weaker than those of picolinic acid, we feel that this is added confirmation that the nitrogen atom in picolinic acid is bound to the metal ion in these complexes. Moreover, since it has been shown that the predominant species in solutions of the pyridine carboxylic acids is that in which the nitrogen atom is protonated,[15] it would seem even more conclusive that the nitrogen atom is coordinated to the rare earth ion.

Although it would be of interest to compare the stabilities of the picolinic acid complexes with those of the corresponding glycine complexes, this is not possible since there are no reliable values for the glycine complexes. The available numbers,[2] however, can be considered to be upper estimates and a qualitative comparison can be made. When this is done, it is found that the picolinic acid complexes are the more stable, in agreement with similar observations for the alkaline earths.[7]

The reason for this enhancement of stability for the rare earth–picolinic acid complexes is possibly due to the fact that the heterocyclic ring fixes the closest distance of approach of the oxygen atoms of the carboxyl group to the nitrogen atom. Since models indicate that this distance is larger than for aliphatic compounds, such as glycine, this geometrical effect should favor coordination by the larger ions, such as the rare earths. This argument was suggested previously to account for the relative stabilities of the alkaline earth complexes.[7] The possibility of π-bonding in complexes of this kind cannot at present be ruled out but must await more detailed studies on related systems.

It is difficult to assess the relative donor capabilities of the pyridyl and hydroxyl groups because picolinic acid is considerably more basic than glycolic acid, which is used as a reference compound. Examination of the data given by Powell and his students for ligands containing the hydroxyl group would seem to indicate that the two groups have nearly the same effect on the formation constants. This is in agreement with the observations made previously on the ligands 2-picolyliminodiacetic acid and N-hydroxyethyliminodiacetic acid.[1]

Since the mercapto group apparently does not coordinate to the rare earth ions in the mercaptoacetic acid complexes, the pyridyl group is obviously a more effective donor to these ions.

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[15] R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

Notes

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Reductions of Hexahalorhenate(IV) Salts with Alkali Metals in Liquid Ammonia[1]

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This paper reports the reductions of two hexahalorhenate(IV) salts with alkali metals in anhydrous liquid ammonia at the boiling point of the solutions. In one product we have found a hydridorhenate like that recently characterized by Ginsberg and coworkers.[2]

Experimental

Apparatus.—The liquid ammonia reactions were carried out in a type of apparatus described previously.[3] Generally, between 0.2 and 1.5 g. of hexahalorhenate(IV) salt was put in the reactor, dissolved in 40–50 ml. of ammonia, and alkali metal added in excess.

Infrared spectra were recorded of products in potassium bromide pellets with a Perkin-Elmer Infracord. Pellet mixes were loaded into the pellet press in a gloved bag. During the recording of two consecutive spectra the pellets were bathed with a stream of dry nitrogen. Only in the case of potassium amide did the second spectrum differ appreciably from the first.

Preparation of K_2ReCl_6.—Potassium hexachlororhenate(IV) was prepared according to the method of Hurd and Reinders.[4]

Anal. Calcd. for K_2ReCl_6: Cl, 44.6; Re, 39.0. Found: Cl, 44.3; Re, 39.6.

Exposure of K_2ReCl_6 to NH_3.—Samples of potassium hexachlororhenate(IV) were dissolved in liquid ammonia and allowed to stand for several hours at about $-33°$. Weights of three samples initially and after recovery, respectively, were: 0.5115 g., 0.5210 g.; 0.3027 g., 0.3108 g.; and 0.6547 g., 0.6601 g. The 35-line X-ray diffraction pattern for one residue was practically identical with that for the original K_2ReCl_6. No loss or gain of lines was noted. Some samples of K_2ReCl_6 on longer standing in ammonia, and with delayed evacuation, became discolored.

Preparation of $(NH_4)_2ReBr_6$.—Ammonium hexabromorhenate(IV) was prepared by an adaptation of the method of Rulfs and Meyers.[5]

Anal. Calcd. for $(NH_4)_2ReBr_6$: NH_4^+, 5.1; Re, 26.5; Br, 68.3. Found: NH_4^+, 4.7; Re, 26.0; Br, 67.7.

Exposure of $(NH_4)_2ReBr_6$ to NH_3.—One sample of ammonium hexabromorhenate(IV) weighing 77.1 mg. was dissolved in ammonia at $-33°$. The ammonia was allowed to evaporate slowly, leaving a brilliant yellow solid behind. On being carefully evacuated at room temperature the solid began to turn orange and maintained this color as constant weight was attained. An X-ray

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[1] Part of this work is from the master's thesis of C. L. Ottinger, The University of Tennessee, Knoxville, Tenn., Dec., 1954.

