347. *Researches on Residual Affinity and Co-ordination. Part XL. Some Complex Compounds of Rhenium.*

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A number of alkali and organic rhenium dioxocyanides have been prepared of the general formula $M_3[ReO_2(CN)_4]$, where M is a univalent metal or radical. Although attempts to determine the valency of rhenium in these compounds were not entirely satisfactory, the results for the most part favoured a quinquevalency in the co-ordinating metal. Some salts of rhenichloric acid and per-rhenic acids with 2 : 2'-dipyridyl and 2 : 2' : 2''-tripyridyl have also been made. From the former base two rhenichlorides were obtained in which the dipyridyl functioned respectively as a mono- and a di-acid base; tripyridyl gave rise only to one salt. Such rhenichlorides are more stable to heat and water than are the corresponding alkali salts.

Australian molybdenite has been investigated for its rhenium content, which is about 1 part in a million.

SEVERAL attempts have been made to obtain complex cyanides of rhenium but, invariably, there have resulted only oxocyanides. In 1932 Turkiewicz (*Rocz. Chem.*, **12**, 589) obtained a substance $K_3[ReO(CN)_4OH]$, and later one of us announced the preparation of potassium–sodium and potassium derivatives to which were assigned the formula $X[ReO(CN)_4]$, where $X = K_2Na$ or K_3 (J., 1935, 568). More recently, Klemm and Frischmuth (*Z. anorg. Chem.*, 1937, **230**, 215) have described the preparation of the compound $K_3[ReO_2(CN)_4]$. Further investigation of the above alkali salts obtained by us has revealed that they also are of this type, $X_3[ReO_2(CN)_4]$, that is, derivatives of quinquevalent rhenium containing two atoms of oxygen instead of one as was formerly suggested (*loc. cit.*).

Attempts to determine the valency of rhenium in these substances by oxidation methods did not give entirely satisfactory results, for the values obtained depended on the oxidising agent used and on the duration and the temperature of the process. With ceric sulphate, the results varied between 3·8 and 5·2, whereas with potassium dichromate they ranged from 5 to 5·7. A direct determination of the oxygen by the ter Meulen method revealed that these oxocyanides contained two atoms of this element. Although this estimation worked satisfactorily with the sodium derivative, low values were experienced with potassium rheniumdioxocyanide owing to the reduction product sintering and so enclosing some of the original material, which remained unattacked by the hydrogen. Accordingly, certain organic derivatives were made, these being more easily reduced and leaving only a powdery residue of rhenium together with a little carbon. The compounds prepared were the *9-ω-phenanthridylmethyl-*N*-pyridinium*, *phenanthridinium* and *2 : 2'-dipyridyl rheniumdioxocyanides*, and they were obtained as colourless or pale brown precipitates on addition of the hydrochloride of the base to an aqueous solution of one of the alkali oxocyanides. When the precipitation with dipyridyl was carried out in 3—4N-hydrochloric acid, a different product was formed consisting of pale blue needles as compared with the light brown powder of $(C_{10}H_8N_2H_2)_3[ReO_2(CN)_4]_2,3H_2O$ obtained in neutral solution. These needles are more stable to heat and are less easily hydrolysed than is the brown powder, and they are but slowly attacked by hydrogen peroxide. A similar type of compound, consisting also of blue needles, is obtained when the phenanthridinium rheniumdioxocyanide is warmed with hydrochloric acid. Analyses of these coloured products indicate that they are acid *salts*, the formulæ of the dipyridyl and the phenanthridine derivative being respectively $(C_{10}H_8N_2H)_2H[ReO_2(CN)_4]$ and $(C_{13}H_9NH)_2H[ReO_2(CN)_4]$.

Some polypyridyl derivatives of rhenichloric and per-rhenic acids have also been made. With 2 : 2′-dipyridyl there is formed both a *mono-* and a *bis-dipyridyl rhenichloride*, depending on whether interaction is allowed to take place under acid or neutral conditions. The former, $(C_{10}H_8N_2H_2)ReCl_6$, is converted into the latter, $(C_{10}H_8N_2H)_2ReCl_6$, on heating with a dilute aqueous solution of the dipyridyl hydrochloride. These rhenichlorides are much more stable than the alkali salts and may be heated with water for long periods without decomposition. They are, however, decomposed by alkalis, with the separation of hydrated rhenium dioxide.

