parts a–c, respectively. Apparently, the lability of the bismuth ligand can be traced to its electropositive character (Figure 7a), while the one for nitrogen is due to its small orbital size (Figure 7c). To elucidate the lability/inertness ordering among P, As, and Sb from a single-parameter variation is not possible, in part because the differences in overlap population values (given in Table X) are fairly small. Also, the s orbitals or s–p hybridization may play a more important role in influencing the lability of the E′ ligands. However, for both group 15 and group 16 ligand sets, the rationalization of the trend based on a single parameter variation is still only a first rough picture, since the change in Fe–E(E′) bond length was not accounted for, the s orbital contributions were left aside, and it is the combination of all the parameters in the semiempirical method that really defines and characterizes an element.

We do not think, however, that the difference between the group 15 and group 16 elements is due to the second lone pair and the possibility for E to Fe π bonding by the former. To probe this assumption, we protonated the EH_2 group, thereby tying up its second lone pair in E–H bonding and making it unavailable for a potential π bond to the metal. On comparing the Fe–E overlap populations for the nonprotonated and protonated case (Table IX; compare column 1 with 6 and 7), we find only a very small difference. In the case of S, Se, and Te, the protonated EH_3^+ group even leads to a very slightly larger Fe–E overlap population than its conjugated base, indicating that if the (second) lone pair has any effect at all, that effect is antibonding. As for the increasing electron density on the iron center in the order S- < Se- < Te-complex I, which was deduced from experimental NMR data (high-field shift of C_{Cp} ($Cp = C_5H_5$) from S to Te and of C_{CO} from Te to S) and IR data (lower ν_{CO} from S to Te),[4a] we are able to theoretically reproduce this trend. The computed net charges on iron are included in Table IX (column 5).

We think we can also provide an understanding of the photosubstitution of a CO group, rather than the conceivable photosubstitution of an ER_2 group. The latter is not observed experimentally.[4a,4b] Figure 8 gives the orbital diagram between the two CO's and the $[C_5H_5Fe(SeH_2)]^+$ fragment. As in Figure 5, the HOMO and the orbitals directly below are mostly Fe d in character. And so is the LUMO. Hence, the lowest energy, HOMO–LUMO, absorption would correspond to a "forbidden" d–d transition ($\Delta l = 0$)—although the LUMO might still be the photoactive state. Two to six orbitals above the LUMO, still very close in energy to it, lie orbitals which are primarily the four CO π^* levels, but which also contain an Fe–CO antibonding component. The Fe–C_{CO} overlap populations for these normally unfilled levels are listed in Table XI. These CO π^* orbitals can give rise to metal–ligand charge-transfer processes, involving the formal oxidation of Fe^{2+} to Fe^{3+}. Promoting electrons to these Fe–CO antibonding orbitals upon irradiation then leads to more labile carbonyl ligands, leaving, however, the Fe–ER_2 group bonding untouched (the Fe–E overlap populations are included in parentheses in Table XI). We note that the Fe–C_{CO} bond strengths as given by the overlap populations are rather similar for all complexes with E = O–Te (see values in Table XI).

Acknowledgment. H.S. is indebted to Profs. Dr. R. W. Parry and T. G. Richmond (University of Utah) for their support and interest in this work during his stay at the University of Utah (1987/1988) and to the Studienstiftung Des Deutschen Volkes, Bonn, FRG, for a stipend. R.H. and C. J. thank the Deutscher Akademischer Austauschdienst (DAAD) for the award of a NATO postdoctoral fellowship for C.J. and the National Science Foundation for its generous support through Grant CHE-89-12070.

Supplementary Material Available: Structural figures of Ia–d and listings of thermal and positional parameters, complete bond distances and angles, least-squares planes, and crystal data (30 pages); tables of calculated and observed structure factors for complexes 1a–d (45 pages). Ordering information is given on any current masthead page.

