sequent decrease in ν(CO). Since this counteracts the predicted rise in ν(CO) based solely on a back-bonding criterion, net cancellation is possible.

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Registry No. Ia, 36250-00-7; Ib, 76391-66-7; $Cp_2Re_2(CO)_5H^+$, 76391-67-8; $(C_5H_4CH_3)_2Re_2(CO)_5H^+$, 76391-68-9; $(C_5H_4CH_3)Re(CO)_3$, 33309-95-4; $ReCl(CO)_5$, 14099-01-5; $HOSO_2CF_3$, 1493-13-6.

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Preparation and Structure of Ethylenediaminetetraacetate Complexes of Ruthenium(II) with Dinitrogen, Carbon Monoxide, and Other π-Acceptor Ligands

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Complexes of $Ru^{II}(H_nedta)L_n$ (n = 1, 2; L = N_2, CO, NO, RCN) were prepared by reacting aqueous solutions of $Ru^{II}(Hedta)H_2O^-$, formed by reducing $Ru^{III}(Hedta)H_2O$ with H_2 on platinum black, with the appropriate ligand. In the case of L = N_2, a terminal complex and a bridging complex were identified in solution and were isolated as solid derivatives by using alternative procedures. $(Ru(edta))_2N_2^{4-}$ was found to dissociate at 25 °C with $\Delta H^* = 44$ kJ mol^{-1} and $\Delta S^* = -140$ J K^{-1}. The complexes were characterized by analytical and spectroscopic procedures, including ^{13}C NMR, and were shown to accommodate L, in both the tetradentate and pentadentate complexes, in the equatorial positions. The electronic and vibrational spectra of the complexes were found to be analogous with those of the corresponding ruthenium(II) tetraammine and pentaammine complexes with the same L.

Introduction

Ruthenium(II) and osmium(II) are the only metal centers which are known to form mononuclear and binuclear dinitrogen complexes in which the other ligands are σ donors with no π-acceptor capabilities. Thus, pentaammine,[1] tetraammineaquo,[2] bis(ethylenediamine)aquo,[3] triethylenediaminebromo and -aquo,[4] and pentaaquo[5] complexes of ruthenium(II) have been reported in which the sixth coordination position is occupied by terminal or bridging dinitrogen, often by direct substitution of an aquo ligand. The sixth coordination site in these complexes can also attach other π-accepting ligands such as CO,[6] HCN,[7] N_2O,[8] RCN,[9] and NO^+.[10]

Ethylenediaminetetraacetate, although normally a hexadentate ligand, can form six-coordinate complexes in which only five[11,12] or even four[13,14] of the potential donor atoms in the ligand are attached to the metal, the remaining coordination positions being occupied by other ligands. Ruthenium(III) also forms chloro complexes of this type,[15] which, in dilute acid solution, give rise to the uncharged species $Ru(Hedta)H_2O$.[16] It was considered that the ruthenium(II) complex formed by the reduction of the above species would contain a coordination site which, by analogy with the ammine complexes, would bind dinitrogen and other π-acceptor ligands. This paper reports the preparation and chemistry of such complexes of ruthenium(II) with ethylenediaminetetraacetate. Recently the reaction of $Ru^{III}(edta)H_2O^-$ and $Ru^{II}(edta)H_2O^{2-}$ with a number of ligands to form pentadentate complexes has been reported.[17] Acetonitrile and a number of nitrogen heterocyclic bases were shown to substitute in the ruthenium(II) system; however, no solid derivatives were reported as isolated or characterized.

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 nitrogen and industrial hydrogen, argon, and carbon monoxide were used as received. Dinitrogen oxide was passed through chromous chloride to remove oxygen and then through P_2O_5 towers. Nitric oxide was purged by passing through concentrated sulfuric acid, through a cold trap, and finally over potassium hydroxide pellets.

Analyses. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, and by the Levels Institute of Technology, Adelaide. The ruthenium(II) content of reduced $Ru^{III}(edta)H_2O^-$ solutions was estimated by reducing a solution of Fe(III) and determining the Fe(II) formed as the phenanthroline complex spectrophotometricaly.[18a] Magnesium was estimated by edta titration.[18b]

Physical Measurements. Solid-state infrared spectra were obtained from KBr pellets and Nujol mulls with use of a Perkin-Elmer spectrometer, Model 457; Raman spectra were recorded at the University of Tasmania with use of a Rhodamine 6G dye laser at 587.7 nm. Electronic spectra were recorded under dinitrogen with use of a

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Perkin-Elmer 402 or a Shimadzu QR50 spectrophotometer. Proton NMR spectra were measured in D_2O solution with use of 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-90E. Conductance measurements were made in aqueous solution by using a Philips PR-9500 AC bridge, and base titrations were carried out in aqueous solution and followed with a Philips PR-9400 pH meter.

Preparations. $[RuCl_5H_2O]K_2$ was prepared by the method of Mercer and Buckley;[19] $[RuCl_5NO]K_2$ by the method of Werner.[20]

A. $[Ru(Hedta)Cl]K{\cdot}2H_2O$. This was prepared by a modification of the method of Ezerskaya and Solovykh.[15] A hot solution of $Na_2(H_2edta)$ (0.5 g) in 0.001 mol dm^{-3} $HClO_4$ (10 cm^3) was added to a warm solution of $[RuCl_5H_2O]K_2$ (0.5 g) in 0.001 mol dm^{-3} $HClO_4$ (10 cm^3), and the mixture was refluxed for 30 min. Concentration of the yellow solution on a steam bath gave a yellow precipitate which was washed with cold water and ethanol; yield 0.25 g (40%).

B. $[Ru(H_2edta)Cl_2]K{\cdot}H_2O$. This was obtained by evaporation of the filtrate remaining after isolation of the above chloro complex. The yellow powder was dissolved in a minimum of 2.5 mol dm^{-3} HCl solution. The filtered solution was warmed on a steam bath until yellow crystals appeared. These were collected and washed with ethanol.

$Ru^{II}(Hedta)H_2O^-$. An aqueous solution containing $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.25–0.50 g in 3–5 cm^3) was placed in a Schlenk tube fitted with a side arm. The solution was saturated with argon prior to the introduction of dihydrogen which was bubbled over a platinum-black mesh. A deep yellow solution was produced after several minutes. The side arm permitted the introduction of ligands without interrupting the flow of dinitrogen.

C. $[(Ru(edta))_2N_2]Mg_2{\cdot}8H_2O$. An aqueous solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.25 g in 3–5 cm^3) was passed through a cation-exchange column in the magnesium form. The effluent was acidified to pH 1 and concentrated to its original volume. After saturation of the solution with N_2 and cooling it in ice, magnesium metal (30 mg) was added while a strong stream of N_2 was maintained through the solution. The pH of the solution was maintained below 3. At higher pH values the color changed from yellow to brown and eventually to violet; however, these changes could be reversed by the addition of a few drops of 2 mol dm^{-3} HCl. Consumption of the reductant required that there be several additions of the metal during the preparation. After 4 h the solution was filtered rapidly under N_2 and the product precipitated by the addition of cold ethanol which was saturated with N_2. The canary yellow solid which was precipitated was collected, washed with ethanol, and dried over P_2O_5 in vacuo; yield 0.12 g (48%). It was stored at approximately 5 °C under N_2 and over a desiccant.

D. $[Ru(edta)N_2](NH_4)_2{\cdot}5H_2O$. Hydrazine hydrate (0.5 cm^3) was added dropwise, against a current of N_2, to a N_2-saturated methanolic solution of $Ru(H_2edta)(NO)Cl$ (for the preparation of this compound see below) (0.1 g in 3 cm^3). Effervescence occurred, followed by the precipitation of a yellow solid. The product was collected under N_2, washed with ethanol, and dried over P_2O_5 in vacuo; yield 0.075 g (68%). It was stored at approximately 5 °C under N_2 over a desiccant.

