427. *A Nitrido- and other Complex Cyanides of Rhenium-*(V) *and* -(VI).

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The octacyano-complex ions of rhenium-(V) and -(VI) have been confirmed; the former is readily hydrolysed by water to the dioxotetracyanorhenate(V) and with aqueous hydrochloric acid solutions in air the oxohydroxotetra-cyanorhenate is formed. Investigation of the anomalous infrared spectrum of potassium dioxotetracyanorhenate prepared by Morgan and Davies's original method and a comparison with authentic material shows that the former product contains substantial amounts of a rhenium nitrido-complex salt of previously unrecognised type, $K[ReN(H_2O)(CN)_4]$, which has been isolated. The infrared spectrum of potassium nitridotetrabromoaquo-osmate(VI) is also given and a note on cyanide analysis appended.

OCTACYANO-COMPLEXES of rhenium(V) and rhenium(IV) and possibly a hydroxo-octacyano-complex of rhenium(VII) have been claimed.[1] The stability of the octacyanorhenate(V) ion in water has been questioned [2] for under somewhat similar preparative conditions the potassium salt of the dioxocyanorhenate ion was obtained. The hydroxo-octacyano-rhenate(VII) has also been questioned [3] and since our attempts to prepare corresponding halogeno-octacyano- and enneacyano-complex anions were unsuccessful, the product always being the oxohydroxocyanorhenate(V) ion, we have therefore re-examined all of these complex cyanides.

It is confirmed that potassium octacyanorhenate(V), $K_3[Re(CN)_8]$, can be prepared by the original procedure,[1] although the samples always contained a small amount of impurity, probably potassium dioxotetracyanorhenate(V). However, purification by repeated evaporation with water followed by extraction with methanol, as recommended,[1] leads to hydrolysis and decomposition, the main product being potassium dioxotetra-cyanorhenate (V) plus small amounts of potassium per-rhenate and rhenium dioxide. The octacyanorhenate(V) is thus similar to the octacyano-complex ions of molybdenum-(IV) and -(V) and of tungsten-(IV) and -(V) which also readily hydrolyse.

The infrared (i.r.) spectrum of potassium octacyanorhenate(V) contained a band at 780 cm.$^{-1}$ which was assigned to an Re–C stretch or possibly a C≡N wagging mode.[1] If the latter assignment were correct, a similar absorption should be observed in the i.r. spectra of the octacyanomolybdate(IV) and octacyanotungstate(IV) ions. If the former were correct, the M–C stretch in the molybdenum and tungsten complexes should be observed at frequencies comparable, if not actually higher, since the M–CN bond could be stronger here owing to increased π-bonding associated with the lower formal charge on the metal atom. No such band is observed. Since pure potassium dioxotetracyanorhenate(V) has a strong i.r. absorption at 780 cm.$^{-1}$ assigned to the Re=O stretch,[4,5] we therefore assign the peak at 780 cm.$^{-1}$ in the samples of $K_3[Re(CN)_8]$ to impurity of $K_3[ReO_2(CN)_4]$. It was possible to reduce the intensity of the peak by carefully drying the methanol used in the preparation, but it was never possible to eliminate it. It has been claimed [6] that it is impossible to prepare pure potassium hexaiodorhenate(IV) which is used as the starting product in the preparation of the octacyanorhenate, and the dioxotetracyanorhenate impurity may originate in this way, or from some decomposition of K_2ReI_6 by interaction with methanol. The red methanol solutions of K_2ReI_6 certainly become brown rapidly when heated but this reaction has not been investigated yet.

[1] Colton, Peacock, and Wilkinson, *J.*, 1960, 1374.
[2] Walter, Kleinberg, and Griswold, *Inorg. Chem.*, 1962, **1**, 10.
[3] Griffith, *Quart. Rev.*, 1962, **16**, 188.
[4] Johnson, Lock, and Wilkinson, *Chem. and Ind.*, 1963, 333.
[5] Schwochau and Herr, *Z. anorg. Chem.*, 1962, **318**, 198.
[6] Morrow, *J. Phys. Chem.*, 1956, **60**, 19.

The preparation of salts of the octacyanorhenate(VI) ion, $[Re(CN)_8]^{2-}$, described earlier [1] by the action of oxygen in hydrochloric acid has also been confirmed. This reaction did not occur in the absence of oxygen. However, the supposed cyano-complexes of rhenium(VII) obtained from them are shown to be salts of the oxyhydroxotetracyano-rhenate(V) ion. This ion had been prepared long ago [7] but the salts were incorrectly formulated as $B_2H[ReO_2(CN)_4]$ instead of $B_2[ReO(OH)(CN)_4]$ (B = base such as 2,2'-bipyridyl).

