Electron Spin Resonance Study of Iron(III) and Ruthenium(III) in a Trinuclear Complex of Tris(2-mercaptoethylamine)cobalt(III)

R. E. DeSIMONE,*[1a] T. ONTKO,[1b] L. WARDMAN,[1b] and E. L. BLINN[1b]

The new heteronuclear complexes $Ru^{III}(CoL_3)_2X_3$ (L = 2-mercaptoethylamine(1-); X = I^-, BPh_4^-) have been prepared and characterized and found to be analogous to the previously prepared Fe(III) complexes. A study of the electron spin resonance of these unique Fe(III) and Ru(III) species indicates that they are severely distorted from octahedral geometry, a fact responsible in part for their room-temperature spectra and that substantial metal–metal interaction occurs via direct metal orbital–metal orbital overlap. Hyperfine structure from two equivalent Co nuclei indicates that the unpaired electron is delocalized over all three metal ions in the complex. A comparison with other systems is given.

Introduction

The low-spin d^5 (t_{2g}^5) configuration has been one of the most fruitful configurations for the study of low-symmetry ligand fields in transition metal complexes.[2-5] Recently the subject of sulfur coordination has been approached through studies of the electron spin resonance of the t_{2g}^5 configuration in complexes of Fe(III), Ru(III), and Os(III).[6] In these studies, attention was directed toward chelate complexes of typical organic sulfur-donor ligands, and some interesting observations and conclusions were reported concerning the nature of sulfur vs. oxygen or nitrogen bonding in trigonal t_{2g}^5 coordination complexes.

We now wish to report the results of a study of a different type of MS_6 coordination complex, one in which the sulfur atoms forming the coordination sphere of the paramagnetic ion form part of another complex, and are not as in the usual case, simple organic ligands.

The complex $Fe(CoL_3)_2Cl_3\cdot 2H_2O$ ($L^- = NH_2CH_2CH_2S^-$) was first reported by Freeh, Chapman, and Blinn[7] in 1973 among a small group of trinuclear complexes of similar structure. It was postulated that the iron was low spin and, on the basis of Mossbauer spectroscopy and magnetic susceptibility studies, at least partially sulfur coordinated; $\Delta E q = 1.62$ mm/sec, $\delta = 0.567$ mm/sec, and $\mu = 2.10$ BM at 30°, typical of low-spin Fe(III). However, in this case, magnetic susceptibility and Mossbauer spectra do not yield information about metal–metal interaction, nor do they unequivocally confirm the expected FeS_6 structure shown in Figure 1. The ESR experiment should do both. Also, as part of this work, it is our intention to observe the effect on the ESR spectrum of low-spin Fe(III) of sulfur ligands shared between two metals.

In addition, we have expanded this study to include the analogous Ru(III) complexes, e.g., $Ru(CoL_3)_2X_3$. Comparison with the iron complex might be expected to reveal a trend in extent of electron delocalization in these systems.

Experimental Section

Materials. 2-Aminoethanethiol hydrochloride was purchased from Matheson Coleman and Bell and $RuCl_3\cdot xH_2O$ was purchased from Ventron (Alfa Inorganics). $Co(NH_2CH_2CH_2S)_3$ was prepared following established procedures as was $Fe(CoL_3)_2Cl_3\cdot 2H_2O$.[7]

Synthesis. $Ru[Co(NH_2CH_2CH_2S)_3]_2I_3$. To a suspension of 2.87 g (0.01 mol) of CoL_3 in 100 ml of water was added 0.242 g (0.001 mol) of "ruthenium trichloride", $RuCl_3\cdot xH_2O$, dissolved in a small quantity of water. The reaction was allowed to proceed for approximately 1 hr with continuous stirring. The reaction mixture was then filtered of excess CoL_3 and reduced in volume with a rotary evaporator to about 40 ml. After warming to ∼40°, a saturated solution, ∼1.5 g (0.01 mol), of sodium iodide was slowly added, after which the mixture was cooled for a few hours in the refrigerator. Filtration gave a dark brown powder in ∼60% yield.