Australian molybdenite has been investigated for its rhenium content, and has been found to contain about 1 part of the metal in a million of the mineral.

EXPERIMENTAL.

Potassium Sodium Rheniumdioxocyanide, $K_2Na[ReO_2(CN)_4],6H_2O$.—A solution of potassium per-rhenate (1 g.), potassium cyanide (double salt) (2 g.), and hydrazine hydrate (0·5—0·7 c.c.) in water (30 c.c.) was heated for 24 hours on a steam-bath in a flask fitted with a Bunsen valve. The deep red liquor was concentrated to about 20 c.c., and methyl alcohol added until about one-quarter of the product was precipitated. The filtrate from this material was poured into alcohol (75 c.c.), whereby a buff-coloured deposit was obtained, which was separated by filtration and then dissolved in a little water. The above process was repeated, the methyl alcohol precipitates being combined and resubmitted to the treatment. The ethyl alcohol deposits were added together, dissolved in water (8—10 c.c.), alcohol introduced until a faint turbidity appeared, this being cleared with a drop of water, and the solution then placed in a small desiccator containing anhydrous potassium carbonate. Massive red octagonal plates were slowly formed, together with a little potassium and sodium carbonate. The former crystals were removed by hand and recrystallised. The red crystals of the *dioxocyanide* effloresce in air, and on drying over phosphoric oxide fall into a pale pinkish-yellow powder, readily soluble in water to an orange-red solution. The analysis was carried out on the dried powder (Found : C, 11·3; N, 13·2; Na, 5·7; K, 18·6; Re, 43·7. $C_4N_4O_2NaK_2Re$ requires C, 11·3; N, 13·2; Na, 5·4; K, 18·4; Re, 44·0%. Found : loss of water on drying the crystals, 20·1. $6H_2O$ requires loss, 20·3%).

Sodium Rheniumdioxocyanide, $Na_3[ReO_2(CN)_4],2H_2O$.—This was prepared from sodium per-rhenate, sodium cyanide, and hydrazine hydrate in a like manner to the foregoing, but in this case the product precipitated by ethyl alcohol was crystallised from water–methyl alcohol. Methyl alcohol does not readily precipitate the complex *sodium* salt from solution, and so the removal of any carbonate is made easier than with the potassium sodium derivative. When left over potassium carbonate, yellow transparent nodules were formed which did not effloresce in air but dissolved readily in water to an orange solution (Found : O, 15·1; N, 12·9; Na, 16·0; Re, 43·7; H_2O, 8·4. $C_4H_4O_4N_4Na_3Re$ requires O, 15·0; N, 13·1; Na, 16·15; Re, 43·6; H_2O, 8·4%).

Potassium Rheniumdioxocyanide, $K_3[ReO_2(CN)_4]$.—Attempts to reduce potassium per-rhenate by the method previously employed proved intolerably slow, and so the oxocyanide was made by heating a suspension of hydrated rhenium dioxide (2 g.) in an excess of an aqueous solution of potassium cyanide (3·5 g. in 30 c.c. of water). The mixture was kept just boiling for 12 hours, after which it was filtered, and the deep red filtrate treated with one or two drops of hydrogen peroxide until it became wine-red. The solution was then concentrated to about 20 c.c. and left to crystallise; large red monoclinic crystals slowly formed, and were hand-picked from any potassium carbonate crystals. The oxocyanide crystals tend to occlude some potassium per-rhenate, which is always present, and were best purified by dissolving them in a 20% solution of potassium acetate, removing any residue of per-rhenate, and then concentrating the solution sufficiently to obtain small crystals. These separated slowly, and were washed with a mixture of alcohol and water (1 : 1), being finally ground with more of the mixture in order to remove any occluded acetate. The *potassium rheniumdioxocyanide* is less soluble in water than the foregoing alkali derivatives, but is still readily soluble. Estimation of oxygen in this compound did not give good results for, when heated in hydrogen, the metallic residue sintered and in doing so enclosed a little of the material which remained unaffected (Found: C, 10·9; O, 6·7; N, 12·8; K, 26·5; Re, 42·5. $C_4O_2N_4K_3Re$ requires C, 10·9; O, 7·3; N, 12·7; K, 26·6; Re, 42·4%). These crystals contained no water of crystallisation.

