Inorganica Chimica Acta, 56 (1981) L27–L28

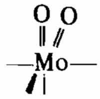
^{95}Mo NMR Spectra of Dioxomolybdenum(VI) Complexes

KENNER A. CHRISTENSEN, PHILIP E. MILLER, M. MINELLI, T. W. ROCKWAY and JOHN H. ENEMARK*

Department of Chemistry, University of Arizona, Tucson, Ariz. 85721, U.S.A.

Received April 30, 1981

Previous ^{95}Mo NMR results [1] for symmetric molybdenum complexes [2] and for molybdenum(0) complexes [3, 4] encouraged us to investigate the ^{95}Mo NMR spectra of low-symmetry molybdenum complexes in oxidation states relevant to molybdenum in xanthine oxidase, sulfite oxidase and related enzymes. Dioxomolybdenum(VI) complexes provide a convenient starting point for more general ^{95}Mo NMR studies of molybdenum complexes. A large number of complexes with a wide variety of ligands and donor atoms are known [5]. All are six-coordinate, and all contain the MoO$_2^{2+}$ unit, but the stereochemistries deviate significantly from *cis*-octahedral geometry (*1*) [6, 7].



(*1*)

The symmetry at the molybdenum atom can be no higher than C$_2$, and many complexes have no symmetry. The ^{95}Mo NMR spectra of such complexes are relevant to molybdenum-containing enzymes because the EXAFS spectrum of sulfite oxidase [8] suggests a six-coordinate MoO$_2^{2+}$ center in the oxidized form of that enzyme.

The ^{95}Mo NMR spectra obtained at 16.3 MHz* are summarized in Table I. A representative spectrum is

---

*Author to whom correspondence should be addressed.

*All spectra were obtained using a Bruker WM 250 NMR spectrometer equipped with a 15 mm broad band probe capable of operating from 10–35 MHz. The 90° pulse for ^{95}Mo was found to be 125 μsec. For these studies pulse widths of 20–30 μsec were used to give adequate power distribution over the 50 kHz spectral width. A data table of 4k or 8k points was used in collection. The digital resolution was 1.5 ppm for 4k spectra and 0.75 ppm for 8k spectra. The corresponding acquisition times were 0.04–0.08 sec/per transient. An acquisition delay of 200 μsec was used to reduce the effects of probe ringing. Additional data points were shifted from the free induction decay (FID) as necessary to obtain a maximum total of 400 μsec. All spectra were recorded without field frequency lock. The position of the external standard was checked before and after each spectrum. No appreciable drift of the field was observed. Solution concentrations were usually 0.1 *M*. Less soluble complexes were studied as saturated solutions.

TABLE I. ^{95}Mo Spectra of Dioxomolybdenum(VI) Complexes.

	Compound^a	Solvent	Chemical Shift^b (ppm)	Linewidth (Hz)	Reference
1	MoO$_4^{2-}$	H$_2$O, pH 11	0	2	3
2	MoS$_4^{2-}$	H$_2$O, pH 7.8	2265	2	2^c
3	MoO$_2$(acac)$_2$	DMF	−45	225	^{c}
4	MoO$_2$(acam)$_2$	DMF	−4	160	^{c}
5	MoO$_2$(ox)$_2$	DMF	58	100	^{c}
		CH$_2$Cl$_2$	59	104	^{c}
6	MoO$_2$(sip)(DMF)	DMF	34	350	^{c}
7	MoO$_2$(sma)(DMF)	DMF	222	360	^{c}
8	MoO$_2$(mae)	DMF	491	500	^{c}
9	MoO$_2$(mpe)^a	DMF	543	260	^{c}
10	MoO$_2$[N(CH$_2$CH$_2$S)$_2$ (CH$_2$CH$_2$N(CH$_3$)$_2$)]^d	CH$_2$Cl$_2$	604	45	^{c}
11	MoO$_2$[SC(CH$_3$)$_2$C(CH$_3$)$_2$NH(CH$_3$)]$_2$^{e}	CH$_2$Cl$_2$	581	320	^{c}
12	MoO$_2$[NH$_2$C(CH$_3$)$_2$C(CH$_3$)$_2$S]$_2$^{e}	CH$_2$Cl$_2$	452	270	^{c}
13	MoO$_2$(dedtc)$_2$	CH$_2$Cl$_2$	176	275	^{c}

[a] Ligand abbreviations and references to the syntheses of the complexes are: acac = acetylacetone [9]; acam = N,N-diethylacetoacetamide [10]; ox = 8-hydroxyquinolinate [11]; sip = *o*-(salicylideneimino)phenol [12]; sma = salicylaldehyde-2-mercaptoanil [13]; mae = 1,2-bis-(2-mercaptoanilino)ethane [14]; mpe = N,N'-bis-(2-mercapto-2-methylpropyl)ethylenediamine [15]; dedtc = diethyldithiocarbamate [16]. [b] The estimated precision on chemical shifts in ≤6 ppm. [c] This work. [d] Ref. 17. [e] Ref. 7.

