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Communications

Stepwise Synthesis and Structural Characterization of the $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)_2\}^{6-}$ and $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}OH)\}^{5-}$ Doubly Bridged Double Cubanes Obtained by the Coupling of $[MoFe_3S_4]$ Clusters

Recent advances in Fe/Mo/S chemistry,[1] inspired by the structural (Mo[2] and Fe[3] EXAFS analyses) and spectroscopic characteristics[4] of the multimetallic center in nitrogenase, have made available numerous new heterometallic clusters including[1] $[MoFe_4S_4(SEt)_3(cat)_3]^{3-}$,[5] $[MoFe_3S_4(SR)_3(R_2cat)L]^{2-}$,[1] $[M_2Fe_6S_8(SR)_6(R_2cat)_2]^{4-}$ (M = Mo, W),[6] $[Fe_6S_6L_6(M(CO)_3)_2]^{n-}$ (M = Mo, L = Cl, Br, n = 3, 4;[7a] M = Mo, L = ArO^-, n = 3;[7b] M = W, L = ArO^-, n = 3[7c]), $[MoOFe_5S_6(CO)_{12}]^{2-}$,[8] and $[MoFe_6S_6(CO)_{16}]^{2-}$.[9] In this communication we report on the stepwise syntheses of the first examples of doubly bridged (μ_2-S^{2-} and μ_2-OH^-) double $MoFe_3S_4$ cubane clusters and on the structure and properties of the $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)_2\}^{6-}$ and $\{[MoFe_3S_4Cl_2(Cl_4cat)_2](\mu_2\text{-}S)(\mu_2\text{-}OH)\}^{5-}$ anions. The latter demonstrate the feasibility of coupling of cubane clusters by μ_2-S^{2-} bridges in a planned fashion. Such cluster coupling reactions are expected to be useful in the synthesis of specific, "mixed", double-cubane clusters appropriate as models for the Fe/Mo/S center in nitrogenase.

The reaction of Na_2S with $(Et_4N)_2(Fe_4S_4Cl_4)$ in CH_3CN in a 1:2 molar ratio affords in modest yield a crystalline material with electronic and Mössbauer spectra very similar to those of $(Et_4N)_2(Fe_4S_4Cl_4)$ but with a different X-ray powder pattern, electrochemistry, and far-IR spectrum. The analytical data and a partial structure determination[10] show that this compound is the $(Et_4N)_4[(Fe_4S_4Cl_3)_2S]$ salt that contains the singly bridged double-cubane anion.[11] Further exploration of the scope of the μ_2-sulfide coupling reaction led us to the synthesis of the new Fe/Mo/S clusters described herein. The reaction of $(Et_4N)_2S$ with $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]$, in a 1:1 molar ratio, in CH_3CN solution, gives in good yield $(Et_4N)_6\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(S)_2\}$[12] (I) that is obtained as I·DMF single crystals, after recrystallization from a DMF/diethyl ether mixture.[12]

The reaction of Na_2S, $(Et_4N)_2(Fe_4S_4Cl_4)$, and $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]$, in a 1:1:1 molar ratio in CH_3CN, affords a microcrystalline solid with an EPR spectrum different from that of $[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-}$ but indicative of a $S = {}^3/_2$ ground state. Analytical data for this material[13] are consistent with the $\{[Fe_4S_4Cl_2](\mu_2\text{-}S)_2[MoFe_3S_4(Cl)_2(Cl_4cat)]\}^{5-}$ formulation (II). Attempts to obtain single crystals of II, from a CH_3CN/benzene mixture, gave, after prolonged (ca. 1 week) standing, an oily substance and a small amount of single crystals. A structure determination showed the latter to be $(Et_4N)_6\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(S)_2\}\cdot 2CH_3CN\cdot{}^1/_2C_6H_6$ (III) (apparently a disproportionation product of II) and to contain an anion identical with that in I. The reaction of $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]$,[1] in CH_3CN solution with 0.5 equiv of Et_4NOH, followed by 0.5 equiv of Li_2S, gives in good yield the $\{[MoFe_3S_4Cl_2(Cl_4cat)_2](S)(OH)\}^{5-}$ cluster that can be isolated as a microcrystalline Et_4N salt[14] (IV). The presence of the OH^-

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(1) Holm, R. H.; Simhon, E. D. In *Molybdenum Enzymes*; Spiro, T., Ed.; Wiley Interscience: New York, 1985; pp 1–87.