Contribution from the Corporate Research Science Laboratories,
Exxon Research and Engineering Company, Annandale, New Jersey 08801,
and the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Magnetostructural Correlations in Magnetically Coupled (μ-Oxo)diiron(III) Complexes

Sergiu M. Gorun*[1a] and Stephen J. Lippard*[1b]

Received November 27, 1990

A quantitative magnetostructural relationship has been found for dinuclear iron(III) centers bridged by a ligand oxygen atom (oxo, hydroxo, alkoxo, etc.) and at least one other bridging ligand (carboxylate, sulfate, phosphate, etc.). A correlation exists between the antiferromagnetic exchange-coupling constant J (in cm^{-1}) and P, a parameter having units of distance (in Å) defined as half the shortest superexchange pathway between two iron(III) ions. Specifically, $-J = A \exp(BP)$ where $A = 8.763 \times 10^{11}$ and $B = -12.663$. Results for 36 dinuclear metal centers, including Fe_2 and Fe_3, complexes have been used to derive this relationship, which can also be applied to tetranuclear complexes and metalloproteins. This magnetostructural correlation is shown to have powerful predictive properties, although it does not apply to (μ-oxo)diiron(III) centers unsupported by other bridging ligands. Attempts to correlate J with any other structural parameters such as the Fe–O–Fe angle or Fe···Fe distance for ligand-bridged $[Fe_2O]^{4+}$ cores were unsuccessful.

It has long been recognized that for open-shell, ligand-bridged polymetallic compounds, some correlation must exist between the type and magnitude of magnetic interactions and the relative positions of the metal ions.[2] Magnetic studies on copper acetate[3] and basic metal carboxylates[4] revealed antiferromagnetic interactions, from which their respective dinuclear and trinuclear structures[5] were correctly predicted. A major thrust of numerous subsequent papers has been to establish quantitative correlations between structural and magnetic properties. This interest stems in part from the desire to understand at a fundamental level what determines the size and magnitude of exchange-coupling inter-

---

(1) (a) Exxon Research and Engineering Co. (b) Massachusetts Institute of Technology.

(2) (a) Néel, L. *Compt. Rend.* **1936**, *203*, 304 and references therein. (b) Goodenough, J. B. *Phys. Rev.* **1955**, *100*, 564. (c) Goodenough, J. B. *Phys. Chem. Solids* **1958**, *6*, 287. (d) Kanamori, J. *Phys. Chem. Solids* **1959**, *10*, 87.

(3) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

(4) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.

(5) (a) Van Niekerk, J. N.; Schoening, F. K. L. *Acta Crystallogr.* **1953**, *6*, 227. (b) Figgis, B. N.; Robertson, B. G. *Nature* **1965**, *205*, 694.

0020-1669/91/1330-1625$02.50/0

actions. An equally motivating factor has been the presence or postulate of dinuclear, oxygen-bridged copper and iron units at the active centers of numerous metalloproteins including hemocyanin,[6] tyrosinase,[7] hemerythrin,[8] ribonucleotide reductase,[9] uteroferrin,[10a,b,e,f] purple acid phosphatase,[10c-f] and methane monooxygenase.[11] Iron oxo clusters of various nuclearity are also present in the iron storage proteins ferritin and hemosiderin.[12]

For some types of dinuclear Cu and Cr complexes, semiquantitative relationships have been established between magnetic exchange coupling and geometric features such as the M–O–M angle and M–O bond lengths.[13] In the case of dinuclear bis(μ-hydroxo)dicopper(II) complexes, a correlation exists between *J* and the Cu–O–Cu angle,[13a] the Cu–O distance being less important. This relationship fails, however, when the OH^- bridges are replaced by OR^- or halide bridges.[13a] For oxygen atom bridged systems, variations in *J* were linked to the degree of tetrahedral distortion around copper.[13,14] Dihedral, twist, and bifold angles have also been considered.[13a] In the case of bis(μ-hydroxo)dichromium(III) complexes, both the Cr–O distance and Cr–O–Cr angle are important. The major factor, however, seems to be the hybridization of the bridging oxygen atom, as reflected in the variation of the angle between the O–H vector and the Cr_2O_2 plane.[13b] It can be concluded from these results that for copper or chromium neither one single parameter nor any combination of structural parameters can correlate all the magnetic data and, therefore, that the complexes must be divided into classes having as many constant structural parameters as possible.

For solid-state materials there exists an empirical power dependence of the isotropic exchange-coupling constant *J* on the intermetallic distance *R*, known as the "magnetic Grüneisen law"[15a] (eq 1). From the study of Mn^{2+} ions in MgO and CaO lattices,

$$J = AR^{-n} \qquad (1)$$

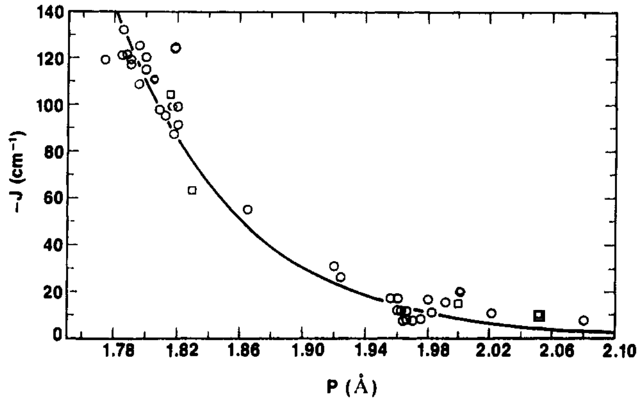

Figure 1. Plot of $-J$ vs *P* data of Table I. The circles represent experimental values, the solid line is the least-squares fit to the experimental data. The squares are the experimental values for entries 3 and 7 of Table III. See text for details.

