experimental evidence strongly suggests that *at least* two of these structures may coexist in the gas. The large number of observed infrared and Raman bands can easily be explained if appreciable amounts of VIII exist. The observed dipole moment can also be accounted for by VIII. Although the electron diffraction experiments cannot give us the hydrogen positions, the recent work may well be correct to the extent that it requires *long* boron–boron distances, as found here. We also point out that the crystallization of I requires no hydrogen rearrangements. This is not true of any other structure considered, although the hydrogen rearrangements necessary in II and VIII are minimal.

Finally, it is well-known that many metal borohydrides undergo rapid intramolecular hydrogen tautomerism, making the hydrogens equivalent on the nmr time scale. Although the nmr spectrum of beryllium borohydride has not yet been observed, the three structures I, VIII, and II provide a convenient and obvious path for such a tautomerism.[26]

Acknowledgments. We would like to thank E. Clementi and the IBM Corporation for generously supplying most of the computer time for this work. We also thank the Office of Naval Research for support of this investigation.

(26) As this manuscript was being submitted a similar independent SCF–CI study on beryllium borohydride appeared: R. Ahlrichs, *Chem. Phys. Lett.*, **19**, 174 (1973). This study employs a Gaussian basis set and the independent electron pair approximation for correlation corrections. It does not consider structures III, VI, XI, X, or XI, no configuration interaction results are reported for structure IV or V, and structure IV was not optimized. Our basic conclusions are, however, very similar.

Mechanistic Studies of One- and Two-Equivalent Oxidations of the Mercury(I) Dimer

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Abstract: Kinetic studies on the reactions of mercury(I) dimer with the one-equivalent oxidants $Fe(phen)_3{}^{3+}$ and $Ru(bipy)_3{}^{3+}$ and the two-equivalent oxidant $BrO_3{}^-$ are described. These and other reactions of the mercury(I) dimer previously reported can be summarized as follows. One-equivalent oxidants usually react by a mechanism $(Hg^I)_2$ + oxidant (1 e^-) $\rightarrow Hg^I + Hg^{II}$ and Hg^I + oxidant (1 e^-) $\rightarrow Hg^{II}$ (fast), with a rate law first order in $(Hg^I)_2$ and oxidant. Two-equivalent oxidants react by a mechanism $(Hg^I)_2 \rightleftharpoons Hg^0 + Hg^{II}$ (fast) and Hg^0 + oxidant (2 e^-) $\rightarrow Hg^{II}$, with a rate law which is first order in both reactants, but which is in addition dependent on $[Hg^{II}]^{-1}$.

Different reaction sequences are generally observed in redox reactions involving one- and two-equivalent oxidants. As a result a distinction between the two based on differences in stoichiometry, reaction products, and/or rate law is often possible. Well-known examples are the reactions of one- and two-equivalent oxidants with hydrazine[1] and with sulfite,[2] where the stoichiometries and products often enable a clearcut distinction to be made.[3]

With mercury(I) dimer as reductant a similar distinction is not at present clearly defined.[4,5] Reactions of mercury(I) dimer with thallium(III),[6] cobalt(III),[7] manganese(III),[8] cerium(IV) (in the presence of sulfate[9] and catalyzed by silver(I)[10] and hexachloroiridate(III)[11]), and neptunium(VII)[5] have been studied previously. The mechanisms of the reactions of the one-equivalent oxidants tris(1,10-phenanthroline)iron(III) and tris(2,2′-bipyridine)ruthenium(III) and the two-equivalent oxidant bromate are considered in this paper. The stoichiometries (in equivalents) are the same and mercury(II) is the product in all cases. The rate laws differ, however, and with information from previous studies we feel it is now possible to differentiate between the two types of reactant.

Experimental Section

Preparation of Solutions of the Mercury(I) Dimer. Stock solutions of the perchlorate salt of $(Hg^I)_2$ in perchloric acid (*ca.* 1 *M*) were prepared in three different ways. (i) Analar BDH mercury (23.5 g) and 50 ml of water were heated together in a 250-ml beaker. and concentrated nitric acid was added a little at a time to the hot solution until all the mercury dissolved. Nitrogen dioxide was given off. Mercury oxide. HgO, was precipitated by adding Analar anhydrous sodium carbonate. The HgO was dried by suction and then dissolved in 2 *M* $HClO_4$. The mercury(II) in solution was converted to mercury(I) dimer by shaking with a slight excess of mercury for *ca.* 24 hr.[12] (ii) Yellow HgO, May and Baker Labor-

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(1) See, for example, W. C. E. Higginson, *Chem. Soc., Spec. Publ.*, No. 10, 95 (1957).

(2) W. C. E. Higginson and J. Marshall, *J. Chem. Soc.*, 447 (1957).

(3) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 232 (1967).

(4) Reference 3, pp 218–219.

(5) M. A. Thompson, J. C. Sullivan, and E. Deutsch, *J. Amer. Chem. Soc.*, **93**, 5667 (1971). We note also that no reaction between mercury(I) dimer and neptunium(VI) is observed over *ca.* 1 hr at 50° with neptunium(VI) concentrations 100 times greater than reported in this paper (personal communication, J. C. Sullivan).

(6) A. M. Armstrong, J. Halpern, and W. C. E. Higginson, *J. Phys. Chem.*, **60**, 1661 (1956); A. M. Armstrong and J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957).

(7) D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 31 (1960).

(8) D. R. Rosseinsky, *J. Chem. Soc.*, 1181 (1963).

(9) W. H. McCurdy and G. C. Guilbault, *J. Phys. Chem.*, **64**, 1825 (1960).

(10) W. C. E. Higginson, D. R. Rosseinsky, B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 49 (1960).

(11) K. B. Yatsimirskii, L. P. Tikhonova, and I. P. Svarkovskaya, *Russ. J. Inorg. Chem.*, 14, (11), 1572 (1969).

(12) W. Pugh, *J. Chem. Soc.*, 1824 (1937).

atory Chemicals, was dissolved in 2 *M* $HClO_4$, procedure then as above. (iii) G. F. Smith mercury(II) perchlorate was dissolved in 2 *M* $HClO_4$, procedure then as in i. Stock solutions which were prepared by i and ii gave inconsistent results at first. We consider it advisable to prepare solutions of mercury(I) dimer by all three methods and to check one against the other. It is also important to use relatively fresh (up to *ca.* 10 days) mercury(I) dimer solutions. All the results reported gave satisfactory reproducibility.