(2) Conradson, S. D.; Burgess, B. K.; Newton, W. E.; Mortenson, L. E.; Hodgson, K. O. *J. Am. Chem. Soc.* **1987**, *109*, 7507 and references therein.

(3) (a) Antonio, M. R.; Teo, B. K.; Orme-Johnson, W. H.; Nelson, M. J.; Groh, S. E.; Lindahl, P. A.; Kauzlarich, S. M.; Averill, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4703. (b) Arber, J. M.; Flood, A. C.; Garner, C. D.; Hasnain, S. S.; Smith, B. E. *J. Phys.* (*Les Ulis, Fr.*) **1986**, *47*, C8–1159.

(4) Orme-Johnson, W. H. *Annu. Rev. Biophys. Biophys. Chem.* **1985**, *14*, 419–459 and references therein.

(5) Wolff, T. E.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 174.

(6) (a) Armstrong, W. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 6246. (b) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4373.

(7) (a) Coucouvanis, D.; Salifoglou, A.; Kanatzidis, M. G.; Dunham, W. R.; Simopoulos, A.; Kostikas, A. *Inorg. Chem.* **1988**, *27*, 4066–4077 and references therein. (b) Coucouvanis, D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 5005. (c) Salifoglou, A.; Kanatzidis, M. G.; Coucouvanis, D. *J. Chem. Soc., Chem. Commun.* **1986**, 559.

(8) Bose, K. S.; Lamberty, P. E.; Kovacs, J. E.; Sinn, E.; Averill, B. A. *Polyhedron* **1986**, *5*, 393.

(9) Eldredge, P. A.; Bryan, R. F.; Sinn, E.; Averill, B. A. *J. Am. Chem. Soc.* **1988**, *110*, 5573.

(10) Physical data for $(Et_4N)_4[(Fe_4S_4Cl_3)_2S]\cdot C_6H_6$ are as follows. Anal. Calcd for $Fe_8Cl_6S_9N_4C_{38}H_{86}$ (MW 1547): Fe, 29.0; Cl, 13.76; S, 18.62; N, 3.62; C, 29.47; H, 5.56. Found: Fe, 27.3; Cl, 14.4; S, 19.3; N, 3.5; C, 29.6; H, 5.4. Cyclic voltammetry (CH_3CN vs SCE): $E_{1/2} = -0.79$ V (qrev); $E_{1/2} = -1.07$ V (qrev). Mössbauer spectrum: a broad line quadrupole doublet; IS_{av} = 0.48 mm/s; $\Delta_{Eq,av}$ = 0.98 mm/s. EPR: silent at temperatures >24 K. Partial crystal data for this compound have been deposited as supplementary material.

(11) The synthesis of a possibly similar $[(Fe_4S_4L\text{-}S_3)_2S]$ cluster (L-S_3 = a sterically encumbered, tridentate, benzenethiolate ligand) has been reported very recently: Stack, T. D. P.; Carney, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1670.

(12) Anal. for I·DMF. Calcd for $Mo_2Fe_6S_{10}Cl_{12}O_5N_7C_{63}H_{127}$ (MW 2333): Mo, 8.22; Fe, 14.40; S, 13.71; Cl, 18.26; N, 4.20; C, 32.40; H, 5.44. Found: Mo, 7.88; Fe, 14.89; S, 14.13; Cl, 18.10; N, 4.70; C, 31.41; H, 5.3. Cyclic voltammetry (CH_3CN vs SCE): $E_{1/2} = -0.20$ V (rev); $E_{1/2} = -1.32$ V (qrev); $E_a = +0.13$ V (irr). Mössbauer spectrum: an excellent fit was achieved by assuming two doublets in a 2:1 intensity ratio; major doublet, IS = 0.53 mm/s; Δ_{Eq} = 1.14 mm/s; minor doublet, IS = 0.34 mm/s; Δ_{Eq} = 1.13 mm/s. EPR: silent at temperatures >24 K. Crystal data for I have been deposited as supplementary material.

