275. *Complex Cyanides of Rhenium.*[1]

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The preparation and properties of 8-co-ordinate complex cyanide anions of rhenium(V) and rhenium(VI) are described, and in addition a new 6-co-ordinate cyanide anion of rhenium(III) is reported. Evidence is also presented for the first nitrosyl complex of rhenium, $[Re^{IV}(CN)_7NO]^{3-}$.

Potassium octacyanorhenates [(V), (VI)] have been prepared; these were the first true complex cyanides of rhenium to be obtained although several oxy-[2-5] and carbonyl[6] cyanides were known previously, and a hexaco-ordinate cyanide of rhenium(I) has been reported.[7] The octacyanides provided the first example of rhenium in an 8-co-ordinate complex; another example has since been observed in the diarsines.[8]

The Octacyanorhenate(V) *Ion and its Properties.*—The brown potassium salt $K_3[Re(CN)_8]$ is obtained from the reaction of potassium hexaiodorhenate(IV), K_2ReI_6, with potassium cyanide in hot methanol. The anion is diamagnetic. Potassium octacyanorhenate(V) gives a stable aqueous solution which is yellowish-brown when dilute, but reddish-brown when more concentrated.

The oxidation of rhenium from rhenium(IV) to rhenium(V) during preparation of potassium octacyanorhenate(V) provides a good example of the loss of an electron in a high-lying orbital in a complex as in the well-known case of cobaltous complexes. An 8-co-ordinate rhenium(IV) complex with d^4sp^3 hybridisation would have one electron in excess of the number required completely to fill the $5d$ shell. This extra electron would be promoted to either an antibonding orbital or the $7s$ shell and would be easily lost from either of these levels. Presumable an 8-co-ordinate species of the type $K_4[Re^{IV}(CN)_8]$ is formed as an intermediate but it was never isolated.

The polarographic reduction of potassium octacyanorhenate(V) has been described separately.[9]

The Octacyanorhenate(VI) *Ion.*—Treatment of potassium octacyanorhenate(V) solution with dilute hydrochloric, acetic, or perchloric acid in presence of air yields a purple solution; this colour change occurs only in the presence of oxygen, and when the pH of the solution is reduced below about pH 5; there is no oxidation of $[Re(CN)_8]^{3-}$ by oxygen in basic solution. A potassium salt cannot be isolated from this solution, but immediate addition of hexamminecobaltic chloride gives an insoluble purple precipitate which is $[Co(NH_3)_6]_2[Re(CN)_8]_3$, the hexamminecobaltic salt of the octacyanorhenate(VI) ion, $[Re(CN)_8]^{2-}$. The gross reaction is thus $2[Re(CN)_8]^{3-} + \frac{1}{2}O_2 + 2H^+ = 2[Re(CN)_8]^{2-} + H_2O$.

Since the octacyanorhenate(V) ion is diamagnetic, the octacyanorhenate(VI) ion would be expected to be paramagnetic with one unpaired electron. The magnetic moment of the insoluble hexamminecobaltic salt is indeed 2·0 B.M., but the behaviour of the $[Re(CN)_8]^{2-}$ ion in solution is most unusual. When aqueous potassium octacyanorhenate(V) in air is made faintly acid with hydrochloric acid, the purple solution is paramagnetic, as expected, but becomes rapidly diamagnetic without any apparent colour change. The change in susceptibility is exponential, with a half-life of 5 ± 2 sec. A log plot allows extrapolation to zero time, and the moment at zero time (addition of acid) is found to be 2·0 B.M., agreeing with the moment of the hexamminecobaltic salt.

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[1] Preliminary note: Colton, Peacock, and Wilkinson, *Nature*, 1958, **182**, 393.
[2] Turkiewicz, *Roczniki Chem.*, 1932, **12**, 589.
[3] Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 215.
[4] Morgan and Davis, *J.*, 1938, 1858.
[5] Morgan, *J.*, 1935, 568.
[6] Hieber and Schuster, *Z. anorg. Chem.*, 1956, **287**, 218.
[7] Clauss and Lissner, *Z. anorg. Chem.*, 1958, **297**, 300.
[8] Fergusson and Nyholm, *Chem. and Ind.*, 1958, 1555.
[9] Colton, Dalziel, Griffith, and Wilkinson, *J.*, 1960, 71.

If hexamminecobaltic chloride is added to the potassium octacyanorhenate(VI) solution immediately after addition of acid, the *whole* of the purple species is precipitated from the solution. On the other hand, if the solution is kept and hence becomes diamagnetic before the addition of hexamminecobaltic chloride, only a small amount of precipitate (about 5% of that expected) is obtained.