The concentrations of mercury(I) dimer solutions ($\sim$0.1 *M*) were determined by titration against 0.025 *M* NaCl (100 ml) with the addition of 0.5 ml of Bromophenol Blue as indicator. The precipitate changes from a creamy white to a lilac color at the end point. Following an initial determination the indicator was, subsequently, not added until just before the end point. Mercury(II) perchlorate solutions were determined by addition of 10 ml of 6 *M* HNO_3 to 100 ml of mercury(II) solution (containing $\sim$0.1 g Hg^{2+}) and cooling to $<15°$. The solution was slowly titrated with 0.1 *M* thiocyanate (solution was well shaken) with the addition of 1 ml of saturated ferric alum indicator, until a reddish brown coloration became permanent. Hydrogen ion concentrations of stock solution were determined by an ion-exchange procedure.

The Preparation of Tris(1,10-phenanthroline)iron(III). The preparation was as described by Schilt and Taylor.[13] Samples were protected from light throughout the preparation and during storage. *Anal.* Calcd for $FeC_{36}H_{24}N_6Cl_3O_{12}\cdot H_2O$: C, 47.34; H, 2.85; N, 9.2. Found: C, 47.75; H, 2.9; N, 9.2. For kinetic runs a stock solution of $Fe(phen)_3{}^{3+}$ *ca.* 5×10^{-3} *M* was made up in 5 *M* $HClO_4$ (the complex is much less soluble in more dilute $HClO_4$), and stored at 0° (fresh solutions were made each day although such stock solutions are in fact stable for longer periods). To commence runs the stock solutions of $Fe(phen)_3{}^{3+}$ was added from a micropipette to $\sim$15 ml of mercury(I) dimer containing $HClO_4$–$LiClO_4$ as required. Solutions of $Fe(phen)_3{}^{3+}$ were standardized by adding 1 ml of stock solution and excess 1,10-phenanthroline to excess hydroxylamine hydrochloride. The pH was adjusted to $\sim$5 (sodium acetate) and the solution made up to 100 ml. Reduction occurred and the absorbance of $Fe(phen)_3{}^{2+}$ was measured at 510 nm.

Preparation of Tris(2,2′-bipyridine)ruthenium(II). Details were taken from ref 14 and 15. We also wish to acknowledge helpful comments from Dr. J. D. Miller of the University of Aston and Dr. J. Burgess of the University of Leicester. BDH laboratory reagent ruthenium trichloride, $RuCl_3\cdot H_2O$ (0.22 g), was dissolved in hot water (20 ml) containing 1 drop of 2 *M* HCl, and 0.55 g of 2,2′-bipyridine was added with shaking. The solution was boiled for a few minutes until the color changed to a deep greenish brown. A solution of sodium hypophosphite, NaH_2PO_2 (0.3 g), in cold water (5 ml) was added slowly with stirring. The solution was refluxed for *ca.* 15 min when a deep orange–red solution was obtained. While the solution was hot, ruthenium metal was filtered off and the perchlorate salt of $Ru(bipy)_3{}^{2+}$ precipitated by addition of concentrated $NaClO_4$. The sample was recrystallized from hot water. *Anal.* Calcd for $RuC_{30}H_{24}N_6Cl_2O_8$: C, 46.9; H, 3.13; N, 10.9. Found: C, 45.9; H, 3.16; N, 10.4.

Preparation of Tris(2,2′-bipyridine)ruthenium(III). A solid sample of $Ru(bipy)_3{}^{3+}$ was first prepared by oxidation of a solution of $Ru(bipy)_3{}^{2+}$ with chlorine (*ca.* 0.5 hr).[15] Unreacted $Ru(bipy)_3{}^{2+}$ was precipitated by addition of $NaClO_4$ and filtered off. The blue solution was left at 0° for 2 days when a sample of the perchlorate salt of $Ru(bipy)_3{}^{3+}$ was obtained. This was filtered off, washed with alcohol and ether, and dried by suction. The above was found to be less stable in dilute $HClO_4$ solutions than fresh solutions prepared by cerium(IV) oxidation of a solution of $Ru(bipy)_3{}^{2+}$. Isosbestic points were observed at 328 and 565 nm during the addition of cerium(IV) to $Ru(bipy)_3{}^{2+}$. On exceeding a 1:1 ratio no further changes in absorption were apparent, and there was no evidence for the formation of ruthenium(IV). The following procedure was therefore adopted for preparation of solutions of $Ru(bipy)_3{}^{3+}$. A solution of $Ru(bipy)_3{}^{2+}$ was made up with $LiClO_4$–$HClO_4$ as required and an equivalent of cerium(IV) perchlorate (G. F. Smith solution of 0.56 *M* cerium(IV) in 6.0 *M* perchloric acid added. Oxidation to $Ru(bipy)_3{}^{3+}$ was rapid.[16] The solution was thermostatted in a 4-cm cell and mercury(I) dimer solution added. High hydrogen ion concentrations were used throughout (1.0–2.9 *M*) to avoid decomposition of $Ru(bipy)_3{}^{3+}$, which appears to have an $[H^+]^{-2}$ dependence.

The reactant products $Fe(phen)_3{}^{2+}$ and $Ru(bipy)_3{}^{2+}$ have intense absorption bands in the visible range, which are suitable for monitoring reactions by conventional spectrophotometry using a Unicam SP500. With bromate as the oxidant the decrease in absorbance of mercury(I) dimer (in the uv range) with time was followed on either a Unicam SP800 or SP500 spectrophotometer. For the slower reactions the SP800 was programmed to record absorbance readings at a fixed wavelength at 5–15-min intervals over periods of 1–3 days. Both instruments were complete with thermostatted cell housings.

Solutions of Analar potassium bromate and reagent grade sodium bromate were determined by standard volumetric procedures. Both solutions were used in kinetic studies and gave satisfactory agreement. A solution of vanadium(V) perchlorate was prepared by dissolving Analar ammonium vanadate in perchloric acid. BDH sodium dichromate and Johnson and Matthey sodium hexachloroiridate(IV) were used.

