Non-Linear Least Square Fitting Program*; Kossuth L. University: Debrecen, Hungary, 1982.

(16) Khoe, G. H.; Robins, R. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2015.

Scheme I



The most fundamental question is whether the final absorbance values (A_∞) can be used as real equilibrium data or whether they are corrupted because of side reactions. On the basis of an excessively conservative estimate, less than 3% of the chlorite ion decomposed in the first 50 ms in any of the SF runs. Therefore, the ClO_2^- concentration can be considered constant during the complex formation. Furthermore, none of the products, including the chloride ion, is formed in sufficiently high concentration to alter the equilibria.

As a catalyst, iron(III) is also involved in the decomposition of the chlorite ion, and the various iron species are not necessarily in true equilibria. However, stable oxidation states of iron other than +3 are unlikely in this system. Accordingly, when the complex formation is completed, the iron(III) species are in quasi-equilibria.

The stability constant of the $FeClO_2^{2+}$ complex was calculated by using the program PSEQUAD.[17] With fixed stability constants, chlorous acid, $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, and $Fe_3(OH)_4^{5+}$ were also included in the calculations. The corresponding log K_p and log β values are 1.72,[6] −2.74,[18] −2.85,[18] and −6.92,[16] respectively. The calculated absorbance values at 510 nm are listed in Table I. The stability constant and molar absorptivity of $FeClO_2^{2+}$ are

$$K_1 = 13.8 \pm 0.6\ \mathrm{M}^{-1} \qquad \epsilon_{510} = 636 \pm 10\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$$

In principle, the chlorite ion can coordinate to the metal ion via either chlorine or oxygen. Tracer experiments in the oxidation of uranium(IV) by chlorine(III) indicated that oxygen is directly bonded to the metal center in the $UClO_2^{3+}$ activated complex.[2] This finding is in concert with the molecular orbital structure of ClO_2^- proposed by Henke et al.[19] According to that report, the valence electrons of Cl are mainly involved in the Cl–O bonds. Lone electron pairs, available to form coordinative bonds, are located on principally oxygen 2p molecular orbitals with a small chlorine 3d character. Considering these results, ClO_2^- is very likely coordinated via oxygen in the $FeClO_2^{2+}$ complex.

Kinetics and Mechanism of the Complex Formation. The rate of $FeClO_2^{2+}$ formation is characterized by the pseudo-first-order rate constants (k) in Table I. As a working hypothesis, first only ligand substitution reactions were considered for the evaluation of these data. However, it should be kept in mind that chlorine dioxide formation was observed in the early phase of the overall reaction. Accordingly, an additional reaction step or steps, related to iron-catalyzed chlorite ion decomposition, also may prove significant in the interpretation of the results.

In the most general case, pathways involving Fe^{3+}, $Fe(OH)^{2+}$, and both protonated and deprotonated forms of the ligand have to be considered for the ligand substitution reactions of Fe(III).[20]

Table II. Kinetic Parameters for the Formation of $FeClO_2^{2+}$

reaction	rate constant	
$Fe^{3+} + ClO_2^- = FeClO_2^{2+}$	k_1, $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	269 ± 55
	k_{-1}, s^{-1}	49.6 ± 4.5
	$k_{-1}'^{a}$	19.5
$Fe(OH)^{2+} + ClO_2^- + H^+ = FeClO_2^{2+}$	k_3, $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	940 ± 430
	$k_3'^{b}$	5000
	k_{-3}/K_4, $\mathrm{M}\ \mathrm{s}^{-1}$	0.66 ± 0.06

[a] $k_{-1}' = k_1/K_1$. [b] $k_3' = k_{-3}K_1/K_hK_4$.

