Table II. Rate Parameters for the Acid-Catalyzed Aquation Reactions of α- and β-$Co(EDDA)CO_3^-$ Ions[a] ([Complex] = 10^{-3} M; I = 2.0 M (KNO_3))

A. α-$Co(EDDA)CO_3^-$

Temp, °C	$10^3 k_0$, sec^{-1}		k_1, M^{-1} sec^{-1}		k_2, sec^{-1}
15	1.1 ± 0.1		58 ± 1		28.5
20	1.7 ± 0.8	(1.1)	76 ± 1	(50)	39.5
25	2.9 ± 0.2	(2.2)	118 ± 1	(83)	55.0
30.3	.....	(3.9)	.....	(136)	...
$\Delta H^\ddagger$, kcal/mol	17 ± 2	(21 ± 3)	12 ± 1	(16 ± 1)	11.1 ± 0.6
$\Delta S^\ddagger$, eu	−14 ± 7	(0 ± 12)	−8 ± 8	(5 ± 3)	−13 ± 2

B. β-$Co(EDDA)CO_3^-$

Temp, °C	$10^4 k_0$, sec^{-1}		k_1, M^{-1} sec^{-1}		k_2, sec^{-1}
15	2.8 ± 0.8		1.25 ± 0.02		0.90
20	7.3 ± 2.9	(1.9)	1.73 ± 0.07	(1.82)	1.40
25	9.8 ± 4.3	(3.8)	2.44 ± 0.11	(3.04)	2.31
30.3	...	(6.9)	...	(5.23)	...
$\Delta H^\ddagger$, kcal/mol	21 ± 6	(21 ± 3)	10.8 ± 0.3	(17 ± 1)	16.3 ± 1.5
$\Delta S^\ddagger$, eu	−2 ± 20	(2 ± 12)	−20 ± 1	(2 ± 3)	−2 ± 5

[a] Parenthesized values are from ref 4; I = 1.0 M ($NaClO_4$).

Table III. Rate Parameters for Acid-Catalyzed Ring-Opening Reactions of Some Chelated Cobalt(III) Carbonato Complexes at 25°

Complex ion[a]	k_1, M^{-1} sec^{-1}	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, eu	Ref
$Co(py)_4CO_3^+$	8.9×10^{-6}	24.0	−1	18
$Co(phen)_2CO_3^+$	1.5×10^{-4}	20.4	−9	19
$Co(bpy)_2CO_3^+$	2.2×10^{-4}	22.3	−2	19
α-$Co(dmtr)CO_3^+$	1.8×10^{-2}			20
β-$Co(dmtr)CO_3^+$	5.6×10^{-4}			20
$Co(en)_2CO_3^+$	0.6	13.8	−7	3
$Co(tren)CO_3^+$	2.0	11.1	−20	3
α-$Co(trien)CO_3^+$	5.2	15.0	−5	3
β-$Co(trien)CO_3^+$	0.2	17.0	−5	3
$Co(NTA)CO_3^{2-}$	47	18.6	+11	2
α-$Co(EDDA)CO_3^-$	118	12	−8	This work
β-$Co(EDDA)CO_3^-$	2.4	10.8	−20	This work

[a] py = pyridine; phen = *o*-phenanthroline; bpy = bipyridine; dmtr = 4,7-dimethyl-triethylenetetramine; en = ethylenediamine; tren = β,β′,β″-triaminotriethylamine; trien = triethylenetetramine.

parameters for which are almost identical with those for the β-EDDA complex and differ from the α-EDDA species mainly in the increased $\Delta S^\ddagger$ for the latter.

Clearly, the overall ionic charge of the complex ion is not a factor of prime significance, as is illustrated by rate comparisons of β-EDDA with tren species and of α-EDDA with NTA. Neither do considerations of ligand basicity nor diaquo complex acidity afford clean-cut correlations of reactivities including the anionic species, contrary to a previous suggestion with respect to the tetraammine complexes.[19] One notes that the average pK_a's of the ligands dmtr, tren, trien, NTA, and EDDA are 6.3,[20] 9.5,[21a] 7.3,[21a] 4.7,[21a] and 5.9,[21b] respectively. Similarly, the first pK's of the various diaquo complexes $CoL(H_2O)_2^{3+}$ are 5.4,[22] 5.4,[23] 5.3,[23] 6.2,[24] 7.4,[25] and 6.0[25] for L = tren, α-trien, β-trien, NTA, α-EDDA, and β-EDDA, respectively. The factors which govern the relative magnitudes of the rate constants for acid-catalyzed ring opening of chelated carbonato complexes obviously include a stereochemical component, as outlined before.[3] The influence of the electronic structure of the ligand, however, at least as evidenced by the type of pK_a data quoted, is not yet clearly delineated for this type of reaction. Indeed, the contrasts in k_1 as between the dmtr and trien complexes or between the tren and NTA species, for example, might perhaps better be ascribed to differences in solvation resulting from methyl substitution in the first case and ionic charge reversal in the second.