Results

The Reaction with $Fe(phen)_3{}^{3+}$. The complex tris(1,10-phenanthroline)iron(III) is reduced by the mercury(I) dimer with the formation of tris(1,10-phenanthroline)iron(II). Uv–visible spectra of $Fe(phen)_3{}^{3+}$ and $Fe(phen)_3{}^{2+}$ give crossover points at 377 and 575 nm, and in the redox process isosbestic points at these wavelengths are observed for up to, in the most favorable cases, *ca.* 30% reaction. Our observations are consistent with a 1:2 reaction as in eq 1. Isosbestic

$$(Hg^I)_2 + 2Fe(phen)_3{}^{3+} \longrightarrow 2Hg^{II} + 2Fe(phen)_3{}^{2+} \qquad (1)$$

points are not retained over longer periods owing to the incidence of eq 2. Rate constants (510 nm) for the

$$Fe(phen)_3{}^{2+} + 6H_2O \longrightarrow Fe(H_2O)_6{}^{2+} + 3phen \qquad (2)$$

dissociation of $Fe(phen)_3{}^{2+}$ (eq 2) with and without the addition of both mercury(I) dimer and mercury(II) are *ca.* 6.2×10^{-5} sec^{-1}, in agreement with values *ca.* 7.2×10^{-5} sec^{-1} obtained by Shakhashiri and Gordon[17] at 25°, $\mu = 1.0$ *M* (sulfate solution), and the value 7×10^{-5} sec^{-1} obtained by Basolo, *et al.*,[18] at 25°, $\mu = 1.0$ *M* (in HCl). One consequence of eq 2 is that a further reaction (eq 3), which is known to be rapid (3.7

$$Fe^{2+} + Fe(phen)_3{}^{3+} \longrightarrow Fe^{3+} + Fe(phen)_3{}^{2+} \qquad (3)$$

$\times 10^4$ l. mol sec^{-1} at 25°, $\mu = 0.5$ *M*)[19] is also effective. A full study of eq 1 is difficult therefore. It has been possible to obtain relevant kinetic information by monitoring the formation of $Fe(phen)_3{}^{2+}$ at 510 nm (ϵ 10,900 l. mol^{-1} cm^{-1}),[19] at which wavelength $Fe(phen)_3{}^{3+}$ also absorbs (ϵ $\sim$300 l. mol^{-1} cm^{-1}). Plots of absorbance changes log ($OD_\infty - OD_t$) against time, where OD_∞ is as calculated assuming eq 2 and 3 do not contribute, are linear for *ca.* 20 min, Figure 1. It is concluded that over such times, which correspond to the period of retention of isosbestics, eq 2 and 3 can be neglected. Nor does the dissociation of $Fe(phen)_3{}^{3+}$ (rate constant 0.14×10^{-4} sec^{-1} at 25°, $[H^+] = 0.1$ *M*, reaction inhibited by increasing $[H^+]$)[18] make any significant contribution in the initial stages. From plots as in Figure 1 second-order rate constants k_1 for (eq 1) were obtained, Table I. Similar rate constants were

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(13) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

(14) F. H. Burstall, *J. Chem. Soc.*, 173 (1936).

(15) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, **83**, 174 (1949).

(16) P. George and D. H. Irvine, *J. Chem. Soc.*, 587 (1954).

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(18) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, **76**, 3807 (1954); discussion in F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 218–219.

(19) N. Sutin and B. M. Gordon, *J. Amer. Chem. Soc.*, **83**, 70 (1961), report ϵ 11,100 l. mol^{-1} cm^{-1} in good agreement with this value.

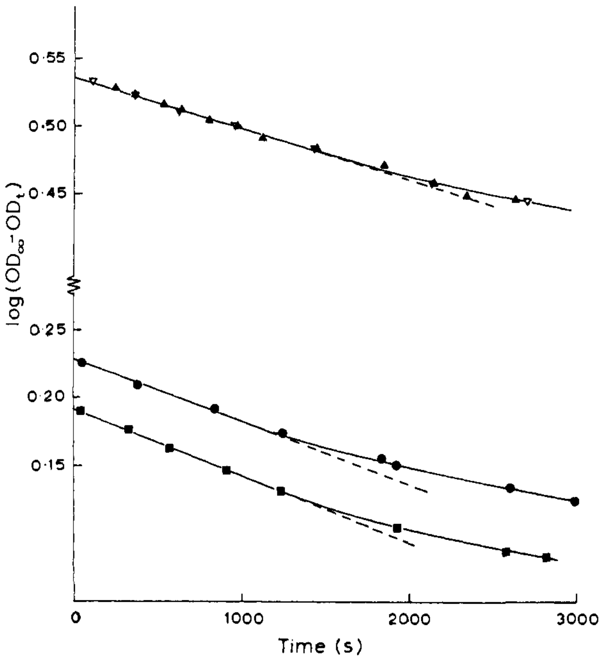

Figure 1. First-order plots for the reaction of mercury(I) dimer with tris(1,10-phenanthroline)iron(III) at 25° and $\mu = 1.0\ M$ ($LiClO_4$). Concentrations were $[(Hg^I)_2] = 0.10\ M$ in all cases and for ∇, $[Fe(phen)_3{}^{3+}] = 9.6 \times 10^{-6}\ M$, $[H^+] = 0.7\ M$; ▲, $[Fe(phen)_3{}^{3+}] = 9.7 \times 10^{-6}\ M$, $[H^+] = 0.2\ M$; ●, $[Fe(phen)_3{}^{3+}] = 4.9 \times 10^{-6}\ M$, $[H^+] = 0.55\ M$, $[Hg^{II}] = 0.05\ M$: ■, $[Fe(phen)_3{}^{3+}] = 4.7 \times 10^{-6}\ M$, and $[H^+] = 0.70\ M$.

