that can be formulated as a bicyclic compound with little boron–boron bonding. Such a system contains strained four-membered C–B–C–B rings which should be susceptible to ring-opening reactions generating open polyhedral faces suitable for cage fusions. Indeed, the proposed 1,2,8,10-$C_4B_7H_{11}$ structure can be envisioned as containing two such open-cage $C_2B_3H_5$ fragments: 1,8,3,4,7-$C_2B_3H_5$ and 2,10,5,6,11-$C_2B_3H_5$ cages. The thermally induced process leading to the formation of IV thus may be formally related to the metal-promoted cage fusions of nido carboranes which have been used to generate the other large-cage four-carbon carborane systems.[26]

The formation of $C_4B_7H_{11}$ from 1,5-$C_2B_3H_5$ is also quite unusual since the molecule contains one more B–H unit than two $C_2B_3H_5$ groups. Two reasonable possibilities for a reaction sequence were suggested. First, diborane, produced by decomposition of 1,5-$C_2B_3H_5$, could be involved in the reaction to produce IV. Supporting this possibility was the report[31] that mass spectroscopic evidence for a compound of the same formula had been obtained as a product of the pyrolysis of 2,4-$C_2B_4H_8$ and diborane. Second, since 1,5-$C_2B_3H_5$ is known[5]

to thermally convert to 1,6-$C_2B_4H_6$ and both 1,6-$C_2B_4H_6$ and 2:2′-[1,5-$C_2B_3H_4$][1,6-$C_2B_4H_5$] were observed as minor products of the reaction, 1,6-$C_2B_4H_6$ could combine with 1,5-$C_2B_3H_5$ to produce IV. It was found, however, that neither additional diborane nor 1,6-$C_2B_4H_6$ affected the yield of IV formed in the 1,5-$C_2B_3H_5$ pyrolysis reaction. Thus, the mechanism of formation of this unusual species is unknown and is the subject of continuing investigation in this laboratory.

The pyrolysis reactions of 1,6-$C_2B_4H_6$ were found to yield only polymerization, but when equimolar quantities of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ were pyrolyzed, the mixed-cage carborane 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$] was formed in good yield based on consumed 1,6-$C_2B_4H_6$, suggesting that reactive fragments derived from 1,5-$C_2B_3H_5$ are the key species in the reaction. This reaction method is a significant improvement over the previous photochemical procedure,[2] and we would expect that the reaction yields could be further improved by employing more efficient quenching of the product.

Further investigations are now in progress concerning the synthesis and properties of the compounds reported herein and related linked- and fused-cage polyhedral boranes. The results of these studies will be reported in future publications.

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Preparation and Coordination Geometry of Quadridentate Ethylenediaminetetraacetate Complexes of Ruthenium(II) and -(III)

ALEX A. DIAMANTIS* and JULES V. DUBRAWSKI

Complexes of $Ru^{II}(H_2edta)L$ (L = bis(pyridine), bis(4-methylpyridine), 1,10-phenanthroline, 2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane, and dimethylglyoximate) and $Ru^{III}(H_2edta)L$ (L = $(SCN)_2$, acetylacetonate, dimethylglyoximate, and diethyldithiocarbamate) were prepared by substitution reactions on $Ru^{II}(Hedta)H_2O^-$ and $Ru^{III}(Hedta)H_2O$, respectively. Substitution of the ligands L on $Ru(H_2edta)(py)_2$ and $Ru(H_2edta)(C_6H_5CN)_2$ with a variety of other entering ligands was investigated. The carboxylic acid functions in the free glycinate arms in $[Ru^{II}(Hedta)CO]K·2H_2O$ and $Ru(H_2edta)(py)_2$ were shown to react with diazomethane and *p*-toluidine. The complexes were characterized by analytical and spectroscopic procedures, including ^{13}C NMR, and were shown to accommodate L in the equatorial positions, giving rise to molecules possessing a C_2 axis. The complexes prepared in this work, together with complexes with π-acceptor ligands reported in an earlier study, were investigated by cyclic voltammetry. Resistance to oxidation was found to depend on the ligand L and followed the sequence NO, CO > RCN > bipyridine, phenanthroline > pyridine > N_2(terminal) > SCN^- > N_2(bridging) > acetylacetonate > dimethylglyoximate. The effect of the ligand L on the stability of the oxidation state of the complex is discussed.

Introduction

In an earlier study[1] we reported the preparation of complexes of the type $Ru(H_nedta)L_n$ (L = N_2, CO, NO (*n* = 1) and L = RCN (*n* = 2)) by substitution of the ligand on $Ru^{II}(Hedta)H_2O^-$ in dilute acid solution and in the presence of H_2/Pt. Matsubara and Creutz[2] investigated the kinetics of substitution on $Ru^{III}(edta)H_2O^-$ and on $Ru^{II}(edta)H_2O^{2-}$ and found rate constants higher than those of corresponding

ruthenium complexes with oxygen and nitrogen donors, especially in the case of ruthenium(III) in which substitution was faster by as much as 10 orders of magnitude. Thus, the ready preparation of the complexes can be explained as proceeding by substitution on ruthenium(II) or on ruthenium(III) followed by rapid electron transfer.

In this paper we report the preparation and properties of complexes of ruthenium(II) and ruthenium(III) containing quadridentate edta, in which the remaining two positions are occupied by a variety of ligands, mainly bidentate, ranging in their coordinating ability from strong π-acceptors to σ- and π-donors.

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Thus, a series of complexes is available in which the electronic effects of the introduced ligands on the properties of the complex as a whole can be examined in a systematic way. Ligands capable of accepting electron density are known to stabilized the +2 oxidation state of ruthenium; conversely electron-donating ligands favor the +3 state.[3,4] Evidence for this behavior was sought by studying the preparation of complexes in the two oxidation states and by examining their stability in solution. This chemical behavior was correlated with their electrochemical properties. Examination of the electronic spectra has provided qualitative information about the effect of the ligands on the electronic energy levels in the ruthenium center.

Experimental Section

Materials. Hydrated ruthenium trichloride, $RuCl_3 \cdot nH_2O$, was purchased from Johnson and Matthey. Analytical grade chemicals were used in all cases. Gases were obtained from CIG Australia Ltd. High-purity dinitrogen, industrial dihydrogen, and argon were used as received.

Analyses. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and by the Levels Institute of Technology, Adelaide. Total ruthenium content was determined gravimetrically.

Physical Measurements. Solid-state infrared spectra were obtained from KBr pellets and Nujol mulls with a Perkin-Elmer spectrometer, Model 457. Electronic spectra were recorded under dinitrogen with a Perkin-Elmer 402 spectrophotometer. Proton NMR spectra were measured in D_2O solution with a Varian T-60 spectrometer. Broad-band decoupled ^{13}C NMR spectra were recorded in D_2O or CF_3CO_2D with a Bruker HX-90 spectrometer. Conductance measurements were made in aqueous solution by using a Philips PH-9500 AC bridge, and base titrations were carried out in aqueous solution and followed with a Philips pH 9400 meter.

Cyclic and single-sweep voltammograms were carried out with a Princeton Applied Research Model 174 polarographic analyzer and Model 175 programmer and recorded on a Houston Instrument Corp. Model HR-97 or displayed on a Tektronix 603/604 cathode ray oscilloscope. The electrochemical measurements were carried out with use of a spherical platinum working electrode, a platinum gauze counterelectrode, and a saturated calomel electrode utilizing a Luggin probe. Solutions contained approximately 0.001 mol dm^{-3} of complex and were purged with N_2 gas.

Preparations. Solutions containing $Ru^{II}(Hedta)H_2O^-$ were prepared by the in situ reduction of $[Ru^{III}(Hedta)Cl]K \cdot 2H_2O$ by dihydrogen over platinum black as described earlier.[1] The $[Ru^{III}(Hedta)Cl]$-$K \cdot 2H_2O$ was prepared by a modification of the method of Ezerskaya and Solovykh.[5]

Preparation of Ruthenium(II) Complexes of the Type $Ru^{II}(H_2edta)L$.
Method 1. The general method was to add the required ligand to an aqueous solution of $[Ru(Hedta)Cl]K \cdot 2H_2O$ (0.2 g) in water (5.0 cm^3), which had been reduced with H_2/Pt for 10 min and then continue the reduction for a further period of 45 min to 1 h. The method of isolation varied depending on the solubility and sensitivity of the complexes to air. The preparation of the bis(pyridine) complex is described in detail to illustrate the procedure.

A. $Ru(H_2edta)(C_5H_5N)_2 \cdot 2H_2O$. An aqueous solution (4 cm^3) of the chloro complex (0.2 g) was reduced for approximately 10 min prior to the addition of excess pyridine. An orange coloration immediately formed, and reduction was continued for 1 h. Subsequently, the solution was freeze-dried and the product washed liberally with ether. Extraction with dinitrogen-saturated dry methanol (20 cm^3) gave an orange solution, which on concentration and precipitation with ether gave a yellow-orange product. This was dried over phosphorus pentoxide; yield 0.15 g (65%).

Anal. Calcd for $C_{20}H_{28}H_4O_{10}Ru$: C, 41.0; H, 4.82; N, 9.57; Ru, 17.31. Found: C, 40.8; H, 4.73; N, 9.32; Ru, 17.2. Other complexes prepared by the same procedure follow:

B. $Ru(H_2edta)(C_6H_7N)_2 \cdot 2H_2O$. The ligand used was 4-methylpyridine. The method of isolation was the same as for A; yield 0.15 g (65%).

Anal. Calcd for $C_{22}H_{32}N_4O_{10}Ru$: C, 43.1; H, 5.26; N, 9.13; Ru, 16.5. Found: C, 42.7; H, 5.10; N, 9.16; Ru, 15.9.

C. $Ru(H_2edta)(C_{12}H_8N_2) \cdot 3H_2O$. The ligand used was 1,10-phenanthroline (0.8 g) in methanol (5 cm^3). Addition of the ligand resulted in an immediate intense reddish brown coloration. As reduction continued, a solid precipitated. After about 45 min the mixture was filtered in air, yielding a violet-brown solid, which was washed with cold water and ether/methanol mixture. Recrystallization was from aqueous methanol; yield 0.15 g (63%).

Anal. Calcd for $C_{22}H_{28}N_4O_{11}Ru$: C, 42.2; H, 4.51; N, 8.96; Ru, 16.2. Found: C, 42.3; H, 4.38; N, 8.91; Ru, 16.3.

D. $Ru(H_2edta)(C_{10}H_8N_2) \cdot 2H_2O$. The ligand used was 2,2'-bipyridine (0.09 g) in methanol (5 cm^3). The yield and method of isolation was the same as for preparation C.

Anal. Calcd for $C_{20}H_{26}N_4O_{10}Ru$: C, 41.2; H, 4.49; N, 9.60. Found: C, 41.4; H, 4.28; N, 9.59.

E. $[Ru(H_2edta)(C_4H_7N_2O_2)]K \cdot H_2O$. The ligand used was dimethylglyoxime (0.05 g in 5 cm^3 of methanol). The brown reaction mixture was extracted as in preparation A; yield 0.12 g (53%).

Anal. Calcd for $C_{14}H_{23}KN_4O_{11}Ru$: C, 29.8; H, 4.11; N, 9.94. Found: C, 30.0; H, 4.03; N, 9.67.

