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Paramagnetic Resonance of Some Complexes of Iron and Chromium in Hexaamminecobalt(III) Hexachlorometalates

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The spin-Hamiltonian parameters are evaluated by epr powder techniques for [FeCl₆]³⁻ and [Cr(NH₃)₆]³⁺ guest ions in three diamagnetic Co(NH₃)₆MCl₆ hosts (M = In, Sb, Bi) and for [CrCl₆]³⁻ in the Co(NH₃)₆InCl₆ host. The significance of the parameters is discussed in terms of molecular and lattice properties. A comparison of the relative magnitudes of the zero-field splitting parameters and sizes of the complex ions provides an interesting model for the guest-host interactions in these systems.

Introduction

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

The present work involves an epr investigation of three complex ions, [FeCl₆]³⁻, [CrCl₆]³⁻, and [Cr(NH₃)₆]³⁺, which were introduced as ~1% guests into a diamagnetic Co(NH₃)₆MCl₆ host. Specifically, [FeCl₆]³⁻ and [Cr(NH₃)₆]³⁺ were studied in three Co(NH₃)₆MCl₆ hosts (M = In, Sb, Bi), while the [CrCl₆]³⁻ ion was prepared only in the indium host. The spin-Hamiltonian parameters evaluated from the epr spectra provide information about the properties of the complex ion as well as the hosts, and the conclusions drawn from the parameters for the compounds studied are consistent with results reported elsewhere.³⁻⁶

Experimental Section

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

Co(NH₃)₆FeCl₆ was magnetically diluted into the corresponding indium host following the general procedure given by Hatfield, *et al.*,¹ and into the antimony host as described by Schroeder and Jacobson.² A sample employing the Co(NH₃)₆BiCl₆ host was prepared in a similar manner to the antimony sample. It was found that strong epr signals could be obtained in the indium host by preparing the sample from a solution containing a 1:99 guest to host ratio. However, suitable sam-

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

Cr(NH₃)₆MCl₆ was diluted into the corresponding cobalt hosts (M = In, Sb, Bi) by the same methods as above.^{1,2} It was found that epr signals of similar intensities as for iron could be obtained in all cases using a 1% chromium to 99% cobalt ratio in solution.

Co(NH₃)₆CrCl₆ gave a suitable epr spectrum only in the indium host. The procedure involved preparing a large excess of Cr³⁺ in hot 12 N HCl, followed by treatment with Zn metal in an attempt to promote ligand exchange and formation of the desired species in solution. A small amount of indium metal was then dissolved in the chromium solution, and to this was added a hot solution of Co(NH₃)₆Cl₃. The product obtained gave epr signals of nearly the same intensity as the other samples; however, attempts to introduce this guest into the antimony and bismuth hosts gave very weak, unidentifiable spectra. In contrast to the [FeCl₆]³⁻ and [Cr(NH₃)₆]³⁺ samples, the [CrCl₆]³⁻ spectra all showed a Mn²⁺ contamination. Manganese(II) appears to have a very strong affinity for these hosts.

Paramagnetic resonance measurements were taken at room temperature on a Varian Model E-12 spectrometer at a frequency of 35 GHz using a Varian Model E-110 microwave bridge. Line positions were measured with a Spectromagnetic Industries Model 5200 nmr gaussmeter. One [FeCl₆]³⁻ sample and the [CrCl₆]³⁻ sample were also examined at 77°K using a frequency of approximately 9.1 GHz.

X-Ray powder patterns of Co(NH₃)₆InCl₆, Co(NH₃)₆SbCl₆, and Co(NH₃)₆BiCl₆ were taken with a Debye-Scherrer camera of 11.46-cm diameter using a copper source with a nickel filter. A comparison of the patterns showed a 1:1 correspondence of the relative line positions for 30 lines, indicating that the three structures are isomorphous. The unit cell dimensions increase only slightly and in an isotropic fashion in going from In to Bi, with the dimensions of the Sb compound being intermediate.

Results

Spectra for all seven epr powder samples displayed extremely high signal-to-noise ratios as can be seen in Figure 1, thus allowing precise measurements of the line positions and also affording further study of unresolved rhombic splittings in the wing lines *via* line shape analysis. Details regarding the interpretation of epr powder spectra for $S \geq 3/2$ have been described elsewhere.^{3,4}

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

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

(1) W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Amer. Chem. Soc.*, **85**, 265 (1963).