The detailed mechanism for the formation of $FeClO_2^{2+}$ is given in Scheme I. In this model, the proton-transfer reactions between Fe^{3+}–$Fe(OH)^{2+}$ and $HClO_2$–ClO_2^- are considered to be fast. It also has to be noted that reaction 1 represents the following two kinetically indistinguishable pathways in the mechanism:

$$Fe^{3+} + ClO_2^- = FeClO_2^{2+} \quad k_{1a} \tag{1a}$$

$$Fe(OH)^{2+} + HClO_2 = FeClO_2^{2+} \quad k_{1b} \tag{1b}$$

Accordingly, k_1 is given as follows:

$$k_1 = k_{1a} + k_{1b}K_hK_p \tag{5}$$

By taking into account that $Fe(OH)ClO_2^+$ is formed at low concentration levels and in steady state, one obtains the pseudo-first-order rate constants in the following form:

$$k = k_+C_{ClO_2^-} + k_- \tag{6}$$

where

$$k_+ = Q\{k_1 + k_2K_p[H^+] + k_3k_4K_h/(k_{-3} + k_4[H^+])\} \tag{7}$$

$$Q = [H^+]/\{([H^+] + K_h)(1 + K_p[H^+])\}$$

$$k_- = k_{-1} + k_{-2}[H^+] + k_{-3}k_{-4}/(k_{-3} + k_4[H^+]) \tag{8}$$

In excellent agreement with eq 6, at constant pH, rate constant k is a linear function of the chlorite ion concentration. At pH 1.51, 1.76, and 2.03, the slopes (k_+) and intercepts (k_-) are 115 ± 20, 146 ± 20, 221 ± 14 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and 69 ± 5, 98 ± 5, 121 ± 3 s^{-1}, respectively.

Rate constants k_- and k_+ increase with increasing pH. This observation suggests that the complex formation via $Fe(OH)ClO_2^+$ is superior compared to the other pH-dependent pathway of the mechanism. Consequently, the middle term in eqs 7 and 8 can be rejected. This conclusion is also supported by literature data for ligand substitution reactions of iron(III).[20] The rate constants for the reaction of the protonated form of the ligands (HL) and Fe^{3+} always were found to be considerably smaller than for other steps. If the protonated and deprotonated forms of the ligand are in comparable concentration, as in our case, the kinetic role of the Fe^{3+} + HL step is negligible in the complex formation.

Since simple proton-transfer reactions are generally diffusion controlled, the assumption that $k_4[H^+] \gg k_{-3}$ seems to be plausible for our conditions. By taking into account the previous considerations, one obtains the following simplified expression for the rate constant:

$$k = Q(k_1 + k_3K_h/[H^+]) + k_{-1} + k_{-3}/(K_4[H^+]) \tag{9}$$

Parameters k_1, k_3, k_{-1}, and k_{-3}/K_4 were simultaneously calculated on the basis of eq 9 and by using the least-squares-fitting program.[15] The results are given in Table II. As seen, k_3 is very poorly defined and its value should be considered valid within a factor of 2–3. Although the calculated first-order rate constants are in good agreement with those obtained from the SF experiments (Table I), the kinetic parameters are internally somewhat inconsistent. On the basis of Scheme I, the following equations should hold for the rate and equilibrium constants:

$$K_1 = k_1/k_{-1} \qquad K_3K_4 = K_1/K_h = k_3K_4/k_{-3}$$

where

$$K_3 = [Fe(OH)ClO_2^+]/([Fe(OH)^{2+}][ClO_2^-])$$

$$K_4 = [FeClO_2^{2+}]/([Fe(OH)ClO_2^+][H^+])$$

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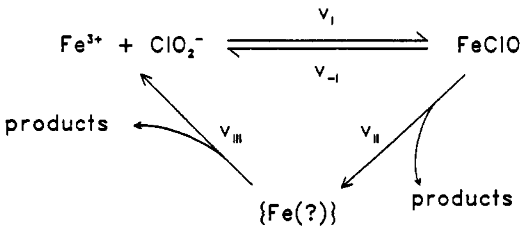
(17) Zékány, L.; Nagypál, I. In *Computational Methods for the Determination of Formation Constants*; Leggett, D. J., Ed.; Plenum: New York, 1985; p 291.

