Table IV. Average Values of Bond Distances and Bond Angles in $[(Fe(TPP))_2SO_4]^a$

	Bond Distances, Å		
Fe-N	2.062 (8)	C_a-C_b	1.446 (13)
N-C_a	1.381 (16)	C_b-C_b	1.340 (10)
C_a-C_m	1.389 (17)		
	Bond Angles, deg		
Fe-N-C_a	125.8 (15)	C_a-N-C_a	106.6 (13)
N-C_a-C_m	126.2 (14)	C_b-C_a-C_m	124.7 (12)
N-C_a-C_b	109.1 (10)	C_a-C_b-C_b	107.6 (7)
C_a-C_m-C_a	124.1 (10)		

[a] The numbers in parentheses are the estimated standard deviations calculated from the averaged population.

angle between the two porphinato cores is 24° as a consequence of the monodentate bridge. This bridge leads to an intramolecular Fe···Fe separation of 6.049 Å. Figure 2 presents a view of the crystallographically unique portion of the $[(Fe(TPP))_2SO_4]$ molecule and gives the labels assigned to each atom. Also entered on Figure 2 are the interatomic distances. Table III (supplementary material) presents a listing of individual values of the bond distances and angles. Averaged values for the chemically distinct bond distances and bond angles are given in Table IV. The numbers in parentheses are the estimated standard deviations calculated from the deviation from the average of the individual values.

The features of the iron coordination group are those expected for a five-coordinate high-spin iron(III) porphyrinate.[9] The average Fe–N_P bond distance is 2.062 (8) Å. The iron(III) is displaced by 0.44 Å from the mean plane of the 24-atom core and 0.43 Å from the mean plane of the four nitrogen atoms. The porphinato core displays a moderate D_{2d} ruffling of the core. A formal diagram of the porphinato core that displays the perpendicular displacements of each atom from the mean plane of the 24-atom core is given in Figure 2S (supplementary material).

The axial Fe–O bond distance is 1.894 (4) Å. This is significantly shorter than the 2.029 (4) Å Fe–O bond in $Fe(TPP)OClO_3$[3a] and the 2.067 (9) Å distance in $Fe(OEP)OClO_3$.[10] This axial distance is somewhat longer than the Fe–O(methoxy) distance[11] of 1.842 (4) Å or the 1.847 (2) Å distance in a binuclear phenoxy iron(III) porphyrinate.[12] The distance is shorter than the Fe–$O(SO_4)$ distances observed in a number of six-coordinate high-spin iron(III) sulfate minerals[13] and ferric ammonium sulfate[14] (average value 1.96 Å; range 1.92–2.006 Å). The pattern of somewhat shorter axial distances in five-coordinate porphyrinates relative to six-coordinate iron(III) species has been noted previously.[15] The two independent S–O distances in $[(Fe(TPP))_2SO_4]$ are 1.512 (6) Å (coordinated oxygen) and 1.430 (7) Å (uncoordinated oxygen). These bond length differences are typical for coordinated sulfate.[13,14]

The sulfate bridging ligand does not lead to any exceptionally short intramolecular C···C distances; the smallest such distance is between phenyl carbon atoms on the two opposite porphyrin rings (3.48 Å). The molecules of $[(Fe(TPP))_2SO_4]$ are well-separated in the lattice with no unusally short intermolecular contacts.

Acknowledgment. We are pleased to acknowledge support from the National Institutes of Health (Grant HL-15627).

Registry No. $[(Fe(TPP))_2SO_4]\cdot CHCl_3\cdot H_2O$, 90791-29-0.

Supplementary Material Available: Figure 1S, the infrared spectrum of $[(Fe(TPP))_2SO_4]$, Figure 2S, a formal diagram of the porphinato core showing mean plane displacements, Table II, anisotropic temperature factors, Table III, a table of individual bond distances and angles for $[(Fe(TPP))_2SO_4]$, Table V, idealized hydrogen atom coordinates, and listings of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

---

(9) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543–555.

(10) Masuda, H.; Taga T.; Osaki, K.; Sugimoto, H.; Yoshida, Z.-I.; Ogoshi, H. *Inorg. Chem.* **1980**, *19*, 950–955.