E. $[Ru(Hedta)CO]K{\cdot}2H_2O$. Hydrogen and carbon monoxide were simultaneously bubbled over platinum black through an aqueous solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.15 g in 3–5 cm^3) for 90 min. The yellow solution was concentrated, and a pale yellow solid was precipitated with cold ethanol. The product was washed with ether and dried in vacuo; yield 0.072 g (48%).

F. $Ru(H_2edta)(NO)Cl{\cdot}2H_2O$. This was prepared by a number of methods, none of which required inert-atmosphere techniques.

(a) An ethanolic solution of MNTS (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) (5 g in 5 cm^3) was added to a solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.3 g) in 0.01 mol dm^{-3} HCl (10 cm^3) and the mixture heated on a steam bath. A brown coloration developed, and after 20 min the solution was cooled and filtered to remove copious amounts of a white solid, the decomposition product of MNTS. The filtrate was concentrated, cooled, and filtered again. The procedure was repeated until no further precipitate was formed. The solution was evaporated to dryness and the product extracted with methanol and filtered. From the concentrated solution a brown product was precipitated with ether, filtered, washed with dry chloroform, and dried over P_2O_5; yield 0.21 g (70%).

(b) A solution of $[RuCl_5(NO)]K_2$ (0.2 g) in 0.01 mol dm^{-3} HCl (10 cm^3) was refluxed with a hot solution of $Na_2(H_2edta){\cdot}2H_2O$ (0.2 g) in 0.01 mol dm^{-3} HCl (10 cm^3) for 30 min. The resulting brown solution was evaporated to dryness, extracted with methanol, filtered, and treated as in method a, yielding a pale brown solid; yield 0.14 g (54%).

(c) $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.3 g) was dissolved in a minimum of 0.01 mol dm^{-3} HCl. Argon was passed through the solution for 10 min prior to the introduction of nitric oxide. The passage of NO through the solution caused a red-brown coloration. After 30 min the flow of NO was stopped and N_2 was passed through the solution for 15 min, followed by concentration of the solution to dryness. The product was extracted with methanol and filtered. A brown solid was obtained which was warmed in dilute hydrochloric acid for 10 min. The solution was evaporated to dryness and treated as in method a; yield 0.2 g.

(d) An aqueous solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.2 g in 5 cm^3) was reduced with dihydrogen over platinum black for 15 min prior to the addition of potassium nitrite (0.07 g). The solution immediately darkened to red-brown. The flow of hydrogen was maintained for about 1 h, and the solution was treated as in method b; yield 0.12 g (60%). Excess $NOPF_6$ could be substituted for KNO_2 in the above preparation and then the solution treated in a similar manner; yield 0.12 g (60%).

G. $Ru(H_2edta)(CH_3CN)_2{\cdot}H_2O$. An excess of acetonitrile was added during the reduction of an aqueous solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.2 g) and the reduction continued for 90 min. Concentration of the solution followed by the addition of small amounts of N_2-saturated ethanol led to the separation of crystalline potassium chloride. From the filtrate, which was cooled under dinitrogen, yellow-orange needles were obtained. Further concentration or addition of ethanol was needed if no product appeared at this stage. The product was washed with dry ethanol and diethyl ether and recrystallized from aqueous methanol; yield 0.09 g (45%).

H. $Ru(H_2edta)(C_6H_5CN)_2{\cdot}2H_2O$. Excess benzonitrile was added during the reduction of an aqueous solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ (0.2 g in 4 mL). An emulsion was formed as the reduction was continued and a yellow solid precipitated after 15 min. After 1 h the reduction was stopped and the product collected and washed with ice-cold ethanol and dry diethyl ether. It was purified by dissolving in N_2-saturated methanol and precipitating with ether; yield 0.10 g (40%).

I. $Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2{\cdot}2H_2O$. A suspension of phthalodinitrile (0.055 g) in ethanol was added to a solution of $[Ru(Hedta)Cl]K{\cdot}2H_2O$ in water (0.1 g in 3 cm^3) while it was being reduced by dihydrogen. An immediate red-orange coloration resulted, and an orange solid precipitate separated eventually from the solution. This was collected in air and washed with cold ethanol, chloroform, and dry diethyl ether. The mother liquor yielded more product upon standing; yield 0.06 g (44%).

The analytical data for the compounds which were prepared are summarized in Table I.

Because the instability of the bridged dinitrogen complex $[(Ru(edta))_2N_2]Mg_2{\cdot}8H_2O$ gave rise to low analytical figures for its nitrogen content, the amount of ligated dinitrogen was determined in gas-release experiments in which a variety of reagents were used to decompose the complex. The complex was decomposed by adding weighed amounts to the frozen and degassed reagent, evacuating the reaction vessel, and allowing the reaction to proceed on thawing. The volume of the gas was determined by measuring the pressure in a manometer of known volume. The gas was shown to be N_2 by using a RMU-7D Hitachi Perkin-Elmer mass spectrometer. The following results were obtained

method of decompn	% recovery of N_2 calcd as 1 mol/mol of complex
ceric sulfate	91
0.9 mol dm^{-3} H_2SO_4	83
thermal decompn of solid	92
hydrolysis ($P(N_2)$ ~0.02 atm)	77

Results and Discussion

Formation of $Ru(Hedta)H_2O^-$ in Solution. Solutions containing the air-sensitive $Ru(Hedta)H_2O^-$ complex were prepared by reducing $[Ru(Hedta)Cl]K{\cdot}H_2O$ in dilute acid with

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Table I. Results of Elemental Analysis

	% calcd						% found				
compd	C	H	N	Cl	other		C	H	N	Cl	other
A	24.0	3.42	5.59	7.08			23.5	3.27	5.27	7.47	
B	23.1	3.11	5.39	13.6			23.6	3.06	5.67	13.3	
C	24.0	4.04	8.41		Mg 4.87		24.0	4.17	7.65		Mg 4.48
D	22.1	5.56	15.5		Ru 18.6		21.9	5.49	15.2		Ru 16.7
E	26.8	3.47	5.68				25.8	3.28	5.65		
F	24.4	3.68	8.53	7.19		(a)	24.6	3.53	8.21	7.90	
						(b)	23.6	3.49	8.30	7.80	
						(c)	23.7	3.33	8.25	8.20	
						(d)[a]	22.9	3.10	7.85		
G	34.2	4.51	11.4		Ru 20.6		34.2	4.30	11.1		Ru 20.4
H	45.5	4.45	8.84		Ru 15.9		45.0	4.32	8.76		Ru 15.3
I	45.7	3.83	12.3		Ru 14.8		44.5	3.72	11.8		Ru 15.8

[a] Using NO_2^-/H^+.

Table II. Complexes of Ru^{II}(edta) with π-Acceptor Ligands and Infrared Absorptions of the Free and Coordinate Carboxylate Groups of edta[a]

complex	color	ν(COOH),[b] cm^{-1}	ν(COOH),[c] cm^{-1}
$[Ru(Hedta)CO]K\cdot 2H_2O$[d]	pale yellow	1725 m	1600 s, br
$[Ru(H_2edta)(NO)Cl]\cdot 2H_2O$	brown	1725 s, br	1640 s, br
$[Ru(H_2edta)(CH_3CN)_2]\cdot H_2O$	yellow	1725 s	1655 s, sp; 1580 s, br
$[Ru(H_2edta)(C_6H_5CN)_2]\cdot H_2O$	yellow	1725 s	1655 s, sp; 1580 s, br
$[Ru(H_2edta)(1,2\text{-}C_6H_5(CN)_2)_2]\cdot 2H_2O$	orange	1720 s	1635 s, br; 1575 s, br
$[Ru(edta)N_2](NH_4)_2\cdot 5H_2O$	yellow		1590 s, br
$[(Ru(edta))_2N_2]Mg_2\cdot 8H_2O$	yellow		1610 s, br; 1580 ms

[a] Key: s, strong; m, medium; br, broad; sp, sharp. [b] Free carboxylic arm of edta. [c] Carboxylate of edta. [d] Shimizu[22] has reported the isolation of $Na_2[Ru(edta)CO]$ by reducing $Ru^{III}(Hedta)H_2O$ in formic acid and formate buffer.

zinc amalgam, magnesium metal, or dihydrogen on platinum black. The resulting solution had a yellow color and absorption bands at 280 nm (ϵ 3 × 10^3 mol^{-1} dm^3 cm^{-1}) and at 425 nm (ϵ 4 × 10^2 mol^{-1} dm^3 cm^{-1}), which are in good agreement with those reported by Matsubara and Creutz.[17] On oxidation by air, the solutions were converted rapidly and quantitatively to the initial ruthenium(III) species.