(2) D. R. Schroeder and R. A. Jacobson, *Inorg. Chem.* **12**, 210 (1973).

(3) L. E. Mohrmann, Jr., B. B. Garrett, and W. B. Lewis, *J. Chem. Phys.*, **52**, 535 (1970).

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(6) B. B. Garrett, K. DeArmond, and H. S. Gutowsky, *J. Chem. Phys.*, **44**, 3393 (1966).

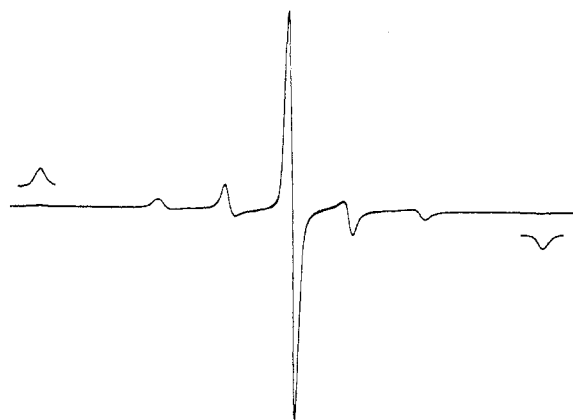


Figure 1. First-derivative epr powder spectrum of $[\text{FeCl}_6]^{3-}$ in the $\text{Co}(\text{NH}_3)_6\text{InCl}_6$ host. The two extreme wing lines are shown with a factor of 20 magnification.

with the hyperfine term $I \cdot A \cdot S$ included for $^{53}\text{CrCl}_6]^{3-}$. An additional fourth-order spin-operator term with the coefficient $a - F$ was necessary for the iron spectra. The fitting of the spin-Hamiltonian parameters for the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ spectra involved a manual iteration procedure using an exact diagonalization of the spin Hamiltonian along each of the three principal axes of the zero-field splitting tensor.

An attempt to fit the iron spectra to a spin Hamiltonian of tetragonal symmetry proved unsuccessful. Here, the same techniques were employed as in the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ situation, and the attempted fitting involved the exact diagonalization of the $S = 5/2$ spin Hamiltonian of tetragonal symmetry.⁴ Therefore, it was necessary to resort to use of a spin Hamiltonian which places the z axis along the trigonal axis of the complex, that is, along the (1, 1, 1) direction with respect to the metal-ligand bonds. The formalism of the second-order perturbation theory solution of such a spin Hamiltonian of trigonal symmetry has been given by Bleaney and Trenam,⁷ and the present data were evaluated by solving simultaneous equations to arrive at the parameters for the iron complex in the three hosts. In all cases these spin-Hamiltonian parameters predict the line positions to within experimental error. In addition, the parallel wing lines were found to be Lorentzian in shape; and using such a line shape for an analysis of the unresolved rhombic splittings in the perpendicular spectrum, we obtained splittings in excellent agreement with the spin-Hamiltonian parameters derived from the positions of the peaks of the perpendicular lines. Pertinent experimental data and spin-Hamiltonian parameters are listed in Tables I-III.

The epr spectra assigned to $[\text{CrCl}_6]^{3-}$ in $\text{Co}(\text{NH}_3)_6\text{InCl}_6$ contained only one major resonance line with two weak satellite lines appearing as shoulders on the main line. These satellites were of approximately the correct intensity and spacing to represent hyperfine lines associated with the (9%) ^{53}Cr isotope. The main resonance line was narrow (about 11-G extremum slope width) with no indication of any splitting at either room temperature or liquid nitrogen temperature. It was concluded that the species observed is the undistorted $[\text{CrCl}_6]^{3-}$ ion which occupies a fixed and definite orientation at the anion site for the following reasons. (1) The ^{53}Cr hyperfine coupling constant of 16.2 G and the 1.9856 isotropic g factor serve as a positive identification for chromium. (2) The zero-field splitting is too small to be observed, as opposed to being too large, on the basis of the

Table I. Fields at Resonance for $[\text{FeCl}_6]^{3-}$ in $\text{Co}(\text{NH}_3)_6\text{InCl}_6$

Line type	Line position, G ^a
Parallel	13374.0
Perpendicular	12871.9
Perpendicular	12559.6
Perpendicular	12277.1
Perpendicular	12009.4
Perpendicular	11721.3
Parallel	11212.9

^a Error limits are estimated to be 2 G for parallel lines (due to low intensities) and 1 G for perpendicular lines.