Acknowledgment. R.v.E. gratefully acknowledges financial support for his participation in this research from the South African Council for Scientific and Industrial Research.

Registry No. α-K[$Co(EDDA)CO_3$], 56144-83-3; β-K[$Co(EDDA)CO_3$], 53029-88-2.

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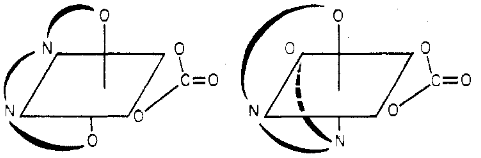

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(12) The rate constant for this isomerization is reported to be 3×10^{-4} sec^{-1} at 29.3°: P. J. Garnett and D. W. Watts, personal communication. This suggests a half-time of the order of magnitude of 100 min at room temperature.
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Synthesis and Acid Hydrolysis of *trans*-Dichlorobis(ethylenediamine)ruthenium(III) and Related Compounds

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Further to our studies on the reactions of ruthenium(III) ethylenediamine complexes[1-3] we report the synthesis of the new *trans*-dichlorobis(ethylenediamine)ruthenium(III) complex

Table I. Infrared Spectra (cm^{-1}) for Ruthenium(III) Complexes^{a}

Compd	NH_2 vibration	CH_2 rock	NH asym deform	H–OH bending	Ru–X stretch	Other bands
trans-$[RuCl_2en_2]Cl\cdot O\cdot 5H_2O$	1123 s, 1105 w	885 m	1585 s	1597 sh	325 s	484 m, 434 m, 265 s, 250 m
trans-$[RuBr_2en_2]Br$	1126 m, 1107 s	879 m	1577 s		213 s	474 m, 427 m, 264 s, 229 m
cis-$[RuCl_2en_2]Cl\cdot H_2O^{b}$	1157 m, 1134 m, 1116 m, 1100 m	886 m, 867 m	1567 s	1633 s	322 w, sh 311 m, 273 s	488 m, 439 m, 251 m
cis-$[RuBr_2en_2]Br\cdot H_2O^{b}$	1151 m, 1128 m, 1111 m, 1096 m	881 m, 864 m	1558 s	1616 s	207 s	478 m, 429 m, 249 m

^{a} In Nujol. ^{b} Reference 1.

and the dibromo analog together with acid hydrolysis studies on the dichloro complex. The *trans*-$RuCl_2en_2^+$ ion (en = ethylenediamine) has been isolated as the chloride and iodide salts following the isomerization of *cis*-$[RuCl_2en_2]Cl$ in boiling ethylene glycol.

Experimental Section

cis-Dichlorobis(ethylenediamine)ruthenium(III) chloride monohydrate and *cis*-dibromobis(ethylenediamine)ruthenium(III) bromide monohydrate were prepared as described previously.[1]

trans-**Dichlorobis(ethylenediamine)ruthenium(III)chloride Hemihydrate.** *cis*-$[RuCl_2en_2]Cl\cdot H_2O$ (0.5 g) was dissolved in ethylene glycol (25 cm^3) by heating to 60° in a large test tube. The solution was next heated to the boiling point for 1 min whereupon the original orange color deepened. The reaction vessel was immediately cooled and the solution passed down a Dowex 50W-X cation exchange column in the hydrogen form (bed volume 2 cm^3). The column was washed with water (10 cm^3) to remove the ethylene glycol and the complex was eluted using hydrochloric acid (2 *M*, 20 cm^3). The eluate was concentrated in a rotary evaporator to 10 cm^3 and orange crystals of the trans complex were obtained. These were filtered off at the pump (the filtrate being reserved) and washed with ethanol then acetone. The yield was 0.32 g. Anal. Calcd for $C_4H_{17}Cl_3N_4O_{0.5}Ru$: C, 14.3; H, 5.1; N, 16.6: Found: C, 14.3; H, 5.1; N, 16.4.