For preparative work the most convenient reducing agent was dihydrogen on platinum black as this introduced only hydrogen ions into the solution. With use of this reagent, however, the conversion was not quantitative. The extent of the reaction was monitored by determining the ability of the reduced solutions to convert iron(III) to iron(II). With a freshly coated electrode at total ruthenium concentrations in the range 10^{-4}–10^{-3} mol dm^{-3} at pH values from 1 to 3, conversions between 50 and 70% were achieved within 1 h. As no further reaction was observed after several hours, it was concluded that such solutions contained the reduced ruthenium(II) complex in equilibrium with the corresponding ruthenium(III) species. In addition, it is possible that some of the ruthenium(II) species is present in the form $Ru(H_2edta)(H_2O)_2$.[21] Attempts to isolate solid derivatives of the ruthenium(II) complex by the addition of large cations and ethanol were unsuccessful; the isolated precipitates were mainly compounds of ruthenium(III). Reduction of solutions of $[Ru(H_2edta)Cl_2]K$ produced solutions with almost identical spectra. However, these solutions had a distinct green tinge, and as they contained twice the amount of potassium chloride in solution, they were not used for preparative work.

Preparation of the Complexes. Solutions containing $Ru(Hedta)H_2O^-$, produced in the way described above, were used to prepare complexes with π-acceptor ligands. Although the conversion to ruthenium(II) was at most 70%, in the presence of the ligand as well as dihydrogen and the catalyst, complete conversion was achieved. With the use of dinitrogen, organonitriles, carbon monoxide, and nitrosonium ion, substitution products were formed which, except in the case of dinitrogen, could be isolated in pure form from the reaction mixture. As the pH of the solution was below 3, the complexes which were isolated contained the free arm of the ethylenediaminetetraacetate ligand in the protonated form. The dinitrogen complexes were prepared by alternative routes, which are outlined below, and contained the free arm of the ethylenediaminetetraacetate ligand in the ionic form. The complexes containing π-acceptor ligands which have been isolated and characterized are shown in Table II. The structures are proposed on the basis of analytical figures and the vibrational spectra of the solids, as well as their properties in solution, which are discussed below.

The recent investigation of the substitution reactions of $Ru(edta)H_2O^-$ and $Ru(edta)H_2O^{2-}$ by Matsubara and Creutz[17] provides a ready explanation for the formation of the complexes. Although substitution of an aquo ligand on ruthenium(III) ammines[23,24] is generally slower than substitution on ruthenium(II),[25,26] in $Ru(edta)H_2O^-$ substitution of the aquo ligand proceeds very rapidly by an associative pathway. This coupled with the expected more positive $E°$ of the π-acceptor complexes provides a ready mechanism by substitution of the ligand on the ruthenium(III) complex followed by reduction by H_2. It is possible, however, that in the case of N_2 and CO, which are not known to form stable bonds with ruthenium(III), the reaction proceeds via substitution on the ruthenium(II) aquo species. The formation of complexes in which edta occupies only four coordination positions requires the displacement of a carboxylate ligand by either the incoming ligand or the solvent. The aquation of $Ru^{II}(NH_3)_5(carboxylate)^+$ is known to proceed rapidly, especially when the ligand is protonated,[27] and hence provides an explanation for the observed products.

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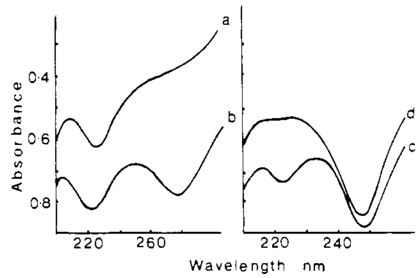

Figure 1. Absorption spectra of the bridging- and terminal-dinitrogen complexes at different concentrations of ruthenium (Ru_T): (a) $[Ru_T] = 10^{-4}$ mol dm^{-3} (path length 10 mm); (b) $[Ru_T] = 5 \times 10^{-4}$ mol dm^{-3} (path length 5 mm); (c) $[Ru_T] = 10^{-3}$ mol dm^{-3} (path length 2 mm); (d) $[Ru_T] = 3 \times 10^{-3}$ mol dm^{-3} (path length 1 mm).

Table III. Formation of the Terminal- and Bridging-Dinitrogen Complexes in Solution

$10^4[Ru^{III}{}_T]$, mol dm^{-3}	% terminal concn[a]	% bridging concn[b]	% yield[c]
1.34	26	8.2	42
3.72	23	9.7	42
5.87	18	10	39
8.16	18	12	43
16.4	17	17	50
25.5	16	18	53

[a] % terminal concn = $([Ru(Hedta)N_2^-]/[Ru^{III}{}_T]) \times 100$. [b] % bridging concn = $([(Ru(Hedta))_2N_2^{2-}]/[Ru^{III}{}_T]) \times 100$. [c] % yield = $\{([Ru(Hedta)N_2^-] + 2[(Ru(Hedta))_2N_2^{2-}])/[Ru^{III}{}_T]\} \times 100$.

The formation of the dinitrogen complexes could be observed in solution through the development of absorption peaks with molar absorbances of the order of 10^4 mol^{-1} dm^3 cm^{-1} at 225 and 278 nm. These were attributed to the terminal $Ru(Hedta)N_2^-$ and bridging $(Ru(Hedta))_2N_2^{2-}$ dinitrogen complexes formed according to equilibria 1 and 2. Analogous

$$Ru(Hedta)H_2O^- + N_2 \rightleftarrows Ru(Hedta)N_2^- \quad (1)$$

$$Ru(Hedta)N_2^- + Ru(Hedta)H_2O^- \rightleftarrows (Ru(Hedta))_2N_2^{2-} \quad (2)$$

spectral changes have been used to study the kinetics of the formation of the pentaammine dinitrogen[28] and other ammine dinitrogen systems.[29] Reaction 1 predominates at low concentrations of ruthenium (ca. 10^{-4} mol dm^{-3}) and reaction 2 at higher concentrations (10^{-3} mol dm^{-3}). Spectra recorded over a range of concentrations of ruthenium show the gradual decrease of the peak of 225 nm, and the corresponding increase of that at 278 nm as can be seen in Figure 1. The reaction represented by (2) can be demonstrated by adding a solution of the terminal-dinitrogen complex to a solution containing $Ru(Hedta)H_2O^-$ where the absorption peak at 278 nm is produced immediately. An estimate of the yield of the two complexes in solution was obtained from the molar absorbances of the two complexes which were determined with the use of solid samples prepared by alternative routes. The results in Table III show that, on the basis of the total ruthenium concentration, the formation of the two complexes does not represent more than a 50% yield. This is because when the dihydrogen atmosphere is replaced with dinitrogen, no further reduction of the ruthenium(III) ethylenediaminetetrakis(acetato)aquo complex could take place. Moreover, the lability and low stability of the dinitrogen complexes precluded the use of mixtures of the ligand and dihydrogen, unlike the case of the corresponding carbonyl complex which could be prepared by this method. The results also show that the high concentrations, which are necessary for the isolation of solid samples of the complexes, favor the formation of the bridging species. For these reasons alternative methods were used for the preparation of the two dinitrogen complexes. The bridging complex was isolated as the magnesium salt by reducing solutions of $Ru^{III}(Hedta)H_2O$ with magnesium under N_2 at low temperatures and a final pH of 3. Reduction with zinc amalgam gave compounds which had similar spectra; these, however, were not fully characterized. The terminal complex was isolated by reacting $Ru(H_2edta)(NO)Cl$ with hydrazine hydrate in methanol. This method has been used to prepare the dinitrogenpentaamineruthenium(II) complex from the corresponding nitrosyl.[30] Kane-Maguire et al.[31] suggested that $Ru(Hedta)N_2^-$ could be formed by acidifying the azido complex $Ru^{III}(edta)N_3^{2-}$ in a manner analogous to the behavior of other ruthenium(III) azidoammines. Attempts to prepare the complex by this route resulted in products which may have contained both the azido and the dinitrogen ligands.

