Tetrameric Cyano-rhenium Complexes with Sulphur and Selenium Bridges: Preparation and *X*-Ray Crystal Structures of $(Ph_4P)_4[Re_4S_4(CN)_{12}]\cdot 3H_2O$ and $(Ph_4P)_4[Re_4Se_4(CN)_{12}].3H_2O$

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Summary The anions $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$ and $[Re_4(\mu_3\text{-}Se)_4(CN)_{12}]^{4-}$ each contain a tetrahedron of Re atoms held together by short Re–Re bonds, with one triply bridging S or Se atom per face of the tetrahedron.

The preparation of salts of $[Re(CN)_6]^-$ from $K_2[ReCl_6]$ in a KSCN melt with excess of KCN and a variety of cations has been reported.[1] Our attempts to repeat this have given salts of $[Re(CN)_7]^{4-}$ mixed with those of empirical formula $[ReS(CN)_3]^-$, whose i.r. spectra (CN stretching region) and electronic spectra are identical with those reported[1] for $[Re(CN)_6]^-$. We find that substitution of KSeCN for KSCN gives salts containing $[ReSe(CN)_3]^-$; with KOCN in place of KSCN, ReO_2 is formed.

These thio- and seleno-complexes have been fully characterised by elemental analyses. They are chemically very stable. The tetraphenylphosphonium salts have the stoicheiometry $(Ph_4P)_4[Re_4L_4(CN)_{12}]\cdot 3H_2O$ (L = S, Se) and are obtained as deep brown crystals by slow evaporation of their water–methanol solutions. The crystals are monoclinic, space group $P2_1/c$. L = S: a = 15·43, b = 24·12, c = 28·54 Å, β = 106·8°, U = 10,166 Å^3, Z = 4. L = Se, a = 15·45, b = 24·18, c = 28·60 Å, β = 106·6, U = 10,242 Å^3, Z = 4. The two compounds are exactly isomorphous. Data were measured on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0·7107 Å) for θ between 3 and 20°; 9750 and 9821 data for L = S and Se, respectively. The structures were solved independently by the Patterson method and refined by block-diagonal least-squares (Re, Se or S, and P atoms anisotropic). R = 0·08 for 8100 data (L = S), and 0·07 for 7484 data (L = Se).†

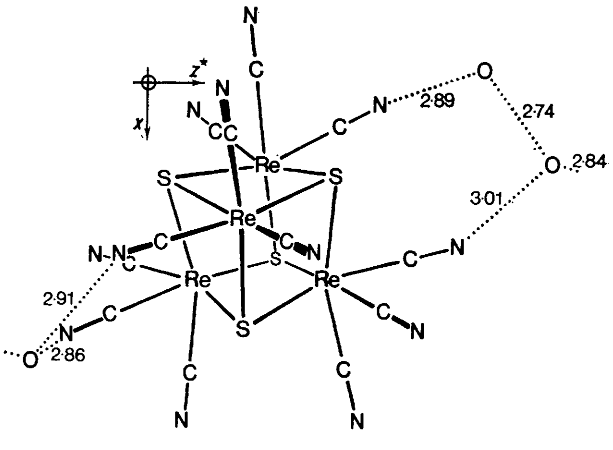

Figure. $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$ anion: a projection down y showing the O atoms of the three waters of crystallization and the hydrogen bonds between the water molecules and the CN groups. The Se analogue is essentially identical in structure: the O . . . . O and N . . . . O separations are similar in both structures.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The anions contain a tetrahedron of bonded Re atoms [mean Re–Re = 2·755(5) for L = S; 2·805(5) Å for L = Se] with one S or Se atom per face of the tetrahedron, equally bonded to each Re atom [mean Re–S = 2·34(1); Re–Se = 2·46(1) Å]. The nearest S–C and Se–C approaches are (mean values) 3·04 and 3·06 Å, respectively, thus making it clear that there are no remaining SCN^- or $SeCN^-$ ligands or ions. To each Re atom are attached three CN groups, mean Re–C = 2·09(2) Å and mean C–Re–C angle of 80(1)°. The co-ordination number of each Re atom is thus 9 if we assume direct Re–Re bonding. The anions are linked in chains by hydrogen bonds formed between one CN on each Re atom and the three H_2O molecules of crystallization (Figure).

These compounds belong to a new class of tetrameric cyano complexes in which the sulphur (or selenium) atoms, which help to hold the metal framework together, have been abstracted from thio- or seleno-cyanate ions. The Re_4S_4 skeleton differs from that in $[Re_4(SMe)_4(CO)_{12}]$[2] in that the new complex contains strong rhenium–rhenium bonding; in this respect it more closely resembles the cubane-like skeleton in $[Fe_4S_4(NO)_4]$.[3] The observed diamagnetism of both complexes is consistent with the bonding scheme which has been proposed for analogous cubane-like systems containing M_4S_4 units.[3] The selenium bridged complex is the first structurally characterised example of an M_4Se_4 cubane-like system.

We thank the South African C.S.I.R. for financial support, Drs. G. Gafner and M. Thackeray of the National Physical Research Laboratory, C.S.I.R. for collecting the intensity data, and the S.R.C. for a grant (P.M.K.).

(*Received*, 21*st December* 1976; *Com.* 1392.)

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