F. $Ru(H_2edta)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2] \cdot 2H_2O$. A solution (4 cm^3) of $[Ru(Hedta)Cl]K$ (0.1 g) was reduced (H_2/Pt) prior to the addition of 5 cm^3 of an ethanol/chloroform solution of the ligand (0.085 g). As reduction proceeded, the mixture became cloudy. After 2 h the mixture was filtered and the yellow filtrate allowed to stand under dinitrogen overnight. A yellow microcrystalline solid precipitated and was collected, washed with ethanol, and dried over silica gel; yield 0.065 g (40%).

Anal. Calcd for $C_{36}H_{42}N_2O_{10}P_2Ru$: C, 52.4; H, 5.13; N, 3.39. Found: C, 51.9; H, 5.00; N, 3.54.

G. $[Ru(Hedta)(NCS)]K_2 \cdot 2H_2O$. The ligand used was potassium thiocyanate (0.1 g) in 5 cm^3 of methanol. The reduction was allowed to proceed for about 1 h before the solution was transferred, under hydrogen, to a vacuum line and concentrated to a small volume. A green product was precipitated by the addition of dinitrogen-saturated acetone (5 cm^3), collected, and washed with ethanol. The complex was dissolved in a minimum amount of water, precipitated with acetone, collected, washed with ethanol, and dried over phosphorus pentoxide; yield 0.14 g.

Anal. Calcd for $C_{11}H_{17}K_2N_3O_{10}SRu$: C, 23.5; H, 3.05; N, 7.47; S, 5.70. Found: C, 23.1; H, 3.02; N, 7.41; S, 6.0. A second sample gave 7.6% S, suggesting the presence of some bis(thiocyanato) complex.

The complexes with 1,10-phenanthroline (preparation D) and 2,2'-bipyridine (preparation D) could also be prepared from the compound of preparation A by substitution (method 2) and from $[Ru(Hedta)Cl]K \cdot H_2O$ with excess of the ligand as the reducing agent (method 3).

Method 2. A methanolic solution (30 cm^3) of phenanthroline (0.04 g) and $Ru(H_2edta)(C_5H_5N)_2 \cdot 2H_2O$ (0.1 g) acidified with 2 mol dm^{-3} HCl (1 cm^3) was refluxed under dinitrogen. Refluxing for 15 min yielded a dark red-brown solution which, on standing for several days, deposited crystalline plates of the phenanthroline complex; yield 0.03 g. From 2,2'-bipyridine the complex of preparation D was obtained on concentrating the solution.

Method 3. Addition of a methanolic solution (5 cm^3) of the ligand (0.10 g) to a solution of $[Ru(Hedta)Cl]K \cdot 2H_2O$ (0.2 g) and warming resulted in a gradual change in color to red-brown over a period of 10 min. After 20 min a brown precipitate was obtained, filtered off, and discarded. The remaining filtrate was allowed to stand overnight, yielding a violet-brown microcrystalline product. The solid was treated as above; yield 0.1 g (40%).

From 2,2'-bipyridine the complex of preparation D was obtained on allowing the reaction mixture to stand for several days.

Esterification of the carboxylic acid functions of coordinated edta was achieved by the use of an ice-cold ethereal solution of diazomethane, which was prepared by the addition of an ice-cold ethereal solution of N-nitroso-N-methylurea to a cold solution of sodium hydroxide and then drying over KOH pellets.

H. $Ru(Me_2edta)(C_5H_5N)_2 \cdot 2H_2O$. Excess diazomethane was added to a colid solution of $Ru(H_2edta)(C_5H_5N)_2$ (0.08 g) in freshly distilled methanol (20 cm^3). The mixture was allowed to stand at room temperature for 1 h before being evaporated to dryness. The orange

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product was washed with ether and recrystallized from chloroform by the addition of a small amount of petroleum ether (80 °C); yield 0.055 g (66%).

Anal. Calcd for $C_{22}H_{32}N_4O_{10}Ru$: C, 43.1; H, 5.26; N, 9.13; Ru, 16.5. Found: C, 43.4; H, 5.25; N, 8.95; Ru, 15.6.

I. [Ru(Meedta)CO]K·2H₂O. Excess diazomethane was added to a chilled solution of [Ru(Hedta)CO]K·2H₂O[1] (0.06 g) in dinitrogen-saturated methanol (50 cm³). The solution was allowed to stand at ambient temperature for approximately 45 min before being concentrated to a small volume, and the product was precipitated with diethyl ether. The yellow solid was washed with ether and dried in vacuo.

Anal. Calcd for $C_{12}H_{19}N_2O_{11}K$: C, 28.4; H, 3.77; N, 5.52. Found: C, 27.9; H, 3.46; N, 5.69.

Preparation of Ruthenium(III) Complexes of the Type Ru^{III}-(H_2edta)L. These were prepared by adding the appropriate ligand to an aqueous solution of [Ru(Hedta)Cl]K·2H₂O. The method of isolation of the solids depended on the solubility and stability of the complex species in solution.

J. [Ru(H₂edta)(NCS)₂]K·2H₂O. A solution of the chloro complex (0.26 g) and potassium thiocyanate (0.11 g) in 0.2 mol dm⁻³ hydrochloric acid (3–5 cm³) was warmed on a steam bath, resulting in a deep red coloration. The mixture was concentrated and the product washed with ice-cold acetone, followed by extraction with a chloroform/acetone (1:10) mixture (15 cm³). The resultant red solution was concentrated, and the product precipitated with ether. The red solid was collected and the procedure repeated. The product was washed with ether and dried under vacuum; yield 0.14 g (48%).

Anal. Calcd for $C_{12}H_{18}KO_{10}N_4S_2Ru$: C, 24.7; H, 3.11; N, 9.62; S, 11.0. Found: C, 24.7; H, 3.00; N, 9.20; S, 10.4.

K. Ru(H₂edta)(CH₃COCHCOCH₃)·2H₂O. Excess acetylacetone was added to a warm solution (5 cm³) of the chloro complex (0.1 g). The solution color gradually changed to violet. The mixture was warmed again and allowed to stand for 20 min before being concentrated to dryness. The violet product was extracted with a methanol/chloroform (10:1) mixture (15 cm³), filtered, and the filtrate concentrated to dryness again. The extraction was repeated, the solution concentrated, and the product precipitated with ether, collected, washed with ether, and dried in vacuo; yield 0.05 g (45%).

Anal. Calcd for $C_{15}H_{25}N_2O_{12}Ru$: C, 34.2; H, 4.79; N, 5.32. Found: C, 34.2; H, 4.51; N, 5.18.

L. Ru(H₂edta)(C₄H₇N₂O₂)·2H₂O. The complex was prepared as described for the acetylacetonato complex. From dimethylglyoxime (0.03 g) and [Ru(Hedta)Cl]K·2H₂O (0.1 g) a brown product (0.07 g, 65%) was obtained.

Anal. Calcd for $C_{14}H_{25}O_{12}N_4Ru$: C, 31.0; H, 4.65; N, 9.94. Found: C, 30.3; H, 4.49; N, 10.4.

The following two preparations gave compounds that were mixtures of at least two components. However, evidence from solution studies suggested that the mixtures contained the sought compound to an appreciable extent; hence, details of the preparation methods are given below:

Reaction of p-Toluidine with Ru(H₂edta)(py)₂·2H₂O. A mixture of p-toluidine (0.035 g) and the bis(pyridine) complex (0.14 g) in freshly distilled methanol (10–20 cm³) was refluxed under a dinitrogen atmosphere for approximately 30 min. The orange solution was filtered and concentrated to a small volume. The addition of diethyl ether yielded an orange product. This was redissolved in methanol (10 cm³), precipitated with ether, collected, washed with ether, and dried in vacuo; yield 0.08 g. Thin-layer chromatography revealed the presence of two components. However, attempts to separate them on fluorosil columns resulted in extensive decomposition. From the IR spectra and other spectroscopic investigations it was concluded that the solid consisted in the main of Ru[(p-toluidide)₂edta](py)₂ contaminated with the starting material, which is also formed by the hydrolysis of the sought product.

Anal. Calcd for Ru[(p-CH₃C₆H₄NHCO)₂C₈O₄N₂H₁₂](py)₂·2H₂O: C, 53.5; H, 5.54; N, 11.0; Ru, 13.2. Found: C, 50.0; H, 5.53; N, 9.77; Ru, 14.1.

Reaction of Ru^{III}(Hedta)H₂O with Sodium Diethyldithiocarbamate. The addition of sodium diethyldithiocarbamate (0.1 g) to a solution (5 cm³) of the chloro complex (0.1 g) resulted in the rapid development of a red coloration. After 30 min the solution was concentrated to dryness and the solid extracted with methanol (10 cm³) and filtered. The solution was then concentrated and precipitated with ether. The red powder was collected, washed with dry chloroform and ether, and

dried over phosphorus pentoxide; yield 0.11 g. Reduction of the chloro complex (0.1 g) with H₂/Pt followed by the addition of the ligand (0.15 g) rapidly gave a red solution, which was treated as above, yielding the same product; yield 0.10 g.

Anal. Calcd for [Ru(edta)(dtc)]Na₂·2H₂O: C, 29.1; H, 4.23; N, 6.78; S, 10.3. Found: C, 25.2; H, 3.60; N, 5.30; S, 8.2.

Results and Discussion

Preparation of Complexes. The complexes of $Ru^{II}(H_2$edta) were prepared by adding the suitable ligand to a solution containing an equilibrium mixture of $Ru^{II}(Hedta)H_2O^-$/$Ru^{III}(Hedta)H_2O$ produced as described previously.[1] In the presence of H₂/Pt complete conversion to the reduced form could be achieved. As the pH of the solution was below 3, the complexes that were isolated contained the free glycinate arms in the protonated form. With the heterocyclic nitrogen bases, the chelating phosphine, and dimethylglyoxime, stable complexes could be prepared in good yields. However, with acetylacetone and thiocyanate, although the complexes obtained were quite distinct from the corresponding ruthenium-(III) compounds, they were unstable, were difficult to characterize completely, and were readily oxidized to the ruthenium(III) complexes.

The preparation of the corresponding ruthenium(III) complexes was attempted by reacting the same ligands with $Ru^{III}(Hedta)H_2O$. Solutions containing this species were prepared by dissolving [Ru(Hedta)Cl]K·2H₂O, which is known to aquate rapidly.[1] In the resulting aquo complex the carboxylic acid function of the free glycinate arm has a pK_a of 2.37.[2,6] No products could be isolated from such solutions on the addition of excess pyridine, CH₃CN, or C₆H₅CN. As reported previously,[1] attempts to oxidize $Ru^{II}(H_2$edta)(RCN)₂ with Ag₂O to the corresponding ruthenium(III) complexes were also unsuccessful. The addition of methanolic solutions of 1,10-phenanthroline produced initially a brown solid, which was shown to be a mixture of the purple ruthenium(II) complex and the starting material and, on subsequent standing, yielded the same purple ruthenium(II) complex described above. The isolation of the ruthenium(II) complex from the above reaction is not unusual since reduction of ruthenium(III) to ruthenium(II) can occur in the presence of methanol and phenanthroline[7,8] under certain conditions.

