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Coordination of S_8 to an Organotransition-Metal System: $Re_2X_2(CO)_6(S_8)$ (X = Br, I)

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Summary: Labile and reversible S_8 adducts containing the hexacarbonyldihalodirhenium(I) moiety are reported.

No examples of coordination of S_8 to transition-metal complexes have been reported as yet, although *cyclo*-octasulfur is known[1] to coordinate to d^{10} silver(I) in $[Ag(S_8)_2]AsF_6$. On the other hand, several compounds containing "lattice" S_8 have been studied by X-ray diffraction, namely the iodides $CHI_3{\cdot}3S_8$,[2] $SnI_4{\cdot}2S_8$,[3] and $AI_3{\cdot}3S_8$ (A = Sb,[4] As[5]), the chlorides $SbCl_3{\cdot}S_8$,[6] $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$,[7] $WCl_6{\cdot}S_8$,[8] and $WCl_4S{\cdot}S_8$,[9] and the sulfides $S_4(NH)_4{\cdot}3S_8$,[10] $Co_6(\mu_3\text{-}S)_8(CO)_6{\cdot}3S_8$,[11] $(PPh_4)_4(Ag_2S_{20}){\cdot}S_8$,[12] and $(PPh_3)_2N[Ag(S_9)]{\cdot}S_8$.[13] In these compounds, van der Waals interactions appear to be responsible for the retention of octasulfur. As far as solution chemistry is concerned, in contrast with the well-established[14] formation of charge-transfer complexes of I_2, no clear-cut evidence of similar adducts has been reported for S_8.[15,16] However, S_8 is one of the candidates, together with H_2[17] and I_2,[18] to coordinatively add to transition-metal centers, possibly as a preliminary step to the ultimate oxidative-addition process.

In line with earlier findings that an oxidatively stable metal center such as rhenium(I) of d^6 configuration is very appropriate to study both I_2 addition to $ReI(CO)_{5-n}L_n$[19] (the triiodo complexes $Re(I_3)(CO)_{5-n}L_n$ being the products) and the coordination of organic dichalcogenides to $Re_2X_2(CO)_6(THF)_2$[20] to form the $Re_2X_2(CO)_6(E_2R_2)$ dimers,[21] we have succeeded in detecting what we believe to be the

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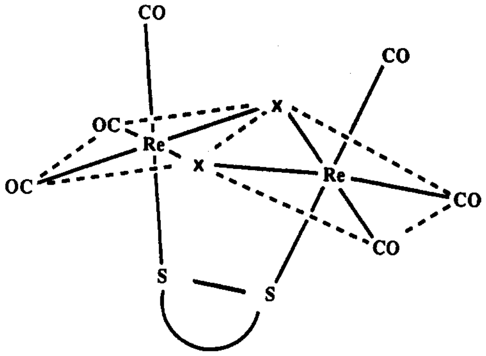
first adducts of S_8 to a transition-metal center in solution and isolating them.

We have found that a CS_2 solution of $Re_2I_2(CO)_6(THF)_2$, characterized by carbonyl stretching vibrations at 2027 and 1922 cm^{-1}, upon treatment with an equimolar quantity of S_8 shows new bands at 2052 m, 2037 s, 1967 s, and 1942 s cm^{-1}. Similar findings were obtained with the bromide derivative $Re_2Br_2(CO)_6(THF)_2$ (bands at 2031 m and 1922 s cm^{-1} in CS_2, shifted to 2056 m, 2041 s, 1968 s, and 1940 s cm^{-1} upon treatment with S_8). Removal of THF by addition of solid $ZrCl_4$ at about −10 °C to a CS_2 solution of $Re_2Br_2(CO)_6(THF)_2$ and S_8 or repeated evaporation of the medium (heptane) at room temperature or lower in the case of $Re_2I_2(CO)_6(CO)_6(THF)_2$ caused the *cyclo*-octasulfur adduct to be formed almost exclusively (see equilibrium 1).[22] The new coordination compounds are

$$Re_2X_2(CO)_6(THF)_2 + S_8 \rightleftarrows Re_2X_2(CO)_6(S_8) + 2THF \quad (1)$$

poorly soluble in aliphatic and aromatic hydrocarbons, have a limited stability at room temperature, and are decomposed by coordinating solvents. Thus, treatment with neat THF gives S_8.[20] The $\tilde{\nu}_{CO}$'s of the *cyclo*-octasulfur coordination compounds are similar to those of the dialkyl and diphenyl disulfide adducts of formula $Re_2X_2(CO)_6(S_2R_2)$ reported earlier[21] (e.g. for R = Me and X = Br,[21a] in heptane, $\tilde{\nu}_{CO}$ = 2060 m, 2043 s, 1966 s, 1961 m, 1935 s cm^{-1}), which were established crystallographically to possess a dimeric structure with bridging halides and disulfide. Similarly, a structure with part of the *cyclo*-octasulfur acting as a bidentate bridging ligand is suggested for the compounds of the present study. In such a structure (Chart I) the $Re_2(CO)_6$ core[23] of idealized C_{2v} symmetry should give five infrared-active $\tilde{\nu}_{CO}$'s ($2A_1$, $2B_1$, B_2), close to the experimental observation.

Chart I



No X-ray-quality crystals of these compounds have yet been obtained, but chemical and spectroscopic evidence leaves little doubt about the nature of these new species. The appears to be a finding relevant to the understanding of the preliminary steps in the oxidation of metal complexes by sulfur to give higher valent sulfides[24] or polysulfides.[25]

Work is in progress to extend this study to other metal systems and to elemental selenium.

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[22] $Re_2Br_2(CO)_6(THF)_2$ (0.575 g, 0.68 mmol) was dissolved in 35 mL of CS_2 together with S_8 (0.178 g, 0.69 mmol). The yellow solution was cooled to about −10 °C, and anhydrous $ZrCl_4$ (2.34 g, 10.0 mmol) was added. The suspension was stirred at about −5 °C for 4 h and then filtered. The dark red solution was concentrated in vacuo (0 °C) to about 5 mL, and heptane (10 mL) was added. The red precipitate was filtered off and dried under reduced pressure (0.32 g; 49% yield). Anal. Found (calcd) for $C_6Br_2O_6Re_2S_8$: C, 7.4 (7.5); H, 0.0 (0.0); Br, 17.2 (16.7); Re, 38.5 (38.9); S, 26.7 (26.8). Similarly, $Re_2I_2(CO)_6(THF)_2$ (1.09 g, 1.16 mmol) and S_8 (0.40 g, 1.56 mmol) were added to 50 mL of heptane. The resulting colorless suspension was stirred in the dark at 23–25 °C for 1 day, and the solvent was evaporated under reduced pressure in order to remove THF from the system. The operation was repeated until no more starting material was observed (IR for the resulting solid dissolved in CS_2). The final suspension was filtered, washed with heptane, and dried to afford the brick red product (0.75 g; 61% yield). Anal. Found (calcd) for $C_6I_2O_6Re_2S_8$: C, 6.9 (6.9); H, 0.0 (0.0); I, 22.8 (24.1); Re, 35.8 (35.4); S, 23.4 (24.4).

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[24] At room temperature, in CS_2, $Re_2X_2(CO)_6(S_8)$ species slowly decompose to give unidentified rhenium sulfides: the decomposition follows approximate first-order kinetics, $\tau_{1/2}$ being about 3.5 h for X = Br and 2.5 h for X = I.

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