(13) Anal. for II. Calcd for $MoFe_7Cl_8S_{10}N_5O_2C_{46}H_{100}$ (MW 1846): Mo, 5.20; Fe, 21.23; Cl, 15.38; S, 17.33; N, 3.80; C, 29.90; H, 5.42. Found: Mo, 5.37; Fe, 20.48; Cl, 15.72; S, 16.38; N, 2.93; C, 28.97; H, 4.74. The complete characterization of this compound will be reported shortly.

(14) Anal. for IV·CH_3CN. Calcd for $Mo_2Fe_6S_9Cl_{12}O_5N_6C_{54}H_{104}$ (MW 2156): Mo, 8.91; Fe, 15.52; S, 13.36; Cl, 19.76. Found: Mo, 8.45; Fe, 15.06; S, 12.43; Cl, 20.1. Cyclic voltammetry (CH_2Cl_2 vs SCE): $E_{1/2} = -1.20$ V (qrev); $E_{1/2} = -0.05$ V (qrev); $E_{1/2} = +0.15$ V (qrev). Mössbauer spectrum: an excellent fit was achieved by assuming two doublets in a 2:1 intensity ratio; major doublet, IS = 0.53 mm/s; Δ_{Eq} = 1.19 mm/s; minor doublet, IS = 0.34 mm/s; Δ_{Eq} = 1.06 mm/s. EPR: silent at temperatures >24 K.

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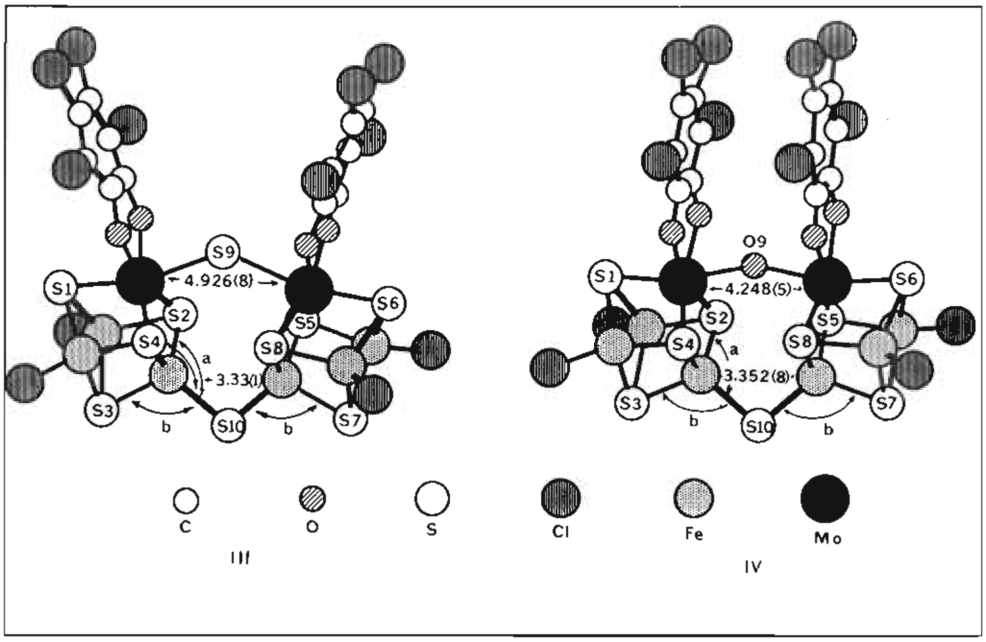
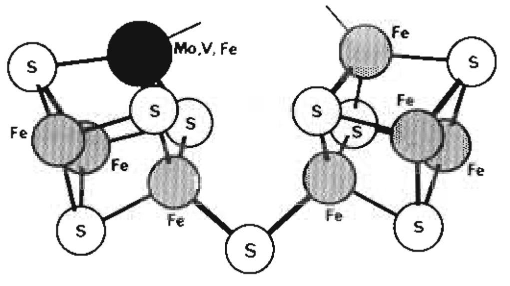


