dithiophosphinate or dithiophosphate from its coordination to the vanadium atom, the ^{31}P nucleus of this chelate no longer experiences significant hyperfine interactions because the spatial arrangement leads to a substantial decrease in the interaction between the vanadium $d_{x^2-y^2}$ orbital and the P-S σ orbitals. The hyperfine splitting of the ^{31}P nucleus of the dithiophosphinate chelate which has not been displaced is altered because the bonding in the

$$
\begin{array}{c}
\text{S} \\
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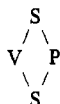
grouping will be modified by the asymmetry of the coordination at the other equatorial sites. In the species D which result from the phenyl and ethoxy complexes in solutions con-

taining low concentrations of pyridine, C_{3s}^{P} has the value 0.084 and 0.100, respectively. It would appear that changes in the coordination trans to the dithiophosphinate chelate lead to lengthening of one or both of the P-S bonds and a decrease in the amount of phosphorus s character in the P-S σ bonds. The HMP adducts of the phenyl and ethoxy complexes show smaller ^{31}P hyperfine splittings than the pyridine adducts. This may be attributable to differences in the effects of oxygen and nitrogen ligand coordination on the V-S and, hence, the P-S bonding.

Oxidative Dehydrogenation of Ethylenediamine Complexes of Ruthenium(II)

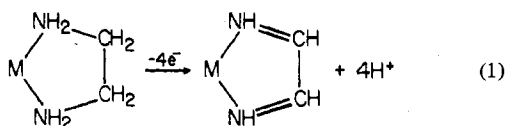DENNIS F. MAHONEY and JAMES K. BEATTIE*[1]

Ethylenediamine coordinated to ruthenium(II) is readily oxidized to the coordinated diimine ligand (diim = NH=CHCH=NH). The new complexes [Ru(phen)$_2$diim]I$_2$ and [Ru(en)$_2$phen]I$_2$ have been characterized by elemental analyses, visible absorption spectra, and analysis of their 220-MHz pmr spectra. Improved procedures are reported for the preparation of [Ru(phen)$_2$en]I$_2$ and [Ru(en)$_2$diim]I$_2$. The electrochemical properties of these complexes have been investigated by redox titration and cyclic voltammetry. A correlation between the oxidative dehydrogenation reaction and the formal reduction potential of the ruthenium(III)–ruthenium(II) couple is observed.

Introduction

The oxidative dehydrogenation of coordinated macrocyclic ligands has been examined;[2-4] recently examples have been reported of the analogous reactions of coordinated diamines and monoamines. The four-electron oxidation of ethylenediamine to α-diimine (diim) has been observed for

$$
\underset{\text{NH}_2}{\overset{\text{NH}_2}{\text{M}}}\!\!\begin{array}{c}\text{CH}_2\\ \\ \text{CH}_2\end{array} \xrightarrow{-4e^-} \underset{\text{NH}}{\overset{\text{NH}}{\text{M}}}\!\!\begin{array}{c}\text{CH}\\ \\ \text{CH}\end{array} + 4\text{H}^+ \qquad (1)
$$

both tris(ethylenediamine)ruthenium(II)[5] and tetracyanoethylenediamineferrate(II)[6] ions; similarly, oxidation of hexakis(methylamine)ruthenium(II) ion produces coordinated cyanide.[7] In each case the oxidized ligand remains coordinated in the metal complex.

We report here some preparative and electrochemical studies of further examples of oxidative dehydrogenation of ethylenediamine coordinated to ruthenium(II) which per-

mit a correlation between the ease of the reaction and the electrochemical properties of the reactant complex.

Experimental Section

Preparation of Complexes. [Ru(phen)$_2$en]I$_2$. An improved procedure was developed for the synthesis of this complex which results in a better yield in a much shorter period of time than the original method.[8] The procedure of Liu, Liu, and Bailar[9] was used to prepare Ru(phen)$_2$ox. This was converted to Ru(phen)$_2$Cl$_2$ by suspension in concentrated HCl (5 ml of HCl/g of Ru(phen)$_2$ox) for 4-6 hr at room temperature. The crude product was then recrystallized from 1:1 water–ethanol.[10] Conversion to the desired product followed a procedure similar to that of Dwyer.[8] In a typical preparation 0.5 g of Ru(phen)$_2$Cl$_2$ was refluxed in 100 ml of 1:1 water–ethanol. After dissolution the hot solution was filtered and the ethanol was removed by heating the filtrate on a steam bath. A solution of 0.5 ml of 96% ethylenediamine in 10 ml of methanol was added to the resulting solution. This solution was heated for a further 10-20 min during which time the color changed from brown to bright red-orange. After cooling, 0.6 g of NaI in 2 ml of water was added to form a dark red precipitate. This product was collected on a filter, washed with water followed by ethanol, and recrystallized from 1:1 0.01 M trifluoroacetic acid–methanol. The final product was collected by filtration, washed with water, ethanol, and ether, and dried. The complex is not stable indefinitely in air, but decomposes slowly, presumably to the diimine analog. *Anal.* Calcd for RuC$_{26}$H$_{24}$N$_6$I$_2$: C, 40.3; H, 3.12; N, 10.8; Ru, 13.0; I, 32.7. Found: C, 40.3; H, 2.98; N, 11.0; Ru, $\geqslant$12.6; I, 32.4.