With acetylacetone and dimethylglyoxime, stable ruthenium(III) complexes were obtained. Normally, in the preparation of complexes starting with these protonated ligands, a base such as acetate is added to encourage proton abstraction from the ligand. In our system this function is fulfilled internally by the coordinated glycinate arm, which is displaced by the ligand during the reaction according to

$$Ru^{III}(Hedta)(H_2O) + (L-L)H \rightleftharpoons$$
$$Ru^{III}(H_2edta)(L-L) + H_2O$$
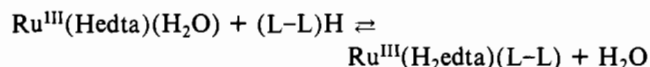
where (L–L)H represents acetylacetone or dimethylglyoxime. Excess potassium thiocyanate resulted in the rapid formation of a red solution from which a solid containing two SCN⁻ ions per ruthenium was obtained. With diethyldithiocarbamate in acid solution the same ruthenium(III) complex was obtained irrespective of whether the ruthenium(II) or ruthenium(III) Hedta aquo complex was used initially. The isolation of a ruthenium(III) complex upon addition of a sulfur-donor ligand to a ruthenium(II) compound is not unprecedented.[9] How-

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Table I. Complexes of $Ru^{II}(H_2edta)$ and $Ru^{III}(H_2edta)$ with Various Ligands and Their Main Infrared Absorptions

complex[a]	color and form	$\nu(COOH),$[b,c] cm^{-1}	ligand[d]
	(a) Ruthenium(II) Complexes		
$Ru(H_2edta)(py)_2\cdot2H_2O$	yellow-orange powder	1725 s, 1580 s, br	1560 s, 1480, 775, 765, 705
$Ru(H_2edta)(4\text{-}Mepy)_2\cdot2H_2O$	yellow-orange powder	1730 s, 1590 s, br	
$Ru(H_2edta)phen\cdot3H_2O$	brown, microcrystalline	1730 s, 1590 s, br	3080 w, 1510, 855 s, 840, 790, 730 s
$Ru(H_2edta)bpy\cdot2H_2O$	brown, microcrystalline	⌈1705 s, 1570 s ⌊1750 s	3080 w, 1530, 1560 sh, 770 s, 740 s, 690, 640
$[Ru(H_2edta)dmg]K\cdot H_2O$	intense brown	1725 s, 1600 s	3170 s, br, 985
$Ru(H_2edta)dppe\cdot2H_2O$	yellow, microcrystalline	⌈1750 s ⌈1570 s ⌊1715 s ⌊1580 s	1400–1350 s, 1210, 1100 s, shp, 830 sh, 760, 750, 710 s
$[Ru(Hedta)NCS]K_2\cdot2H_2O$	green	1725 s, 1600 s, br	2100 s, 2070 s, sh
$[Ru(H_2edta)acac]K\cdot nH_2O$	bronze, violet on standing		
	(b) Ruthenium(III) Complexes		
$Ru(H_2edta)acac\cdot2H_2O$	violet	1725 s, 1630 s, br	1520 s, 1540 s
$Ru(H_2edta)dmg\cdot2H_2O$	brown	1725 s, 1610 s	3200 s, 985 ms
$[Ru(H_2edta)(NCS)_2]K\cdot2H_2O$	dark red	1725 s, 635 s, br	2100, 2068 s, 705 w, br (?)
$[Ru(edta)(dtc)]Na_2\cdot nH_2O$	red powder	. . ., 1610	1520
	(c) Ester and Amide edta Complexes		
$Ru(Me_2edta)(py)_2\cdot2H_2O$	orange	1742 s, 1615 s, br	1560 s, 1480
$[Ru(Meedta)CO]K\cdot H_2O$[e]	yellow	1735 s, 1620	1940
$Ru((p\text{-}tol)_2edta)(py)_2\cdot nH_2O$	yellow	1720,[f] 1620 s, br	3170, 1560 s, 1515 ms

[a] Abbreviations for ligands used throughout paper: py = pyridine; 4-Mepy = 4-methylpyridine; phen = 1,10-phenanthroline; bpy = 2,2'-bipyridine; dmg = dimethylglyoximate; dppe = 1,2-bis(diphenylphosphino)ethane; acac = acetylacetonate; dtc = diethyldithiocarbamate; edta = ethylenediaminetetraacetate; H_2edta and Hedta = diprotonated and monoprotonated edta; Me = methyl; *p*-tol = *p*-toluidide. [b] First figure is stretch of free carboxylic arm of edta; second figure is asymmetric stretch of coordinated carboxylate arm. [c] s = strong, w = weak, br = broad, shp = sharp, and sh = shoulder. [d] Only important, characteristic bands due to the ligand are given. [e] In [Ru(Hedta)CO]K corresponding bands are at 1725 s, 1600 s, br, and 1940 s cm^{-1}.[1] [f] Due to $Ru(H_2edta)(py)_2$ contaminant.

ever, because of the instability of diethyldithiocarbamate in acid solutions, the complex isolated could not be completely characterized although it was shown to contain coordinated diethyldithiocarbamate and to have a magnetic moment of 1.6 μ_B by the Gouy method.

The complexes of $Ru^{II}(H_2edta)$ and $Ru^{III}(H_2edta)$ with these ligands are shown in Table I together with the infrared absorptions in the carbonyl region, which are characteristic of the coordinated carboxylate and free carboxylic functions of edta, and significant ligand absorptions. The structures are proposed on the basis of analytical figures and infrared spectra of the solids as well as their properties in solution, including electrochemical behavior, which are discussed below.

The complexes described above, together with those in a previous paper,[1] permit us to form a concise picture of the coordination chemistry of Ru(Hedta)L and $Ru(H_2edta)L_2$. In these compounds the metal can be in the oxidation state of +2 and/or +3 depending on the nature of the ligand L, which can cover the range from π-acceptors such as CO and N_2, organonitriles, and mono- and bidentate aromatic nitrogen bases to anionic ligands capable of σ- and π-donation.
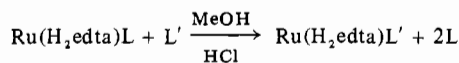
The influence of electron-withdrawing ligands in stabilizing the oxidation state of +2 ruthenium compounds and particularly in the substituted ruthenium(II) ammines is well-known.[10] It is not surprising, therefore, that an analogous situation exists in the Ru(edta)L complexes. Thus, when L was an electron-withdrawing ligand, only the ruthenium(II) complexes could be prepared. Conversely, with ligands that are capable of σ- and π-donation, both the ruthenium(II) and ruthenium(III) complexes were formed, with only the latter, however, being stable and well characterized.

The facile formation of these complexes by ligand substitution on $Ru^{II}(Hedta)H_2O^-$ and $Ru^{III}(Hedta)H_2O$ can be attributed to the lability of the aquo ligand. This is especially so in the case of the oxidation state +3, where substitutions proceed through an associative path and can be several times faster than in the corresponding aquoammine systems.

Matsubara and Creutz[2] attribute this both to the ability of the free glycinate arm to hydrogen bond to the aquo ligand and to the incomplete d shell present in the d^5 configuration of the metal atom. Substitution on the +3 complex also provides a ready mechanism for the formation of the ruthenium(II) complexes because of the facile electron transfer between the two oxidation states and the presence of excess reducing agent. However, with ligands that are unlikely to substitute on aquoruthenium(III) such as CO and N_2, a direct substitution on the aquoruthenium(II) complex is the more likely path. The further substitution on an adjacent site by another ligand molecule or by the second donor atom of a bidentate ligand presents no problem, even if this requires the displacement of the coordinated glycinate arm, as it is known that carboxylate ligands on ruthenium(II) complexes aquate readily in acid solution.[11] With CO, N_2, and NO^+ only one coordination position is occupied in spite of the presence of the ligand in excess. The reasons for this could be kinetic as the rate of substitution of the aquo ligand in *cis*-Ru^{II}-$(NH_3)_4(OH_2)L$ is slower when L is a π-acceptor than when it is a σ-donor.[12] In addition ruthenium(II) ammines containing two strong π-acceptors such as CO or N_2 either are very unstable or have not been prepared.[13]

Substitution Reactions. The complexes $Ru(H_2edta)L_2$ (where L = pyridine, C_6H_5CN) can be used to provide an alternative route for the preparation of several of the compounds that were obtained by direct substitution on the aquo complex. Advantages of this method are the absence of alkali chloride as a byproduct and the possibility of using solvents other than water as the reaction medium. The reaction proceeds only in acidified media and requires elevated temperatures for convenient rates. Refluxing in methanol acidified with concentrated HCl was found to be an effective way of carrying out the reaction. With these conditions, the following results were obtained:

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$$\text{Ru}(\text{H}_2\text{edta})\text{L} + \text{L}' \xrightarrow[\text{HCl}]{\text{MeOH}} \text{Ru}(\text{H}_2\text{edta})\text{L}' + 2\text{L}$$

L'	observation
1,10-phenanthroline 2,2'-bipyridine NO	complete reaction
acetylacetone dimethylglyoxime	ruthenium(III) complex formed
N$_2$O triphenylphosphine	starting material plus oxidation product
CO	mixture of carbonyl products

Reactions of the Uncoordinated Carboxylic Acid Function in Ruthenium(II) edta Complexes. The ability of the free carboxylic acid function in ruthenium edta complexes to undergo esterification and amidation reactions was investigated by using complexes that are soluble in methanol. The most suitable proved to be Ru(H$_2$edta)(py)$_2$ and [Ru(Hedta)-CO]K·2H$_2$O, while some evidence of reaction was obtained with the phenanthroline and bipyridine complexes. Reaction with an ethereal solution of diazomethane gave compounds that are formulated in Table I as the methyl esters on the basis of analysis, infrared spectra of the solids, and their properties in solution. Reaction of the pyridine complex with *p*-toluidine in methanol gave a product that was a mixture of the starting material and the ditoluidide, as deduced from the ^{1}H NMR spectra described below.

However, extension of the reactions of the carboxylic acid group to other systems was disappointing, yielding intractable oils and mixtures of compounds. This was due largely to the instability of the products toward hydrolysis and the difficulty in achieving anhydrous conditions in reactions in which the starting materials are hydrates or, as in the amidation reaction, in whcih water is formed during the reaction.

Vibrational Spectra of the Complexes. The vibrational spectra of the complexes have provided information about the structure of the complexes in three respects: the presence of lattice water, the coordination of the edta moiety, and the presence of the ligand L in the complex.

All the complexes prepared were found to contain lattice water, in most cases two molecules, giving rise to a broad ν(OH) absorption in the range 3300–3400 cm^{-1}, indicating extensive hydrogen bonding.