Figure 1. Structures of the $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(S)_2\}^{6-}$ (III) and $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(S)(OH)\}^{5-}$ (IV) anions. Selected structural parameters (distances, Å; angles, deg) are as follows. For III: Mo–Mo, 4.926 (8); Mo–Fe, 2.75 (2); Fe–Fe(intracube), 2.73 (2); Fe–Fe(intercube), 3.33 (2); Mo–S(intracube), 2.35 (2); Mo–S(9), 2.60 (2), 2.69 (2); Fe–S(intracube), 2.28 (2); Fe–S(10), 2.23 (2), 2.17 (2); Mo–O(catechol), 2.04 (4); Mo–S(9)–Mo, 137.2 (7); Fe–S(10)–Fe, 98.7 (8); S(10)–Fe–S, a, 115.8 (8); S–Fe–S(10), b, 111.0 (8). For IV: Mo–Mo, 4.248 (5); Mo–Fe, 2.75 (1); Fe–Fe(intracube), 2.73 (3); Fe–Fe(intercube), 3.35 (1); Mo–S(intracube), 2.36 (2); Fe–S(intracube), 2.28 (2); Fe–S(10), 2.24 (2), 2.20 (2); Mo–O(9), 2.15 (3), 2.17 (3); Mo–O(catechol), 2.10 (4); Mo–O(9)–Mo, 158 (2); Fe–S(10)–Fe, 97.8 (8); S(10)–Fe–S, a, 112.3 (7); S–Fe–S(10), b, 118.4 (5).

ligand in IV is suggested by a sharp O–H vibration in the infrared spectrum at 3490 cm^{-1} and is verified by isotopic substitutions (^2H, ^{18}O).

The $[M_2Fe_6S_8(SR)_6(R_2cat)_2]^{4-}$ anions (M = Mo, W) are other double-bridged double cubanes known,[6] and contain centrosymmetric cores with two heterometallic M–μ-SR–Fe bridges. In donor solvents (Sol) these anions solvolyze to the $[MoFe_3S_4(SR)_3(R_2cat)(Sol)]^{2-}$ single cubanes.[6] In contrast, I, III, and IV appear stable in donor solvents, presumably due to a greater stability of the S^{2-} bridge. A crystal structure determination[15] of III shows the hexaanion (Figure 1) as a bis(μ_2-sulfido) doubly bridged double cubane with two homometallic M–μ_2-S–M bridges (M = Mo, Fe). The pentaanion in IV has a similar structure[15] (Figure 1), with a Mo–μ_2-OH–Mo bridge in place of the Mo–μ_2-S–Mo in III. Both anions show nearly exact, noncrystallographically required C_{2v} symmetry. Among the outstanding structural features in III and IV are included short Fe–S bonds in the Fe–μ_2-S–Fe bridge and oblique Mo–μ_2-E–Mo angles of 137.2 (7)° (E = S^{2-}) and 158 (2)° (E = OH^-). The structures of III and IV (Figure 1) show a remarkable steric flexibility in accepting widely different Mo–Mo distances. This is accomplished by a pivoting of the two cubane subunits around each of the two Fe atoms within the Fe–μ_2-S–Fe bridges. A decrease in the Mo–Mo distance, from 4.926 (8) Å in III to 4.248 (5) Å in IV, is dictated by the short Mo–O bonds in the latter and accommodated by an opening of the external μ_2-S–Fe–μ_3-S angle (b, Figure 1) from 111.0 (8) to 118.4 (7)° and a closing of the internal μ_2-S–Fe–μ_3-S angles (a, Figure 1) from 115.8 (8) to 112.3 (7)°. The Fe–μ_2-S–Fe angles and the Fe–Fe distances within the intercubane bridges remain relatively unaffected at 98.7 (8)° and 3.33 (1) Å in III and 97.8 (8)° and 3.35 (2) Å in IV. The rather long Mo–μ_2-S bonds in III, (2.60 (2) and 2.69 (2) Å) which may be suggestive of possible ease of solvolytic bridge rupture, or of S^{2-} replacement by other ligands, are similar to the Mo–μ_2-SR bonds in the $[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]^{4-}$ cluster[6] (2.689 (2) Å). The oblique Mo–μ_2-S(OH)–Mo angles in III and IV arise as a result of intercluster S–S repulsions, involving S(2), S(5), S(4), and S(8), that can be minimized with the longest possible Mo–Mo distances. Clearly, the core structures in III and IV are highly strained and should be reactive. We already have demonstrated that the reaction of IV with $(R_3Si)_2S$, in CH_3CN solution, readily gives I. Similar reactions of IV with $(R_3Si)X$ (X = CN, N_3) occur readily, and the crystalline products (analogues of IV) are currently under investigation.

