dinates and isotropic temperature factors for non-hydrogen atoms are given in Tables II and III.

The structure of **1** is centrosymmetric (imposed) and involves two six-membered PN_2C_3 rings linked at the nitrogens by a pair of $-CH_2CH_2-$ fragments. Alternatively the structure may be described as a puckered, 14-membered cyclam ring in which two $>\ddot{P}Me$ moieties bridge across the 1,11 and 4,8 pairs of nitrogens. The four nitrogens form a plane with projecting $>\ddot{P}Me$ groups on either side. The planarity at nitrogen and the P–N bond distance, 1.694 (2) Å, resemble the geometry of acyclic $>PN<$ compounds.[7] The closest known structures to **1** are the compounds in which a single P,[8] Ti,[9] or V[10] atom has been inserted in the cavity of macrocyclic rings.

Compound **1** is novel in that it contains two extra donor atoms (2 P's) that are 4.131 (2) Å apart. This separation may be compatible (in view of some flexibility in the $-CH_2CH_2-$ link) with P···P distances in trans square-planar (ca. 4.4–4.6 Å) or tetrahedral (3.7–3.9 Å) transition-metal complexes. In view of the high inversion barriers at phosphorus and the constraints of the ring system of **1**, structures in which both P donors bind a metal in a cis fashion are unlikely. Compound **1** may be therefore a member of a rare class[11] of bidentate ligands that should bind trans rather than cis to a metal center. More flexibility could, of course, be introduced by increasing the size of the macrocyclic ring, affording greater movement on the part of the phosphorus atoms and increasing their separation.

The structure of **2**, having a crystallographically imposed center of symmetry, consists of a 14-membered $C_{10}N_4$ backbone with the pairs of $-CH_2PPh_2$ groups on N_1,N_4 and N_8,N_{11} on opposite sides of the cyclam ring. The ligand is therefore potentially an octadentate N_4P_4 ligand with four pairs of bidentate $>PCH_2N<$ units. Ligands of this type have been used extensively to form complexes in which two different transition metals are in close proximity.[12] The bond distances and angles in **2** are normal (see Figure 2 legend), and the P···N separations (2.801 (2) Å for P(1)···N(1)) are close to those found in other $>PCH_2N<$ systems.[12]

The syntheses described for **1** and **2** are likely to be applicable to most macrocycles containing $>\ddot{N}H$ groups and also to primary phosphines. The extension of these methods to allow the isolation of macrocycles with three-dimensional cavities (cavitands) is in progress.

Acknowledgment. We are grateful to the Research Corp. and the NSF (Grant CHE-8116355) for generous financial support and to Dr. Marilyn Olmstead for helpful discussions.

Registry No. **1**, 90696-72-3; **2**, 90696-71-2; cyclam, 295-37-4; $P(Me)(NMe_2)_2$, 14937-39-4; $PHPh_2$, 829-85-6; CH_2O, 50-00-0.

Supplementary Material Available: Listings of bond distances, bond angles, hydrogen atom coordinates, isotropic and anisotropic temperature factors, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

---

(7) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Horwood-Wiley: Chichester, 1978.

(8) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955. Dupart, J.-M.; Grand, A.; Pace, S.; Reiss, J. G. *Ibid.* **1982**, *104*, 2316–2318.

(9) Olmstead, M. M.; Power, P. P.; Viggiano, M. *J. Am. Chem. Soc.* **1983**, *105*, 2927–2928.

(10) Olmstead, M. M.; Power, P. P., unpublished work.

(11) Di Stefano, N. J.; Johnson, D. K.; Lane, R. M.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59*, 2674–2679. Constable, A.; McDonald, W. S.; Shaw, B. L.; *J. Chem. Soc., Dalton Trans.* **1979**, 496–500, 1109–1111.

(12) Olmstead, M. M.; Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 4060–4967. Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Ibid.* **1980**, *20*, 1182–1187. Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792–798. Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229–1235.

Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556,
and Department of Pharmaceutical Science,
Nagoya City University, Nagoya, Japan 467

Stereochemistry of (μ-Sulfato)bis[(*meso*-tetraphenylporphinato)iron(III)]

W. Robert Scheidt,*[1] Young Ja Lee,[1] T. Bartzcak,[1]
and Keiichiro Hatano*[2]

Received November 23, 1983

Oxyanionic ferric porphyrinates have recently received much attention. The first oxyanionic ligand to be studied was perchlorate.[3] The unusual magnetic properties[3a–c] of these admixed intermediate spin species led in turn to the study of other oxyanionic ligands. Phillippi et al.[4] showed that the nitrato complex, $[Fe(TPP)NO_3]$,[5] was high spin and contained a bidentate nitrato ligand. They also showed that the binuclear sulfato complex $[(Fe(TPP))_2SO_4]$ contains high-spin iron(III) with small or negligible antiferromagnetic coupling between the two iron(III) ions. They suggested on the basis of NMR spectra that the binuclear species had a bridging sulfate ligand in which the sulfate was bound in a bidentate manner. We have investigated the molecular structue of $[(Fe(TPP))_2SO_4]$ and found that the complex contains (in the solid state) a monodentate bridging sulfate ligand.