Table II. Spin-Hamiltonian Parameters of $[\text{FeCl}_6]^{3-}$ in $\text{Co}(\text{NH}_3)_6\text{MCl}_6$ Hosts

	M				Error limit
	In	In (77°K)	Sb	Bi	
D , G	274.9	316.9	279.3	273.3	±1.0
E , G	3.0	1.5	3.0	2.8	±0.4
$a - F$, G	14.3	18.3	11.6	12.0	±1.0
g_{\parallel}	2.0118	... ^a	2.0120	2.0119	±0.0004
g_{\perp}	2.0122	... ^a	2.0124	2.0124	±0.0004
ν , GHz	34.614	9.1 ^a	34.614	34.623	±0.002

^a Boiling of the liquid nitrogen precluded accurate measurement of the frequency and the g factors.

Table III. Spin-Hamiltonian Parameters for $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in $\text{Co}(\text{NH}_3)_6\text{MCl}_6$ Hosts

	M			Error limit
	In	Sb	Bi	
D , G	490.3	1013.7	1159.3	±1.0
E , G	4.7	2.7	2.3	±0.4
g_{\parallel}	1.9855	1.9860	1.9859	±0.0004
g_{\perp}	1.9854	1.9858	1.9857	±0.0004
ν , GHz	34.614	34.615	34.625	±0.002

line shape and the 11-G width of the center line. (3) The center line width also demonstrates that the species occupies a definite orientation with respect to the lattice, since a random distribution of zero-field splittings would result in line broadening. (4) The observation of ^{53}Cr hyperfine coupling excludes exchange narrowing as the cause of the narrowness of the center line. (5) It was also shown that the paramagnetic species is probably not undergoing a rapid rotational averaging in the host, as the center line width remains constant in going to liquid nitrogen temperature. (6) The possibility that the species observed is $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ at the cobalt site can be excluded since such an ion would be too large to avoid lattice distortions. Deliberate attempts to coprecipitate $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in the indium host gave a broad, weak spectrum with a significant zero-field splitting. Other possible chromium species must have large axial distortions of molecular origin.

Having exhausted these possibilities, it appears that the observed species is $[\text{CrCl}_6]^{3-}$ with a zero-field splitting of 0 ± 5 G and is probably the first reported case of an octahedral guest in a host of rhombic symmetry.

Discussion

Recent epr studies of MX_5Y type complexes have demonstrated that the spin-Hamiltonian parameters of these species are molecular properties if the guest and host have similar symmetries and similar charge distributions.⁴⁻⁶ This conclusion was reached experimentally by noting that the epr spectra were essentially superimposable for any one of these complexes in a series of widely varied host lattices. One can reconcile such an invariance to the host on the grounds that alterations of the molecular framework in tetragonal MX_5Y type complexes in these lattices would effectively involve

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lengthening or shortening of bonds, as required by the symmetry of the host.

For the present situation, however, the spin-Hamiltonian parameters involve both molecular properties and lattice effects, since the distortions from octahedral symmetry involve angular displacements rather than changes in bond distances within the complex ion, as observed in the X-ray results² for $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$. It can be concluded that the g factors for all three paramagnetic species and the cubic parameters a for the iron complexes are essentially of molecular origin, while the axial and rhombic parameters, D and E , respectively, arise from the tendency of the guest ion to adopt the symmetry of its environment.

The fact that the g factors are found to be isotropic and identical in these hosts indicates that the angular distortions of the complex ion induced by the host are insufficient to distinguish g_{\parallel} and g_{\perp} from the value expected for the undistorted octahedral complex. Again, changes in the metal-ligand bond distances are not expected, as in the case of the MX_5Y compounds. Similarly, the cubic parameter for $[\text{FeCl}_6]^{3-}$ should reflect only the local chloride ion environment of the metal, with insignificant changes being brought about by very slight angular distortions. On the other hand, it is apparent that D and E are determined by lattice effects, since both parameters must be zero for an undistorted octahedron.