(18) Perrin, D. D. *J. Chem. Soc.* **1959**, 1710.

(19) Henke, B. L.; Perera, R. C. C.; Urch, D. S. *J. Chem. Phys.* **1968**, *68*, 3692.

(20) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Vol. 2, pp 1–220 and references therein.

Scheme II



On the basis of the kinetic parameters, $K_1 = 5.4$ M^{-1} and $K_3K_4 = 1400$ M^{-2}. These data compare unfavorably to the results obtained from direct equilibrium studies, 13.8 M^{-1} and 7600 M^{-2}, respectively. Because of the uncertainty in rate constant k_3, this comparison is not necessarily appropriate in the case of K_3K_4 $(=K_1/K_h)$. The discrepancy in the values for K_1 is most likely the consequence of the simplified kinetic model used for the evaluation of the parameters. As discussed earlier, the catalytic decomposition of the chlorite ion may be significant in the overall complex formation reaction. The generalized mechanism given in Scheme II offers a consistent interpretation of the results.

In this model, step I corresponds to the overall ligand substitution reaction and is equivalent with Scheme I. Step II represents all the possible pathways of the redox decomposition of the $FeClO_2^{2+}$ complex. At this point, the oxidation state of the product iron species is not obvious. The decomposition may proceed via either Fe(II) or Fe(IV). The formation of iron(IV) species was postulated in several redox reactions of Fe(III).[7,21] However, in aqueous solution, no simple iron species in oxidation state +4 has been experimentally confirmed.

If the primary product of step II is Fe(II), it is rapidly oxidized by the chlorite ion or the byproduct oxychlorine species.[1] Therefore, neither Fe(IV) nor Fe(II) is expected to be stable in this system. Since {Fe(?)} is presumably in steady state, Fe(III) must be rapidly regenerated from this transient species in step III. Chlorine dioxide can be the immediate product of either steps II and III or additional reactions between the byproducts. It should be added, both steps II and III can be a composite of several parallel and/or consecutive elementary reactions.

The proposed mechanism is far from complete. Because of experimental limitations, it is open to question under what circumstances the exact details of steps II and III can be elucidated. Nevertheless, this model is suitable to resolve the anomalies in the kinetic parameters for the complex formation. Formally, steps II and III can be regarded as a new pathway for the dissociation of $FeClO_2^{2+}$. Since the apparent dissociation rate is increased by this pathway, the equilibrium constants calculated from the kinetic parameters are smaller than expected.

Providing that $d[Fe(?)]/dt \sim 0$, the following rate equation is given for the formation of $FeClO_2^{2+}$:

$$d[FeClO_2^{2+}]/dt = v_I - v_{-I} - v_{II} \qquad (10)$$

In eq 10, v_I and v_{-I} are the overall rates for the formation and dissociation of $FeClO_2^{2+}$ in Scheme I, respectively, and v_{II} is the rate of step II in Scheme II.

Tentatively, we propose that the $FeClO_2^{2+} \rightarrow$ {Fe(?)} transition consists of only one kinetically significant reaction step. It is the decomposition of $FeClO_2^{2+}$ in a first-order intramolecular electron-transfer process. The spectroscopic observations lend some support to this theory. It is well-known that d–d transitions are forbidden for Fe^{3+}. Therefore, similar to case of other iron(III) complexes, the intense absorbance band in the visible spectral range corresponds to charge-transfer (CT) transition in $FeClO_2^{2+}$.[7] Ultimately, the CT phenomena easily can result in a formal oxidation–reduction reaction between the metal ion and the ligand.

