this investigation exhibited only a single band in this region, this would strongly support the assignment of a trans geometry.

An independent synthesis and structure proof of *trans*-$Cr(tn)_2Cl_2^+$ has been developed by Professor House,[8] at the University of Canterbury.

If as in the case of the ethylenediamine complexes of the type *trans*-$Cr(en)_2X_2^+$ the bands near 500 and 440 cm^{-1} are essentially pure Cr–N stretching modes in the trimethylenediamine complexes, the complexes studied in this investigation may possibly represent two different cases.

The diacetato and difluoro complexes have similar infrared spectra in that they both have bands near 550 cm^{-1} and the dichloro and dibromo complexes are similar in that the band near 550 cm^{-1} is absent. However, the assignment of the 550-cm^{-1} band is in doubt and further speculation is not warranted at this time.

The products formed in the reaction of hydrated chromium(III) chloride, a diamine, and a weak acid in aqueous solution under a rather specific set of conditions appear to depend on the nature of the acid used in the synthesis.

(8) D. A. House, submitted for publication.

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Synthesis and Characterization of Oxalatobis(ethylenediamine)rhodium(III) Nitrate

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Although various diacidotetraammine complexes of rhodium(III) have been synthesized and characterized,[1,2] there appear to be no reports of the preparation of oxalatotetraammine complexes of rhodium(III). In continuance of our investigations on oxalato complexes[3,4] it has become desirable to examine the reactivity of the oxalatobis(ethylenediamine) rhodium(III) ion. The preparation and characterization of this complex, which involve several interesting features, are described herein.

Experimental Section

cis-Dichlorobis(ethylenediamine)rhodium(III) nitrate was prepared as described by Johnson and Basolo[1] except for some modifications in the procedures of adding the potassium hydroxide. In one procedure, after adding to the refluxing solution[5] the second 0.426-g portion of potassium hydroxide (in 50 ml of water added in 5-ml increments at 1–2 min intervals) a further 0.5 g of potassium hydroxide in 10 ml of water was added at one time. Following the last addition of potassium hydroxide the solution was evaporated to half its original volume, after which 20 ml of concentrated nitric acid was added. On standing for 1.5–2 hr the trans isomer along with some cis isomer precipitated, as expected.[1] The solid was separated by filtration, and the filtrate was allowed to stand at room temperature for 2 days during which time the bright yellow *cis*-$[Rh(en)_2Cl_2]NO_3$ separated. This method resulted in a 0.30-g (22%) yield of cis isomer without any contamination from the trans isomer.

The yield of the *cis*- and *trans*-$[Rh(en)_2Cl_2]NO_3$ mixture, as described by Johnson and Basolo,[1] was certainly significantly increased by the addition of two to three pellets of solid potassium hydroxide to the refluxing reaction solution. However, we failed to notice a brownish black substance or other indications of decomposition following the addition of the potassium hydroxide pellets. Also, the predicted 70% yield of cis product has not been approached in spite of several attempts. Yields of up to ~40% have been obtained.

Pure *trans*-$[Rh(en)_2Cl_2]NO_3$ was obtained easily following the method of Johnson and Basolo.[1]

The purity of the above cis and trans complexes was confirmed by comparing uv, visible, and ir spectra with those reported in the literature.[1]

