Additional support for the carbonyl protonation mechanism is provided by the recent report by Bunton, *et al.*,[4] on the oxygen exchange reactions of $H_2C_2O_4$, $Co(C_2O_4)_3^{-3}$, and $Cr(C_2O_4)_3^{-3}$ in strongly acidic media. Under comparable conditions the calculated rate constants, activation energies, and frequency factors are essentially identical, from which the authors conclude that oxygen exchange proceeds in all three cases *via* prior protonation of a carbonyl oxygen. Although these reported values are quite similar to the reaction parameters for $Pt(C_2O_4)_2^{-2}$, an exact comparison is inappropriate because experiments on the latter complex were carried out under conditions involving much lower ionic strength and acidities.

The carbonyl protonation mechanism is also consistent with the report[25] that the carbonyl oxygen in $Co(NH_3)_5C_2O_4^+$ is the most labile. In the corresponding bidentate complex, $Co(NH_3)_4C_2O_4^+$, only half the oxygens, presumably the outer oxygens, exchange rapidly. This result might be predicted because the bond breakage necessary for the equilibration of ligand oxygens should be inhibited in a cationic species.

The carbonyl protonation mechanism is thus consistent with all reported data for oxygen exchange in oxalate species. Also, since protonation of a carbonyl oxygen would weaken the corresponding metal–oxygen bond in a bidentate oxalato ligand, it is likely that acid-catalyzed hydrolysis and racemization reactions proceed through initial protonation of a carbonyl oxygen.

The mechanism predicts that under comparable acidic conditions all nonlabile oxalato complexes of the type $M(C_2O_4)_n{}^{-n}$ will exchange oxygen at a similar rate. A convenient test of the mechanism would be provided by a study of the oxygen and oxalate exchange reactions of the bis(oxalato)palladate(II) ion. Since palladium–ligand bonds are usually more labile than corresponding platinum bonds, the oxalate exchange reaction in the palladium complex (which involves Pd–O bond breakage) should be much faster than exchange in the platinum complex under comparable conditions, whereas the oxygen exchange reactions should proceed at rates independent of the metal.

[25] C. Andrade, R. B. Jordan, and H. Taube, Abstracts of Papers, 141st National Meeting of the American Chemical Society, March 1962, p. 13M.

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The Preparation and Properties of $[Re(amine)_4O_2]^+$ Type Ions

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Methods of preparation are given for $[Re(amine)_4O_2]^+$ type ions and related oxohydroxy and dihydroxy complexes, where amine = py, CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $^1/_2$en. The en and py complexes react with dilute and concentrated HCl to produce $[Re(amine)_2Cl_2O(OH)]$ and $[Re(amine)_2Cl_2(OH)_2]Cl$, respectively. $[Re(en)Cl_2(OH)_2]^+$ reacts further with concentrated HCl to produce $[ReCl_4(OH)_2]^-$, and the rates of formation of both these complexes have been followed spectrophotometrically in 12.4 *M* HCl solution. These complexes of Re^{+5} are diamagnetic but, after making the diamagnetic corrections for the ligands, a small residual, temperature-dependent paramagnetism exists for the rhenium ion.

Introduction

In recent years, there has been an interest in the coordination chemistry of rhenium. Much of this activity has centered around the +3, +4, and +5 oxidation states. With simple amine ligands, only a few complexes have been prepared and little is known about their reactivities or the products of their reactions. It was our intention to study the rates of isotopic and ligand-exchange reactions of the amine complexes of Re^{+5} having the general formula $[Re(amine)_4O_2]^+$. This paper reports the preparation of these complexes and some of their physical and chemical properties. The kinetics and products of the interactions with HCl were especially interesting.

Lebedinskii and Ivanov-Emin[1] prepared and characterized the first compound of this group, $[Re(en)_2O_2]Cl$, and found that it was basic toward HCl, giving $[Re(en)_2O(OH)]Cl_2$ and $[Re(en)_2(OH)_2]Cl_3$ reversibly. Improved methods of preparation have been given.[2,3] Burovaya[4] prepared $[Re(py)_4O_2]Cl$ and determined its crystal structure. Various methods have been used for preparing this complex,[5-8] but there is at present no complete description of a method producing a reasonable yield of pure material. Lebedinskii and Ivanov-Emin[6] started with K_2ReOCl_5 because, they claimed, K_2ReCl_6 or K_3ReCl_6 reacted with 50% H_2O–pyridine to give only hydrated ReO_2. However, Sur and Sen[7] obtained $[Re(py)_4O_2]Cl$, together with other products, by

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[1] V. V. Lebedinskii and B. N. Ivanov-Emin, *Zh. Obshch. Khim.*, **13**, 253 (1943).

[2] R. K. Murmann, *J. Inorg. Nucl. Chem.*, **18**, 226 (1961).

[3] R. K. Murmann, *Inorg. Syn.*, in press.

[4] E. E. Burovaya, *Krist. Nauk SSSR*, **5**, 197 (1949); *Chem. Abstr.*, **47**, 3749*d* (1953).

[5] A. S. Kotel'nikov and V. G. Tronev, *Russ. J. Inorg. Chem.*, **3**, 1008 (1958).

[6] V. V. Lebedinskii and B. N. Ivanov-Emin, *ibid.*, **4**, 794 (1959).

[7] B. Sur and D. Sen, *Sci. Cult.* (Calcutta), **26**, 85 (1960).

[8] M. C. Chakravorti, *J. Indian Chem. Soc.*, **40**, 81 (1963).

boiling a mixture of pyridine and aqueous K_2ReCl_6 in the presence of air.

The analogous compounds with monodentate primary amines such as methylamine have not been described previously.

