

plexes to change by a factor of about 10 for a unit change in charge. Acid-independent aquation *via* an intramolecular proton-transfer mechanism, therefore, may be expected to occur less readily with the singly charged dicyanotetraaquo chromium(III) cation than with the doubly charged monocyano cation, with its

much more strongly acidic coordinated water molecules. This expectation is in agreement with experiment and is in contrast to the relative rates observed for singly and doubly substituted aquo complexes containing less basic ligands which do not aquate *via* a mechanism involving proton transfer.

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## Electrochemical Investigation of Molybdenum(III)-Chloro Complexes with Pyridine, 2,2'-Bipyridine, and 1,10-Phenanthroline in Acetonitrile

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A series of molybdenum(III)-chloro complexes with pyridine, 2,2'-bipyridine, and 1,10-phenanthroline were prepared and their electrochemistry in acetonitrile was studied. The compounds investigated included  $\text{MoCl}_3(\text{py})_3$ ,  $\text{MoCl}_3(\text{py})\text{bipy}$ ,  $\text{MoCl}_3(\text{py})\text{phen}$ ,  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4(\text{py})_2]$ ,  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{bipy}]$ ,  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{phen}]$ ,  $[\text{MoCl}_2(\text{bipy})_2][\text{MoCl}_4\text{bipy}]$ ,  $[\text{MoCl}_2(\text{phen})_2][\text{MoCl}_4\text{phen}]$ , and  $[\text{MoCl}_2(\text{phen})_2]\text{Cl}$ . Current-voltage curves of acetonitrile solutions of all of the compounds exhibited at least one reversible one-electron reduction step. In addition, a second reversible one-electron reduction step was observed for the compounds containing the  $\text{MoCl}_2(\text{phen})_2^+$  and  $\text{MoCl}_2(\text{bipy})_2^+$  cations. These steps are attributed to the reduction of the metal. At potentials more negative than those required for metal reduction, cathodic waves were found which, on the basis of the electrochemical evidence, have been ascribed to reduction of the ligands. Compounds containing  $\text{MoCl}_4$ -amine anions gave reversible one-electron oxidation steps involving the conversion of the metal in the anion to the tetrapositive state. Anodic steps, at more positive potentials than for the  $\text{MoCl}_4$ -amine anions, occur for the other molybdenum complex species. Of the complexes studied,  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4(\text{py})_2]$ ,  $[\text{MoCl}_2(\text{phen})_2][\text{MoCl}_4\text{phen}]$ , and  $[\text{MoCl}_2(\text{phen})_2]\text{Cl}$  were prepared for the first time.

### Introduction

It is generally recognized that low oxidation states of transition metals may be stabilized by coordination with ligands which permit back-donation of d electrons from the metal to the  $\pi$  system of the ligands.<sup>1,2</sup> However, few quantitative data, in terms of redox potentials, which reflect the effect of systematic changes in the aromatic  $\pi$  system of the coordination sphere are available. The present communication describes a study in acetonitrile as the solvent of a series of tetrachloro-, trichloro-, and dichloromolybdenum(III) complexes containing as ligands with  $\pi$  character pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and mixtures thereof. In connection with the investigation, several of the complexes were prepared for the first time.

### Experimental Section

**Materials.**—Acetonitrile (Baker Analyzed reagent) was purified by distillation first from sodium hydride and then from phosphorus(V) oxide. Pyridine (Baker Analyzed reagent) and 2,2'-bipyridine and 1,10-phenanthroline, both obtained from Aldrich Chemical Co., were used without further purification. Tetraethylammonium perchlorate was precipitated by mixing

aqueous solutions of tetraethylammonium bromide and sodium perchlorate. The precipitate was recrystallized six times from water and then vacuum dried under an infrared lamp. Tetraethylammonium perchlorate, from Eastman Chemical Co., was also found to be suitable for electrochemical work after one or two recrystallizations from water and appropriate drying.