an exponential dependence of *J* vs *R* has also been suggested.[15b] An attempt to correlate long metal–metal distances (up to ~25 Å) with *J* for various bridged metal systems has been described, but no simple relationship was found.[15d] As a general trend, however, *J* decreases with increasing metal–metal distance.

For iron, the bridging angle seems to be less important,[16] as compared with the Cu and Cr cases, but no quantitative relationship has been established thus far. For a limited series of singly bridged compounds with constant Fe–O bond lengths, the exchange-coupling interactions increase as the Fe–O–Fe angle increases.[16e] This trend, however, is not found in the related $[Cl_3Fe-O-FeCl_3]^{2-}$ class.[16f]

The present paper reports the discovery of a novel magnetostructural relationship for multiply bridged polyiron(III) complexes and some of its applications.[17]

Calculations

Various attempts were made to correlate the variation of *J* with one or more structural parameters by using literature data for 36 compounds obtained and characterized in over 20 different laboratories. *J* values reported in the literature are most often obtained from a fit of the variable-temperature magnetic susceptibility data, measured with a magnetometer or by NMR spectroscopy, to the theoretical expression derived from the Heisenberg–Dirac–van Vleck formalism (HDVV).[18] In some cases the molecular field approximation was used.[19] Occasionally, the *J* values resulted from measurements that were not extended to liquid helium temperature, a technique that allows corrections for paramagnetic impurities. Moreover, the experimental errors in measuring *J* usually exceed the estimated standard deviations that result from least-squares fits of the exchange-coupling constants to variable-temperature magnetic susceptibility data. Thus, no estimated standard deviations for *J* were included in our correlations. Structural parameters of metal complexes considered here were also taken from the literature. Unlike the *J* values, the bond distances and angles have well-defined errors associated with them. We have used standard nonlinear least-squares programs[20] to fit

---

(6) For a review see: Prêaux, G.; Gielens, C. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC Press, Inc.: Boca Raton, FL, 1984; Vol. II, pp 159–205.

(7) (a) Schoot Uiterkamp, A. J. M.; Mason, H. S. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 993–996. (b) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Lerch, K.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 7339.

(8) (a) Hendrickson, W. A. In *Invertebrate Oxygen-Binding Proteins: Structure, Active Site and Function*; Lamy, J.; Lamy, J., Eds.: Marcel-Dekker: New York, 1981; pp 503–515. (b) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618 and references therein. (c) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273 and references therein.

(9) (a) Thelander, L.; Reichard, P. *Ann. Rev. Biochem.* **1979**, *48*, 133. (b) Petersson, L.; Gräslund, A.; Ehrenberg, A.; Sjöberg, B.-M.; Reichard, P. *J. Biol. Chem.* **1980**, *255*, 6706. (c) Atkin, C. L.; Thelander, L.; Reichard, P.; Lang, G. *J. Biol. Chem.* **1973**, *248*, 7464. (d) Backes, G.; Sahlin, M.; Sjöberg, B. M.; Loehr, T. M.; Sanders-Loehr, J. *Biochemistry* **1989**, *28*, 1923.

(10) (a) Antanaitis, B. C.; Aisen, P.; Lilienthal, H. R. *J. Biol. Chem.* **1983**, *258*, 3166. (b) Sim, E.; O'Connor, C. J.; De Jersey, J.; Zerner, B. *Inorg. Chim. Acta* **1983**, *78*, L13. (c) Averill, B. A.; Davis, J. C.; Burman, S.; Zirino, T.; Sanders-Loehr, J.; Loehr, T. M.; Sage, J. T.; Debrunner, P. G. *J. Am. Chem. Soc.* **1987**, *109*, 3760. (d) Kauzlarich, S. M.; Teo, B. K.; Zirino, T.; Burman, S.; Davis, J. C.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 2781. (e) Que, L., Jr.; Scarrow, R. C. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372; American Chemical Society: Washington, DC, 1988; p 152 (see also references therein). (f) Doi, K.; Antanaitis, B. C.; Aisen, P. *Struct. Bonding* **1988**, *70*, 1.

