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Hexachlororhenates(IV) by Action of Carbon Tetrachloride on Perrhenates[1]

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Perrhenates of Li, Na, K, Cs, Cu(I), Ag, Tl(I), Ba, and Cu(II) react at 400° with carbon tetrachloride to form hexachlororhenates(IV). Pure products were not obtained from the copper salts. Copper(I) perrhenate gave $CuReCl_6$. Rhenium(V) chloride, also formed, can be separated from the mixture by extracting with carbon tetrachloride.

Anhydrous metal chlorides[2] have been prepared from the reaction of a metal oxide with carbon tetrachloride at elevated temperature (400°) and pressure (order of 100 atm.). The same conditions have led to reaction between perrhenates and carbon tetrachloride.

In each case investigated the hexachlororhenate of the associated cation was isolated in nearly quantitative yield. In the case of copper(I) perrhenate, copper(II) hexachlororhenate(IV) was formed. The process is described by the reaction

$$4MReO_4 + 16CCl_4 = 2M_2ReCl_6 + 2ReCl_5 + 5Cl_2 + 16COCl_2 \qquad (1)$$

The process was used to prepare hexochlororhenates(IV) of Li, Na, K, Cs, Ag, Tl(I), Ba, and Cu(II).

Experimental

Preparation and Purification of Reagents.—Reagent grade chemicals were used where grade is not specified. Preparations of lithium,[3] copper(I),[4] and copper(II)[5] perrhenates have been described. An article by Wilke-Dörfurt[6] contains references pertinent to the preparation of other perrhenates.

Apparatus and Procedure. (A) **The Reaction with Carbon Tetrachloride at 400°.**—The reaction mixture consisted of 2.0 g. of the appropriate perrhenate salt unless otherwise specified and 20–32 ml. of CCl_4. The mixture was sealed in a Pyrex ampoule of 60–120-ml. capacity and heated at 400° in a bomb (Aminco reaction vessel No. 41-4150) containing CCl_4 to counterbalance the pressure generated in the ampoule. Heating time was 2 hr. unless otherwise specified. The volumes of CCl_4 used in loading both the ampoule and the bomb were carefully adjusted to $^8/_{26}$ of the empty space in each vessel as prescribed by Knox, *et al.*[2]

(B) **Isolation of Reaction Products.**—The products were separated on the basis of their solubility in carbon tetrachloride.

(1) **Insoluble Residue.**—After cooling, the reaction mixture was transferred from the ampoule in a stream of dry nitrogen to a Soxhlet extractor equipped with a Pyrex thimble, extracted successively with 100 ml. each of CCl_4 and CH_2Cl_2, and the insoluble residue dried under vacuum. Manipulations of the dried product were performed in a drybox.

(2) **The Solvent-Soluble Products.**—In all cases the CCl_4 extraction gave a red solution from which lustrous black crystals of $ReCl_5$ separated. Only in the case of the $KReO_4$ reaction mixture were they collected, weighed, and analyzed. In the other cases their presence was noted.

The methylene chloride extract, upon evaporation under nitrogen, yielded traces of a residue which was not characterized.

Measurement of Magnetic Susceptibility.—Magnetic susceptibility was determined using a Gouy balance and permanent magnet described earlier.[7]

Analyses. (A) **Rhenium.**—Samples (75–150 mg.) were hydrolyzed and rendered basic with NaOH, and the rhenium was oxidized with hydrogen peroxide to perrhenate. The rhenium was determined gravimetrically as tetraphenylarsonium perrhenate.[8]

When thallium was present rhenium was determined in the manner described by Smith.[9]

(B) **Chlorine.**—Samples (75–150 mg.) were hydrolyzed by slowly admitting water through the ground-glass stopper of the weighing pig immersed in a beaker of water. The rhenium was oxidized to perrhenate as described for the rhenium determination. The resulting basic solution, after being boiled to remove excess H_2O_2, was cooled, acidified, and filtered. Chloride was determined gravimetrically on the filtrate.

(C) **Oxidation State Determination.**—The oxidation state of rhenium was determined in the manner described by Geilmann and Wrigge[10] using an excess of cerium(IV) solution and back titrating with iron(II) solution. When thallium(I) was present it was simultaneously oxidized to thallium(III).