Anal. Calcd for $Ru[Co(NH_2CH_2CH_2S)_3]_2I_3$: C, 13.68; H, 3.40; N, 7.95. Found: C, 14.01; H, 3.70; N, 8.06.

$Ru[Co(NH_2CH_2CH_2S)_3]_2[B(C_6H_5)_4]_3\cdot 4H_2O$. Preparation was similar to the iodide complex except for the addition of $NaB(C_6H_5)_4$ instead of NaI with immediate formation of a precipitate.

Anal. Calcd for $Ru[Co(NH_2CH_2CH_2S)_3]_2[B(C_6H_5)_4]_3\cdot 4H_2O$: C, 59.18; H, 6.10; N, 4.92. Found: C, 57.49; H, 6.07; N, 4.88.

Physical Measurements. Magnetic susceptibilities were determined by the Gouy method. Samples were prepared in air and compared with $Hg[Co(NCS)_4]$ as standard. Diamagnetic corrections were obtained using Pascal's law and employing tabulated constants.[8] Electronic spectra were recorded on a Beckman DK-2 spectrophotometer. Conductivity measurements were obtained using a Model RC-18 conductivity bridge manufactured by Industrial Instruments Inc. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Microanalytical Laboratory.

ESR spectra were recorded on a Varian E-4 spectrometer system at X-band frequencies. Calibration with DPPH ($g = 2.0036$) is expected to give magnetic fields accurate to ±1%. The best resolved spectra were obtained in either methanol or ethylene glycol solutions at room temperature and in ethylene glycol glass at 77°K. Spectra at 77°K in H_2O, MeOH, and ethylene glycol were virtually identical (except for resolution) and we feel that the species in all cases is the same. Unlike the situation observed in most t_{2g}^5 systems, we find that saturation, with accompanying loss in resolution, occurs rather easily and microwave power levels were kept at 0.5 mW or less for the Fe complex and at a 1–2 mW for the Ru complex.

Results and Discussion

Characterization of the $[Ru(CoL_3)_2]^{3+}$ Ion. The $(CoL_3)_2RuX_3\cdot nH_2O$ complexes (X = Cl, I, $B(C_6H_5)_4$) are prepared by the reaction of $RuCl_3$ with large excesses of CoL_3. If large excesses of CoL_3 are not employed, both $[(CoL_3)_2Co]X_3$ and $[(CoL_3)_2Ru]X_2$ can be isolated. The products obtained are highly sensitive to experimental conditions such as temperature and reaction time as well as to the amount of excess CoL_3 employed in the reaction. There are other examples of reactions of CoL_3 with various metal ions (other than Co(II)) which resulted in a rearranged product, $[(CoL_3)_2Co]X_3$. For example, the reaction of Fe^{2+} with CoL_3 results in the trinuclear ion $[(CoL_3)_2Co]^{3+}$ as does the reaction of Fe^{3+} with CoL_3 in the presence of iodide ion.[7] Although the mechanism of such a rearrangement is not fully understood, it is believed that the presence of a potential reducing agent is necessary to cause such a rearranged product. Therefore any ruthenium(II) present in the reaction mixture should cause such a rearrangement.

The Onsager slope obtained from conductivity data (slope is 272) indicates that $[(CoL_3)_2Ru]I_3$ is a 3:1 electrolyte in water. Therefore it can be concluded that the iodide ions are not coordinated in aqueous solution. The electronic spectrum of $(CoL_3)_2RuI_3$ in water shows a peak at 437 mμ (ϵ 6910) and a shoulder at 550 mμ (ϵ 1970). The electronic spectrum of $[(CoL_3)_2Co]^{3+}$ in water has a peak at 438 mμ (ϵ 6300) and at 590 mμ (ϵ 2150) while $[(CoL_3)_2Fe]^{3+}$ has bands at 445 mμ (ϵ 5300), 505 mμ (ϵ 4700), 595 mμ (ϵ 2000), and 920 mμ (ϵ