**Preparation of Compounds. Pyridinium Perchlorate.**—A solution of pyridine in absolute ethanol was made just acidic by the addition of 60% perchloric acid. The white precipitate was filtered, washed with ethanol, recrystallized from hot ethanol, and dried in air. *Anal.* Calcd for  $\text{C}_5\text{H}_5\text{N} \cdot \text{HClO}_4$ : equiv wt, 180. Found: equiv wt, 186.

**Phenanthroline Perchlorate.**—This compound was prepared by a procedure similar to that given above. *Anal.* Calcd for  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{HClO}_4$ : equiv wt, 281. Found: equiv wt, 292.

**Ammonium Hexachloromolybdate(III) Monohydrate, Ammonium Pentachloroquomolybdate(III), and Potassium Hexachloromolybdate(III).**—These substances were made according to published procedures.<sup>3,4</sup> *Anal.* Calcd for  $(\text{NH}_4)_3\text{MoCl}_6 \cdot \text{H}_2\text{O}$ : Cl, 56.0. Found: Cl, 56.3. Calcd for  $(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ : Cl, 54.2. Found: Cl, 54.3. Calcd for  $\text{K}_2\text{MoCl}_6$ : Cl, 49.9. Found: Cl, 47.4.

**Tetraethylammonium Tetrachlorodiaquomolybdate(III).**—A modification of the procedure for the synthesis of the hexachloromolybdate complexes listed above was used to prepare this compound. This consisted of substituting tetraethylammonium chloride for ammonium or potassium chloride. The infrared spectrum confirmed the presence of water and the tetraethyl-

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ammonium cation in the compound. *Anal.* Calcd for  $(C_2H_5)_4N[MoCl_4(H_2O)_2]$ : Cl, 35.2. Found: Cl, 35.5.

**Trichlorotris(pyridine)molybdenum(III).**—The complex was prepared according to the method of Jonassen and Bailin.<sup>5</sup> *Anal.* Calcd for  $MoCl_3(py)_3$ : Mo, 21.8; Cl, 24.2. Found: Mo, 21.7; Cl, 24.2.

**Trichloropyridinebipyridinemolybdenum(III) and Trichloropyridinephenanthrolinemolybdenum(III).**—These were made by a modification of the general procedure of Marzilli and Buckingham<sup>6</sup> to avoid substantial formation of  $[MoCl_2(bipy)_2]$ ,  $[MoCl_4bipy]$ ,  $[MoCl_2(phen)_2][MoCl_4phen]$ , and  $[MoCl_2(phen)_2]Cl$ . This was accomplished by decreasing the ratio of ligand to  $MoCl_3(py)_3$  starting compound and the reaction time.<sup>7</sup> *Anal.* Calcd for  $MoCl_3(py)bipy$ : Mo, 21.9; Cl, 24.3. Found: Mo, 21.5; Cl, 23.9. Calcd for  $MoCl_3(py)phen$ : Mo, 20.8; Cl, 23.0. Found: Mo, 20.6; Cl, 22.9.

**Tetraethylammonium Tetrachlorobis(pyridine)molybdate(III).**—Tetraethylammonium tetrachlorodiaquomolybdate(III) (1.00 g) was added to a solution of 1.0 g of pyridine in 50 ml of acetonitrile and the mixture was refluxed under purified nitrogen for 15 hr. The golden yellow crystals obtained from the cooled reaction mixture were recovered by filtration, washed with benzene, and vacuum dried at room temperature. The yield was 0.99 g. *Anal.* Calcd for  $(C_2H_5)_4N[MoCl_4(py)_2]$ : Mo, 18.2; Cl, 26.9. Found: Mo, 17.9; Cl, 26.9.