Oxalatobis(ethylenediamine)rhodium(III) Nitrate. (a) **Preparation from *cis*-Dichlorobis(ethylenediamine)rhodium(III) Nitrate.**[6]—A mixture consisting of 0.460 g (1.29×10^{-3} mol) of *cis*-$[Rh(en)_2Cl_2]NO_3$, 0.447 g (3.34×10^{-3} mol) of $Na_2C_2O_4$, and 35 ml of water was refluxed for about 2 hr, during which time the solution changed from a deep yellow to a pale yellow. The hot solution was filtered twice and then cooled in an ice bath. Between 3 and 4 ml of saturated sodium nitrate solution was then added and the solution was placed in a refrigerator. After about 3 hr a very pale yellow crystalline solid precipitated. The yield was increased by adding a further 1 ml of saturated sodium nitrate solution and leaving in the refrigerator overnight. The pale yellow crystalline solid was collected by suction filtration, washed with cold dilute nitric acid, cold 95% ethanol, and cold ether, sucked dry, and stored in a vacuum desiccator; yield 0.34 g. The product was recrystallized by dissolving in 10 ml of water at 80°, filtering while hot, cooling slowly, and washing and drying as before; overall yield, 0.20 g (40%). *Anal.* Calcd for $[Rh(N_2C_2H_8)_2C_2O_4]NO_3 \cdot H_2O$: C, 18.4; H, 4.64; N, 17.9; Rh, 26.3. Found: C, 18.4; H, 4.37; N, 18.1; Rh, 26.2.[7,8]

(b) **Preparation from *trans*-Dichlorobis(ethylenediamine)-rhodium(III) Nitrate.**—The complex can be prepared in poor yield from *trans*-$[Rh(en)_2Cl_2]NO_3$; therefore it may also be obtained from trans–cis mixtures of the dichloro complexes. For these purposes the same procedure as under (a) has been followed, except that considerably longer times are needed before the refluxing solution changes from bright to pale yellow. Typically, in preparations from *trans*-$[Rh(en)_2Cl_2]NO_3$, 12–16 hr was used. In such preparations from the *trans*-dichloro complex, which had been carefully purified by repeated recrystallization,[1] yields of ~6% were obtained following two or three recrystallizations of the oxalato product. Although the yields were very low, they were significantly greater than those which could be attributed to any *cis*-$Rh(en)_2Cl_2^+$ impurity in the *trans*-$Rh(en)_2Cl_2^+$ starting material. From ir and visible–uv spectra we estimate the maximum amount of any such *cis*-dichloro impurity to

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(1) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

(2) S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 214 (1963).

(3) (a) L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **90**, 3884 (1968); (b) L. Damrauer and R. M. Milburn, Proceedings of the XIIth International Conference on Coordination Chemistry, Sydney, Australia, 1969, p 38.

(4) M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, **8**, 2201 (1969).

(5) Containing 1.00 g of $RhCl_3 \cdot 3H_2O$, 1.00 g of en·2HCl, 50 ml of water, and 0.426 g of potassium hydroxide.

(6) L. Damrauer, Ph.D. Dissertation, Boston University, 1969.

(7) C, H, and N analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

(8) Rhodium analysis in this laboratory by the stannous chloride method: (a) E. B. Sandell, "Colorimetric Determination of Trace Metals," Interscience, New York, N. Y., 1959, p 769; (b) I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry," Part II, Vol. 8, Interscience, New York, N. Y., 1963, p 468.

be ~2% of the dichloro sample used. In all probability the level of impurity would be considerably less than this upper limit because of the recrystallization procedures used.

(c) **Physical Properties.**—In water, the solubility of [Rh(en)$_2$C$_2$O$_4$]NO$_3$·H$_2$O at room temperature is ~100 mg/100 ml; the solubilities of the perchlorate and iodide salts are very much less. Visible and uv spectral data from the Rh(en)$_2$C$_2$O$_4^+$ ion and related complexes in dilute aqueous solution are in Table I.