The action of hot aqueous HCl on $[Re(en)_2O_2]^+$ is said to produce green, insoluble $[Re(en)_2O_2]_2[ReOCl_5]$.[6] With $[Re(py)_4O_2]^+$ various authors suggest different formulas for the insoluble green product obtained by the action of HCl. Lebedinskii and Ivanov-Emin[6] conclude that the green complex is $[Re(py)_4O_2]_2[ReOCl_5]$, while Sur and Sen[7] formulate it as $Re(py)_2(OH)_2Cl_5$, and Chakravorti[8] suggests that it is $Re(py)_2OCl_3$. No previous attempt has been made to explain these different results.

This paper reports new or improved preparative methods for the pyridine and alkylamine compounds, an investigation of the products of their reaction with HCl solutions, and some kinetic studies on the stability of the complexes toward ligand replacement. Also, magnetic and spectral measurements are reported for the complexes.

Experimental

Analyses for C, H, N, and halogen were determined by Galbraith Laboratories, Knoxville, Tenn., and for oxygen by the Microchemical Laboratory, Imperial College, London. Our results show that analyses for these elements are more inaccurate and less reproducible when rhenium is present. Rhenium was determined either spectrophotometrically[9] or by precipitation as $(C_6H_5)_4AsReO_4$.

K_2ReCl_6 was prepared by reduction of $KReO_4$ by the method of Watt, *et al.*[10]

$[Re(en)_2O_2]Cl$ was prepared by the method described previously.[2,3] It was twice recrystallized from methanol–water mixtures and gave the same infrared spectrum as an authentic analyzed sample.

$[Re(py)_4O_2]^+$.—After several trials, the following method gave the highest yield of pure material. To 1.0 g. of finely divided K_2ReCl_6 was added a solution of 2.0 ml. of H_2O and 5.0 ml. of pyridine. The mixture was warmed gently for several minutes until all the K_2ReCl_6 had reacted to give a blood-red solution. It was cooled to room temperature and oxygen was bubbled through it for 4 hr. The resultant yellow-brown solution was evaporated to dryness under vacuum to remove the excess pyridine, whose presence increases the difficulty of isolating the product. The residue was dissolved in 15 ml. of H_2O, passed through a filter to remove traces of an insoluble red impurity, and evaporated to dryness under vacuum. Extraction with absolute ethanol followed by evaporation of the alcohol removed most of the insoluble KCl. The complex was isolated in a pure form as either the sparingly soluble iodide or the perchlorate by the addition of excess NaI or $NaClO_4$ to a concentrated aqueous solution of the complex chloride. After washing the orange-yellow crystalline salt with ice-cold water, it was dried under vacuum at room temperature; yield of iodide 0.66 g., 48% of theory; yield of perchlorate 0.76 g., 57% of theory. Both the iodide and perchlorate were slightly soluble in water but very soluble in acetone. The dry salts are stable at room temperature, but aqueous solutions decompose in the absence of a large excess of pyridine.

Because of its high solubility, we were not able to precipitate the pure chloride complex from aqueous solution. However, we did manage to recrystallize it from a pyridine solution containing a small amount of water, but analysis indicated that the sample was still contaminated. On standing in air the orange-yellow crystalline complex crumbled to a yellow powder and became more highly hydrated.

Both the iodide and perchlorate salts are easily isolable in pure form.

Anal. Calcd. for $[Re(py)_4O_2]Cl \cdot H_2O$: C, 40.80; H, 3.77; N, 9.52; Cl, 6.03; Re, 31.66; (O), 8.16. Found for sample recrystallized from pyridine solution: C, 39.05; H, 4.42; N, 8.91; Cl, 6.91; Re, 29.23, 29.41; (O), 7.86. Calcd. for $[Re(py)_4O_2]ClO_4$: C, 37.7; H, 3.19; N, 8.83; Cl, 5.59; Re, 29.4. Found: C, 37.47; H, 3.03; N, 8.77; Cl, 5.46; Re, 28.5. Calcd. for $[Re(py)_4O_2]I$: C, 36.13; H, 3.05; N, 8.46; I, 19.41; Re, 28.14; (O), 4.84. Found: C, 37.2, 36.8; H, 3.20, 3.35; N, 8.56, 8.46; I, 19.41; Re, 28.32; (O), 4.76.

In strong HCl solution, $[Re(py)_4O_2]^+$ changes to a red species having the formula $[Re(py)_4O(OH)]^{+2}$. This has been separated as the $PtCl_6^{-2}$ and $[Cr(NH_3)_2(SCN)_4]^-$ salts, and these give a medium strength infrared band at 945 and 975 cm.$^{-1}$, respectively; these bands are in the region considered to be characteristic of a single Re=O bond.[11] However, these complexes also have a medium-weak band at 810 cm.$^{-1}$ (characteristic[12] of O=Re=O), but the band is much weaker than that for the corresponding complexes isolated from neutral solution. We have concluded from the infrared spectra and from analysis that these salts are a mixture of the dioxo and the oxo–hydroxo forms of the complex.

Anal. Calcd. for $[Re(py)_4O_2]_2PtCl_6$: Re, 25.2. Calcd. for $[Re(py)_4O(OH)]PtCl_6$: Re, 19.73. Found: Re, 22.64, 22.57.

$[Re(py)_2Cl_2(OH)_2]Cl$.—This complex was obtained as a pale green precipitate by boiling a solution of $[Re(py)_4O_2]^+$ in concentrated HCl for about 35 min. The precipitate was collected by vacuum filtration, washed with concentrated HCl, and dried under vacuum at room temperature; yield 65.5%.

Anal. Calcd. for $[Re(py)_2Cl_2(OH)_2]Cl$: C, 24.75; H, 2.50; N, 5.78; Cl, 21.94; Re, 38.41; (O), 6.60. Found: C, 25.51; H, 2.28; N, 5.82; Cl, 22.56; Re, 41.4, 41.3; (O), 6.49.

$[Re(py)_2Cl_2O(OH)]$.—This complex was obtained as a dark green precipitate by the action of 1 *M* HCl on $[Re(py)_4O_2]^+$. The reaction went to completion within 10 hr. at room temperature, and within 15 min. when the solution was boiled. The precipitate was collected by vacuum filtration, washed with 1 *M* HCl, and dried under vacuum at room temperature; yield 60%.

