# Studies on Transition-metal Cyano-complexes. Part 2.[1] Unsubstituted Cyanorhenates, $[Re(CN)_x]^{n-}$, and Cyanorhenates with Thio-, Seleno-, and Nitrosyl Ligands

By **William P. Griffith** * and **Patrick M. Kiernan**, Inorganic Chemistry Research Laboratories, Imperial College of Science and Technology, London SW7 2AY
**Jean-Marie Brégeault**, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France

The preparation and structural characterisation of salts of the species $[Re(CN)_7]^{4-}$, $[Re_4(CN)_{12}(\mu_3\text{-}S)_4]^{4-}$, $[Re_4(CN)_{12}(\mu_3\text{-}Se)_4]^{4-}$, $[Re_2(CN)_8(\mu_2\text{-}S)_2]^{4-}$, and $[Re(CN)_5(NO)]^{3-}$ are described. Reinvestigation of all the reactions reported to give unsubstituted cyanorhenates confirms the existence of $[Re(CN)_7]^{4-}$ and $[Re(CN)_6]^{5-}$ only; the other species are reformulated. The nature of some cyano-oxorhenates reported in the literature is also discussed.

OUR interest in octa- and hepta-cyano-complexes [1] has led us to study the cyanorhenates, since rhenium is known to be capable of giving species with a variety of oxidation states, often with high co-ordination numbers. A wide range of unsubstituted cyanorhenates has been reported,[2] *viz.* $[Re^{I}(CN)_6]^{5-}$,[3,4] $[Re^{0}(CN)_6]^{6-}$,[5] $[Re^{II}(CN)_6]^{4-}$,[6-8] $[Re^{II}(CN)_5]^{3-}$,[9] $[Re^{III}(CN)_6]^{3-}$,[10,11] $[Re^{V}(CN)_6]^{-}$,[12] $[Re^{V}(CN)_8]^{3-}$,[10,13,14] and $[Re^{VI}(CN)_8]^{2-}$.[10] We have repeated all these literature preparations and can confirm the existence only of $[Re(CN)_6]^{5-}$. In our hands, most of the preparations gave $[Re(CN)_7]^{4-}$ and, in some cases, substituted cyano-species. In this paper we first describe the species $[Re(CN)_7]^{4-}$, $[Re_4(CN)_{12}L_4]^{4-}$ (L = S or Se), $[Re_2(CN)_8S_2]^{4-}$, and $[Re(CN)_5(NO)]^{3-}$, and then consider the probable nature of the complex ions listed above.

---

[1] Part 1, P. M. Kiernan and W. P. Griffith, *J.C.S. Dalton*, 1975, 2489; P. M. Kiernan, *Inorg. Chim. Acta*, 1976, **20**, 89.

[2] W. P. Griffith, *Co-ordination Chem. Rev.*, 1975, **17**, 177.

[3] D. Clauss and A. Lissner, *Z. anorg. Chem.*, 1958, **297**, 300.

[4] K. Schwochau and W. Herr, *Z. anorg. Chem.*, 1962, **319**, 148.

[5] R. Colton, 'The Chemistry of Rhenium and Technetium,' Interscience, London, 1965, p. 141.

[6] S. Sen, *Z. anorg. Chem.*, 1965, **340**, 82.

[7] S. Sarkar, *J. Indian Chem. Soc.*, 1969, **46**, 871.

[8] S. Sarkar, *Indian J. Chem.*, 1970, **8**, 296.

[9] S. Sen, *Z. anorg. Chem.*, 1962, **315**, 315.

[10] R. Colton, R. D. Peacock, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1374.

[11] O. E. Skolozdra, A. N. Sergeeva, and K. N. Mikhalevich, *Russ. J. Inorg. Chem.*, 1971, **16**, 861.

[12] R. A. Bailey, M. Elguindy, and S. L. Kozak, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2275.

[13] C. J. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 2281.

[14] O. E. Skolozdra, K. N. Mikhalevich, and A. M. Sergeeva, *Visn. L'vivs'k Politekhn. Inst.*, 1971, **60**, 23 (*Chem. Abs.*, 1972, **77**, 55792e).

## RESULTS AND DISCUSSION

*New Cyanorhenates*.—(*a*) *The heptacyanorhenate*(III) *ion*, $[Re(CN)_7]^{4-}$. We have already briefly reported that the reaction product of $K_2[ReCl_6]$ with potassium cyanide in a potassium thiocyanate or selenocyanate melt, after recrystallisation from water, is $K_4[Re(CN)_7]\cdot 2H_2O$.[15] The literature preparation [6] of $K_4[Re(CN)_6]\cdot 3H_2O$ also gives the heptacyano-salt in high yield as does reaction of $K_2[ReI_6]$ with K[CN] in refluxing methanol. Both these latter methods can be adapted to give the mixed salt $NaK_3[Re(CN)_7]\cdot 3H_2O$. The potassium salt is also formed by reaction of $Re_3Cl_9$ with aqueous K[CN] in air.

TABLE 1

Vibrational spectra (cm$^{-1}$) of cyanorhenates as the solids unless stated otherwise. For other spectra see Experimental section

| Complex | | | Other metal–ligand modes | $H_2O$, OH, or NO modes |
|---|---|---|---|---|
| $K_4[Re(CN)_7]\cdot 2H_2O$ | Raman | 2 125(10), 2 115(3), 2 103(3), 2 094w, 2 068(5), 2 063(7) 2 041w | 512(2), 472(2), 456(2), 431(5), 419(5), 370(1) | |
| | Raman [a] | 2 123(10)p, 2 106(6)dp, 2 061(6)p | 504(1)dp, 469(2)dp, 438(3)p, 425(4)p, 407(1)dp, 155w, 109w | |
| | I.r. | 2 144w, 2 125m, 2 112m, 2 101m, 2 092vs, 2 069m, 2 062w, 2 040vs, 2 005w | 521s, 516 (sh), 455w, 434m, 405m, 382(sh), 368m | 3 605s, 1 625s |
| | I.r. [a] | 2 080s, 2 019vs | | |
| $[PPh_4]_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ | Raman [b] | 2 169(10)p, 2 158(7)dp, 2 150w | 464w, 440(3)p, 335(1)p, 215(5)p, 177(2)dp, 110m | |
| | I.r. | 2 162m, 2 152s | 490w, 442w, 426m, 418m, 403m, 358s, 317w, 110m | 3 420s,1 630m |
| | I.r. [b] | 2 165s | | |
| $[PPh_4]_4[Re_4(CN)_{12}Se_4]\cdot 3H_2O$ | Raman [b] | 2 157(10)p, 2 150(8)dp, 2 147w | 448(1)p, 280(4)p, 197(5)p, 158(1)dp, 106w | |
| | I.r. | 2 157m, 2 149 (sh), 2 147s | 445w, 431s, 423m, 385s, 294w, 207m | 3 420, 1 630m |
| | I.r. [b] | 2 160s | | |
| $[PPh_4]_4[Re_2(CN)_8S_2]\cdot 6H_2O$ | Raman [b] | 2 136(10)p, 2 125(7)dp, 2 112(1)dp | 558(1)dp, 445(6)p, 336(1)dp, 241(4)p, 183(6)p | |
| $Cs_4[Re_2(CN)_8S_2]\cdot 4H_2O$ | I.r. | 2 120m, 2 103s, 2 070s, 2 025m, 2 003m | 516w, 490w, 453m, 435w, 420w, 395w, 375w, 350m, 340s | 3 500s, 1 630m |
| $K_3[Re(CN)_5(NO)]\cdot 3H_2O$ | Raman [a] | 2 135(4)p, 2 115(10)p, 2 090(5)dp | 621(4)dp, 602(8)p, 442w, 412(2)dp, 370(8)p | 1 640(1)p |
| | I.r. | 2 141m, 2 110m, 2 080s, 2 045s | 632m, 594w, 480s, 445s, 425m, 398m, 375m, 362m, 310w | 1 650s |