Table I

	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle_{iso}{}^{a}$	$|A_{\parallel}{}^{Co}|$	$|A_{\perp}{}^{Co}|$	$\langle A \rangle_{iso}{}^{a}$
Fe(CoL$_3$)$_2$Cl$_3$·2H$_2$O						
Solid	2.02	2.08				
Glass^c	2.01	2.08		14.0	1.6^b	
Soln			2.06			5.8
Ru(CoL$_3$)$_2$I$_3$						
Glass^c	1.99	2.03		21.5		

^{a} $\langle g \rangle_{iso} = {}^1\!/_3 g_{\parallel} + {}^2\!/_3 g_{\perp}$, $\langle A \rangle_{iso} = {}^1\!/_3 A_{\parallel} + {}^2\!/_3 A_{\perp}$. All A values in gauss. ^{b} Calculated from above equations. ^{c} At 77°K in ethylene glycol.
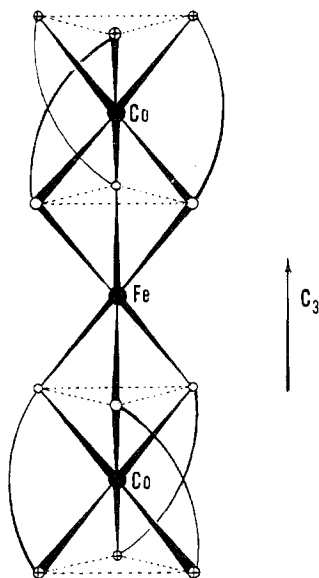

Figure 1. Proposed structure of the M(CoL$_3$)$_2{}^{3+}$ complex where M = Fe or Ru, ⊕ = N, and ○ = S.

Figure 2. Electron spin resonance spectrum of Fe(CoL$_3$)$_2$Cl$_3$ in ethylene glycol glass at 77°K. Horizontal marker indicates 50-G interval.

320). In all of the above complexes a band around 437 mμ is observed and hence this band is attributed to the ligand CoL$_3$; the band at 550 mμ must involve in some way the Ru(III) ion. The high extinction coefficient of all bands suggests that metal-to-ligand or ligand-to-metal charge transfer is involved in all observed electronic transitions.

The magnetic moment of (CoL$_3$)$_2$RuI$_3$ is 1.8 BM at 30°. This is indicative of one unpaired electron and is typical of Ru(III) in sulfur coordination.[9]

Electron Spin Resonance Spectra. One might expect that perhaps reduced covalency toward the iron, as a result of Co–S interactions, would produce a spectrum different from that normally found for FeS$_6$ systems, perhaps more like mixed sulfur–oxygen donors.[10] We find that the ESR spectral properties of this complex and of the Ru(III) analog which we have also prepared are in some ways totally unlike those of any heretofore studied low-spin d^5 complex and in other ways quite characteristic of other t$_{2g}{}^5$ species in MS$_6$ coordination.