Attempts to form the dinitrogen oxide complex, by introducing dinitrogen oxide into solutions of $Ru(Hedta)H_2O^-$, led to a rapid quantitative oxidation to form $Ru^{III}(Hedta)H_2O$ with no evidence for the formation of a dinitrogen intermediate as in the case of ruthenium(III) aquopentaammine[32] complex. In the presence of zinc amalgam, introduction of dinitrogen oxide even at pressures of 30 atm produced no evidence for the formation of a dinitrogen complex in contrast with the ruthenium(II) pentaammine system for which these conditions provide a convenient method for the preparation of the dinitrogen complex.[33] Reaction of hydrazine hydrate at −10 to −40 °C and of hydroxylamine at room temperature on $Ru(H_2edta)(NO)Cl$ also failed to give any evidence for the presence of a dinitrogen oxide complex as expected from the behavior of these reagents with $Ru(NH_3)_5NO^{3+}$.[30]

The nitrosyl complex was prepared from $Ru(Hedta)H_2O^-$ by using $NOPF_6$ or nitrite ions as a source of NO^+. In the latter case the nitrosonium ion is a possible intermediate because of the equilibrium

$$NO_2^- + 2H^+ \rightleftarrows NO^+ + H_2O$$

However, equally valid is a mechanism involving coordination of nitrite followed by oxide abstraction;[34] nitrite ions in dilute acid have been used previously to produce a chromium ethylenediaminetetraacetate nitrosyl complex.[35] The complex could also be prepared from the chloro complexes $[Ru(Hedta)Cl]K\cdot 2H_2O$ or $[Ru(H_2edta)Cl_2]K\cdot 2H_2O$ by reacting either with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) or with nitric oxide. Nitric oxide has been used previously to prepare $[Ru(NH_3)_5NO]Cl^{36}$ and $[Ru(NH_3)_4(NO)X]X_2{}^{37}$ from the corresponding ruthenium(III) ammines. The most convenient synthesis, leading to a product free of nitrite, was by the reaction of $[RuCl_5NO]K_2$, in acidic solution, with the disodium salt of ethylenediaminetetraacetic acid.

Solution Properties of the Complexes. The nitrosyl and carbonyl complexes were stable in aqueous solution toward substitution of the π-acceptor ligand and oxidation; the latter

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Table IV. Observed Rates (k_{obsd}) of Decomposition for $(\mathrm{Ru(edta)})_2\mathrm{N}_2{}^{4-\,a}$

10^3k_{obsd},[a] s^{-1}	temp, K	10^3k_{obsd},[b] s^{-1}	temp, K
1.4	292.8	2.7	287.8
3.1	300.2	3.5	293.5
3.6	303.7	5.9	300.9
6.4	310.9	10.0	308.4

[a] Concentration range (5.7–6.5) × 10^{-5} mol dm^{-3}; N_2 atmosphere; solution pH 5. [b] $k_{\mathrm{obsd}} \pm 0.1\ \mathrm{s}^{-1}$; Ar atmosphere.

Table V. Molar Conductance and Neutralization Equivalents of Ru(edta) Complexes

complex	Λ_M,[a] S cm^2	molar ratio H^+/Ru	$\mathrm{p}K_{\mathrm{av}}$[b]
$[\mathrm{Ru(edta)N_2}](\mathrm{NH_4})_2$	235	*c*	
$[\mathrm{Ru(Hedta)CO}]\mathrm{K}$	276	1.0 ± 0.1	2.6
$\mathrm{Ru(H_2edta)(CH_3CN)_2}$	221	1.9 ± 0.2	2.7
$\mathrm{Ru(H_2edta)(C_6H_5CN)_2}$	227	2.0 ± 0.1	2.7
	13[d]		
	11[e]		
$\mathrm{Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2}$	*f*	1.9 ± 0.1	
$\mathrm{Ru(H_2edta)(NO)Cl}$	450	2.0 ± 0.1	2.4
	45[d]		

[a] At 1.0 × 10^{-3} mol dm^{-3} at 23–25 °C. [b] From pH at half-neutralization. [c] No acid properties. [d] In methanol. [e] In dimethylformamide. [f] Insufficiently soluble.

was confirmed by the absence of an oxidation wave in cyclic voltammograms up to +0.8 V vs. SCE, which was the limit of the decomposition of the electrolyte solution. The stability of these complexes which can be attributed to the electron-withdrawing effects of the π-acceptor ligands is paralleled by the stability of the nitrosyl pentaammines[10] and acido tetraammines[37] of ruthenium(II) as well as the carbonyl ammines.[2,38] The organonitrile complexes were sufficiently stable to be studied under N_2 in aqueous solution, methanol, dimethylformamide, and trifluoroacetic acid. Slow decomposition, however, was observed in aqueous solution which became rapid under neutral and alkaline conditions and resulted in the production of violet colorations. Thus the complexes appear to be less stable toward substitution than the $\mathrm{Ru(NH_3)_5RCN^{2+}}$ complexes studied by Ford and Clarke[9] and unlike the latter, on oxidation with $\mathrm{Ag_2O}$, form $\mathrm{Ru(edta)H_2O^-}$ and not the corresponding ruthenium(III) organonitrile complexes.

By contrast, the dinitrogen complexes were found to be unstable because of substitution of the dinitrogen ligand and aerial oxidation. Their stability in solution was followed conveniently by the changes in their electronic spectra. The spectra of the dinitrogen complexes were found to be independent of pH over the range 1–5. Over the concentrations used (10^{-5}–10^{-3} mol dm^{-3}), both the bridging- and terminal-dinitrogen complexes were converted to the aquo complex at moderate rates, even in solutions saturated with dinitrogen. Loss of dinitrogen was accelerated on passing dihydrogen or argon through the solution. The decomposition of the bridging-dinitrogen complex in water was followed by monitoring the decay of the absorption at 278 nm. The spectral changes produced a sharp isosbestic point at 234 nm; there was, however, no corresponding increase at 225 nm, the region of the maximum absorption of the terminal-dinitrogen complex. The decay was found to follow pseudo-first-order kinetics; this enabled an accurate determination of the molar absorbance of the complex by extrapolation to zero time, as well as the calculation of the rate constant of the reaction. Observed rates, derived from plots of log $[(A - A_0)/(A - A_t)]$ vs. t, where A, A_0, and A_t refer to absorbances at infinite time, initial time, and time t, are given in Table IV.