A key point in the original assignment [1] of the 780 cm.$^{-1}$ band referred to above was the comparison with a sample of potassium dioxotetracyanorhenate(V), $K_3[ReO_2(CN)_4]$, prepared by Morgan and Davies's method.[7] This product had strong i.r. absorptions at 780, 975, and 1000 cm.$^{-1}$ which were assigned [1] as the Re–C stretch and the two Re=O stretches, respectively. However, as we have shown, pure $K_3[ReO_2(CN)_4]$ has no band at 975 or 1000 cm.$^{-1}$. We have repeated Morgan and Davies's preparation with results similar to those just mentioned. However, it proved possible to separate the product into two components by treatment with water. The more soluble product has a strong i.r. absorption at 780 cm.$^{-1}$ and from this fact, and analyses, it is clearly $K_3[ReO_2(CN)_4]$. The less soluble, pink fraction shows two strong absorptions at 974 and 997 cm.$^{-1}$ but none at 780 cm.$^{-1}$. The analytical data and its i.r. spectrum (see Table) are consistent with the formulation as $K_2[ReN(CN)_4(H_2O)]$; other nitrido-complexes of rhenium have been characterised.[8] The compound has only a single strong C≡N stretching frequency which is in keeping with a planar $Re(CN)_4$ and *trans*-N≡Re–OH$_2$ group. The latter is also to be

Infrared spectra of cyano-complexes of rhenium.

Compound	Main bands in cm.$^{-1}$ (in Nujol mulls)
$K_3[Re(CN)_8]$	2140s, 2100s, 2050s (CN str); 780w (Re=O str, impurity)
$[Co(NH_3)_6]_2[Re(CN)_8]_3$	~3150m (NH str); 2090s (CN str); ~1600m, b (NH bend)
$K_3[ReO_2(CN)_4]$	2110s (CN str); 780vs (Re=O str)
$K_2[ReN(H_2O)(CN)_4]$	3720m, 3625mw (OH str); 2160s (CN str); 1620ms (HOH bend); 997s, 974s (Re≡N str)
$[di\ py\ H_2][ReO(OH)(CN)_4]$ ...	2090s (CN str); 950 (Re=O str)
$[Ph_4As]_2[ReO(OH)(CN)_4]$ ...	2190, 2150m (CN str); 956 (Re=O str)
$K[OsN(H_2O)Br_4],H_2O$	3470m, 3370m (OH str); 1590 (HOH bend), 1110s (Os≡N str); 917w, b (Os–OH$_2$ wag)

expected considering the strong *trans* effect of a nitrido-group since a non-π-bonding ligand, in this case water, is more likely to be in the *trans*-position than a cyanide group; a *trans*-cyanide would also require splitting of the C≡N stretching frequencies which is not observed. Although the i.r. spectral data do not unequivocally eliminate the alternative formulations with O=Re–NH$_2$ or HO–Re≡NH groups, there are strong absorptions consistent with the presence of co-ordinated water [9] and there already exists an analogous osmium complex $K[OsNBr_4(H_2O)]$ which is known to have a linear N≡Os–OH$_2$ group with the bromide ions in a plane perpendicular to it.[10] The strong bands in the rhenium complex at 974 and 997 cm.$^{-1}$ are presumably due to the R≡N stretch, split by solid-state interaction; the lowering of this frequency compared to the similar frequencies in the other rhenium [8] and osmium complexes is probably due to the effect of the cyanide ligands. Thus the σ-bond between the strongly donating cyanide ion and the metal atom must here place considerable electron density on the metal atom which cannot, as is usual in complexes of π-bonding ligands, be dissipated by back-bonding to empty orbitals on the cyanide ligand since the metal d_{xz} and d_{yz} orbitals normally used for this purpose are utilised in
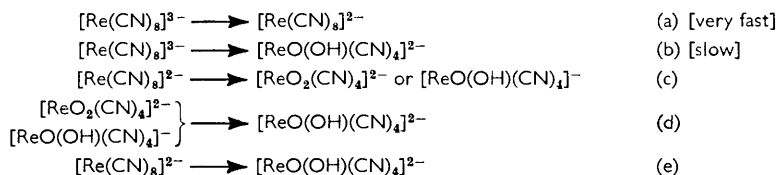
[7] Morgan and Davies, *J.*, 1938, 1858.

