Inorganica Chimica Acta, 54 (1981) L131–L132
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Molybdenum-95 NMR of Molybdenum–Sulfur and –Selenium Species. Structural Characterisation of the $[(CN)CuS_2MoS_2]^{2-}$ Anion

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Received May 19, 9181

The ^{95}Mo nucleus has been shown [1, 2] to have an extended NMR chemical shift range and it is expected that subtle electronic and structural effects can be detected by ^{95}Mo NMR. Consequently, the technique has potential for application to the molybdo-enzyme and related areas where a sensitive spectroscopic probe of molybdenum in the diamagnetic states is currently unavailable. However, quadrupolar line broadening associated with this nucleus ($I = 5/2$) in sites of reduced symmetry might be expected to restrict the chemical usefulness of ^{95}Mo NMR in these areas. This letter reports that a combination of acceptably narrow linewidths (<50 Hz) and rapid data accumulation (presumably associated with favourable relaxation processes) is observed for various molybdenum–sulfur species of reduced symmetry. New chemical shift data are shown schematically in Fig. 1. It should be noted that the chemical shifts are solvent-dependent (*e.g.* $[MoS_4]^{2-}$: H_2O, 2254; MeOH, 2230; MeCN, 2207; DMF, 2192; DMSO, 2176 ppm) and can vary by 100 ppm from the values of Fig. 1.

The series of anions $[MoO_{4-n}S_n]^{2-}$ ($n = 0–4$) show [3] narrow experimental linewidths (<10 Hz) and a systematic decrease in shielding of the molybdenum nucleus as the number of sulfido ligands increases. The related series $[MoO_{4-n}Se_n]^{2-}$ exhibits a similar chemical shift variation (Fig. 1) and solvent dependency, which gives considerable confidence to the assignments. $[MoSe_4]^{2-}$ has the most deshielded signal observed to date and extends the known chemical shift range to 5500 ppm ($[MoSe_4]^{2-}$ in MeCN:3339; $[(\eta\text{-}C_5H_5)Mo(CO)_3]^-$ in CH_2Cl_2: −2120). ^{95}Mo shielding increases in the order Se < S < O, an order at variance with a recent prediction [4]. While detailed systematic study is required to understand the factors which determine the ^{95}Mo chemical shift, an essentially linear correlation of the chemical shifts with the inverse of the energy of the first allowed electronic transtion [5] suggests [6] that a major contribution to the chemical shift in these $[MoO_{4-n}X_n]^{2-}$ systems may arise from temperature-independent paramagnetism.

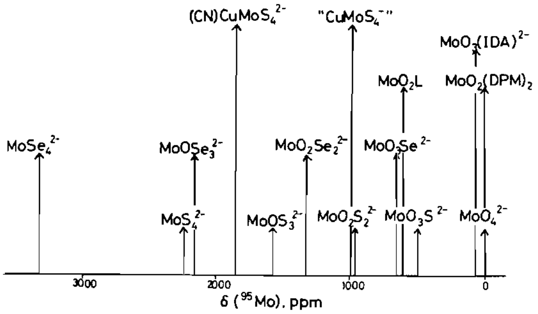

Fig. 1. ^{95}Mo chemical shift scale ($H_2(IDA)$:$HN(CH_2CO_2H)_2$; H(DPM):$OC(Bu^t)CHC(Bu^t)OH$; H_2L: $(-CH_2N(Et)CH_2CH_2SH)_2$.

Compounds containing the $Mo(VI)O_2$- and $Mo(VI)O_3$-structural units also provide useful NMR data (Fig. 1). In particular, the narrow band widths (*ca.* 40 Hz) and the sensitivity of the chemical shift to minor changes in the quadridentate ligand in the species $[MoO_2L]$ containing *trans* thiolate ligands (confirmed in solution by ^{13}C NMR) is noteworthy: $\delta(^{95}Mo)$ in MeCN:H_2L = $(-CH_2N(Me)CH_2CH_2SH)_2$, 599 ppm ($w_{h/2}$ 55 Hz); $N(CH_2CH_2SH)_2$ $(CH_2CH_2NMe_2)$, 605(35); $(-CH_2N(Et)CH_2CH_2SH)_2$, 629(40).

There is current interest in the chemical basis of the Cu–Mo–S interaction [7, 8] in higher animals. We have synthesised red, diamagnetic, crystalline $(Pr^n_4N)_2[(CN)CuS_2MoS_2]$ in high yield by extraction of $(NH_4)CuMoS_4$ [9] with aqueous cyanide followed by recrystallisation from ethanol (infra-red data: ν(CN), 2120 cm^{-1}, ν(MoS), 500, 489, 452, 410 br cm^{-1}; electronic spectral maxima (ϵ, M^{-1} cm^{-1} in MeCN), 470 nm (6500) 317 nm (19,800). Conductance measurements Λ (10^{-3} *M*), 268 ohm^{-1} mol^{-1} cm^2) suggest the presence of a 2:1 electrolyte in MeCN [10].

The compound was structurally characterised by a single crystal X-ray diffraction study**. The molecular structure (Fig. 2) reveals a pseudo-tetrahedral MoS_4 group acting as a bidentate ligand to an essentially linear Cu–CN unit. The $Cu(\mu\text{-}S)_2Mo$ moiety is essentially planar and coordination of the Cu–CN unit has increased the bridging MoS bond lengths by

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**See footnote overleaf.