Anal. Calcd. for $[Re(py)_2Cl_2O(OH)]$: C, 26.76; H, 2.47; N, 6.25; Cl, 15.82; Re, 41.53; (O), 7.14. Found: C, 26.31; H, 2.31; N, 6.36; Cl, 16.87; Re, 41.86, 42.06; (O), 7.06.

$[Re(CH_3NH_2)_4(OH)_2]Cl_3$.—Both the dioxo and oxo–hydroxo species are somewhat unstable with respect to loss of amine. Thus this complex is best isolated in the dihydroxo form from strong HCl solution. Two grams of finely ground K_2ReCl_6 was added to a screw-top high pressure glass Carius tube. Anhydrous CH_3NH_2 (10 ml.) was condensed into the tube by cooling it in a Dry Ice–acetone mixture, and then 2 ml. of H_2O was added. The tube was sealed and the contents were allowed to come to room temperature. Reaction was slow and H_2 was evolved.[13] The reaction was allowed to proceed at room temperature for about 8–10 hr. The excess amine was then allowed to evaporate and, when this was nearly complete, the mixture was added to 40 ml. of cold concentrated HCl solution. The pale blue precipitate was collected on a filter, washed with concentrated HCl and with acetone, and dried under vacuum at room temperature; yield 1.46 g., 77% of theory.

Recrystallization was accomplished in the following manner: to 50 ml. of 0.1 *M* HCl was added 1.0 g. of the impure complex. Vigorous stirring was applied and water added dropwise until almost all of the blue species was in solution. (The slight residue contained another blue species which was not very soluble.)

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(9) J. Guyon and R. K. Murmann, *Anal. Chem.*, **36**, 1058 (1964).

(10) G. W. Watt and R. J. Thompson, *Inorg. Syn.*, **7**, 187 (1963).

(11) (a) C. J. L. Lock and G. Wilkinson, *Chem. Ind.* (London), 40 (1962); *J. Chem. Soc.*, 4019 (1962); (b) J. Chatt and G. W. Rowe, *Chem. Ind.* (London), 92 (1962).

(12) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *ibid.*, 333 (1963).

(13) We are indebted to Robert Shandles for the hydrogen determination, which was carried out by gas phase chromatography.

The purple solution was filtered and an equal volume of concentrated HCl added. After 3 hr. at 0° the blue crystals were collected on a filter, washed with concentrated HCl and with acetone, and dried at room temperature under vacuum; yield about 80% of theory.

The corresponding complexes of $C_2H_5NH_2$, $C_3H_7NH_2$, and $C_4H_9NH_2$ were prepared by a similar method to that described above for the CH_3NH_2 complex. The yield was in the range of 75–85% of theory.

Anal. Calcd. for $[Re(CH_3NH_2)_4(OH)_2]Cl_3$: C, 10.51; H, 4.88; N, 12.41. Found: C, 11.13; H, 4.79; N, 13.02. Calcd. for $[Re(C_2H_5NH_2)_4(OH)_2]Cl_3$: C, 18.91; H, 5.90; N, 11.03. Found: C, 18.88; H, 5.76; N, 10.79. Calcd. for $[Re(C_3H_7NH_2)_4(OH)_2]Cl_3$: C, 25.60; H, 6.76; N, 9.77. Found: C, 25.38; H, 6.67; N, 9.77.

Alkylamine complexes of the type $[Re(RNH_2)_4O_2]^+$ and $[Re(RNH_2)_4O(OH)]^{+2}$ were also isolated in pure form by the methods used for the ethylenediamine series. The former were unstable in water solution and in the solid state and released the alkylamine.

$[Re(en)Cl_2O(OH)]$.—The purple color of a concentrated solution of $[Re(en)_2O(OH)]Cl_2$ in 2 *M* HCl gradually changed to yellow and, after 3 days, dark green crystals of $[Re(en)Cl_2O(OH)]$ were precipitated. The crystals were separated by vacuum filtration, washed with 2 *M* HCl, and dried under vacuum at room temperature; yield 35%.

Anal. Calcd. for $[Re(en)Cl_2O(OH)]$: C, 6.85; H, 2.57; N, 8.00; Cl, 20.2; Re, 53.2. Found: C, 6.69; H, 2.72; N, 8.40; Cl, 21.2; Re, 53.0.

$[Re(en)(OH)_2Cl_2]Cl$.—The blue solution of $[Re(en)_2(OH)_2]Cl_3$ in concentrated HCl precipitates green crystals when left for 2 days. The precipitate was collected by vacuum filtration, washed with concentrated HCl, and dried under vacuum at room temperature; yield 70%.

Anal. Calcd. for $[Re(en)(OH)_2Cl_2]Cl$: C, 6.20; H, 2.58; N, 7.24; Cl, 27.4. Found: C, 6.48; H, 2.37; N, 7.46; Cl, 29.3.

$Cs[ReCl_4(OH)_2]$.—To a mixture of 8 ml. of H_2O and 9 ml. of concentrated HCl, 1.0 g. of $[Re(en)_2O_2]Cl$ was added. The mixture was heated to about 85° for about 30 min. During this time the color of the mixture changed from purple to blue to green and finally to yellow. The addition of solid CsCl (1.0 g.) produced an orange-yellow crystalline precipitate of the product. After cooling the solution, the product was collected on a filter, washed with concentrated HCl, and finally with acetone containing a trace of concentrated HCl. It was dried over SiO_2 at atmospheric pressure. The $(C_6H_5)_4As^+$ salt can be made by replacing the CsCl with excess $(C_6H_5)_4AsCl$; yield (Cs^+) 1.1 g., 83% of theory; ($(C_6H_5)_4As^+$) 1.8 g., 91% of theory.

Anal. Calcd. for $Cs[ReCl_4(OH)_2]$: Re, 37.6. Found: Re, 37.6. Calcd. for $(C_6H_5)_4As[ReCl_4(OH)_2]$: C, 38.7; H, 2.96; Cl, 19.10; N, 0.0; Re, 25.0. Found: C, 39.52; H, 2.88; Cl, 19.79, 18.55; N, 0.0; Re, 26.0.