The rate of decomposition of the dinitrogen complex is accelerated by replacing the dinitrogen atmosphere by argon as can be seen from the k_{obsd} values in Table IV. This indicates that the rate is not simply determined by the dissociation of the dimer. From the observed rates at various temperatures a good Arrhenius plot was obtained for the decomposition reaction in an argon atmosphere from which $\Delta H^{\ddagger}$ was estimated at 44 kJ mol^{-1} and $\Delta S^{\ddagger}$ at −140 J K^{-1} at 25 °C. These values differ from values obtained in related systems such as $\mathrm{Ru^{III}(edta)(N_3)^{2-}}$,[31] $\mathrm{Ru(NH_3)_5N_2^{2+}}$,[39] and $\mathrm{Ru(NH_3)_5N_2O^{2+}}$.[32b] However, as it is not known to what processes our activation parameters refer, comparisons are not appropriate at this stage. The dimeric complexes $(\mathrm{Ru(NH_3)_5})_2\mathrm{N_2}^{4+}$ and $(\mathrm{Ru(trien)H_2O})_2\mathrm{N_2}^{4+}$ have also been reported to dissociate in inert atmospheres in dilute alkaline solutions;[4,40] however, in aqueous solution the latter complex dissociates more slowly.[4]

Aerial oxidation of the bridging complex produced initially $\mathrm{Ru^{III}(Hedta)H_2O}$, as judged from the appearance of a plateau at 280 nm (ϵ 3 × 10^3 $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$); gradually new peaks appeared at 390 and 630 nm. The same peaks appear more quickly on dissolving the complex in 0.001 mol dm^{-3} sodium hydroxide in the presence of air and are consistent with the formation of the μ-hydroxo μ-dioxygen ruthenium ethylenediaminetetraacetate complex which was described by Ezerskaya et al.[41] Solutions of $\mathrm{Ru(edta)N_2}^{2-}$ are also readily oxidized, giving, in the presence of chloride, intensely blue solutions characteristic of the mixed-oxidation μ-chloro complexes described by Mercer.[42]

Although our observations on the stability and lability of the terminal-dinitrogen complex are at best semiquantitative, it is evident that the complex is less stable and much more labile than the corresponding $\mathrm{Ru(NH_3)_5N_2^{2+}}$. Thus, although it is sufficiently stable to allow the determination of properties such as conductance and absorption spectra in N_2-saturated solutions, it decomposes fairly rapidly on bubbling argon through the solution, forming at first some of the dimer complex and eventually $\mathrm{Ru(Hedta)H_2O^-}$. By contrast, the aquation of $\mathrm{Ru(NH_3)_5N_2^{2+}}$ has a rate constant of 2.0 × 10^{-6} s^{-1} at 25 °C.[39] Although aquation of π-acceptor ligands on ruthenium(II) ammines is generally a slow reaction,[43] faster reactions have been observed when the ligand being replaced is less firmly held such as N_2O in $\mathrm{Ru(NH_3)_5N_2O^{2+}}$ [32b] or the first replaceable N_2 in $\mathrm{Ru(en)_2(N_2)_2^{2+}}$.[3] Thus a weaker Ru–$N_2$ bond in the edta complexes may be the reason for the observed lability. The data in Table III suggest an equilibrium constant for the formation of the terminal complex of 1–2 orders of magnitude smaller than the formation constant of $\mathrm{Ru(NH_3)_5N_2^{2+}}$.[39]

The state of protonation of the free arm of the ligated edta and the overall ionic charges of the complex ions in solution were investigated by pH titration with sodium hydroxide and by conductance measurements. The results, which are summarized in Table V, confirm the structures which have been proposed in Table II for the solid compounds, in which the protonation of the free arm was deduced from microanalytical and infrared spectroscopic data. The nitrosyl complex undergoes rapid dissociation in dilute solution according to the equilibrium

$$\mathrm{Ru(H_2edta)(NO)Cl} \rightleftarrows \mathrm{Ru(Hedta)(NO)} + \mathrm{H^+} + \mathrm{Cl^-}$$

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Table VI. Electronic Spectra of the Ru(edta) Complexes[a]

	high energy		low energy		
compd	λ_{max}, nm	ϵ, mol^{-1} dm^3 cm^{-1}	λ_{max}, nm	ϵ, mol^{-1} dm^3 cm^{-1}	ref
		Principal Spectra			
$Ru(edta)N_2^{2-}$	224	1.6×10^4			this work
$(Ru(edta))_2N_2^{4-}$	278	3.2×10^4			
Ru(Hedta)CO	<190	ca. 10^4	425	65	
	260 sh	2.2×10^3			
$Ru(H_2edta)(NO)Cl$			350	1.7×10^2	
			500	ca. 25	
			360[b]	1.7×10^2	
			360[c]	2.0×10^2	
$Ru(H_2edta)(CH_3CN)_2$	205	1.5×10^4	375	1.9×10^2	
	217 sh	1.2×10^4			
$Ru(H_2edta)(C_6H_5CN)_2$	227	3.5×10^4	330	1.1×10^4	
	250 sh	1.5×10^4			
			345[b]	1.2×10^4	
			366[d]	9.2×10^3	
			410 sh	7.0×10^3	
$Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2$	239	3.3×10^4	372	1.2×10^4	
	270 sh	1.6×10^4			
$[Ru^{III}(Hedta)Cl]K \cdot 2H_2O$[e]	225	$(4.4 \pm 0.3) \times 10^3$	350	$(7.7 \pm 0.4) \times 10^2$	
	280	$(3.0 \pm 0.2) \times 10^3$			
$Ru^{II}(Hedta)H_2O^-$[f]	280	ca. 3×10^3	425	ca. 4×10^2	
		Related Spectra			
$Ru(NH_3)_5N_2^{2+}$	221	1.8×10^4			39
$(Ru(NH_3)_5)_2N_2^{4+}$	262	4.7×10^4			28
$Ru(NH_3)_5CO^{2+}$	<200		360	17	38
	277	2.58×10^2			
cis-$Ru(NH_3)_4(NO)Cl^{2+}$	<200		345	1.28×10^2	37
			480	19	
trans-$Ru(NH_3)_4(NO)Cl^{2+}$	243	4.22×10^3	330	2.64×10^2	38
			440	17	
$Ru(NH_3)_5CH_3CN^{2+}$	229	1.55×10^4	350	2.51×10^2	9
cis-$Ru(NH_3)_4(C_6H_5CN)_2^{2+}$	226	2.51×10^4	344	1.07×10^4	9
$Ru(NH_3)_5H_2O^{2+}$	267	5.70×10^2	410	44	32b, 45

[a] Spectra determined in aqueous solution unless otherwise stated. [b] In methanol. [c] In 2.0 mol dm^{-3} KCl. [d] In dimethylformamide. [e] Completely hydrolyzed to $Ru^{III}(Hedta)H_2O$; $\epsilon_{280} = 2.80 \times 10^3$.[17] [f] $\epsilon_{282} = (2.9 \pm 0.1) \times 10^3$;[17] $\epsilon_{427} = 260 \pm 15$.[17]

giving rise to a molar conductance higher than that of hydrochloric acid (Λ_M(HCl) = 421 S cm^2 at 25 °C[44]) and releasing chloride ions which are rapidly precipitated by silver nitrate. Only one end point is observed in the titration corresponding to 2H$^+$/Ru; the absence of further end points precludes the existence of species containing coordinated aquo ligands which in $Ru(Hedta)H_2O$ have a pK_a of 7.63.[21] The rapid aquation of the chloride in $Ru(H_2edta)(NO)Cl$ is to be contrasted to the inertness towards aquation observed by Pell and Armor[37] in *cis*-$Ru(NH_3)_4(NO)Cl^{2+}$ and suggests that the ease of substitution of H_2O observed by Matsubara and Creutz[17] in $Ru(edta)H_2O^-$ and $Ru(edta)H_2O^{2-}$ may also extend to other ligands. Evidence for the equilibrium is also obtained from the ^{13}C nuclear magnetic resonance spectra in D_2O which are consistent with the presence of two species in dilute solution, but only one at higher concentrations.

The anionic charge on the terminal-dinitrogen complex was demonstrated by absorbing the anion on an anion exchanger. The conductance, which is typical of a 2:1 electrolyte, has a linear plot over a range of concentrations very similar to that of an authentic 2:1 electrolyte such as $[RuCl_5NO]K_2$ as shown in Figure 2. By contrast, $Ru(H_2edta)(CH_3CN)_2$ and [Ru(Hedta)CO]K show appreciable deviation from linearity, consistent with the behavior of weak electrolytes.