**Tetraethylammonium Tetrachlorobipyridinemolybdate(III) and Tetraethylammonium Tetrachlorophenanthrolinemolybdate(III).**—These compounds were prepared in a manner similar to that for the corresponding tetrachlorobis(pyridine)molybdate(III). For the bipyridine complex 1.30 g of the starting molybdate and 1.6 g of ligand were employed and the solution was refluxed for 12 hr. There was isolated 1.18 g of a purple solid which was dried under a stream of nitrogen. *Anal.* Calcd for  $(C_2H_5)_4N[MoCl_4bipy]$ : Mo, 18.3; Cl, 27.0. Found: Mo, 18.2; Cl, 27.0. In the case of the phenanthroline complex, 2.10 g of starting molybdate and 2.10 g of amine were used. After 8 hr of refluxing under nitrogen in acetonitrile, 2.32 g of a mixture of the desired compound and  $[MoCl_2(phen)_2][MoCl_4phen]$  were isolated by filtration from the cooled mixture. The tetraethylammonium compound, which made about three-fifths by weight of the mixture, was extracted with acetonitrile under nitrogen. Cooling of the extract and the addition of benzene yielded the desired product, which was washed with benzene and dried under nitrogen. *Anal.* Calcd for  $(C_2H_5)_4N[MoCl_4phen]$ : Mo, 17.5; Cl, 25.9. Found: Mo, 17.5; Cl, 25.2.

**Dichlorobis(phenanthroline)molybdenum(III) Tetrachlorophenanthrolinemolybdate(III).**—The residue left after extraction of  $(C_2H_5)_4N[MoCl_4phen]$  (see above) was dried under a stream of nitrogen. *Anal.* Calcd for  $[MoCl_2(phen)_2][MoCl_4phen]$ : Mo, 20.3; Cl, 22.5. Found: Mo, 18.2; Cl, 21.0. The compound exhibited a molar conductivity of  $60.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in nitromethane, a value of the order of magnitude expected for a 1:1 electrolyte.

**Dichlorobis(bipyridine)molybdenum(III) Tetrachlorobipyridinemolybdate(III).**—Tetraethylammonium tetrachlorobipyridinemolybdate(III) (1.39 g) and 2,2'-bipyridine (4.03 g) were placed in 50 ml of acetonitrile and the mixture was refluxed under nitrogen for 12 days. There was isolated, by filtration, 0.81 g of a red-purple solid which was washed with acetonitrile and dried under nitrogen. The compound was also prepared by a modification of the method used for the synthesis of  $(C_2H_5)_4N[MoCl_4bipy]$ . Tetraethylammonium tetrachlorodiaquomolybdate(III) (1.30 g) and 2,2'-bipyridine (5.00 g) were dissolved in acetonitrile and the solution was refluxed for 11 days. The yield of red-purple solid was 0.71 g. *Anal.* Calcd for  $[MoCl_2(bipy)_2][MoCl_4bipy]$ : Mo, 22.0; Cl, 24.4. Found: Mo, 20.8;

Cl, 22.9. The molar conductivity in nitromethane was  $63.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

**Dichlorobis(phenanthroline)molybdenum(III) Chloride.**—Trichlorotris(pyridine)molybdenum(III) (1.00 g) was added to 100 ml of xylene containing 1,10-phenanthroline (5.00 g) and the resulting mixture was refluxed under nitrogen for 6 hr. The mixture was cooled, and the orange solid was removed by filtration, washed with oxygen-free xylene, and dried under nitrogen; yield, 1.10 g. *Anal.* Calcd for  $[MoCl_2(phen)_2]Cl$ : Mo, 17.0; Cl, 18.9. Found: Mo, 16.0; Cl, 18.6. The molar conductivity in nitromethane was  $66.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

All of the compounds investigated appeared to be unaffected by the residual water in the acetonitrile during the electrochemical studies, and all except trichlorotris(pyridine)molybdenum(III) were sensitive to air oxidation.

**Analytical Methods.**—Molybdenum was determined gravimetrically as the 8-quinolinolate. The molybdenum-containing complex was digested in a mixture of equal volumes of concentrated nitric, sulfuric, and perchloric acids until evolution of nitrogen dioxide ceased. The solution was then diluted to 50 ml and the pH adjusted to 5–7 prior to the addition of 8-quinolinol in acetone.

Chloride was determined potentiometrically. The sample was first treated with 50 ml of 1.5 M nitric acid and digested on a hot plate.

**Conductance Measurements.**—An Industrial Instruments, Inc., conductivity bridge, Model RC-16B2, was used to measure the conductance of a number of the complexes in nitromethane solution. The conductivity cell had a cell constant of  $0.1 \text{ cm}^{-1}$ .