The most prominent absorptions associated with the edta moiety are the carbonyl stretches of the carboxylic acid function and the symmetric and asymmetric stretches of the coordinated carboxylate groups. The complexes formulated as containing uncoordinated carboxylic acid arms exhibit intense broad absorptions at 1725–1730 cm^{-1}. In the case of Ru(H$_2$edta)(dppe) and Ru(H$_2$edta)(bpy), which could be obtained as microcrystalline solids, this peak was split into two with a separation of about 40 cm^{-1}. The position of the bands suggests intramolecular hydrogen bonding comparable in extent to that found in dimeric carboxylic acids (e.g., 1720–1760 cm^{-1})[14] and considerably less than the intermolecular hydrogen-bonding interactions found in the uncoordinated molecule (e.g.: Na$_2$H$_2$edta·2H$_2$O, ν(CO) = 1675 cm^{-1}; H$_2$edta·0.5H$_2$O, ν(CO) = 1690 cm^{-1}).[15] The asymmetric ν(CO) of the coordinated carboxylate ranges from 1580 to 1640 cm^{-1}, and the energy of the band is believed to depend on the covalent character of the metal to carboxylate group bond.[16] The symmetric stretches of the coordinated carboxylate are less sensitive to the mode of bonding and are observed in the range 1350–1450 cm^{-1}. Esterification of the carboxylic acid function

increases the ν(CO) of the free carboxylic acid arm and, to a greater extent, the frequency of the asymmetric stretch of the coordinated carboxylate, indicating the loss of a hydrogen-bonding interaction between the two.

The ligand vibrations provide little information other than to confirm the presence of the ligand in the complex. In [Ru^{III}(H$_2$edta)(NCS)$_2$]K·2H$_2$O the ν$_1$ mode of the ligand[17] is clearly visible and split both in Nujol mull and in methanolic solution; this suggests a cis arrangement for the ligands, as was found in the Ru^{III}(H$_2$edta)(RCN)$_2$ complexes.[1] The ν$_3$-(SCN) stretch in complexes normally appears in the range 700–860 cm^{-1}, the low end of the range indicating coordination through the sulfur atom;[17,18] because of the occurrence of many other bands in this region, assignment is difficult. However, comparison with the spectrum of [Ru^{III}(H$_2$edta)Cl$_2$]K·H$_2$O suggests that a weak broad band at 705 cm^{-1} may be due to the ligand. Such a low value would suggest coordination through the S atom although this would appear unlikely in view of the structure of [Ru(NH$_3$)$_5$NCS]$^{2+}$, where the ligand is believed to be attached through the nitrogen atom.[19]

In the dimethylglyoximato complex the second ν(OH) at 3200 cm^{-1} is assigned to the hydroxyl group of the oxime ligand, i.e. at the same frequency at which it is observed in the uncoordinated ligand. Obviously in this compound there is not the opportunity for the strong hydrogen bonding that produces the large shifts to lower energies in complexes containing two such ligands in the same plane.[20,21]

Electronic Spectra. The electronic spectra of the ruthenium(II) and ruthenium(III) edta complexes contain bands that in most cases can be interpreted as arising from one or more of the following types of transitions: (i) intraligand, (ii) metal to ligand charge transfer (MLCT), (iii) ligand to metal charge transfer (LMCT), and (iv) ligand field. In the cases where tetraammine or pentaammine complexes of ruthenium containing the same ligand L are known, their spectra show strong similarities with those of the edta complexes and can be used to assign bands.[1] The spectra of the complexes prepared together with those of some related ruthenium complexes are given in Table II.

Ru^{II}(H$_2$edta)L$_2$ (L = py, 4-Mepy) and Ru(Me$_2$edta)(py)$_2$ have spectra similar to that of *cis*-Ru(NH$_3$)$_4$(py)$_2$$^{2+}$; with use of the assignments made by Ford,[22] the high-energy bands are attributed to a π–π* intraligand transition showing a hypsochromic shift on coordination, while the band at low energy is assigned to MLCT. There is a small hypsochromic effect in this band when L = Mepy, consistent with the inductive effect of the 4-methyl substituent. Similar shifts have been observed in ruthenium(II) ammines containing substituted pyridines.[22,10] Esterification of the free carboxylic acid function produces no appreciable change in the spectrum.

The complexes Ru(H$_2$edta)L (L = phen, bpy) have spectra typical of coordinated 2,2'-bipyridine and 1,10-phenanthroline. The correct number of π–π* intraligand bands are present,

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and they show the small red shift expected on coordination.[28] In addition, for L = bpy, the absorption at 290 nm is split by about 1000 cm^{-1}, as is normally observed on coordination.[28] The low-energy bands are MLCT, characteristic of these ligands when coordinated to metals of low oxidation state.[28,29] The spectra are very similar to those of the corresponding tetraammine complexes (see Table II). The complexes Ru^{II}(H$_2$edta)L (L = dppe, acac) have low-energy bands that are attributed to ligand field transitions by analogy to similar bands in the range 350–425 nm found in Ru^{II}(edta)L complexes.[1] The band at 270 nm in the acac complex is probably a π–π^* intraligand transition.[30] The ruthenium(II) complexes where L = SCN$^-$ or dmg have intense bands at 465 and 635 nm. These, because of their low energy and high intensity, are unlikely to be ligand field bands nor are they likely to be metal to ligand charge-transfer bands as the ligands are negatively charged.

The ruthenium(III) complexes that have been prepared contain L = acac, SCN$^-$, dtc, and dmg in the two positions not occupied by the edta moiety. These ligands are negatively charged and contain donor atoms capable of σ- and π-donation; moreover, the first three are known to give rise to intense LMCT when coordinated to Fe(III).[31-33] Acetylacetonate,[25] dithiocarbamates,[24] and thiocyanate[23] are also known to give rise to similar bands in ruthenium(III) complexes. For these reasons the low-energy band in each case is assigned to a similar charge transfer. In the case where L = acac, the spectrum is very similar to that of Ru(acac)$_3$ (see Table II), in which the bands at 270 and 350 nm have been assigned to LMCT.[25]

Thus, it can be seen that the presence of π-acceptor ligands in the ruthenium(II) edta complexes not only stabilizes the +2 oxidation state but also give rise to MLCT bands in their spectra because of the acceptor properties of the ligands. Conversely, ligands that give rise to complexes in the +3 oxidation state because of their σ- and π-donor ability also give rise to charge-transfer bands in the spectra but in the reverse direction. As a consequence of this, most of the complexes examined have characteristic absorptions in the visible region, which arise from the specific interaction of the ligand L with the ruthenium atom in its appropriate oxidation state. Because such bands are not present in the parent aquo complexes or in the ligands, it is convenient to use spectrophotometric techniques to study the formation of the complexes, e.g. in the ruthenium(III) thiocyanate system. Similarly, their reactions in which the ligand L is replaced or a change in the oxidation state of the metal takes place can be followed in the visible region.

Solution Properties. All the complexes, with the exception of Ru(H$_2$edta)(dppe), were found to be soluble in water. Dilute solutions were unstable to varying degress; e.g., Ru-(H$_2$edta)(py)$_2$ lost 20% of the absorbance of the low-energy absorption band in 45 min, while peaks characteristic of free pyridine gradually appeared at 250, 255, and 263 nm. Similar aquation reactions were observed with the other ruthenium(II) complexes but proceeded at a slower rate when the two cis positions were occupied by a bidentate ligand. Solutions in aqueous potassium carbonate, which presumably contained the [Ru(edta)L]$^{2-}$ ion, were less stable than in acid although
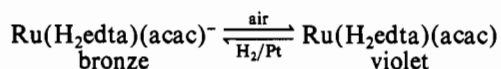
still satisfactory for the recording of proton NMR spectra. Most of the complexes were also soluble in methanol, forming stable solutions. Trifluoroacetic acid solutions were very useful for NMR experiments although, in these solutions too, decomposition of the complex was eventually observed.

Aquation was also observed in the ruthenium(III) complexes: the reactions of the thiocyanate complex are discussed in some detail below. In Ru(H$_2$edta)(acac) the absorbance of the low-energy band decreased by 40% in 30 min; at the same time the molar conductance also decreased, suggesting aquation according to

$$Ru(H_2edta)(acac) \rightleftharpoons Ru(Hedta)H_2O + acacH$$

The ease with which the ligands are replaced by water in these complexes appears to be greater than when the same ligands are present in other ruthenium(III) complexes. It seems that the same mechanism that facilitates substitution of the aquo ligand in Ru(Hedta)H$_2$O[2] may also operate in the reverse reaction. Thus, aquation reactions of Ru^{III}(Hedta)L are much faster than in the corresponding ammine complexes. Examples of this are the rapid dissociations of [Ru^{III}(H$_2$edta)X$_2$]K (X = Cl$^-$, SCN$^-$) and Ru(H$_2$edta)(NO)Cl[1] that take place when the complexes are dissolved in water, in contrast with the behavior of analogous ammine complexes.[34,35] With ligands of higher pK_a such as acac and dmg, the possibility also exists for the protonation of the ligand by the pendant carboxylic acid group, which is well placed for such an internal proton-transfer reaction. Similar considerations probably apply to the ruthenium(II) complexes, which seem to undergo aquation reactions more easily than compounds such as Ru(NH$_3$)$_4$L$_2$$^{2+}$, where L = py or RCN.[10]

Solutions of the ruthenium(II) complexes were also unstable toward oxidation. Exposure to air accelerated decomposition because of the oxidation of Ru(Hedta)H$_2$O$^-$. However, in the complexes Ru^{II}(H$_2$edta)L, where L = acac, dmg, and SCN$^-$, oxidation to the corresponding ruthenium(III) complexes was observed. In the case of L = dmg, the conversion was quantitative on allowing the solution to stand overnight in air. With the very unstable and not fully characterized L = acac complex, the reaction was reversible according to

$$\underset{\text{bronze}}{Ru(H_2edta)(acac)^-} \underset{H_2/Pt}{\overset{air}{\rightleftharpoons}} \underset{\text{violet}}{Ru(H_2edta)(acac)}$$

The dark green Ru^{II}(Hedta)(NCS)$^{2-}$ complex could also be converted quantitiatively to the corresponding ruthenium(III) complex by aerial oxidation. The characteristic peak at 635 nm, which was stable under N$_2$, was replaced on exposure to air by a new peak at 465 nm with an isosbestic point at 540 nm. The ruthenium(II) complex was also found to be remarkably sensitive to copper(II) ions: this was first noted when metal syringes were used to dispense solutions under dinitrogen. The effect of added copper(II) ions was to replace the maximum at 635 nm by a new maximum at 560 nm with an isosbestic point at 595 nm. Eventually the ruthenium(III) thiocyanate complex was formed.

Conductance measurements in dilute aqueous solution and pH titration of the complexes with sodium hydroxide have provided confirmation for the ionic charges of the complex ions and for the protonation of the free arms of the ligand, as proposed on the basis of microanalysis and infrared spectroscopic data. The results are summarized in Table II.