TABLE I

VISIBLE AND UV ABSORPTION MAXIMA FOR SOME RELATED COMPLEXES

Complex	λ, nm	ε, M^{-1} cm^{-1} (molar absorbance)	Ref
Rh(en)$_2$C$_2$O$_4^+$	325	260	*a*
Co(en)$_2$C$_2$O$_4^+$	500	113	*b*
	360	138	
cis-Rh(en)$_2$Cl$_2^+$	352	155	*c*
	295	180	
trans-Rh(en)$_2$Cl$_2^+$	406	75	*c*
	286	130	
cis-Rh(C$_2$O$_4$)$_2$Cl$_2^{3-}$	433	247	*d*
	353	358	
trans-Rh(C$_2$O$_4$)$_2$Cl$_2^{3-}$	465	58	*e*
	400	40	

[a] This work. [b] S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962). [c] Reference 1. [d] The values given are from W. R. Keel and R. M. Milburn, unpublished results. There is disagreement about the λ_{max} values and corresponding absorbancy coefficients for this complex. C. K. Jørgensen, *Acta. Chem. Scand.*, **11**, 151 (1957), reported the two band maxima at 437 nm (22.9 kK) and 352 nm (28.4 kK) with ε values of 190 and 275, respectively. Gillard and Wilkinson[e] have reported the band maxima at the same wavelengths as Jørgensen, but with ε values of 170 and 262, respectively. [e] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 870 (1964).

The ir spectrum of [Rh(en)$_2$C$_2$O$_4$]NO$_3$ measured in KBr disks (using a Perkin-Elmer Model 237B grating spectrometer) is shown in Figure 1A. For comparative purposes the ir spectrum for [Co(en)$_2$C$_2$O$_4$]NO$_3$ was measured and this is represented in Figure 1B.

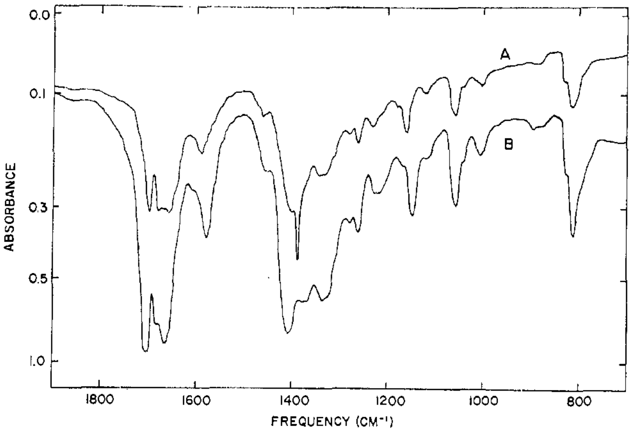

Figure 1.—Infrared spectra (in KBr disks) for (A) [Rh(en)$_2$C$_2$O$_4$]NO$_3$ and (B) [Co(en)$_2$C$_2$O$_4$]NO$_3$.

Discussion

Based on the observations of Johnson, *et al.*,[9] it seems likely that the reaction of *cis*-Rh(en)$_2$Cl$_2^+$ with oxalate would proceed through intermediates which would include *cis*-Rh(en)$_2$(OCOCO$_2$)(H$_2$O)$^+$ and *cis*-Rh(en)$_2$(OCOCO$_2$)Cl^0. Regardless of these details, the expected product Rh(en)$_2$C$_2$O$_4^+$ is obtained. More difficult to visualize is the formation of the chelated oxalato complex from *trans*-Rh(en)$_2$Cl$_2^+$. Johnson, *et al.*, did not observe any cis → trans or trans → cis isomerization during base hydrolysis and re-formation of *cis*- and *trans*-Rh(en)$_2$Cl$_2^+$, respectively, nor did they find any racemization in solution when resolved *cis*-Rh(en)$_2$Cl$_2^+$ underwent hydrolysis and re-formation.[9] In related experiments we have refluxed, for periods of approximately 12 hr, solutions containing *trans*-Rh(en)$_2$Cl$_2^+$ in 1 *M* sodium chloride and *trans*-Rh(en)$_2$Cl$_2^+$ in 1 *M* sodium chloride and 0.01 *M* hydrochloric acid, and, through spectral observations, we have likewise failed to observe any indications of *cis*-Rh(en)$_2$Cl$_2^+$ formation. Clearly the equilibrations among the dichloro species are, for the conditions examined, extremely slow. When *trans*-Rh(en)$_2$Cl$_2^+$ is refluxed in the presence of oxalate, one would anticipate intermediate species which would include *trans*-Rh(en)$_2$(OCOCO$_2$)(H$_2$O)$^+$ and *trans*-Rh(en)$_2$(OCOCO$_2$)Cl^0. The rearrangement of such monodentate oxalate species to the required chelated product, under the conditions used, can perhaps be understood in terms of the high effective concentration which a dangling carboxylate group would have with respect to the metal center. An alternative possibility is that conversion of trans intermediates to the Rh(en)$_2$C$_2$O$_4^+$ product is catalyzed by small amounts of Rh(I) which might be formed during the prolonged refluxing.