For the first time, we have observed a well-resolved ESR spectrum of low-spin Fe(III) at room temperature, both in the solid and in solution. The Ru(III) analog is not nearly as well resolved at room temperature but is still observable. In addition, we clearly observe well-resolved hyperfine structure from two equivalent cobalt nuclei, both in frozen glass and in room temperature solution. Also, perhaps a bit unexpectedly, we find the g values to be entirely typical of other sulfur-coordinated FeS$_6$ systems.[6] For the predicted ground state (see below) a very large axial distortion is most effective in producing rather long relaxation times leading to observable room-temperature spectra, and this is apparently the case here. There was some concern that in fact we were not looking at low-spin Fe(III) but rather at the $-{}^1\!/_2 \rightarrow +{}^1\!/_2$ transition of a trivial amount of high-spin impurity which could not be detected by other means. The analogous Ru(III) complex,
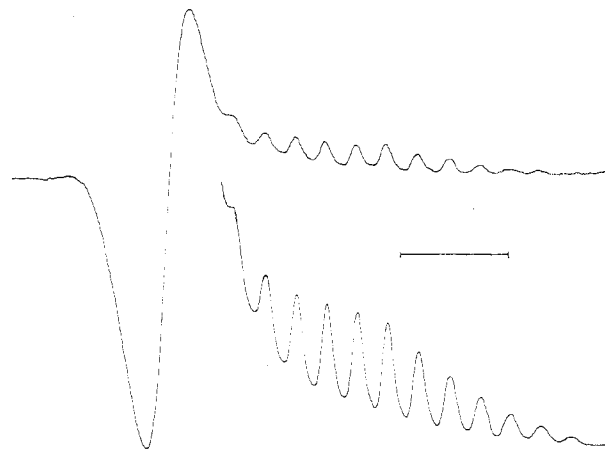
Ru(CoL$_3$)$_2$I$_3$, however dispelled these fears, yielding a spectrum very similar to that of the iron(III) complex. Its spectrum was also observable but not as well resolved in the room temperature solid, and its solution spectrum is of no real value. The spectrum of the Ru(III) ion in ethylene glycol glass at 77°K is very well resolved, however. One might surmise that the larger Ru(III) ion can better accommodate the CoL$_3$ ligand without so extensive a distortion as required by Fe(III). This would be reflected in shorter relaxation times and broader, less easily observed resonances.

Table I contains the results of the EPR experiments and Figure 2 illustrates the spectrum of the Fe(III) complex. $A_{\parallel}$ is taken as half the separation between the seventh and ninth hyperfine lines, and $g_{\parallel}$ is measured at the field of the eighth hyperfine line of $A_{\parallel}$. Since not all $A_{\parallel}$ lines are observed due to the large $g_{\perp}$ resonance in the Fe(III) complex, the question of uncertainty in these measurements arises. The Fe(III) spectrum is intense enough to define unambiguously the highest field hyperfine component of $A_{\parallel}$. The Ru(III) spectrum allows us to confirm that there are indeed 15 lines due to $A_{\parallel}$; in this case the spread of $A_{\parallel}$ is larger, extending on both sides of the $g_{\perp}$ resonance. Thus identification of the midpoint of the $A_{\parallel}$ multiplet poses no problems. $g_{\perp}$ is obtained by inspection as usually must be done, but the result is consistent with $g_{\parallel}$ and g_{iso}, both also measured quantities.

The existence of three g values >2.00 for Fe(CoL$_3$)$_2$Cl$_3$ might be called anomalous behavior, although it has been observed before, in tris(dimethyldithiocarbamato)iron(III).[11] Typically in t$_{2g}{}^5$ systems g values occur on both sides of g = 2.00.

The usual treatment of t$_{2g}{}^5$ due to Bleany[12] and Stevens[13] would, based on past experience, lead to rather meaningless values of the ligand field parameters in the case where all three g values are >2.00. This results from the mathematical behavior of the equations relating the g_i and the energy level separations and has been discussed in detail.[6] This will not be pursued further here nor will the equations[6] be duplicated. For our purposes we state only that the spectra may be interpreted *via* a spin Hamiltonian such as

$$\mathcal{H} = \beta S^{Fe} \cdot g^{Fe} \cdot H + I^{Co} \cdot A^{Co} \cdot S^{Fe}$$

with the ground state being some linear combination of the usual trigonal orbitals, t_2^0, $t_2^{\pm}$. The fact that $g_{\parallel} < g_{\perp}$ indicates that the unpaired electron (or the hole) resides in the t_2^0 orbital, associated with d_{z^2} in D_3 symmetry. This leads to a prediction that the trigonal distortion is one of *elongation* along the C_3 axis. There is no way to distinguish D_3 from D_{3d}, so that the possibility of trigonal-prismatic coordination about the iron cannot be ruled out. When the trigonal distortion becomes very large and a high degree of covalency exists, the t_2^0, $t_2^{\pm}$ orbitals are no longer satisfactory approximations to the true molecular orbitals and the constraint requiring at least one g value <2.00 is removed. Also, in this case, the presence of cobalt with its large spin–orbit interaction, is expected to shift the g values further to >2.00.

