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REACTIONS OF THE OCTAHALODIRHENATE (III) ION WITH SODIUM SELENOCYANATE IN DIFFERENT SOLVENTS

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The reactivity of the $\left[Re_2X_8\right]^{2-}$ ion, where X = Cl or Br, toward a variety of donor molecules has recently been investigated by Cotton c.s. (1-3). An interesting result of these studies is that within a wide variety of ligand substitutions (carboxylic acids, phosphines and sulfur ligands) the Re - Re bond is remained as a quadruple bond. In the case of 2,5 - dithiahexane however, the Re - Re bond becomes a triple bond (4-6). Changing X from Cl to Br usually has little effect upon the reactivity of the $\left[Re_2X_8\right]^{2-}$ species. We have investigated the reaction of $\left[Re_2Cl_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ with sodium selenocyanate to get more information about the effect of the nature of X upon the stability and reactivity of the $\left[Re_2X_8\right]^{2-}$ species. In a previous paper we have already mentioned the reaction of the $SeCN^-$ ion with $\left[Re_2Cl_8\right]^{2-}$, and from the analyses we formulated the reaction product as $\left[Re_2SeCN_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ (7). Here we report the same reactions in acetonitrile and ethanol, the chro - matographic separation of the reaction products and their characterization by means of spectral data, analytical results, magnetic susceptibility and Thermogravimetric (TG) measurements.

Experimental

Materials.

$\left[Re_2Cl_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ was prepared as described previously (8). All used chemicals were reagent grade. The reaction of $\left[Re_2Cl_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ with KSeCN in acetonitrile gave a deep purple product (I).

Anal.Calcd. for $\left[Re_2SeCN_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ C , 28.30; H , 4.25; N , 8.25; Re , 21.93. Found C , 28.11; H , 4.29; N , 8.16; Re , 21.60. The compound is very slightly soluble in acetonitrile and acetone and insoluble in other organic solvents. The reaction of $\left[Re_2Cl_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ with KSeCN in alcohol gave after extraction with diethylether a badly defined black product (II). The compound has the same solubilities as (I), but the analytical results are quite different. Anal.Found C , 19.37; H , 3.15; N , 4.88; Re , 10.11.

Techniques.

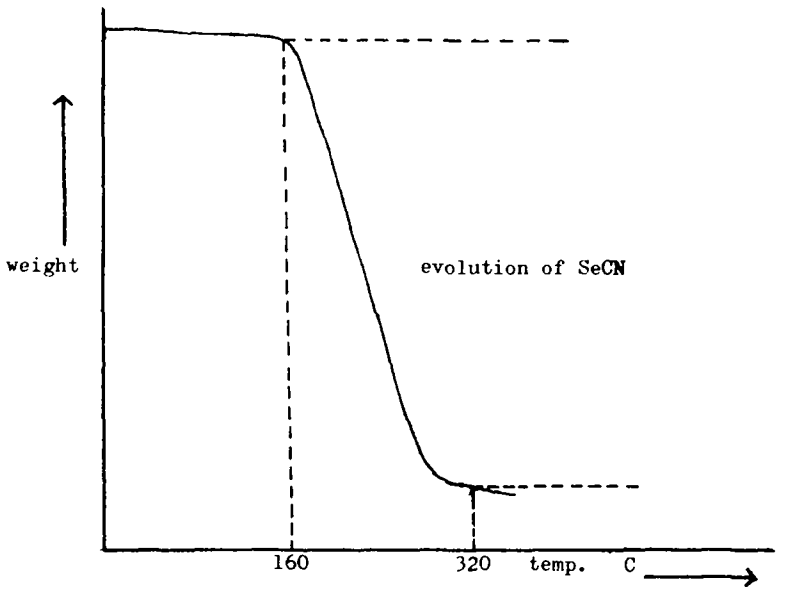
Analyses were carried out by the Micro Analytical Department of Organisch Chemisch Instituut TNO, Croesestraat 79 Utrecht. Infrared spectra were recorded in the range 4000 - 400 cm^{-1} using the Hitachi EPI - G 81 spectrophotometer and in the range 400 - 50 cm^{-1} using the Coderg interferometer. Magnetic susceptibility measurements were performed by the Faraday method. Electronic spectra were recorded on the Shimadzu MP 50-L recording spectrophotometer in the 250 - 1200 nm. region. Electrolytic conductivities were measured using a commercial Wheatstone bridge circuit. A Dupont Thermogravimetric Analyzer was used for the TG measurements.

Results and Discussions

As a part of a program dealing with special stacking patterns of square rhenium complexes in crystalline phases it is necessary to obtain pure crystalline materials. The products obtained in the forementioned reaction are mixtures. Therefore, suspensions of (I) in acetonitrile and (II) in alcohol were passed through a chromatographic column for separation. Inspection of the I.R. and electronic spectra of the compounds before and after passing through the alumina column shows however, that both products are decomposed at the surface of the column. For example, the selenocyanate C-N stretching frequency, which was observed as a very strong band at 2050 cm^{-1} disappeared completely after the chromatographic separation. Purification of the solids by recrystallisation is not possible, because of the poor solubility in the common organic solvents. Conductivity measurements of the compounds in acetonitrile (which seems to be a good solvent at first sight) confirm this. Above concentrations of 10^{-4} equiv./l both products give nonlinear ($\Lambda_0 - \Lambda_e$) vs. $\sqrt{c}$ plots. (Λ_e = equivalent conductivity, Λ_0 =conductivity at zero concentration). The explanation is that at concentrations higher than 10^{-4} equiv./l a suspension of very

small particles is formed. Another suggestion is to prepare single crystals from the melt. However, the results of the TG and DSC measurements showed, that $[Re_2SeCN_8]$ $[(n\text{-}C_4H_9)_4N]_2$ loses selenocyanate in the temperature range from 160 - 320 °C without melting at lower temperatures. Fig.1 gives the TG curve of compound (I).