The primary distortions in the host were found to be trigonal at both cation and anion sites according to the X-ray analysis of Schroeder and Jacobson,² and this is in accord with the epr data. Certainly, the fact that the $[\text{FeCl}_6]^{3-}$ spectra could only be fitted to a spin-Hamiltonian of three-fold symmetry leaves little doubt as to the nature of the distortion at the anion site in the host. Spectra of d^5 systems for trigonal⁷ and tetragonal⁸ symmetries are distinguishable because the principal axes for the cubic and the quadratic zero-field splitting tensors are coincident in the latter symmetry but not in the former case. It does not appear feasible to insert a d^5 ion into the cation site in order to check the site symmetry directly with the spin Hamiltonian. Evidence for a trigonal distortion at the cation site can be obtained by noting the difference in the magnitude of the axial parameter, D , for $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in the three hosts. An increase in D from an already large value of 490 G in the indium host to 1014 G in the antimony host with a further increase to 1159 G in the bismuth host must necessarily favor the easier angular distortion as opposed to distortions along the bond directions, since these hosts are very similar.

Although the small rhombic splittings at both anion and cation sites demonstrated by the nonzero E parameters are not reflected in the bond distances and angles,² the X-ray structure does indicate metal site symmetries below axial. Hence, the presence of the E parameter merely shows the sensitivity of the epr spectrum to small rhombic distortions.

While the present data suggest a primarily molecular origin of the g factor, this conclusion need not be drawn from the $\text{Co}(\text{NH}_3)_6\text{MCl}_6$ data alone. In fact, a comparison of the g factors of similar complexes in a wide variety of different hosts provides strong supportive evidence for this observation. We note from the data in Table IV that several $\text{Cr}(\text{NH}_3)_5\text{X}$ complexes ($\text{X} = \text{NH}_3, \text{H}_2\text{O}, \text{Cl}, \text{Br}$) have g factors in the range 1.9856 ± 0.0005 . Similarly, the g factors of chlorochromium(III) and chloroiron(III) complexes fall into narrow ranges as is shown in Table IV. The theoretical basis for these comparisons has been given previously.^{5,6}

Such an extensive comparison of the cubic parameter, a , for iron(III) in a chloride environment is not possible due to

Table IV. Spectroscopic Splitting Factors for Some Chromium and Iron Complexes

Paramagnetic ion	Host	g factor
$[\text{CrCl}_6]^{3-}$	$\text{Co}(\text{NH}_3)_6\text{InCl}_6$	$g = 1.9856$
$[\text{CrCl}_5]^{2-}$	$(\text{NH}_4)_2\text{SbCl}_5$	$g_{\parallel} = 1.9853^a$
$[\text{CrCl}_6]^{3-}$	AlCl_3	$g_{\parallel} = 1.9860^b$
$[\text{Cr}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$	$(\text{NH}_4)_2\text{In}(\text{H}_2\text{O})\text{Cl}_5$	$g_{\parallel} = 1.9871^c$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\text{Co}(\text{NH}_3)_6\text{InCl}_6$	$g = 1.9855$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\text{Co}(\text{NH}_3)_6\text{SbCl}_6$	$g = 1.9859$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\text{Co}(\text{NH}_3)_6\text{BiCl}_6$	$g = 1.9858$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$	$g = 1.9857^d$
$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$	$g_{\parallel} = 1.9860^d$
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$g_{\parallel} = 1.9861^d$
$[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$	$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	$g_{\parallel} = 1.9853^d$
$[\text{FeCl}_6]^{3-}$	$\text{Co}(\text{NH}_3)_6\text{InCl}_6$	$g = 2.0120$
$[\text{FeCl}_6]^{3-}$	$\text{Co}(\text{NH}_3)_6\text{SbCl}_6$	$g = 2.0122$
$[\text{FeCl}_6]^{3-}$	$\text{Co}(\text{NH}_3)_6\text{BiCl}_6$	$g = 2.0122$
$[\text{Fe}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$	$(\text{NH}_4)_2\text{In}(\text{H}_2\text{O})\text{Cl}_5$	$g_{\parallel} = 2.0109^e$

^a H. H. Dearman, private communication. ^b J. Schmidt, *Phys. Lett. A*, 28, 419 (1968). ^c See ref 6. ^d See ref 5. ^e See ref 4.

the limited amount of suitable data. It would not be reasonable to draw any conclusion about the origin of a as a molecular parameter from the experimental results of this work alone, since none of the parameters for $[\text{FeCl}_6]^{3-}$ showed any significant variation in these hosts. But a comparison of the present results of $a - F \approx 14$ G can be made with the $[\text{Fe}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ result of $a \approx 20$ G. It is not expected that cubic terms of molecular origin would be vastly different in these two situations, while the hosts are very dissimilar.