If $FeClO_2^{2+}$ decomposes in a simple first-order reaction, i.e. $v_{II} = k_{II}[FeClO_2^{2+}]$, rate constant k_{II} is incorporated in k_{-1}:

$$k_{-1} = k_{-1}' + k_{II} \qquad (11)$$

Table III. Formation Rate Constants for $Fe^{3+} + L^- = FeL^{2+}$ Reactions and the pK_a of the Ligands

ligand	pK_a	k_1, M^{-1} s^{-1}	I, M	T, °C	ref
$C_2H_5COO^-$	4.7	4.2×10^5	1.0	20	28
CH_3COO^-	4.6	3.4×10^5	1.0	20	28
N_3^-	4.2	1.6×10^5	1.0	25	22
F^{-a}	2.9	5.4×10^3	0.5	25	29
CH_2ClCOO^-	2.6	4.9×10^3	1.0	20	28
ClO_2^-	1.7	269	1.0	25	*b*
$H_2PO_2^-$	0.9	270	1.0	25	30
SCN^-	0.9[c]	127	0.4	25	31
Cl^-		4.8	1.5	25	32
Br^-		1.6	2.0	25	33

[a] The rate constant was estimated on the basis of the corresponding activation parameters obtained from the 0–12.1 °C range. [b] This work. [c] From ref 8b at $I = 0$ M.

Rate constant k_{-1}' is the "real" dissociation rate constant for reaction 1. Since $k_{-1}' = k_1/K_1$, both components of k_{-1} in eq 11 can be estimated from the equilibrium and kinetic parameters:

$$k_{-1}' = 19.5 \text{ s}^{-1} \qquad k_{II} = 30.1 \text{ s}^{-1}$$

According to these data, the redox decomposition and the dissociation of $FeClO_2^{2+}$ are equally important in the overall complex formation reaction.

Formally, an analogous interpretation can be given for the difference in the k_{-3}/K_4 values. In this case, another redox decomposition step should be included in the mechanism. The rate of this reaction should be inversely proportional to the hydrogen ion concentration. While this possibility cannot a priori be rejected, it is questionable whether a chemically admissible reaction step or steps can be found to support such a rate law.

The ambiguity between rate constants k_{1a} ($Fe^{3+} + L^-$) and k_{1b} ($(Fe(OH)^{2+} + HL$) was demonstrated in several papers on ligand substitution reactions of Fe(III).[22-24] One of the most complete discussions of this problem was given by Gouger and Stuehr.[24] According to these authors, unambiguous assignment of k_1 is possible only with ligands of very low ($k_1 = k_{1a}$) or relatively high ($k_1 = k_{1b}$) basicity. In the case of other ligands, and chlorite ion falls into this category, the data appear to be consistent with both interpretations. If k_1 is assigned to k_{1a}, the trend of the rate constants suggests an associative interchange mechanism (I_a) for reaction 1. On the basis of the other possibility, the same kinetic data are consistent with a dissociative interchange mechanism (I_d).

Activation parameters have increasingly been used to differentiate between possible mechanisms of ligand substitution reactions.[25] In aqueous solutions of Fe(III), the activation parameters of water exchange are consistent with associative activation in $Fe(H_2O)_6^{3+}$ and dissociative activation in $Fe(H_2O)_5OH^{2+}$.[26,27] Activation parameters for reactions analogous to reaction 1 also indicate an I_a mechanism.[25] These data, coupled with previous considerations, strongly suggest that k_1 has to be assigned to k_{1a}; i.e., $k_{1a} = 269$ M^{-1} s^{-1}. In the case of associative activation, the rate constants of the complex formation reactions should correlate with the pK_a of the ligands. As shown in Table III, the kinetic data for simple monodentate ligands, including the chlorite ion, fulfill this expectation. It has to be emphasized,

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(21) Conocchioli, T. J.; Hamilton, E. J.; Sutin, N., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 926.

(22) Seewald, D.; Sutin, N. *Inorg. Chem.* **1963**, *2*, 643.

(23) Fogg, P. G. T.; Hall, R. J. *J. Chem. Soc. A* **1971**, 1365.

(24) Gouger, S.; Stuehr, J. *Inorg. Chem.* **1974**, *13*, 379.

(25) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549 and references therein.

(26) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.

(27) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

(28) Accascina, F.; Cavasino, F. P.; Didio, E. *Trans. Faraday Soc.* **1969**, *65*, 489.