trans-**Dichlorobis(ethylenediamine)ruthenium(III) Iodide Hemihydrate.** To the filtrate from the above sodium iodide (ca. 3 g) was added to give bright red crystals of the iodide salt. The yield was 0.16 g. Anal. Calcd for $C_4H_{17}Cl_2IN_4O_{0.5}Ru$: C, 11.2; H, 4.0; Cl, 16.7; I, 29.6; N, 13.1. Found: C, 11.5; H, 4.0; Cl, 17.4; I, 29.8; N, 13.2.

trans-**Dibromobis(ethylenediamine)ruthenium(III) Bromide.** This complex was prepared by an analogous method to that used for the dichloro complex. The completion of the cis–trans conversion was marked by a change in color from dark-brown to yellow-brown. The yield was 60%. Anal. Calcd for $C_4H_{16}Br_3N_4Ru$: C, 10.4; H, 3.5; Br, 51.9; N, 12.1. Found: C, 10.8; H, 3.8; Br, 52.5; N, 11.8.

Physical Measurements

Infrared spectra were measured using a Grubb-Parsons DB1-G54 spectrophotometer calibrated against polystyrene in the 4000–400 cm^{-1} region. Far-infrared measurements (500–200 cm^{-1}) were made on a Grubb-Parsons DM4 instrument. Ultraviolet and visible spectra were measured on a Cary 14 spectrophotometer using matched 1 cm silica cells.

Results and Discussion

Characteristic infrared and ultraviolet–visible absorption spectra for the *trans*-$[RuX_2en_2]^+$ complexes (X = Cl or Br) are given in Tables I and II. We have previously discussed the use of the three following infrared regions, viz., 1560–1600, 1100–1160, and 870–900 cm^{-1}, in the characterization of cis–trans isomers. The spectra of the new complexes are consistent with earlier findings showing only two bands for trans isomers in the region 1090–1160 cm^{-1} whereas there are four bands for the corresponding cis isomers. The splitting observed by Baldwin[4] in the CH_2 rocking region for cis but not for trans isomers is also absent here. In the far-infrared region the D_{2h} symmetry of the *trans*-$RuX_2en_2^+$ complexes predicts one metal–halogen stretching vibration whereas the C_2 symmetry of the cis species requires two such vibrations. The assignments for the trans isomers shown in Table I have been made by replacement of coordinated chloride by bromide and confirm these predictions.

Table II. Visible and Ultraviolet Spectra of Trans-Disubstituted Bis(ethylenediamine)ruthenium(III) Complexes

Complex	Solvent	λ_{max}, nm (ϵ M^{-1} cm^{-1})
trans-$[RuCl_2en_2]Cl\cdot O\cdot 5H_2O$	0.1 *M* HCl	342 (4080); 295 sh (745); 268 sh (810)
trans-$[RuBr_2en_2]Br$	0.2 *M* HBr	409 (4680); 382 (770)
trans-$[Ru(H_2O)_2en_2]^{3+\,a}$	0.1 *M* $HClO_4$	340 br (540)
trans-$[RuClH_2Oen_2]^{2+\,a}$	0.1 *M* CH_3SO_3H	310 (2800)

^{a} Prepared by reaction of *trans*-$[RuCl_2en_2]Cl\cdot 0.5H_2O$ with the theoretical amount of silver *p*-toluenesulfonate.

Table III. Rate Data for *trans*-$RuCl_2en_2^+$

Temp, °C	$10^4K_{H_2O}$,^{a} sec^{-1}	Temp, °C	$10^4K_{H_2O}$,^{a} sec^{-1}
39.9	0.239	61.8	3.40^{b}
50.1	0.75	68.9	4.90, 5.05^{c}
59.3	1.97	78.7	11.0

^{a} Measured spectrophotometrically at 342-nm in 0.1 *M* methanesulfonic acid at ionic strength 0.1 *M* unless otherwise stated; average reproducibility ±4%. ^{b} By titration. ^{c} 1 *M* acid.

The ultraviolet and visible spectra reported in Table II are certainly charge transfer in type although showing bands or shoulders of much weaker intensity. The true intensities will be less than those measured here but unfortunately curve resolution has not been possible.

The kinetics of the primary aquation reaction

$$trans\text{-}RuCl_2en_2^{\ +} + H_2O \rightleftarrows trans\text{-}RuClH_2Oen_2^{\ 2+} + Cl^- \qquad (1)$$

have been studied chiefly by a spectrophotometric method and checked titrimetrically. The spectrophotometric method was similar to that used previously.[2] The complex concentration was 2×10^{-4} *M*. Chloride ion was determined by Volhard titration after first removing the complex cations on an ion exchange column (Acid Dowex 50W-X). Since hydrolysis in nitric or perchloric acids leads to the formation of nitrosyl complexes[5] work was carried out in methanesulfonic acid.