Perhaps the most interesting result of this study lies in comparisons of the zero-field splittings, especially when one recognizes the sensitivity of the axial parameter to very small distortions in the paramagnetic complex. Clearly, the existence of an undistorted octahedral paramagnetic complex, $[\text{CrCl}_6]^{3-}$, in a host of lower symmetry is an unexpected result. But, the fact that the zero-field splitting for $[\text{FeCl}_6]^{3-}$ remains unchanged in three different hosts while that of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ undergoes large changes in these same hosts is equally surprising, considering the sensitivity of the zero-field splitting parameters as generally observed for both trivalent iron and chromium.⁴⁻⁶ Taken collectively, however, these results make very strong suggestions as to the nature of the guest-host interactions.

The host lattice structures consist of an NaCl type arrangement of ions with the chlorine ligands of the anions projecting into the region between the ammine ligands of the cations. If the lattice dimensions in the sequence of hosts containing In, Sb, and Bi do not increase as rapidly as the expected metal-chlorine bond distances, then the trigonal distortions at the cation sites should increase in this sequence. At the anion sites, the guest ions are significantly smaller than the host ions; thus much smaller changes in the anion distortions are expected in this sequence of hosts. Indeed, if the guest ions are sufficiently smaller than the host ions, then minor changes in the lattice dimensions may not be reflected in the epr spectra of the guest ions at all.

The In-Cl distance should be in the neighborhood of 2.55 Å as in $(\text{NH}_4)_2[\text{InCl}_5\text{H}_2\text{O}]$,⁸ while the Sb-Cl bond length in $\text{Co}(\text{NH}_3)_6[\text{SbCl}_6]$ is 2.65 Å.² A further increase of about 0.1 Å is expected on going to the Bi-Cl bond length, if one uses interpolated ionic radii.⁹ Therefore, a range of about 0.2 Å in the M-Cl bond distances is expected for $\text{M} = \text{In}, \text{Sb},$ and Bi , whereas the unit cell dimensions obtained from the

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(9) R. C. Evans "An Introduction to Crystal Chemistry," 2nd ed, Cambridge University Press, New York, N. Y., 1964.

X-ray powder data for $\text{Co}(\text{NH}_3)_6\text{MCl}_6$ would allow for only about a 0.05 Å variation in the bond length in these lattices.

The axial zero-field splitting parameter D for $[\text{Cr}(\text{NH}_3)_6]^{3+}$ increases from 490 G in the In host to 1014 G in the Sb host and to 1160 G in the Bi host, in accord with the above model of the lattice interactions. At the anion site, D for $[\text{FeCl}_6]^{3-}$ is the same (276 ± 4 G) in all three lattices at room temperature which suggests that the iron complex is large enough to suffer some trigonal distortion by the host lattice but not so large that it feels small variations in the lattice. The 15% increase in the magnitude of D for $[\text{FeCl}_6]^{3-}$ in the indium host which occurs when the temperature is lowered to liquid nitrogen temperature suggests that the iron complex may be experiencing a further distortion by compression in this the smallest of the three hosts used, but other effects may also be involved at low temperatures.

The absence of any zero-field splitting for $[\text{CrCl}_6]^{3-}$ in the indium host suggests that this ion is somewhat smaller than the iron complex and is thus able to occupy the anion site without suffering any distortion from the lattice. This size effect could also account for our failure to obtain $[\text{CrCl}_6]^{3-}$ substitution in the antimony and bismuth hosts.