**Electrochemical Measurements. Polarography.**—Polarograms were obtained with a Kelly-Fisher-Jones controlled-potential polarograph.<sup>8</sup> A three-compartment cell, with the compartments separated by fritted-glass disks of medium porosity, was used. The working electrode was placed in the center compartment and the reference [saturated calomel electrode (sce)] and auxiliary (platinum) electrodes were placed in the other compartments. The dropping mercury electrode (dme) had a drop time of 4.6 sec and flow rate of 1.44 mg/sec in a 0.10 M solution of tetraethylammonium perchlorate in acetonitrile on open circuit and a mercury height of 60 cm. In some instances, a rotating platinum electrode (rpe) was used in place of a dme. The former was a platinum wire sealed into glass so that 1 mm of the wire extended from the tip of the glass; a Sargent synchronous rotator was used. Solutions investigated were degassed by means of purified nitrogen presaturated with acetonitrile. The solutions were  $10^{-3}$ – $10^{-4}$  M in concentration of complex.

**Cyclic Voltammetry.**—The cyclic voltammetric circuit has been described previously.<sup>9</sup> A Moseley 7030A X-Y recorder was employed. The solutions examined had the same concentrations of complexes and the electrochemical cell was the same as in the polarographic work. A hanging mercury drop and the platinum electrode described above served as working electrodes.

**Coulometry.**—A Wenking potentiostat, Model 61-RS, was used for the controlled-potential coulometric studies. The current was integrated directly from the external recorder output of the potentiostat with the aid of a 10-ohm standard resistor (General Radio Co. Type 1440), a Hewlett-Packard 2120 voltage to frequency converter, and a Hewlett-Packard 3734A electronic counter. Three-compartment cells similar to that described for the voltammetric studies were used. The working electrode, in the center compartment, was either a mercury pool or a platinum gauze. A magnetic stirring bar placed on the mercury pool served to agitate the solution of complex. The platinum gauze electrode was rotated at 600 rpm. All electrolyses were carried out under a nitrogen atmosphere and the concentration of starting complex was between  $10^{-3}$  and  $10^{-4}$  M.

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TABLE I

SUMMARY OF THE REDOX DATA FOR THE PROCESSES INVOLVING THE METAL IN SOME MOLYBDENUM(III)-CHLORO COMPLEXES WITH PYRIDINE, 2,2'-BIPYRIDINE, AND 1,10-PHENANTHROLINE IN ACETONITRILE (HALF-WAVE POTENTIALS *vs.* SCE)

Compound	Anodic steps at rpe			Cathodic steps at dme		
MoCl <sub>3</sub> (py) <sub>3</sub>	+0.94 (1-2) <sup>a,b</sup>			-1.47 (1) <sup>d</sup>		
MoCl <sub>3</sub> (py)bipy	+0.83 (2) <sup>a</sup>			-1.00 (1)		
MoCl <sub>3</sub> (py)phen	+0.82 (2) <sup>a</sup>			-1.01 (1)		
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> (py) <sub>2</sub> ]	+0.50 (1)			-1.85 (1)		
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> bipy]	+0.48 (1)			-1.20 (1)		
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> phen]	+0.48 (1)			-1.20 (1)		
[MoCl <sub>2</sub> (phen) <sub>2</sub> ]Cl	+0.92 (2) <sup>a</sup>		-0.2 <sup>a,c</sup>	-0.64 (1)	-1.08 (1)	
[MoCl <sub>2</sub> (phen) <sub>2</sub> ][MoCl <sub>4</sub> phen]	+0.92 (1) <sup>a</sup>	+0.48 (1)		-0.64 (1)	-1.08 (1) -1.20 (1)	
[MoCl <sub>2</sub> (bipy) <sub>2</sub> ][MoCl <sub>4</sub> bipy]	+0.92 (1-2) <sup>a</sup>	+0.48 (1)		-0.63 (1)	-1.08 (1) -1.20 (1)	

<sup>a</sup> Signifies an irreversible process. <sup>b</sup> The numbers in parentheses denote the moles of electrons required for 1 mol of electroactive species. <sup>c</sup> This measurement was made with the dme. <sup>d</sup> The one-electron character and reversibility of this step was confirmed by controlled-potential coulometry and polarographic examination of the reduced solution.