Experimental Section

Needlelike crystals of $[(Fe(TPP))_2SO_4]$ were obtained by using procedures similar to those reported by Phillippi et al.[4] except that more dilute (1 M) sulfuric acid was used. These crystals diffracted poorly. Recrystallization of these needles from a saturated benzene solution in which *n*-pentane was allowed to diffuse yielded homogeneous crystals of rhombic habit. These crystals did not diffract adequately. Anal. Calcd for $Fe_2SO_4N_8C_{94}H_{62}$: C, 74.71; H, 4.14; N, 7.42. Found: C, 75.12; H, 4.18; N, 7.19. Satisfactory crystals were finally obtained by layering a saturated $CHCl_3$ solution of $[(Fe(TPP))_2SO_4]$ on 50% sulfuric acid and allowing *n*-pentane to diffuse into the two-layered system. Inhomogeneous crystal mixtures were thus obtained. Purple rhombic crystals picked from the mass were found to be adequate for X-ray diffraction studies. Crystals prepared by both methods had characteristic IR spectra in the 800–1000-cm^{-1} region as shown in Figure 1S (supplementary material).

Preliminary examination of a crystal with dimensions of 0.12 × 0.50 × 0.52 mm established a rhombohedral cell with systematic absences consistent with the space groups $R3c$ or $R\bar{3}c$. Lattice constants (hexagonal setting) ($\bar{\lambda}$ 0.71073) a = 32.431 (7) Å and c = 36.355 (8) Å came from a least-squares refinement that utilized the setting angles of 60 reflections given by the automatic centering routine supplied with the Syntex $P\bar{1}$ diffractometer. These constants gave a calculated density of 1.418 g/cm^3 for a cell content of 18 molecules (including the chloroform and water molecules of crystallization); the experimental density was 1.42 g/cm^3. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C.

Diffracted intensities were measured by θ–2θ scanning with graphite-monochromated Mo Kα radiation. A total of 12836 data to 2θ of 42.93° were measured. Net intensities were reduced as described previously.[6] After they were averaged (merging R factor 0.056), reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 3499 unique observed data were thus obtained. No absorption

---

(1) University of Notre Dame.

(2) Nagoya City University.

(3) (a) Reed, C. A.; Mashiko, T., Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948–2958. (b) Dolphin, D. H.; Sams, J. R.; Tsin, T. B. *Inorg. Chem.* **1977**, *16*, 711–713. (c) Goff, H. M.; Shimomura, E. *J. Am. Chem. Soc.* **1980**, *102*, 31–37. (d) Ogoshi, H.; Watanabe, E.; Yoshida, Z.-I. *Chem. Lett.* **1973**, 989–992.

(4) Phillippi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3904–3911.

(5) Abbreviations: TPP and OEP, dianions of tetraphenylporphyrin and octaethylporphyrin, respectively; N_p, porphinato nitrogen atom.

(6) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84–89.

0020-1669/84/1323-2552$01.50/0 © 1984 American Chemical Society

Table I. Fractional Coordinates[a,b]