[8] Clifford and Olsen, *Inorg. Synth.*, 1960, **6**, 167; Chatt, Garforth, and Rowe, *Chem. and Ind.*, 1963, 332.

[9] Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 156.

[10] Bokii, Atovmyan, and Khodasheva, *Doklady Akad. Nauk, S.S.S.R.*, 1959, **128**, 78.

multiple bonding to the nitrogen atom. Hence the effect of the cyanide groups is to cause electron drift into the Re≡N bond, weakening it and lowering the Re–N stretching frequency.

The present knowledge of the cyanide complexes discussed here is summarised in the Scheme; i.r. spectra are collected in the Table. There still remains one unusual feature, namely the rapid oxidation by molecular oxygen in acid solution of the octacyano-rhenate(v) ion and the slower reduction of the resulting octacyanorhenate(vi) ion under the same conditions to the oxohydroxotetracyanorhenate(v). There is not necessarily any conflict here. The overall reactions which must be considered are:

$$[Re(CN)_8]^{3-} \longrightarrow [Re(CN)_8]^{2-} \qquad \text{(a) [very fast]}$$
$$[Re(CN)_8]^{3-} \longrightarrow [ReO(OH)(CN)_4]^{2-} \qquad \text{(b) [slow]}$$
$$[Re(CN)_8]^{2-} \longrightarrow [ReO_2(CN)_4]^{2-} \text{ or } [ReO(OH)(CN)_4]^{-} \qquad \text{(c)}$$
$$\left.\begin{matrix}[ReO_2(CN)_4]^{2-}\\ [ReO(OH)(CN)_4]^{-}\end{matrix}\right\} \longrightarrow [ReO(OH)(CN)_4]^{2-} \qquad \text{(d)}$$
$$[Re(CN)_8]^{2-} \longrightarrow [ReO(OH)(CN)_4]^{2-} \qquad \text{(e)}$$

In the oxygenated acid solution, we have competition between reactions (a) and (b) and the experimental evidence is that (a) is very fast (complete in less than *ca.* 30 sec.) while (b), which takes place in the absence of oxygen, is quite a slow reaction, taking more than

Scheme. *Cyano-complexes of rhenium*
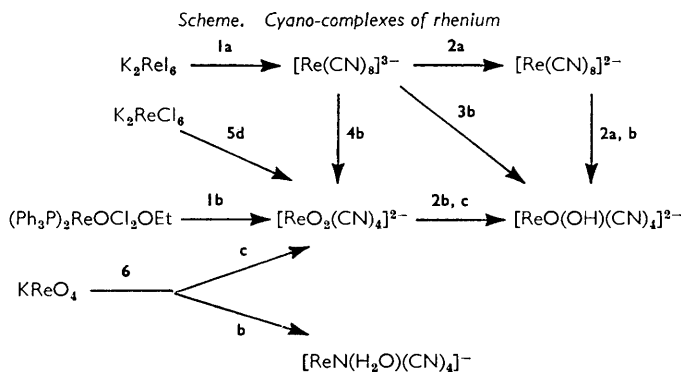
References: (a) Colton, Peacock, and Wilkinson, *J.*, 1960, 1374. (b) This work. (c) Morgan and Davies, *J.*, 1938, 1858. (d) Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 215.

Reagents: 1, KCN in CH₃OH. 2, 4м-HCl in air. 3, 4м-HCl, (CN)₂. 4, H₂O. 5, KCN, H₂O₂. 6, KCN, N₂H₅OH, H₂O₂.

half an hour for completion. The product of (a) is unstable to acid hydrolysis according to either reaction (c) or (b); although this reaction is quite fast (approximate half-time 5 sec.) the $[Re(CN)_8]^{2-}$ can be isolated by rapid addition of a precipitant. If the decomposition proceeds by reaction (c) the hydrolysis product is a rhenium(vi) complex which is evidently unstable and is reduced rapidly as in (d).

EXPERIMENTAL

Microanalyses are by the Microanalytical Laboratory, Imperial College.