[a] In aqueous solution. [b] In methanol.

The salt $K_4[Re(CN)_7]\cdot 2H_2O$ forms pale yellow crystals which are very soluble in air-free water to give a pale yellow solution, stable under nitrogen if some free cyanide ion is present. Single-crystal Weissenberg photographs show the crystals to be monoclinic, and a full *X*-ray study on the salt is in progress. The *X*-ray powder-diffraction pattern of $K_4[Re(CN)_7]\cdot 2H_2O$ is very similar to that of $K_4[V(CN)_7]\cdot 2H_2O$. The anion in the vanadium complex is approximately pentagonal bipyramidal ($D_{5h}$),[16] suggesting a similar stereochemistry for $[Re(CN)_7]^{4-}$. The rhenium complex is diamagnetic, as expected for a low-spin $d^4$ seven-co-ordinate complex.

The vibrational spectra of $[Re(CN)_7]^{4-}$ are listed in Table 1. For the aqueous solution the presence of 10 Raman shifts, four of which are polarised, is consistent with $D_{5h}$ symmetry [11 Raman shifts predicted, $4A_1'$-(polarised) $+ 3E_1'' + 4E_2'$, all non-coincident with i.r. vibrations]. For the lower symmetries greater spectral complexity would be expected: for the $C_{3v}$ capped octahedron 23 Raman shifts (10 polarised) are expected, and for the $C_{2v}$ capped trigonal prism 39 (12 polarised) are expected, with many i.r.–Raman coincidences. In the C≡N stretching region (2 000—2 200 cm$^{-1}$) the solution shows three Raman shifts, two of which are polarised, and two i.r. bands at frequencies not coincident with the Raman, as expected for $D_{5h}$ symmetry ($2A' + E_2'$, $A_1'$ polarised in the Raman; $A_2'' + E_1'$ for the i.r.). The Raman and i.r. spectra of the solids in the C≡N stretching region, although more complex owing presumably to solid-state splitting effects, are similar in profile to those of the solutions, and this is also the case for Raman spectra of the solid and solution from 50 to 4 000 cm$^{-1}$.

We conclude therefore that the $[Re(CN)_7]^{4-}$ ion has essentially $D_{5h}$ symmetry in $K_4[Re(CN)_7]\cdot 2H_2O$. The electronic spectra of solid $K_4[Re(CN)_7]\cdot 2H_2O$ and its aqueous solution are very similar, suggesting no major stereochemical change for the anion from solid to solution. In this respect the complex differs from $K_4[Mo(CN)_7]\cdot 2H_2O$, which is believed to change from $C_{2v}$ (solid) to $D_{5h}$ (solution).[17] The salt $K_5[Mo(CN)_7]\cdot H_2O$ has an essentially $D_{5h}$ anion in the solid,[18] and $[Mo(CNBu^t)_7][PF_6]_2$ has a $C_{2v}$ structure in the solid state and

---

[15] P. M. Kiernan and W. P. Griffith, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 377.

[16] R. A. Levenson and R. L. R. Towns, *Inorg. Chem.*, 1974, **13**, 105.

[17] G. R. Rossman, F-D. Tsay, and H. B. Gray, *Inorg. Chem.*, 1973, **12**, 824.

[18] M. G. B. Drew, P. C. H. Mitchell, and C. F. Pygall, *J.C.S. Dalton*, 1977, 1071.

may be fluxional in solution.[19] Reduction of $K_4[Re(CN)_7]\cdot 2H_2O$ with potassium amalgam gives $K_5[Re(CN)_6]$, but there is no reaction with hydroxylamine in basic solution. Oxidation of the anhydrous salt with nitrosyl chloride in dimethylformamide gives an unstable yellow salt which may be $K_3[Re(CN)_7]$.

(*b*) *The tetra-*$\mu_3$*-thio- and -seleno-dodecacyanotetrarhenate*(IV) *ions*, $[Re_4(CN)_{12}(\mu_3\text{-}S_4)]^{4-}$ *and* $[Re_4(CN)_{12}(\mu_3\text{-}Se)_4]^{4-}$. We have already briefly reported the preparation and crystal structures of the tetraphenylphosphonium salts of these ions.[20] Salts of the anions are made from $K_2[ReCl_6]$ and K[CN] in potassium thiocyanate or selenocyanate melts at 250 and 320 °C respectively $\{[Re(CN)_7]^{4-}$ is always a by-product$\}$ followed by extraction and treatment with the appropriate cation. The potassium, caesium, tetraphenylphosphonium, and tetraphenylarsonium salts were also isolated.

The crystal structures of $[PPh_4]_4[Re_4(CN)_{12}L_4]\cdot 3H_2O$ (L = S or Se) show the anions to contain cubane-like $Re_4L_4$ units (Re–Re 2.755 Å for L = S and 2.805 Å for L = Se), the cyanide ligands occupying terminal positions on the rhenium atoms. These have, assuming the direct metal–metal bonding suggested by the *X*-ray study, nine-co-ordinate trigonal-prismatic geometry. The complexes are diamagnetic both in the solid state and in acetone solution, as would be expected from the bonding scheme of Toan *et al.*[21] for analogous cubane-like systems.