Atom	x	y	z
Fe	0.22526(4)	0.05718(4)	0.17951(2)
N(1)	0.1689(2)	0.0596(2)	0.1558(1)
N(2)	0.2139(2)	0.0050(2)	0.1421(1)
N(3)	0.2947(2)	0.0708(2)	0.1846(1)
N(4)	0.2497(2)	0.1262(2)	0.1964(1)
S	0.21440(8)	0	0.25000
O(1)	0.1959(2)	0.0222(2)	0.2228(1)
O(2)	0.2195(2)	-0.0363(2)	0.2318(1)
C(a1)	0.1521(3)	0.0900(3)	0.1646(2)
C(a2)	0.1334(3)	0.0242(3)	0.1337(2)
C(a3)	0.1738(3)	-0.0214(3)	0.1202(2)
C(a4)	0.2406(3)	-0.0162(3)	0.1392(2)
C(a5)	0.3082(3)	0.0376(3)	0.1766(2)
C(a6)	0.3281(3)	0.1046(3)	0.2073(2)
C(a7)	0.2918(3)	0.1539(3)	0.2154(2)
C(a8)	0.2243(3)	0.1499(3)	0.1982(2)
C(b1)	0.1060(3)	0.0731(3)	0.1484(2)
C(b2)	0.0944(3)	0.0332(3)	0.1302(2)
C(b3)	0.1769(3)	-0.0596(3)	0.1033(2)
C(b4)	0.2170(3)	-0.0580(3)	0.1156(2)
C(b5)	0.3527(3)	0.0520(3)	0.1959(2)
C(b6)	0.3641(3)	0.0918(3)	0.2145(2)
C(b7)	0.2921(3)	0.1968(3)	0.2288(2)
C(b8)	0.2513(3)	0.1940(3)	0.2178(2)
C(m1)	0.1366(3)	-0.0124(3)	0.1158(2)
C(m2)	0.2842(3)	-0.0027(3)	0.1564(2)
C(m3)	0.3274(2)	0.1437(3)	0.2223(2)
C(m4)	0.1786(3)	0.1330(3)	0.1836(2)
C(1)	0.0967(3)	-0.0447(3)	0.0915(2)
C(2)	0.0878(3)	-0.0289(3)	0.0584(2)
C(3)	0.0503(4)	-0.0595(4)	0.0356(2)
C(4)	0.0214(3)	-0.1057(4)	0.0450(2)
C(5)	0.0298(3)	-0.1222(3)	0.0765(3)
C(6)	0.0670(3)	-0.0920(3)	0.1000(2)
C(7)	0.3044(3)	-0.0355(3)	0.1536(2)
C(8)	0.3386(3)	-0.0287(4)	0.1289(2)
C(9)	0.3552(4)	-0.0612(5)	0.1263(3)
C(10)	0.3372(4)	-0.0992(4)	0.1500(4)
C(11)	0.3048(4)	-0.1046(4)	0.1751(4)
C(12)	0.2874(4)	-0.0735(4)	0.1766(3)
C(13)	0.3670(3)	0.1746(3)	0.2482(2)
C(14)	0.3574(3)	0.1751(3)	0.2850(2)
C(15)	0.3933(4)	0.2013(4)	0.3096(2)
C(16)	0.4390(4)	0.2251(3)	0.2976(3)
C(17)	0.4490(3)	0.2252(3)	0.2621(2)
C(18)	0.4135(3)	0.1997(3)	0.2372(2)
C(19)	0.1558(3)	0.1633(3)	0.1893(2)
C(20)	0.1772(3)	0.2095(3)	0.1738(2)
C(21)	0.1559(3)	0.2371(3)	0.1784(2)
C(22)	0.1138(4)	0.2204(4)	0.1973(3)
C(23)	0.0931(3)	0.1755(4)	0.2119(2)
C(24)	0.1144(3)	0.1470(3)	0.2082(2)
C(25)	0.4459(2)	0.0014(2)	0.2564(2) *
Cl(1)	0.4964(2)	0.0052(2)	0.2347(2) *
Cl(2)	0.3965(2)	-0.0302(2)	0.2271(2) *
Cl(3)	0.4557(2)	0.0599(2)	0.2613(2) *
O(5)	0.0538(5)	0.0040(6)	0.2386(4) *

[a] The estimated standard deviations of the last significant digits are given in parentheses. [b] Asterisks denote atoms with site occupation factors 0.5.

correction was applied. With $\mu = 0.59$ mm^{-1} and the mounting of the crystal, scans around the diffraction vector showed a maximum variation of ±4% on F. The structure was solved by the heavy-atom method. The space group $R\bar{3}c$ was assumed; this choice was consistent with all subsequent developments in the structure solution. This choice of space group requires that the [(Fe(TPP))$_2$SO$_4$] molecule have C_2 symmetry. The sulfur atom of the bridging sulfate ligand was found to be located on a twofold axis. Final cycles of least-squares refinement utilized two blocks with anisotropic temperature factors for all heavy atoms and fixed idealized(C–H = 0.95 Å) hydrogen atom positions.[7]