(11) (a) Woodland, M. P.; Patil, D. S.; Cammack, R.; Dalton, H. *Biochim. Biophys. Acta* **1986**, *873*, 237. (b) Woodland, M. P.; Dalton, H. *J. Biol. Chem.* **1984**, *259*, 53.

(12) (a) Theil, E. C. *Adv. Inorg. Biochem.* **1983**, *5*, 1 and references cited therein. (b) Ford, G. C.; Harrison, P. M.; Rice, D. W.; Smith, J. M. A.; Treffry, A.; White, J. L.; Yariv, J. *Philos. Trans. R. Soc. London B* **1984**, *304*, 551. (c) Lowenstam, H. A. *Science* **1981**, *211*, 1126.

(13) For a review see: (a) Willett, R. D. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; pp 389–420 (see also references therein). (b) Hodgson, D. J. *Ibid.*, pp 497–522 (see also references therein).

(14) Mikuriya, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1086.

(15) (a) Bloch, D. *J. Phys. Chem. Solids* **1966**, *27*, 881. (b) Harris, E. A. *J. Phys. C: Solid State Phys.* **1972**, *5*, 338. (c) Shrivastava, K. N.; Jaccarino, V. *Phys. Rev. B* **1976**, *13*, 299. (d) Coffmann, R. E.; Buettner, G. R. *J. Phys. Chem.* **1979**, *83*, 2367.

(16) (a) Thich, J. A.; Ou, C. C.; Powers, D.; Vasiliou, B.; Mastropaolo, D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1976**, *98*, 1425. (b) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 2781. (c) Thich, J. A.; Toby, B. H.; Powers, D. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1981**, *20*, 3314 and references cited therein. The angular dependence of the magnetic superexchange is also inferred: (d) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1 and references therein. (e) Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 1850. (f) Adler, J.; Ensling, J.; Gütlich, P.; Bominaar, E. L.; Guillin, J.; Trautwein, A. X. *Hyperfine Interact.* **1988**, *42*, 869.

(17) Aspects of this work were communicated in preliminary form at the 3rd International Conference on Bioinorganic Chemistry. See: Gorun, S. M.; Lippard, S. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 417. The reported *A* and *B* values were 7.513×10^{11} and -12.633, respectively. The new parameters reported here are derived from a larger statistical sample.

(18) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(19) (a) Jameson, D. L.; Xie, C.-L.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 740. (b) Drüecke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Bominaar, E. L.; Sawaryn, A.; Winkler, H.; Trautwein, A. X. *Inorg. Chem.* **1989**, *28*, 4477.