Acid hydrolysis was observed to follow a first-order rate law for up to two half-lives after which time the reverse of reaction 1 interferes. Rate constants have been calculated from the slopes of $1 + \log (A_t - A_\infty / A_0 - A_\infty)$ vs. time plots. The results are given in Table III. Arrhenius parameters calculated from the data are $E_a = 21.8$ kcal mol^{-1}, $\Delta S^\ddagger = 10.4$ cal deg^{-1} mol^{-1}, and $\log A = 10.63$. From the extinction coefficients of Table II and the final optical densities of the solutions an equilibrium quotient for reaction 1 of 0.30 ± 0.05 at 60.1° and ionic strength 0.1 is obtained.

The acid hydrolysis rate constants and Arrhenius parameters for the *trans*-$RuCl_2en_2^+$ complex are very similar to those found previously for the cis isomer. In general the trans isomer hydrolyzes somewhat more slowly than the cis counterpart but the differences are not significant. In 0.1 *M* chloride ion the hydrolysis product is converted completely back into the *trans*-dichlorobis(ethylenediamine)ruthenium(III) species which is identified by its spectrum. Unlike the corresponding acid hydrolysis of *trans*-$CoCl_2en_2^+$ which is accompanied by some 35% isomerization to the cis form,[6] the trans ruthenium(III) system shows complete retention of geometry. Retention of configuration during both acid and base hydrolysis of *cis*-$RuCl_2en_2^+$ has previously been found.[3]

Registry No. *cis*-$[RuCl_2en_2]Cl$, 22294-93-5; *cis*-$[RuBr_2en_2]Br$, 55822-57-6; *trans*-$[RuCl_2en_2]Cl$, 55822-58-7; *trans*-$[RuCl_2en_2]I$, 55822-59-8; *trans*-$[RuBr_2en_2]Br$, 55870-35-4; *trans*-$[Ru(H_2O)_2en_2]^{3+}$, 55870-36-5; *trans*-$[RuClH_2Oen_2]^{2+}$, 55870-37-6.

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Magnetic Exchange Interactions in Transition Metal Dimers. VI. The Tetracyanonickelate(II) Ion as a Bridging Group

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Very recently we reported[3] the results of a single-crystal X-ray, infrared, and ESR study of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, where tren = 2,2',2''-triaminotriethylamine. It was found that the copper atom environment is trigonal bipyramidal and that the complex is dimeric by virtue of the coordinated cyanide on each copper atom hydrogen bonding through its nitrogen to a primary amine of the tren ligand coordinated to the second copper. Attempts to prepare the analogous nickel(II) complex have given complexes with the composition $Ni_3(tren)_2(CN)_4X_2$, where $X^- = ClO_4^-$, I^-, and PF_6^-. Data will be presented in this note to show the presence of an $Ni(CN)_4^{2-}$ bridging group in $Ni_3(tren)_2(CN)_4X_2$.

Experimental Section

Samples of $Ni_3(tren)_2(CN)_4X_2$ were prepared by dissolving $NiSO_4{\cdot}6H_2O$, NaCN, and tren in boiling 50% H_2O/ethanol in a 3:4:2 ratio, and then adding a boiling 50% H_2O/ethanol solution containing an excess of NaX. Cooling the resulting solution in an ice bath gave bluish purple, crystalline products. Analytical data for all compounds are given in Table I.[4]

Variable-temperature (4.2–283°K) magnetic susceptibility measurements were made with a PAR Model 150A magnetometer as described in a previous paper.[5] Infrared spectra were run with a Perkin-Elmer Model 457 spectrometer using 13 mm KBr pellets. Electronic absorption data were measured using a Cary 14 spectrophotometer; KBr pelleted samples were run and pellet dispersion was compensated by employing a pellet of ~1% $Na(BPh_4)$ in KBr in the reference beam.