(11) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312–2319.

(12) Goff, H. M.; Shimomura, E. T.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 315–321.

(13) Fanfani, L.; Nunzi, A.; Zanazzi, P. F. *Am. Mineral.* **1970**, *55*, 78–89. Fang, J. H.; Robinson, P. D. *Ibid.* **1970**, *55*, 1534–1540. Robinson, P. D.; Fang, J. H. *Ibid.* **1971**, *56*, 1567–1572. Robinson, P. D.; Fang, J. H. *Ibid.* **1973**, *58*, 535–539. Thomas, J. N.; Robinson, P. D.; Fang, J. H. *Ibid.* **1974**, *59*, 582–586.

(14) Palmer, K. J.; Wong, R. Y.; Lee, K. S. *Acta Crystallogr., Sect. B* **1972**, *B28*, 236–241.

(15) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 317–380. Scheidt, W. R. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 463–511.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721,
and Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

^{95}Mo NMR Measurements of Dioxomolybdenum(VI) Complexes. 3. Inverse Halogen Dependence of the Molybdenum Chemical Shifts of $[MoO_2]^{2+}$ Complexes

Martin Minelli,[†] Katsumoto Yamanouchi,[†] John H. Enemark,*[†] P. Subramanian,[‡] Bharat B. Kaul,[‡] and Jack T. Spence[‡]

Received October 12, 1983

Dioxomolybdenum(VI) complexes have attracted special attention because the oxidized state of the Mo centers of molybdenum-containing enzymes such as sulfite oxidase and nitrate reductase as well as the desulfo forms of xanthine oxidase and xanthine dehydrogenase are believed to have a $[MoO_2]^{2+}$ core.[1,2] One direct probe of $[MoO_2]^{2+}$ complexes is ^{95}Mo NMR, as has been demonstrated by us and others.[3-8]

In this study we report the ^{95}Mo NMR properties of two new series of octahedral $[MoO_2]^{2+}$ complexes, establish the halide dependence for $[MoO_2]^{2+}$ complexes, and show the effects of thioether ligands on the ^{95}Mo nucleus.

Experimental Part

The MoO_2LX complexes, where L = hydrotris(3,5-dimethylpyrazolyl)borate ($HB(3,5\text{-}Me_2Pz)_3$) and X = NCS^-, OCH_3^-, Cl^-, and Br^-, have been synthesized according to Yamanouchi et al.[9] The complexes MoO_2L^x (L^1H_2 = *N,N'*-bis(3-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane (I), L^2H_2 = *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane (II), L^3H_2 = *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-*cis*-1,2-diaminocyclohexane (III), L^4H_2 = *N,N'*-bis(2-hydroxybenzyl)-1,2-diaminoethane (IV); see Figure 1) and the complex $MoO_2(dttd)$ (V) ($dttdH_2$ = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane, Figure 1) have been synthesized according to Spence et al.[10] The complex $(Et_4N)_2[MoO_2(NCS)_4]$ has been prepared according to the method of Brisdon and Edwards,[11] and $MoO_2(mab)$ ($mabH_2$ = 2,3-bis(2-mercaptoanilino)butane, Figure 1) has been prepared according to the method of Minelli.[12]

The NMR spectra were obtained on a Bruker WM250 NMR spectrometer, by using a 10-mm molybdenum probe (16.3 MHz) with a 35-μs 90° pulse. A delay of 200 μs prior to acquisition was used to reduce the effects of probe ringing. A 2 M Na_2MoO_4 solution in D_2O at pH 11 served as external standard. The solution concentrations were generally 0.1 M; less soluble compounds were measured as saturated solutions.

[†] University of Arizona.

[‡] Utah State University.