(29) Pouli, D.; Smith, W. M. *Can. J. Chem.* **1960**, *38*, 567.

(30) Espenson, J. H.; Dustin, D. F. *Inorg. Chem.* **1969**, *8*, 1760.

(31) Below, J. F.; Connick, R. E.; Coppel, C. P. *J. Am. Chem. Soc.* **1958**, *80*, 2961.

(32) Hasinoff, B. B. *Can. J. Chem.* **1976**, *54*, 1820.

(33) Hasinoff, B. B. *Can. J. Chem.* **1979**, *57*, 77.

Inorg. Chem. **1991**, *30*, 3999–4007

however, that the alternative pathway cannot be completely ruled out. If k_1 is assigned to reaction 1b, $k_{1b} = 2.8 \times 10^3$ M^{-1} s^{-1}.

Conclusions

The results presented in this paper and in our previous report[6] confirm the formation of relatively weak chlorito complexes with the two most common transition-metal ions. In the absence of specific effects, similar complexes are formed between Cu^{2+} or Fe^{3+} and simple monodentate ligands such as NO_3^-, Cl^-, and Br^- (cf. ref 8). Also, the rate constants obtained for the formation of $FeClO_2^{2+}$ are in good correlation with literature data for ligand substitution reactions of Fe(III). Providing that the results are typical for the chlorite ion, these findings suggest that no special interactions between the metal ion and ClO_2^- need be considered for the interpretation of the coordination chemistry of this ligand. Furthermore, both $CuClO_2^+$ and $FeClO_2^{2+}$ can be regarded as models for chlorito complexes with di- and trivalent metal ions, respectively.

In the presence of Fe^{3+}, fast catalytic decomposition of the chlorite ion was observed. This reaction is kinetically coupled with the complex formation and must be included in the interpretation of the experimental data. The results also provide some evidence that the $FeClO_2^{2+}$ complex is the precursor in the decomposition reaction. However, the exact kinetic role of this species is not known. Further studies in this system should focus on the intrinsic mechanism of the iron(III)-catalyzed decomposition of ClO_2^-.

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Oxidation of Thiosulfate by $[Os(phenanthroline)_3]^{3+}$ and Related Complexes

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The kinetics of oxidation of thiosulfate by $[Os(phen)_3]^{3+}$ (phen = phenanthroline) in aqueous media at 25.0 °C and 0.10 M ionic strength has been investigated by stopped-flow spectrophotometry. With excess thiosulfate, the reaction has the stoichiometry $2[Os(phen)_3]^{3+} + 2S_2O_3^{2-} \rightarrow 2[Os(phen)_3]^{2+} + S_4O_6^{2-}$, and the rate law is $-d[Os(III)]/dt = 2k_1[Os(III)][S_2O_3^{2-}] + 2k_2[Os(III)][S_2O_3^{2-}]^2$. Oxidations by $[Os(4,7\text{-}Me_2phen)_3]^{3+}$, $[Os(5,6\text{-}Me_2phen)_3]^{3+}$, and $[Os(5\text{-}Cl\text{-}phen)_3]^{3+}$, having reduction potentials that span a range of 0.65 to 0.94 V, show similar rate laws. Both the k_1 and k_2 rate constants increase as the reduction potential of the oxidant increases. An outer-sphere electron-transfer mechanism is inferred for both terms, with $S_2O_3^-$ and $S_4O_6^{3-}$ as the primary intermediates.