[Ru(phen)$_2$diim]I$_2$. A mixture of freshly precipitated AgCl and 1 g of [Ru(phen)$_2$en]I$_2$·2H$_2$O was stirred in 100 ml of H$_2$O for 20 min at room temperature. The resulting mixture was filtered,

(1) Fellow of the Alfred P. Sloan Foundation, 1971-1973. Address correspondence to this author at The University of Sydney.

(2) N. F. Curtis, *Chem. Commun.*, 881 (1966); *J. Chem. Soc. A*, 2834 (1971).

(3) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 108 (1971); V. L. Goedken and D. H. Busch, *ibid.*, **10**, 2679 (1971).

(4) J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *J. Amer. Chem. Soc.*, **94**, 5502 (1972).

(5) B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).

(6) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).

(7) W. R. McWhinnie, J. D. Miller, J. B. Watts, and D. Y. Waddan, *Chem. Commun.*, 629 (1971).

(8) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, **16**, 544 (1963).

(9) C. F. Liu, N. C. Liu, and J. C. Bailar, Jr., *Inorg. Chem.*, **3**, 1197 (1964).

(10) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, **19**, 2229 (1966).

the filtrate was heated to about 50°, and 5-10-ml portions of a sodium hypochlorite solution (10% Clorox) were added periodically. Visible absorption spectra of diluted aliquots of the solution were recorded after each addition. The oxidation was considered complete when the absorption maximum has shifted from 480 to 452 nm. (The absorption band of the product solution is asymmetric with half-widths of 75 nm to shorter wavelengths and 35 nm to longer wavelengths; see Figure 1.) The solution was cooled and filtered to remove a small amount of insoluble material and 1.5 g of NaI was added. This solution was concentrated on a rotary evaporator with formation of a dark brown precipitate which was collected on a filter, washed with water, and dried. *Anal.* Calcd for RuC_{26}-$H_{20}N_6I_2$: C, 40.4; H, 2.62; N, 10.9; Ru, 13.1; I, 32.9. Found: C, 39.3; H, 2.86; N, 9.04; Ru, $\geqslant$12.0; I, 31.4.

[Ru(en)$_2$Cl$_2$]Cl. The double salt [Ru(en)$_2$ox][Ru(en)$_2$(ox)$_2$] was prepared as described previously[11] and then converted to [Ru-(en)$_2$ox]BPh$_4$ by stirring 1 g of the double salt with 5 g of sodium tetraphenylborate in 80 ml of H$_2$O at room temperature for 1 hr. The resulting mixture was filtered and the precipitate was then suspended with stirring in concentrated HCl for 1 hr (1 g of complex/ 10 ml of 12 *M* HCl). The mixture was then filtered, the filtrate evaporated to dryness with a rotary evaporator, and the product recrystallized from 1 *M* HCl. The purity was checked by the absorption spectrum using the published extinction coefficients.[12]

[Ru(en)$_2$phen]I$_2$. A solution of 0.35 g of [Ru(en)$_2$Cl$_2$]Cl in 10 ml of H$_2$O was adjusted to pH 3 with acetic acid. Stirring with several pieces of lightly amalgamated mossy zinc for 20 min produced a green solution to which a solution of 0.17 g (0.95 equiv) of phenanthroline in 5 ml of methanol was added. This solution was heated on a steam bath for about 30 min during which time the color changed from green to dark red. A solution of NaI (4 g/5 ml of H$_2$O) was added to give a dark precipitate which was collected and recrystallized from 1:1 0.01 *M* trifluoroacetic acid–methanol. *Anal.* Calcd for $RuC_{16}H_{24}N_6I_2$: C, 29.3; H, 3.66; N, 12.8; Ru, 15.4; I, 38.8. Found: C, 29.6; H, 3.63; N, 12.7; Ru, 15.4; I, 38.8.

