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Molybdenum-95 NMR Chemical Shifts of some Ionic Molybdenum(0) Carbonyl Complexes

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Introduction

Molybdenum-95 NMR spectroscopy has recently been established as a sensitive probe of both electronic and structural effects in diamagnetic molybdenum complexes [1–4]. The chemical shift range is *ca.* 7000 ppm for species in all oxidation states; values extend from –450 to –2100 ppm for Mo(0) complexes, which are the most extensively studied. For the substituted carbonyl compounds, $Mo(CO)_{6-x}L_x$ (x = 1–3, L = PR_3, AsR_3, SbR_3, NR_3), a correlation is apparent between the ^{95}Mo chemical shift and the position of the ligand in a spectrochemical series [3]. Shifts of $\delta(^{95}Mo)$ of up to 40 ppm have been reported for substituent effects involving ligand atoms six bonds away from the molybdenum atom [5, 6].

A recent paper [7] has reported the identification in DMSO solution of unstable complexes of the type *cis*-$M(CO)_4L\text{–}L]^-$ (MO = Cr, Mo, W; L–L = diethyldithiocarbamate and ethylxanthate anions) by their IR spectra in the carbonyl stretching frequency region. This paper demonstrates the usefulness of ^{95}Mo NMR spectroscopy in characterizing a wider range of these non-isolable molybdenum(0) species. The chemical shift data for the $[Mo(CO)_5L]^-$ and $[Mo(CO)_4L\text{–}L]^-$ (L = Cl, Br, dithiocarbamato; L–L = dithiocarbamato, xanthato and phosphorodithioato) species represent the first available $\delta(^{95}Mo)$ values for molybdenum(0) complexes of sulfur ligand.

Experimental

Molybdenum-95 NMR spectra were obtained from naturally abundant samples with a Bruker WH-400 NMR spectrometer in the pulsed Fourier transform mode. The probe was specifically tuned for ^{95}Mo at 26.08 MHz using a field strength of 9.3956 T. All samples were measured at ambient temperature (293 ± 2 K) with chemical shifts referenced to aqueous 2 *M* K_2MoO_4 at pH 11. Pulse widths of 75 msec were found to give adequate S/N with approximately 1000 transients on 0.1 mol dm^{-3} solutions. A typical spectral width of 10 KHz was used for an FID of 4000 or 16000 data points.

Solution IR spectra were obtained using matched KBr sealed cells with a path length of 0.2 mm. Solution concentrations of approximately 0.01 mol dm^{-3} were found to give good spectra on a Perkin-Elmer 180 grating infrared spectrophotometer which was previously calibrated against polystyrene film.

All complexes were prepared according to published procedures [7, 8]. The compounds $[R_4N][Mo(CO)_5X]$ (R = Me, Et; X = Cl, Br) were prepared [8] by heating a degassed diglyme solution of $Mo(CO)_6$ and the appropriate tetraalkylammonium halide to 120 °C for 2 h followed by addition of petroleum ether (30–60 °C) to the cooled solution until incipient crystallisation. Chilling in the freezer resulted in bright yellow crystals in greater than 90% yield.

Compounds of the type $[Cat][Mo(CO)_5L]$ and $[Cat][Mo(CO)_4L\text{–}L]$ (Cat = Na, K, NH_4; L, L–L = dithiocarbamato, xanthato, phosphorodithioato) were prepared [7] by heating (60–65 °C) $Mo(CO)_6$ and the ligand salt in degassed DMSO for 30–45 min. $[NH_4][Mo(CO)_4S_2CN(CH_2)_4]$ was prepared in N-methylpyrole (NMP). These complexes could not be isolated; NMR spectra were recorded on the cooled solutions while IR spectra were recorded on diluted solutions from the NMR tube subsequent to NMR analyses.

Results and Discussion

Molybdenum hexacarbonyl readily reacts with dithiocarbamate, xanthate and phosphorodithioate anions in warm DMSO to form ionic complexes of the type $[Cat][Mo(CO)_4L\text{–}L]$ [7]. Displacement of the carbonyl groups is apparently stepwise, as $[M(CO)_5L\text{–}L]^-$ anions are also detected in this work in some cases. Identification of these latter species is assisted by comparison of their ^{95}Mo NMR chemical shifts with those found for $[M(CO)_5X]^-$ (X = Cl, Br) anions. For NaS_2CNPh_2, only the pentacarbonyl derivative is found by ^{95}Mo NMR and IR spectral measurements of the DMSO solutions. The possible occurrence of unidentate dithiocarbamate groups is unprecedented in Group VI chemistry. For reactions of $Mo(CO)_6$ and $NH_4S_2P(OEt)_2$ or $NH_4S_2N(CH_2)_4$, a competing reaction leads to the formation of sulphido bridged Mo(V)

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TABLE I. Molybdenum-95 NMR Data for Some Ionic Molybdenum(0) Complexes.