Introduction

Thiosulfate is one of the most industrially and biologically important sulfur oxyanions. Unlike sulfate, thiosulfate has an extensive redox chemistry. Although there have been numerous mechanistic studies of these reactions, much remains to be learned regarding the sulfur-containing intermediates. It is clear that in many cases, oxidation of thiosulfate by coordination complexes occurs via an inner-sphere mechanism.[1-3] The body of literature on outer-sphere mechanisms is much smaller, but such processes are of interest because of the implied free-radical intermediates. The only data available pertain to the oxidations by $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Mo(CN)_8]^{3-}$, and $[CoW_{12}O_{40}]^{5-}$.[4-6] The reaction of $[CoW_{12}O_{40}]^{5-}$ is difficult to interpret because of the extreme electrostatic problems associated with the 5−/2− charge product.[6] Related problems are found for the reaction of $[Mo(CN)_8]^{3-}$, which is catalyzed by alkali-metal cations.[5] Difficulties also arise in comparing the reactions of $[Fe(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, and $[IrBr_6]^{2-}$ because of the differing properties of these oxidants.[4]

The objective of this paper is to study a homologous series of reactions, in which thiosulfate is oxidized in an outer-sphere mechanism. Criteria for selection of the oxidants are that they be substitution inert so as to ensure an outer-sphere mechanism and cationic so as to avoid alkali-metal cation catalysis and have smoothly varying reduction potentials so as to facilitate construction of LFERs (linear free energy relationships). $[Os(phen)_3]^{3+}$ (phen = phenanthroline) and its relatives constitute such a series. An advantage of these oxidants is that they are weaker oxidants than the corresponding Fe(III) and Ru(III) series. This weakly oxidizing power allows us to explore the transition from outer-sphere electron transfer to the alternative mechanisms exhibited by very weak oxidants such as $[Fe(CN)_6]^{3-}$. There have been a few reports in the literature in which these Os(III) complexes acted as outer-sphere electron-transfer oxidants.[7,8] These reports demonstrated the applicability of Marcus's theory to reactions of these oxidants. In the present paper we report on the reactions of $S_2O_3^{2-}$ with $[Os(phen)_3]^{3+}$ and three of its relatives.

Experimental Section

Reagents. Distilled deionized water was obtained from a Barnstead Fi-Streem glass still. Sodium thiosulfate and sodium acetate were recrystallized from hot water. Osmium tetroxide was from Alfa Products, and the ligands 1,10-phenanthroline (phen), 4,7-dimethylphenanthroline (4,7-Me_2phen), 5,6-dimethylphenanthroline (5,6-Me_2phen), and 5-chlorophenanthroline (5-Cl-phen) were purchased from Aldrich Chemical Co. Trifluoromethanesulfonic acid (HCF_3SO_3) was from 3M, and sodium trifluoromethanesulfonate (sodium triflate) was prepared by neutralization of concentrated HCF_3SO_3 with sodium carbonate. After neutralization the solution was boiled to drive off excess CO_2, and the solid was recrystallized from hot water. Br_2/CH_3CN solutions used for in situ oxidation of Os(II) to Os(III) were prepared by the method of Callahan et al.[9] Tetra-*n*-propylammonium bromide was recrystallized from ethanol by addition of ethyl ether. Potassium salts of the polythionates were prepared and purified by literature methods.[10] Trithionate was made from the reaction of SO_2 with an aqueous solution of $K_2S_2O_3$. Tetrathionate was prepared by the oxidation of thiosulfate by iodine, and pentathionate, by the reaction of thiosulfate with HCl in the presence of arsenious acid. All other materials were of certified or reagent grade.

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† Preliminary investigations conducted at Rice University, Houston, TX, as reported in the Ph.D. dissertation (1987) of S.B.R.

(1) Nord, G.; Skibsted, L. H.; Halonin, A. S. *Acta Chem. Scand. A* **1975**, *29*, 505–512.
(2) Panda, R. K.; Neogi, G.; Ramaswamy, D. *Int. J. Chem. Kinet.* **1981**, *13*, 1001–1010.
(3) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 889–893.
(4) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155–179.
(5) Lamprecht, G. J.; Leipoldt, J. G.; Dennis, C. R.; Basson, S. S. *React. Kinet. Catal. Lett.* **1980**, *13*, 269–275.
(6) Ali, M.; Saha, S. K.; Banerjee, P. *Indian J. Chem.* **1990**, *29A*, 528–530.
(7) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731–1736.
(8) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233–2238.
(9) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443–1453.
(10) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; Vol. 1; pp 393–403.

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