The vibrational spectra of the salts are given in Table 1. Raman spectra could be measured for the methanolic solutions only, the solids decomposing in the beam. The Raman spectra are consistent with the overall $T_d$ symmetry of the free ion, although the small ' spread ' of CN frequencies prevents resolution of the four expected C≡N stretching bands ($A_1 + E + 2F_2$: three only are seen, one polarised as expected). The polarised band near 400 cm$^{-1}$ is assigned to the $A_1$ metal–carbon stretch. The polarised shifts at 335 (L = S) and 280 cm$^{-1}$ (L = Se) are assigned to the totally symmetric ($A_1$) $Re_4S_4$ and $Re_4Se_4$ stretches respectively. {In the analogous $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ ion the corresponding mode has been located at 275 cm$^{-1}$.[22]} The strong polarised shifts at 215 (L = S) and 197 cm$^{-1}$ (L = Se) are likely to be due to the symmetric ($A_1$) $Re_4$ breathing modes, and we tentatively assign the depolarised 110 and 177 (L = S) and 106 and 158 cm$^{-1}$ (L = Se) shifts to the *E* and $F_2$ modes respectively of the $Re_4$ tetrahedron. Similar frequencies and relative intensities were found for these modes in $[Ir_4(CO)_{12}]$ which also has $T_d$ symmetry.[23]

In the i.r. spectra of the solids the broad bands at 3 470 and 1 630 cm$^{-1}$ clearly arise from the hydrogen-bonded water molecules. Two C≡N stretching frequencies (one for the solution) are probably the $F_2$ modes: they are slightly lower in frequency for the seleno- than for the thio-complex, as in $[Re_4(LC_6H_4)_4(CO)_{12}]$ (L = S or Se).[24] The bands between 350 and 450 cm$^{-1}$ probably arise from ν(ReC) and δ(ReCN) modes since they appear with similar profiles in the spectra of both thio- and seleno-species, rendering involvement of chalcogen bridges improbable. The weak sharp absorptions at 358 (L = S) and 207 cm$^{-1}$ (L = Se) probably arise from the asymmetric ($F_2$) Re–L stretch. The far-i.r. spectra (20—200 cm$^{-1}$) were recorded for the solid thio-complex only: the band at 110 cm$^{-1}$ is probably the *E* stretching mode of the $Re_4$ tetrahedron.

The electronic spectra of the complexes are listed in the Experimental section. A single-crystal electronic spectrum of $[AsPh_4]_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ is similar to that of the complex in methanol, suggesting that there has been no major stereochemical change from solid to solution.

(*c*) *The di-*$\mu_2$*-thio-octacyanodirhenate*(IV) *ion*, $[Re_2(CN)_8(\mu_2\text{-}S)_2]^{4-}$. We find that reaction of sodium perrhenate in excess of aqueous sodium cyanide solution with hydrogen sulphide yields, after extraction and precipitation with the appropriate cation, salts of the dimeric $[Re_2(CN)_8S_2]^{4-}$ ion. The caesium, tetraphenylphosphonium, and tetraphenylarsonium salts were isolated, and are diamagnetic in the solid state.

Preliminary results for the *X*-ray crystal structure of $[PPh_4]_4[Re_2(CN)_8S_2]\cdot 6H_2O$ show the sulphur atoms to bridge the two rhenium atoms, there being a short rhenium–rhenium distance suggesting strong metal–metal interaction (Re–S 2.33, Re–Re 2.60 Å).[25] The $Re_2S_2$ system is planar. The sulphur atoms function as single bridging ligands rather than as bridging $S_2$ since the S · · · S distance is long (3.86 Å). There are four terminal cyanide ligands on each rhenium atom (Re–C 2.20, C–N 1.15 Å) giving seven-co-ordination to the rhenium. The structure of the anion and bond parameters are similar to those reported for $[Mo_2(CN)_8S_2]^{6-}$, which is made in analogous fashion from molybdate, cyanide, and $H_2S$.[26]

These data permit us to compare metal–metal bond lengths of a dimer and tetramer where the ligand environment ($[CN]^-$) and metal oxidation state ($Re^{IV}$) are the same; the dimer bond length of 2.60 Å in $[Re_2(CN)_8S_2]^{4-}$ is substantially shorter than that of the tetramer $[Re_4(CN)_{12}S_4]^{4-}$ (2.755 Å). This sequence has been observed in other systems, *e.g.* $[Fe_2Cl_4S_2]^{2-}$ (2.716 Å) and $[Fe_4Cl_4S_4]^{2-}$ (2.755 Å), although in this latter case the formal oxidation states are not the same.[27] Elec-

---

[19] D. L. Lewis and S. J. Lippard, *J. Amer. Chem. Soc.*, 1975, **97**, 2697.

[20] M. Laing, P. M. Kiernan, and W. P. Griffith, *J.C.S. Chem. Comm.*, 1977, 221.

[21] T. Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1977, **99**, 408.

[22] S. P. W. Tang, T. G. Spiro, G. Antanaitis, T. H. Moss, R. H. Holm, T. Herzkovitz, and L. E. Mortensen, *Biochem. Biophys. Res. Comm.*, 1975, **62**, 1.

[23] C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, 1969, **8**, 2011.

[24] E. W. Abel, P. J. Hendon, R. A. N. McLean, and M. M. Qurashi, *Inorg. Chim. Acta*, 1969, **3**, 77.

[25] M. Laing, J.-M. Brégeault, and W. P. Griffith, *Inorg. Chim. Acta*, 1978, **26**, L27.

[26] M. G. B. Drew, P. C. H. Mitchell, and C. F. Pygall, *Angew. Chem.*, 1976, **15**, 784.

[27] M. A. Bobrik, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, 1977, **16**, 1851.

tronic rather than steric factors may be responsible for the effect.[27]

The Raman spectrum of the blue solid could not be measured owing to decomposition in the laser beam, but it was recorded for the methanolic solution. Three of the four C≡N stretches expected for a $D_{2h}$ symmetry of the anion were observed, one polarised. There is no evidence from the i.r. spectrum that SH or $SH_2$ groups are co-ordinated rather than sulphur atoms, and the $^1H$ n.m.r. spectrum in deuteriated acetic acid shows no shifts attributable to such ligands. The bands near 400 cm$^{-1}$ in the Raman and i.r. we assign to Re–C stretching modes, the Raman band at 241 cm$^{-1}$ to a symmetric Re–S stretch, and the i.r. band at 345 cm$^{-1}$ to an asymmetric Re–S mode {the corresponding band of $K_6[Mo_2(CN)_8S_2]$ is at 320 cm$^{-1}$ (ref. 26)}. The strong polarised Raman shift at 183 cm$^{-1}$ is probably the $Re_2S_2$ stretching vibration; bands in this region have been found for other binuclear rhenium species with short Re–Re bonds.[28]