[Ru(en)$_2$diim]I$_2$. Portions of solid I$_2$ were added to a warm solution of 2.9 g of [Ru(en)$_3$]ZnCl$_4$[13] dissolved in 10 ml of 0.01 *M* NaOH. The progress of the oxidation was monitored by the change in the pH; 1 *M* NaOH was added to maintain pH 7-9. The reaction was judged complete when 1 drop of the solution mixed with 1 drop of AgNO$_3$ solution produced yellow AgI instead of black Ag metal. The solution was filtered before cooling and HI was added to give pH 2. To this solution was added 2 g of NaI and the volume was reduced on a rotary evaporator to yield a brown-black precipitate. This crude product was recrystallized from 12 ml of 0.01 *M* trifluoroacetic acid and 3 ml of concentrated HI. The final product was collected by filtration, washed with water and ethanol, and dried under vacuum at room temperature. *Anal.* Calcd for $RuC_6H_{20}N_6I_2$: C, 13.5; H, 3.75; N, 15.8; Ru, 19.0; I, 47.8. Found: C, 13.7; H, 3.78; N, 15.3; Ru $\geqslant$18.3; I, 47.8.

Electronic Absorption Spectra. Spectra were recorded with either a Beckman Acta V or a Cary 14 spectrophotometer using solutions in 0.01 *M* trifluoroacetic acid.

Pmr Spectra. The iodide salts of the ruthenium(II) complexes were converted to the more soluble chloride salts by stirring with freshly precipitated AgCl in D$_2$O. Deuteriotrifluoroacetic acid was added to the filtered solutions to a concentration of 0.01 *M* and the acidified solutions were concentrated to near saturation. Spectra were recorded on Varian A-60, HA 100, or HR 220 MHz instruments at ambient probe temperatures using DSS as an internal reference.

Electrochemistry. Cyclic voltammetry experiments were performed with a Princeton Applied Research Model 173 potentiostat-galvanostat and a locally designed function generator and were recorded with either a Tektronix Model 563 storage oscilloscope or a Houston Instruments Omnigraphic XY recorder. The cell comprised a platinum working electrode, a gold counter electrode, and a calomel reference electrode. A tin oxide electrode replaced the platinum electrode for the study of the Ru(phen)$_2$diim^{2+} complex due to the high potentials required. The Pt and Au electrodes were soaked in dichromate cleaning solution and then rinsed with distilled water before each experiment. Solutions of approximately 10^{-3} *M* Ru(II) were prepared by exchanging the iodide anion with chloride ion by stirring with AgCl in 0.01 *M* trifluoroacetic acid. The solu-
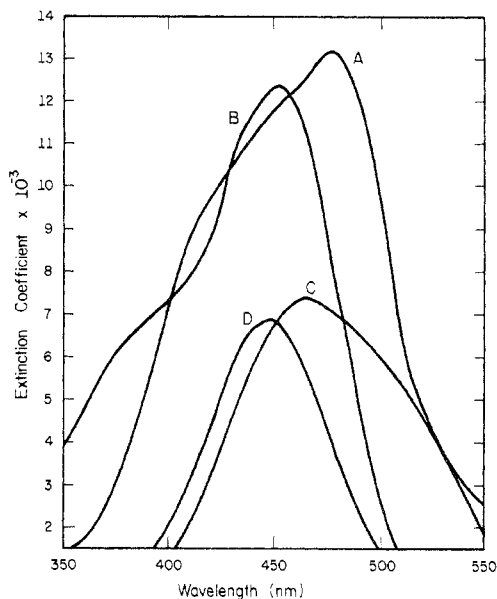

Figure 1. Visible absorption spectra: (A) [Ru(phen)$_2$en]I$_2$ (λ_{max} 478 nm, ϵ_{max} 13,800 M^{-1} cm^{-1}); (B) [Ru(phen)$_2$diim]Cl$_2$ (λ_{max} 452 nm, ϵ_{max} 12,400 M^{-1} cm^{-1}); (C) [Ru(en)$_2$phen]I$_2$ (λ_{max} 468 nm, ϵ_{max} 7950 M^{-1} cm^{-1}); (D) [Ru(en)$_2$diim]I$_2$ (λ_{max} 448 nm, ϵ_{max} 6900 M^{-1} cm^{-1}).

tions were then mixed with supporting electrolyte to give the desired conditions summarized in Table II. All solutions were deoxygenated by bubbling nitrogen through them and were maintained under a nitrogen atmosphere during the experiments.

The redox titrations were preformed with a Radiometer automatic titrator assembly using a platinum electrode and a calomel reference electrode. Solutions of 10^{-3} *M* Ru(II) were titrated with 0.07 *M* ceric ammonium sulfate in 1 *M* sulfuric acid.

