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^{95}Mo Nuclear Magnetic Resonance Spectra of Tetrathiomolybdate(VI) Complexes of d^{8} Metals

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^{95}Mo NMR spectroscopy is now established as a valuable probe of the environment of this element in diamagnetic systems [1]. Recent studies have shown that the molybdenum chemical shift provides a sensitive probe of the particular chemical environment of this element in M–Mo–S (M = Cu, Ag, or Au) clusters [2–4]. Herein we report an extension of these studies to the $[M'(MoS_4)_2]^{2-}$ (M′ = Ni, Pd, or Pt) complexes reported by Müller *et al.* [5] and Callahan and Piliero [6]. $[PPh_4]_2[Ni(MoS_4)_2]$ has been structurally characterised; two bidentate $\{MoS_4\}$ groups provide a planar coordination geometry at the nickel and the Ni----Mo separation of 2.80 Å was not considered indicative of a direct metal–metal bond [7].

^{95}Mo NMR spectra were recorded on a Varian XL 300 spectrometer operating at a frequency of 19.55 MHz for solutions of the $[NPr_4]_2[M'(MoS_4)_2]$ salts (*ca.* 0.05 M) in DMF at *ca.* 21 °C. The spectra recorded are shown in Fig. 1 and the chemical shifts and linewidths are summarised in Table I.

Clearly, these results show that coordination of $[MoS_4]^{2-}$ to Ni(II), Pd(II), or Pt(II) results in an increased shielding of the molybdenum nucleus. The magnitude of this shielding increases down the group (Pt > Pd > Ni) in contrast to observations for $\{MoS_4\}$ complexes of Cu, Ag and Au. Thus, for $[MoS_4(MCN)]^{2-}$ (M = Cu or Ag) [2], $MoS_4(MPPh_3)(M(PPh_3)_2)]$ (M = Cu or Ag) [4], and $[MoS_4(MPPh_3)_2]$ (M = Ag or Au) [4] the increased shielding varies as Au > Cu > Ag.

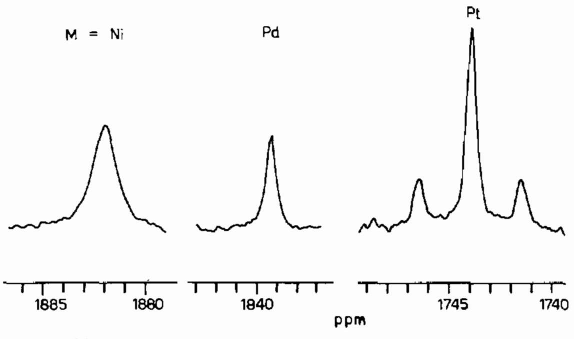

Fig. 1. ^{95}Mo NMR spectra of $[NPr_4]_2[M'(MoS_4)_2]$ (M′ = Ni, Pd or Pt) in DMF at *ca.* 21 °C, the linewidths are not directly comparable due to the use of different exponential weightings in the free induction decay.

TABLE I. ^{95}Mo NMR Chemical Shifts (δ)^{a} of $[NPr_4]_2[M'(MoS_4)_2]$ (M′ = Ni, Pd or Pt) in DMF Solution at *ca.* 21 °C

Compound	δ (ppm)	$J(M'-Mo)$ (Hz)
$[NPr_4]_2[Ni(MoS_4)_2]$	1882 ± 2	
$[NPr_4]_2[Pd(MoS_4)_2]$	1839 ± 2	
$[NPr_4]_2[Pt(MoS_4)_2]$	1744 ± 2^{b}	96 ± 1

^{a}Chemical shifts were referenced externally to a solution of $Na_2[MoO_4]$ (2 M) in D_2O at 21 ± 1 °C and an apparent pH of 11, linewidths at half-height <20 Hz in each case. Acquisition parameters; transmitter frequency = 19.545 MHz; acquisition time = 0.4 s; pulse width = 17 μs; number of points = 32×10^3. ^{b}For central resonance.

A notable aspect of the ^{95}Mo NMR spectrum of $[NPr_4]_2[Pt(MoS_4)_2]$ is the appearance of a doublet centred on the main resonance which is attributed to ^{95}Mo–^{195}Pt coupling (^{195}Pt, $I = ½$, natural abundance 33.8%), $J(^{95}Mo, ^{195}Pt) = 96$ Hz. This represents the first reported NMR observation of molybdenum–metal (M) coupling in an Mo–S–M cluster and, also, provides a novel example of Mo–Pt coupling. The magnitude of this coupling implies the existence of a significant interaction between the metals of $[Pt(MoS_4)_2]^{2-}$ and, presumably, this is also true for the corresponding nickel and palladium systems.

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