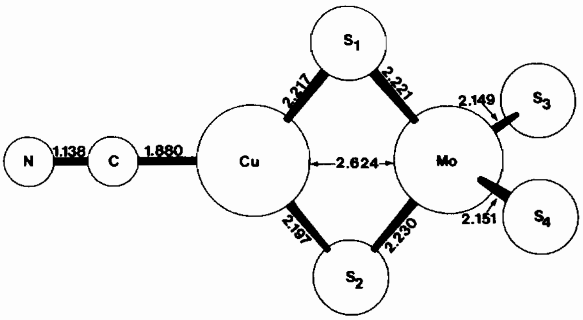

Fig. 2. A three-dimensional representation [13] of the $[(CN)CuS_2MoS_2]^{2-}$ anion showing relevant bond lengths. Bond angles: NCCu, 179.3(5); CCuS, 125.7(1); $CCuS_2$; CCuMo, 179.3(2); S_1CuS_2, 108.1(1); CuS_2Mo, 72.7(2); CuS_1Mo 72.5(2), S_1MoS_2, 106.7(1), S_1MoS_3 110.0(1); S_1MoS_4, 109.9(1); S_2MoS_3, 109.9(1); S_2MoS_4, 109.9(1); S_3MoS_4, 110.4(1)°.

0.10 Å from their value [5] in $[MoS_4]^{2-}$. The other structurally characterised CuMoS species are polymeric $(NH_4)CuMoS_4$ [9], tetranuclear $[(CuPPh_3)_3\text{-}MoS_4Cl$ [13] and trinuclear $[(PPh_3)_2CuS_2MoS_2Cu\text{-}(PPh_3)]$ [14].

The ^{95}Mo NMR signal of $(Pr^n_4N)_2[(CN)CuS_2\text{-}MoS_2]$ in MeCN is shielded relative to $[MoS_4]^{2-}$ (Fig. 1) and the linewidth is increased ($W_{h/2}$, 38 *vs.* 0.3 Hz), presumably as a consequence of the lower effective symmetry at the molybdenum nucleus due to the presence of the adjacent (quadrupolar) copper nucleus. The more highly shielded signal for the structurally uncharacterised species $(Et_4N)CuMoS_4$ in MeCN illustrates the potential of ^{95}Mo NMR in the examination of diamagnetic, metal–molybdenum–sulfur systems.

Factors influencing the chemical shift, linewidths, relaxation processes and solvent dependencies of the ^{95}Mo NMR of the present compounds and related species are currently under investigation.

Acknowledgements

We thank the Wool Research Trust Fund (Australian Wool Corporation) and the Australian Research Grants Committee for financial support.

References

1 (a) W. D. Kautt, H. Krüger, O. Lutz, H. Maier and A. Nolle, *Z. Naturforsch., 31a,* 356 (1976).
(b) O. Lutz, A. Nolle and P. Kroneck, *Z. Naturforsch., 31a,* 454 (1976).
2 (a) A. F. Masters, R. T. C. Brownlee, M. J. O'Connor, A. G. Wedd and J. D. Cotton, *J. Organometal. Chem., 195,* C17 (1980).
(b) A. F. Masters, S. F. Gheller, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem., 19,* 3866 (1980) and unpublished work.
(c) A. F. Masters, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, submitted to *Inorg. Chem.,* 1981.
3 O. Lutz, A. Nolle and P. Kroneck, *Z. Naturforsch., 32a,* 505 (1977). *Z. Physik A, 282,* 157 (1977).
4 R. G. Kidd, *Ann. Reports NMR Spectr., 10A,* 20 (1980).
5 E. Diemann and A. Müller, *Coord. Chem. Rev., 10,* 79 (1973).
6 R. G. Kidd and R. J. Goodfellow, in 'NMR and the Periodic Table', Ed., R. K. Harris and B. E. Mann, Academic Press, London, 195 (1978).
7 M. P. Coughlan, Ed., 'Molybdenum and Molybdenum-Containing Enzymes', Pergamon, 1980.
8 E. J. Underwood, 'Trace Elements in Human and Animal Nutrition', 4th ed., Academic Press, New York, 1977.
9 W. P. Binnie, M. J. Redman and W. J. Mallio, *Inorg. Chem., 6,* 1449 (1970).
10 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971);
J. A. Davis, F. R. Hartley and S. J. Murray, *Inorg. Chim. Acta, 43,* 69 (1980).
11 G. M. Sheldrick, 'SHELX-Program for Crystal Structure Determination', University of Cambridge, 1976.
12 W. D. S. Motherwell, 'PLUTO-Program for Molecular Plotting', University of Cambridge, 1977.
13 A. Müller, H. Bögge and U. Schimanski, *J. Chem. Soc. Chem. Commun.,* 91 (1980).
14 A. Müller, H. Bögge and U. Schimanski, *Inorg. Chim. Acta, 45,* L249 (1980).

**Crystal Data: $C_{25}H_{56}CuMoN_3S_4$, MW = 686.5, anorthic, $P\bar{1}$, a = 9.712(1), b = 12.686(3), c = 14.474(2) A, α = 76.07(1), β = 83.98(1), γ = 81.19(1)°, V = 1705.96 A^3; Z = 2, d_c = 1.33 g cm^{-3}, d_m = 1.299 g cm^{-3}; $F(000)$ = 721; μ(Mo-Kα) = 12.10 cm^{-1}. The positions of the Mo and Cu atoms were located by direct methods using the SHELX [11] system of programs. The remaining non-hydrogen atoms were located from subsequent difference Fourier synthesis [12]. The hydrogen atom positions were calculated using standard geometry with all C–H distances fixed at 0.965 A. The final R-factors are R = 3.99%, R_w = 4.77% where $w = 4.3384/(\sigma^2(F_o) + 0.0001\ F_o^2)$ for 3709 independent reflections. [$I \geqslant 2.5\sigma(I)$, $1.5° \leqslant \theta \leqslant 27°$, Enraf-Nonius CAD-4 diffractometer]. Full details will be provided in a detailed paper to be published subsequently.