TABLE II

SUMMARY OF THE REDUCTION STEPS FOR LIGAND AND FOR COORDINATED LIGAND IN SOME MOLYBDENUM(III)-CHLORO COMPLEXES WITH PYRIDINE, 2,2'-BIPYRIDINE, AND 1,10-PHENANTHROLINE IN ACETONITRILE<sup>a,b</sup>

Compound	Half-wave potentials <i>vs.</i> sce at the dme			Total no. of electrons	
				Exptl	Expected
Pyridine			-2.65 (2)	2	2 <sup>d</sup>
1,10-Phenanthroline	-2.11 (2) <sup>c</sup>	-2.28 (2)	-2.54 (2)	6 <sup>e</sup>	...
2,2'-Bipyridine	-2.20 (2)	-2.50 (2)	-2.66 (2)	6 <sup>f</sup>	...
MoCl <sub>3</sub> (py) <sub>3</sub>	-2.05 (1)	-2.34 (2)	-2.69 (3)	6	6
MoCl <sub>3</sub> (py)bipy	-1.96 (2)	-2.5 (ca. 5)	-2.7 (ca. 2)	Ca. 9	8
MoCl <sub>3</sub> (py)phen	-1.92 (2)	-2.3 (7)		9	8
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> (py) <sub>2</sub> ]		-2.37 (2-1)	-2.66 (0-1)	Ca. 2	4
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> bipy]	-2.20 (2)	-2.5 (4)		6	6
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N[MoCl <sub>4</sub> phen]	-2.08 (2)	-2.4 (4)		6	6
[MoCl <sub>2</sub> (phen) <sub>2</sub> ]Cl	-1.90 (2)	-2.3 (8)		10	12

<sup>a</sup> The number of electrons involved in each reduction step for coordinated ligands was estimated by comparison of the diffusion current with that for the first one-electron step involving the metal. <sup>b</sup> All reduction steps were irreversible. <sup>c</sup> The numbers in parentheses denote the number of moles of electrons required for 1 mol of electroactive species. <sup>d</sup> See P. H. Given, *J. Chem. Soc.*, 2684 (1958), and C. Parkyani and R. Zahradnik, *Bull. Soc. Chim. Belges*, **73**, 57 (1964). Also determined by us from comparison of the diffusion current of pyridine with that of pyridinium ion in pyridinium perchlorate. <sup>e</sup> Estimated by comparison of the diffusion current with that of the phenanthroline ion. <sup>f</sup> Estimated by comparison of the diffusion current with that of 1,10-phenanthroline.

## Results

The current-voltage curves of all of the complexes showed both oxidation and reduction waves. The potentials and the numbers of electrons in the oxidation and reduction steps involving the metal in the complexes are summarized in Table I. Reduction data for steps involving the ligands in the complexes are given in Table II. No oxidation waves for free ligand were observed before about +1.8 V, a value much more positive than those shown for the anodic steps in Table I. Assignment of reduction steps to processes involving coordinated ligands was made on the basis of similarities in potentials and also in the number of electrons transferred for the complexes and the free ligands.

Although specific redox steps have been attributed to either metal or ligands in the complexes, in each case electrons may be regarded as being added to or removed from molecular orbitals of the whole complex. When a

process is described, for example, as involving the metal, we believe that electrons are being added to or removed from a molecular orbital which has primarily metal character.