Analyses of Complex Cyanides.—Some difficulty has been experienced in the determination of cyanide in complexes. Standard microanalysis for carbon and nitrogen generally gave poor carbon analyses (even in presence of vanadium pentoxide catalyst) and nitrogen values were not always reliable. The conversion of cyanide into carbon monoxide by concentrated sulphuric acid [1] is difficult and not very accurate; we have found that the composition of the gases and the amount varies with the sulphuric acid concentration and the method was accordingly discarded. A method based on a suggestion by Heintz [11] has proved very satisfactory. The sample (*ca.* 10 mg.) was fused with potassium (300 mg.) in a nickel bomb at 550° for 1 hr. When

[11] Heintz, *Inorg. Synth.*, 1963, **7**, 142.

cool, sufficient methanol was added to destroy the excess of potassium. The residue was dissolved in water, the solution filtered, and the cyanide determined by precipitation with silver nitrate.

Other Measurements.—Magnetic measurements on solids were made by the Gouy method (all diamagnetic unless otherwise stated). Infrared spectra were studied as Nujol mulls and were recorded on a Perkin-Elmer model 21 instrument with sodium chloride optics.

Potassium Octacyanorhenate(v).—The procedure is a modification of that given previously.[1] Freshly prepared potassium hexaiodorhenate (2 g.) was dissolved in methanol (distilled from sodium) and the solution run into a refluxing solution of potassium cyanide (1 g.) in methanol (100 ml.) and allowed to reflux for 10 min. The brown solid which separated was filtered off, suspended in more dry methanol (100 ml.), and refluxed for 10 min. The *product* was filtered off, washed with hot methanol, and dried at 25°/0·1 mm. (yield 0·7 g.; 71%) [Found: K, 22·9; CN, 40·2. Calc. for $C_8K_3N_8Re$: K, 23·1; CN, 40·7%].

Hydrolysis of Potassium Octacyanorhenate(v).—The complex salt (0·5 g.) was dissolved in water (5 ml.), and the solution evaporated to dryness on a steam-bath. The evaporation was repeated four more times, additional 5 ml. portions of water being used. The dirty-white residue was slurried with methanol (50 ml.), filtered off, and dried at 25°/0·1 mm. {Found: CN, 22·0. Calc. for $K_3[ReO_2(CN)_4]$: CN, 23·7%}. The i.r. spectrum of this mixture showed peaks characteristic of $K_3[ReO_2(CN)_4]$, $KReO_4$, and ReO_2.

Potassium Dioxotetracyanorhenate(v).—While Morgan and Davies's original method gives a mixture of products, Klemm and Frischmuth [12] have obtained this complex by treatment of K_2ReCl_6 with an aqueous solution of potassium cyanide and hydrogen peroxide. The following procedure, from $(Ph_3P)_2ReOCl_2$·OEt as starting material, is simpler and gives a pure product. Recrystallisation from water gave fine orange crystals free from potassium chloride which is difficult to remove in the earlier procedure.

Oxodichloroethoxobis(triphenylphosphine)rhenium(v) (2 g.) was suspended in methanol (50 ml.) containing potassium cyanide (1 g.). The mixture was refluxed for 4 hr. and the solution filtered hot. The creamy white complex was washed thoroughly with hot methanol and dried *in vacuo* (yield, 0·5 g.; *ca.* 50%) [Found: K, 27·0; O, 6·5; CN, 24·3; Cl, 0. Calc. for $C_4K_3N_4O_2Re$: K, 26·7; O, 7·3; CN, 23·7%].

Hexamminecobalt(iii) *Octacyanorhenate*(vi).—Potassium octacyanorhenate(v) (0·5 g.) was dissolved in oxygenated cold water (5 ml.), and the solution acidified with concentrated hydrochloric acid (2 ml.). A saturated solution of hexamminecobalt(iii) chloride (5 ml.) was added immediately. The black precipitate was collected, washed thoroughly with water, and dried (0·1 mm./100°) (yield, 0·2 g.; *ca.* 100%) (Found: Co, 7·8; CN, 42·7. Calc. for $C_{24}H_{36}Co_2N_{36}Re_3$: Co, 7·8; CN, 41·5%). The compound was paramagnetic, $\mu_{eff} = 1·9$ B.M. (corrected for diamagnetism and at 289°k). The solid slowly dissolves in water giving a purple solution.

Tetraphenylarsonium Oxohydroxotetracyanorhenate(v).—*Method* 1. Potassium octacyanorhenate(v) (1 g.) in water (10 ml.) was treated with concentrated hydrochloric acid (2 ml.). The solution was set aside for 15 min. and an excess of an aqueous solution of tetraphenylarsonium chloride then added. The purple precipitate was filtered off and dissolved in acetone (15 ml.) containing a few drops of water. The salt was reprecipitated by slowly pouring the acetone solution into vigorously stirred water (400 ml.). The blue-purple salt was collected and dried (0·1 mm./25°) (yield, 1·9 g.; 95%) [Found: As, 14·1; CN, 9·9; O, 3·1. $C_{52}H_{41}As_2N_4O_2Re$ requires As, 14·1; CN, 9·6; O, 2·9%]. Contrary to the earlier report,[1] the compound was not very soluble in anhydrous acetone but it dissolved readily if a few drops of water were added even though the compound is virtually insoluble in water.