TABLE 2

Cyanorhenates reformulated

| Species in literature | Reaction | Our formulation of products |
|---|---|---|
| (*a*) Unsubstituted species | | |
| $[Re(CN)_6]^{5-}$ | $[ReCl_6]^{2-}$ + K–Hg + $[CN]^-$<br>$[ReCl_6]^{2-}$ + $[BH_4]^-$ + $[CN]^-$ | $[Re(CN)_6]^{5-}$ |
| $[Re(CN)_6]^{6-}$ | $[ReCl_6]^{2-}$ + $[BH_4]^-$ + $[CN]^-$ | $[Re(CN)_6]^{5-}$ |
| $[Re(CN)_6]^{4-}$ | $[ReO_4]^-$ + K–Hg + $[CN]^-$ | $[Re(CN)_7]^{4-}$ |
| $[Re(CN)_5]^{3-}$ | $[Re(CN)_5(OH_2)]^{3-}$ + K[OH] | $[Re(CN)_7]^{4-}$ |
| $[Re(CN)_6]^{3-}$ | $Re_3Cl_9$ + $[CN]^-$ | $[Re(CN)_7]^{4-}$ + $[Re(CN)_6]^{5-}$ |
| | $[ReCl_6]^{2-}$ + 7$[CN]^-$ (under $N_2$) | $[Re(CN)_6]^{5-}$ |
| $[Re(CN)_6]^-$ | $[ReCl_6]^{2-}$ + $[CN]^-$ + $[SCN]^-$ (melt) | $[Re_4(CN)_{12}S_4]^{4-}$ + $[Re(CN)_7]^{4-}$ |
| $[Re(CN)_8]^{3-}$ | $[ReI_6]^{2-}$ + $[CN]^-$ (in MeOH) | $[Re(CN)_7]^{4-}$ + $[Re(CN)_4O_2]^{3-}$ |
| | $[ReCl_6]^{2-}$ + $[CN]^-$ (in water, in air) | $[Re(CN)_7]^{4-}$ + $[Re(CN)_4O_2]^{3-}$ + $[Re_2(CN)_9(OH)_3]^{5-}$ |
| | $Re_3Cl_9$ + $[CN]^-$ (in water, in air) | $[Re(CN)_7]^{4-}$ |
| $[Re(CN)_8]^{2-}$ | $[Re(CN)_8]^{3-}$ + $H^+$ + $O_2$ | ? |
| (*b*) Substituted species | | |
| $[Re(CN)_7(NO)]^{3-}$ | $[ReO_4]^-$ + $[CN]^-$ + $NH_2OH$ | $[Re(CN)_5(NO)]^{3-}$ |
| $[Re(CN)_4O_2]^{4-}$, $[Re_2(CN)_8O_3]^{6-}$ | $[ReCl_6]^{2-}$ + 40 $[CN]^-$ (in $N_2$) | $[Re(CN)_4O_2]^{3-}$ + $[Re_2(CN)_9(OH)]^{5-}$, $[Re(CN)_6]^{5-}$ |

(*d*) *The pentacyanonitrosylrhenate*(3—) *ion*, $[Re(CN)_5(NO)]^{3-}$. The reported cyanonitrosyl complexes of rhenium are $Ag_3[Re(CN)_n(NO)]$ ($n$ = 5 or 7),[10] $[Re(CN)_5(NO)]^{2-}$,[29] and $K_3[Re(CN)_7(NO)]\cdot 4H_2O$, this latter species being made by reaction of perrhenate, K[CN], and hydroxylamine hydrochloride in alkaline solution.[30] We have repeated the latter preparation and obtain red crystals of $K_3[Re(CN)_5(NO)]\cdot 3H_2O$. This salt is diamagnetic, as expected for $Re^I$ with co-ordination from $[NO]^+$. The vibrational spectra (Table 1) are consistent with a $C_{4v}$ configuration of the ion. The Raman spectrum of the solid is difficult to record owing to sample decomposition, but that of the solution shows three bands (two polarised) in the CN stretching region [four, $2A_1$ (polarised) + $B_1$ + $E$ are expected for $C_{4v}$ symmetry, but the $B_1$ and $E$ modes probably coincide]. The Re–N stretching ($A_1$) and Re–N–O deformation ($E$) modes are easily identified, as in analogous complexes,[31] by the former being strong and polarised in the Raman with the latter depolarised and weaker. The N–O stretch is weak in the Raman but strong in the i.r., and is partly obscured in the latter by the $H_2O$ deformation mode. Deuteriation of the complex shows it to lie, however, at 1 640 cm$^{-1}$.

(*e*) *The identity of* $[Re(CN)_6]^{n-}$ ($n$ = 1 *or* 3—6). Our conclusions regarding the identity of these and cyano-oxorhenates are summarised in Table 2.

(*i*) $[Re(CN)_6]^{5-}$ *and* $[Re(CN)_6]^{6-}$. Of all the unsubstituted cyanorhenates described in the literature we can confirm the existence only of $[Re(CN)_6]^{5-}$. Reaction of $Re_3Cl_9$, Na[CN], and sodium amalgam is said to give an unidentified rhenium(I) cyano-complex,[32] and reduction of $K_2[ReCl_6]$ in K[CN] solution with potassium amalgam to give deep green $K_5[Re(CN)_6]\cdot 3H_2O$.[3] This salt was later reported [4,33] to be anhydrous, and was also made from $K_2[ReCl_6]$ in K[CN] solution with potassium tetrahydroborate.[34] The isomorphism of $K_5[Re(CN)_6]$ with $K_5[Mn(CN)_6]$ and $K_5[Tc(CN)_6]$ has been demonstrated by *X*-ray powder photography,[4] and the i.r.,[4,33] Raman,[33] and electronic [4] spectra of anhydrous $K_5[Re(CN)_6]$ recorded. We find that reduction of $K_2[ReCl_6]$ in K[CN] with potassium amalgam does give anhydrous $K_5[Re(CN)_6]$, this product having the same i.r. and *X*-ray powder patterns as given in the literature.

It has been suggested that $K_6[Re(CN)_6]$ could be the product of reaction of $K_2[ReCl_6]$ with K[CN] and $K[BH_4]$,[5] and a yellow cyano-complex with a K : Re ratio of *ca.* 6 : 1 is said to be formed in low yield from the reduction with potassium amalgam.[3] Nevertheless, we find only $K_5[Re(CN)_6]$ to be formed in both cases.