**The Trichloromolybdenum(III)-Amine Complexes.**—All three complexes—MoCl<sub>3</sub>(py)<sub>3</sub>, MoCl<sub>3</sub>(py)bipy, and MoCl<sub>3</sub>(py)phen—gave reversible one-electron cathodic steps at the dme and two-electron irreversible anodic steps at the rpe (Table I), in addition to irreversible reduction steps (Table II) at the dme. Cyclic voltammetry at low scan rates (*ca.* 1–5 V min<sup>-1</sup>) at the hanging mercury drop electrode confirmed the reversible nature of the one-electron reduction steps and similar studies at a stationary platinum electrode confirmed the irreversible character of the two-electron oxidation steps. (The criteria used to evaluate the reversibility of the reductions and oxidations with cyclic voltammetry were the anodic-cathodic peak potential separations and peak currents. For a reversible process the separa-

tion of the peak potentials is  $57/n$  mV and the peak currents for the anodic and cathodic scans are equal.<sup>10</sup>) In the cyclic voltammetric experiments at the stationary platinum electrode at high scan rates, *ca.* 30 V  $\text{min}^{-1}$ ,  $\text{MoCl}_3(\text{py})_3$  appeared to show an irreversible one-electron oxidation. The anodic peak current at +0.9 V was equal to the cathodic peak current observed at -1.47 V, the potential at which the complex is reduced in a one-electron step at the dme and at the hanging mercury drop electrode. The cathodic peak current at +0.9 V on reverse scan was not, however, of the same height as the anodic peak current and the separation in peak potentials was about 100 mV. For  $\text{MoCl}_3(\text{py})$ -bipy and  $\text{MoCl}_3(\text{py})\text{phen}$ , regardless of scan rate, no cathodic peaks were found on reverse scan at +0.8 V, the potential at which oxidation occurred in each case, nor was there indication of a change to one-electron oxidation.

All polarographic reduction steps attributable to ligands (Table II) were shown either by the drawn-out character of the polarographic waves or by cyclic voltammetry at low scan rates to be irreversible. However, the first ligand-reduction step of  $\text{MoCl}_3(\text{py})_3$  became reversible at high scan rates.

**The Tetrachloromolybdenum(III)-Amine Anionic Complexes.**—The three complexes of this type— $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4(\text{py})_2]$ ,  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{bipy}]$ , and  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{phen}]$ —gave reversible one-electron cathodic steps at the dme and reversible one-electron oxidations at the rpe, involving the metal (Table I). Cyclic voltammetry at low scan rates at the hanging mercury drop electrode and at the stationary platinum electrode confirmed the voltammetric results. All polarographic steps due to ligands (Table II) were shown to be irreversible by cyclic voltammetry or by the drawn-out polarographic waves.

**The Dichloromolybdenum(III)-Amine Cationic Complexes.**— $[\text{MoCl}_2(\text{phen})_2]\text{Cl}$  gave two reversible one-electron cathodic steps attributable to reduction of metal and one irreversible anodic step at the dme. At the rpe, a single irreversible two-electron oxidation was observed (Table I). The anodic step at the rpe at +0.92 V apparently involves both a one-electron oxidation of molybdenum(III) and a simultaneous one-electron oxidation of chloride ion. The oxidation of the latter ion was indicated by the one-electron oxidation step at +0.92 V in the current-voltage curve of a solution of  $[\text{MoCl}_2(\text{phen})_2][\text{MoCl}_4\text{phen}]$ , a compound which contains no unbound chloride ion. The oxidation step at -0.2 V at the dme was shown to be due to the dissolution of mercury in the presence of free chloride ion. The cathodic steps at -1.90 and -2.3 V at the dme (Table II) resulting from ligand reduction were shown to be irreversible by cyclic voltammetry.

As the data of Table I show, the potential values and numbers of electrons transferred for processes due

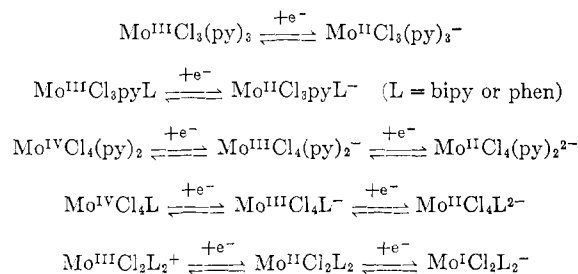
to the metal in the case of  $[\text{MoCl}_2(\text{phen})_2][\text{MoCl}_4\text{phen}]$  are a composite of those for  $[\text{MoCl}_2(\text{phen})_2]\text{Cl}$  and  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{phen}]$ . A similar situation is indicated for the redox characteristics of  $[\text{MoCl}_2(\text{bipy})_2][\text{MoCl}_4\text{bipy}]$ .