Method 2. Potassium dioxotetracyanorhenate(v) (0·5 g.) was dissolved in 4m-hydrochloric acid (5 ml.). A 4m-hydrochloric acid solution of tetraphenylarsonium chloride was added and the precipitate collected and purified as above (yield, 1·1 g.; 95%) [Found: CN, 10·0; O, 3·2%].

2,2′-Bipyridylium Oxohydroxotetracyanorhenate(v).—Potassium dioxotetracyanorhenate(v) (0·5 g.) was dissolved in 4m-hydrochloric acid (5 ml.) and a solution of 2,2′-bipyridyl (1 g.) in 4m-hydrochloric acid (5 ml.) added. The purple *salt* was collected, washed with two portions of 4m-hydrochloric acid (5 ml. each), and dried (0·1 mm./25°) (yield, 0·2 g.; 45%) [Found: CN, 22·2; O, 6·3. $C_{14}H_{11}N_6O_2Re$ requires CN, 21·7; O, 6·7%].

[12] Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 215.

Barium Oxohydroxotetracyanorhenate(v) *Dihydrate.*—Potassium octacyanorhenate(v) (1 g.) was dissolved in deoxygenated water (50 ml.), and concentrated hydrochloric acid (5 ml.) added. Cyanogen was bubbled through the solution for 2 hr. A saturated solution of barium chloride (5 ml.) was added and the purple precipitate was collected, washed with a little cold water, ethanol, and ether, and dried (0·1 mm./25°) (yield, 0·3 g.; 29%) [Found: H, 1·0; Ba, 27·0; N, 10·6; O, 12·2. $C_4H_5BaN_4O_4Re$ requires H, 1·0; Ba, 27·6; N, 11·3; O, 12·9%].

Potassium Nitridoaquotetracyanorhenate(v).—Potassium per-rhenate (1 g.) was suspended in an aqueous solution (30 ml.) of potassium cyanide (2 g.). Hydrazine hydrate (5 ml.) was added, and the mixture heated on a steam-bath for a week under nitrogen. The solution slowly became an intense red. The solution was filtered and thrown into excess of methanol, a red oil being precipitated. The oil was dissolved in the minimum of water, and the solution again poured into methanol. The oil was finally dissolved in water (10 ml.) and methanol (5 ml.) added. The solution was allowed to evaporate in a desiccator containing anhydrous potassium carbonate for a week. The red crystals, which slowly separated, were filtered off and then slurried with water (3 × 2 ml.) to remove the more soluble products, mainly $K_3[ReO_2(CN)_4]$. The residual pink crystals of the *nitrido-complex salt* were dried (0·1 mm./25°) (yield, 0·4 g.) [Found: C, 12·1; H, 0·9; K, 20·1; N, 18·0; O, 3·4; CN, 26·2. $C_4H_2K_2N_5ORe$ requires C, 12·0; H, 0·4; K, 19·5; N, 17·5; O, 4·0; CN, 26·0%]. The valency of rhenium in the compound was determined by Geilmann and Wrigge's method [13] to be 4·91. The water is tightly bound in the complex ion and there is no observable exchange with deuterium oxide when the latter is shaken with 0·1 g. of the salt for 14 hr. The salt is sparingly soluble in water but dissolves readily in dilute hydrochloric acid giving a yellow solution.

Potassium Nitridotetrabromoaquo-osmate(vi) *Monohydrate.*[14]—Potassium nitrido-osmate(vi) (1 g.) was dissolved in concentrated hydrobromic acid (5 ml.) in a flat dish and the solution allowed to evaporate overnight. The pink crystals were collected, dried between filter paper to remove excess of hydrobromic acid and afterwards at 25°/0·1 mm. [Found: K, 6·5. Calc. for $H_4Br_4KNO_2Os$: K, 6·7%].

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[13] Geilmann and Wrigge, *Z. anorg. Chem.*, 1935, **222**, 56.
[14] Werner and Dinklage, *Ber.*, 1906, **39**, 500.