The visible spectra of the Cs^+ and $(C_6H_5)_4As^+$ salts were identical. Concentrated HCl and dimethylformamide, respectively, were used as the solvent.

Properties of Complexes

Visible Spectra.—For the majority of the work a thermostated Beckman DU spectrophotometer was used, but a Cary Model 12 recording spectrophotometer was used for preliminary investigations. The reflectance spectra of solids were determined with a Cary Model 11 instrument, which was fitted with a Model 1011 diffuse reflectance attachment; magnesium carbonate was used as the standard. In Table I are listed the wave lengths of maximum absorbance and the extinction coefficients of freshly prepared solutions. $[Re(CH_3NH_2)_4O_2]^+$ was stable only in 70% CH_3NH_2–H_2O solution. The previously published data on the en complex[14] are included for comparison.

Acid Association.—Each of the dioxo complexes associates with H^+ in acid media. The approximate $[H^+]$ for half of the complex to be converted to its protonated form at 25° was determined spectrophotometrically using the spectral data in Table I. The values −0.57 and −0.43 were obtained for the pH of one-half acid dissociation for $[Re(py)_4O(OH)]^{+2}$ and $[Re(CH_3NH_2)_4(OH)_2]^{+3}$, respectively.

Because of simultaneous decomposition and the high ionic strength, accurate values could not be obtained. A puzzling feature of both the en and CH_3NH_2 systems is that the formation of the dihydroxy complex is not instantaneous, but requires 0.5–2 min. to come to equilibrium. This observation is not understood, but the change is reversible and does not involve ligand substitution. No evidence has been found for polymerization in these systems which leads one to suspect that *cis–trans* isomerization may be occurring.

Infrared Spectra.—Nujol mulls were used in either a Perkin-Elmer Model 137 or 237B spectrophotometer. The Re=O and O=Re=O bonds are in the region 700–1000 cm.$^{-1}$. The important bonds in this region for the compounds prepared are (cm.$^{-1}$): $[Re(py)_4O_2]Cl$: 695 (s), 705 (s), 770 (s), 785 (s), 820 (s). $[Re(py)_4O_2]I$: 695 (s), 702 (s), 768 (s), 777 (s), 815 (s), 822 (s). $[Re(py)_4O_2]ClO_4$: 692 (s), 698 (sh), 765 (s), 770 (sh), 823 (s). $[Re(py)_4O_2][Cr(NH_3)_2(SCN)_4]$: 690 (m), 702 (m), 727 (m), 760 (m), 765 (m), 770 (m), 823 (s), 980 (w), 1020 (w). $[Re(py)_4O_2]_2PtCl_6$: 700 (s), 725 (w), 775 (s), 823 (s), 957 (w), 1015 (w). $[Re(py)_4O(OH)]PtCl_6$: 691 (m), 720 (m), 763 (m), 810 (w), 945 (m), 1016 (w). $[Re(py)_4O(OH)][Cr(NH_3)_2(SCN)_4]_2$: 690 (s), 720 (sh), 765 (m), 812 (m), 975 (m), 1012 (m). $[Re(py)_2(OH)_2Cl_2]Cl$: 680 (s), 758 (s), 940 (m), 970 (s). $[Re(py)_2O(OH)Cl_2$: 640 (s), 662 (s), 687 (s), 757 (m), 767 (s), 980 (m). $[Re(en)_2O_2]Cl$: 700 (s), 727 (m), 757 (s), 830 (s), 890 (w), 907 (w), 1008 (m), 1012 (m). $[Re(en)_2O(OH)]Cl_2$: 780 (w), 890 (w), 985 (s), 1005 (m). $[Re(en)_2(OH)_2]Cl_3$: 805 (w), 885 (w), 1000 (s), 1010 (s). $[Re(en)(O)(OH)Cl_2]$: 720 (s), 875 (w), 980 (w), 1000 (vw). $[Re(en)(OH)_2Cl_2]Cl$: 695 (w), 720 (w), 745 (w), 867 (vw), 890 (vw), 970 (s), 987 (s), 1005 (m). $Cs[Re(OH)_2Cl_4]$: 960 (s). $[Re(CH_3NH_2)_4(OH)_2]Cl_3$: 707 (w), 712 (w), 1000 (s), 1010 (s). $[Re(CH_3NH_2)_4O(OH)][Cr(NH_3)_2(SCN)_4]_2$: 696 (s), 719 (s), 989 (s), 999 (m), 1034 (w).

Magnetic Susceptibility.—All measurements were made on a Gouy balance previously described.[15] We assumed that the diamagnetic corrections for the ligands are the same in the complex as for the free ligands, and that they are temperature independent. The diamagnetic corrections for the ligands were calculated from

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[14] R. K. Murmann and D. R. Foerster, *J. Phys. Chem.*, **67**, 1383 (1963).

[15] J. E. Young and R. K. Murmann, *ibid.*, **67**, 2647 (1963).