Tetraphenylarsonium chloride also gives a purple precipitate with potassium octacyanorhenate(VI) solution. If precipitated immediately, the solid is paramagnetic, with moment 2·0 B.M. If the solution is allowed to become diamagnetic before the reagent is added, the *whole* of the purple species is still precipitated but in this case the magnetic moment of the solid is very low. About 95% of this solid can be dissolved in and recrystallised from acetone; this fraction is *diamagnetic* but the 5% of original precipitate insoluble in acetone is *paramagnetic,* with moment 2·0 B.M. Analyses of both samples correspond to $[Ph_4As]_2[Re(CN)_8]$.

These reactions might suggest that there is an equilibrium in the solutions between two species (95% diamagnetic, 5% paramagnetic). However, if this were correct the addition of hexamminecobaltic chloride should displace the equilibrium to the paramagnetic side, since it precipitates only the paramagnetic species from solution. In fact when hexamminecobaltic chloride is added to the diamagnetic solution, there is a small amount of paramagnetic precipitate formed at first and then no more.

High-resolution nuclear magnetic resonance studies on an anhydrous acetone solution of the diamagnetic tetraphenylarsonium salt show the absence of any peak in the characteristic metal–hydride region, but a peak appears on the low-field side relative to water (310 c./sec. at 40 Mc./sec.) in the regions where the protons of soluble metal hydroxides usually show resonances. Addition of traces of water to the acetone solution causes the peak to broaden and finally disappear, suggesting that exchange is taking place between the water and the protons responsible for the peak. A solution of the potassium salt in acid or alkaline solution does not show the resonance, presumably because of exchange with the water.

We therefore suggest that the diamagnetic species is obtained by further oxidation, and that the rhenium is utilising its remaining 5*d* orbital to form a 9-co-ordinate hydroxycyanide complex, $[Re^{VII}(CN)_8OH]^{2-}$. The presence of one hydroxyl group cannot be detected in a compound with molecular weight about 1200 by conventional analytical methods, but it would be difficult otherwise to account for the diamagnetism of the species, the analyses, and the peak in the nuclear magnetic resonance spectrum. That there are still eight cyanide radicals attached to the rhenium is shown by the nearly quantitative reduction of the diamagnetic species to potassium octacyanorhenate(V) with zinc and acid or with sodium borohydride. Whilst the diamagnetic species as obtained here in feebly acid solutions apparently has a hydroxy-group present, yet in more concentrated acid a chloride complex may be present; further work on this system is in progress.

The Hexacyanorhenate(III) *Ion.*—Meier and Treadwell [10] reported that potassium cyanide reacts with rhenium trichloride in aqueous solution to give a complex series of colour changes, and claimed that a Re(I) compound was formed. We have confirmed the colour changes; the initial red solution turns blue on warming, quickly changes to green, and finally after a long time with excess of potassium cyanide in air the solution becomes yellowish-brown. This final product is potassium octacyanorhenate(V). From the green solution a green product is precipitated by addition of a large excess of potassium hydroxide. This is potassium hexacyanorhenate(III), $K_3[Re(CN)_6]$. However, the compound thus prepared is difficult to purify, and a better preparation is obtained when potassium octacyanorhenate(V) solution is reduced with potassium borohydride. The compound gives an insoluble hexamminecobaltic salt which has a magnetic moment of 2·6 B.M. at 298° K consistent with the two unpaired electrons expected in the complex.

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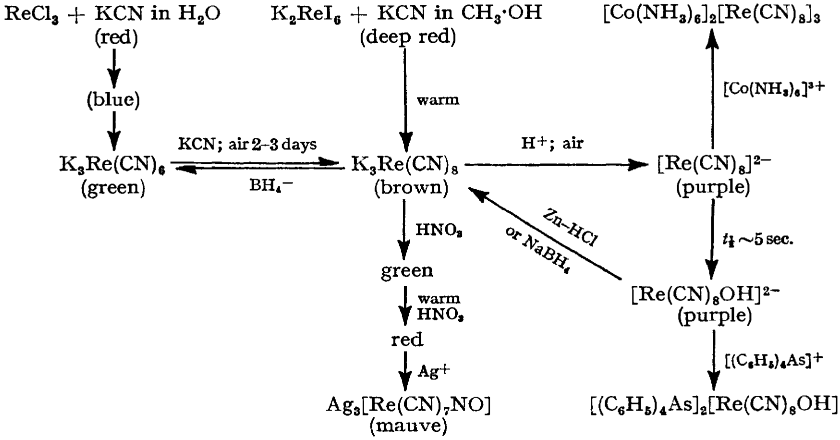
[10] Meier and Treadwell, *Helv. Chim. Acta,* 1955, **38**, 1679.