In comparing the visible–uv spectra of Rh(en)$_2$C$_2$O$_4^+$ and Co(en)$_2$C$_2$O$_4^+$ (Table I), bands corresponding to the $^1A_1 \rightarrow {}^1T_1$ transition appear with the respective maxima at 325 and 500 nm, consistent with the expected larger ligand field splitting for the second-row transition element.[10] When Rh(en)$_2$C$_2$O$_4^+$ and *cis*-Rh(en)$_2$Cl$_2^+$ are compared, corresponding bands have maxima at 325 and 352 nm, respectively, in accord with oxalate being higher in the spectrochemical series.[11] Any second ligand field band at higher energy for Rh(en)$_2$C$_2$O$_4^+$ seems to be completely masked by a strong band which may be associated with an internal transition in the oxalate group.[12]

The infrared spectra of [Rh(en)$_2$C$_2$O$_4$]NO$_3$ and [Co(en)$_2$C$_2$O$_4$]NO$_3$ are almost indistinguishable (Figure 1) and provide very strong support for the similar nature of the two metal complexes. Nakamoto, *et al.*,[13] have interpreted the infrared spectrum of the closely related [Co(NH$_3$)$_4$C$_2$O$_4$]Cl in terms of bidentate oxalate and have identified the C–O stretching frequencies unambiguously (1705, 1663, 1395, and 1260 cm^{-1}). There is a very close correspondence between these frequencies and those observed for the two oxalatobis(ethylenediamine) complexes above. Oxygen-exchange studies confirm the view that the oxalate is chelated in the Co-

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[9] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 1741 (1963).

[10] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p 114.

[11] Reference 10, p 109.

[12] Reference 10, p 196.

[13] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, **79**, 4904 (1957).

$(NH_3)_4C_2O_4^+$ and $Co(en)_2C_2O_4^+$ ions.[14] The correctness of the conclusion that the oxalate in $Rh(en)_2C_2O_4^+$ is chelated therefore seems assured.

Acknowledgment.—We wish to thank Mrs. Nancy S. Rowan for her help in checking some experimental details.

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[14] (a) R. B. Jordan, C. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, pp 381–394; (b) C. Andrade, R. B. Jordan, and H. Taube, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 13-M; (c) C. Andrade, Ph.D. Thesis, University of Chicago, 1964; (d) C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, **9**, 711 (1970).

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Complexes of Aziridine with Nickel(II) Chloride

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Reports on the complexes of aziridine with transition metal ions have appeared since 1961.[1–4] We have undertaken an investigation of the coordinating properties of the three-membered heterocycle as it occurs in aziridine and its *N*-aminoalkyl derivatives which are capable of chelate ring formation. The potential for ring-opening reactions of the coordinated aziridine ring is also under investigation.

Complexes of the type $[Ni(Az)_6]X_2$ (Az = aziridine, $X^- = NO_3^-, Br^-, I^-$) have been reported by Jackson and Edwards.[1] The previously unreported chloride salt has been prepared by the reaction of anhydrous nickel(II) chloride directly with aziridine. The use of a solvent leads to the formation of $Ni(Az)_4Cl_2$ which has been reported but not completely characterized.[1] The violet hexaaziridinenickel(II) chloride, $[Ni(Az)_6]Cl_2$, has absorption bands at 17,100, 27,400, and 42,000 cm^{-1} in the solid state in agreement with the published spectrum of the nitrate salt in solution.[3] The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition could not be observed due to decomposition of the sample by the heat of the infrared source of the spectrophotometer.