TABLE I

VISIBLE AND ULTRAVIOLET SPECTRA[a]

Compound	Solvent	Absorption maxima					
		Solution			Solid		
$[Re(py)_4O_2]I$, Cl, or ClO_4^-	Water		331 (ε 19,400)	445 (ε 1240)	337	425	485 sh
$[Re(py)_4O(OH)]Cl_2$	Concd. HCl			513 (ε 540)			
$[Re(py)_4(OH)_2]^{3+}$	Concd. H_2SO_4			605			
$[Re(py)_2(OH)_2Cl_2]Cl$					350		800
$[Re(py)_2O(OH)Cl_2]$	Acetone		320 (ε 6,400)	733 (ε 320)	350		705
$[Re(CH_3NH_2)_4O_2]Cl$	70% $C_2H_5NH_2$ in H_2O		445	550 sh			
$[Re(CH_3NH_2)_4O(OH)]Cl_2$	0.5 *M* HCl			500 (ε 30.8)			
$[Re(CH_3NH_2)_4(OH)_2]Cl_3$	Concd. HCl			685 (ε 30.2)			
$[Re(en)_2O_2]Cl$	Water		440 (ε 20.0)	580 sh			
$[Re(en)_2O(OH)]Cl_2$	2 *M* HCl		487 (ε 19.0)	650 sh			
$[Re(en)_2(OH)_2]Cl_3$	Concd. HCl		610 (ε 20.8)	840 sh			
$[Re(en)Cl_2(OH)_2]Cl$	Concd. HCl		780 (ε 23.1)				
$Cs[ReCl_4(OH)_2]$	Concd. HCl	408 (ε 33.2)	480 (ε 27.3)	820 (ε 23.8)			

[a] sh denotes shoulder; ε = extinction coefficient.

available tabulations.[16] The measurements were conducted at two or three field strengths and since χ_m had no field strength dependence, ferromagnetic impurities were absent. Table II lists the observed values.

TABLE II

MAGNETIC SUSCEPTIBILITIES

Compound	Temp., °K.	$10^6\chi_m$[a]	$10^6\chi_m'$[b]	μ_{eff}, B.M.[c,d]
$[Re(en)_2O_2]Cl$	298	−76	87	0.46 (3)
	77	−64	99	0.25 (3)
$As(C_6H_5)_4[Re(OH)_2Cl_4]$	298	−121	252	0.78 (3)
	77	+39	411	0.51 (2)
$[Re(py)_4O_2]I$	298	−12	283	0.82 (2)
	195	−47	247	0.62 (2)
	77	+114	402	0.50 (2)
$[Re(py)_4O_2]ClO_4$	298	−218	58	0.37 (2)
$[Re(py)_2O(OH)Cl_2]$	298	+32	224	0.73 (2)
	77	+59	250	0.39 (2)
$[Re(py)_2(OH)_2Cl_2]Cl$	298	−170	46	0.31 (2)
$[Re(CH_3NH_2)_4(OH)_2]Cl_3$	298	−165	59	0.38 (2)

[a] χ_m is the molar susceptibility of the complex. [b] χ_m' is the molar susceptibility of the complex corrected for the diamagnetism of the ligands, etc. [c] μ_{eff} is the effective magnetic moment of the rhenium ion. [d] The figure in parentheses is the number of field strengths used.

Kinetics of Reaction of $[Re(en)_2(OH)_2]^{+3}$ with Concentrated HCl Solution.—The spectral changes which occur as a function of time for a solution of $[Re(en)_2(OH)_2]Cl_3$ in concentrated (12.4 *M*) HCl solution are shown in Figure 1. A careful inspection of these curves suggests that three species are involved in the reaction. These have been shown to be $[Re(en)_2(OH)_2]^{+3}$ (A), $[Re(en)Cl_2(OH)_2]^+$ (B), and $[ReCl_4(OH)_2]^-$ (C). Each of these complexes has been isolated in the solid phase. $[Re(en)_2(OH)_2]Cl_3$ and $Cs[ReCl_4(OH)_2]$ give solution spectra (in concentrated HCl) identical with those shown, respectively, by the t_0 and t_∞ spectra of Figure 1. Solid $[Re(en)Cl_2(OH)_2]Cl$ in concentrated HCl solution gives the same spectrum as that estimated for the intermediate B from Figure 1. For kinetic measurements the wave lengths chosen for study (mμ) were 395 (B = C), 465 (A = B), 535 (B = C), 685 (A = C), and 765 (B = C). At these wave lengths the molar absorbancies of the species shown are equal. Thus absorption measurements at constant temperature at these wave lengths give a measure of [A], [C], [A], [B], and [A], respectively. At each wave length, $(D - D_\infty)/(D_0 - D_\infty)$ was used as a measure of the concentration of that species at time *t*. Figure 2 shows a graph of the absorbance changes as a function of time. A graph of $\ln (D - D_\infty)/(D_0 - D_\infty)$ for 395, 535, 765 mμ gave straight lines with the same slope ±1%, showing that our interpretation of the spectra is correct and that the disappearance of A is a first-order process. Figure 2 shows that B builds up to a maximum and then diminishes while an induction period is observed in the formation of C. This behavior is suggestive of two consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. Since A → B is first order with respect to [A], it was necessary to know the rate expression for B → C. This was determined by starting with B, $[Re(en)Cl_2(OH)_2]^+$, and following its decomposition as a function of time. When studied in this manner the reaction B → C was found to be first order with respect to [B] within experimental error. Since B is very slow to dissolve the results of this method were not very accurate.

For two consecutive first-order reactions it can be shown[17] that the "time for maximum [B]" = $(\ln k_1/k_2)/(k_1 - k_2)$. Since k_1 can be determined directly, and the time at which [B] reaches a maximum can be determined from graphs similar to Figure 2, k_2 can be evaluated. When this was done, k_2 was the same as found in the direct measurement of B → C. It was found that more consistent results were obtained when k_2 was determined using the "time of maximum [B]," and the results quoted were determined in this manner. Table III gives the average of three separate determinations at each temperature, the reproducibility being within ±5%.

A graph of $\ln k_1$ *vs.* $1/T$ was linear, and the rate may be described by the Arrhenius expression $k_1 = 6.5 \times 10^{13}e^{-25,500/RT}$ sec.$^{-1}$. The graph of $\ln k_2$ *vs.* $1/T$ was

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(16) (a) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956; (b) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, Chapter 6.

(17) S. Glasstone, "Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Princeton, N. J., 1961, pp. 1075–1077.