It is interesting to note that 2,2'-bipyridine and 1,10-phenanthroline exert identical effects on the electrochemical characteristics of the metal in the complexes studied.

Although the data are not given in Table II, it was found, as expected, that the ligand-reduction steps for  $[\text{MoCl}_2(\text{phen})_2][\text{MoCl}_4\text{phen}]$  are a composite of those for  $[\text{MoCl}_2(\text{phen})_2]\text{Cl}$  and  $(\text{C}_2\text{H}_5)_4\text{N}[\text{MoCl}_4\text{phen}]$ . It also appears that a similar situation exists with regard to ligand-reduction steps for  $[\text{MoCl}_2(\text{bipy})_2][\text{MoCl}_4\text{bipy}]$ .

### Discussion

A summary of the reversible redox steps involving the metal in the complexes investigated is shown as



The tendency for reduction of the metal in the complexes investigated is dependent on the nature of the aromatic  $\pi$  system of the coordination sphere, *i.e.*, its ability to accept d electrons from the metal. For the neutral trichloromolybdenum(III) complexes and the tetrachloro anionic complexes, replacement of two pyridine ligands by one bipyridine or phenanthroline causes a marked decrease in the potential at which reduction occurs (Table I). This may be regarded as a reflection of the much greater acceptor character of the aromatic  $\pi$  system of the latter ligands as compared with pyridine. This effect can also be seen by a comparison of the potentials for reduction in the following sequence:  $\text{MoCl}_4(\text{py})_2^-$ , -1.85 V;  $\text{MoCl}_3(\text{py})_3$ , -1.47 V;  $\text{MoCl}_4\text{phen}^-$ , -1.20 V;  $\text{MoCl}_3(\text{py})\text{phen}$ , -1.01 V;  $\text{MoCl}_2(\text{phen})_2^+$ , -0.64 V. It is particularly worth noting that the only complex species which exhibit two reversible reduction steps are the  $\text{MoCl}_2(\text{phen})_2^+$  and  $\text{MoCl}_2(\text{bipy})_2^+$  cations, which would be expected to have the highest degree of acceptor character. The second step is attributable to the reduction of molybdenum from the bipoisitive to the monopoisitive state.

One may ask whether the trends in potentials observed for the redox processes reflect effects of chelation. The potential data for the anodic step for the tetrachloromolybdenum(III)-amine anionic complexes at the rpe (Table I) indicate that this factor apparently has little effect.

(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

Within the tetrachloro series of compounds as well as for the trichloromolybdenum(III)-amine complexes, the potential data for the anodic process also show little dependence on the  $\pi$ -acceptor character of the coordination sphere in contrast to the situation for the cathodic processes. This point emphasizes the important role

that the  $\pi$ -acceptor character of ligand plays in the stabilization of lower oxidation states.

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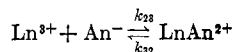
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## A Kinetic Investigation of Lanthanide(III) Complexation. II. Deuterium Isotope Effects and Activation Parameters for the Lanthanide(III)-Anthranilate Reaction

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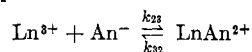
Deuterium isotope effects and activation parameters have been measured for the rate constants  $k_{23}$  and  $k_{32}$  in the reaction



where  $\text{Ln}^{3+}$  and  $\text{An}^-$  represent the 3+ lanthanide and the anthranilate (*o*-aminobenzoate) ions. The kinetics of several other selected lanthanide-ligand systems have been partially examined. Possible interpretations of the results in terms of the solvation of the 3+ lanthanide are discussed. The kinetic experiments were carried out using temperature-jump relaxation techniques.