9-ω-Phenanthridylmethyl-N-pyridinium Rheniumdioxocyanide, $(C_{19}H_{15}N_2H)_3[ReO_2(CN)_4],4H_2O$.— The addition of an aqueous solution of 9-ω-phenanthridylmethyl-*N*-pyridinium chloride to one of potassium (or sodium) rheniumdioxocyanide produced a white precipitate, which was washed with water and dried in air. The resulting pale-coloured powder could be obtained in the form of small colourless needles on crystallising it from hot water, but such treatment tended to produce some hydrolysis. This *oxocyanide* is almost insoluble in cold water and sparingly so in hot water (Found: C, 60·4; H, 4·6; O, 7·8; N, 12·0; Re, 15·7; H_2O, 6·1. $C_{61}H_{56}O_6N_{10}Re$ requires C, 60·5; H, 4·6; O, 7·9; N, 11·55; Re, 15·4; H_2O, 5·95%).

Phenanthridinium Rheniumdioxocyanide, $(C_{13}H_9NH)_3[ReO_2(CN)_4],2H_2O$.—Excess of phenanthridine in the least possible quantity of N/2-hydrochloric acid was added to an aqueous solution of potassium rheniumdioxocyanide; the pale brown precipitate obtained was washed first with water and then with a mixture of alcohol and ether (1 : 2) in order to remove any phenanthridine which usually contaminated the product. The *oxocyanide* dried to a light brown powder not appreciably soluble in cold water, more soluble in alcohol. It is hydrolysed on heating with water (Found: C, 57·2; H, 3·6; O, 7·4; N, 11·0; Re, 20·4; H_2O, 4·0. $C_{43}H_{34}O_4N_7Re$ requires C, 57·4; H, 3·8; O, 7·1; N, 10·9; Re, 20·7; H_2O, 4·0%).

If this compound is dissolved in hot 4N-hydrochloric acid then, on cooling, there separate out pale blue crystals of *phenanthridinium hydrogen rheniumdioxocyanide,* which when dried in a vacuum has the formula $(C_{13}H_9NH)_2H[ReO_2(CN)_4]$ (Found: N, 12·3. $C_{30}H_{21}O_2N_6Re$ requires N, 12·3%).

2 : 2′-*Dipyridyl Rheniumdioxocyanide,* $(C_{10}H_8N_2H_2)_3[ReO_2(CN)_4]_2,3H_2O$.—Obtained in a similar fashion to the previous compound as a pinkish-brown crystalline precipitate, this *compound* is somewhat soluble in hot water or alcohol but is easily hydrolysed. When heated above 80°, it decomposes, some dipyridyl being vaporised along with the water of crystallisation and a violet residue remaining (Found: C, 39·0; H, 3·2; N, 16·7; O, 9·7; Re, 31·8; H_2O, 4·5. $C_{38}H_{36}O_7N_{14}Re_2$ requires C, 38·9; H, 3·1; N, 16·7; O, 9·55; Re, 31·8; H_2O, 4·6%).

When 2 : 2′-dipyridyl hydrochloride is added to a solution of potassium rheniumdioxocyanide in 4N-hydrochloric acid, a blue product is obtained which, on recrystallisation from hydrochloric acid of the same strength, separates as pale blue needles of the *acid salt,* $(C_{10}H_8N_2H)_2H[ReO_2(CN)_4],4H_2O$. Dried in a vacuum desiccator over phosphoric oxide the crystals lose their water of crystallisation without any appreciable change in colour. The analysis was carried out on the anhydrous product (Found: C, 45·3; H, 2·8; N, 17·7; Re, 28·8, 29·5. $C_{24}H_{19}O_2N_8Re$ requires C, 45·2; H, 3·0; N, 17·6; Re, 29·2%. Found: loss of water on drying, 9·9. $4H_2O$ requires loss, 10·15%).

Bis-2 : 2′-*dipyridyl Rhenichloride,* $(C_{10}H_8N_2H)_2ReCl_6$.—A solution of potassium rhenichloride (0·3 g.) in water (25 c.c.) was treated with 2 : 2′-dipyridyl (0·3 g.) dissolved in the least possible quantity of dilute hydrochloric acid, and a pale greenish-white precipitate was formed. This product may be obtained as pale green rods or needles by carefully crystallising it from warm water. If too high a temperature is employed, or if heating is continued for too long, then the solution slowly becomes yellow and deposits hydrated rhenium dioxide. This *rhenichloride* is moderately soluble in warm water but only slightly so in the cold (Found: N, 8·1; Cl, 29·8; Re, 27·1. $C_{20}H_{18}N_4Cl_6Re$ requires N, 7·85; Cl, 29·9; Re, 27·0%).