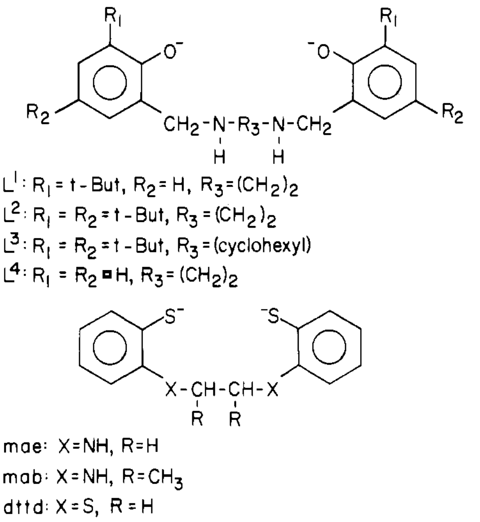
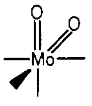


Figure 1. Ligands.

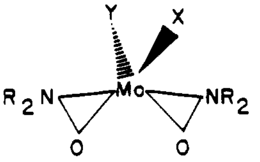
Results and Discussion

The total known chemical shift range for six-coordinate $[MoO_2]^{2+}$ complexes is over 900 ppm.[3-8] These complexes



1

have either approximate octahedral (**1**) or skew-trapezoid bipyramid geometry (**2**). Complexes with ligands containing



2

N and O donor atoms absorb from −219 to 58 ppm, whereas the ^{95}Mo NMR resonances of complexes of ligands with S donor atoms are more deshielded.

In this study we have looked at a new group of octahedral complexes with the general formula MoO_2LX, where L = $HB(3,5\text{-}Me_2Pz)_3$ and X = NCS^-, OCH_3^-, Cl^-, and Br^-. These complexes absorb over a range of 164 ppm (Table I), depending on X. This is the first example of a group of six-coordinate $[MoO_2]^{2+}$ complexes in which one ligand can be readily replaced while the rest of the molecule remains unchanged. It is therefore possible to monitor specifically the effect of the ligand X on the ^{95}Mo nuclues. When Cl^- is replaced by Br^-, the ^{95}Mo NMR nucleus becomes more deshielded and the molybdenum chemical shift increases by 44 ppm. The effect of halide replacement has been studied for several nuclei,[13] and a downfield chemical shift, as observed for this system, is referred to as *inverse halogen dependence*. Increased shielding upon replacement of chloride by bromide is referred to as *normal halogen dependence*.

Table I

compd	solvent	chem shift,[a] ppm	line width, Hz
$(Et_4N)_2[MoO_2(NCS)_4]$	acetone	−155	330
$MoO_2(OCH_3)(HB(3,5\text{-}Me_2Pz)_3)$	CH_2Cl_2	−35	100
$MoO_2(L^1)$ (I)	CH_2Cl_2	−19	120
$MoO_2(L^2)$ (II)	CH_2Cl_2	−15	220
$MoO_2(L^3)$ (III)	CH_2Cl_2	−11	140
$MoO_2(NCS)(HB(3,5\text{-}Me_2Pz)_3)$	DMF	−5	250
$MoO_2(L^4)$ (IV)	CH_2Cl_2	0	50
$MoO_2Cl(HB(3,5\text{-}Me_2Pz)_3)$	CH_2Cl_2	85	400
$MoO_2Br(HB(3,5\text{-}Me_2Pz)_3)$	DMF	129	270
MoO_2(dttd) (V)	CH_2Cl_2	409	65
MoO_2(mab)	DMF	499	550

[a] Relative to 2 M $NaMoO_4$ in D_2O, pH 11.

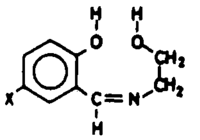
Table II. Halogen Dependence of the Chemical Shifts (ppm vs. MoO_4^{2-}) for Mo Complexes

	$[MoO_2LX]$	$[MoO_2\text{-}(sae\text{-}X)]$[a]	[MoCp-$(NO)_2X$]	[MoCp-$(CO)_3X$]
X = Cl	85	32	−852	−836
X = Br	129	26	−883	−956
change[b]	+44	−6	−31	−120

[a] sae = dianion of 2-(salicylideneamino)ethanol; X is on the 5-position of the aromatic ring.[7] [b] Positive chemical shift change = inverse halogen dependence; negative chemical shift change = normal halogen dependence.