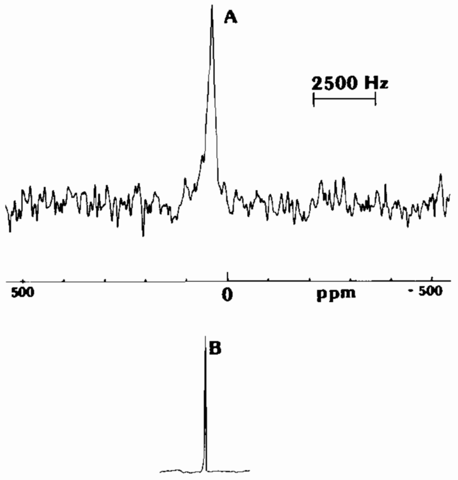
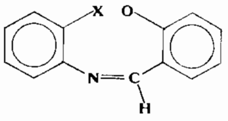


Fig 1 Typical spectrum

shown in Fig 1 Chemical shifts are referenced to external aqueous 2 *M* Na_2MoO_4 at pH 11 [3] The six-coordinate dioxomolybdenum complexes studied show chemical shifts of −45 to +600 ppm and line widths ranging from 45 to 500 Hz

The results in Table I show that significant chemical shift differences are observed for complexes of the MoO_2^{2+} group upon changing the donor atoms of the ligands For the compounds studied to date small negative chemical shifts occur for MoO_2^{2+} ligated exclusively by O atoms, whereas the largest positive chemical shifts relative to MoO_4^{2-} are found for complexes *8–12* which have two N and two S atoms in the coordination sphere The results for the pair of complexes MoO_2(sip)(DMF) (*2a*) and MoO_2(sma)-DMF (*2b*) show that replacement of an O atom of the



2a sip X=O
2b sma X=S

terdentate ligand by an S atom results in an increase in the chemical shift of +188 ppm, substantially less than the 500 ppm increase observed upon substitution of an O atom by an S in tetrahedral MoO_4^{2-} [2] The chemical shifts for Mo(VI) complexes are all much more positive than those observed for Mo(CO)$_6$ and its ligand substituted derivatives [3, 4]

The preliminary results show that dioxomolybdenum(VI) complexes of a variety of bidentate, terdentate, and tetradentate ligands can be conveniently studied by ^{95}Mo NMR spectroscopy Investigations of the ^{95}Mo NMR spectra of molybdenum compounds in other oxidation states and stereochemistries are in progress

Acknowledgements

We thank Mr S Walter and Professor M Barfield for assistance with the initial experiments and for numerous helpful discussions We thank Dr E I Stiefel for samples of compounds *10–12* We gratefully acknowledge support from the National Institutes of Environmental Health Sciences (Grant ES 0966) and a grant from the National Science Foundation for purchase of the NMR spectrometer We thank Dr A G Wedd for providing us a copy of ref 3 prior to publication, we thank Dr B E Mann for a preprint of reference 4

References

1 R K Harris and B E Mann, Eds 'NMR and the Periodic Table', Academic Press, New York (1978), pp 6, 213
2 a) W D Kautt, H Kruger, O Lutz, H Maier and A Nolle, *Z Naturforsch*, *31a,* 351 (1976), b) O Lutz, A Nolle and P Kroneck, *Z Naturforsch*, *31a,* 454 (1976), c) *32a,* 505 (1977)
3 A F Masters, R T C Brownless, J D Cotton, M J O'Connor and A G Wedd, *J Organometal Chem*, *195,* C17 (1980)
4 S Dysart, I Georgii and B E Mann, submitted for publication
5 E I Stiefel, *Prog Inor Chem*, *22,* 1 (1977)
6 a) R J Butcher, B R Penfold and E Sinn, *J Chem Soc*, *Dalton Trans*, 668 (1979), b) K Yamanouchi and J H Enemark, *Proceedings of the Third International Conference on the Chemistry and Uses of Molybdenum*, H F Barry and P C H Mitchell, Eds, Climax Molybdenum Co, Ann Arbor, Michigan (1979) p 24
7 E I Stiefel, K F Miller, A E Bruce, J L Corbin, J M Berg and K O Hodgson, *J Am Chem Soc*, *102,* 3624 (1980)
8 S P Cramer, H B Gray and K V Rajagopalan, *J Am Chem Soc*, *101,* 2772 (1979)
9 W C Fernelius, K Terada and B E Bryant, *Inorg Syn*, *6,* 147 (1960)
10 M Minelli, unpublished results
11 H Fleck and A M Ward, *Analyst, 58,* 388 (1933)
12 R D Taylor, J P Street, M Minelli and J T Spence, *Inorg Chem*, *17,* 3207 (1978)
13 a) O A Rajan and A Chakravorty, *Inorg Chem Acta, 37,* L503 (1979), b) O A Rajan, S Ashikari and A Chakravorty, *Indian J Chem Sect A, 15,* 209 (1977)
14 J K Gardner, N Pariyadath, J L Corbin and E I Stiefel, *Inorg Chem*, *17,* 897 (1978)
15 J T Spence, M Minelli, P Kroneck, M I Scullane and N D Chasteen, *J Am Chem Soc*, *100,* 8002 (1978)
16 F W Moore and M L Larson, *Inorg Chem*, *6,* 998 (1967)
17 J M Berg, K O Hodgson, S P Cramer, J L Corbin, A Elsburry, N Pariyadath and E I Stiefel, *J Am Chem Soc*, *101,* 2774 (1979)