Table I. Structural and Magnetic Data

no.	complex	Fe–Fe, Å	Fe–O–Fe, deg	⟨Fe–O⟩,[a] Å	P,[b] Å	$-J$, cm^{-1}
1	$[Fe(Chel)(H_2O)(OH)]_2\cdot 4H_2O$[c]	3.078	103.2	1.964	1.964 (3)	7.3
2	$[Fe_2L(OH)Cl_2]$[d]	3.162	102.5	2.02	1.97 (1)	7.4
3	$[Fe(Salen)Cl]_2$[e]	3.291	105	2.08	2.08 (2)	7.5
4	$[Fe_2L(OCH_3)Cl_2]$[f]	3.139	102.5	2.013	1.975 (7)	8.0
5	$[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$[g]	3.023	98.2	2.019	1.966 (7)	8.0
6	$[FeL(OH)]_2\cdot 2H_2O\cdot 2Py$[h]	3.155	102.8	2.021	2.021 (4)	10.4
7	$[Fe_2(acac)_4(OC_2H_5)_2]$[i]	3.116	103.6	1.982	1.982 (3)	11.0
8	$[Fe(Dipic)(H_2O)(OH)]_2$[j]	3.089	103.6	1.966	1.966 (4)	11.4
9	$\{Fe[(CH_3)_2(NC_7H_2NO_4)](H_2O)(OH)\}_2\cdot 2H_2O$[k]	3.118	105.3	1.962	1.962 (8)	11.7
10	$[Fe_2L(OH)(H_2O)_2]$[l]	3.137	102.6	1.985	1.960 (4)	12.0
11	$[Fe_2L(OC_2H_5)_2Cl_2]$[m]	3.144	104.3	1.991	1.991 (2)	15.4
12	$[Fe_2L(OCH_3)_2Cl_2]$[n]	3.106	102.5	1.989	1.98 (1)	16.3
13	$[Fe_2(OH)(OAc)_2(HBpz_3)_2](ClO_4)$[o]	3.439	123.6	1.984	1.956 (3)	17.0
14	$[Fe_2(SALPA)_2(SALPAH)_2]$[p]	3.217	109.4	1.97	1.96 (1)	17.0
15	$[Fe_2L_2(OPh)_2](ClO_4)_2$[q]	3.21	107.4	2.00	2.00 (2)	20.5
16	$K_5[Fe_3O(SO_4)_6(H_2O)_3]$[r]	3.332	120.0	1.944	1.924 (3)	26.0
17	$[Fe_3O(alanine)_6(H_2O)_3](ClO_4)_7$[s]	3.32	120.0	1.981	1.92 (1)	31.0
18	$[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$[t]	3.667	159.1	1.865[mm]	1.865 (5)	55.0
19	$\{Fe_2O[O_2PO(OPh)]_2(Me_3TACN)_2\}^{2+}$[u]	3.198	123.2	1.928	1.817 (5)	87.0
20	$[Fe_2O(CO_3)_2(TACN)_2]$[v]	3.048	113.8	1.905	1.820 (8)	91.0
21	$\{Fe_2O[O_2PPh_2]_2(HBpz_3)_2\}$[w]	3.292	130.6	1.946	1.812 (3)	95.0
22	$\{Fe_2O(TACN)_2[O_3P(OPh)]_2\}NaClO_4\cdot 2H_2O$[x]	3.198	123.2	1.928	1.817 (5)	98.0
23	$\{Fe_2O[O_2P(OPh)_2]_2(HBpz_3)_2\}$[y]	3.337	134.7	1.930	1.808 (4)	98.0
24	$[Fe_2O(SO_4)_2(Me_3TACN)_2]$[z]	3.224	122.1	1.938	1.82 (1)	99.0
25	$\{Fe_2O(OAc)_2[(OP(OEt)_2)_3Co(Cp)]_2\}$[aa]	3.174	124.4	1.950	1.795 (5)	108.5
26	$[Fe_2O(OAc)_2(Me_3TACN)_2](ClO_4)_2$[bb]	3.120	119.7	1.956	1.800 (3)	115.0
27	$\{Fe_2OL_2[O_2C(CH_3)_3]_2\}(ClO_4)_2$[cc]	3.075	117.0	1.966	1.803 (6)	116.0
28	$[Fe_2O(O_2CPh)_2(N_3)_2](ClO_4)_2$[dd]	3.079	118.7	1.954	1.790 (5)	117.0
29	$[Fe_2O(MPDP)(4,4'\text{-}Me_2bpy)_2Cl_2]$[ee]	3.130	124.0	1.991	1.773 (3)	119.0
30	$[Fe_2O(TPA)_2(O_2CPh)]^{3+}$[ff]	3.241	129.7	1.903	1.790 (5)	119.0
31	$[Fe_2O(OAc)_2(TIP)_2]^{2+}$[gg]	3.150	122.7	1.962	1.800 (5)	120.0
32	$[Fe_2O(OAc)_2(HBpz_3)_2]$[hh]	3.146	123.6	1.956	1.784 (1)	121.0
33	$[Fe_2O(MPDP)(BIPhMe)_2Cl_2]$[ii]	3.183	125.9	1.980	1.787 (5)	122.0
34	$[Fe_2O(TACN)_2(CrO_4)_2]$[jj]	3.285	129.1	1.911	1.819 (2)	124.0
35	$[Fe_2O(MPDP)(HBpz_3)_2]$[kk]	3.161	123.4	1.967	1.795 (5)	125.0
36	$[Fe_2O(bpy)_2(OAc)_2Cl_2]$[ll]	3.151	123.9	1.982	1.785 (5)	132.0