Results

New Complexes. Two new complexes, Ru(en)$_2$phen^{2+} and Ru(phen)$_2$diim^{2+}, have been prepared and characterized by elemental analyses of their iodide salts and by their electronic absorption and proton magnetic resonance spectra.

Synthesis of Ru(en)$_2$phen^{2+} was achieved by first reducing a solution of Ru(en)$_2$Cl$_2^+$ to ruthenium(II) over zinc amalgam and then adding a stoichiometrically deficient quantity of phenanthroline. Addition of phenanthroline without prior reduction produces the same product but in much lower yield.

The oxidation of Ru(phen)$_2$en^{2+} with sodium hypochlorite solution at approximately neutral pH results in the oxidative dehydrogenation of the coordinated ethylenediamine ligand to produce Ru(phen)$_2$diim^{2+}. The oxidation is not stoichiometric and an insoluble by-product is produced.

Electronic Absorption Spectra. Ruthenium(II) complexes containing at least one phenanthroline ligand are red or red-brown due to a strong charge-transfer band with a maximum in the region 450-500 nm. The brown complex [Ru(en)$_2$-diim]I$_2$ also gives a yellow solution with a strong absorption band at 448 nm.[5,14] The visible spectra and extinction coefficients for these complexes are presented in Figure 1. In contrast, Ru(en)$_3^{2+}$ is colorless with the lowest energy absorption a weak band at 302 nm.[15,16] The strong visible absorption bands of the complexes possessing an α-diimine chromophore are undoubtedly $t_{2g} \rightarrow \pi^*$ metal-to-ligand

(11) J. K. Witschy and J. K. Beattie, *Inorg. Nucl. Chem. Lett.*, 5, 969 (1969).

(12) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

(13) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

(14) H. Elsbernd and J. K. Beattie, *J. Chem. Soc. A*, 2598 (1970).

(15) Other workers[13,16] have reported a peak at 370 nm; however, it has been our experience that this peak is of varying strength and is greatly attenuated or absent after recrystallization.

(16) H. Elsbernd, Ph.D. Thesis, The University of Illinois, Urbana, Ill., 1970.

charge-transfer transitions typical of low-spin d^6 complexes containing these ligands.[17]

Proton Magnetic Resonance Spectra. Pmr spectra, especially at 220 MHz, were used conveniently to characterize these complexes. Several related spectra have been reported previously. In $Ru(en)_3^{2+}$, the three ethylenediamine ligands are equivalent and each ligand is symmetric, but there is a large chemical shift difference between the axial and equatorial methylene protons, resulting in an $AA'BB'$ spectrum.[18] In $Ru(phen)_3^{2+}$, the phenanthroline ligands are equivalent and symmetric, giving an ABCM spectrum.[19] Finally, in $Ru(en)_2diim^{2+}$, a sharp singlet at δ 8.8 characterizes the CH imine protons.[5]

The aromatic regions of the 220-MHz spectra of the new complexes $Ru(phen)_2en^{2+}$ and $Ru(phen)_2diim^{2+}$ are presented in Figures 2 and 3, respectively. The C_{2v} symmetry of these complexes requires the equivalence of the two phenanthroline ligands, but each ligand is no longer symmetric and an ABCMNXYZ spectrum results. Using 100-MHz decoupling experiments, the ABC portion (protons 2, 3, and 4) was distinguished from the XYZ portion (protons 7, 8, and 9). These two sets of protons were then identified by the large upfield chemical shift of proton 2 which occurs upon oxidation of the ethylenediamine ligand to diimine. Thus protons 2, 3, and 4 are identified as those cis to the ethylenediamine or diimine ligand while protons 7, 8, and 9 are identified as those cis to the adjacent phenanthroline. It was not possible to distinguish protons 5 and 6. The resulting chemical shifts and coupling constants are given in Table I, together with those observed for $Ru(en)_2phen^{2+}$ and those previously reported for $Ru(phen)_3^{2+}$.[19] The ethylenediamine protons in $Ru(phen)_2en^{2+}$ at 220 MHz produce an $AA'BB'$ spectrum centered at δ 3.64. The appearance and half-width of 40 Hz are similar to those of $Ru(en)_3^{2+}$ but the peak occurs further downfield. After oxidation to $Ru(phen)_2diim^{2+}$, the two remaining diimine protons appear as a singlet at δ 9.26 (Figure 3).