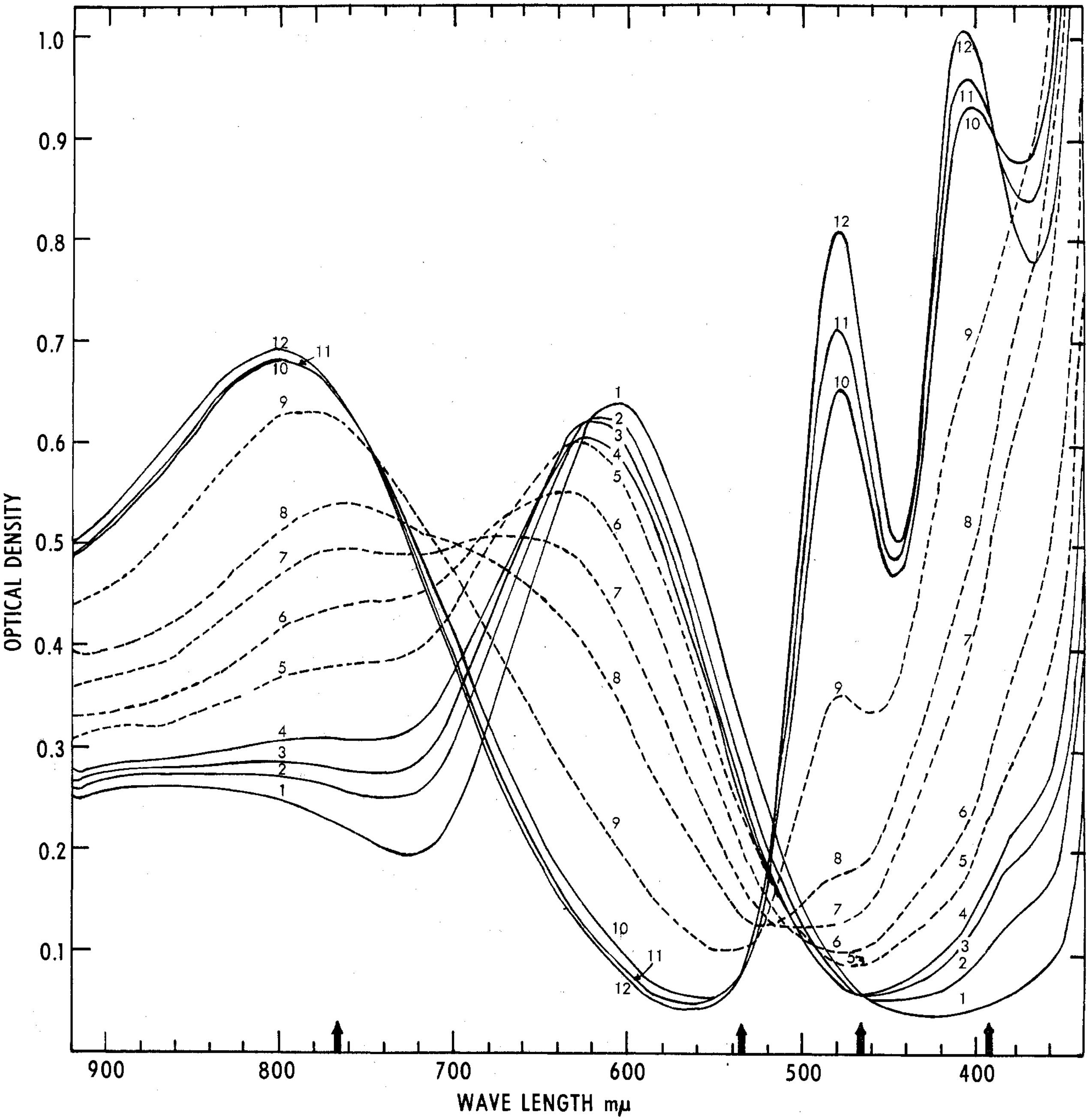


Figure 1.—Spectral changes of [Re(en)$_2$(OH)$_2$]Cl$_3$ in 12.4 M HCl (26–30°) as a function of time [curve no., time (min.)]: 1, 10; 2, 55; 3, 77; 4, 115; 5, 170; 6, 250; 7, 345; 8, 415; 9, 630; 10, 1420; 11, 1825; 12, 2880.

not linear, reflecting the increased measurement error. However, the E_a for k_2 is also about 25 kcal./mole.

In an attempt to determine the effect of [Cl$^-$], kinetic measurements were carried out in 8.0 M HCl. However, the apparent spectra of B and C are different in this media since some coordinated Cl$^-$ is replaced by H$_2$O and the reaction rates could not be reliably determined. Within an estimated error of 15% the 8.0 M rates were the same as in 12.4 M HCl. Thus, the rate dependence on Cl$^-$ is not known.

Discussion

The compounds [Re(en)$_2$O$_2$]$^+$ and [Re(py)$_4$O$_2$]$^+$ are structurally analogous and have the *trans*-dioxo configuration. The [Re(aliphatic amine)$_4$(OH)$_2$]$^{+3}$ type compounds have nearly the same properties as [Re(en)$_2$(OH)$_2$]$^{+3}$, and they probably have the *trans*-dihydroxo structure. The color of the ions changes progressively from yellow to red-purple to blue, [Re(amine)$_4$O$_2$]$^+$, [Re(amine)$_4$O(OH)]$^{2+}$, [Re(amine)$_4$(OH)$_2$]$^{+3}$, as the acidity increases. This is reflected in the similarity of their absorption spectra (Table I). The acid dissociation constants, given as the pH at half-dissociation, for these equilibria are about the same with en and RNH$_2$, but are different from those with pyridine, [Re(en)$_2$(OH)$_2$]$^{+3}$ = −0.9, [Re(en)$_2$O(OH)]$^{+2}$ = 3.26.[14] The addition of the second proton to the pyridine complex was only achieved in concentrated H$_2$SO$_4$. We could not isolate this blue diprotonated species from solution, but deduced its existence by comparison of the

Table III

Rate Constants of Reaction in 12.4 *M* HCl Solution[a]

$$2Cl^- + 2H^+ + [Re(en)_2(OH)_2]^{+3} \xrightarrow{k_1} [Re(en)(OH)_2Cl_2]^+ + enH_2^{+2}$$

$$2Cl^- + 2H^+ + [Re(en)(OH)_2Cl_2]^+ \xrightarrow{k_2} [ReCl_4(OH)_2]^- + enH_2^{+2}$$

Temp. °C.	$t_{1/2}$, sec.$^{-1}$	k_1, sec.$^{-1}$	"time for max. [B]," sec.	k_2, sec.$^{-1}$
25.3	4.44×10^4	1.57×10^{-5}	5.88×10^4	9.2×10^{-6}
36.7	9.12×10^3	7.7×10^{-5}	1.50×10^4	6.7×10^{-5}
50.0	1.68×10^3	4.2×10^{-4}	2.58×10^3	3.3×10^{-4}

[a] Each value listed is an average of three determinations. Individual rates agreed within ±5%.