[a] ⟨Fe–O⟩ is the average distance between the metal and the bridging ligands. [b] *P* is the shortest superexchange pathway defined as the shortest distance between the metal and the bridging ligand(s). See the text for details. [c] Chel = 4-hydroxo-2,6-pyridinedicarboxylate; ref 16a. [d] L = trisalicylidenetriethylenetetramine; ref 16b. [e] Reference 21. [f] See footnote *d*; ref 22. [g] TIEO = 1,1,2-tris(1-methylimidazol-2-yl)ethoxide; ref 23. [h] L = *N*,*N*′-ethylenebis(salicylamine); ref 24. [i] Reference 25. [j] Dipic = 2,6-pyridinedicarboxylate; ref 16a. [k] $(CH_3)_2(NC_7H_2NO_4)$ = 4-(dimethylamino)-2,6-pyridinedicarboxylic acid; ref 26. [l] L = *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylylene)bis[*N*-(carboxymethyl)glycine]; ref 27. [m] L = 1,4-piperazinediylbis(*N*-ethylenesalicylaldiminato); ref 25. [n] See footnote *m*; ref 28. [o] $HBpz_3$ = hydrotris(1-pyrazolyl)borate; ref 29. [p] SALPAH = *N*-(3-hydroxypropyl)salicylaldimine; refs 26 and 30. [q] L = 2-[bis(2-benzimidazolylmethyl)amino]ethanol; ref 57. [r] Reference 16c. [s] Reference 31a. [t] TIEO = 1,1,2-tris(1-methylimidazol-2-yl)ethoxide; ref 23. [u] Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane; ref 32. [v] TACN = 1,4,7-triazacyclononane; ref 33. [w] See footnote *o*; ref 34. [x] Reference 58. [y] See footnote *o*; ref 35. [z] See footnote *u*; ref 32. [aa] Reference 36. [bb] See footnote *u*; ref 37. [cc] L = bis(benzimidazol-2-ylmethyl)amine; ref 59. [dd] N_3 = bis(2-benzimidazolylmethyl)amine; ref 38. [ee] MPDP = *m*-phenylene dipropionate; ref 39. [ff] TPA = tris(2-pyridylmethyl)amine; ref 40b. [gg] TIP = tris(*N*-methylimidazolyl)phosphine; ref 41. [hh] See footnote *o*; ref 42. [ii] BIPhMe = bis(*N*-methylimidazol-2-yl)phenylmethoxymethane; see footnote *ee*; ref 39. [jj] Reference 58. [kk] See footnote *ee*. [ll] Reference 43. [mm] 1.969 Å if the third Fe is considered a ligand.

various analytical expressions to the experimental curves that describe the dependence of J on various structural parameters for the complexes considered. The estimated standard deviations (σ's) of the crystallographically measured bond lengths were included in the fitting program by setting the weights equal to $1/\sigma$. All calculations were performed on a VAX-750 computer.

Results and Discussion

Presented in Table I are structural and magnetic data for 36 di- and trinuclear high-spin Fe(III) complexes.[16,21–44,57–59] The metals are either five- or six-coordinate, doubly or triply bridged, with first coordination spheres composed of Cl, O, or N atoms

---

(20) BBN Software products, Cambridge, MA 02139.

(21) (a) Reiff, W. M.; Long G. J.; Baker, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 6347. (b) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1900.

(22) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 2444.

(23) (a) Gorun, S. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 4568. (b) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244.

(24) Borer, L.; Thalken, L.; Cecarrelli, C.; Glick, M.; Zhang, J. H.; Reiff, W. M. *Inorg. Chem.* **1983**, *22*, 1719.

(25) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1984**, *23*, 3398 and references cited therein.

(26) Ou, C. C.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2053.

(27) (a) Murch, B. P.; Boyle, P. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *107*, 6728. (b) Murch, B. P.; Bradley, F. L.; Boyle, P. D.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 7993.

(28) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 1396.

(29) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4632.

(30) Bertrand, J. A.; Eller, P. G. *Inorg. Chem.* **1974**, *13*, 927.

(31) (a) Holt, E. M.; Holt, S. L.; Tucker, W. F.; Asplund, R. O.; Watson, K. J. *J. Am. Chem. Soc.* **1974**, *96*, 2621. (b) White, R. P.; Al-Basset, J. D.; Cannon, R. D.; Kearley, G. J.; Jayasooriya, U. A. *Physica B* **1989**, *156 & 157*, 367 and references therein.

(32) Wieghardt, K. Private communication.

(33) Drüecke, S.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 1414.

(34) Turowski, P. N.; Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *112*, 681.

(35) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3730.

(36) Feng, X.; Bott, S. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 8046.

(37) Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 778.

(38) Gomez-Romero, P.; Casan-Pastor, N.; Ben-Hussein, A.; Jameson, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 1988.

(39) Beer, R. H.; Tolman, W. B.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1989**, *28*, 4557.

(40) (a) Yan, S.; Que, L., Jr.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 5222. (b) Yan, S.; Cox, D. D.; Pearce, L. L.; Juarez-Garcia, C.; Que, L., Jr.; Zhang, J. H.; O'Connor, C. J. *Inorg. Chem.* **1989**, *28*, 2509.