Compound	Solvent	δ ^{95}Mo (ppm)	$\Delta\nu_{1/2}$ (Hz)
$[NH_4][Mo(CO)_5S_2P(OEt)_2]$	DMSO	−1626	90
$Na[Mo(CO)_5S_2CNPh_2]$	DMSO	−1596	46
$[Et_4N][Mo(CO)_5Br]$	CH_2Cl_2	−1551	102
$[Me_4N][Mo(CO)_5Cl]$	CH_2Cl_2	−1538	76
$Na[Mo(CO)_5S_2CNMe_2]$	DMSO	−1534	98
$[Et_4N][Mo(CO)_5Cl]$	CH_2Cl_2	−1513	108
$K[Mo(CO)_4S_2COEt]$	DMSO	−1417	172
$Na[Mo(CO)_4S_2CNMe_2]$	DMSO	−1414	273
$Na[Mo(CO)_4S_2CNEt_2]$	DMSO	−1409	169
$[NH_4][Mo(CO)_4S_2P(OEt)_2]$	DMSO	−1390	148
$K[Mo(CO)_4S_2CN(CH_2)_4]$	DMSO	−1388	254
$[NH_4][Mo(CO)_4S_2CN(CH_2)_4]$	NMP	−1380	271

dimeric species [9] that are not detected by ^{95}Mo NMR spectroscopy. We have circumvented this problem for the $NH_4S_2CN(CH_2)_4$ reaction by either converting the commercially available ammonium salt to the potassium salt or by performing the reaction in N-methylpyrole. Except for the previous report of data for $[Mo(CO)_5X]^-$ [3, 10], this note represents the first ^{95}Mo NMR study of ionic Mo(0) complexes as well as the initial report involving Mo(0) and sulphur ligands.

The ^{95}Mo NMR chemical shifts for some ionic pentacarbonyl and tetracarbonyl species incorporating either halide or potentially bidentate sulfur ligands are listed in Table I. The $\delta(^{95}Mo)$ values for $[Mo(CO)_5L]^-$ (−1626 to −1513 ppm) and $[Mo(CO)_4L{-}L]^-$ (−1417 to −1380 cm^{-1}) are intermediate between those reported earlier for $Mo(CO)_{6-x}L_x$ (x = 1,2) complexes with L being phosphines and amines [3]. It is noteworthy that shielding of the molybdenum atom in the present pentacarbonyl anions is comparable for the halide and monodentate sulphur ligands. This shielding correlates with the relative positions of these ligands in the spectrochemical series [11], with deshielding (w.r.t. $Mo(CO)_6$ near −1850 ppm [3]) being expected for ligands with smaller ligand field splitting ΔE according to the Ramsey formalism for the paramagnetic shielding term [3, 12]. Contributions due to the inverse dependence on the cube of the d-electron radius, as well as covalency effects, must also be important, as shown by the higher shielding found for the heavier halide ions [3]. The high polarizability of the dithiocarbamato, xanthato, and phosphorodithioato ligands places them high in the nephelauxetic series [13], thus a contribution to increased molybdenum shielding is expected. Alternatively, the order of chemical shifts, assuming nearly constant σ donor ability of the sulfur ligands, reflects a decreased π acceptor ability (or increased π donor ability) in the order $S_2COEt > S_2CNMe_2 > S_2CNEt_2 > S_2P(OEt)_2 > S_2CN(CH_2)_4$ (for the $[Mo(CO)_4L{-}L]^-$ series). The reversal of the order for $S_2P(OEt)_2$ and S_2CNMe_2 in the two types of complexes shows that different factors are important to the shielding in the two series of complexes and caution is warranted in assessing their relative importance of comparing $\delta(^{95}Mo)$ values between the series. It can however be stated that the order of chemical shifts for the dithiocarbamates follows the anticipated order of decreasing π-acceptor ability from aryl to alkyl derivatives.

The tetracarbonyl complexes are characterized, as noted earlier [7], by the occurrence of four carbonyl bonds in their IR spectra; for example, $[Mo(CO)_4S_2CN(CH_2)_4]^-$ has bands at 1995, 1871, 1841 and 1795 cm^{-1}. Three IR carbonyl stretching frequencies are expected for the pentacarbonyl complexes, and hence the presence of $[Mo(CO)_5S_2CNPh_2]^-$ in DMSO solution is assigned because the three observed bands (2061, 1925 and 1865 cm^{-1}) compare favourably with those found for $[Mo(CO)_5X]^-$. When both tetracarbonyl and pentacarbonyl species exist simultaneously, as for the $S_2P(OEt)_2$ case, the infrared carbonyl region shows the expected complexity; this work confirms the previous speculation [7] that a band at *ca.* 1920 cm^{-1} is indicative of the presence of a pentacoordinate species. The existence and relative proportion of the two species is much more clearly shown by ^{95}Mo NMR spectroscopy. The identification of mixtures of substituted molybdenum(0) carbonyl complexes by ^{95}Mo NMR spectroscopy is under continuing investigation in our laboratory.

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