(*ii*) $[Re(CN)_6]^{4-}$ *and* $[Re(CN)_5]^{3-}$. These ions we believe to be identical with $[Re(CN)_7]^{4-}$. The reaction

---

[28] J. San Filippo and H. J. Sniadoch, *Inorg. Chem.*, 1973, **12**, 2326.

[29] S. Sen, *Z. anorg. Chem.*, 1965, **335**, 222; B. K. Sen and P. B. Sarkar, *Science and Culture*, 1961, **27**, 404.

[30] A. Sergeeva, A. V. Mazera, and V. S. Mazuroki, *Koord. Khim.*, 1975, **1**, 1681.

[31] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

[32] J. Meier and W. D. Treadwell, *Helv. Chim. Acta*, 1955, **38**, 1679.

[33] W. Krasser, E. W. Bohres, and K. Schwochau, *Z. Naturforsch.*, 1972, **A27**, 1193.

[34] P. H. L. Walter, J. Kleinberg, and E. Griswold, *Inorg. Chem.*, 1962, **1**, 10.

of $[ReO_4]^-$ and cyanide followed by sodium-amalgam reduction, neutralisation, and treatment with K[CN] was said to give $K_4[Re(CN)_6]\cdot 3H_2O$,[6-8] although this product is not isomorphous with $K_4[Fe(CN)_6]\cdot 3H_2O$.[7] We find this preparation gives $K_4[Re(CN)_7]\cdot 2H_2O$ in high yield, as does the preparation [9] for $K_3[Re(CN)_5]$. The published *X*-ray data for $K_4[Re(CN)_6]\cdot 3H_2O$ [7] are insufficient for us to demonstrate its identity with the heptacyano-complex. However, electronic spectra in aqueous solution of '$[Re(CN)_6]^{4-}$' (refs. 6 and 7) and $[Re(CN)_7]^{4-}$ are very similar, '$Ag_4[Re(CN)_6]$' and $Ag_4[Re(CN)_7]$ have similar broad i.r. bands in the CN stretching region [2 082 and 2 030 cm$^{-1}$ (ref. 7) and 2 090 and 2 040 cm$^{-1}$ respectively], and potassium and rhenium analyses for $K_4[Re(CN)_6]\cdot 3H_2O$ [6] are close to those expected for the heptacyanide. The reported diamagnetism [6] or slight paramagnetism [7] variously reported for the complex are inconsistent with the $d^5$ configuration of $[Re(CN)_6]^{4-}$ but would be expected for $[Re^{III}(CN)_7]^{4-}$. The observed oxidation of $[Re(CN)_6]^{4-}$ to $[Re(CN)_6]^{3-}$ ($E^\ominus$ 0.72 V) [35] could be from $[Re(CN)_7]^{4-}$ to $[Re(CN)_7]^{3-}$. It is possible that '$[Re(CNMe)_6]^{2+}$',[36] made by methylation of '$[Re(CN)_6]^{4-}$', is in fact $[Re(CNMe)_7]^{3+}$.

(*iii*) $[Re(CN)_6]^{3-}$. Reaction of $Re_3Cl_9$ with aqueous K[CN] solution is reported to give this ion as the green anhydrous potassium salt.[10] {The same reaction has also been said to give $[Re^{II}(CN)_4\cdot Re^{IV}(CN)_4]^{2-}$, although no salts of this ion were isolated.[32]} Green $K_3[Re(CN)_6]\cdot 3H_2O$ has also been postulated as the product of reaction of $K_2[ReCl_6]$ with K[CN] under nitrogen,[11] and $[Co(NH_3)_6][Re(CN)_6]$ is said to be formed when '$[Re(CN)_8]^{3-}$' is reduced with $Na[BH_4]$.[10]

We find that $Re_3Cl_9$ reacts with aqueous K[CN] to give $K_4[Re(CN)_7]\cdot 2H_2O$ together with an air-sensitive green material which has an i.r. spectrum similar to that of $K_5[Re(CN)_6]$. In air the only identifiable product is $K_4[Re(CN)_7]\cdot 2H_2O$. We find that reaction of $K_2[ReCl_6]$ with K[CN] under nitrogen gives $K_5[Re(CN)_6]$. Since *X*-ray powder data show that '$K_3[Re(CN)_6]\cdot 3H_2O$' is identical with $K_5[Re(CN)_6]$ {which is also isomorphous with $K_5[Mn(CN)_6]$ and $K_5[Tc(CN)_6]$ [4]} the report [11] of the rhenium(III) species is clearly in error. The reported [11] i.r. spectrum of '$K_3[Re(CN)_6]\cdot 3H_2O$' is identical to that of $K_5[Re(CN)_6]$ [4,33] with the exception of an extra band for the former at 907 cm$^{-1}$ which may plausibly be attributed to an $ReO_2$ impurity. Spectra of our products reveal no such band, and our analyses support the formulation $K_5[Re(CN)_6]$.

(*iv*) $[Re(CN)_6]^-$. Tetraphenylarsonium and tetrabutylammonium salts of this ion are said to be formed when $K_2[ReCl_6]$ is treated with cyanide in a K[SCN] melt. The product is precipitated from aqueous solution with the organic cations.[12] The caesium salt has also been reported without preparative details.[37] There seems little doubt that these are in fact the $[Re_4(CN)_{12}S_4]^{4-}$ salts referred to above: the carbon and hydrogen analyses for $[AsPh_4][Re(CN)_6]\cdot H_2O$ and for $[AsPh_4]_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ are very similar. The reported i.r. spectra in the CN stretching region for '$[AsPh_4][Re(CN)_6]$' [12] and for '$Cs[Re(CN)_6]$' [37] and the reported electronic spectra for $[AsPh_4][Re(CN)_6]$ [12] are very close to those which we find for the $[Re_4(CN)_{12}S_4]^{4-}$ analogues. The reported paramagnetism [12] of '$[Re(CN)_6]^-$' salts must have arisen from an impurity. The previously unidentified [12] by-product of this reaction is $K_4[Re(CN)_7]\cdot 2H_2O$.

(*f*) *Other unsubstituted cyanorhenates.* (*i*) $[Re(CN)_8]^{3-}$ *and* $[Re(CN)_8]^{2-}$. Reaction of $K_2[ReI_6]$ with K[CN] in hot methanol is said to give $K_3[Re(CN)_8]$,[10,13] together with some $K_3[Re(CN)_4O_2]$,[13] and that of $K_2[ReCl_6]$ with K[CN] in air [14] to give $K_3[Re(CN)_8]\cdot H_2O$. In our hands these reactions give a mixture containing $K_4[Re(CN)_7]\cdot 2H_2O$ and $K_3[Re(CN)_4O_2]$ and, in addition for the latter reaction, a dark brown species which we tentatively formulate as $K_5[Re_2(CN)_9(OH)_3]\cdot 2H_2O$ (see below). The reaction of $Re_3Cl_9$ with K[CN] in air is also said [10] to give $K_3[Re(CN)_8]$, but again we obtain $K_4[Re(CN)_7]\cdot 2H_2O$. Oxidation of $[Re(CN)_8]^{3-}$ is said to give $[Re(CN)_8]^{2-}$,[10,13] but analogous oxidation of $[Re(CN)_7]^{4-}$ affords no isolable product.