Table II. Dinuclear Complexes Incompletely Characterized

no.	complex[a]	$-J_{calc}$, cm^{-1}	$-J_{obs}$, cm^{-1}	P_{calc}, Å	P_{obs}, Å
1	$(PIP)_3[Fe_2L_4(OAc)]$[b]	7	10[m]	1.99	2.02 (1)
2a	$[Fe_2O(OAc)_2(Me_3TACN)_2](PF_6)_2$[c]		119	1.794	
2b	$[Fe_2O(OAc)_2(Me_3TACN)_2](PF_6)_2$[d]		95	1.812	
3	$[Fe_2O(OAc)_2(TACN)_2]I_2 \cdot 0.5NaI \cdot 3H_2O$[e]	142	84	1.822	1.78 (1)
4	$[Fe_2L(OAc)_2(Me_4N)]$[f]	8			2.008 (2)
5	$[Fe_2OL_2(O_2CPh)](BPh_4)$[g]	129			1.788 (6)
6	$[Fe_2(TPA)_2O(OAc)]^{3+}$[h]	118			1.795 (5)
7	$[Fe_2OMg(OAc)_6(Py\text{-}d_5)_3]$[i]		62	1.846	
8	$[Fe_2OL_2(OAc)](ClO_4)_3$[j]		104.3	1.805	
9	$[Fe_2O(TACN)_2(HPO_4)_2]$[k]		80	1.826	
10	$[Fe_2O(TACN)_2(HAsO_4)_2]$[l]		70	1.836	

[a] See footnotes, Table I, for abbreviations. [b] PIP = piperidinium, L = 1,2-benzenediolato; ref 46. [c] Reference 47. [d] Reference 48. [e] TACN = 1,4,7-triazacyclononane; ref 49. [f] L = See footnote *e*, Table I; ref 50. [g] L = (*o*-hydroxybenzyl)bis(2-pyridylmethyl)amine; ref 40a. [h] TPA = See footnote *ff*, Table I; ref 40b. [i] This complex probably comprises a triangular arrangement of the metal ions; ref 41b. [j] L = tris(benzimidazol-2-ylmethyl)amine; ref 60. [k,l] Reference 58. [m] Quoted as an approximate value in ref 46.

of a large variety of ligands, both mono- and polydentate. The bridging ligands are binary and ternary combinations of μ_2-oxo, μ_2-hydroxo, μ_2-alkoxo, μ_2-carboxylato, μ_2-sulfato, μ_2-aryl phosphato, μ_2-aryl phosphinato, μ_2-carbonato, μ_2-chromato, and μ_3-oxo groups. The charges on the metal complexes range from −5 to +7. All complexes share the common feature that the metal ions are linked by *more* than one bridge. Considering the above variety, it is not surprising that the Fe···Fe distances vary from 3.023 to 3.667 Å while the Fe–O–Fe angles range from 98 to 159°. The *J* values are spread over more than 1 order of magnitude, from −7 to −134 cm^{-1}.

Examination of data in Table I and Figures S1 and S2 (supplementary material) does not reveal any major correlation between metal–metal distances or the bridging angle and *J*. In fact, the least strongly coupled complex, $J = -7.3$ cm^{-1}, entry 1 in Table I, exhibits one of the shortest metal–metal distances, 3.078 Å. It can be concluded that the empirical power law (eq 1) and the exponential form which contains the metal–metal distance as variable are not adequate.

In order to correlate the magnetic data for dinuclear iron(III) complexes, we introduce a new structural parameter *P*, defined as half of the shortest superexchange pathway between two metals. This parameter has the same order of magnitude as a metal–ligand bond length. The parameter *P* represents the average of the shortest distance between the metals and the bridging atom(s), which are part of the superexchange pathway between the two metals. Averaging is necessary only when the distances are not related by crystallographic symmetry. When multiple-atom bridges like carboxylate anions are present, only the metal–carboxylato oxygen distances are used to calculate the *average* length of the pathway, ⟨Fe–O⟩. The two C–O bonds are arbitrarily excluded since they are considered to play a secondary role in diminishing the exchange interactions as compared with the longer metal–oxygen bonds. In other words, the O⎓C⎓O moiety is considered to be much better at facilitating magnetic exchange coupling compared to the Fe–O(carboxylate) units.