The g values for Ru(CoL$_3$)$_2$I$_3$ are typical for RuS$_6$ complexes,[6] although again we have chosen not to place undue validity on the crystal field parameters derived from the usual treatment of the data since the undoubtedly substantial effect of the cobalt spin–orbit interaction has been neglected, and the parameters are very sensitive to small error in the region described by the experimental g values. In this complex we likewise predict the odd electron to be in d_{z^2}, the orbital pointing along the C_3 axis directly at the cobalt. We were unable to measure the isotropic hyperfine coupling in solution for the Ru(III) complex, so we do not know $A_{\perp}^{Co}$ in this case, but there is no reason to expect that it is not quite as small as in the Fe(III) complex.

Metal–Metal Interaction. There has been considerable interest in recent years in metal–metal interactions in polynuclear complexes. Polynuclear compounds of iron and ruthenium are not especially rare although not numerous. Magnetic properties of a number of homonuclear ruthenium complexes have been studied, but we are not aware of any heteronuclear systems of either iron or ruthenium such as those discussed here. In view of this a brief comparison with certain other systems seems warranted. Heteronuclear ruthenium species vary considerably in magnetic properties, from the essentially diamagnetic ruthenium red,[14] Ru$_3$O$_2$(NH$_3$)$_{14}^{6+}$, where oxygen bridging between terminal Ru(III) and bridging Ru(IV) is presumably involved, to the high-spin $(S = 3/2)$ Ru$_2$(OAc)$_4$Cl$_{14}$.[15] This latter compound exhibits a strong metal–metal bond with Ru^{II}–Ru^{III} of only 2.28 Å.[16] Creutz and Taube[17] have prepared a series of pyrazine-bridged ruthenium ammines, the most studied of which is the (NH$_3$)$_5$Ru^{II}–pyr–Ru^{III}(NH$_3$)$_5^{5+}$ species. Various indications of substantial delocalization exist.[17–18] The g values[19] $(g_{\parallel} = 2.04, g_{\perp} = 2.32)$ indicate deviation from t_{2g}^5 but this is more likely due to extensive metal–ligand covalency than to metal–metal interaction. The somewhat high magnetic moment of 2.23 BM[19] would tend to support this. In the Ru(II,III) complex Ru$_2$((C$_6$H$_5$)$_3$As)$_3$Cl$_6$ $S = 1/2$ and the ESR spectrum is entirely typical of mononuclear t_{2g}^5 systems.[20] Metal–metal interaction, if any, might be revealed by use of ^{101}Ru to show hyperfine structure.[6]

It is apparent that the trinuclear species described in this work are quite unique. The nuclear spin of the cobalt atom provides a sensitive probe of metal–metal interaction, while the diamagnetic CoL$_3$ does not substantially "interfere" with the magnetics of the d^5 ion.

The fact that unpaired spin is localized primarily in an iron orbital pointing directly at the cobalt atom (see Figure 1) provides an obvious explanation for the mechanism of the hyperfine interaction, i.e., direct $d_{z^2}^{Fe}$–$d_{z^2}^{Co}$ overlap. It would appear from the values of $A_{\parallel}^{Co}$ that the magnitude of this interaction—and of the overlap—is relatively small. To put this statement in perspective we compare our observation to the situation found in other cobalt complexes. In a wide variety

of high- and low-spin cobalt(II) complexes, values for A vary considerably, but the combination of the usual polarization and/or direct mechanism for electron–nuclear coupling produces values on the order of 100×10^{-4} cm^{-1}, considerably larger than we find here. None of these complexes are suitable for comparison however, due to the different ground states involved. Typical of complexes where the unpaired electron resides in a d_{z^2} orbital is Co(CN)$_5^{3-}$ where $A_{\parallel} = 82.7$ and $A_{\perp} = -23.7 \times 10^{-4}$ cm^{-1}.[21] The cobalamines and cobinamides are similar.[22]