[2] (a) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961); (b) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

[3] G. W. Watt and C. W. Keenan, *J. Am. Chem. Soc.*, **71**, 3833 (1949).

[4] L. C. Hurd and V. A. Reinders, *Inorg. Syn.*, 1, 178 (1939).

[5] C. L. Rulfs and R. J. Meyers, *J. Am. Chem. Soc.*, **77**, 4505 (1955).

TABLE I

COMPOSITION OF K–K_2ReCl_6 REDUCTION PRODUCT

Wt. of reactants, g.		Times ppt.	Product composition, %		
K	K_2ReCl_6	washed	K	Re	Cl
1.268	1.248	3	36.6	30.9	28.6
1.845	1.330	5	35.7	30.2	28.6
0.391	0.698	10	36.1	30.8	28.2
			36.0 ± 0.3	30.6 ± 0.4	28.4 ± 0.2

diffraction photograph of the product showed no lines, whereas the original material gave a well-defined pattern.

Anal. Calcd. weight increase for $2NH_3$, 3.7 mg.; found, 3.7 mg.

Reaction of K with K_2ReCl_6 in NH_3.—When potassium, either as the metal or in liquid ammonia solution, was added to a liquid ammonia solution of potassium hexachlororhenate(IV), the reaction took place in two steps. At first there was no evidence of the blue color of potassium in liquid ammonia but instead a light brown precipitate formed. After about 1 g.-atom of potassium had been added for each mole of potassium hexachlororhenate(IV) present, the blue color appeared but faded rapidly. Thereafter, if the precipitate was allowed to settle and potassium added, the solution became blue; the blue color faded quickly when the suspension was stirred. At a point corresponding to just over 5 g.-atoms of potassium added per mole of potassium hexachlororhenate(IV), a slow evolution of gas began from the stirred suspension. Finally, a point was reached after which further addition of potassium was marked by rapid gas evolution and an increase in the time required for the blue color to fade. In all cases except one, all excess potassium reacted in a well-stirred mixture within 4 to 5 min. as indicated by the disappearance of the blue color.

The precipitates from the K–K_2ReCl_6 reactions were finely divided, black while in contact with liquid ammonia but gray and pyrophoric upon evacuation. The precipitates were washed with three to ten freshly condensed 15-ml. portions of ammonia. The filtrates gave no test for rhenium, but contained potassium and about 18% of the total chlorine. The analyses of the precipitates for ammonia were erratic, varying from 2 to 4%,[6] but were reproducible for major components, as shown in Table I.

A typical X-ray diffraction pattern for the solid product gave the lines: 5.20 (m), 3.42 (s), 3.14 (s), 2.47 (w), 2.48 (w), 2.21 (m), and 1.72 (w) Å. (It is to be noted that KCl gives the lines 3.13 (s), 2.21 (m), 1.81 (w), and 1.57 (w) Å.)

Reactions were carried out in an effort to determine the potassium:rhenate reaction ratio. One method was to measure the amount of hydrogen evolved and equate this with excess potassium. Results of five such determinations, in which the K:K_2ReCl_6 mole ratio mixed varied from 6.7 to 17.0, showed a mole reaction ratio of 5.8 ± 0.5.

The K:K_2ReCl_6 reaction ratio was also calculated on the basis of approximate end points observed when well-stirred rhenate solutions were titrated with standard potassium solutions. End points, characterized by slow fading of the blue color and beginning of rapid gas evolution, were difficult to determine precisely due to the presence of the finely divided, suspended black precipitate. Results of four determinations showed a mole reaction ratio of 5.6 ± 0.5.

Several attempts were made to determine the oxidation state of the solid reduction product. Weighed samples of the solid were placed in flasks of standard ceric sulfate or potassium dichromate. Titration of the excess oxidant with standard ferrous sulfate gave erratic results with reacting ratios of moles of oxidizing agent:rhenium much lower than expected. More satisfactory results were obtained by treating the washed solid reduction product with silver nitrate in the original reaction vessel and determining the amount of silver ion reduced.[7] The mole reaction ratio of Ag^+:Re in the product was 6.8 ± 1.2.