The Heptacyanonitrosylrhenate(IV) *Ion.*—When a solution of potassium octacyanorhenate(V) is made 2N in nitric acid, a green solution is obtained with no apparent evolution of hydrogen cyanide. This solution turns red when warmed and hydrogen cyanide is evolved. The red anion can be isolated as a mauve silver salt, but when silver ions are added to the green solution a green precipitate is formed which rapidly becomes mauve with evolution of hydrogen cyanide. This final product is identical with the compound obtained when the silver ions are added to the red solution. It is diamagnetic, and the infrared spectrum shows a large sharp peak at 1875 cm.$^{-1}$ attributable to the stretching frequency of nitric oxide donating as a NO$^+$ group.[11] Unfortunately, some silver cyanide is always precipitated with the compound, so that, although the analytical figures are sufficient to show that the atomic ratio of silver to rhenium was 3 : 1, yet they do not distinguish between the two possible formulæ $As_3[Re(CN)_5NO]$ and $Ag_3[Re(CN)_7NO]$, each of which would be diamagnetic. However, it was found by use of a gas burette that only one equivalent of hydrogen cyanide is liberated; it seems probable therefore that the compound is in fact $Ag_3[Re(CN)_7NO]$. This compound is the first nitrosyl complex of rhenium to be reported.

Nitric oxide itself has no effect upon potassium octacyanorhenate(V) solution, but in the presence of oxygen the same unstable green solution as given by nitric acid is obtained. It thus seems likely that nitrogen dioxide is the attacking species and so the green solution may contain a nitro-compound. No hydrogen cyanide has been detected in this first step, so there is, however, the possibility that the green compound is an unstable 9-co-ordinate species. Attempts to precipitate a solid have failed; in all cases the red nitrosyl salt has been obtained.

These reactions are summarized in the diagram:

Reactions of rhenium cyanide complexes.



Infrared Spectra.—The infrared spectrum of potassium octacyanorhenate(V) in Nujol mulls shows three cyanide stretching frequencies at 2140, 2100, and 2050 cm.$^{-1}$, a spectrum very similar to that of the complex molybdenum and tungsten octacyanides.[12] In aqueous solution, however, the compound shows only one peak [as does the molybdenum octacyanide(IV) ion [13]] at 2100 cm.$^{-1}$, suggesting that the splitting in the solid-state spectra is due to crystal interaction. It seems, therefore, that these octacyano-ions have the same duodecahedral structure.[14]

The spectrum also has a strong sharp peak at 780 cm.$^{-1}$, and there is no other peak

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[11] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[12] Brame, Johnson, Larsen, and Meloche, *J. Inorg. Nuclear Chem.*, 1958, **6**, 99.
[13] Colton, Griffith, and Wilkinson, unpublished work.
[14] Hoard and Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

in the potassium bromide region. This peak could be due to either a C≡N wagging mode or the Re–C stretching frequency; if it were the former it might be expected to occur in the spectra of the molybdenum and tungsten octacyanides(IV), but no band is found in these cases.[12] A similar peak (at 730 cm.$^{-1}$) occurs in the hexacyanorhenate(III), and we have also observed it (at 780 cm.$^{-1}$) in the spectrum of the well-known complex oxycyanide, $K_3[ReO_2(CN)_4]$.[3,4] Thus it appears that the band may be due to the Re–C stretching frequency. The only compound to which this frequency has been assigned[15] is rhenium carbonyl (650 cm.$^{-1}$). The cyano-oxyrhenate, $K_3[ReO_2(CN)_4]$, also shows two strong peaks at 975, 1000 cm.$^{-1}$ which can be assigned to the Re=O stretching by analogy with the values obtained from per-rhenyl chloride, ReO_3Cl (*ca.* 970 cm.$^{-1}$),[16] and potassium perrhenate (900 cm.$^{-1}$).

EXPERIMENTAL

Potassium Octacyanorhenate(V).—Potassium hexaiodorhenate(IV) (2 g.) was dissolved in methanol and run into a refluxing solution of potassium cyanide (1 g.) in methanol (100 ml.); the colour changed immediately from deep red to light yellow-brown. After addition of the reactant, the solution was refluxed for about 10 min., then allowed to cool and settle. The brown solid was centrifuged and purified by extracting excess of potassium cyanide with methanol. A better procedure was to evaporate to dryness with water several times to hydrolyse the potassium cyanide and then extract the resulting potassium hydroxide with methanol. The *octacyanorhenate*(V) was finally recrystallised from water as brown flakes (Found: K, 21·9; C, 18·6; H_2O, 3·3; Re, 34·4. $K_3[Re(CN)_8],H_2O$ requires K, 22·1; C, 18·1; H_2O, 3·4; Re, 35·1%). Other salts were made by precipitation or ion-exchange methods; these are listed in the following Table.