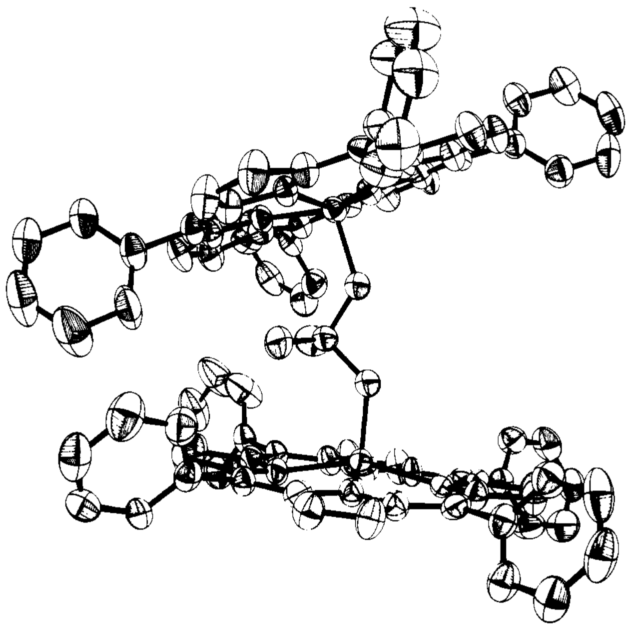

Figure 1. Overall view of the [(Fe(TPP))$_2$SO$_4$] molecule. Atomic ellipsoids are contoured to enclose 50% probability distributions. Values for angles subtended at the sulfur atom are O(1)–S–O(1)′ = 101.3 (4)°, O(2)–S–O(1) = 108.9 (3)°, O(2)–S–O(1)′ = 110.1 (4)°, and O(2)–S–O(2)′ = 116.5 (5)°. The Fe–O(1)–S angle is 129.0 (4)°.

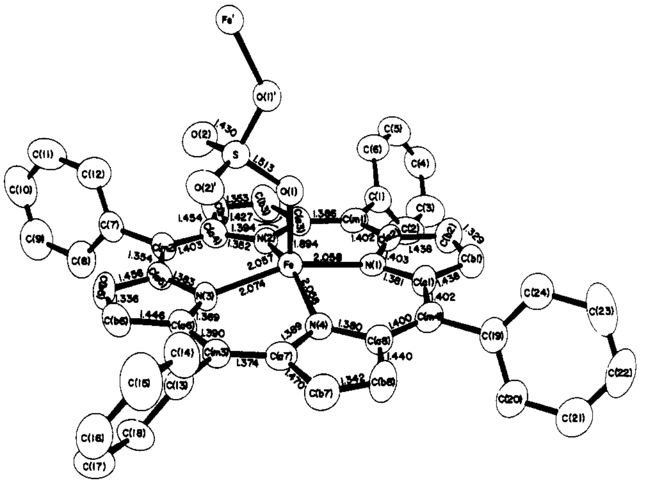

Figure 2. View of the crystallographically independent half of the [(Fe(TPP))$_2$SO$_4$] molecule. Shown are the atom labels assigned. Also displayed on the figure are the interatomic distances in the core. Estimated standard deviations for Fe–N bond distances are 0.008 Å and for C–N and C–C bonds in the core are 0.008–0.015 Å.

The solvate molecules (18 of each per cell) were found to lie close to twofold axes and were refined with occupancy factors of 0.5 for each atom. The chloroform molecule was refined as rigid group.

Final least-squares refinement led to a conventional residual (R_1) of 0.088, a weighted residual (R_2) of 0.086,[8] and an error of fit of 3.33. A final difference Fourier synthesis displayed density (0.7 e/Å^3) near the iron atom and smaller density elsewhere. Atomic coordinates are given in Table I, and the associated anisotropic temperature factors are given in Table II (supplementary material). A listing of the observed and calculated structure amplitudes is available (supplementary material).

Discussion of Results

An overall view of the binuclear complex is given in Figure 1. As is clearly seen in the figure, the sulfato ligand bridges the two iron atoms in a monodentate fashion. The dihedral

---

(7) In addition to various local programs, the SHELX system of programs was employed with real and imaginary corrections for the form factors of the iron, sulfur, and chlorine atoms.

(8) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table IV. Average Values of Bond Distances and Bond Angles in [(Fe(TPP))$_2$SO$_4$][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))$_2$SO$_4$] 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))$_2$SO$_4$] 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))$_2$SO$_4$] 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))$_2$SO$_4$]·CHCl$_3$·H$_2$O, 90791-29-0.

Supplementary Material Available: Figure 1S, the infrared spectrum of [(Fe(TPP))$_2$SO$_4$], 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))$_2$SO$_4$], 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$_2$LX complexes, where L = hydrotris(3,5-dimethylpyrazolyl)borate (HB(3,5-Me$_2$Pz)$_3$) and X = NCS$^-$, OCH$_3^-$, Cl$^-$, and Br$^-$, have been synthesized according to Yamanouchi et al.[9] The complexes MoO$_2$L^x (L^{1}H$_2$ = *N,N'*-bis(3-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane (I), L^{2}H$_2$ = *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane (II), L^{3}H$_2$ = *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-*cis*-1,2-diaminocyclohexane (III), L^{4}H$_2$ = *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$_4$N)$_2$[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$_2$MoO$_4$ solution in D$_2$O 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.