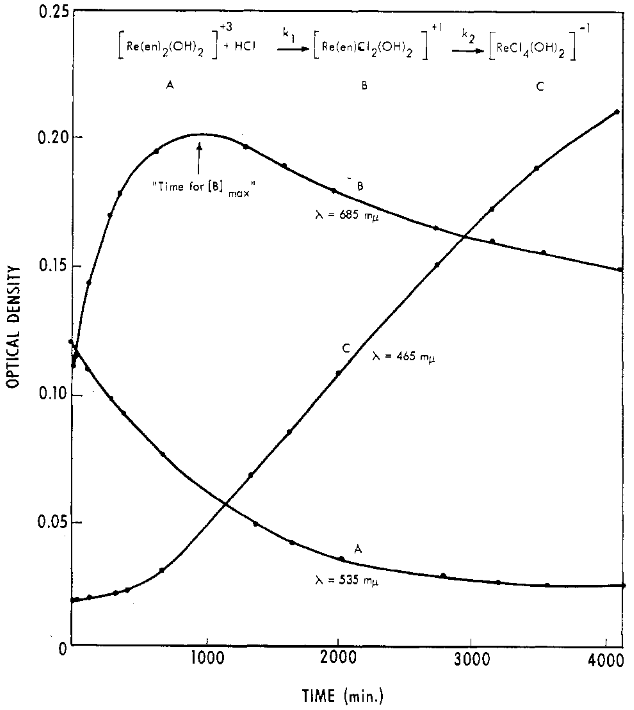
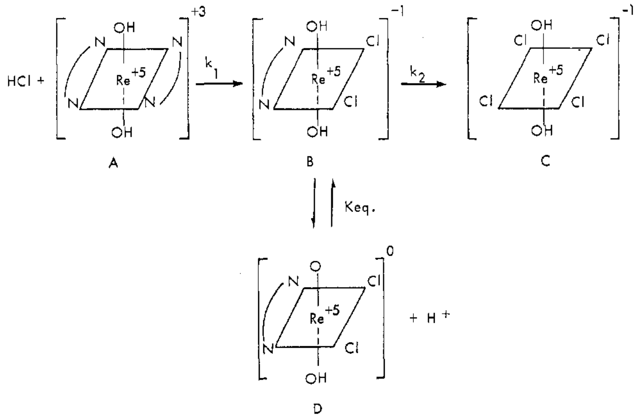


Figure 2.—Absorbance changes at various wave lengths of $[Re(en)_2(OH)_2]Cl_3$ in 12.4 *M* HCl as a function of time; temperature 25.3°.

wave length of the absorption band with those of the corresponding en and CH_3NH_2 complexes. This was confirmed by diluting the H_2SO_4 solution with an equal volume of water: the diluted solution had a band at 517 mμ and a shoulder at 605 mμ, and therefore contained a mixture of the mono- and diprotonated species. The spectra of the pyridine complexes have higher ε values than those of the aliphatic amine complexes, and the absorption spectrum of $[Re(py)_4O_2]^+$ is extremely sensitive to the solvent, as will be described later.[18]

The en, py, and aliphatic amine (RNH_2) complexes dissociate very slowly in strongly acidic media. In water $[Re(RNH_2)_4O_2]^+$ decomposes rapidly, $[Re(py)_4O_2]^+$ slowly, and $[Re(en)_2O_2]^+$ not at all. Even at pH 12 the last complex is stable for hours in the presence of a small excess of en.

In 12.4 *M* HCl-H_2O, $[Re(en)_2(OH)_2]^{+3}$ reacts according to the equations



In the first step, two coordinated nitrogens are replaced by two chloride ions to give the compound B, $[Re(en)Cl_2(OH)_2]Cl$, which has a low solubility and can be isolated in the solid state. Compound B is in equilibrium with D, $[Re(en)Cl_2O(OH)]$, which was isolated from dilute acid solution. A subsequent reaction of the en complex, proceeding at a slightly lower rate, replaces the last two coordinated nitrogens by two chloride ions giving C, $[ReCl_4(OH)_2]^-$, which can be isolated as the Cs^+ and $(C_6H_5)_4As^+$ salts.

The reactions of $[Re(py)_4O_2]^+$ with HCl are analogous to those of the corresponding en compound, but are much slower. Compound D is converted to B only when it is boiled with concentrated HCl for 2 or 3 hr., and B is converted to C when it is treated similarly for 20 hr. A possible explanation for the difficulty of these conversions in the pyridine case is the extreme insolubility of both B and D. Compound D, $[Re(py)_2Cl_2O(OH)]$, has the same empirical formula as the intermediate postulated (but not isolated) by Wilkinson, *et al.*,[19] in the reaction of $ReCl_5$ with aqueous pyridine.

Isolation of complexes B and D has not been accomplished with the CH_3NH_2 or $C_3H_7NH_2$ complexes due to their extremely high solubility. However, the spectral changes which occur as a function of time suggest that $[Re(RNH_2)_2Cl_2(OH)_2]^+$ is the major intermediate between the starting material $[Re(RNH_2)_4(OH)_2]^{+3}$ and the final product $[ReCl_4(OH)_2]^-$.