TABLE I

RESULTS OF SYNTHESES OF HEXACHLORORHENATE(IV) SALTS

Reactant	Product	Color	Yield, g. Found	Yield, g. Calcd.
$KReO_4$[a]	K_2ReCl_6	Yellow	3.3	3.30
	$ReCl_5$	Black	1.8	2.50
$LiReO_4$	Li_2ReCl_6	Yellow	1.5	1.60
$NaReO_4$	Na_2ReCl_6	Yellow	1.6	1.66
$CsReO_4$	Cs_2ReCl_6	Yellow	1.7	1.73
$AgReO_4$	Ag_2ReCl_6	Red-brown	1.4	1.71
$TlReO_4$[b]	Tl_2ReCl_6	Orange	1.7	1.78
$Ba(ReO_4)_2$[c]	$BaReCl_6$	Yellow	1.5	1.65
$Cu(ReO_4)_2$[c]	$CuReCl_6$	Black	2.0	1.64
$CuReO_4$	$CuReCl_6$	Black	2.3	2.95

[a] 4 g. of $KReO_4$ was used. [b] 16 hr. reaction time. [c] 4–5 hr. reaction time.

Products of Reaction of Perrhenates with Carbon Tetrachloride.—In all cases the products consisted of a cake of solid hexachlororhenate(IV) overlaid by a layer of lustrous black crystals of $ReCl_5$ under a red solution. Results of the syntheses are tabulated in Table I. Analytical data are given in Table II. In the case of Cs_2ReCl_6 the initial reaction product obtained by this method was finely ground and allowed to react with CCl_4 a second time in the bomb (5 hr.) to effect complete conversion

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(1) From work performed by W. W. Horner in partial fulfillment of requirements for the Ph.D. degree in Chemistry at the University of North Carolina at Chapel Hill.

(2) K. Knox, S. Y. Tyree, Jr., R. D. Srivastava, V. Norman, J. Y. Bassett, Jr., and J. H. Holloway, *J. Am. Chem. Soc.*, **79**, 3358 (1957).

(3) W. T. Smith, Jr., and S. H. Long, *ibid.*, **70**, 354 (1948).

(4) W. T. Smith, Jr., *ibid.*, **73**, 77 (1951).

(5) H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J. Chem. Soc.*, 2211 (1931).

(6) E. Wilkie-Dörfurt and Th. Gunzert, *Z. anorg. allgem. Chem.*, **215**, 369 (1933).

(7) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

(8) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

(9) W. T. Smith, *Anal. Chem.*, **20**, 937 (1948).

(10) W. Geilmann and F. W. Wrigge, *Z. anorg. allgem. Chem.*, **222**, 61 (1935).

TABLE II

ANALYTICAL DATA FOR HEXACHLORORHENATE(IV) SALTS

Product	% Re Found	% Re Calcd.	% Cl Found	% Cl Calcd.	Cl/Re Found	Cl/Re Calcd.	Av. ox. state Re
K_2ReCl_6	39.25	39.04	43.88	44.58	5.87	6.00	4.00
$ReCl_5$	51.3	51.24	48.0	48.76	4.91	5.00	...
Li_2ReCl_6	44.55	45.23	50.99	51.65	6.01	6.00	3.97
Na_2ReCl_6	40.83	41.87	47.18	47.81	6.07	6.00	3.95
Cs_2ReCl_6	28.48 28.72 28.45	28.03	31.94 31.13	32.00	5.81	6.00	4.04
Ag_2ReCl_6	30.52	30.31	34.52	34.61	5.94	6.00	3.82
Tl_2ReCl_6	23.05 23.02	23.06	26.61 26.45	26.33	6.05	6.00	...
$BaReCl_6$	33.83	34.73	38.83	39.65	6 03	6.00	
$CuReCl_6$[a]	38.44 38.83 38.64	40.27	45.29	45.99	6.17	6.00	3.93
$CuReCl_6$[b]	36.66	40.27	45.35	45.99	6.50	6.00	3.96

[a] From $Cu(ReO_4)_2$. [b] From $CuReO_4$.

of $CsReO_4$ to Cs_2ReCl_6 and give the product reported. Magnetic moments of 3.2–3.4 B.M. were observed for rhenium in each hexachlororhenate(IV) salt except $CuReCl_6$, for which the value 2.7 B.M. was obtained.