Results and Discussion

Cooling a 50% H_2O/ethanol solution of Ni^{2+}, tren, CN^-, and X^- (PF_6^-, I^-, and ClO_4^-) gives a compound that analyzes as $Ni_3(tren)_2(CN)_4X_2$ as indicated by the analytical data given in Table I.[4] The fact that the $Ni_3(tren)_2(CN)_4^{2+}$ cation can be precipitated by a variety of anions, differing greatly in size, suggests that the trinickel(II) cation is a molecular species. The $[Ni_2(tren)_2(CN)_4]X_2$ compounds are not sufficiently soluble for effective molecular weight determination by vapor-pressure osmometry; however, their insolubility does support the proposal for the presence of the $Ni_3(tren)_2(CN)_4^{2+}$ cation. It seems unlikely that for the series of X^- anions used that one would isolate in each case the same collection of Ni(II) monomers.

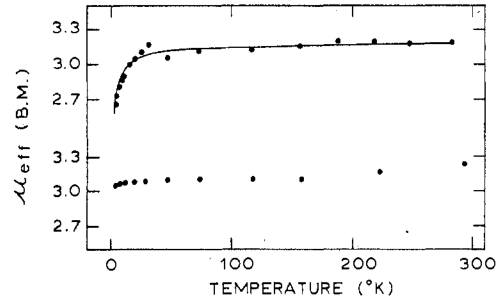

Figure 1. Magnetic susceptibility data for $[Ni_3(tren)_2(CN)_4](ClO_4)_2$ (top) and $Ni(tren)(SCN)_2$ (bottom) as a function of temperature. The data for the former are plotted as μ_{eff} per paramagnetic nickel ion and the solid line is a least-squares theoretical fit line.

Electronic absorption spectroscopy is very sensitive to the nickel(II) coordination geometry.[6] Three peaks are seen in the spectra (KBr pellets) of the $[Ni_3(tren)_2(CN)_4]X_2$ compounds in the region of ~400 to 1200 nm; the spectra show little sensitivity to the X^- counterion. The presence and appearance of the three bands are very characteristic of an octahedral nickel(II) environment. The three bands can be assigned as follows: 11,060 cm^{-1} [$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$], 12,580 cm^{-1} [$^1E_g(P) \leftarrow {}^3A_{2g}(F)$], and 17,860 cm^{-1} [$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$], which when least-squares fit to the theoretical equations for octahedral Ni(II) give the parameters $Dq = 1106$ cm^{-1}, $B = 940$ cm^{-1}, and $C = 2750$ cm^{-1}. Thus, electronic spectroscopy implies either that all *three* nickel atoms in $Ni_3(tren)_2(CN)_4^{2+}$ have the same environment or more probably that absorptions are to be seen for only one of the nickel atom environments. From what is known about the $Ni(CN)_4^{2-}$ ion, it is reasonable at this point to speculate that one of the nickel atom environments in $Ni_3(tren)_2(CN)_4^{2+}$ approximates that in the tetracyanonickelate ion, which is known[7] to have two low intensity bands at 22,500 cm^{-1} (ϵ 2) and 30,500 cm^{-1} (ϵ 250). Both of these bands would be difficult to see because of dispersion effects associated with KBr pellets in the near-uv and uv regions. The $Ni_3(tren)_2(CN)_4^{2+}$ cation could be viewed then as two $Ni(tren)^{2+}$ moieties *bridged* by $Ni(CN)_4^{2-}$; bis-bidentate bridging would be required to secure an octahedral environment for the two $Ni(tren)^{2+}$ centers. The electronic spectrum of the μ-oxalato $[Ni_2(tren)_2(C_2O_4)](ClO_4)_2$ compound is, in fact, very similar to those for the $[Ni_3(tren)_2(CN)_4]X_2$ compounds. It is our proposal, thus, that the bridging function of the $C_2O_4^{2-}$ anion is fulfilled by the $Ni(CN)_4^{2-}$ anion. Feller and Robson[8] have reported a compound $[Ni(DPK)_2^{2+}][Ni(CN)_4^{2-}]$, where DPK = di-2-pyridyl ketone. The nickel center in the cation was shown to be octahedrally coordinated by virtue of the $Ni(CN)_4^{2-}$ acting as a bidentate ligand; there are two bridging cyanide groups. Also, very recently the single-crystal X-ray structures of a series of Hofmann-type clathrates of the composition $M(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$, where M = Ni, Cd, Cu, and Mn, have been reported.[9] In these solids there are two-dimensional networks of $[M(NH_3)_2Ni(CN)_4]_\infty$ wherein $Ni(CN)_4^{2-}$ units are bridging between $M(NH_3)_2^{2+}$ moieties with end-to-end CN^- bridging.

Infrared spectra (KBr pellets) were run for the [Ni3-