The results of this study demonstrate unequivocally the feasibility of rationally assembling $MoFe_3S_4$ and Fe_4S_4 units into μ_2-S^{2-}-bridged double-cubane clusters. The latter contain a relatively structurally invariant Fe–μ_2-S–Fe bridge and suggest yet another structural analogue for the Fe/Mo/S site in nitrogenase. Indeed, a realistic model for the Fe/Mo/S center in nitrogenase could be a composite cluster that contains the known Fe_4S_4[16] and $MoFe_3S_4$[1] structural subunits coupled in a Fe–μ_2-S–Fe, singly bridged, double cubane:



The attractive features of the single $MoFe_3S_4$ cubanes as a partial model for the nitrogenase center have been discussed previously.[1] The coupling of a Fe_4S_4 cubane to a MFe_3S_4 cluster (M = Mo,[1] V[17]) will result in a new cluster that retains the undisputedly attractive structural features of the MFe_3S_4 clusters and in addition will (a) possess an acceptable Fe/M/S stoichiometry of 7:1:9, (b) contain a site for the bimetallic activation of molecular nitrogen as proposed previously,[18] (c) contain at least four distinct iron sites, and (d) have a flexible (M) site capable

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[15] Crystal and refinement data for III and IV have been deposited as supplementary material.

[16] Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578.

[17] (a) Kovacs, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 340. (b) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702. (c) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 713.

[18] Hardy, R. W. F.; Burns, R. C.; Parshall, G. W. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; pp 745–793.

of accommodating Mo, V (or Fe). Feature c is compatible with ENDOR results[19] obtained for the Fe/Mo/S center in nitrogenase, and feature d is significant in view of the recent recognition of active nitrogenases where Mo is replaced by either vanadium (in an apparently similar Fe/V/S core structure[20]) or even iron.[21]

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Supplementary Material Available: A discussion presenting crystal and structural data for I, III, and IV and Tables S1-1-4 and S2-1-4, listing positional and thermal parameters and bond distances and angles for the Et_4N^+ salts of II and III (18 pages); Tables S1-5 and S2-5, listing structure factors for the Et_4N^+ salts of II and III (19 pages). Ordering information is given on any current masthead page.

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(19) Hoffman, B. M.; Venters, R. A.; Roberts, J. E.; Nelson, M.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 4711.

(20) (a) Eady, R.; Robson, R.; Postgate, J. *New Sci.* **1987**, *18*, 59. (b) Hales, B. J.; Case, E. E.; Morningstar, J. E.; Djeda, M. F.; Mauterer, L. A. *Biochemistry* **1987**, *25*, 7251. (c) George, G. N.; Coyle, C. L.; Hales, B. J.; Cramer, S. P. *J. Am. Chem. Soc.* **1988**, *110*, 4057.