Table I. Rate Constants k_1 for the Reduction of $Fe(phen)_3{}^{3+}$ by Mercury(I) Dimer at 25°, $\mu = 1.0\ M$ ($LiClO_4$)

Temp, °C	$[H^+]$, M	$[(Hg^I)_2]$, M	$[Hg^{II}]$, M	$10^6[Fe(phen)_3{}^{3+}]$, M	$10^4 k_1$, l. mol^{-1} sec^{-1}
25.0	0.70	0.10		9.62	4.5
	0.70	0.10		4.71	5.15
	0.70	0.08		9.96	5.05
	0.70	0.06	0.01	8.74	4.75
	0.70	0.05	0.05	9.40	4.6
	0.55	0.10	0.05	4.91	4.9
	0.20	0.10		9.75	4.5

also evaluated at 354 nm at which wavelength the complex $Fe(phen)_3{}^{3+}$ absorbs most strongly. As far as the mechanism is concerned what is particularly important is that addition of mercury(II) (up to 0.05 M) clearly has no effect on k_1. The alternative mechanism involving initial dismutation of mercury(I) dimer gives an inverse mercury(II) dependence, which has a pronounced effect on rates (see for example the bromate study). There is no dependence on $[H^+]$ over the range 0.2–0.7 M, and results obtained are consistent with the rate law

$$-d[Fe(phen)_3{}^{3+}]/dt = 2k_1[(Hg^I)_2][Fe(phen)_3{}^{3+}] \quad (4)$$

where at 25°, $k_1 = ca.\ 5.0 \times 10^{-4}$ l. mol^{-1} sec^{-1}.

The Reaction with $Ru(bipy)_3{}^{3+}$. Kinetic data obtained using a solid sample believed to be $Ru(bipy)_3(ClO_4)_3$ were unsatisfactory, and the complex was therefore prepared *in situ* by cerium(IV) oxidation of $Ru(bipy)_3{}^{2+}$ (see Experimental Section). Solutions of $Ru(bipy)_3{}^{3+}$ undergo a side reaction at low $[H^+]$, and $[H^+]$ values in the range 1.0–2.9 M (and a correspondingly high ionic strength, $\mu = 3.0\ M$) had to be used to minimize contributions from this process. Quantitative formation of $Ru(bipy)_3{}^{2+}$ was observed and the overall reaction is assumed to be as in eq 5. The reaction was

$$(Hg^I)_2 + 2Ru(bipy)_3{}^{3+} \longrightarrow 2Hg^{II} + 2Ru(bipy)_3{}^{2+} \quad (5)$$

followed at 452 nm at which wavelength ϵ 12,900 l. mol^{-1} cm^{-1} for $Ru(bipy)_3{}^{2+}$ and a value $\epsilon \sim 300$ l. mol^{-1} cm^{-1} was obtained for $Ru(bipy)_3{}^{3+}$.[20] No subsequent reaction of the product $Ru(bipy)_3{}^{2+}$ was observed. The mercury(I) dimer reactant was in large excess, and plots of log ($OD_\infty - OD_t$) against t were generally linear to >70% reaction. Second-order rate constants, k_2, are given in Table II. Variation of the mercury(I) dimer concentration over a fivefold range was consistent with a first-order dependence on this reactant. At lower mercury(I) dimer concentrations linear plots were not observed due to side reactions of $Ru(bipy)_3{}^{3+}$. Addition of mercury(II) had no effect on rates, and the rate law is therefore of the same form as eq 4. Activation parameters (Table VI) were evaluated by a least-squares treatment (no weighting) from rate constants with $[(Hg^I)_2] = 0.05\ M$. Runs at the high mercury(I) dimer concentrations were excluded from the computation because variations in perchlorate ion concentration may be relevant.

Table II. Rate Constant for the Reduction of $Ru(bipy)_3{}^{3+}$ by Mercury(I) Dimer, $\mu = 3.0\ M$ ($LiClO_4$)

Temp, °C	$[H^+]$, M	$[(Hg^I)_2]$, M	$10^6[Ru(bipy)_3{}^{3+}]$, M	$10^4 k_2$, l. mol^{-1} sec^{-1}
20.0	2.85	0.055	4.55	4.32
	2.75	0.050	4.55	4.13
25.0	2.85	0.05	5.20	6.8
	2.75	0.05	4.15	7.0
	2.55	0.15	3.70	7.0
	2.55	0.10[a]	2.70	6.7
	2.55	0.05[b]	2.04	6.8
	2.00	0.05	2.20	7.55
	1.50	0.12	2.43	6.8
	1.25	0.04	4.35	7.1
	1.00	0.05	3.42	6.9
35.5	2.85	0.05	3.95	3.13
	2.55	0.05[c]	3.92	3.11
	2.40	0.20	3.10	3.47
	2.40	0.26	3.10	3.56
	2.00	0.05	3.85	3.16
45.0	2.85	0.05	3.23	6.95
	2.00	0.05	3.80	6.65

[a] $[Hg^{II}] = 0.05\ M$. [b] $[Hg^{II}] = 0.01\ M$. [c] $[Hg^{II}] = 0.05\ M$.

The Reaction with $BrO_3{}^-$. The stoichiometry was determined at 50°, $\mu = 1.0\ M$ ($LiClO_4$), by analyzing reaction solutions, $[BrO_3{}^-] = ca.\ 4 \times 10^{-3}\ M$ and $[(Hg^I)_2] = ca.\ 0.8 \times 10^{-3}\ M$, at varying time intervals. Concentrations of bromate were determined iodometrically after first removing all metal ions using a cation exchange resin. The concentration of mercury(I) dimer was determined at 236 nm (ϵ 2.77×10^4 l. mol^{-1} cm^{-1})[21] after applying corrections for absorbance due to bromate and final products. There was no detectable change in stoichiometry over the course

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(20) A. J. McCafferty, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1428 (1969); J. D. Miller and R. H. Price, *ibid.*, 1048 (1966); R. R. Miller, W. W. Brandt, and M. Puke, *J. Amer. Chem. Soc.*, 77, 3178 (1955).