Reaction of K with $(NH_4)_2ReBr_6$ in NH_3.—Reduction of ammonium hexabromorhenate(IV) with potassium gave a black precipitate which contained no bromine and a filtrate which contained only a trace of rhenium. After being washed and evacuated overnight the precipitate was obtained as a brown powder. Two preparations were analyzed with the following results. *Anal.* Found: Re, 69.3, 67.3; K, 21.8, 21.3; NH_3, 5.2, 4.7; H_2, 1.5, not determined.

The hydrogen in the solid product was determined by thermal decomposition *in vacuo* at 450°. The residue consisted of black brittle granules and a white rhenium-containing crystalline material which distilled out of the hottest region of the tube. Some white rhenium-containing material was found in the liquid nitrogen trap. Also, some elemental potassium distilled out of the hottest region of the tube.[8]

The brown powder was found to be diamagnetic. An infrared spectrum showed a prominent sharp band at 1850 cm.$^{-1}$, a broad band at about 730 cm.$^{-1}$, and some other features in common with a spectrum reported for a potassium rhenium hydride.[2a] In a search for evidence of amide in our solid product, an infrared spectrum of potassium amide was made; this amide spectrum was completely unlike the spectrum of our reaction product.

An X-ray powder diffraction pattern was obtained with difficulty. A long exposure revealed some lines, but the intensity of the background made measurements difficult. Results are shown in Table II.

TABLE II

X-RAY DATA. PRODUCT OF K + $(NH_4)_2ReBr_6$

d for product, Å.	*d* for K_2ReH_9,[a] Å.	
4.72 (m)	4.77	(100)
	4.58	(70)
. . .	3.60	(30)
3.32 (w)	3.31	(80)
3.02 (w)	. . .	
2.77 (s)	2.76	(90)
	2.71	(70)
2.40 (w)	2.39	(60)
1.97 (w)	1.95	(60)
1.81 (s)	1.80	(60)
. . .	1.59	(30)
. . .	1.51	(30)
1.44 (m)	1.44	(20)
1.30 (s)	. . .	

[a] Pattern of K_2ReH_9 by private communication from A. P. Ginsberg; Cu $K\alpha$ radiation was used. Only the most prominent lines found by Dr. Ginsberg are recorded here. The line at 1.30 Å. is thought to be spurious; it occurred in some other apparently unrelated exposures made at the same time. Our lines at 4.72 and 2.77 Å. were broad.

Discussion

There is evidently a great difference in the tendency toward ammonolysis of the hexachloro- and hexabromorhenate ions. Our finding that the former does not ammonolyze appreciably upon solution at the boiling point of the solvent was not expected on the basis of work previously reported.[9]

The reduction of potassium hexachlororhenate(IV) with potassium leads to a product with the composition shown in Table I. Due to the reproducibility of this composition with differing ratios of reactants and somewhat different washing procedures, it is felt that the substance produced may be a compound. The X-ray powder pattern suggests that potassium chloride could

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[6] Analyses for ammonia nitrogen in air-sensitive materials may be low and unreproducible. See G. W. Watt and P. I. Mayfield, *J. Am. Chem. Soc.*, **75**, 6179 (1953).

[7] V. J. Christensen, J. Kleinberg, and A. W. Davidson, *ibid.*, **75**, 2495 (1953).

[8] Compare with description of thermal decomposition of K_2ReH_9 in, ref. 2b.

[9] V. V. Lebedinskii and B. N. Ivanov-Emin, *J. Gen. Chem. USSR*, **13** 253 (1943); *Chem. Abstr.*, **38**, 928 (1944).

be present, but this is unlikely due to the solubility of this compound. On the basis of the analysis in Table I, 95% of the product has the approximate empirical formula $K_{11}Re_2Cl_{10}$. The mole reaction ratios of $K:K_2ReCl_6$ of about 5.6–5.8 indicate that the effective oxidation state of rhenium is below zero, having been reduced from +4 to −1 or −2. The great reducing equivalency of the solid product is also consistent with an oxidation state of rhenium below zero. Another explanation for the high reducing equivalency of the product would be the existence of hydridorhenate groups.

The brown solid product recovered from the reduction with potassium of ammonium hexabromorhenate(IV) is evidently a mixture of white potassium enneahydridorhenate(VII) and a rhenium–nitrogen compound.[10] Rhenium(IV) amide is possibly the source of nitrogen and the brown color, but, from the infrared spectrum, amide does not appear to be present. Rhenium(III) amide would be a possibility, also; Thompson found this compound to be formed by the reaction of potassium amide and rhenium(III) iodide in liquid ammonia.[11]

Potassium enneahydridorhenate(VII) and -technate(VII) have been produced in liquid ammonia by Ginsberg[12]; for the former, he added potassium to potassium perrhenate in ammonia which contained about 10% ethanol or water.