While not denying the possibility of the existence of octacyanorhenates-(V) or -(VI), we are unable to repeat their preparations. The reported *X*-ray powder-diffraction pattern for $K_3[Re(CN)_8]\cdot H_2O$ [38] and our data for $K_4[Re(CN)_7]\cdot 2H_2O$ are very similar. Infrared spectra in the CN stretching region for $K_3[Re(CN)_8]$ [13] and $K_4[Re(CN)_7]\cdot 2H_2O$ are similar, and the electronic spectrum for $[Re(CN)_8]^{3-}$ reported by Basu and Basu [39] is close to that which would be expected for a mixture of $[Re(CN)_4O_2]^{3-}$ (ref. 40) and $[Re(CN)_7]^{4-}$ (the spectrum reported by Adamson *et al.*[41] is quite different, however). Both $K_3[Re(CN)_8]$ [10,13] and $K_4[Re(CN)_7]\cdot 2H_2O$ are diamagnetic.

(*g*) *Oxo- and hydroxo-cyanorhenates.* The ions *trans*-$[Re(CN)_4O_2]^{3-}$ (ref. 42) and *trans*-$[Re_2(CN)_8O_3]^{4-}$ (ref. 43) are well established. The reaction of $K_2[ReCl_6]$ with excess of aqueous K[CN] at room temperature under nitrogen is said to give $K_4[Re(CN)_4O_2]$,[34] later reformulated as $K_6[Re_2(CN)_8O_3]\cdot 4H_2O$.[44] We have repeated the preparation several times and find the products, from their i.r. spectra and *X*-ray powder-diffraction patterns, to be a mixture of $K_3[Re(CN)_4O_2]$, $K_5[Re(CN)_6]$, and $K_5[Re_2(CN)_9(OH)_3]\cdot 2H_2O$.

If $K_2[ReCl_6]$ is treated with hot aqueous K[CN]

---

[35] B. K. Sen, N. N. Ghosh, and P. B. Sarkar, *J. Indian Chem. Soc.*, 1963, **40**, 815.

[36] S. Sarkar, *J. Indian Chem. Soc.*, 1972, **49**, 189; S. Sarkar, P. Bandyopadhyay, and P. B. Sarkar, *ibid.*, 1968, **45**, 992.

[37] B. Jezowska-Trzebiatowska, J. Hanuza, and M. Baluka, *Spectrochim. Acta*, 1971, **A27**, 1753.

[38] O. E. Skolozdra and A. N. Sergeeva, *Russ. J. Inorg. Chem.*, 1973, **18**, 290.

[39] M. Basu and S. Basu, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3669.

[40] D. E. Grove and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1224.

[41] J. E. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1963, **85**, 249.

[42] R. H. Fenn, A. J. Graham, and N. P. Johnson, *J. Chem. Soc.* (*A*), 1971, 2880.

[43] R. Shandles, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, 1971, **10**, 2785.

[44] W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 211.

solution, a mixture of $K_4[Re(CN)_7]\cdot 2H_2O$ and a dark brown material, amorphous to *X*-rays, is formed. This latter material gives consistent analyses corresponding to the formula $K_5[Re_2(CN)_9(OH)_3]\cdot 2H_2O$, and is paramagnetic ($\mu_{eff.}$ 0.7 B.M. per rhenium atom at 298 K).* The complex gives a deep red-brown aqueous solution with a very strong band in its electronic spectrum at 398 nm. This, the paramagnetism, and its stoicheiometry lead us tentatively to suggest that it is a mixed-oxidation-state complex, perhaps with a hydroxo-bridge. An i.r. absorption near 530 $cm^{-1}$ could arise from an Re–OH–Re mode, as found in other $\mu$-hydroxo-species.[45] The same species is also formed together with $K_4[Re(CN)_7]\cdot 2H_2O$ when $K_2[ReI_6]$ reacts with K[CN] in aqueous methanol.

## EXPERIMENTAL

*Potassium Heptacyanorhenate*(III), $K_4[Re(CN)_7]\cdot 2H_2O$.—*Method* (1). Potassium hexachlororhenate(IV) (1 g) was added to molten potassium selenocyanate (20 g) under nitrogen, followed by potassium cyanide (2 g). The light golden solution was maintained at 250 °C with stirring for 10 min, then cooled. The selenocyanate was extracted with methanol and the pale yellow product recrystallised from water–methanol, yield 90%.

*Method* (2). Rhenium trichloride (0.3 g) was added to a solution of K[CN] (2 g) in water (5 $cm^3$), and the mixture stirred for 2 h in air and then heated under reflux under nitrogen. On cooling to 0 °C the product separated and was recrystallised from water–methanol under nitrogen, yield 85%.

*Method* (3). The procedure of Sen[6] was used. The violet-brown solution was heated under reflux with aqueous K[CN], concentrated by distillation, and the salt precipitated by addition of methanol, followed by recrystallisation from water–methanol, yield 82%.

*Method* (4). The literature procedure for $K_3[Re(CN)_8]$ (ref. 4) was used, the dark brown product being recrystallised from water–methanol, yield 40%.

Electronic spectrum ($\lambda$/nm, $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parentheses); aqueous solution, 203 ($2.5 \times 10^4$), 214 ($3.0 \times 10^4$), 253 ($2.0 \times 10^4$), 272 ($5.7 \times 10^3$), 318 ($8.5 \times 10^2$), and 347 ($3.8 \times 10^2$); solid, 235, 240, 260, 266, 290, and 325 (Found: C, 15.1; H, 0.8; K, 27.9; N, 17.5; O, 6.2; Re, 32.8. $C_7H_4K_4N_7O_2Re$ requires C, 15.0; H, 0.7; K, 27.9; N, 17.5; O, 5.7; Re, 33.2%).