(21) W. C. E. Higginson, *J. Chem. Soc.*, 1438 (1951).

of the reaction (30–100%) investigated, and a ratio of 2.8 (±0.2) mol of mercury(I) dimer per mole of bromate is, we feel in accordance with an overall reaction as in eq 6. A stoichiometry of 3:1 was assumed in evaluating all rate constants below. Absorption changes at 212 nm were consistent with the formation of $HgBr^+$, $\epsilon \sim 6 \times 10^3$ l. mol^{-1} cm^{-1}, as compared with $\epsilon \sim 400$ l. mol^{-1} cm^{-1} for Hg^{2+} (absorption coefficients determined in presence of an equivalent amount of mercury(I) dimer).

$$3Hg^{I}_2 + BrO_3^- \longrightarrow 6Hg^{II} + Br^- + 6H_2O \qquad (6)$$

Absorbance changes in kinetic runs were monitored at the mercury(I) dimer peak at 236 nm. For reactions with high bromate concentrations a correction was applied for absorbance due to bromate. The reaction was studied over a temperature range of 35–50°. It was assumed that the first stage of the stepwise reduction of bromate $BrO_3^- \rightarrow BrO_2^- \rightarrow BrO^- \rightarrow Br^-$ is rate determining and that subsequent reactions are fast. Consistent with this it was found in separate experiments that the $BrO^- \rightarrow Br^-$ step is indeed fast. Bromine solutions also react rapidly with mercury(I) dimer under conditions of high [H$^+$], when the extent of formation of hypobromous acid is small. Spectra (200–400 nm) recorded during the course of the reaction showed no evidence for the buildup of intermediates. The reaction was slowed down by addition of mercury(II), which suggests a reaction sequence

$$(Hg^I)_2 \overset{K}{\rightleftharpoons} Hg^0 + Hg^{II} \qquad (7)$$

$$Hg^0 + BrO_3^- \xrightarrow[+2H^+]{k_3} Hg^{II} + BrO_2^- + H_2O \qquad (8)$$

The equilibration in eq 7 is known to be rapid,[6,22] and the rate law is therefore as in (9).

$$\frac{-d[(Hg^I)_2]}{dt} = 3k_3\frac{K[(Hg^I)_2][BrO_3^-]}{[Hg^{II}]} \qquad (9)$$

With a large excess of bromate this may be written in the form

$$\frac{3dx}{dt} = \frac{3k'(a - 3x)}{6x} \qquad (10)$$

where $k' = k_3K[BrO_3^-]$, a is the initial concentration of mercury(I) dimer, and x is the number of moles of mercury(I) dimer consumed by eq 7 and 8 at time t. On integration eq 11 is obtained. Graphs of the left-hand

$$-3x - a \ln (a - 3x) = 1.5k't + \text{constant} \qquad (11)$$

side against t were linear to *ca.* 70% completion. Bromate concentrations were varied over the range 7×10^{-4}–7×10^{-3} *M* (Figure 2) without any evidence for a $[BrO_3^-]^2$ dependence as observed by Thompson[23] in the bromate oxidation of cerium(III), manganese(II), and neptunium(V). Other values of k_3K are listed in Table III. When mercury(II) as well as bromate is in large excess eq 12 is obtained on integration, where

$$-\ln (a - 3x) = 3k''t + \text{constant} \qquad (12)$$

both $[BrO_3^-]$ and $[Hg^{II}]$ are included in k''; *i.e.*, $k'' = k_3K[BrO_3^-]/[Hg^{II}]$. Under these conditions the reaction is extremely slow. Graphs of log $(OD_\infty - OD_t)$ against t were linear to at least 60% completion. Rate constants k'' are given in Table IV, and the linear dependence of k'' on $[Hg^{II}]^{-1}$ is illustrated in Figure 3. From this figure $k_3K = 4.3 \times 10^{-7}$ sec^{-1} at 45° which is in good agreement with values in Table III. An upper limit for reaction by an $[Hg^{II}]$-independent path

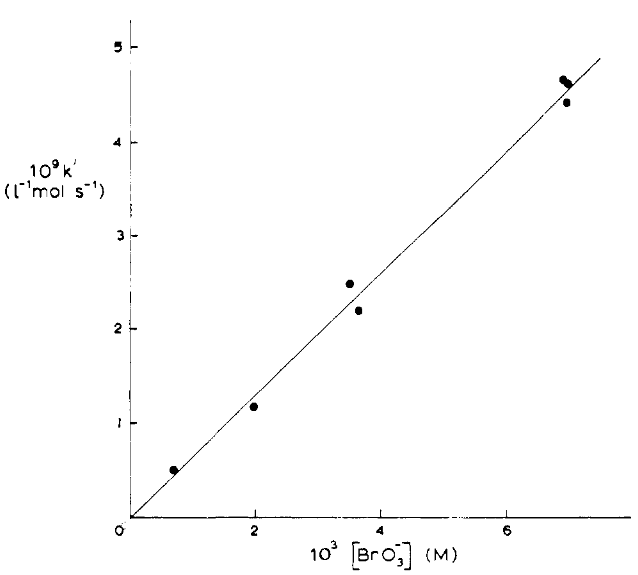

Figure 2. The dependence of first-order rate constants k' on bromate ion concentration for the reaction of mercury(I) dimer with bromate (50°, μ = 1.0 *M* (LiClO$_4$), [H$^+$] = 0.8 *M*, $[(Hg^I)_2] = 3.1 \times 10^{-5}$ *M*).

Table III. Rate Constants for the Reduction of Bromate Ions by Mercury(I) Dimer, μ = 1.0 *M* (LiClO$_4$)

Temp, °C	[H$^+$], *M*	$10^5[(Hg^I)_2]$, *M*	$10^3[BrO_3^-]$, *M*	10^7k_3K, sec^{-1}
35.0	1.00	3.89	1.33	1.04
	1.00	3.78	2.15	0.910
	0.90	4.03	1.94	0.873
	0.80	3.90	2.65	0.641
	0.70	3.63	2.65	0.693
	0.60	3.26	2.65	0.607
	0.40	4.08	2.65	0.411
40.0	1.00	4.25	2.10	1.95
	1.00	4.24	2.20	1.79
	0.80	4.07	2.65	1.36
	0.70	3.62	2.65	1.33
	0.60	4.95	2.65	1.05
	0.40	4.14	2.65	0.79
45.0	1.00	4.21	1.94	4.33
	1.00	3.98	2.00	4.40
	1.00	2.11	2.00	4.20
	1.00	3.96	0.97	4.57
	0.90	4.01	1.94	3.78
	0.90	3.83	2.00	3.70
	0.80	4.05	1.94	2.96
	0.80	3.83	2.00	2.83
	0.75	3.67	2.00	2.78
	0.70	4.28	2.00	2.34
	0.65	4.43	2.00	2.23
45.0	0.50	4.53	1.94	1.79
	0.50	4.64	2.00	1.81
	0.40	4.32	2.40	1.43
	0.10	2.81	2.00	0.641
50.0	1.00	3.99	1.96	9.01
	0.90	3.47	1.96	7.80
	0.80	3.81	1.96	6.02
	0.70	3.81	1.96	5.13
	0.60	4.00	1.96	3.51
	0.40	4.28	1.96	2.25
	0.30	4.10	1.96	1.54

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[23] R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971).