The two acid functions in complexes of the type Ru-(H$_2$edta)L give rise to a molar conductance of about 200 S cm^2 at a concentration of 0.001 mol dm^{-3}. The molar con-

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Table II. Electronic Spectra, Molar Conductance, and Neutralization Equivalents of $Ru^{II}(H_2edta)L$ and $Ru^{III}(H_2edta)L^n$

complex	λ_{max}, nm	molar absorptivity, mol^{-1} dm^3 cm^{-1} $\times 10^3$	concn $\times 10^3$, mol dm^{-3}	Λ_M,[a] S cm^2	H^+:Ru molar ratio	pK_a(av)
		Ruthenium(II) Complexes				
Ru(H₂edta)(py)₂	⌈245	8.5		217	1.9 ± 0.2	3.0
	⌊263 sh	3.2		12[b]		
	368	7.9		10[c]		
	⌈245[b]	8.3				
	⌊260 sh	2.8				
	375	8.2				
Ru(H₂edta)(4-Mepy)₂	⌈245	8.2				
	⌊260 sh	4.2		220	2.0 ± 0.1	3.0
	360	7.2				
	⌈241[b]	8.7		13[b]		
	⌊260 sh	4.0				
	370	7.7				
Ru(Me₂edta)(py)₂	⌈245	9.1				
	⌊260	3.1				
	365	8.2				
Ru(H₂edta)phen	226	28.0	1.0	190	2.0 ± 0.1	3.0
	⌈272	37.0	0.71	225		
	⌊292 sh	12.0	0.49	242		
	465	6.4	0.25	265		
			0.12	325		
			0.06	360		
Ru(H₂edta)bpy	242	11.0				
	⌈284 sh	20.0				
	⌊293	28.0		187	1.8 ± 0.1	2.7
	352	6.1				
	505	4.1				
Ru(H₂edta)dppe	⌈232[b]	39.0		*f*		
	⎮267 sh	5.7				
	⌊274 sh	4.8				
	332	2.6				
	398	0.65				
[Ru(H₂edta)(dmg)]K	465[d]	3.5				
	295[e]	2.8				
	360[e]	2.1				
	470[e]	1.4				
[Ru(Hedta)(SCN)]⁻	635[d]	ca. 0.5				
[Ru(H₂edta)acac]⁻[g]	220[d]	4.2				
	⌈270	4.0				
	⌊340 sh	0.65				
		Ruthenium(III) Complexes				
Ru(H₂edta)dmg	295	2.5		234	2.0 ± 0.1	2.9
	360	2.3				
	470	1.3				
[Ru(H₂edta)(NCS)₂]K	295[h]	3.0		557	2.0 ± 0.1	2.7
	360	0.89				
	486	2.7		620[j]	ca. 1	7.2
	482[l]	3.1				
	505[m]	2.7				
Ru(H₂edta)acac	240[b]	4.0				
	288	8.4,[i] 6.8[j]		254	1.8 ± 0.1	2.7
	332	4.1, 3.1		240[k]		
	520	0.6, 0.5				
[Ru(edta)dtc]Na₂	235	15.0		285		
	335	2.2				
	445	0.60				
	525	0.67				
		Related Ruthenium Complexes				
cis-[Ru(NH₃)₄(py)₂]²⁺	245	7.24		ref 22		
	⌈375 sh	6.45				
	⌊410	7.94				
trans-[Ru(NH₃)₄(py)₂]²⁺	245	8.51		ref 22		
	423	16.6				
[Ru(NH₃)₅NCS]²⁺	278	0.21		ref 23		
	321	0.40				
	496	3.62				
Ru(Me₂dtc)₃	362, 399 sh	8.32		ref 24		
	464	2.40				
	558	1.52				
Ru(acac)₃	205	16				
	270	18		ref 25		
	250	16				
	520	ca. 2				

Table II (*Continued*)

complex	λ_{max}, nm	molar absorptivity, mol^{-1} dm^3 $cm^{-1} \times 10^3$	concn $\times 10^3$, mol dm^{-3}	Λ_M,[a] S cm^2	H^+:Ru molar ratio	pK_a(av)
[Ru(NH$_3$)$_4$(bpy)]$^{2+}$	244	10				
	286	21.4		ref 26		
	294	32				
	367	5.7				
	523	3.5				
[Ru(NH$_3$)$_4$(phen)]$^{2+}$	265	35		ref 27		
	471	6.7				

[a] Molar conductance at 20 °C of a 0.001 M solution unless otherwise stated. [b] In methanol. [c] In dimethylformamide. [d] Under dinitrogen. [e] On standing overnight in air. [f] Insoluble. [g] Solid not characterized; bronze solid from copper-colored solution. Spectrum has same absorption maximum as Ru(H$_2$edta)acac reduced by H$_2$/Pt from which solution molar absorbances were determined. [h] In 4.0 M potassium thiocyanate. [i] Initial molar absorbances in aqueous solution. [j] After 30 min. [k] After 12 h. [l] In acetone. [m] In ethanol. [n] Figures bracketed together indicate complex absorption bands with peaks at wavelengths indicated. All measurements in aqueous solution unless otherwise stated.

ductance depends on concentration in a manner characteristic of weak electrolytes, as can be seen from the values of Ru-(H$_2$edta)(phen). Similar behavior was found in Ru-(H$_2$edta)(CH$_3$CN)$_2$.[1] The two acid functions titrate with a single inflection point corresponding to 2:1 H$^+$:Ru and with an average pK_a value of 2.7–3.0. In [Ru^{II}(H$_2$edta)(dmg)]K the Λ_m value is 300 S cm^2 corresponding to the value of a 1:1 electrolyte plus the contributions from the carboxylic acid functions. Ru(Me$_2$edta)(py)$_2$ showed initially a low value expected from a nonelectrolyte that, however, increased rapidly on standing due to hydrolysis. High values were also obtained with aged samples immediately on dissolution. Values higher than what is expected for 1:1 electrolytes were obtained from [Ru^{II}(Meedta)CO]K because of the presence of hydrolysis products. Conductance measurements of aqueous solutions of [Ru(H$_2$edta)(NCS)$_2$]K·2H$_2$O indicate that coordinated SCN$^-$ is being replaced by water. The molar conductance (Table II) is not as high as the Λ_m (0.001 M) for [Ru-(H$_2$edta)Cl$_2$]K·H$_2$O (741 S cm^2),[5] which suggests that unlike the chloro complex, the thiocyanato complex is not completely ionized, although ionization increases with time. Titration of an aqueous solution of the parent compound with base gives two end points. The first (pK_a(av) = 2.7) corresponds to 2:1 H$^+$:Ru; the second more diffuse end point (pK_a = 7.2) corresponds to the proton of a coordinated water. The latter is consistent with Ru(Hedta)H$_2$O being formed eventually.

Aquation of Ru^{III}(H$_2$edta)(NCS)$_2^-$. The displacement of the thiocyanate ligands by water is also evident in the spectra of the complex in various media. Thus, in the presence of high thiocyanate concentrations or in nonaqueous solvents, the complex appeared to be stable and undissociated (Table II). However, the spectrum of the solid in water, determined immediately after dissolution, had a visible absorption maximum at 468 nm (molar absorptivity 1.2 $\times$ 10^3 mol^{-1} dm^3 cm^{-1}). With time, the visible absorption decreased and the color faded from pink to yellow; addition of thiocyanate restored the red color to an intensity greater than that of the original band. These observations are consistent with the presence of the equilibria shown in eq 1 and 2. In the absence of excess SCN$^-$

$$Ru(H_2edta)(NCS)_2^- \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}}$$
$$Ru(H_2edta)(NCS)(H_2O) + SCN^- \quad fast \quad (1)$$

$$Ru(H_2edta)(NCS)(H_2O) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}}$$
$$Ru(Hedta)H_2O + SCN^- + H^+ \quad slow \quad (2)$$
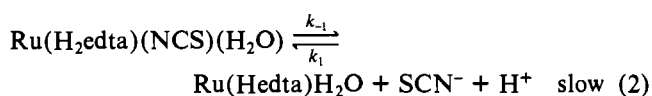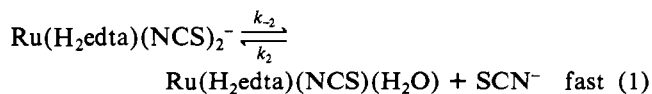
reaction 1 proceeds to the right immediately on dissolving the solid while equilibrium 2 is established more slowly. The formation of the complexes according to the equilibrium 1 and
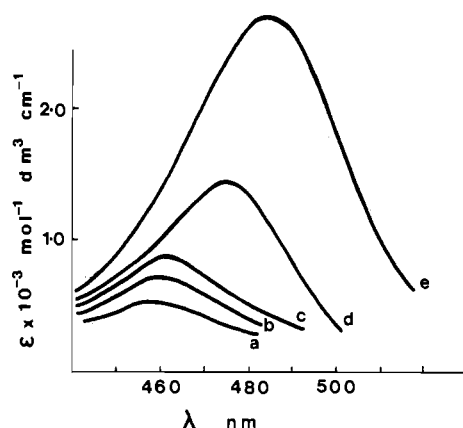

Figure 1. Visible spectrum of Ru(Hedta)H$_2$O (concentration 5.35 $\times$ 10^{-4} mol dm^{-3}) in the presence of increasing concentrations of thiocyanate ions. [SCN$^-$] (mol dm^{-3}): a, 5 $\times$ 10^{-4}; b, 5 $\times$ 10^{-3}; c, 5 $\times$ 10^{-2}; d, 0.5; e, 2.0.

2 was also demonstrated by recording the spectra of Ru-(Hedta)H$_2$O in the presence of increasing concentrations of thiocyanate. The spectra, shown in Figure 1, are consistent with a mono(thiocyanato) species, formed at low concentrations (λ_{max} ca. 460 nm; molar absorptivity ca. 1.0 $\times$ 10^3 mol^{-1} dm^3 cm^{-1}), and a bis(thiocyanato) species (with the same spectral characteristics as [Ru^{III}(H$_2$edta)(NCS)$_2$]K·H$_2$O), formed at high concentrations. Matsubara and Creutz[2] also established the sequential formation of two thiocyanato complexes. However, the rate constants estimated by them for the dissociation of the two species, i.e. $k_{-2} = 1.6 \times 10^{-3}$ s^{-1} and $k_{-1} = 0.5$ s^{-1}, are in conflict with our qualitative observations. Their values suggest that the second thiocyanate ligand is lost faster than the first and that, consequently, simultaneous rather than consecutive dissociation of the complex should be observed.

NMR Spectra. The main purpose in determining the ^{1}H NMR and ^{13}C NMR spectra of the complexes was to obtain information concerning the stereochemical arrangement of the ligands in the complexes. At the same time, of course, the presence of the ligand in the complexes was established and additional confirmation was obtained for the proposed formulations of the complexes.

In general, ^{1}H NMR spectra produced little information of structural value because of the complexity of the incompletely resolved signals, which, in addition, were often broadened in acid solution.[36] By contrast, the ^{13}C NMR

(36) (a) Sudmeir, J. L.; Reilley, C. N. *Inorg. Chem.* **1966**, *5*, 1047. (b) Reed, G. H.; Kula, R. J. *Ibid.* **1971**, *10*, 2050.