Acknowledgments.—We are indebted to Dr. A. P. Ginsberg for making available to us preprints of several of his papers and for supplying us with X-ray data and a powder diffraction photograph of K_2ReH_9. We thank Dr. W. H. Fletcher for helping with the interpretation of our infrared spectra. I. E. M. especially thanks the National Science Foundation for support under NSF-G15447.

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(10) On the basis of our analytical results and the infrared spectrum, Dr. Ginsberg has suggested the product could be mainly a mixture of K_2ReH^9 and $(NH_4)_2ReH_9$.

(11) R. J. Thompson, Ph.D. Dissertation, Texas University, 1959.

(12) A. P. Ginsberg, private communication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Cyanide Stretching Frequencies of Some Mixed Ligand Complexes of Iron, Ruthenium, and Osmium

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The infrared absorption properties of some mixed cyanide and aromatic diimine complexes of iron, ruthenium, and osmium have been examined in an attempt to gain evidence concerning their configurations and bonding. This work was prompted in part by reports by Hamer and Orgel[1] and by Shriver[2] that the neutral dicyanobis(1,10-phenanthroline)iron(II) complex and its adducts with methyl sulfate, boron trifluoride, and diborane display two close-lying bands in the C≡N stretch region, suggesting a *cis* configuration for the complexes.[1,2] Since spectra obtained by the author in an earlier study[3] did not exhibit splitting of the cyanide frequencies, it was of interest to explore the possible effects of solvation and various recrystallization procedures on the spectra and also to extend the study to additional, related compounds.

Experimental

Analyzed samples of most of the complexes were available from earlier work: the osmium and ruthenium complexes,[3] the tetracyano complexes of iron(II) and (III),[4] and the dicyano complexes of iron(III).[4] Fresh samples of the dicyano complexes of iron(II) with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) were prepared as described earlier but not recrystallized.[4] Assay of these by potentiometric titration with standard cerium(IV) sulfate in 6 *M* H_2SO_4 indicated equivalent weights corresponding to the formulas $[Fe(phen)_2(CN_2]\cdot 2H_2O$ and $[Fe(bipy)_2(CN)_2]\cdot 3H_2O$.

Spectra were obtained using a Beckman IR-8 spectrophotometer and the mull technique in Nujol. Frequency calibration was confirmed to within ±4 cm.$^{-1}$ by the spectrum of a polystyrene film.

Recrystallization from $CHCl_3$ involved dissolution in the boiling solvent, filtration, and evaporation of the filtrate to dryness to yield a chloroform solvated complex (as evidenced by strong absorption at 1350 cm.$^{-1}$). Heating above 100° gave the nonsolvated form. The formula $[Fe(phen)_2(CN)_2]\cdot 2CHCl_3$ was indicated by a loss in weight of 31.2% (theory, 33.8%) on drying the product at 120° for 1 hr. Recrystallization from concentrated H_2SO_4 by dilution with water was performed as previously described.[4] The solubility of $[Fe(bipy)_2(CN)_2]$ enabled recrystallization from hot water; the 1,10-phenanthroline analog was too insoluble for similar treatment. Water of solvation was removed by heating at 160° for 1 hr.

Results

Frequencies measured for the cyanide stretching motions are compiled in Table I. Relative intensities were estimated on the basis of peak heights, assigning the number 10 to the highest peak to be found for the compound and proportionately smaller numbers to the smaller peaks. Band widths at half-heights ranged from about 5 to 20 cm.$^{-1}$. As an illustration of typical band shape and resolution, spectra in the 2000 to 2400 cm.$^{-1}$ region for two of the complexes are shown in Fig. 1.

In the spectral region from 2000 to 625 cm.$^{-1}$ the 1,10-phenanthroline complexes showed little or no differences among themselves. The same was true for the bipyridine complexes. The only appreciable differences found were those expected due to the presence of water or chloroform of solvation. Since spectra in this region resemble those reported earlier for the simple *tris* aromatic diimine complexes of iron,[5] details are omitted here.

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(1) N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

(2) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963).

(3) A. A. Schilt, *ibid.*, **85**, 904 (1963).

(4) A. A. Schilt, *ibid.*, **82**, 3000 (1960).

(5) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).