2 : 2′-*Dipyridyl Rhenichloride,* $(C_{10}H_8N_2H_2)ReCl_6$.—When the reaction between potassium rhenichloride and dipyridyl is carried out in 3—4N-hydrochloric acid, the product is a yellow crystalline precipitate which, on recrystallising from hot dilute hydrochloric acid, is obtained as fine crocus-yellow needles (Found: Cl, 38·2; Re 33·5. $C_{10}H_{10}N_2Cl_6Re$ requires Cl, 38·2; Re, 33·4%).

2 : 2′ : 2″-*Tripyridyl Rhenichloride,* $(C_{15}H_{11}N_3H_2)ReCl_6,H_2O$.—2 : 2′ : 2″-Tripyridyl forms only one rhenichloride whether the reaction is carried out in neutral or in strongly acid solution; under both conditions a *monotripyridyl* derivative is obtained as a microcrystalline, almost colourless, precipitate which, after being washed with dilute hydrochloric acid, dries to a pale green powder practically insoluble in water. It is distinguished from the dipyridyl compounds in possessing 1 molecule of water of crystallisation and in a greater tendency to hydrolyse on

treatment with hot water (Found : Cl, 32·5, 32·6; Re, 28·8, 28·5; H_2O, 2·7. $C_{15}H_{15}ON_3Cl_6Re$ requires Cl, 32·65; Re, 28·6; H_2O, 2·8%).

2 : 2'-*Dipyridyl Per-rhenate,* $(C_{10}H_8N_2H)ReO_4$.—This *salt* was prepared by treating a concentrated solution of per-rhenic acid with a slight excess of dipyridyl dissolved in dilute acetic acid; the colourless crystalline precipitate recrystallised from hot water as well-defined leaf-shaped clusters of fine needles. It is fairly easily soluble in warm water, and its solubility at 19° is 2·1 g. per 100 c.c. of solution (Found : Re, 45·6. $C_{10}H_9O_4N_2Re$ requires Re, 45·7%).

2 : 2' : 2''-*Tripyridyl Per-rhenate,* $(C_{15}H_{11}N_3H)ReO_4$.—Prepared in a like manner to the previous compound, this *per-rhenate* is obtained as a white precipitate much less soluble in cold water than the dipyridyl per-rhenate. It is, however, moderately soluble in hot water and, depending on the rate of cooling, there separate from the solution either colourless spangles or clusters of fine, hair-like needles. Also unlike the dipyridyl salt, it may be obtained from potassium per-rhenate by double decomposition with the hydrochloride of the base (Found : Re, 38·3. $C_{15}H_{12}O_4N_3Re$ requires Re, 38·4%).

Rhenium from Australian Molybdenite.—The finely ground molybdenite (50 lbs.) was treated with 14·5N-nitric acid (90 l.) in a tantiron pan fitted with a steam-jacket, the temperature being maintained at 70—80°. A white pasty mass was formed to which was added enough water to make the volume up to 90 l., the mixture being stirred well and filtered. The precipitate was washed thoroughly with water, after which the filtrate (85 l.) was concentrated to 20 l., the molybdenum trioxide which separated during this process being removed at intervals. A further separation was obtained by precipitating molybdenum as ammonium phosphomolybdate, but this was disappointing, for the reaction was far from being quantitative on the large scale and, indeed, was omitted during the treatment of a second batch of molybdenite. The molybdenum and rhenium were now precipitated as sulphides, which were converted into oxides and these distilled from concentrated sulphuric acid in a current of hydrogen chloride after the manner described by Geilmann and Weibke (*Z. anorg. Chem.*, 1931, **199**, 120). A considerable enrichment was thereby achieved, since molybdenum is much less volatile than rhenium under these conditions. The distillate was carefully concentrated to small bulk, and molybdenum removed from it with 8-hydroxyquinoline, the rhenium being recovered as tripyridyl per-rhenate. This final separation was also carried out with 2 : 2'-dipyridyl, for the dipyridyl molybdate is only slightly soluble in cold water whereas dipyridyl per-rhenate is moderately soluble. The amount of rhenium extracted from 100 lbs. of molybdenite was 49·5 mg., the content of the mineral being thus of the order of 1·1 × 10^{-4}%.

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