Table III. Proton NMR Spectra of Some Ruthenium(II) edta Complexes

complex	major peaks rel to Me₄Si, ppm
Ru(H₂edta)(py)₂·2H₂O in TFA[a,b]	3.3, 3.7, 3.8, 4.1, 4.5 (edta)
	6.9, 7.0, 7.1, 7.5, 7.8, 8.1 (aromatic)
rel ratio	edta:py 12:9.5[c]
in D₂O/K₂CO₃	3.2, 3.5, 3.7, 3.9, 4.0, 4.2 (edta)
	7.2, 7.3, 7.4, 7.6, 7.8, 7.9, 8.5, 8.6 (aromatic)
pyridine in TFA	7.8, 7.9, 8.0, 8.3, 8.5, 8.6
Ru(H₂edta)(4-Mepy)₂·2H₂O in TFA[b]	2.0 s (Me), 3.3, 3.8, 4.1, 4.5 (edta)
	6.8, 6.9, 7.8, 7.9 (aromatic)
rel ratio	Me:edta:aromatic 6:12:~8[c]
4-methylpyridine in TFA	2.5 (Me), 7.6, 7.7, 8.3, 8.4, 8.5 (aromatic)
Ru(Me₂edta)(py)₂·2H₂O in CDCl₃	3.2, 3.3, 3.5, 3.7 s (Me), 4.0, 4.1, 4.2, 4.3 (Me₂edta)
	7.0, 7.2, 7.4, 7.5, 7.7, 8.5, 8.6 (aromatic)
rel ratio	Me₂edta:py 18:10
Ru((p-tol)₂edta)(py)₂·nH₂O in CDCl₃/TFA[b]	2.1 s (Me), 3.4, 3.5, 3.9, 4.2, 4.5 (edta)
	6.9, 7.0, 7.5, 8.2 (aromatic)
rel ratio	edta:Me ~12:3
Ru(H₂edta)phen·2H₂O in TFA[b]	3.5, 3.9, 4.3, 7.3, 7.6, 8.0
in D₂O/K₂CO₃	3.6, 3.7, 3.8, 4.0, 4.2, 4.3, 4.5 (edta)
	7.1, 7.8, 9.9 (aromatic)
rel ratio	edta:phen 12:8
Ru(H₂edta)bpy·2H₂O in TFA[b]	3.6, 4.1, 4.4, 7.3, 7.6, 7.8, 8.0
in D₂O/K₂CO₃	3.4, 3.7, 3.8, 4.1, 4.3, 4.6 (edta)
	7.5, 7.7, 7.8, 7.9 (aromatic)
rel ratio	edta:bpy 12:8
[Ru(H₂edta)(dmg)]K·H₂O	2.1 (Me), 3.3, 3.6, 3.8, 4.1
[Ru(Meedta)CO]K·2H₂O in D₂O	3.5, 3.8 (Me, prominent peak), 3.9, 4.0, 4.2, 4.4

[a] Trifluoroacetic acid. [b] Broadened spectrum. [c] Integration not accurate due to proximity of TFA peaks. [d] s = singlet.

spectra have been shown to be more useful in this type of study.[1] However, the requirements of a high concentration

and of long periods of accumulation of data restricted the number of complexes that could be studied in this way because of the difficulty in finding solvents in which the complexes were both soluble and stable.

The results of the proton NMR spectra are summarized in Table III. In all cases, and within the limitations stated in the table, the spectra confirm the ratio between the protons of edta and those of the ligand, in agreement with the formulations. Decomposition to form the free ligand was observed in the case of Ru(H₂edta)(py)₂. In the case of the 4-methylpyridine analogue, a single methyl resonance at 2.0 ppm indicated equivalent environments for the two methyl groups. The methylation of the free carboxylic acid function in the complexes Ru(Me₂edta)(py)₂ and Ru(Meedta)CO⁻ was clearly seen in the spectra. In the former case, again a single resonance was observed from the two methyl groups. The product of the amidation reaction was shown to be a mixture and appeared to contain the toluidine to the extent of about 60%, the other substances present being complexes containing coordinated edta.

The complexes, which were formulated as ruthenium(III) compounds in Table I, gave broad signals as expected from paramagnetic molecules containing a ruthenium d⁵ metal atom.

Satisfactory ¹³C NMR spectra were obtained only for the complexes Ru(H₂edta)L, where L = (py)₂, bpy, and phen. The pyridine complex was investigated in trifluoroacetic acid solution, although it did show slow decomposition and the production of uncoordinated pyridine. The phenanthroline and bipyridine complexes were extensively decomposed in this solvent, showing sharp resonances due to free edta together with weaker, broader peaks due to the aromatic α-diimine ligands. This problem was overcome by recording the spectra of the complexes in their unprotonated forms in deuterium oxide neutralized with potassium carbonate to obtain intensely red-brown solutions containing the Ru(edta)L²⁻ ion.

The results are shown in Table IV, together with the resonances of the free ligands. The peaks of coordinated edta have been assigned by comparison with other ruthenium(II) edta complexes.[1] The assignment of the ligand resonances was made by comparison with the spectra of known heterocyclic and polycyclic aromatic systems.[37,38] In such compounds the

Table IV. ¹³C NMR Chemical Shifts[a] in Some Ru(H₂edta)L Complexes and Free Ligands L

phen   py   bpy

complex	carboxylate axial	carboxylate free	methylenic axial	methylenic free	ethylenic	ligand			solvent
Ru(H₂edta)(py)₂	188.9	172.6	65.0	63.4	60.2	155.5 (Cα)	138.7 (Cβ)	127.4 (Cγ)	TFA
pyridine (free)[b]						148.3 (Cα)	142.1 (Cβ)	128.8 (Cγ)	TFA
pyridine (from decompn of complex)						149.5	143.4	129.4	TFA
Ru(edta)bpy²⁻	185.2	175.4	64.4	60.7	57.5	161.6 (Cε)	136.3 (Cγ)	123.4 (Cδ)	D₂O/K₂CO₃
						155.7 (Cα)	125.9 (Cβ)		
bipyridine[c]						156.2 (Cε)	138.1 (Cγ)	122.0 (Cδ)	D₂O/methanol
						149.5 (Cα)	124.6 (Cβ)		
Ru(edta)phen²⁻	185.2	175.4	64.8	60.6	57.6	156.6 (Cα)	135.0 (Cβ)	127.1 (Cγ)	D₂O/K₂CO₃
						151.6 (Cε)	129.8 (Cδ)	124.6 (Cζ)	
phenanthroline[c]						146.6 (Cα)	136.4 (Cβ)	127.1 (Cγ)	TFA
						141.8 (Cε)	129.6 (Cδ)	125.3 (Cζ)	
Ru(H₂edta)phen		172.6		57.0	54.0				TFA

[a] In ppm relative to Me₄Si, 1,4-dioxane used as internal reference. [b] As the pyridinium ion. See also ref 37. [c] Assignments other than for Cα and Cε are tentative.
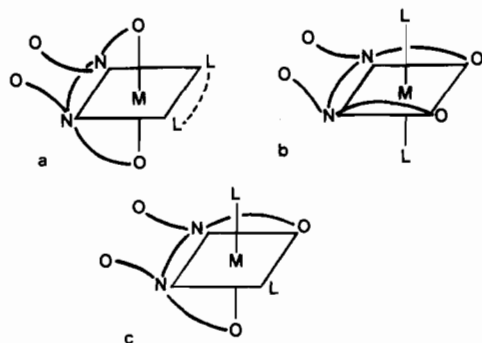
Figure 2. Some geometric isomers of four-coordinate edta with ligand L occupying remaining positions: a, cis equatorial; b, trans axial; c, cis arrangement of L in a nonsymmetric complex.

Table V. Half-Wave Potentials of Ruthenium edta Complexes[a]

complex	$E_{1/2}{}^{b,c}$	$E^{b,d}$	$i_p{}^a/i_p{}^c$	$\Delta E_p{}^b$
Ruthenium(II) Complexes				
Ru(Hedta)(CO)$^-$	>0.85	−0.5		
Ru(H$_2$edta)(NO)Cl	>0.85	−0.5		
Ru(H$_2$edta)(1,2-C$_6$H$_4$(CN)$_2$)$_2$,[e]	0.65	−0.3, −0.6		
Ru(H$_2$edta)(C$_6$H$_5$CN)$_2$	0.51	−0.3, −0.6		
Ru(H$_2$edta)(CH$_3$CN)$_2$	0.44	−0.3, −0.7		
Ru(H$_2$edta)phen, A[f]	0.31	−0.6	0.98	60
B[g]	0.30	−0.6	0.95	70
Ru(H$_2$edta)bpy, C[f]	0 33	−0.6	0.91	70
D[g]	0.35	−0.6	0.94	70
Ru(H$_2$edta)(py)$_2$, 0 °C	0.17	−0.6	0.94	60
25 °C	0.16	−0.6	0.92	80
Ru(Me$_2$edta)(py)$_2$	0.17	−0.6	0.99	80
Ru(H$_2$edta)(CH$_3$py)$_2$, 0 °C	0.12	−0.6	0.95	60
25 °C	0.13	−0.6	0.94	80
Ru(edta)(N$_2$)$^{2-}$	0.09			
(Ru(edta))$_2$N$_2{}^{4-}$	−0.15	−0.4		
Ruthenium(III) Complexes				
Ru(H$_2$edta)(NCS)$_2$$^-$	0.02	−0.6	1.0	65
Ru(H$_2$edta)(NCS)(H$_2$O)	−0.13	−0.6	0.95	70
Ru(Hedta)H$_2$O	−0.26	−0.6	1.0	65
Ru(Hedta)(N$_3$)$^-$	−0.32	−0.6		
Ru(H$_2$edta)dmg	−0.5			
Ru(H$_2$edta)acac	−0.5	−0.3		

[a] In 0.5 mol dm^{-3} KCl solution at 25 °C unless otherwise stated. Scan rates in the range 50–1000 mV/s. [b] $E_{1/2}$ and E_p in volts vs. SCE (±0.02 V). ΔE_p in millivolts. [c] For Ru(II) complexes $E_{1/2}$ refers to an anodic process; for Ru(III) complexes $E_{1/2}$ refers to a cathodic process. [d] Peak potential of other cathodic waves observed. [e] Low solubility in aqueous solution. [f] A and C were prepared according to method 1 (see Experimental Section). [g] B and D were prepared according to method 3 (see Experimental Section).

carbon atoms directly attached to the nitrogen are shifted to lower field compared with the other carbon members of the ring. In addition, bridgehead carbons fusing two ring systems give rise to the weakest signals because of the absence of nuclear Overhauser enhancement. These observations allowed the two peaks at lower field in the spectra of the α-diimine complexes to be assigned with certainty. The remaining peaks cannot be assigned with equal certainty except, of course, that they are unambiguously due to the α-diimine ligand. The resonances of the carbon atoms directly attached to the nitrogen atom experience an appreciable shift downfield on coordination. However, the stereochemical significance of the results lies in the total number of ^{13}C resonances observed: eight, ten, and eleven for L = (py)$_2$, bpy, and phen, respectively. The significance of this will be discussed below.

Coordination Geometry of Complexes. The complexes reported provide examples of edta acting as a quadridentate ligand; that is, two glycinate arms of the ligand are coordinated, two remain free, and two coordination positions on the metal are occupied by two monodentate ligands or one bidentate. Earlier it was shown that, when four coordination positions are occupied by edta, the number of possible isomers is 7. Arguments have been presented to suggest that the isomer which has two free equatorial glycinate arms is the most likely isomer of all. On the basis of ^{13}C NMR spectra and infrared and Raman spectra, this structure was proposed for Ru^{II}.(H$_2$edta)(CH$_3$CN)$_2$.[1]

In their ^{13}C NMR spectra, the complexes Ru^{II}(H$_2$edta)L, where L = phen or bpy, produced just half the number of possible ^{13}C resonances in each case. This indicates that the molecule possesses a C_2 axis of symmetry. As the two donor atoms in L can only occupy cis positions, the only possible arrangement is the cis equatorial (Figure 2). The ^{13}C NMR spectrum of Ru(H$_2$edta)(py)$_2$ shows eight sharp resonances for a molecule containing 20 carbons, the two pyridine ligands giving rise to only three peaks because of the symmetry within the pyridine moieties. The presence of a C_2 axis in the molecules is consistent with either a cis equatorial or a trans axial arrangement of the ligand (Figure 2), the NMR evidence being unable to distinguish between these two possibilities. Support for the cis configuration comes from the electronic spectrum which resembles more that of the *cis*-[Ru(NH$_3$)$_4$-(py)$_2$]$^{2+}$ rather than that of the trans isomer in having three absorption bands (Table II). In addition, the substitution of two pyridine ligands by phenanthroline and bipyridine under mild conditions is consistent with a cis arrangement of the monodentate ligands.