In $Ru(en)_2phen^{2+}$ the two ethylenediamine ligands are equivalent but not symmetric. Together with the chemical shift difference between the axial and equatorial protons on each carbon atom, this results in the ABCD spectrum shown in Figure 4. A reasonable assignment is obtained if the average chemical shift of the axial protons occurs at a higher field than for the equatorial protons, as is observed in other complexes. Thus the multiplets at δ 2.54 and 2.98 are associated with the axial protons, while those at δ 2.75 and 3.20 belong to the equatorial protons. Using this assignment, a first-order analysis yields the approximate coupling constants J_{gem} = 13 Hz, J_{aa} = 10 Hz, J_{ae} = 4 Hz, and J_{ee} = 4 Hz, consistent with the usual observation that trans vicinal coupling constants are larger than gauche vicinal coupling constants.[20]

Electrochemical Properties. Each of the ruthenium(II) complexes can be oxidized to ruthenium(III) both by cyclic voltammetry and by titration with cerium(IV) solutions. The relative stability of the ruthenium(III) solutions decreases markedly as the ruthenium(III)–ruthenium(II) reduction potential increases. Furthermore, the stability of the ruthenium(III) ions is strongly dependent on the acidity of the solution. For the complexes $Ru(phen)_2diim^{3+}$ and
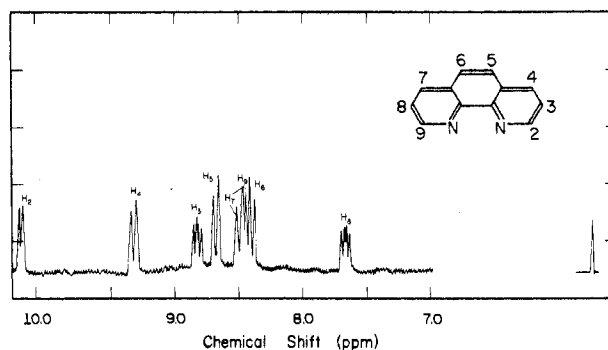
(17) P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 139 (1971).
(18) J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).
(19) J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 3185 (1965).
(20) J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, **10**, 2010 (1971).

Figure 2. The phenanthroline pmr spectrum of $Ru(phen)_2en^{2+}$ at 220 MHz.

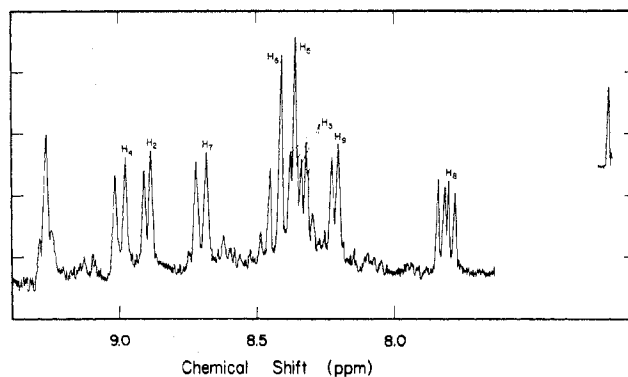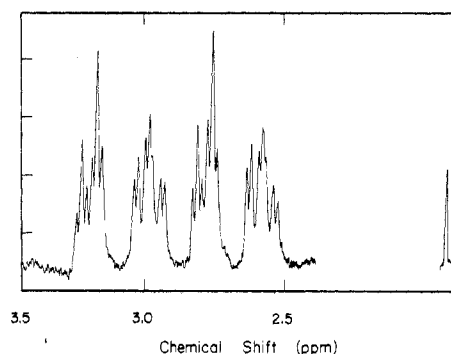**Figure 3.** The 220-MHz pmr spectrum of $Ru(phen)_2diim^{2+}$. The strong peak at δ 9.26 is due to the imine protons.

Figure 4. The 220-MHz pmr spectrum of the ethylenediamine protons of $Ru(en)_2phen^{2+}$.

Table I. Chemical Shifts (ppm) of Protons of Ruthenium(II)-Coordinated Phenanthroline

Proton[a]	Ru-(phen)$_3^{2+}$[b]	Ru(phen)$_2$-en^{2+}	Ru(phen)$_2$-diim^{2+}	Ru(en)$_2$-phen^{2+}
H$_2$	8.09	10.20	8.90	9.50
H$_3$	7.60	8.81	8.34	7.92
H$_4$	8.57	9.34	9.00	8.41
H$_5$, H$_6$	8.16	8.39, 8.66	8.34, 8.44	8.05
H$_7$		8.48	8.70	
H$_8$		7.66	7.82	
H$_9$		8.45	8.21	

[a] Numbering system as in Figure 2; the coupling constants are nearly identical for each complex, with values J_{23} = 5 Hz, J_{24} = 1 Hz, J_{34} = 8 Hz, and J_{56} = 9 Hz. [b] Reference 19.