Compound	Colour	Solubility in H_2O	Compound	Colour	Solubility in H_2O
$[Co(NH_3)_6][Re(CN)_8]$	Dark green	Insol.	$Sr_3[Re(CN)_8]_2$	Brown	Sol.
$Zn_3[Re(CN)_8]_2$	V. dark brown	Insol.	$Ba_3[Re(CN)_8]_2$	Brown	Sol.
$Ca_3[Re(CN)_8]_2$	Brown	Sol.	$Na_3[Re(CN)_8]$	Brown	Sol.

Oxidation of Octacyanorhenate(V) *in Solution.—Hexamminecobalt*(III) *octacyanorhenate*(VI). Potassium octacyanorhenate(V) (1 g.) was dissolved in water (10 ml.), and the solution acidified by hydrochloric acid. A concentrated solution of hexamminecobaltic chloride was added; the purple precipitate was washed several times with water, finally with acetone and ether, and dried (Found: Re, 36·0; Co, 7·8. $[Co(NH_3)_4]_2[Re(CN)_8]_3$ requires Re, 36·5; Co, 7·8%); $\chi_M^{298} = 191 \times 10^{-5}$ c.g.s.u. (corrected for diamagnetism of cation and ligands), $\mu_{eff.} = 2{\cdot}0$ B.M.

Tetraphenylarsonium Octacyanorhenate(VI) *and Hydroxycyanide.*—The octacyanorhenate(VI) ion was made as above; immediate addition of tetraphenylarsonium chloride solution gave a purple precipitate, which was centrifuged, washed, and dried {Found: Re, 16·2. $[(C_6H_5)_4As][Re(CN)_8]$ requires Re, 16·1%}; $\chi_M^{298} = 176 \times 10^{-5}$ c.g.s.u. (corrected); $\mu = 2{\cdot}0$ B.M. If the purple species was allowed to become diamagnetic before addition of tetraphenylarsonium salt, the precipitate was digested with acetone, the small amount of insoluble material was centrifuged off, and the *product* crystallised by evaporation of the acetone solution {Found: Re, 16·1; CN, 8·0. $[(C_6H_5)_4As]_2[Re(CN)_8OH]$ requires Re, 16·0; CN, 8·3%}, diamagnetic.

Heptacyanonitrosylrhenate(IV).—Potassium octacyanorhenate(V) (1 g.) was dissolved in water (10 ml.), and the solution made about 2N with nitric acid. The solution was warmed and it quickly turned red, with evolution of hydrogen cyanide. Silver nitrate solution was added, and the precipitate centrifuged, washed, and dried. By measuring in a gas burette the volume of hydrogen cyanide liberated in this reaction, it was found that 0·95 equiv. of hydrogen cyanide was liberated per mole of octacyanorhenate(V) used.

Hexamminecobalt(III) *Hexacyanorhenate*(III).—Potassium octacyanorhenate(V) (1 g.) was dissolved in water and reduced by addition of potassium borohydride. Hexamminecobaltic chloride solution was added to the resulting green solution and the resulting green precipitate

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[15] Cotton, Liehr, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 141.

[16] Wolf, Clifford, and Johnston, *J. Amer. Chem. Soc.*, 1957, **79**, 4257.

was washed with water and dried {Found: Re, 37·3; Co, 11·4; C, 15·0. $[Co(NH_3)_6][Re(CN)_6]$ requires Re, 37·2; Co, 11·5; C, 14·2%}; $\chi_M^{298} = 274 \times 10^{-5}$ c.g.s.u.; $\mu_{eff.} = 2{\cdot}6$ B.M.

Analyses.—*Rhenium.* The complexes were fused with a mixture of sodium peroxide and sodium hydroxide, the mass extracted with water, and the solution diluted to 250 ml. An aliquot part was taken, and the rhenium determined colorimetrically as the furil α-dioxime complex.[17] *Potassium.* This was determined gravimetrically as potassium tetraphenylboron.[18] *Cobalt.* This was determined by heating the complexes to fuming with sulphuric acid and estimating the metal colorimetrically by use of nitroso-R-salt.[19] *Carbon.* Carbon analyses in the cyanide complexes were performed by heating the complexes with concentrated sulphuric acid and measuring the volume of carbon monoxide evolved.[20]

Physical Measurements.—Magnetic measurements on solid and solution samples were made by the Gouy method. Infrared spectra were recorded on a Perkin–Elmer model 21 instrument; samples were studied in Nujol mulls or in aqueous solution between calcium fluoride plates. Nuclear magnetic resonance spectra were taken on a Varian Associates Model 4300B spectrometer, by using 15 mm. non-spinning tubes in the large insert.

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[17] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.
[18] Raff and Brotz, *Z. analyt. Chem.*, 1951, **133**, 241.
[19] Hall and Young, *Analyt. Chem.*, 1950, **22**, 497.
[20] Adie and Browning, *J.*, 1900, **77**, 150.