The same halogen dependence is *not* found in all classes of molybdenum complexes. For complexes of the type $Mo(Cp)X(NO)_2$[14] and $Mo(Cp)X(CO)_3$[15] a normal halogen dependence has been found. For $[Mo(NO)_2]^{2+}$ complexes the normal halogen dependence is similar in *magnitude* to the inverse halogen dependence determined here for $[MoO_2]^{2+}$ complexes. The magnitude and signs of the halogen dependence for several molybdenum complexes are given in Table II.

In another ^{95}Mo NMR study[7] the efffect of halide substitution on the 5-position of the aromatic ring of the sae ligand (**3**) bound to the $[MoO_2]^{2+}$ unit has been investigated. For such ligands the shielding increases when chloride is replaced by bromide, exactly the opposite of the effect reported here for halide ligands bound directly to the Mo atom (Table II).



5-X-sae-H_2

3

The ^{95}Mo NMR results in Table I demonstrate the sensitivity of the chemical shift of $[MoO_2]^{2+}$ complexes to the

---

(1) (a) Coughlan, M. P., Ed. "Molybdenum and Molybdenum Containing Enzymes"; Pergamon Press: Oxford, 1980. (b) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59.

(2) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.

(3) Christensen, K. A.; Miller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27.

(4) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.

(5) Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183.

(6) Gheller, S. F.; Gazzana, P. A.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Rodgers, J. R.; Snow, M. R. *Inorg. Chim. Acta* **1981**, *54*, L131.

(7) Alyea, E. C.; Topich, J. *Inorg. Chim. Acta* **1982**, *65*, L95.

(8) Buchanan, I.; Minelli, M.; Ashby, M. T.; King, T. J.; Enemark, J. H.; Garner, C. D.; *Inorg. Chem.* **1984**, *23*, 495.

(9) Yamanouchi, K.; Enemark, J. H., manuscript in preparation.

(10) Subramanian, P.; Spence, J. T.; Ortega, R.; Enemark, J. H. *Inorg. Chem.*, in press. Spence, J. T. manuscript in preparation.

(11) Brisdon, B. J.; Edwards, D. A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 301.

(12) Minelli, M. Dr. rer. nat. Dissertation, University of Konstantz, Konstanz, West Germany, 1980.

(13) Kidd, R. G. In "The Multinuclear Approach to NMR Spectroscopy"; Lambert, J. B., Riddell, F. G., Eds.; Reidel Publishing Company: Dordrecht, 1983; p 443.

(14) Minelli, M.; Hubbard, J. L.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 970.

(15) LeGall, J.-Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

change of just one ligand in the coordination sphere of the molybdenum atom. Comparison of the dioxo and dinitrosyl complexes, $MoO_2Cl(L)$ and $Mo(NO)_2Cl(L)$, shows that the dinitrosyl complex is more shielded by 469 ppm. The same is true for the complexes $Mo(X)_2$(2,4-pentanedionate)$_2$ and $Mo(X)_2(S_2CNEt_2)_2$ (X = O or NO), where the dinitrosyl complexes are more shielded by several hundred ppm.[14]

The second group of $[MoO_2]^{2+}$ complexes studied in this paper have the general formula MoO_2L^x, where L^x is a sterically hindered O_2N_2 ligand (Figure 1). These complexes have distorted octahedral geometry around the molybdenum center.[10] The complex with the least hindered ligand has the most deshielded molybdenum core, but there is no simple correlation between the number of R groups and the chemical shift of these complexes. The line width increases from IV to I to II as the number of *tert*-butyl groups increases.

The first ^{95}Mo NMR spectrum for a $[MoO_2]^{2+}$ complex with two thiolate and two thioether sulfurs, V, is also shown in Table I. The chemical shift of V (409 ppm) is smaller than those for a wide range of $[MoO_2]^{2+}$ complexes of N_2S_2 ligands.[3,5,6,8] The only other $[MoO_2]^{2+}$ complex with four sulfur ligands to be studied by ^{95}Mo NMR is $MoO_2(S_2CNEt_2)_2$, which absorbs at 176 ppm. No dioxomolybdenum(VI) complexes with four thiolate sulfur ligands are known.

