Inorganica Chimica Acta, 116 (1986) L39

Synthesis and Structural Characterization of [ReO(Et_2NCS_2)(NHNC(S)SMe)], a Complex with a N,S-chelating Hydrazido(2–) Ligand

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(Received January 21, 1986)

Recently several hydrazido(1–), hydrazido(2–) and diazenido complexes of rhenium have been prepared and structurally characterized [1–4]. As part of a systematic study of the ligation of *S*-methyl dithiocarbazate, $NH_2NHC(S)SCH_3$ [5–7], we have investigated reactions of this ligand with oxo-rhenium compounds. Using oxo-molybdenum complexes as starting materials, we obtained mono- and dinuclear complexes with linear diazenido and (N,S)-chelating hydrazido(1–) or (3–) (for the terminology of the latter see ref. 8) ligands derived from *S*-methyl dithiocarbazate. In these reactions generally, the oxygen atoms were abstracted and replaced by diazenido ligands [5–7]. As shown in this paper, oxo-rhenium(V) compounds do not react with *S*-methyl dithiocarbazate to form diazenido complexes. Therefore more reactive species like the silylated diazene Me_3SiN_2Ph have to be used [3].

The complex [ReO(Et_2NCS_2)(NHNC(S)SMe)], **I**, was prepared in very good yields by reacting $Re_2O_3(Et_2NCS_2)_4$ with excess $NH_2NHC(S)SCH_3$ in refluxing methanol. In the 3000–3500 cm^{-1} region **I** shows just one strong band at 3220 cm^{-1} assignable to νNH. The bands at 1540, 1500 and 960 cm^{-1} can be assigned to δNH, νCN of the dithiocarbazate ligand and νReO, respectively. The presence of a NH– group is supported by a singlet at 7.35 ppm in the ^1H NMR spectrum (further signals: $\delta = 2.05$ (t, CH_2), 2.90 (s, SCH_3), 3.10 (q, CH_2), acetone-d_6). Black, plate-like crystals of **I** suitable for X-ray diffraction were grown from methanol dichloromethane. Crystal data: space group *Ia* (non-standard setting of space group *Cc*), $a = 14.71(3)$, $b = 9.73(4)$, $c = 13.79(6)$ Å, $\beta = 101.6(3)°$, $V = 1933(1)$ Å^3, $Z = 4$. Structure solution and refinement were based on 1216 reflections to give a final discrepancy factor of 0.092.

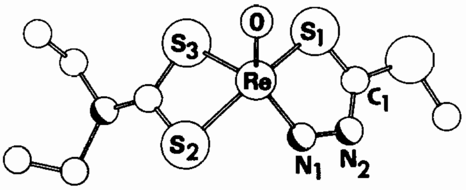

Fig. 1. ORTEP diagram of ReO(Et_2NCS_2)(NHNCSSMe). Selected bond distances (Å) and angles (deg): Re–S1, 2.282(9); Re–S2, 2.44(2); Re–S3, 2.36(2); Re–O, 1.93(5); Re–N1, 2.01(4); N1–N2, 1.38(4); C1–S1, 1.73(3); C1–N2, 1.36(4); S1–Re–S2, 140(1); S3–Re–N1, 120(1); O–Re–N1, 142(2); O–Re–S2, 127(2).

An ORTEP view of the molecule is presented in Fig. 1, including selected bond lengths and angles. The overall geometry of the rhenium is highly distorted square pyramidal, unusual for oxo-rhenium(V) complexes. The coordination polyhedron can equally be described as a trigonal bipyramid with the ligands O, N1 and S3 in the equatorial plane. It is difficult to give any reasons for the distortion. According to the spectroscopic and structural results the *S*-methyl dithiocarbazate is singly deprotonated at both nitrogen atoms and acts therefore like a hydrazido(2–) ligand, but the second negative charge is mainly localized at S1 as shown by the bond lengths in the –NCS– group and by the rather short Re–S1 distance. The Re–N1 bond is considerably shorter than the Mo–N bond in [Mo(N_2CSSEt)(NH_2NCSSMe)($(Me_2NCS_2)_2$)] [5], where the nitrogen atom is not deprotonated. The remaining rhenium–ligand bond distances are normal.

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