(21) Hales, B. J. Personal communication.

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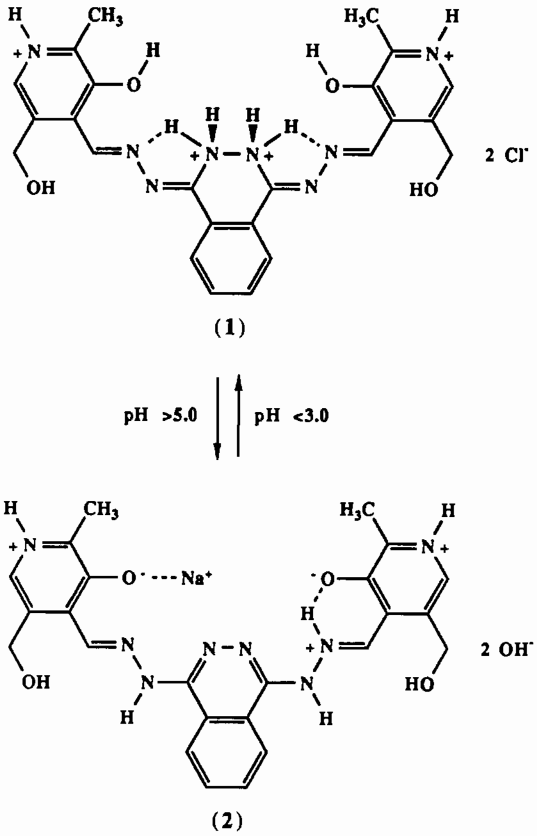
A Novel Ferromagnetic Inorganic-Organic Host-Guest System. Synthesis of Crystalline Small Magnetite Particles Complexed with Bis(pyridoxylidenehydrazino)phthalazine (DPDHP) at Ambient Temperature and Neutral pH

The naturally occurring "magnetic stone"—magnetite (Fe_3O_4)—was produced on earth some thousands of millions of years ago. Synthetically it is produced by the high-temperature oxidation of iron[1] or from mixed iron salts (Fe(II) and Fe(III)) in water and OH^- (pH > 13).[2] Polymer-anchored magnetite is produced from iron salts in water, O_2, OH^-, and polymeric lignosulfonate at elevated temperatures (90-140 °C) and pH (>12).[3] Magnetic bacteria and other biological systems, in contrast, can produce small magnetite particles at ambient temperature and pressure and neutral pH with defined crystallochemical characteristics by an unknown process.[4]

We wish to report the formation and characterization of novel types of host-guest molecules of general structures **3** and **4**, containing in crystalline forms small particles of magnetite sequestered by the title compound DPDHP[5] (L_A, **1**), by allowing ferrous sulfate to react with **1** at ambient temperature and pressure and neutral pH. The organic component (**1** and/or **2**) contains three azine (N-N) groups linked to two pyridoxylidene residues, thus forming a compartmental open-chain macrocycle with N_4O_2 sites for metal coordination[7,8] (see Schemes I and II).

Scheme I



Aqueous solutions of DPDHP hydrochloride[9] (**1**; 0.61 g, 1 mmol, in 150 mL of H_2O) and $FeSO_4{\cdot}7H_2O$ (1.12 g, 4 mmol, in 50 mL of H_2O) were first neutralized (pH 6.0)[13] separately by

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(1) Brett, M. E.; Graham, M. J. *J. Magn. Magn. Mater.* **1986**, *60*, 175.

(2) (a) Elmore, W. C. *Phys. Rev.* **1938**, *54*, 309. (b) David, I.; Welch, J. E. *Trans. Faraday Soc.* **1958**, *52*, 1642. (c) McNab, I. K.; Fox, B. A.; Boyle, Y. F. *J. Appl. Phys.* **1968**, *39*, 5703. (d) Brett, M. E.; Graham, M. J. *J. Magn. Magn. Mater.* **1986**, *60*, 171.