Fig.1 TG curve of the $[Re_2SeCN_8]$ $[(n\text{-}C_4H_9)_4N]_2$



Summarizing, all methods to obtain good crystalline products have failed till now.

Spectra.

The I.R.spectra of the compounds (I) and (II) are nearly identical except for the two weak bands at 910 and 945 cm^{-1} in the spectrum of (II). The position of the two bands is characteristic for complexes in which alkoxy groups are present with the following assignments

910 cm^{-1} (Re=O) stretching.

945 cm^{-1} (CH_2) rocking (part of the OC_2H_5 group) (9).

However, in this kind of complexes the two bands are strong, while in our case they are very weak. Therefore the assignments are rather uncertain. The amount of oxygen is also very doubtful, because the oxygen analyses were seriously disturbed by the presence of Se. Shortly, from the elemental analyses and I.R. spectra it is not possible to derive a definite formulation of the reaction product. In $[Re_2SeCN_8]$ $[(n\text{-}C_4H_9)_4N]_2$ the selenocyanate C-N stretching frequency is observed

as a strong band at 2050 cm^{-1}. (Fig.2).

Fig.2. I.R. spectrum of $[Re_2SeCN_8][(n\text{-}C_4H_9)_4N]_2$.

This is within the range of 2080 - 2040 cm^{-1}, which is characteristic for the selenocyanate ion as a terminal group (10). Whether the selenocyanate groups are N-or Se bonded cannot be concluded from the position and nature of ν(CN) only.It is possible to distinguish the two forms by the combined evidence of ν (C-Se) and δ(SeCN). Unfortunately, none of these two vibrations were observed with certainty in the range 670 - 360 cm^{-1} (11). It is more likely, that the two bands at 300 and 273 cm^{-1} are M-N vibrations rather than M-Se vibrations because ν (M-Se) occurs at much lower frequencies. Thus, the selenocyanate group is terminal and probably N bonded.

Fig.3 shows the dilute solution spectrum of $[Re_2SeCN_8][(n\text{-}C_4H_9)_4N]_2$ in acetonitrile. This spectrum is rather different from the solution spectrum of the $[Re_2Cl_8]^{2-}$ ion.

In Table 1 the spectral data and their possible assignments are compared.

TABLE 1

Spectral data of $[Re_2Cl_8][(n\text{-}C_4H_9)_4N]_2$ and $[Re_2SeCN_8][(n\text{-}C_4H_9)_4N]_2$

$[Re_2Cl_8][(n\text{-}C_4H_9)_4N]_2$	$[Re_2SeCN_8][(n\text{-}C_4H_9)_4N]_2$
39000 $^1B_{2g} \rightarrow {}^1B_{1u}$ ($\delta \rightarrow \delta^*$)	37700 $^1B_{2g} \rightarrow {}^1B_{1u}$
32500 $^1E_u \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \sigma_\pi$)	30300 $^1E_u \rightarrow {}^1A_{2u}$
14700 $^1B_{2g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \sigma$)	43500(s); 22200(sh)
21000(w); 17500(sh)	19600 (electronic transfer)

w = weak; s = strong; sh = shoulder

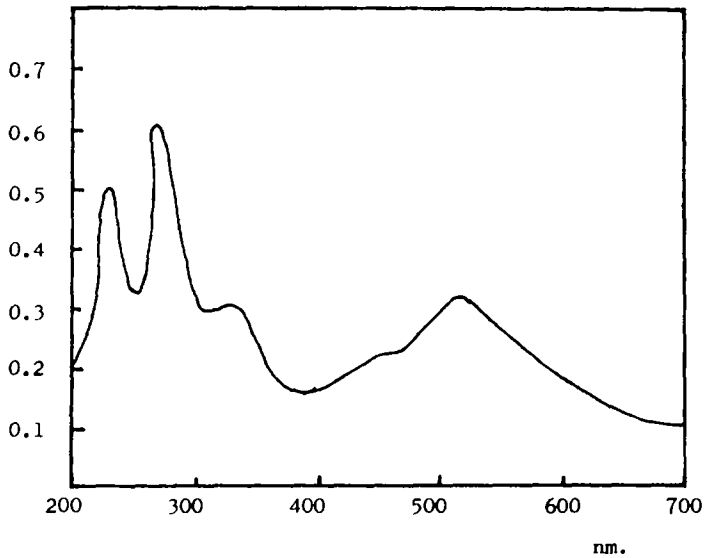


Fig.3. The solution spectrum of $\left[Re_2SeCN_8\right]\left[(n\text{-}C_4H_9)_4N\right]_2$ in acetonitrile.

A possible explanation for the shifts of the bands to lower energies could be the increasing interaction of the orbitals of the $SeCN^-$ ion with the metal $d\pi$ orbitals, which weakens the Re - Re π bonding, and thus the Re-Re distance will increase. The δ overlap is sensitive to the Re - Re π bonding, because this accounts for more than half of the total Re-Re bond strength, and a decrease of the $\delta \rightarrow \delta^*$ transition energy might occur. The strong band at 19600 cm^{-1} is probably an electronic transfer band. It cannot be the $^1B_{2g} \rightarrow {}^1A_{2u}$ transition, since this should occur at frequencies < 14700 for reasons mentioned above.

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