Perhaps more like the situation encountered here is that of the well-known superoxo complexes studied by Weil[23,24] and more recently Basolo.[25] Here delocalization from the superoxide onto a Co(III) ion produces couplings much more like those found in this work, at least in magnitude if not in origin. The complexes studied by Weil probably do not involve delocalization into d_{z^2}, and those studied by Basolo presumably involve d_{yz}. In the case of Co(acacen)O$_2$ [acacen = (CH$_3$CO=CHC(CH$_3$)=NCH$_2$−)$_2$] $A_{\parallel}^{Co} = 19.64$ and $A_{\perp}^{Co} = 10.73$ G.[25]

In the M(CoL$_3$)$_2$X$_3$ complexes it would seem from comparison with the above values that direct delocalization into Co d_{z^2} is sufficient to account for the magnitude of the observed couplings. There is likely some interaction *via* the sulfurs but, in view of the observed anisotropy in A^{Co}, probably very little. One final point is that it is very tempting when comparing the iron and ruthenium complexes to attribute the larger value of $A_{\parallel}^{Co}$ in the Ru complex to greater overlap of the larger Ru $4d_{z^2}$ with Co $3d_{z^2}$ than occurs with Fe. While this may in part be true, the situation is probably not so simple.

It becomes interesting at this point to inquire as to the Fe–Co or Ru–Co distance in these molecules. Analysis of hyperfine structure can often give information as to the radial extent of spin-containing orbitals, but in the absence of detailed knowledge of the mechanism of nuclear spin–electron spin interaction (direct vs. polarization) progress on this point is severely retarded. One would need to know the various mixing coefficients for the cobalt orbitals, as well as good wave functions for both Fe and Co in order to calculate proper overlap integrals and then one must still resort to a fitting process to arrive at an optimum distance. We feel that the accuracy of such a calculation would not allow us to calculate a number significantly better than an educated guess. The only way of directly estimating the distance to our knowledge is from observation of forbidden simultaneous spin flip transitions as satellites on each of the allowed hyperfine lines.[26] The intensities of these are related only to the value of $\langle r^{-6} \rangle$. However the line widths, narrow as they are for a t_{2g}^5 system, are still too broad to allow any such detection of lines as weak as those arising from internuclear separation of >3 Å as we most likely have here.

Registry No. Fe(CoL$_3$)$_2$Cl$_3$, 40510-99-4; Ru(CoL$_3$)$_2$I$_3$, 54385-44-3; Ru(CoL$_3$)$_2$(BPh$_4$)$_3$, 54423-08-4.

References and Notes

(1) (a) Wayne State University; (b) Bowling Green State University.
(2) (a) J. M. Baker, B. Bleany, and K. D. Bowers, *Proc. Phys. Soc., London, Sect. B*, **69**, 1205 (1956); (b) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).
(3) I. A. Miller and E. L. Offenbacher, *Phys. Rev.*, **166**, 269 (1968).
(4) A. Hudson and M. J. Kennedy, *J. Chem. Soc. A*, 1116 (1969).
(5) N. J. Hill, *J. Chem. Soc., Faraday Trans. 2*, **68**, 427 (1972).
(6) R. E. DeSimone, *J. Am. Chem. Soc.*, **95**, 6238 (1973).

(7) G. Freeh, K. Chapman, and E. Blinn, *Inorg. Nucl. Chem. Lett.*, **9**, 91 (1973).
(8) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960, p 403.
(9) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).
(10) S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 803 (1971).
(11) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **53**, 3118 (1970).
(12) B. Bleany and M. C. M. O'Brien, *Proc. Phys. Soc., London, Sect. B*, **69**, 1216 (1956).
(13) K. W. H. Stevens, *Proc. Roy. Soc., Ser. A*, **219**, 542 (1953).
(14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, p 1011.
(15) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).