In MoO_2(mae), which has two NH groups instead of the thioether sulfurs (Figure 1), the chemical shift is 491 ppm (500 Hz).[3] The related complex MoO_2(mab) has a ^{95}Mo chemical shift of 499 ppm (Table I).

Since the coordination geometry at the Mo atom in the mae and dttd complexes is essentially the same,[16,17] the two complexes are related by replacement of the two atoms in the coordination sphere of the Mo atom that are trans to the terminal oxo groups. The ^{95}Mo NMR spectra show that replacement of two amine nitrogens by two thioether sulfurs causes a shielding of the $[MoO_2]^{2+}$ core of 82 ppm. Thus, a thioether sulfur has a greater shielding effect on a $[MoO_2]^{2+}$ center compared to that of amines. Amines that are attached to a delocalized ligand unit generally tend to cause more shielding than amines attached to aliphatic parts of the ligand.[3,5,6]

The increase in the ^{95}Mo shielding upon replacing a coordinated amine by a coordinated thioether contrasts with the decreased shielding observed when a thiolate sulfur atom or a terminal sulfur atom is added to the coordination sphere of $[MoO_2]^{2+}$.[3-6] As shown previously for the MoO_2(sip)(DMF) and MoO_2(sma)(DMF) couple,[3,18] a change from RO^- to RS^- causes deshielding of the ^{95}Mo NMR signal from 34 to 231 ppm.

In the tetrahedral environment of MoO_4^{2-}, deshielding of about 500 ppm per oxygen replaced is observed[19] for the stepwise substitution of terminal oxygen atoms by terminal sulfur atoms. In the related skew-trapezoid bipyramidal dioxomolybdenum(VI) complexes of type **2**, the deshielding increases by about 700 ppm per oxygen replaced.[4,5]

The molybdenum center of the oxidized form of xanthine oxidase is proposed to contain an $[MoOS]^{2+}$ unit that is also ligated by a least two RS^- groups.[1] No $(RS)_2MoOS$ complexes are yet known. It is of special interest to see whether the terminal oxo groups of the complexes of Table I can be replaced by terminal sulfido groups. Previous results (discussed above) show that such a substitution should produce a large deshielding of the Mo atom.[4-6,19] Attempts were made to exchange the terminal oxygen atoms by terminal sulfur atoms for the complexes of Table I by adding $((CH_3)_3Si)_2S$ to the solutions.[4] No new species could be detected by ^{95}Mo NMR. The presence of EPR-active species in the resultant solutions indicated reduction reactions had occurred.

Finally, the chemical shift for the complex $(Et_4N)_2[MoO_2(NCS)_4]$ is the most shielded signal yet observed for a $[MoO_2]^{2+}$ complex of type **1** with approximate octahedral geometry.

Acknowledgment. The authors thank the U.S. Department of Agriculture for supporting this work with Grant No. 81-CRCR-1-626 (J.H.E.), the National Science Foundation for funds for the NMR spectrometer, and the NIH for Grant GM 08347 (J.T.S.). We thank Dr. K. A. Christensen for his technical assistance with the NMR spectrometer.

Registry No. I, 90758-94-4; II, 90758-95-5; III, 90866-53-8; IV, 90858-42-7; V, 90758-93-3; $(Et_4N)_2(MoO_2(NCS)_4)$, 52486-94-9; $MoO_2(OCH_3)(HB(3,5\text{-}Me_2Pz)_3)$, 90858-40-5; $MoO_2(NCS)(HB(3,5\text{-}Me_2Pz)_3)$, 90858-41-6; $MoO_2Cl(HB(3,5\text{-}Me_2Pz)_3)$, 90858-43-8; $MoO_2Br(HB(3,5\text{-}Me_2Pz)_3)$, 90866-54-9; MoO_2(mab), 65293-33-6; ^{95}Mo, 14392-17-7.

---

(16) Enemark, J. H.; Spence, J. T., manuscript in preparation.

(17) Bruce, A.; Corbin, L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917.

(18) The ^{95}Mo NMR chemical shift for MoO_2(sma)(DMF) is 231 ppm (420 Hz). This value is more accurate than the one reported in ref 3.

(19) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch. A* **1976**, *31A*, 454; **1977**, *32A*, 505.