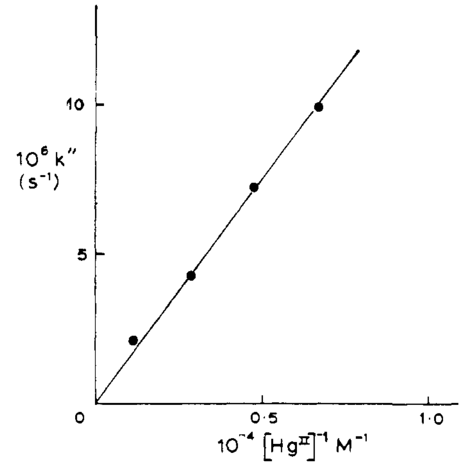

Figure 3. The dependence of first-order rate constant k'' on mercury(II) concentration for the reaction of mercury(I) dimer with bromate (45°, $\mu = 1.0\ M$(LiClO$_4$)).

Table IV. The Reduction of Bromate by Mercury(I) Dimer. Dependence of Rate Constants k'' (eq 12) on the Concentration of Mercury(II) with $[H^+] = 0.99\ M$, 45°, and $\mu = 1.0\ M$ (LiClO$_4$)

$10^3[BrO_3^-]$, M	$10^5[(Hg^I)_2]$, M	$10^4[Hg^{II}]$, M	$10^6k''$, sec^{-1}
3.26	4.64	9.00	2.03
3.26	4.21	3.57	4.12
3.26	3.24	2.13	7.01
3.26	2.16	1.50	9.65

Table V. The Reduction of Bromate by the Mercury(I) Dimer. Computed Values of Constants m and n as Defined in Eq 13

Temp, °C	10^7m, sec^{-1}	10^7n, l.^{2} mol^{-2} sec^{-1}
35.0	0.34	0.66
40.0	0.48	1.58
45.0	0.66	3.65
50.0	0.91	8.23

Table VI. Summary of Rate Constant (25°) and Activation Parameters Obtained for Reactions of Mercury(I) Dimer

Oxidant	μ, M	Rate constant	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Fe(phen)$_3^{3+}$ (k_1)	1.0	ca. 5.0×10^{-4} l. mol^{-1} sec^{-1} [a]		
Ru(bipy)$_3^{3+}$ (k_2)	3.0	7.0×10^{-4} l. mol^{-1} sec^{-1} [b]	21.2 ± 0.3	-1.68 ± 2.4
BrO$_3^-$ (m)	1.0	1.7×10^{-8} sec^{-1} [c]	12.3 ± 3.1	-52.9 ± 9.8
BrO$_2^+$ (n) (or H$_2$BrO$_3^+$)	1.0	1.1×10^{-8} l.^{2} mol^{-2} sec^{-1} [c]	32.6 ± 1.1	14.3 ± 3.3

[a] $-d[Fe(phen)_3^{3+}]/dt = 2k_1(Hg^I)_2][Fe(phen)_3^{3+}]$. [b] $-d[Ru(bipy)_3^{3+}]/dt = 2k_2[(Hg^I)_2][Ru(bipy)_3^{3+}]$. [c] Obtained by extrapolation of data at temperatures 35–50°; $-d[(Hg^I)_2/dt = 3k_3K[(Hg^I)_2][BrO_3^-][Hg^{II}]^{-1} = 3m[(Hg^I)_2][BrO_3^-][Hg^{II}]^{-1} + 3n[(Hg^I)_2][BrO_3^-][H^+]^2[Hg^{II}]^{-1}$.

(obtained from possible intercept of k'' axis, Figure 3) is 1.5×10^{-4} l. mol^{-1} sec^{-1} at 45°. The hydrogen ion dependence of k_3K has been investigated, Table III, and is of the form (13), Figure 4.

$$k_3K = m + n[H^+]^2 \quad (13)$$

From the data values of m and n at four temperatures, Table V, and activation parameters, Table VI, have been evaluated using a nonlinear least-squares program (equal weighting).[24] Values of m and n at 25° were obtained from data at other temperatures by extrapolation.

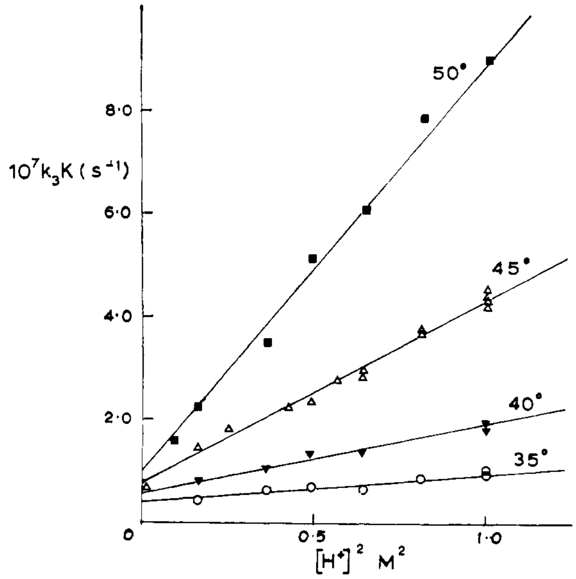

Figure 4. The dependence of the composite rate constant term k_3K on hydrogen ion concentration for the reaction of mercury(I) dimer with bromate.

Other Reactions. Attempts were made to study three other reactions. Hexachloroiridate(III) (1.7×10^{-7}–1.7×10^{-6} M) is known to catalyze the reaction of cerium(IV) with mercury(I) dimer,[11] and eq 14 is

$$(Hg^I)_2 + IrCl_6^{2-} \longrightarrow Hg^I + Hg^{II} + IrCl_6^{3-} \quad (14)$$

believed to contribute. We attempted therefore to study eq 14 directly. With reactant concentrations $[(Hg^I)_2] = 2 \times 10^{-5}$ M, $[IrCl_6^{2-}] = 10^{-5}$ M, and $[H^+] = 0.5$ M, $\mu = 0.5$ M (LiClO$_4$), a yellow precipitate formed. Spectrophotometric equipment available did not enable us to use more dilute solutions.