(16) M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).
(17) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(18) J. H. Elias and R. S. Drago, *Inorg. Chem.*, **11**, 415 (1972).
(19) I. M. Treitel, Ph.D. Thesis, California Institute of Technology, 1971.
(20) R. E. DeSimone, Ph.D. Thesis, University of Illinois, 1970.
(21) F. D. Tsay and H. B. Gray, *J. Chem. Phys.*, **54**, 3760 (1971).
(22) J. H. Bayston, F. D. Looney, J. R. Pilbrow, and M. E. Winfield, *Biochemistry*, **9**, 2164 (1970).
(23) M. Mori, J. A. Weil, and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 103 (1967).
(24) J. A. Weil and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 3341 (1967).
(25) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).
(26) G. T. Trammell, H. Zeldes and R. Livingston, *Phys. Rev.*, **110**, 630 (1958).

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Kinetics, Mechanism, and Stereochemistry of the Aquation and Chloride Anation Reactions of *fac*- and *mer*-Trichlorotriaquorhodium(III) Complexes in Acidic Aqueous Solution. A complete Reaction Scheme for Complex Ions of the General Formula $[RhCl_n(OH_2)_{6-n}]^{3-n}$ [1]

D. A. PALMER and G. M. HARRIS*

Improved procedures for preparing the title compounds are outlined, and their reactions in strongly acidic aqueous solution in the presence of varied concentrations of chloride are described. The *fac* isomer readily undergoes equilibration in the temperature range 35–55° resulting in a mixture of the parent compound and the three anation products *cis*-RhCl$_4$(OH$_2$)$_2^-$, RhCl$_5$(OH$_2$)$^{2-}$, and RhCl$_6^{3-}$ *only*. The *mer* analog under similar conditions establishes a pseudoequilibrium with the aquation product *cis*-RhCl$_2$(OH$_2$)$_4^+$ and the anation product *trans*-RhCl$_4$(OH$_2$)$_2^-$. The latter, at higher temperatures and high chloride concentration, is converted irreversibly to RhCl$_5$(OH$_2$)$^{2-}$. A review of all relevant rate constant data for complexes of the type $[RhCl_n(OH_2)_{6-n}]^{3-n}$ is presented. These data are found to be consistent with a dissociative mechanism involving a square-pyramidal transition state, for both anations and aquations. The kinetic trans effect of ligand chloride is shown to be preeminent in determining the relative rate and steric course of each reaction. The results of this investigation enable a better understanding of some of the previously observed catalytic properties of chloroaquorhodium(III) complexes.
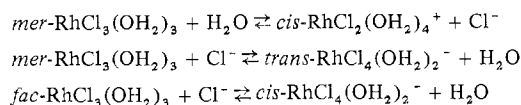
Introduction

Kinetic studies of ligand substitution reactions of the chloroaquorhodium(III) complexes have so far encompassed the chloride anation of the hexaaquo[2] and chloropentaaquo[3] species, both of which reactions are essentially unidirectional, and the aquation–anation equilibria in the systems[4-6]

$$cis\text{-RhCl}_4(\text{OH}_2)_2^- \rightleftarrows \text{RhCl}_5(\text{OH}_2)^{2-} \rightleftarrows \text{RhCl}_6^{3-}$$
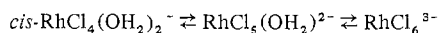
However, no rate data have been published relative to the complex RhCl$_3$(OH$_2$)$_3$, though its *fac* (1,2,3 or cis) and *mer* (1,2,6 or trans) isomers have been prepared and identified.[7] A primary aim of the present work was to fill in the remaining blanks with respect to the rates and equilibria in the reaction sequence symbolized by

