

CCCL.—*The Per-rhenates of Copper, Nickel, and Cobalt, and the Ammines of these Compounds.*By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON,  
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PER-RHENIC acid forms well-characterised compounds with many of the heavy metals and these, in turn, give stable ammines. Those of copper, nickel, and cobalt are here described.

Metallic rhenium was heated in oxygen and the heptoxide thus produced, when dissolved in water, yielded per-rhenic acid. Normal per-rhenates were obtained by adding excess of the appropriate metallic carbonate to this solution and warming it until the reaction was complete.

*Copper Per-rhenate.—Hydrates.* Solution of the carbonate is readily effected, and the pale blue solution yields crystals of the pentahydrate of the same colour which in a desiccator over fused calcium chloride soon reach constant weight corresponding to the tetrahydrate [Found : loss at  $110^{\circ}$ , 10.80.  $\text{Cu}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$  requires  $4\text{H}_2\text{O}$ , 11.32%]. The nearly white anhydrous residue had a very faint greenish tinge and readily reabsorbed moisture from the air [Found : Cu, 11.29.  $\text{Cu}(\text{ReO}_4)_2$  requires Cu, 11.28%]. Curves for the velocity of dehydration at  $100^{\circ}$  showed only one break, occurring when the composition of the residual material corresponded with the hemihydrate,  $\text{Cu}(\text{ReO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Thereafter the loss of weight at  $100^{\circ}$  became so slow that complete dehydration was always effected by raising the temperature to  $115$ — $120^{\circ}$ . Rate of hydration curves in material kept in a desiccator over sodium carbonate decahydrate showed no falling off until the tetrahydrate was reached. Finally, under these conditions the pentahydrate was obtained, which subsequently deliquesced. The pentahydrate when maintained over fused calcium chloride was reconverted to tetrahydrate [Net gain of weight = 13.15% of anhydrous material. Calc. for  $\text{Cu}(\text{ReO}_4)_2 \longrightarrow \text{Cu}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$  : 12.77%].

*Ammines.* By adding aqueous ammonium hydroxide (or, better, gaseous ammonia) to a fairly concentrated hot solution of copper per-rhenate, until the precipitate first formed redissolved, a dark blue solution was obtained from which deep blue crystals separated on cooling. These are only slightly soluble in water and are stable in air at 100° [Found: Cu, 9.73, 9.62, 10.27, mean 9.87; NH<sub>3</sub>, 11.15, 10.17, 10.80, mean 10.71. Cu(ReO<sub>4</sub>)<sub>2</sub>·4NH<sub>3</sub> requires Cu, 10.07; NH<sub>3</sub>, 10.76%]. The *tetrammine* on being strongly heated in air turns pale green and then melts with darkening and decomposition. Varying the conditions gave no evidence of the formation of any other ammine.

*Nickel Per-rhenate.—Hydrates.* From a solution of nickel carbonate in aqueous per-rhenic acid, pale green crystals separated which after drying on a porous plate varied somewhat in water content but nevertheless must be *nickel per-rhenate pentahydrate* [Found: H<sub>2</sub>O, 13.34, 14.00, 13.14, 12.33, 13.86, 13.42, mean 13.35. Ni(ReO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O requires H<sub>2</sub>O, 13.87%]. In the curve for rate of dehydration of pentahydrate at 100°, there is no inflexion until the pale green *tetrahydrate* is reached, whereupon the rate of loss of weight falls to zero. This hydrate is also formed by leaving the pentahydrate in a desiccator over fused calcium chloride [Found: H<sub>2</sub>O, 11.21, 11.42, mean 11.32. Ni(ReO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O requires H<sub>2</sub>O, 11.41%]. The cream-yellow anhydrous *salt* was obtained by heating the tetrahydrate to 170° [Found: Ni, 10.25, 10.39, mean 10.32. Ni(ReO<sub>4</sub>)<sub>2</sub> requires Ni, 10.51%].

*Ammines.* Treatment of an aqueous solution of nickel per-rhenate with ammonia gave eventually a clear blue solution, from which lilac crystals separated. These were washed with aqueous and then with alcoholic ammonia, and dried on a porous plate. They are unstable in air and pass into a light blue material with loss of ammonia [Found: Ni, 9.52, 9.13, 8.84, mean 9.16; NH<sub>3</sub>, 14.52, 15.53, 14.45, mean 14.83. Ni(ReO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> requires Ni, 8.88; NH<sub>3</sub>, 15.44%].

The rate of loss of ammonia from the *hexammine* at 100° gave a smooth curve down to the blue *tetrammine* [Found: loss at 100°, 5.03. Ni(ReO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> requires 2NH<sub>3</sub>, 5.24%], which is stable at this temperature [Found: Ni, 9.55, 9.75, 9.26, mean 9.52; NH<sub>3</sub>, 10.81, 10.73, 9.74, mean 10.43. Ni(ReO<sub>4</sub>)<sub>2</sub>·4NH<sub>3</sub> requires Ni, 9.36; NH<sub>3</sub>, 10.85%]. When heated strongly in air this compound decomposes and eventually leaves a residue of nickel oxide.

*Cobalt Per-rhenate.—Hydrates.* Cobalt carbonate dissolved in aqueous per-rhenic acid gave a pink solution from which somewhat darker pink crystals separated. These were filtered off and dried on a porous plate, and then corresponded most nearly to the *penta-*

*hydrate* [Found :  $\text{H}_2\text{O}$ , 13.32, 13.82, 11.28, 12.41, 13.62, 12.31, mean 12.79.  $\text{Co}(\text{ReO}_4)_2, 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 13.87%]; this hydrate appears to lose water more readily than the corresponding hydrates of copper and nickel, samples having been obtained with as little as 4.1 mols. of water. After standing over fused calcium chloride the material is converted into the *trihydrate* [Found :  $\text{H}_2\text{O}$ , 8.58, 8.92, 8.87, 8.79.  $\text{Co}(\text{ReO}_4)_2, 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 8.81%]. Dehydration leaves the purplish-blue *cobaltous per-rhenate* [Found : Co, 10.53.  $\text{Co}(\text{ReO}_4)_2$  requires Co, 10.55%].

*Ammines.* Passage of ammonia into hot cobaltous per-rhenate solution caused the precipitation of bright violet crystals, more of which separated on cooling. Too much ammonia must be avoided or a brown precipitate of hydrated oxide is formed, and the crystals must be washed with liquids containing ammonia, otherwise they are converted into a bright green powder which is probably a basic per-rhenate since it is insoluble in ammonia-free water, and contains about 20% of cobalt. The violet crystals proved to be *cobaltous per-rhenate tetrammine* [Found : Co, 9.80, 9.86, 9.93, mean 9.86;  $\text{NH}_3$ , 11.09, 10.99, 10.40, mean 10.83.  $\text{Co}(\text{ReO}_4)_2, 4\text{NH}_3$  requires Co, 9.40;  $\text{NH}_3$ , 10.84%]. On being strongly heated in air, the compound decomposes leaving eventually cobalt oxide, whilst in water it is converted into the insoluble green substance already mentioned.

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