*Tripotassium Sodium Heptacyanorhenate*(III), $NaK_3[Re(CN)_7]\cdot 3H_2O$.—This was made as in methods (3) and (4) above, sodium cyanide replacing potassium cyanide. The product was recrystallised from water–methanol, yield 90%. Infrared spectrum of solid: 2 125m, 2 109m, 2 095(sh), 2 091vs, 2 069w, 2 064w, 2 046(sh), 2 042vs, 2 012w, 552m, 529s, 521(sh), 477w, 420m, 337w, 322m, and 308w $cm^{-1}$. Raman spectrum of solid (relative intensities in parentheses): 2 122(7), 2 103(3), 2 094(2), 2 062(10), 2 055w, 515w, 472w, 430(1), 403w, 370w, 220(3), and 168(9) $cm^{-1}$. The electronic spectrum of the solid showed maxima at 233, 242, 266, 275, and 330 nm (Found: C, 14.8; H, 1.1; K, 21.0; N, 17.2; Na, 4.0; Re, 32.9. $C_7H_6K_3N_7NaO_3Re$ requires C, 14.9; H, 1.1; K, 20.9; N, 17.4; Na, 4.1; Re, 33.1%).

*Salts of the Tetra-$\mu_3$-thio-dodecacyanotetrarhenate*(IV) *Ion*, $[Re_4(CN)_{12}(\mu_3\text{-}S)_4]^{4-}$.—The potassium salt $K_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ was made from $K_2[ReCl_6]$ (2 g) dissolved in molten potassium thiocyanate (20 g) under nitrogen. Potassium cyanide (4 g) was added to the dark brown melt which was stirred at 250 °C for 30 min and then cooled. Excess of thiocyanate and cyanide were extracted and the brown residue washed with methanol and dissolved in the minimum quantity of water. Addition of methanol (100 $cm^3$) gave $K_4[Re(CN)_7]\cdot 2H_2O$. Acetone (100 $cm^3$) and diethyl ether (50 $cm^3$) were added to the red filtrate, and the red precipitate was redissolved in the minimum of water and crystallised by concentration under reduced pressure, yield 20% (Found: C, 10.9; H, 0.4; K, 10.9; N, 12.2. $C_{12}H_6K_4N_{12}O_3Re_4S_4$ requires C, 10.3; H, 0.4; K, 11.2; N, 12.0%).

The caesium salt $Cs_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ was made from the potassium salt (1 g) in the minimum of water by addition of caesium chloride (1 g) in water (5 $cm^3$). Slow addition of methanol and cooling to 0 °C gave red crystals of the product which was washed with aqueous ethanol, methanol, and diethyl ether, yield 85%. Infrared spectrum (solid): 2 171w, 2 162m, 2 158s, 2 153m, 488w, 442w, 426m, 406m, 402m, 359s, and 317w $cm^{-1}$ (Found: C, 8.6; H, 0.6; N, 9.7. $C_{12}H_6Cs_4N_{12}O_3Re_4S_4$ requires C, 8.1; H, 0.3; N, 9.5%).

The tetraphenylphosphonium salt $[PPh_4]_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ was made from an aqueous solution of the potassium salt by addition of strong methanolic tetraphenylphosphonium iodide solution in methanol. The red precipitate was redissolved in methanol and slow addition of water followed by slow evaporation gave well formed red crystals (Found: C, 49.9; H, 3.4; N, 6.3; S, 4.5%; $C_{108}H_{86}N_{12}O_3P_4Re_4S_4$ requires C, 49.9; H, 3.3; N, 6.5; S, 4.9%).

The tetraphenylarsonium salt $[AsPh_4]_4[Re_4(CN)_{12}S_4]\cdot 3H_2O$ was made as above. Infrared spectrum (solid, $[AsPh_4]^+$ bands omitted): 2 168w, 2 160m, 2 157s, 2 152m, 488w, 441w, 424m, 416w, 402m, 358s, and 317w $cm^{-1}$. Electronic spectrum in methanol ($\lambda$/nm; $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parentheses): 211 ($1.5 \times 10^5$), 221 ($1.0 \times 10^4$), 229 ($8.0 \times 10^4$), 263 ($1.1 \times 10^4$), 269 ($1.4 \times 10^4$), 276 ($1.3 \times 10^4$), 305 ($4.4 \times 10^3$), 333 ($1.6 \times 10^3$), 341 ($1.2 \times 10^3$), 372 ($1.3 \times 10^3$), 421 ($9.4 \times 10^2$), 478 ($2.8 \times 10^2$), and 566 ($1.0 \times 10^2$) (Found: C, 46.8; H, 3.4; N, 6.1; S, 4.7. $C_{108}H_{86}As_4N_{12}O_3Re_4S_4$ requires C, 46.8; H, 3.1; N, 6.1; S, 4.7%).

*Salts of the Tetra-$\mu_3$-seleno-dodecacyanotetrarhenate*(IV) *Ion*, $[Re_4(CN)_{12}(\mu_3\text{-}Se)_4]^{4-}$.—The caesium salt $Cs_4[Re_4(CN)_{12}Se_4]\cdot 3H_2O$ was made from $K_2[ReCl_6]$ (2 g) in molten potassium selenocyanate (20 g) under nitrogen. Potassium cyanide (4 g) was added to the melt which became very pale green. The temperature was increased to 320 °C and maintained for 30 min until the solution became dark brown. It was cooled, the selenocyanate and cyanide extracted with methanol, and the brown solid filtered off and dissolved in a minimum of water. The caesium salt was then isolated in the same way as its thio-analogue. Infrared spectrum (solid): 2 165w, 2 156m, 2 152s, 2 148m, 445w, 434s, 422m, 386s, 297w, and 209m $cm^{-1}$ (Found: C, 7.7; H, 0.3; N, 9.0. $C_{12}H_6Cs_4N_{12}O_3Re_4Se_4$ requires C, 7.4; H, 0.3; N, 8.6%).

The tetraphenylphosphonium salt $[PPh_4]_4[Re_4(CN)_{12}Se_4]\cdot 3H_2O$ was made in the same way as its thio-analogue (Found: C, 46.7; H, 3.4; N, 6.0; S, 10.9. $C_{108}H_{86}N_{12}O_3P_4Re_4Se_4$ requires C, 46.6; H, 3.1; N, 6.0; Se, 11.3%).

The tetraphenylarsonium salt was made in the same way

---

* Throughout this paper: 1 B.M. ≈ $9.27 \times 10^{-24}$ A $m^2$.