The three complexes of ruthenium(II) that contain methyl groups, i.e. Ru(H$_2$edta)(4-Mepy)$_2$, Ru(Me$_2$edta)(py)$_2$, and

(37) Strothers, J. B. "^{13}C-NMR Spectroscopy"; Academic Press: New York, 1972.
(38) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1973**, 841.

[Ru^{II}(H$_2$edta)(dmg)]$^-$, gave rise to ^{1}H NMR spectra in which a single methyl resonance was present. This indicates the presence of a C_2 axis in these complexes as well and suggests a cis equatorial or trans axial arrangement for the first two and a cis equatorial for the last. The other ruthenium(II) complexes that were prepared were too unstable or not sufficiently soluble for NMR examination.

NMR studies could not be undertaken with the ruthenium(III) complexes because of the paramagnetism of the molecules. The only evidence for a cis equatorial arrangement comes from the infrared spectrum of [Ru^{III}(H$_2$edta)(NCS)$_2$]K, which produced a strong split peak due to ν(CN) both in the solid and in methanolic solution. The two bands were assigned to a symmetric and an asymmetric stretch and hence to a cis arrangement of the ligands, although not necessarily cis equatorial. Within the seven possible arrangements for quadridentate edta there also exists several nonsymmetrical cis arrangements.[1]

In view of the well-established preference of quadridentate and pentadentate[1] edta to have free arms in the equatorial position, it is a reasonable assumption that all the quadridentate complexes prepared have the cis equatorial configuration.

Electrochemical Studies. The electrochemical oxidation and reduction behavior of the complexes that are reported in this paper, together with the complexes that were prepared in an earlier study,[1] was investigated by single-sweep and cyclic voltammetry in 0.5 M aqueous KCl. Because many of the complexes were stable ruthenium(II) species, the anodic processes were studied except for the compounds Ru(H$_n$edta)L (L = dmg, dtc, SCN$^-$, N$_3{}^-$) that were investigated as cathodic processes. The results, which were obtained, extend the range of reduction potentials reported by Matsubara and Creutz[2] for the pentacoordinated ruthenium(III) edta species and

Table VI. $E_{1/2}$ Potentials[k] (in V) of Some Ruthenium(III)/Ruthenium(II) Complexes and Energies of Lower MLCT Bands (in cm^{-1}) of Some of the Ruthenium(II) Complexes

ligand L	Ru(NH$_3$)$_4$L$_2$[j]	Ru(H$_2$edta)L$_2$[b,j]	Ru(NH$_3$)$_5$L	Ru(edta)L[j]
CO				>0.80[b] (52 000)[a]
N$_2$(terminal)			0.81[f,g]	0.09[b,g]
N$_2$(bridging)			0.46[f]	-0.15[b,g] (44 650)[a]
C$_6$H$_5$CN	0.62[c] (29 100)[c]	0.51 (30 300)[a]	0.23[c]	
CH$_3$CN		0.44 (47 650)[a]	0.18[c]	0.01[d]
bpy	0.27[h] (19 120)[h]	0.33 (19 800)		
phen	0.29[i] (21 230)[i]	0.31 (21 500)		
py	0.24[c] (24 400, 26 700 sh)[c]	0.17 (27 200)	0.05[c]	-0.15[d] (26 200)[d]
SCN$^-$		0.02	-0.11[e]	-0.13[b]
				-0.18[d]
H$_2$O			-0.18[c]	-0.24[c]
				-0.26[b]

[a] Reference 1. [b] This work. [c] Refernce 4. [d] Reference 2. [e] Reference 19. [f] Reference 41. [g] Anodic wave only. [h] Reference 26. [i] Reference 27. [j] Figures in parentheses are energies of MLCT bands. [k] $E_{1/2}$ potentials vs. SCE; values from other sources converted to this scale and approximated to two significant figures.

Figure 3. Cyclic voltammogram of Ru(H$_2$edta)phen·3H$_2$O in 0.5 mol dm^{-3} KCl solution (voltage sweep 200 mV/s).

complement an earlier investigation[4,19] of ruthenium(II) pentaammine and tetraammine complexes with heterocyclic aromatic and organonitrile ligands.

The $E_{1/2}$ values determined in this work are given in Table V. The range of values is limited on the positive side by the decomposition voltage of the supporting electrolyte at +0.8 V and on the negative side by a large irreversible peak at -0.7 V, which is associated with a lower, broad cathodic wave at about -0.5 to -0.6 V. Such waves are present in the voltammograms of almost all the compounds investigated, including that of uncoordinated Na$_2$H$_2$edta, and are probably due to the free carboxylic acid function, as they are not present in Ru(edta)N$_2$$^{2-}$, (Ru(edta))$_2N_2$$^{4-}$, and the system Ru(Hedta)H$_2$O/NaN$_3$ (excess) which produces high pH values. A typical cyclic voltammogram exhibiting these features is given in Figure 3. As a consequence of these limits, there is no differentiation between Ru(Hedta)CO$^-$ and Ru(H$_2$edta)-(NO)Cl, both of which are too stable to be oxidized at the potentials allowed by the supporting electrolyte. Similarly, the cathodic peaks due to Ru(H$_2$edta)L (L = acac, dmg, dtc) were observed at -0.5 V and could not be differentiated from the peak due to (H$_2$edta). The acac complex, in addition, shows a shoulder at -0.3 V probably due to Ru(Hedta)H$_2$O arising from the aquation of the complex as reported above.
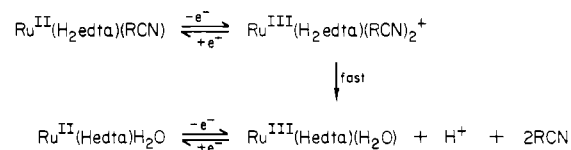
The reduction potentials of the metal complexes provide quantitative confirmation of the observations on the stability of the complexes toward oxidation deduced from the preparative and solution studies. On the basis of the $E_{1/2}$ values, the ability of the ligand to enhance the stability of the ruthenium(II) complexes toward oxidation is as follows: NO, CO > RCN > phen, bpy > py > N$_2$(terminal) > SCN$^-$ > N$_2$(bridging) > H$_2$O > N$_3$$^-$ > acac, dmg, dtc.

With the exception of the N$_2$, the ligands are in agreement with their expected electron-withdrawing and electron-donating abilities. Within groups of related ligands the effects of

electron-withdrawing or electron-releasing substituents are seen to effect the $E_{1/2}$ in the expected way. Thus, the $E_{1/2}$ of the complexes with L = RCN decrease in the sequence 1,2-C$_6$H$_4$(CN)$_2$ > C$_6$H$_5$CN > CH$_3$CN, in agreement with the electron-withdrawing effect of the substituents. In the pyridine ligands the $E_{1/2}$ are in the order H > 4-CH$_3$, in agreement with the electron-releasing effects of the methyl substituents in the 4-position. Similar substituent effects have been noted by Matsubara and Ford in the reduction potentials of Ru(NH$_3$)$_5$L^{3+}, where L = RCN or substituted pyridine.[4]

The relative electron-withdrawing effects of the ligands in the edta complexes are compared with their effect in analogous tetraammine and pentaammine complexes in Table VI. It should be noted that $E_{1/2}$ is greatly altered by the number of electron-withdrawing ligands substituted on the complex.[4] Thus, the monosubstituted species of Matsubara and Creutz[2] have appreciably lower $E_{1/2}$ than the disubstituted complexes with the same ligand. In general, and with the exception of L = bpy and phen, the edta complexes are easier to oxidize than the corresponding pentaammine or tetraammine compounds containing the same L. Except when L = N$_2$, the ligands have the same relative order in their stabilizing effect on the +2 oxidation state, whether substituted on the ruthenium ammine or the ruthenium edta complexes.

The complexes Ru(H$_2$edta)L, where L = bpy, phen, or (py)$_2$, showed reversible or quasi-reversible behavior. In the last case the voltammograms were ill-defined at room temperature but produced distinct, well-defined cathodic and anodic waves at 0 °C. However, irreversible behavior was observed in the case of Ru(H$_2$edta)(RCN)$_2$ where only the anodic wave was observed even at scan rates of 20 V/s. This could be explained as a strictly irreversible reaction or as an oxidation followed by a rapid consecutive reaction that consumed the oxidation product before it could be reduced. A likely scheme could be

$$\text{Ru}^{II}(\text{H}_2\text{edta})(\text{RCN}) \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{Ru}^{III}(\text{H}_2\text{edta})(\text{RCN})_2{}^+$$

$$\downarrow \text{fast}$$

$$\text{Ru}^{II}(\text{Hedta})\text{H}_2\text{O} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{Ru}^{III}(\text{Hedta})(\text{H}_2\text{O}) + \text{H}^+ + 2\text{RCN}$$

Supporting evidence for this is the presence of a second wave at -0.3 V, the region associated with the reduction of Ru(Hedta)H$_2$O. Repeated scanning from +0.8 to 0.0 V followed by a scan to -0.8 V showed a decrease in the wave at 0.5 V and an increase at -0.3 V, consistent with the accumulation of the hydrolysis product at the electrode. Because of the acid conditions prevailing, aquation is a more likely reaction of the oxidation product than the base hydrolysis of the nitrile ligand, which has been reported for ruthenium(III) complexes.[39] The
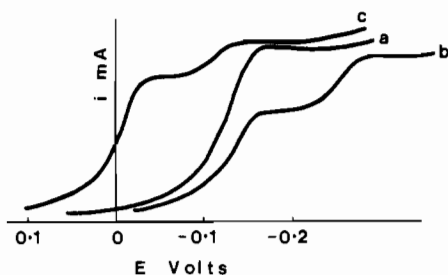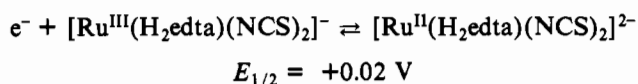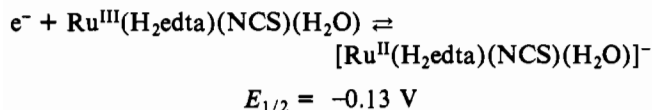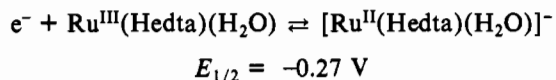
Figure 4. Voltammogram of [Ru(H$_2$edta)(SCN)$_2$]K·2H$_2$O (concentration 10^{-3} mol dm^{-3}; voltage sweep 50 mV/s): a, in 0.5 mol dm^{-3} KCl immediately after dissolving solid; b, in solution a after 40 min; c, in 0.4 mol dm^{-3} KSCN.

postulated scheme is consistent with the failure to prepare ruthenium(III) complexes with nitrile ligands.