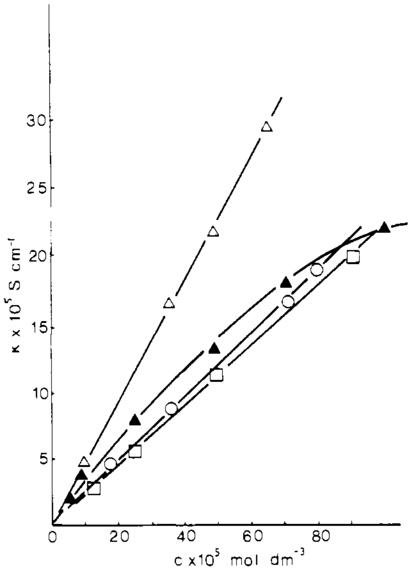

Figure 2. Specific conductivity (κ) in aqueous solution at 24 °C of some ruthenium complexes: △, $[Ru(NH_3)_6]Cl_3$; ○, $[Ru(edta)N_2](NH_4)_2 \cdot 5H_2O$; □, $[RuCl_5NO]K_2$; ▲, $Ru(H_2edta)(CH_3CN)_2 \cdot H_2O$.

Electronic Spectra. The UV–visible spectra of the ruthenium(II) edta complexes are determined by three considerations: (i) charge transfer from the ruthenium(II) center to the π-acceptor ligand, i.e., MLCT, (ii) internal ligand transitions, and (iii) d–d transitions. Because the donor atoms in edta are comparable, in their σ-donor capacity, to ammine and/or aquo ligands, the spectra of the complexes are comparable to those of the corresponding ruthenium(II) ammines containing the same π-acceptor ligands. The spectra of the complexes prepared together with those of some selected ruthenium(II) ammines are given in Table VI.

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Table VII. Electronic Spectra of Some Dinitrogen Complexes of Ruthenium(II)

metal group attached to dinitrogen (M)	λ_{max}, nm terminal complex[a] ($M-N_2$)	λ_{max}, nm bridging complex[b] ($M-N_2-M$)	ref
$Ru(NH_3)_4H_2O$	220	265	2, 29
$Ru(NH_3)_3(H_2O)_2$	221	262	46
$Ru(H_2O)_5$	218	255	5
$Ru(en)_2H_2O$	220	265	31, 29
$Ru(trien)H_2O$	225	268	4
Ru(Hedta)	225	278	this work

[a] Molar absorptivity (1.3–1.8) × 10^4 mol^{-1} dm^3 cm^{-1}. [b] Molar absorptivity (4.0–5.0) × 10^4 mol^{-1} dm^3 cm^{-1}.

The spectra of the terminal- and bridging-dinitrogen–edta complexes have intense absorption bands which parallel those found in other related ruthenium(II) dinitrogen complexes as shown in Table VII. Gray et al.[47] have attributed these to metal to ligand charge transfers. The lower energy of the band observed in the dimeric edta complex suggests that the Ru^{II}(edta) center is a better donor than the other ruthenium(II) ammines and/or aquo complexes. The carbonyl and nitrosyl complexes show rising absorptions toward the high-energy end of the spectrum, suggesting the presence of a band beyond the range of the instrument. Similar "end absorptions" have been noted for $Ru(NH_3)_5CO^{2+}$ [38] and *cis*-$Ru(NH_3)_4(NO)Cl^{2+}$ [37] and have been interpreted as due to MLCT with $\lambda_{max} < 200$ nm.[37,48] In *trans*-$Ru(NH_3)_4(NO)Cl^{2+}$ an intense charge-transfer band is observed at 240 nm.[37,49] The absence of such a band in the spectrum of $Ru(H_2edta)(NO)Cl$ and the general similarity of the spectrum to that of the *cis*-$Ru(NH_3)_4(NO)Cl$ suggest strongly that in the edta complex the NO and Cl ligands are also cis to each other. The spectrum of $Ru(H_2edta)(C_6H_5CN)_2$ parallels that of *cis*-$Ru(NH_3)_4(C_6H_5CN)_2^{2+}$ reported by Ford;[9] accordingly, the high-energy band is assigned to internal ligand transitions, whereas the lower energy, solvent-dependent absorption is due to MLCT. The extra CN substituent in $Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2$ shifts both the MLCT and the internal-ligand transitions to lower energy as would be expected from the electron-withdrawing effect of the substituent. In $Ru(H_2edta)(CH_3CN)_2$ the intense high-energy band is assigned to charge transfer by analogy to $Ru(NH_3)_5CH_3CN^{2+}$.[9]

The lower energy band in $Ru(Hedta)CO^-$ and the shoulder at 260 nm are analogous to the absorption bands observed in $Ru(NH_3)_5CO^{2+}$ [38] and are also assigned to $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ transitions,[48] approximating the coordination sphere to octahedral. The two bands in $Ru(Hedta)H_2O^-$ are similarly assigned to the same transitions. A $^1A_1 \rightarrow {}^1T_1$ transition is also suggested for the low-energy band in $Ru(H_2edta)(CH_3CN)_2$ and the band at 360 nm of $Ru(H_2edta)(NO)Cl$ by analogy with similar assignments which have been made for the corresponding bands in *cis*-$Ru(NH_3)_4(NO)Cl^{2+}$ [37] and $Ru(NH_3)_5CH_3CN^{2+}$.[9] It appears that in the cases in which a comparison of the $^1A_1 \rightarrow {}^1T_1$ transition can be made between the Ru(Hedta)X and the $Ru(NH_3)_5X$ complexes, the former have absorptions at lower energies, suggesting that the Hedta ligand produces a weaker ligand field splitting than the ammine ligands.

Vibrational Spectra. The vibrational spectra of the complexes are of interest because of the information which they provide about bonding interactions between the metal and the π-acceptor ligands. A decrease in the magnitude of the free ligand is usually taken as an indication of the extent of $d\pi \rightarrow \pi^*$ bonding in the complexes.[50] Because in the edta complexes the remaining positions are occupied by σ donors, they can be compared directly to the ruthenium(II) ammine complexes with the same π-acceptor ligands. The vibrational frequencies in the coordinated and free π-acceptor ligands for the prepared complexes and for some related ammine complexes are shown in Table VIII.

Table VIII. Stretching Frequencies[a] (cm^{-1}) in Coordinated and Free π-Acceptor Ligands

complex	coordinated ν(XY)[b] IR	coordinated ν(XY)[b] Raman	free ν(XY)	Δν
$[Ru(edta)N_2](NH_4)_2\cdot 5H_2O$	2110 s		2331	221
$[(Ru(edta))_2N_2]Mg_2\cdot 8H_2O$	2060 vw	2064 s	2331	267
$[Ru(Hedta)CO]K\cdot H_2O$	1940 s		2143	203
$Ru(H_2edta)(NO)ClH_2O$	1890 s		2220	320
$Ru(H_2edta)(CH_3CN)_2H_2O$	2268 m 2278 m, sh	2267 ms 2278 m	2257	−10
$Ru(H_2edta)(C_6H_5CN)_2H_2O$	2226 s 2240 ms 2225[c] 2240 sh[c]	2221 s 2236 ms	2230	4
$[Ru(edta)(C_6H_5CN)_2]K_2\cdot nH_2O$[d]	2220 2240 sh			10
$Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2$	2198 sh 2212 s 2232 s 2242 sh		2237	25
$[Ru(NH_3)_5CO]Cl_2$[e]	1918			225
$[Ru(NH_3)_5N_2]Cl_2$[e]	2105			226
$[(Ru(NH_3)_5)_2N_2](BF_4)_4$[f]		2100		231
cis-$[Ru(NH_3)_4(NO)Cl]Cl_2$[g]	1899			331
trans-$[Ru(NH_3)_4(NO)Cl]Cl_2$[g]	1880			420
cis-$[Ru(NH_3)_4(C_6H_5CN)_2]ZnBr_4$[h]	2219 vs 2232 s			11
trans-$[Ru(NH_3)_4(C_6H_5CN)_2](ClO_4)_2$[h]	2213 vs			

[a] Spectra recorded in Nujol mulls. [b] XY = N_2, CO, NO, CN in RCN. Key: w, weak; m, medium; ms, medium strong; s, strong; sh, shoulder; v, very. [c] In methanol solution. [d] Not fully characterized. [e] From ref 50. The counterion also affects XY. In $[Ru(NH_3)_5N_2]X_2$ the values are as follows for X: Cl, 2105; Br, 2111; I, 2125; BF_4, 2145; PF_6, 2166 cm^{-1}. [f] Reference 51. [g] Reference 37. [h] Reference 9.