The magnetic susceptibilities, shown in Table II, show that the compounds behave according to a consistent pattern. The magnetic susceptibility of the

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[18] J. H. Beard and R. K. Murmann, to be published.

[19] N. P. Johnson, F. I. M. Taha, and G. Wilkinson, *J. Chem. Soc.*, 2614 (1964).

metal ion, χ_m', in all cases increases slightly with decreasing temperature, but the increase does not follow the simple Curie–Weiss law and μ_{eff} decreases with decreasing temperature. The magnetic moment is considerably less than that required by the "spin-only" formula for a d^2 ion. This suggests that the d^2 ion is in a highly distorted octahedral field with two *trans* ligands exerting more influence than the other four. This gives a nondegenerate low-lying energy level (d_{xy}) in which the two d-electrons are paired. The small paramagnetic moment is probably due to an orbital moment. Regardless of the exact reason for the paramagnetism, the moments are in agreement with the +5 oxidation state for the metal ion. It is interesting to note that changes in the ligands, OH for O, py for Cl, RNH_2 for en, do not cause major changes in the magnetic susceptibility.

The visible and ultraviolet and infrared spectra of the complexes are primarily useful for identification purposes, but several points should be amplified. The structure of the green product resulting from the interaction of [Re(amine)$_4$O$_2$]$^+$ with 12.4 *M* HCl cannot be [Re(amine)$_4$O$_2$]$_2$ReOCl$_5$ as previously postulated,[6] since the visible and reflectance spectra of the green complexes in solution and in the solid state, respectively, do not show the [Re(amine)$_4$O$_2$]$^+$ bands. This is also true of the infrared spectra of these compounds. Since the compounds were isolated from 12.4 *M* HCl, it seems more likely that the corresponding mono- or dihydroxo ions would have been obtained, but again the spectra do not show the bands characteristic of these ions. Thus, the conclusion is reached that the solid complexes of py and en (and by analogy those of the alkyl amines) do not contain [Re(amine)$_4$O$_2$]$^+$ or [Re(amine)$_4$O(OH)]$^{+2}$ or [Re(amine)$_4$(OH)$_2$]$^{+3}$. The structures 1,6-dihydroxo-2,3-dichloro(ethylenediamine)-rhenium(V) for [Re(en)Cl$_2$(OH)$_2$]$^+$ and 1-hydroxo-6-oxo-2,3-dichlorodipyridinorhenium(V) for [Re(py)$_2$Cl$_2$O(OH)] are consistent with the visible, ultraviolet, and infrared spectra. Lebedinskii and Ivanov-Emin[1,6] obtained their green compounds from 50% HCl, and it is therefore likely that these compounds consisted of mixtures of [Re(amine)$_2$Cl$_2$O(OH)] and [Re(amine)$_2$Cl$_2$(OH)$_2$]Cl.

We attempted to prepare [Re(en)$_2$O$_2$]$_2$ReOCl$_5$, but we were not able to repeat the preparation of K$_2$ReOCl$_5$ given by Jakob and Jazowska.[20] After four trials no K$_2$ReOCl$_5$ was obtained, even though we used exactly the conditions described.

Another discrepancy, which is more difficult to explain, is the difference in the extent of hydration of our [Re(py)$_4$O$_2$]$^+$ compounds compared to those obtained by Wilkinson, *et al.*[21] The analyses of our compounds clearly indicate that the Cl$^-$ is the monohydrate while both the I$^-$ and ClO$_4^-$ are anhydrous. Wilkinson's analyses, however, indicate that the Cl$^-$ is the dihydrate and the iodide is the monohydrate. It is possible that the variation is caused by a difference in drying time or temperature.

For each of the complexes having two oxo groups a strong infrared band appears in the region 815–830 cm.$^{-1}$ which is characteristic of the Re–O stretching frequency in *trans*-dioxo complexes.[12]

Our results indicate that, when one or both of these oxygens are protonated, this band is lost and another occurs at 960–1010 cm.$^{-1}$ which is characteristic of the Re–O–H group (the band is more intense when both oxygens are protonated). Other results[11,12,21,22] indicate that compounds with a single Re=O group have a band in this region. If this is true, the band for the Re=O group must have a much lower intensity than that for the Re–O–H group. Griffith[23] has studied a series of Os(V) compounds and has assigned the band in this region (1050–1090 cm.$^{-1}$) to a deformation mode of the coordinated hydroxyl group. In addition, protonation gives OH stretching bands at 3500 and 1600 cm.$^{-1}$.

The kinetics of the reaction [Re(en)$_2$(OH)$_2$]$^{+3}$ + HCl (concd.) are especially interesting from two points: (a) the reaction provides an example of two consecutive first-order reactions of which few examples exist; (b) the ratio k_1/k_2 strongly suggests that the two ethylenediamines are removed almost independently of each other.

The first of these points (a) was adequately shown by a comparison of k_2 determined by the "time for maximum [B]" method and by independent measurement starting with [Re(en)Cl$_2$(OH)$_2$]$^+$. Since k_1 and k_2 when measured directly were first-order processes, the overall reaction consists of two consecutive first-order reactions.

Both k_1 and k_2 have activation energies of about 25 kcal./mole and the pz values are 6.5×10^{13} for k_1 and about 5×10^{13} for k_2.

The pz value for k_2 is smaller than k_1 but by less than a factor of two. If it does not make any difference what groups are opposite the leaving ethylenediamine, the ratio should be 2. This suggests that the reactivity of a coordinated ethylenediamine is not strongly affected by changing the group opposite it from ethylenediamine to two chlorides. Further, it is in line with the idea that the electronic energy levels of the Re are primarily determined by the *trans* oxygens.

Acknowledgment.—This investigation supported by Research Grant GP-585 from the National Science Foundation.

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[20] W. F. Jakob and B. Jezowska, *Z. anorg. allgem. Chem.*, **220**, 16 (1934).

[21] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964).

[22] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *ibid.*, 601, 1012 (1964).

[23] W. P. Griffith, *ibid.*, 245 (1964).