$Ru(phen)_3^{3+}$ which have the highest reduction potentials, solutions of 6–9 M H_2SO_4 are required to observe the ruthenium(III) complex. In contrast, $Ru(en)_3^{3+}$ is stable at pH 2–3. The formal reduction potential values determined in this study, under various conditions, together with the values reported for $Ru(phen)_3^{3+}$ and $Ru(en)_3^{3+}$, are collected in Table II.

Table II. Apparent Formal Reduction Potentials

Couple	Cerium-(IV) titration $E°$, V	Cyclic voltammetry[a] $E°$, V	Peak sepn, mV	Conditions
Ru(phen)$_3$$^{3+,2+}$	1.27[b]			0.5 M H$_2$SO$_4$
Ru(phen)$_2$diim$^{3+,2+}$	1.10			9 M H$_2$SO$_4$
		1.30	110	6 M H$_2$SO$_4$
Ru(phen)$_2$en$^{3+,2+}$	0.77	0.80	72	6 M H$_2$SO$_4$
	Irrev	0.87	160	1.5 M HCl
Ru(en)$_2$diim$^{3+,2+}$	0.67	0.74	70	4 M H$_2$SO$_4$
Ru(en)$_2$phen$^{3+,2+}$	0.56			6 M H$_2$SO$_4$
		0.55	66	1.5 M HCl
Ru(en)$_3$$^{3+,2+}$	0.21[c]			0.01 M HClO$_4$

a Scan rate 0.5 V sec^{-1}. *b* Reference 21. *c* Reference 13.

Oxidation of Ru(phen)$_3$$^{2+}$ with cerium(IV) in 0.5 M H$_2$SO$_4$ is reported to produce Ru(phen)$_3$$^{3+}$ with a formal potential of 1.27 V.[21] We have been unable to oxidize reversibly the related Ru(phen)$_2$diim^{2+}. Titration with cerium(IV) in 9 M H$_2$SO$_4$ produces ruthenium(III) with an apparent formal potential of 1.1 V, but even at 0° the intense color of ruthenium(II) returns within a few minutes. Rapid scan cyclic voltammetry in 6 M H$_2$SO$_4$ gives an apparent formal potential of 1.3 V, but the large peak separation of 110 mV indicates substantially irreversible behavior.

The remaining ruthenium(II) complexes can be oxidized to ruthenium(III) if the acid strength is sufficiently high. Thus in 6 M H$_2$SO$_4$ oxidation of Ru(phen)$_2$en^{2+} occurs nearly reversibly with formal potentials of 0.77 and 0.80 V determined by direct titration and by cyclic voltammetry, respectively. However, in 1.5 M HCl the oxidation becomes irreversible as indicated by a 160-mV peak separation in the cyclic voltammogram. In 1.5 M NaCl solution containing 5 × 10^{-3} M trifluoroacetic acid, the cathodic wave disappears completely. In contrast, oxidation of Ru(en)$_2$phen^{2+} is substantially reversible under each of these conditions (*i.e.*, 6 M H$_2$SO$_4$, 1.5 M HCl, and pH 2.3) but at pH 6.8 the oxidation is completely irreversible. Because of the longer time required for the titrimetric oxidations by cerium(IV), irreversible behavior is observed at higher acidities than in the corresponding cyclic voltammetry experiments.

The formation of a diimine product upon oxidation was confirmed for Ru(phen)$_2$en^{2+} by a spectrophotometric titration at pH 10 using an alkaline solution of ferricyanide ion as the oxidant. Four equivalents of oxidant was consumed according to the stoichiometry

Ru(phen)$_2$en^{2+} + 4Fe(CN)$_6$$^{3-}$ → Ru(phen)$_2$diim^{2+} +

$\quad$ 4Fe(CN)$_6$$^{4-}$ + 4H$^+$ $\qquad\qquad\qquad\qquad$ (2)
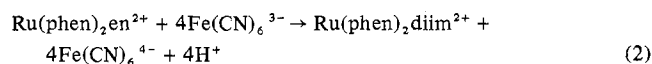
Other, unidentified side reactions occur under different conditions, however, for the titrimetric oxidation of Ru(phen)$_2$en^{2+} with cerium(IV) in 0.5 M H$_2$SO$_4$ required approximately 5 equiv. Spectrophotometric examination of the product solution revealed an unidentified absorbance maximum at 375 nm as well as an absorption band at 450 nm assigned to the expected Ru(phen)$_2$diim^{2+} product.