$$[\text{RhCl}_n(\text{OH}_2)_{6-n}]^{3-n} + \text{Cl}^- \rightleftarrows [\text{RhCl}_{n+1}(\text{OH}_2)_{5-n}]^{2-n} + \text{H}_2\text{O}$$
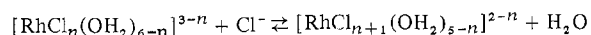
It turns out that in strongly acid solution the only significant processes in addition to those already mentioned above are three equilibrations

$$mer\text{-RhCl}_3(\text{OH}_2)_3 + \text{H}_2\text{O} \rightleftarrows cis\text{-RhCl}_2(\text{OH}_2)_4^+ + \text{Cl}^-$$

$$mer\text{-RhCl}_3(\text{OH}_2)_3 + \text{Cl}^- \rightleftarrows trans\text{-RhCl}_4(\text{OH}_2)_2^- + \text{H}_2\text{O}$$

$$fac\text{-RhCl}_3(\text{OH}_2)_3 + \text{Cl}^- \rightleftarrows cis\text{-RhCl}_4(\text{OH}_2)_2^- + \text{H}_2\text{O}$$

together with the slow unidirectional process

$$trans\text{-RhCl}_4(\text{OH}_2)_2^- + \text{Cl}^- \rightarrow \text{RhCl}_5(\text{OH}_2)^{2-} + \text{H}_2\text{O}$$
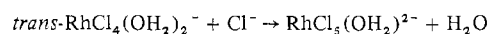
Our data on these systems provide further confirmation of the previously observed[2,3] strong kinetic trans effect of the chloride ligand on reactions of chloroaquorhodium(III) complexes and enable an improved understanding of the well-known catalytic

properties of anionic chlororhodium(III) species in the hydration of acetylenes[8] and in the activation of molecular hydrogen.[9]

Experimental Section

The following complexes were prepared in crystalline form by established methods: Rh(OH$_2$)$_6$(ClO$_4$)$_3$,[10] K$_2$RhCl$_5$(OH$_2$),[5] and K$_3$RhCl$_6$.[5] The complex ions RhCl(OH$_2$)$_5^{2+}$ and *cis*- and *trans*-RhCl$_2$(OH$_2$)$_4^+$ were separated by ion-exchange chromatography using previously published methods.[3] However, separation of the isomers *fac*- and *mer*-RhCl$_3$(OH$_2$)$_3$ by the method of Wolsey, Reynolds, and Kleinberg[7] could not be duplicated effectively so their technique was modified as follows.

The initial mixture of isomers is prepared in either of two ways. Refluxing a solution of Rh(OH$_2$)$_6$(ClO$_4$)$_3$ in 0.5 *M* HCl for 6–8 hr gives predominantly the *mer* isomer, whereas refluxing K$_3$RhCl$_6$ for 15 min in dilute perchloric acid gives mainly the *fac* isomer. Either solution is then passed through an 80–90-cm ion-exchange column containing a mixed-bed resin composed of equivalent amounts of anion resin in the chloride form, Bio-Rad 1-X8 (200–400 mesh), and protonated cation resin, Bio-Rad 50W-X8 (200–400 mesh). The temperature of the column is maintained at aproximately 2° by passing ice-cold water through a water jacket surrounding the column. The neutral trichloro isomers are eluted with a weak perchloric acid solution (pH 3.5). Two distinct bands are obtained, and the initial ~4-cm portions of both bands and the "tail" of the second band are discarded. As with earlier work,[7] the first band was assigned to the *mer* isomer and the second to the *fac*. This assignment, based on the difference in dipole moments of the two isomers, is supported by similar ion-exchange studies of analogous iridium(III)–[11] and ruthenium-(III)–chloroaquo[12] complexes and numerous other studies.[13] The wavelengths of the maxima in the absorption spectra of both isomers agree exactly with those reported by Kleinberg et al.[7] However, the molar extinction coefficients are somewhat different. For *mer*-RhCl$_3$(OH$_2$)$_3$ at 471 nm, ϵ is 85.2 (77.1), and at 370 nm, ϵ is 71.6