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Registry No. $[\text{FeCl}_6]^{3-}$, 19639-41-9; $[\text{Cr}(\text{NH}_3)_6]^{3+}$, 14695-96-6; $\text{Co}(\text{NH}_3)_6\text{InCl}_6$, 17499-93-3; $\text{Co}(\text{NH}_3)_6\text{SbCl}_6$, 17805-63-9; $\text{Co}(\text{NH}_3)_6\text{BiCl}_6$, 16591-55-2; $[\text{CrCl}_6]^{3-}$, 15276-03-6.

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Characterization of the Products Resulting from Electrochemical Reduction of $\text{Rh}(\text{en})_2\text{Cl}_2^+$ at Mercury Electrodes

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An intermediate product resulting from the reduction of $\text{trans-Rh}(\text{en})_2\text{Cl}_2^+$ at mercury electrodes that had been identified as "a rhodium(II) dimer" is shown, instead, to be a mercury(II)-bridged complex of rhodium(I), $[(\text{en})_2\text{Rh}]_2\text{Hg}^{4+}$. The experimental conditions under which the formation of this complex is favored during electrochemical reductions of $\text{Rh}(\text{en})_2\text{Cl}_2^+$ are delineated. Nonelectrochemical production of the same complex *via* homogeneous reactions between $\text{Hg}(\text{II})$ and $\text{Rh}(\text{en})_2\text{H}(\text{OH})_2^{2+}$ is also described.

As part of an investigation of the electrochemical behavior of rhodium(III) complexes, we have been examining the reduction of the $\text{trans-Rh}(\text{en})_2\text{Cl}_2^+$ cation (en = ethylenediamine) at mercury pool electrodes maintained at constant potential. Gillard and coworkers¹ have reported recently on similar studies in which they believed to have produced a relatively stable, binuclear rhodium(II) complex by one-electron reduction of $\text{Rh}(\text{en})_2\text{Cl}_2^+$. In initial attempts to reproduce the results of Gillard, *et al.*,¹ we found that the apparent number of electrons required to reduce solutions of $\text{Rh}(\text{en})_2\text{Cl}_2^+$ at mercury electrodes was a very sensitive function of electrode potential and pH as were the final reduction products obtained. When conditions were optimized for producing the species whose wavelength of maximum absorption matched that reported by Gillard, *et al.*,¹ the solution was found (by atomic absorption analysis) to contain a high concentration of mercury. In addition, a species having the same spectrum could be produced by mixing solutions of mercury(II) salts with solutions of the hydridorhodium(III) complex, $\text{Rh}(\text{en})_2\text{H}(\text{OH})_2^{2+}$, obtained from the two-electron reduction of $\text{Rh}(\text{en})_2\text{Cl}_2^+$. The same species could also be prepared by oxidizing solutions of $\text{Rh}(\text{en})_2\text{H}(\text{OH})_2^{2+}$ at mercury electrodes. These observations, coupled with recent reports of other transition-metal complexes that yield mercury adducts when exposed to mercury

electrodes at appropriate potentials,² led us to try to characterize more carefully the species produced when $\text{trans-Rh}(\text{en})_2\text{Cl}_2^+$ is reduced at mercury electrodes.

Experimental Section

Apparatus. Electrolyses were carried out in a conventional two-compartment cell wrapped in aluminum foil to avoid photodecomposition of reaction products. A Wenking potentiostat (Model TR) was employed and electrolysis currents were integrated using operational amplifiers. The coulomb-time behavior was obtained with a pen and ink recorder.

A Varian Model AA5 atomic absorption apparatus was used for rapid measurements of the total rhodium and mercury in solutions of the complexes. The estimated accuracy of these analyses was ± 5 –10%.

Electronic spectra were recorded with a Cary 11M spectrophotometer. Standard serum cap-syringe techniques were used to exclude oxygen during transferring of solutions between the electrolysis or reaction vessels and spectrophotometer cells.

Reagents. Reagent grade chemicals were used throughout without further purification. Solutions of sodium methanesulfonate were prepared by neutralizing the commercially available acid, $\text{CH}_3\text{SO}_3\text{H}$ (Eastman Kodak) with solid NaOH, filtering, and diluting with triply distilled water. All solutions were deaerated using prepurified N_2 which was passed over hot copper turnings and through a distilled water washing tower before use.

$\text{trans-}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ was prepared by standard procedures³ and its purity was determined by comparison with previously measured extinction coefficients.⁴

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