Discussion

Inspection of Table II reveals that the formal reduction potentials of the complexes are strongly dependent on the nature of the coordinated ligands. As the ethylenediamine ligands are replaced with phenanthroline ligands, the reduction potential increases. Presumably the conjugated

(21) F. P. Dwyer, *J. Proc. Roy. Soc. N. S. W.*, **83**, 134 (1949).

Table III. Anodic Peak Voltages (mV *vs.* Sce) for Oxidation of Ruthenium(II) Complexes

Complex	Ru(II) → Ru(III)	Ru(II) → Ru^{II}diim
Ru(phen)$_2$en^{2+}	600[a]	740[b]
Ru(en)$_2$phen^{2+}	340[b]	425[c]

a 6 M H$_2$SO$_4$. *b* 1.5 M HCl. *c* 1.5 M NaCl, pH 6.8.

phenanthroline ligand stabilizes the ruthenium(II) state. Similar trends have been noted previously[22] with ruthenium ammine complexes and attributed to the π-accepting ability of the ligands involved. It is significant that a similar effect is observed when the ethylenediamine ligand is oxidized to diimine, suggesting that an extensive conjugated π system is not required. The observation that complexes with either diimine or phenanthroline ligands have similar visible electronic spectra further suggests that the metal interacts primarily with the α-diimine system.[17]

The observation that oxidation of these complexes leads to the formation of ruthenium(III) only in acidic solutions is the probable consequence of two separate effects. The strongly oxidizing complexes Ru(phen)$_3$$^{3+}$ and Ru(phen)$_2$diim^{3+} are capable of oxidizing water unless the acid concentration is high. The lower reduction potentials of the other complexes preclude the oxidation of water, even at neutral pH. In these cases oxidation of the coordinated ethylenediamine ligand can occur, which is also a strongly acid-dependent process according to eq 1. Both effects thus lead to the instability of the various ruthenium(III) complexes except in strongly acidic solutions.

Other investigators have observed that macrocyclic ligands coordinated to iron(II) or nickel(II) are readily oxidized, whereas the same ligands coordinated to cobalt(III) are not.[23] From this it has been inferred that the mechanism of oxidation requires the initial oxidation of the metal to a higher oxidation state followed by oxidation of the ligand with concomitant reduction of the metal to the original oxidation state. The present results are consistent with this hypothesis. Comparison of the cyclic voltammetric potentials for the formation of ruthenium(III) and for the oxidation of the ligand given in Table III shows that the anodic peak voltages for the irreversible diimine formation occur at a greater potential than those for oxidation to ruthenium(III). Thus the oxidative dehydrogenation of the coordinated ethylenediamine ligand may be initiated by oxidation of the metal to ruthenium(III). Other mechanisms are possible, however, as studies on the electrochemical oxidation of magnesium(II), zinc(II), and lead(II) porphyrin complexes suggest.[24] Furthermore, side reactions occur upon the chemical oxidation of these ruthenium(II) complexes leading to unidentified products.

The present work helps to account for some of the difficulties experienced by ourselves and others in the preparation of certain ruthenium complexes and also provides a route for the synthesis of the simplest of the α-diimine ligands which may be of some interest for future studies.

(22) H. S. Lim, D. J. Barclay, and F. Anson, *Inorg. Chem.*, **11**, 1460 (1972); A. M. Zwickel and C. Creutz, *ibid.*, **10**, 2395 (1971).
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Paramagnetic Resonance of Some Complexes of Iron and Chromium in Hexaamminecobalt(III) Hexachlorometalates

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The spin-Hamiltonian parameters are evaluated by epr powder techniques for [FeCl$_6$]$^{3-}$ and [Cr(NH$_3$)$_6$]$^{3+}$ guest ions in three diamagnetic Co(NH$_3$)$_6$MCl$_6$ hosts (M = In, Sb, Bi) and for [CrCl$_6$]$^{3-}$ in the Co(NH$_3$)$_6$InCl$_6$ host. The significance of the parameters is discussed in terms of molecular and lattice properties. A comparison of the relative magnitudes of the zero-field splitting parameters and sizes of the complex ions provides an interesting model for the guest–host interactions in these systems.