### Introduction

As part of a continuing study of complexation reactions of the lanthanides,<sup>1</sup> a more extensive kinetic investigation of the reaction between the anthranilate (*o*-aminobenzoate) ion and selected 3+ lanthanides has been carried out. The rate constants  $k_{23}$  and  $k_{32}$  for the reaction



where  $\text{Ln}^{3+}$  is the 3+ lanthanide and  $\text{An}^-$  is the anthranilate ion, have been examined in  $\text{D}_2\text{O}$  and as a function of temperature in  $\text{H}_2\text{O}$ . Possible interpretations of the results in terms of the structure of the solvent about the lanthanide ions are discussed.

### Experimental Section

The general experimental procedures and instrumentation are discussed in a previous paper.<sup>1</sup> All stock lanthanide perchlorate solutions were prepared by adding oxides of greater than 99.9% purity (American Potash and Chemical Corp., Lindsay Chemical Division) to known quantities of dilute perchloric acid. The purity of the oxides was checked by the technique of Stewart and Kato.<sup>2</sup> All of the oxides readily dissolved except that of terbium which required the addition of a small amount of  $\text{H}_2\text{O}_2$ .

The anthranilic acid (Eastman, practical) was recrystallized twice from ethanol containing decolorizing charcoal. After air drying, an uncorrected melting point of 145.0–146.8° was ob-

tained, which was in agreement with the published value of 146.1°.<sup>3</sup> The melting point of methyl red (Matheson Coleman and Bell and Allied Chemical Co.) was 177–179°, uncorrected, which is in agreement with the published value of 178–179°.<sup>4</sup> Reagent grade sodium carbonate, sodium acetate, sodium hydroxide, and perchloric acid were used. All solutions were made up with distilled water which was further purified by passage through an ion-exchange apparatus, Model 306-4, Caw Engineering, Palo Alto, Calif. The density of deuterium oxide (Columbia Organic Chemical Co., Inc., and Bio-Rad Laboratories) was 1.1050 g/ml at 22.1° which agrees well with the value of 1.1049 g/ml reported in the literature.<sup>5</sup>

Stock solutions of lanthanide ions in  $\text{D}_2\text{O}$  were prepared by weighing out the oxide in sufficient 70–72%  $\text{HClO}_4$  to dissolve the solid. After dissolution, sufficient  $\text{D}_2\text{O}$  was added to bring the solutions to the desired concentration. The amounts of 11.8 *M*  $\text{HClO}_4$  added varied from 0.09 to 0.40 ml with a final dilution of the stock solutions to 25.0 ml. This gives a maximum of 0.35 HDO mol % (*e.g.*, erbium solution). Thus, the stock solutions contain a minimum of 99.4%  $\text{D}_2\text{O}$ .

Stock solutions of anthranilic acid and methyl red in  $\text{D}_2\text{O}$  were prepared by adding known amounts of the respective solids to  $\text{D}_2\text{O}$ . The stock anthranilic acid solution was  $2.17 \times 10^{-3}$  *M*, corresponding to the addition of the same concentration of  $\text{H}^+$  to the  $\text{D}_2\text{O}$  (55.17 *M*). The amount of HDO in the solution was 0.004%. The  $\text{NaClO}_4$ - $\text{D}_2\text{O}$  stock solutions were prepared by neutralizing  $\text{Na}_2\text{CO}_3$  with  $\text{HClO}_4$  and gently heating to dryness, care being taken to minimize the decomposition. Since the  $\text{NaClO}_4$  is deliquescent, it was cooled in a closed desiccator, quickly weighed, and dissolved in  $\text{D}_2\text{O}$ .  $\text{NaOD}$ , which was

(3) "Beilstein's Handbuch der Organischen Chemie," 2nd ed, Band XIV, Springer-Verlag, Berlin, 1951, p 205.

(4) S. W. Tobey, *J. Chem. Educ.*, **35**, 514 (1958).

(5) T. L. Chang and L. H. Tung, *Nature*, **163**, 737 (1949).

(1) H. B. Silber and J. H. Swinehart, *J. Phys. Chem.*, **71**, 4344 (1967).

(2) D. C. Stewart and D. Kato, *Anal. Chem.*, **30**, 164 (1958).