The light blue complex $Ni(Az)_4Cl_2$ can be prepared either by the reaction of nickel(II) chloride and aziridine in methanol or by the thermal decomposition of $[Ni(Az)_6]Cl_2$ at 56° and about 5 Torr. At room temperature there is only a suggestion of the splitting in the electronic spectrum which is observed clearly at liquid nitrogen temperature.[5] Bands at 8375, 11,890, 12,800, 13,870, 17,150, and 27,200 cm^{-1} were assigned to the transitions from the ground $^3B_{1g}$ state to ^3E_g, $^3B_{2g}$, ($^1A_{1g}$, $^1B_{1g}$), $^3A_{2g}(^3F)$, $^3E_g(^3F)$, and $^3E_g(^3P)$, respectively, assuming D_{4h} symmetry. On the basis of the magnitude of the splitting observed and the similarity of the spectrum to those of complexes of known structure, the assignment of the trans geometric configuration is made.[5] No evidence of isomerization has been observed. The measured magnetic moment of 3.09 BM supports the assignment of a six-coordinate structure.

By the thermal decomposition of $[Ni(Az)_6]Cl_2$ or $Ni(Az)_4Cl_2$ at 100° *in vacuo*, we have prepared $Ni(Az)_2Cl_2$. This pale green solid could not be prepared by wet chemical methods. In the spectrum of $Ni(Az)_2Cl_2$ run at liquid nitrogen temperature,[6] maxima were observed at ∼7840 (broad and structured), ∼9760, 12,700, 14,700, 19,900, and 24,500 cm^{-1}. The position and relative intensities of these absorption maxima and the magnetic moment of 3.19 BM support assignment of a six-coordinate structure. It is likely that a chloride-bridged polymeric structure similar to that shown to exist for $Ni(py)_2Cl_2$ is assumed by this material.[7,8] The similarity of the electronic spectrum of $Ni(Az)_2Cl_2$ to that of $Ni(py)_2Cl_2$ at liquid nitrogen temperature[6] supports this hypothesis though the lack of quantitative agreement with a tetragonal model having a strong axial field suggests that some other six-coordinate structure might be assumed. It is noted that several diamines of stoichiometry $Ni(diamine)Cl_2$ also appear to have six-coordinate polymeric structures.[9]

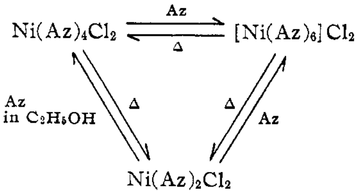
TABLE I

ANALYTICAL AND MAGNETIC RESULTS FOR AZIRIDINE COMPLEXES OF NICKEL(II) CHLORIDE

		Analyses, %								
		Calcd				Found				
Compound	Color	C	H	N	Cl	C	H	N	Cl	μ_{eff}, BM
$[Ni(Az)_6]Cl_2$	Violet	37.14	7.79	21.66	18.27	36.59	7.80	19.91	18.77	3.22
$Ni(Az)_4Cl_2$	Blue	31.83	6.68	18.56	23.49	31.52	6.68	18.31	23.39	3.09
$Ni(Az)_2Cl_2$	Green	22.22	4.67	12.98	32.86	22.33	4.97	12.96	32.58	3.19

For all three complexes a strong absorption occurs between 870 and 900 cm^{-1}. This band is attributed to deformation of the aziridine ring. A band in the 3370–3450-cm^{-1} region is also present and is assigned to the N–H stretching mode of the coordinated aziridine.

The interconversions of compounds of aziridine with nickel(II) chloride are illustrated by



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[5] D. A. Rowley and R. S. Drago, *ibid.*, **7**, 795 (1968).

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