No reactions were observed with vanadium(V), VO$_2^+$, over 20 hr at 25°. Absorbance measurements were at the vanadium(IV) peak at 760 nm (ϵ 17.2 l. mol^{-1} cm^{-1}), and reactant concentrations were $[(Hg^I)_2] = 7.2 \times 10^{-2}$ M, $[VO_2^+] = 5 \times 10^{-3}$ M, $[H^+] = 1.8$ M, $\mu = 2.0$ M (LiClO$_4$).

With chromium(VI) a 7% decrease in chromate absorption was observed over 3 hr, but some precipitation was also apparent. Conditions were $[(Hg^I)_2] = 3.3 \times 10^{-2}$ M, $[Cr^{VI}] = 5.6 \times 10^{-5}$ M, $[H^+] = 0.5$ M, $\mu = 0.6$ M, and the temperature 35°. Mercurous chromate is known to have low solubility.

Discussion

The one-equivalent oxidants Fe(phen)$_3^{3+}$, Ru-

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[24] Los Alamos Report LA2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. T. W. Newton for details of this program.

$(bipy)_3^{3+}$, Co^{III},[7] and Np^{VII} [5] react with mercury(I) dimer by a mechanism

$$(Hg^I)_2 + \text{oxidant } (1\ e^-) \longrightarrow Hg^I + Hg^{II} \qquad (15)$$

$$Hg^I + \text{oxidant } (1\ e^-) \xrightarrow{\text{fast}} Hg^{II} \qquad (16)$$

It is possible that the product in eq 15 is $[Hg]_2^{3+}$ where this dissociates to give Hg^I and Hg^{II} or is itself further oxidized in eq 16. The Ce^{IV} oxidation of the mercury(I) dimer has been studied with Ag^I [10] and $IrCl_6^{3-}$ [11] as catalyst, and from these studies it would appear that Ag^{II} and $IrCl_6^{2-}$ also react with mercury(I) dimer by the above mechanism. Two-electron oxidants, on the other hand, of which BrO_3^- and Tl^{III} are examples,[6] react with mercury(I) dimer by a mechanism

$$(Hg^I)_2 \overset{\text{fast}}{\rightleftharpoons} Hg^0 + Hg^{II} \qquad (17)$$

$$Hg^0 + \text{oxidant } (2\ e^-) \longrightarrow Hg^{II} \qquad (18)$$

The one-equivalent oxidant manganese(III)[8] is also reported to react with Hg^0, but this study does not conform to either of the above reaction sequences.

Standard reduction potentials for the couples $Fe(phen)_3^{3+,2+}$ and $Ru(bipy)_3^{3+,2+}$ are 1.06 and 1.27 V, respectively.[25] An earlier correlation[26] of data for the oxidation with Ag^{II} (1.98 V), Co^{III} (1.84 V) (as above, eq 14 and 15), Mn^{III} (1.51 V). and Tl^{III} (1.25 V) (reactions involving Hg^0) in terms of redox potentials[27] is therefore ruled out. With the exception of the Mn^{III} reaction a classification in terms of one- and two-equivalent oxidants now seems probable. The distinguishing feature of this classification is the rate law. Thus both types of reaction are first order in oxidant and in reductant, but with the two-equivalent oxidants an inverse mercury(II) dependence is observed.

The standard reduction potential for the half-reaction

$$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+} \qquad (19)$$

is 0.92 V.[27] However, no oxidation was observed with vanadium(V), standard reduction potential

$$VO_2^+ + e^- + 2H^+ \longrightarrow VO^{2+} + H_2O\ (1.00\ V) \qquad (20)$$

The reaction of cerium(IV), a much stronger oxidant (*ca.* 1.44 V in 1 *M* H_2SO_4), is also extremely slow in the absence of a catalyst. Furthermore, no reaction is observed with neptunium(VI) (*ca.* 1.14 V),[5] and the reaction with manganese(III) (1.51 V) is slow.[8] The requirement that the reactions with one-equivalent reagents proceed *via* Hg^+ or Hg_2^{3+} clearly introduces a step which is less favorable than the overall process. Although in the present context $Fe(phen)_3^{3+}$ and $Ru(bipy)_3^{3+}$ are not particularly strong oxidants, it is noteworthy that reactions with these oxidants occur much more rapidly than with either cerium(IV) or manganese(III). Enthalpy requirements are high, however, for the reaction of $Ru(bipy)_3^{3+}$, Table VI. The inaccessibility of the electron pair of the mercury(I) dimer may make reactions more critically dependent on the nature of the orbitals which are involved on the oxidant. Evidence indicating extensive complexing of perchlorate to the mercury(I) dimer[28] is of course highly relevant to any detailed consideration of kinetic parameters. The effect of varying the perchlorate ion concentration has not been investigated.

Equation 21 followed by 16 may be considered as an

$$(Hg^I)_2 \rightleftharpoons 2Hg^I \qquad (21)$$

alternative to eq 15 and 16. Moser and Voigt[29] have indicated an upper limit of 10^{-7} mol l.$^{-1}$ for the equilibrium quotient in eq 21. Assuming the equilibration in eq 21 to be rapid then this mechanism will exhibit a dependence on $[(Hg^I)_2]^{1/2}$ instead of $[(Hg^I)_2]$. No evidence for contributions from such a path has been obtained in the present work. Recent studies by Thompson[23] have provided examples of bromate reactions which exhibit a $[BrO_3^-]^2$ dependence. No evidence for contributions from such a term was obtained on varying the concentration of bromate tenfold (bromate in excess). Our results lend support to the suggestion[23,30] that weak one-equivalent reductants such as cerium(III), manganese(II), and neptunium(V) react in a complex manner with bromate, whereas multiequivalent reductants such as Br^-, H_2O_2, HN_3, and now $(Hg^I)_2$ (*via* Hg^0) react according to a simple rate law with a first-order dependence on bromate. The stoichiometry and product analysis are consistent with reduction of bromate to bromide.