[45] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 472.

as its thio-analogue. Infrared spectrum (solid, omitting $[AsPh_4]^+$ modes): 2 150m, 2 144s, 446w, 434m, 384m, 296w, and 209m cm$^{-1}$. Electronic spectrum in methanol ($\lambda$/nm, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ in parentheses): 208 ($9.0 \times 10^4$), 211 ($1.1 \times 10^5$), 218 ($9.0 \times 10^4$), 229 ($8.0 \times 10^4$), 263 ($1.0 \times 10^4$), 269 ($1.2 \times 10^4$), 276 ($1.2 \times 10^4$), 290 ($5.6 \times 10^3$), 328 ($4.0 \times 10^3$), 349 ($1.9 \times 10^3$), 384 ($1.5 \times 10^3$), 446 ($9.0 \times 10^2$), 500 ($3.6 \times 10^2$), and 592 ($1.4 \times 10^2$) (Found: C, 44.1; H, 2.6; N, 5.9; Se, 10.4. $C_{108}H_{86}As_4N_{12}O_3Re_4Se_4$ requires C, 43.8; H, 2.9; N, 5.7; Se, 10.7%).

*Salts of the Di-$\mu_2$-thio-octacyanodirhenate*(IV) *Ion*, $[Re_2(CN)_8(\mu_2\text{-}S)_2]^{4-}$.—Sodium perrhenate (0.7 g) was dissolved in air-free water (6 cm$^3$) with sodium hydroxide (0.5 g), and sodium cyanide (1.96 g) was added under nitrogen. Hydrogen sulphide was passed through the solution for 1 h and acetone (20 cm$^3$) added. After decantation of the yellow supernatant liquid the remaining blue-green oil was triturated with methanol to give a blue-green precipitate which was then dissolved in the minimum quantity of water. The caesium salt $Cs_4[Re_2(CN)_8S_2]\cdot4H_2O$ was made by addition of caesium chloride (0.4 g) to this solution followed by precipitation with methanol and repeated washing of the precipitate with a 20% water–methanol mixture, yield 18% (Found: C, 8.2; H, 0.6; N, 9.1; S, 5.1. $C_8H_8Cs_4N_8O_4Re_2S_2$ requires C, 7.7; H, 0.7; N, 9.0; S, 5.1%). The tetraphenylphosphonium salt $[PPh_4]_4[Re_2(CN)_8S_2]\cdot6H_2O$ was similarly prepared, $[PPh_4]Cl$ replacing caesium chloride (Found: C, 59.2; H, 4.5; N, 5.3; P, 5.9; S, 3.6. $C_{104}H_{92}N_8O_6P_4Re_2S_2$ requires C, 59.2; H, 4.4; N, 5.3; P, 5.9; S, 3.0%). The tetraphenylarsonium salt $[AsPh_4]_4[Re_2(CN)_8S_2]\cdot6H_2O$ was made in analogous fashion (Found: C, 55.2; H, 4.3; N, 4.9; S, 2.9. $C_{104}H_{92}As_4N_8O_6Re_2S_2$ requires C, 54.6; H, 4.1; N, 4.9; S, 2.8%).

*Salts of the Pentacyanonitrosylrhenate*(3–) *Ion*, $[Re(CN)_5(NO)]^{3-}$.—The potassium salt $K_3[Re(CN)_5(NO)]\cdot3H_2O$ was made by the literature method for $K_3[Re(CN)_7(NO)]\cdot4H_2O$.[30] It forms orange-red crystals and is diamagnetic (Found: C, 11.3; H, 1.2; K, 23.4; N, 16.0; Re, 36.0. $C_5H_6K_3N_6O_4Re$ requires C, 11.6; H, 1.2; K, 22.7; N, 16.2; Re, 36.0%). The tetraphenylphosphonium salt $[PPh_4]_3[Re(CN)_5(NO)]\cdot4H_2O$ was made from an aqueous solution of the potassium salt with tetraphenylphosphonium chloride (Found: C, 64.1; H, 4.9; N, 5.7; P, 6.6. $C_{77}H_{68}N_6O_5P_3Re$ requires C, 64.4; H, 4.8; N, 5.8; P, 6.5%). The tetraphenylarsonium salt $[AsPh_4]_3[Re(CN)_5(NO)]\cdot3H_2O$ was made in analogous fashion (Found: C, 59.4; H, 4.7; N, 5.2. $C_{77}H_{66}AsN_6O_4Re$ requires C, 59.6; H, 4.3; N, 5.4%).

Potassium hexacyanorhenate(I), $K_5[Re(CN)_6]$, was made by the literature method [3] (Found: C, 13.5; K, 35.3; N, 15.3. $C_6K_5N_6Re$ requires C, 13.4; K, 36.4; N, 15.6%).

The salt $K_5[Re_2(CN)_9(OH)_3]\cdot2H_2O$ was made by the literature method for $K_3[Re(CN)_8]\cdot H_2O$ [14] after separation of $K_4[Re(CN)_7]\cdot2H_2O$. A better procedure is as follows. To K[CN] (5 g) was added a saturated solution of $K_2[ReCl_6]$ (1 g), the mixture stirred and heated until the black solid first precipitated had redissolved. After cooling, slow addition of methanol gave a black solid which was centrifuged off and redissolved in water. This procedure was twice repeated and acetone and diethyl ether used to crystallise the oil obtained (Found: C, 12.3; H, 0.8; K, 22.2; N, 13.6; Re, 41.6. $C_9H_7K_5N_9O_5Re_2$ requires C, 12.2; H, 0.8; K, 21.9; N, 14.2; Re, 41.9%). Infrared spectrum: 3 600m, 3 400m, 2 060vs, 1 600m, 915w, 852w, 778m, 732m, 518m, 490sh, 405w, and 394vw cm$^{-1}$.

The salts $K_2[ReCl_6]$,[46] $K_2[ReI_6]$,[47] and $Re_3Cl_9$ [48] were made by the literature methods.

Raman spectra were recorded on a Spex Ramalog 5 instrument equipped with a DPC-2 detector and with krypton-ion laser red (6 471 Å) and yellow (5 682 Å) excitation. Infrared spectra were obtained on Perkin-Elmer 325 and 457 instruments with liquid-paraffin mulls in caesium iodide plates or as aqueous solutions in matched calcium fluoride cells. Electronic-absorption spectra were recorded in quartz cells on a Perkin-Elmer 402 instrument. Microanalyses were by the Microanalytical Department, Imperial College, E. Pascher, Bonn, and the C.N.R.S., Paris.

We thank the Royal Society and the C.N.R.S., Paris (to J.-M. B.) and the S.R.C. (to P. M. K.) for the awards of grants.

[7/2060 *Received*, 23*rd November*, 1977]

---

[46] C. I. Rulfs and R. J. Meyer, *J. Amer. Chem. Soc.*, 1955, **77**, 4505.

[47] G. K. Schweitzer and D. L. Wilhelm, *J. Inorg. Nuclear Chem.*, 1956, **3**, 1.

[48] H. Gehrke and D. Bue, *Inorg. Synth.*, 1970, **12**, 193.