The decreases in stretching frequency observed in $Ru(Hedta)N_2^{2-}$ and $Ru(Hedta)CO^-$ are comparable to those observed in the corresponding pentaammine. Apparently, the fact that these complexes carry a negative charge does not affect the back-donating ability of the metal center which, in this case, appears to be determined by the formal oxidation state of the metal. A more precise comparison of the values in the two series is limited by the fact that they contain different counterions which are known to influence the stretching frequency of the coordinated π acceptor as discussed by Chatt et al.[50] However, in the case of the dimeric $(Ru(edta))_2N_2^{4-}$, the stretching frequency is about 36 cm^{-1} lower than in the corresponding $(Ru(NH_3)_5)_2N_2^{4+}$; presumably the difference of eight units of the ionic charge is of significance in this case.

In the case of the nitrosyl complex, the observed ν(NO) frequency is comparable to that of the analogous $[Ru(NH_3)_4(NO)Cl]Cl_2$ (cis 1899 cm^{-1}, trans 1880 cm^{-1} [37]) and is in agreement with a $Ru^{II}NO^+$ formulation. The susceptibility of the nitrosyl group to nucleophilic attack also provides chemical support for this description and is in broad agreement

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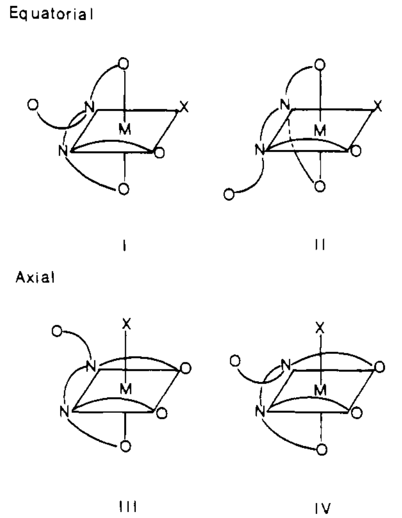

Figure 3. Possible geometric isomers for five-coordinate edta.

with Bottomley's observations on the reactivity of nitrosyls.[52]

The organic nitrile complexes also resemble the corresponding tetraammines. The effect of coordination on the stretching frequency of the attached CN group has been found to be a small increase in the case of $Ru(H_2edta)(CH_3CN)_2$ and small decreases in the case of the benzonitrile and 1,2-dicyanobenzene complexes. In the last case, two distinct absorptions were observed; the one at a frequency close to that of the CN group in the free ligand is attributed to the uncoordinated CN group. This behavior is consistent with the observations of Ford and Clarke,[9] who have found decreases in ν(CN) in the pentaammine and, to a lesser extent, the tetraammine organonitrile complexes of ruthenium(II). This they attributed to the exceptional back-bonding ability of the ruthenium(II) center which offsets the increase in frequency normally encountered when organonitrile ligands are complexed to other metal centers.[53] The smaller effects observed in the case of edta complexes when compared to the corresponding ammines are due in part to the absence of counterion polarization in the neutral edta complexes which is known to increase the frequency shift in the ammine series.[9,50] In the potassium salt of $Ru(H_2edta)(C_6H_5CN)_2$, which was obtained as an unstable, not fully characterized solid, the reduction in ν(CN) is greater than in the neutral complex.

The main absorptions due to coordinated CN in the $Ru(H_2edta)(RCN)_2$ complexes are accompanied by distinct absorptions of lower intensity on the high-energy side; similar patterns are also observed in their Raman spectra. The same behavior was noted with *cis*-$Ru(NH_3)_4(C_6H_5CN)_2$ but not in the trans complex; this suggests strongly that the edta complexes have cis configurations.

The absorptions in the carbonyl region of the spectrum are important in establishing the presence of a protonated free arm in the edta ligand. The positions of the two major absorptions, ν(CO) of the protonated carboxylic group at about 1730 cm^{-1} and $\nu(CO)_{as}$ at about 1600 cm^{-1}, for the coordinated carboxylate are practically independent of the nature of the π-acceptor ligand. The relative intensities of the two peaks also give an indication of the ratio of free to coordinated groups. Thus, in the nitrosyl and organic nitrile complexes the peaks were of almost equal intensity, whereas in the carbonyl complex the band at 1600 cm^{-1} was from 3 to 4 times more intense than that at 1730 cm^{-1}. The unprotonated free carboxylate arm of edta in the dinitrogen complexes does not give rise to a distinct absorption but forms part of the broad band of the coordinated carboxylate at 1640–1580 cm^{-1}.

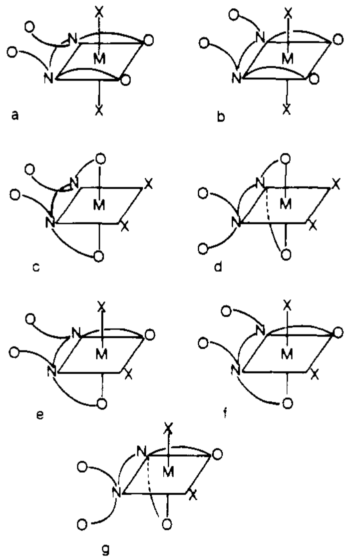

Figure 4. Possible geometric isomers for four-coordinate edta.

Table IX. Proton NMR Spectra of Some Ru^{II}edta Complexes[a]

complex	major peaks, ppm	solvent
$Na_2H_2edta \cdot 2H_2O$	3.8 (en), 4.2 (gly), 4.9 (H_2O)	TFA[b]
$[Ru(Hedta)CO]K \cdot 2H_2O$	3.4, 3.8, 4.1, 4.2, 4.5	D_2O, pH 1.0
$Ru(H_2edta)(CH_3CN)_2 \cdot H_2O$ [rel ratios]	2.2 (CH_3),[d] 3.1 (en), 3.8, 4.0 (gly) [6:4:8]	TFA[b]
$Ru(H_2edta)(C_6H_5CN)_2 \cdot 2H_2O$ [rel ratios]	3.3 (en), 4.1, 4.3 (gly), 7.3 (ar)[e] [4:8:9.5[c]]	TFA[b]
$Ru(H_2edta)(1,2\text{-}C_6H_4(CN)_2)_2 \cdot 2H_2O$ [rel ratios]	3.5 (en), 4.5, 4.6 (gly), 6.9 (ar) [4:8:8[c]]	TFA[b]

[a] Abbreviations: TFA = trifluoroacetic acid; en = ethylenic protons; gly = glycinate arm protons; ar = aromatic. [b] Acid broadened. [c] Integration of aromatic protons not accurate due to proximity of solvent resonance. [d] Resonance of free CH_3CN at 1.7 ppm. [e] Resonance of free C_6H_5CN at 7.5 ppm.