Finally, the hydrogen ion dependence (eq 13) for the reaction with bromate warrants comment. The same dependence has been observed for the bromate oxidation of uranium(IV),[31] and $[H^+]^2$ terms are not uncommon in other bromate reactions (see for example Table 6 of ref 32). The occurrence of an $[H^+]^2$ (but not $[H^+]$) term suggests that BrO_2^+ or $H_2BrO_3^+$ (formation constant K_B) is involved (eq 22). The species BrO_2^+

$$2H^+ + BrO_3^- \rightleftharpoons BrO_2^+ + H_2O\ (\text{or } H_2BrO_3) \qquad (22)$$

has been postulated previously.[33] The oxygen-exchange reaction between BrO_3^- and water solvent has a rate law of the form $k[BrO_3^-][H^+]^2$ with H^+ in the range 0.1–1.0 *M* and is sufficiently rapid ($k = 6.6 \times 10^{-3}$ l.^{2} mol^{-2} sec^{-2} at 30°, $\mu = 0.9$ *M*)[34] to make formation of BrO_2^+ a reasonable possibility. However, it has been suggested that the exchange of oxygen between BrO_3^- and solvent occurs by an associative process,[35] and more recently Barton and Wright[32] have experienced difficulty in explaining results in terms of

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(26) A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press, 2nd printing, 1970, p 172.

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(28) S. Hietanen and L. G. Sillen, *Ark. Kemi*, **10**, 124 (1956), have estimated the extent of complexing of Hg_2^{2+} with ClO_4^- to be ~0.9 l. mol^{-1} at 25°.

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BrO_2^+ participation. Whichever species is relevant the rate constants m and n in eq 13 are composite and may be expressed as k_mK and k_nKK_B (eq 23) where k_m and k_n are rate constants for the reactions of Hg^0

$$kK_3 = k_mK + k_nKK_B[H^+]^2 \qquad (23)$$

with BrO_3^- and BrO_2^+ (or H_2BrO_3), respectively. Using a value for K of 5.5×10^{-9} mol l.$^{-1}$ at 25°[36] $k_m = 3.7$ l. mol^{-1} sec^{-1} at 25°.

Acknowledgments. We are grateful to SRC for a postdoctoral fellowship to R. D., and to the University of Calgary for leave of absence to B. K.

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Ion Association and Charge-Transfer Excitation between Pyridinium Cations and Dianionic Dithiolene Complexes

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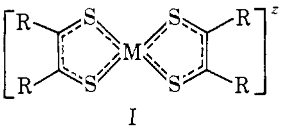
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 24, 1973*

Abstract: A series of salts of anionic dithiolene complexes, $[M(mnt)_2]^{2-}$ (M = Zn, Cu, Ni, Co), $[M(mnt)_2]_n^{n-}$ (M = Cu(n = 1), Co(n = 2), Fe(n = 2)), $[Ni(tfd)_2]^{2-}$, and $[NiS_4C_4Ph_4]^-$ (mnt ≡ maleonitriledithiolate, tfd ≡ 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate) with 1,4-substituted pyridinium cations including the 1-ethyl-4-carbomethoxypyridinium ion, KOS^+, have been prepared and characterized. The existence of a centrosymmetrical sandwich type ion associate of two planar cations enclosing a planar dianion with van der Waals separations has been demonstrated for $(KOS)_2M(mnt)_2$, M = Co, Ni, or Cu, in the crystalline state. Ion association prevails in solution, and in pyridine $K_1 = [(KOS)Ni(mnt)_2^-]/[KOS^+][Ni(mnt)_2^{2-}] = (7 \pm 4) \times 10^4\ M^{-1}$, $\beta_2 = [(KOS)_2Ni(mnt)_2]/[KOS^+]^2[Ni(mnt)_2^{2-}] = (1.1 \pm 0.7) \times 10^9\ M^{-2}$. The ion associates possess charge-transfer (anion to cation) transitions which appear in solid and solution spectra in the range 12–18 kK, with ϵ(solution) $<10^3\ M^{-1}$ cm^{-1}. No anomalous magnetic properties occur, and it is concluded that there is negligible mutual electronic perturbation of anion and cation in the ground state. Nevertheless, the ion association is sufficient to modify the reactivity of some reduced dithiolene complexes.

Recent work on the reactivity patterns of transition metal dithiolene complexes[1] has emphasized the coordinative,[2–6] homogeneous electron-transfer,[4,7] and substitution[3,4,8,9] processes which occur for relatively oxidized, electron-poor, bisdithiolene complexes, I, $z = 0, -1$. Upon reduction to I, $z = -2$,



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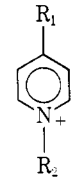

II

the coordinative[6] and substitution[9,10] processes at the metal are markedly inhibited, while there is increased nucleophilicity at the sulfur donor atoms.[11] We are interested in the reactions of reduced, electron-rich, dithiolene complexes with reagents which may function as Lewis acids, cations, or oxidants and report here the results of structural and spectroscopic investigations of the compounds formed by dianionic dithiolene complexes and planar pyridinium cations, II. Under appropriate conditions ion association would be expected;[12] the association between $Ni(mnt)_2^{2-}$[13] and sterically encumbered, electronically insulated cations in acetonitrile has been measured.[14] It is also not unreasonable to anticipate modification of the reactivities of reduced complexes consequent upon such ion association, either *via* the reaction field[15] of the associated cations or *via* a charge-transferred excited state.[16]

Previous studies of anionic dithiolene complexes with nonspherical cations have encompassed a tropylium salt, $(C_7H_7)[Ni(tfd)_2]$,[17] a salt of the N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) cation radical $(TMPD)_2[Ni(mnt)_2]$,[18] phenothiazine and phenoxazine

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[13] Abbreviations: 1,2-dithiolene ligands, as in I: mnt when R = CN; tfd when R = CF_3; $S_2C_2Ph_2$ when R = Ph. Pyridinium cations, as in II: KOS^+ when $R_1 = CH_3COO$, R_2 = Et; 4-CNpyMe$^+$, 4-CNpyEt$^+$, and 4-CNpyBu$^+$ when R_1 = CN, R_2 = Me, Et, and n-Bu, respectively; pyMe$^+$ when R_1 = H, R_2 = Me.

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