The Na, K, and Cs hexachlororhenate(IV) salts were yellow when freshly prepared and became yellow-green in subsequent manipulations.

Equation 1 does not apply to the conversion of $CuReO_4$ to $CuReCl_6$ by CCl_4. A one to one conversion is assumed in obtaining the calculated yield given in Table I.

Discussion

Following the procedure set forth in this paper it has been possible to prepare hitherto unreported hexachlororhenates(IV) that are more soluble in hydrochloric acid than the chloride of the associated cation. For example, dissolution of Na_2ReCl_6 in concentrated HCl causes precipitation of NaCl and leaves a bright green solution. The precipitation of NaCl was predictable from work reported by the Noddacks[11] in which they attempted the preparation of Na_2ReCl_6 from HCl solution. Four of these salts were prepared, those of Li, Na, Ba, and Cu(II), and were found to be very soluble in water. All four were found to be hygroscopic. The high Cl:Re ratio in the $CuReCl_6$ preparation may indicate the formation of some $CuCl_2$ in the reaction. The procedure also was used to prepare several of the well-known[12] water-insoluble hexachlorohenates(IV), the salts of K, Cs. Ag, and Tl(I).

For the water-soluble group of hexachlororhenates(IV) the analytical values obtained for Re and Cl were consistently low despite the fact that Cl:Re ratios very close to 6 were obtained. Deliberate exposure of Li_2ReCl_6 to moist air for about 5 min. resulted in significant lowering of the percentage of Re and Cl but the ratio of Cl:Re remained the same. The infrared spectrum of $BaReCl_6$ freshly prepared by the method described in this work showed small but definite absorption peaks at 3700 and 1620 cm.$^{-1}$. For O–H in water the stretching and bending vibrations are reported to absorb at 3725 and 1600 cm.$^{-1}$, respectively.[13] Infrared results therefore indicate the strongly hygroscopic nature of the compound. However, available analytical data show a maximum limit of about 2% H_2O in $BaReCl_6$ handled in this manner.

It is of practical significance that this method provides a route to $ReCl_5$ directly from $KReO_4$ (the latter being readily prepared and purified). A yield of 72% of the theoretical calculated from eq. 1 was realized in the $KReO_4$ case.

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[11] I. Noddack and W. Noddack, *Z. anorg. allgem. Chem.*, **215**, 159 (1933).

[12] S. Tribalat, "Rhénium et Technétium," Gauthier-Villars, Paris, 1957, pp. 91–95.

[13] M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 487, 490 (1957).

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Studies of Nitro and Nitrito Complexes. I. Some Nitrito Complexes of Nickel(II)

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The results are reported of studies of the infrared and electronic spectra of the blue or blue-green complexes $Ni(py)_4(ONO)_2$ and $Ni(diamine)_2(ONO)_2$ (where diamine represents one of several C- or N-substituted ethylenediamines). In the solid state these nitrito complexes are quite stable with respect to conversion to the nitro analogs. The antisymmetric and symmetric NO_2 stretching frequencies lie between those of the free ion and those of previously known nitrito complexes such as $[Cr(NH_3)_5(ONO)]^{2+}$. It is suggested that steric factors play an important part in the adoption of oxygen coordination by the NO_2^- ion in contrast with the more usual mode of bonding *via* nitrogen. The electronic spectrum of $K_2Ba[Ni(NO_2)_6]$ is reported and a Δ value of 13,400 cm.$^{-1}$ is obtained from the energies of the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions.

Introduction

In a previous communication[1] one of us reported the apparently anomalous infrared frequencies due to the NO_2 groups in the blue complex $Ni(a\text{-dieen})_2(NO_2)_2$.[2] Further investigations have shown that in series of compounds of the types $NiD_2(NO_2)_2$ (where D = a C- or

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[1] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

[2] We shall use the following abbreviations for ligands; py = pyridine; en = ethylenediamine; *a*-dimen = N,N-dimethylethylenediamine; *a*-dieen = N,N-diethylethylenediamine; *s*-dieen = N,N'-diethylethylenediamine; *m*-stien = *meso*-1,2-diphenylethylenediamine.