Stereochemistry. When edta acts as a pentadentate ligand with the sixth position occupied by a substituent ligand, four geometric isomers are possible which are shown in Figure 3. The isomers can be divided into pairs of "equatorial" (I and II) and "axial" (III and IV) configurations. In studying the structure of cobalt edta complexes, Howarth et al.[54] have suggested that acid hydrolysis of $Co(edta)^-$ to $Co(edta)X^{2-}$ (X = Cl, Br) is unlikely to produce II or III since these require the opening of at least two glycinate rings of edta as opposed to only one for the formation of isomers I and II. Therefore, isomers III and IV are provisionally discounted. Deuteration[55] and crystallographic studies[56] have shown that upon coordination the equatorial glycinate arms of edta are more strained than the axial arms and, therefore, more prone to substitution. Considerable evidence has accumulated to indicate that the equatorial isomer is the favored one.[54,57,58]

When four coordination positions are occupied by the edta ligand, the number of possible isomers increases to 7 as shown

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Table X. ^{13}C NMR Chemical Shifts[a] of Some Ru^{II}(edta) Complexes

complex[g]	carboxylate C			methylenic C			ethylenic C	ligand C
	equat	axial	free	equat	axial	free		
Ru(Hedta)CO$^-$	182.9	184.1, 185.7	170.7	65.7	64.8, 63.5	61.3	59.3, 57.9	202.8
Ru(H_2edta)(NO)Cl[b]								
0.4 mol dm^{-3}		182.9, 180.4	170.5, 169.6		65.7, 64.8[c]	64.8,[c] 63.4	59.8[c]	
0.05 mol dm^{-3}		182.8, 180.5	170.8, 170.1		66.4, 66.1	64.7, 63.0	60.9, 60.6	
	181.8	183.6, 180.7	171.1	66.7	65.3	64.4	60.2	
Ru(H_2edta)(CH_3CN)$_2$[d]		188.8	173.7		66.6	64.8	61.8	130.7 (CN), 5.7 (CH_3)[f]
Co(edta)$^-$[e]	182.4	183.0		65.8	66.0		64.0	
Co(Hedta)Cl$^-$[e]	183.8	184.7, 185.2	169.6	66.9	65.5, 65.8	63.8	62.3, 64.8	
Co(edta)Cl^{2-}[e]	183.7	184.8, 185.3	173.4	66.9	65.2, 66.1[c]	66.1[c]	62.3, 64.7	
Co(Hedta)H_2O[e]	182.6	183.8, 184.3	169.6	67.4	66.4, 64.7	62.6	61.8, 63.4	

[a] In ppm relative to Me_4Si. equat = equatorial. [b] Only major peaks shown; tentative assignment of peaks. [c] Superimposed peaks. [d] In trifluoroacetic acid. [e] From ref 54. [f] In free CH_3CN, 6.3 (CH_3) and 117.7 (CN) ppm. [g] Complexes in D_2O unless otherwise stated.

in Figure 4. These configurations may be conveniently labeled as trans-axial (a, b), cis-equatorial (c, d), and nonsymmetrical (e, f, and g). With use of the same argument as above, isomers a, c, and e would be favored over the other members of their respective groups because, in each case, the least number of rearrangements of glycinate arms would be required for their formation from a hexadentate structure. The most likely isomer is c, the logical extension of I, in which both equatorial arms are free.

Evidence for the structure of the ruthenium edta complexes in solution was obtained from ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C spectra provided more useful information as the ^{1}H NMR spectra were complicated because of AB coupling and often poorly resolved as a result of broadening in acid solution.[57,59] The spectra are summarized in Tables IX and X, together with information from the spectra of related complexes obtained by other workers.

The ^{13}C spectrum of [Ru(Hedta)CO]K·2H_2O produced 11 peaks and established the absence of symmetry elements as expected from a pentadentate coordination of edta. The assignments shown in Table X were made by comparison with the reported spectra of Co^{III}(edta) complexes.[54] The observed chemical shifts of the carbonyl complex resembled the values for the protonated cobalt(III) complexes. While it is not possible to assign a configuration unambiguously, the observed spectrum is in agreement with the equatorial isomers of Co(edta)X^{2-} and Co(Hedta)X^-.

The ^{1}H NMR spectra of the nitrile complexes, recorded in trilfuoroacetic acid, produced acid-broadened peaks. The resonances due to edta appeared between 3.0 and 4.0 ppm. The coalesced AB patterns of the glycinate methylenic protons appeared at lower field and the broadened A_2B_2 signals of the ethylenic backbone at higher field. The appearance of a single methyl resonance for Ru(H_2edta)(CH_3CN)$_2$ immediately suggested a symmetrical molecular environment. However, the possibility that acid broadening resulted in the coalescence of two closely separated peaks could not be excluded. A symmetrical structure was confirmed by the ^{13}C spectrum recorded in trifluoroacetic acid solution, which showed seven peaks for a molecule containing 14 carbon atoms. The carboxylate resonances, free and coordinated, appeared at 173.7 and 188.8 ppm, respectively. The nitrile carbons produced a single peak at 130.7 ppm, a downfield shift of 13 ppm from the free-ligand resonance. A doublet at approximately 65 ppm was assigned to the methylenic carbons of the glycinate arms with the resonance at the higher field attributed to the free glycinate arm by analogy with the behavior of the cobalt(III) complexes. The spectrum is compatible with configurations a, b, or c. Further distinction between these was made by comparing ν(CN) in the infrared and Raman spectra of the solids. Both vibrational spectra were identical in producing two absorptions at 2268 and 2278 cm^{-1} (Table VIII) which were assigned to the symmetric and asymmetric stretching modes of two CN groups in a cis configuration. The similarity of the Raman spectra and of the infrared spectra in the solid and in methanol solution of the complex Ru(H_2edta)(C_6H_5CN)$_2$ with those of the acetonitrile complex suggests strongly that this complex also has the same configuration c.

The ^{13}C spectrum of Ru(H_2edta)(NO)Cl measured in D_2O was concentration dependent. In concentrated solution four prominent resonances were seen in the carboxylate region. Of these, the peaks 182.9 and 180.4 ppm were assigned to coordinated carboxylates and those at 170.5 and 169.6 ppm to the free-carboxylic groups. This suggested that in concentrated solution the complex existed largely as the undissociated tetradentate species. Of the four expected methylenic signals from the glycinate arms, only three peaks were observed; however, the signal at 64.8 ppm was especially intense and could have resulted from the superposition of two closely separated peaks. Similarly, only one intense peak was observed for the ethylenic carbons and was explained in the same way. In addition to the major peaks, a number of small resonances were seen and attributed to the presence of the pentadentate complex. The spectrum of a less concentrated solution of Ru(H_2edta)(NO)Cl (0.05 mol dm^{-3}) was more complex than the one described above and clearly indicated a mixture. This was concluded from the appearance of five resonances between 184 and 180 ppm and three in the free carboxylic acid region between 171 and 169 ppm. Up to 12 peaks appeared in the methylenic region of the spectrum. This indicated that both the tetradentate and pentadentate species were present in solution as a result of the dissociation of Ru(H_2edta)(NO)Cl as described above. Although no stereochemical assignment was possible from the ^{13}C spectrum, the similarity between the electronic spectrum of this complex and that of *cis*-Ru(NH_3)$_4$(NO)Cl suggests the cis-equatorial configuration for the tetradentate complex and, therefore, configuration I for the pentadentate species.

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Registry No. A, 76095-13-1; B, 76095-14-2; C, 76068-57-0; D, 76058-08-7; E, 76095-15-3; F, 76058-09-8; G, 76058-10-1; H, 76068-58-1; I, 76058-11-2; [Ru(edta)(C_6H_5CN)$_2$]K_2, 76058-12-3; [RuCl_5H_2O]K_2, 14404-33-2; Ru^{II}(Hedta)H_2O^-, 68122-22-5; [RuCl_5(NO)]K_2, 14854-54-7; MNTS, 80-11-5; KNO_2, 7758-09-0; $NOPF_6$, 16921-91-8; Na_2H_2edta, 139-33-3; [Ru(NH_3)$_6$]Cl_3, 14282-91-8; [Ru(Hedta)N_2]$^-$, 76058-13-4; [(Ru(Hedta))$_2N_2$]$^{2-}$, 76123-93-8.

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