(3) Hassett, K. L.; Stecher, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 416.

(4) (a) Review: Blakemore, R. P. *Annu. Rev. Microbiol.* **1982**, *36*, 217. (b) Mann, S.; Frankel, R. B.; Blakemore, R. P. *Nature (London)* **1984**, *310*, 405. (c) Paoletti, L. C.; Blakemore, R. P. *J. Bacteriol.* **1986**, *167*, 73.

(5) DPDHP was shown[6] to inhibit pyridoxal-dependent enzymes such as (i) glutamic acid decarboxylase, which generates γ-aminobutyric acid (GABA), (ii) DOPA decarboxylase, and (iii) glutamate-pyruvate transaminase.

(6) (a) Ackermann, E.; Oehme, P.; Rex, H.; Lange, P. *Acta Biol. Med. Ger.* **1964**, *12*, 322. (b) Oehme, P.; Rex, H.; Ackermann, E. *Acta Biol. Med. Ger.* **1964**, *12*, 284. (c) Oehme, P.; Niedrich, H.; Jung, F.; Rudel, M. *Acta Biol. Med. Ger.* **1969**, *22*, 345, 359.

(7) The tetraaza analogue dipyridoxylidene-*o*-phthaldehyde dihydrazone (L_B), appearing in **4**, **5**, **6**, and **8**, is assumed to act as a tetradentate sequestrant.

(8) Compare: (a) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1412. (b) Ball, P. W.; Blake, J. E. *J. Chem. Soc. A* **1969**, 1415.

(9) Commerical pyridoxal hydrochloride (0.4 g, 2 mmol) and dihydrazinophthalazine hydrochloride (0.26 g, 1 mmol) were dissolved respectively in 10 and 30 mL of 1:1 H_2O-MeOH and then mixed and stirred for 3 h at room temperature. MeOH (30 mL) was added and a red-orange precipitate (0.66 g) of DPDHP collected. Recrystallization from EtOH afforded red crystals, mp 250 °C. Anal. Calcd for $C_{24}H_{24}N_8O_4{\cdot}3HCl{\cdot}2H_2O$: C, 45.48; H, 4.89; N, 17.67. Found: C, 45.73; H, 4.67; N, 17.64. When it is heated in vacuo (140 °C), it loses $^1/_2$ HCl without a noticeable change in color but its melting point increases to 275 °C. Anal. Calcd for $C_{24}H_{24}N_8O_4{\cdot}2H_2O$: C, 46.81; H, 4.96; N, 18.20; Cl, 14.42. Found: C, 46.67; H, 4.82; N, 17.46; Cl, 14.50. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ 8.87 (s, 2 H, CH=N), 8.39, 8.01 (s, 2 H, pyridinic), 7.97, 7.96, 7.94, and 7.93 (4 H, aromatic), 4.69 (d, 4 H, CH_2O), 3.60-3.34 (m, 6 H, OH and NH), 2.52, 2.51, and 2.49 (s, 6 H, CH_3). UV (EtOH): λ_{max} 417, 391, 385, 305, 274, and 218 nm.[10,11]

(10) UV (EtOH) λ_{max} bands at 390 and 280 nm, for the unprotonated free base of DPDHP (L_A), are reported in: Oehme, P. In *Pyridoxal Catalysis: Enzymes and Model Systems*; Snell, E. E., Braunstein, A. E., Severin, E. S., Torchinsky, Yu. M., Eds.; New York, 1968; pp 677-692.

(11) The observed spectrum is assumed to be composed of three subspectra (λ_{max}): (i) 417, 385, 274 nm; (ii) 391, 274 nm; (iii) 305, 218 nm.[12]

(12) Compare: (a) Heinert, D.; Martell, A. E. *J. Am. Chem. Soc.* **1963**, *85*, 188. (b) Matsushima, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 1322, 1331. Also: Sala, L. F.; Martell, A. E.; Motekaitis, R. J.; Abbott, E. H. *Inorg. Chim. Acta* **1987**, *135*, 123.

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