Irreversible behavior was also observed with the monomeric and dimeric dinitrogen complexes, which produced only anodic waves resulting from the oxidation of ruthenium(II) to ruthenium(III). The nature of the oxidized products, however, was unknown although the dimeric complex did produce a broad plateau on the cathodic cycle with $E_p = -0.4$ V, which could have been due to the ruthenium(III) aquo species at the pH of the solution (5.5). Surprisingly, no such wave was observed in the voltammogram of the terminal dinitrogen complex. It is difficult to explain the electrochemical behavior of the dinitrogen complexes in which the ligand appears to stabilize the ruthenium(II) center to a much lesser extent that CO, NO$^+$, or RCN. The corresponding [Ru(NH$_3$)$_5$N$_2$]$^{2+}$, which also gives only anodic waves even at scan rates of 100 V s^{-1},[41] has a much higher $E_{1/2}$.

The spectrophotometric examination reported above of the Ru(Hedta)H$_2$O/SCN$^-$ system suggested that a ruthenium(III) edta dithiocyanate complex is formed by a stepwise process. The system was investigated further by using single-sweep as well as cyclic voltammetry. A fresh solution of [Ru^{III}(H$_2$edta)(NCS)$_2$]K (10^{-3} mol dm^{-3}) in 0.5 mol dm^3 KCl produced a single cathodic wave with $E_{1/2} = -0.13$ V. When the scan was repeated after a period of time, the height of the wave was found to have decreased and a second wave appeared at -0.27 V (Figure 4a, b). However, when the experiment was repeated by using 0.4 mol dm^{-3} KSCN as supporting electrolyte, a new wave was observed at $+0.02$ V, the wave at -0.13 V was considerably reduced in intensity, and the one at -0.27 V did not appear even after allowing the solution to stand (Figure 4c). The observed reduction potentials were identified with the equations:

$$e^- + Ru^{III}(Hedta)(H_2O) \rightleftharpoons [Ru^{II}(Hedta)(H_2O)]^-$$

$$E_{1/2} = -0.27 \text{ V}$$

$$e^- + Ru^{III}(H_2edta)(NCS)(H_2O) \rightleftharpoons$$
$$[Ru^{II}(H_2edta)(NCS)(H_2O)]^-$$

$$E_{1/2} = -0.13 \text{ V}$$

$$e^- + [Ru^{III}(H_2edta)(NCS)_2]^- \rightleftharpoons [Ru^{II}(H_2edta)(NCS)_2]^{2-}$$

$$E_{1/2} = +0.02 \text{ V}$$

The behavior of the system also confirms the rapid dissociation of the bis(thiocyanato) complex in aqueous solution to form the mono(thiocyanato) and the slow partial aquation of the
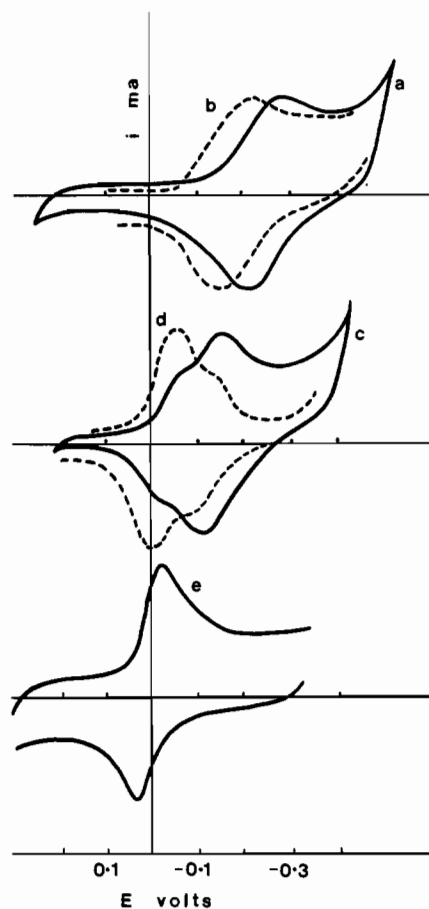
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Figure 5. Cyclic voltammograms of Ru(Hedta)ClK·2H$_2$O (concentration 10^{-3} mol dm^{-3} in 0.5 mol dm^{-3} KCl) at increasing concentrations of thiocyanate ions, determined immediately after addition and dissolution of solid (voltage sweep 1.0 V/s). [SCN$^-$] (mol dm^{-3}): a, 0.0; b, 10^{-3}; c, 0.1; d, 0.5; e, 1.0.

latter as observed in the spectrophotometric investigation. The relative heights of the two reduction steps in the slow single-sweep voltammograms shown in curves b and c of Figure 4 give equilibrium constants for the step formation of about 1500 and 10.

The equilibria in solution were also monitored by cyclic voltammetry of a solution of Ru(Hedta)H$_2$O containing increasing concentrations of thiocyanate. The results, shown in Figure 5, indicate the gradual replacement of the cathodic peak of the aquo complex with that of the mono(thiocyanato) complex and the eventual replacement of the latter by the peak of the bis(thiocyanato). All three species in equilibrium are reduced reversibly, justifying thus the formulation given to the ruthenium(II) edta thiocyanato complexes in the redox equations above.

Kane-Maguire et al.[40] suggested that [Ru^{III}(edta)N$_3$]$^-$ on acidification decomposes to form [Ru(edta)N$_2$]$^{2-}$ in solution. As an earlier attempt to verify this experimentally proved inconclusive,[1] the reaction was investigated electrochemically. Addition of an equimolar quantity of azide to Ru^{III}(Hedta)H$_2$O resulted in a color change from pale yellow to orange and in the shift of the cathodic wave of the aquo complex to a more negative potential. The new cathodic peak ($E_{1/2} = -0.32$ V) of equal height was assigned to the reduction of [Ru^{III}(Hedta)N$_3$]$^-$. Addition of excess azide caused no change in peak position or height. No additional peaks were observed to suggest the formation of the dinitrogen complex even on allowing the solutions to stand.

The effect of the various electron-withdrawing ligands in stabilizing the ruthenium(II) oxidation state is paralleled by their ability to give rise to MLCT in the electronic spectrum

of the complex. Inasmuch as such transitions are usually from the highest occupied MO in the complex to an empty orbital of suitable symmetry on the ligand, they can in principle be related to the complete removal of the electron and hence to $E_{1/2}$. Although linear correlations between $E_{1/2}$ and the energy of the MLCT have been found to hold when limited to complexes containing related ligands,[4] they do not apply when ligands of widely varying types are considered as illustrated in Table VI. In the cases where the energy of the MLCT in the Ru(H$_2$edta) complexes can be compared to that of analogous tetraammine complexes, the electrons in the Ru(edta) center appear to be more firmly bound than in the Ru(NH$_3$)$_4$ moiety. This is in conflict with the relative ease of oxidation of some of the complexes as seen above.

Contribution from the Chemistry Departments,
University of Minnesota, Minneapolis, Minnesota 55455, and University of Sarajevo, Sarajevo, Yugoslavia

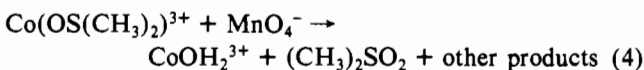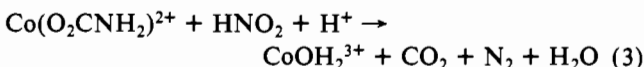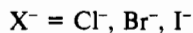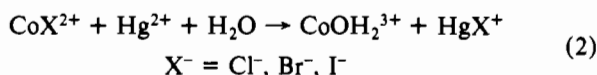# Assisted Aquation of Chloropentaamminecobalt(III) Ion in Different Media

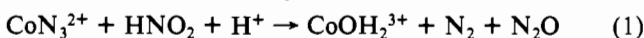W. L. REYNOLDS,* M. GLAVAŠ, and E. DŽELILOVIĆ

The product ratios from competition reactions accompanying the Hg^{2+}-assisted removal of Cl$^-$ from Co(NH$_3$)$_5$Cl^{2+} in aqueous solutions of NaNO$_3$, NaHSO$_4$, H$_3$PO$_4$ and CH$_3$CO$_2$H and in three water + nonaqueous solvent mixtures were determined at 0, 25, and 55 °C. The temperature dependence of these ratios was very small or undetectable outside of experimental error. An I$_d$ interchange of leaving and incoming ligands was postulated which adequately explains the observed data. In mixtures of water with one of the nonaqueous solvents dimethyl sulfoxide, N,N-dimethylformamide, or acetonitrile the product ratios were equal for equal bulk mole fraction of nonaqueous solvent. This result was interpreted to mean that, at equal bulk mole fraction, the three nonaqueous solvents were equally available in the solvation shell of the encounter complex preceding the formation of products and that complete, preferential solvation by one solvent component did occur in some solvent mixtures but not in others.

Introduction

The question concerning the existence of the five-coordinate pentaamminecobalt(III) complex has been an intriguing one. If this complex exists, it is most likely formed in one or more of the so-called assisted aquations shown in reactions[1-4] 1–4

$$CoN_3^{2+} + HNO_2 + H^+ \rightarrow CoOH_2^{3+} + N_2 + N_2O \quad (1)$$

$$CoX^{2+} + Hg^{2+} + H_2O \rightarrow CoOH_2^{3+} + HgX^+$$
$$X^- = Cl^-, Br^-, I^- \quad (2)$$

$$Co(O_2CNH_2)^{2+} + HNO_2 + H^+ \rightarrow$$
$$CoOH_2^{3+} + CO_2 + N_2 + H_2O \quad (3)$$

$$Co(OS(CH_3)_2)^{3+} + MnO_4^- \rightarrow$$
$$CoOH_2^{3+} + (CH_3)_2SO_2 + \text{other products} \quad (4)$$

(Co represents the Co(NH$_3$)$_5$ group in these and subsequent equations) rather than in the unassisted substitution reactions.[5,6] These reactions are still being actively studied.[7-10] Attempts to detect the possible five-coordinate intermediate Co(NH$_3$)$_5$$^{3+}$ involve trapping it with nucleophilic competition reactions. If Co(NH$_3$)$_5$$^{3+}$ exists sufficiently long to qualify as an intermediate in these competition reactions, then it survives sufficiently long to experience loss of the leaving group from its solvation shell and a change in the composition of its solvation shell from diffusional processes. Hence, it can meet and react with nucleophiles not originally present in that solvation shell and the mechanism of ligand exchange is D. If Co(NH$_3$)$_5$$^{3+}$ does not exist sufficiently long to experience the change of composition in, or loss of leaving group from, the solvation shell, then it must react with a component in its solvation shell and the mechanism of ligand exchange is I$_d$. If loss of leaving ligand from the solvation shell and a change in the composition of the solvation shell occur on much different time scales, then, for example, the leaving ligand could be retained in the solvation shell to influence the product ratio while diffusional processes are bringing nucleophiles into the solvation shell for reaction with the vacant first-coordination-shell site. This might happen when the leaving ligand is so large and/or heavy as to be slow moving compared to the entering nucleophiles. In this case, the reaction mechanism would be borderline between D and I$_d$ and would appear to be I$_d$ because of the influence of leaving ligand on the product ratio.

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