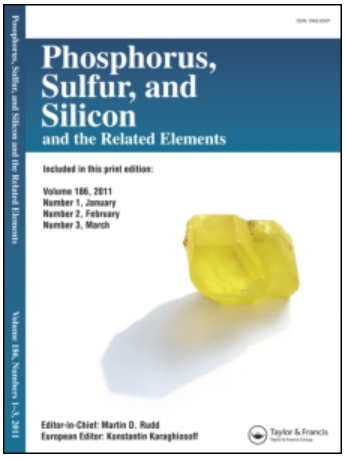

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PREPARATION AND STRUCTURAL STUDIES OF $[Mo(N_3S_2)\{R_2(O)PNP(S)R_2\}_2]$

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Abstract The compounds $[Mo(N_3S_2)\{Ph_2(O)PNP(S)Ph_2\}_2]$ **1** $[Mo(N_3S_2)\{^iPr_2(O)PNP(S)^iPr_2\}_2]$ **2** have been synthesised by treating $[MoCl_3(N_3S_2)]$ with $KN(PPh_2S)_2$ or $KN(P^iPr_2S)_2$. X–Ray structures of **1** and **2** have been solved. On complexation, the MoN_3S_2 ring remained planar, but the $Mo(OPNPS)_2$ rings are puckered.

Keywords: Molybdenum complex; imidodiphosphinate derivatives; metalla–cycles; sulfur–nitrogen; EPR.

INTRODUCTION

There has been much interest in the chemistry of molybdenum in its highest oxidation state when stabilised by the trianionic $N_3S_2^{3-}$ ligand. This area has produced large quantities of publications especially in the 80s.[1] Since then very little chemistry has been reported. However, there are three reported examples of mixed-ligand complexes of

molybdenum containing $N_3S_2^{3-}$ with the halides displaced by catecholate, phenanthroline or bipyridyl (EQUATIONS 1 and 2).[2]

$$[Mo(N_3S_2)Cl_3]_x + 2H_2DTBC \xrightarrow{4NaOMe} Na[Mo(N_3S_2)DTBC_2] \quad \text{Eqn 1}$$

$$[Mo(N_3S_2)Cl_3]_x + H_2DTBC \xrightarrow[L = phen \text{ or } bpy]{2NaOMe} [Mo(N_3S_2)(DTBC)Cl(L)] \quad \text{Eqn 2}$$

Here we report the preparation of $[Mo(N_3S_2)\{Pr_2(O)PNP(S)Ph_2\}_2]$ (**1**) and $[Mo(N_3S_2)\{^iPr_2(O)PNP(S)^iPr_2\}_2]$ (**2**). The X–Ray structures of **1** and **2** are discussed.

RESULTS AND DISCUSSION

1 and **2** were prepared from the treatment of the metal complex $[Mo(N_3S_2)Cl_3]_x$ with $KN(PPh_2S)_2$ or $KN(P^iPr_2S)_2$ in dichloromethane (EQUATION 3). After work-up, the resulting green powder was recrystallised from acetonitrile to give dark emerald green crystals. The crystals are air stable but the compounds are air-sensitive in solution. Both metal complexes have one sulfur atom of each $N(PR_2S)_2$ ligand replaced by oxygen during the course of the reaction. **1** in $CDCl_3$ displayed a group of broad peaks in the $^{31}P - \{^1H\}$ NMR spectrum ($\delta = 55$ ppm). The IR spectra showed that the ν(Mo=N) has shifted to a higher frequency, from 955 cm^{-1} in the starting material to 1047 cm^{-1} for **1** and 1045 cm^{-1} for **2**.

$$[Mo(N_3S_2)Cl_3]_x + 2KN(PR_2S)_2 \longrightarrow [Mo(N_3S_2)\{R_2(O)PNP(S)R_2\}_2]$$
$$R = Ph \text{ or } ^iPr$$

EQUATION 3

During the reaction molybdenum complexes have been reduced from Mo(VI) to Mo(V) forming neutral complexes.

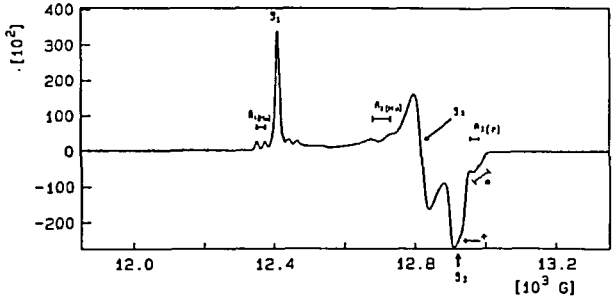

FIGURE 1 EPR spectrum of **1**.

The EPR spectrum for **1** in toluene solution at 298 K gave the parameters $g_{iso} = 1.944$ and $A_{iso(Mo)} = 31$ G, the average of the anisotropic parameters from the frozen solution spectrum ($g_1 = 1.988$, $g_2 = 1.924$, $g_3 = 1.910$, $A_{1(Mo)} = 23$ G, $A_{2(Mo)} = 51$ G and $A_{3(Mo)} = 19$ G) illustrated in FIGURE 1. The largest hyperfine couplings (* and + in FIGURE 1) on the g_3 signal are from the ^{31}P nuclei. **2** has similar EPR patterns as **1**.

The X-ray structures of **1** and **2** show (FIGURES 2 and 3) the metals have octahedral co-ordination with distortions associated with the mixed ligands. In the molecules, the molybdenum atoms are members of nearly planar MoN_3S_2 rings with the MoN bond distances still corresponding to double bonds comparable to the starting metal complex $[Mo(N_3S_2)Cl_3]$. The Mo–O bonds of the $Mo(OPNPS)_2$ rings *trans* to nitrogen are shorter (*ca.* 0.4 Å) than Mo–S *cis* to nitrogens. Its the sulfur atoms that are *trans* to nitrogen have been replaced by oxygen atoms. The $Mo(OPNPS)_2$ rings are puckered.

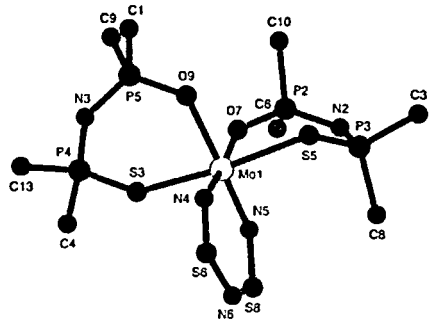

FIGURE 2. Molecular structure of **1**

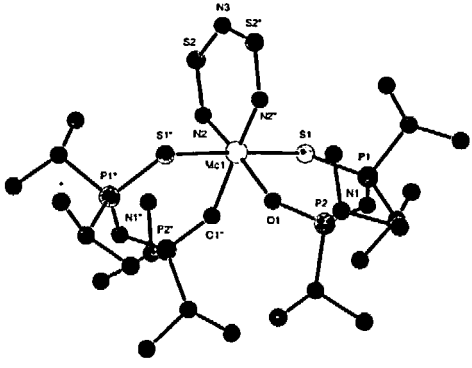

FIGURE 3. Molecular structure of **2**.

Acknowledgement

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