Introduction

The effect of lattice stabilization on the solubility of salts composed of ions of equal and opposite charge and of comparable size has provided a synthetic route for the isolation of highly coordinated transition metal ion complexes. Of particular concern have been the hexaamminecobalt(III) hexachlorometalates. These compounds are relatively easy to prepare and have proven to be of interest not only as a means of isolation and study of the complex ions but also from the standpoint of their own crystal structures.[1,2]

The present work involves an epr investigation of three complex ions, [FeCl$_6$]$^{3-}$, [CrCl$_6$]$^{3-}$, and [Cr(NH$_3$)$_6$]$^{3+}$, which were introduced as ~1% guests into a diamagnetic Co(NH$_3$)$_6$-MCl$_6$ host. Specifically, [FeCl$_6$]$^{3-}$ and [Cr(NH$_3$)$_6$]$^{3+}$ were studied in three Co(NH$_3$)$_6$MCl$_6$ hosts (M = In, Sb, Bi), while the [CrCl$_6$]$^{3-}$ ion was prepared only in the indium host. The spin-Hamiltonian parameters evaluated from the epr spectra provide information about the properties of the complex ion as well as the hosts, and the conclusions drawn from the parameters for the compounds studied are consistent with results reported elsewhere.[3-6]

Experimental Section

Microcrystalline samples suitable for epr were obtained by coprecipitation of host and guest such that the concentration of the paramagnetic species in the product was approximately 1 mol %. Slow crystal growth procedures were found to be unnecessary.

Co(NH$_3$)$_6$FeCl$_6$ was magnetically diluted into the corresponding indium host following the general procedure given by Hatfield, *et al.*,[1] and into the antimony host as described by Schroeder and Jacobson.[2] A sample employing the Co(NH$_3$)$_6$BiCl$_6$ host was prepared in a similar manner to the antimony sample. It was found that strong epr signals could be obtained in the indium host by preparing the sample from a solution containing a 1:99 guest to host ratio. However, suitable sam-

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ples could not be obtained for the antimony or the bismuth host with less than an equimolar solution, and a 5:1 guest to host ratio in solution was required with these hosts to obtain signals of magnitude comparable to the indium case.

Cr(NH$_3$)$_6$MCl$_6$ was diluted into the corresponding cobalt hosts (M = In, Sb, Bi) by the same methods as above.[1,2] It was found that epr signals of similar intensities as for iron could be obtained in all cases using a 1% chromium to 99% cobalt ratio in solution.

Co(NH$_3$)$_6$CrCl$_6$ gave a suitable epr spectrum only in the indium host. The procedure involved preparing a large excess of Cr^{3+} in hot 12 N HCl, followed by treatment with Zn metal in an attempt to promote ligand exchange and formation of the desired species in solution. A small amount of indium metal was then dissolved in the chromium solution, and to this was added a hot solution of Co(NH$_3$)$_6$Cl$_3$. The product obtained gave epr signals of nearly the same intensity as the other samples; however, attempts to introduce this guest into the antimony and bismuth hosts gave very weak, unidentifiable spectra. In contrast to the [FeCl$_6$]$^{3-}$ and [Cr(NH$_3$)$_6$]$^{3+}$ samples, the [CrCl$_6$]$^{3-}$ spectra all showed a Mn^{2+} contamination. Manganese(II) appears to have a very strong affinity for these hosts.

Paramagnetic resonance measurements were taken at room temperature on a Varian Model E-12 spectrometer at a frequency of 35 GHz using a Varian Model E-110 microwave bridge. Line positions were measured with a Spectromagnetic Industries Model 5200 nmr gaussmeter. One [FeCl$_6$]$^{3-}$ sample and the [CrCl$_6$]$^{3-}$ sample were also examined at 77°K using a frequency of approximately 9.1 GHz.

X-Ray powder patterns of Co(NH$_3$)$_6$InCl$_6$, Co(NH$_3$)$_6$SbCl$_6$, and Co(NH$_3$)$_6$BiCl$_6$ were taken with a Debye–Scherrer camera of 11.46-cm diameter using a copper source with a nickel filter. A comparison of the patterns showed a 1:1 correspondence of the relative line positions for 30 lines, indicating that the three structures are isomorphous. The unit cell dimensions increase only slightly and in an isotropic fashion in going from In to Bi, with the dimensions of the Sb compound being intermediate.

Results

Spectra for all seven epr powder samples displayed extremely high signal-to-noise ratios as can be seen in Figure 1, thus allowing precise measurements of the line positions and also affording further study of unresolved rhombic splittings in the wing lines *via* line shape analysis. Details regarding the interpretation of epr powder spectra for $S \geqslant {}^3/_2$ have been described elsewhere.[3,4]

The line positions of the parallel and perpendicular spectra for each complex were measured, and the appropriate spin Hamiltonian was used to fit the spectra. For the chromium samples, the Hamiltonian was of the form

$$\mathcal{H} = \beta H \cdot g \cdot S + D[S_z{}^2 - S(S+1)/3] + E[S_x{}^2 - S_y{}^2]$$