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Synthesis and X-ray Structural Characterization of $[WS(S_2CNEt_2)_3]BF_4$

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While the chemistry of tungsten is in many ways similar to that of molybdenum, some notable differences are apparent in the high-valent chemistry of these elements. In particular, the propensity of oxo–W(VI) complexes to undergo hydrolytic or spontaneous decomplexation and polytungstate formation limits the stability of such complexes. As a striking example, dithiocarbamate complexes such as *cis*-$WO_2(S_2CNR_2)_2$, $WOCl_2(S_2CNR_2)_2$, and $[WO(S_2CNR_2)_3]^+$ are reportedly unstable or unknown [1, 2], in contrast to the well known molybdenum analogues [3–5]. We are exploring the synthesis and reactivity of oxo– and thio–W(VI) complexes and report herein the synthesis and characterization of the $[WS(S_2CNEt_2)_3]^+$ cation which, in contrast to the oxo species above, has no known molybdenum analogue.

The anaerobic reaction of $WSCl_4$ and three equivalents of $Me_3SiS_2CNEt_2$ in dichloromethane results in the formation of at least two metal complexes, known $WS(S_2)(S_2CNEt_2)_2$ [6, 7] and the new complex cation $[WS(S_2CNEt_2)_3]^+$. Workup of the reaction in the presence of added $NaBF_4$ leads to the isolation of air stable, diamagnetic, orange–red crystals of $[WS(S_2CNEt_2)_3]BF_4$. The infrared spectrum of the compound exhibits bands due to bidentate $S_2CNEt_2^-$ ligands [ν(CN) 1550, 1525 cm^{-1}], BF_4^- (br 1100 cm^{-1}) and a terminal thio ligand [ν(W=S) 510 cm^{-1}]. ^1H NMR spectroscopy reveals that the complex is fluxional in $CDCl_3$ at room temperature, in contrast to related $[MoO(S_2CNR_2)_3]^+$ complexes which become fluxional at relatively high temperatures (>65 °C) [5]. Crystals suitable for an X-ray structure determination were grown by slow addition of diethylether to a dichloromethane solution of the compound.

Crystal data: $C_{15}H_{30}BF_4N_3S_7W$, $M = 747.5$, monoclinic, space group $P2_1/a$, $a = 12.293(1)$, $b = 17.229(5)$, $c = 14.257(2)$ Å, $\beta = 113.69(1)°$, $U = 2765(2)$ Å^3, $D_c = 1.796$ g cm^{-3} ($Z = 4$). Data (7237 total, 6345 unique, 3961 with $I > 2.5\sigma(I)$) were collected on a CAD4 diffractometer using monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The structure was solved from the Patterson map and refined by a full-matrix least-squares procedure (SHELX). The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the model at their calculated positions. The refinement converged with $R = 0.039$, $R_w = 0.040$ for $w = [\sigma^2(F) + 0.003|F|^2]^{-1}$.

The seven-coordinate complex (Fig. 1) possesses a distorted pentagonal bipyramidal (PB) geometry. The δ angles [8] derived from the normalized coordination polyhedron are in good agreement with those calculated for an idealized PB geometry. The δ angles, corresponding to the dihedral angles between the polyhedral faces that intersect along the edges S(3)..S(4), S(3)..S(7), and the internal 'edge' S(4)..S(7), are 47.4, 48.9 and −76.7°, respectively. A similar set of δ angles for the corresponding edges on the opposite side of the equatorial plane are 64.1, 62.3 and −61.7°. For an idealized D_{5h} PB geometry the δ angles are 54.4, 54.4 and −72.8° [8]. The terminal thio ligand S(1) occupies an axial position, a unique $S_2CNEt_2^-$ ligand spans the other axial position and an equatorial position while the two remaining $S_2CNEt_2^-$ ligands occupy four equatorial sites. The limited bite angle of the spanning dithiocarbamate ligand is mainly responsible for the distortions from ideal PB geometry. The W atom lies 0.2755(2) Å out

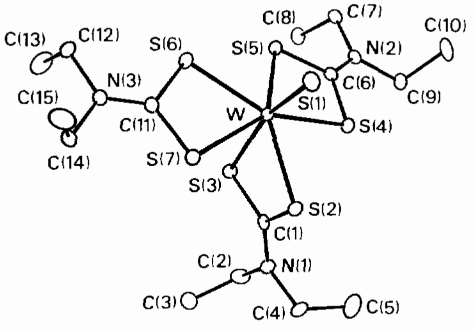

Fig. 1. Structure of the $[WS(S_2CNEt_2)_3]^+$ cation (excluding hydrogen atoms) showing the atom labelling scheme. Selected bond lengths (Å) and angles (°) are: W–S(1), 2.127(2); W–S(2), 2.502(2); W–S(3), 2.575(2), W–S(4), 2.510(2); W–S(5), 2.462(2); W–S(6), 2.464(2); W–S(7), 2.505(2); ⟨S–C⟩, 1.718 ± 0.016 (± indicates maximum deviation from mean); ⟨S_2C–N⟩, 1.306 ± 0.005 Å; S(1)–W–S(2), 96.0(1); S(1)–W–S(3), 165.0(1); S(1)–W–S(4), 93.1(1); S(1)–W–S(5), 104.5(1); S(1)–W–S(6), 102.8(1); S(1)–W–S(7), 94.7(1); S(2)–W–S(3), 69.0(1); S(3)–W–S(4), 81.8(1); S(4)–W–S(5), 68.6(1); S(5)–W–S(6), 71.1(1); S(6)–W–S(7), 68.7(1)°.

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of the plane defined by S(4)–S(7) toward the terminal thio ligand. The W–S(1) bond has a length of 2.127(2) Å. The W–S(3) bond length of 2.575(2) Å is considerably longer than the remaining W–S bonds (2.462–2.510(2) Å) due to the *trans* influence of the W–S(1) bond. Bond lengths within the essentially planar dithiocarbamate ligands are consistent with the values found in other related complexes [9–11].

We are now exploring the chemistry of $[WS(S_2CNR_2)_3]^+$ complexes, in particular the possible formation of mixed-valence $[W_2S(S_2CNR_2)_6]^+$ complexes upon reaction with PPh_3 [12]. Comparative studies of the reactivity of oxo– and sulfido–Mo and –W complexes may provide a clearer understanding of the catalytic inactivity of various tungsten-substituted molybdoenzymes. Variable temperature NMR studies aimed at elucidating the mechanism of the molecular rearrangement (fluxionality) are also in progress.

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