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Molybdenum-95 NMR Spectra of Dioxomolybdenum(VI) Schiff Base Complexes

ELMER C. ALYEA

(GWC)^2, Guelph Campus, University of Guelph, Guelph, Ont. N1G 2W1, Canada

and JOSEPH TOPICH

Department of Chemistry, Virginia Commonwealth University, Richmond, Va 23284, U.S.A.

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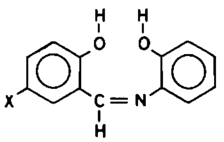
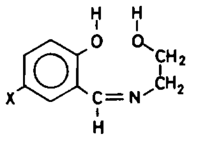
Potential applications of molybdenum-95 (I = 5/2, 15.8%) NMR, until recently known only for a few compounds of high symmetry [1], have now been demonstrated for a variety of less symmetric Mo(0) [2], Mo(II) [3], and Mo(VI) [4] compounds. The establishment of a wide ^{95}Mo NMR chemical shift range (>5500 ppm) and the possibility of observing relatively narrow line widths with short acquisition times *via* FT NMR led us to attempt the observation by ^{95}Mo NMR spectroscopy of more subtle structural and electronic effects for the molybdenum(VI) Schiff base complexes MoO_2 (5-X-SAP) (solvent) (*1a*) and MoO_2 (5-X-SAE) (solvent) (*1b*) [5]. These complexes contain the *cis*-dioxo MoO_2^{2+} group which EXAFS studies show is present in the oxidized forms of xanthine oxidase [6] and sulfite oxidase [7]. Trends in cathodic reduction potentials and charge-transfer transitions were recently discussed for these complexes in terms of ligand substituent (X = NO_2, Br, Cl, H, CH_3O) and ligand structural variations [5].



5-X-SAP-H$_2$

1a



5-X-SAE-H$_2$

1b

The ^{95}Mo NMR spectral data obtained at 26.08 MHz are summarized in Table I. Chemical shifts are relative to external aqueous 2 *M* K_2MoO_4 at pH 11 [1–4, 8]. The two related series of six coordinate dioxomolybdenum(VI) complexes show chemical shifts in the +26 to +47 ppm range with linewidths ranging from 156 to 1170 Hz.

TABLE I. ^{95}Mo NMR Spectral Data[a] for Some Schiff Base Complexes of Dioxomolybdenum(VI).

MoO_2L (Solvent)	δMo (ppm)	$\Delta\nu_{1/2}$ (Hz)
L = 5-CH_3O-SAP[b]	47	860
5-Cl-SAP	40	280
5-Br-SAP	39	1170
5-H-SAP	38[c]	470
5-NO_2-SAP	31	156
5-CH_3O-SAE	34	860
5-Cl-SAE	32	500
5-NO_2-SAE	31	450
5-Br-SAE	29	470
5-H-SAE	26	430

[a] Spectra were obtained on naturally abundant samples with a multinuclear Bruker WH-400 NMR spectrometer operating in the pulsed Fourier Transform mode at 26.08 MHz. Complexes were synthesized by procedures described in reference 5. Samples were measured at ambient temperature in 10 mm diameter cylindrical tubes. Chemical shifts are expressed as δ values in ppm (positive values are downfield) relative to 2 *M* K_2MoO_4. Concentrations in dimethylsulfoxide (DMSO) solutions were 0.1 *M* except for the 5-NO_2-SAP derivative which was a saturated solution. The number of transients varied from 2500 to 12000 except for the 5-NO_2-SAP derivative which was observed after 281000 transients. Digital resolution was 0.2 ppm per data point. [b] Ligand structures are given in *1a* and *1b*. [c] Enemark and coworkers reported a value of 34 ppm in dimethylformamide [4]; we observed similar upfield shifts for some of the other complexes in dimethylformamide.

The results show that the chemical shifts reflect the 'fine-tuning' of the tridentate ligand environments by changing the substituent on the salicylaldehyde moiety. The linear correlation noted previously from cyclic voltammetry measurements [5] between the cathodic reduction potentials and the Hammett σ_p parameter for the ligand substituent followed the substituent order NO_2 > Cl ~ Br > H > CH_3O. As expected, the strongly electron withdrawing group (NO_2, σ_p = 0.8 as compared to –0.3 for CH_3O) allowed the molybdenum to be more easily reduced. The observed trend in chemical shifts is slightly different in each series, with the complexes having the electron donating methoxy substituent being least shielded, *i.e.*, their resonances are significantly downfield. A similar unexpected deshielding of the ^{95}Mo nuclei occurs with increasing methyl substitution on the arene in [(arene)-$Mo(CO)_3$] complexes [2c]. The reversal is qualitatively explicable in that several terms of the Ramsey

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equation [9] become important, in a way not presently well understood [2c, 3b, 10], for quadrupolar nuclei such as molybdenum-95. The apparent correlation of the Ramsey ΔE term with the ligand-to-metal charge-transfer transitions (*i.e.* the most deshielded ^{95}Mo resonance in Table I occurs for MoO_2(5-CH_3O-SAP), which has the lowest LMCT band [5]) is being explored in further ^{95}Mo NMR studies of Schiff base complexes. The downfield chemical shifts observed for the MoO_2(5-X-SAP) as compared to the MoO_2(5-X-SAE) complexes also suggests the influence of the ΔE term of the Ramsey equation since the LMCT bands for the former series occur at considerably lower energy [5]. It is particularly noteworthy that the range of ^{95}Mo chemical shifts for the two series of complexes are significantly different, reflecting the small change in the structural backbone of the two ligands. This sensitivity of ^{95}Mo chemical shifts to the environment of the molybdenum atom is much greater than that observed for Mo 3d binding energies by X-ray photoelectron spectroscopy [11], and indicates that ^{95}Mo NMR spectroscopy is an invaluable new tool in investigations of molybdenum chemistry.

Acknowledgements

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