The *P* and *J* values listed in Table I are plotted in Figure 1. Interestingly, a pattern is revealed and the line through the experimental points is described by eq 2, where *J* is given in inverse

$$-J = A \exp(BP) \qquad (2)$$

centimeters and *P* in angstroms. Values for $A = 8.763 \times 10^{11}$ and $B = -12.663$ were determined by least-squares fitting as described in the preceding section.

The exponential form of the analytical expression (eq 2) has been chosen since, to a first approximation, it represents the variation of the overlap integral of two s type orbitals, which, in turn, determines the magnitude of *J*.[45] We have also tried to fit the data with eq 1 by using *P* instead of the metal–metal distance. A correlation can be found between *J* and *P*, but it is statistically inferior to the exponential form. Moreover, the Grüneisen coefficient is −23 as compared with the −10 value derived previously.[15a] It should be noted that for linear complexes (Fe–O–Fe angle 180°) *P* is half the metal–metal distance and, therefore, the latter could be used in principle in eq 2. Multiply bridged linear oxodiiron(III) complexes of this type, however, are not known. When two or more pathways are comparable in length, within 5σ, *P* is set equal to ⟨Fe–O⟩. This case occurs occasionally when the bridging oxide is protonated, alkylated, or metalated. When this *average* (i.e. ⟨Fe–O⟩) superexchange pathway is considered for all the compounds of Table I and Figure S3 (supplementary material), however, no correlation is found.

It is interesting that only one independent parameter, *P*, is needed to describe such a structural variety of complexes and magnitudes of magnetic exchange-coupling interactions. It seems, therefore, that variations in both the electronic and steric effects

---

(41) (a) Kurtz, D. M., Jr. *J. Inorg. Biochem.* **1989**, *3-4*, 309. (b) Wu, F.-J.; Kurtz, D. M., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6563 and references therein.

(42) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653.

(43) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 6898.

(44) (a) Dawson, J. W.; Gray, H. B.; Hoenig, H. E.; Rossman, G. R.; Schredder, J. M.; Wang, R. H. *Biochemistry* **1972**, *11*, 461. (b) Zhang, K.; Stern, E. A.; Ellis, F.; Sanders-Loehr, J.; Shiemke, A. K. *Biochemistry* **1988**, *27*, 7470.

(45) Herring, C.; Flicker, M. *Phys. Rev. A* **1964**, *2*, A362.

(46) Anderson, B. F.; Webb, J.; Buckingham, D. A.; Robertson, G. B. *J. Inorg. Biochem.* **1982**, *16*, 21.

(47) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387.

(48) Wieghardt, K.; Pohl, K.; Ventur, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 392.

(49) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727.

(50) Murch, B. P.; Bradley, F. L.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5027.

(51) (a) Gorun, S. M. Ph.D. Dissertation, Massachusetts Institute of Technology, 1986. (b) References 15, 17, and 47. (c) Gorun, S. M. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372; American Chemical Society: Washington, DC, 1988; pp 196–220.

(52) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149.

(53) Ponomarev, V. I.; Atovmyan, L. O.; Bobkova, S. A.; Turtĕ, K. I. *Dokl. Akad. Nauk SSSR* **1984**, *274*, 368.

(54) Toftlund, H.; Murray, K. S.; Qwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191.

(55) (a) Scarrow, R. C.; Maroney, M. J.; Palmer, S. M.; Que, L., Jr.; Salowe, S. P.; Stubbe, J. *J. Am. Chem. Soc.* **1986**, *108*, 6832. (b) Scarrow, R. C.; Maroney, M. J.; Palmer, S. M.; Que, L., Jr.; Roe, A. L.; Salowe, S. P.; Stubbe, J. *J. Am. Chem. Soc.* **1987**, *109*, 7857. (c) Bunker, G.; Petersson, L.; Sjöberg, B.-M.; Sahlin, M.; Chance, M.; Chance, B.; Ehrenberg, A. *Biochemistry* **1987**, *26*, 4708.

(56) (a) Reference 11. (b) Prince, R. C.; George, G. N.; Savas, C. J.; Cramer, S. P.; Patel, R. N. *Biochim. Biophys. Acta* **1988**, *952*, 220.

(57) Menage, S.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 4293.

(58) Druecke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Fleischhauer, H.-P.; Gehring, S.; Haase, W. *J. Am. Chem. Soc.* **1989**, *111*, 8622.

(59) Adams, H.; Bailey, N. A.; Crane, J. D.; Fenton, D. E.; Latour, J.-M.; Williams, J. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1727.

Table III. Tetranuclear Complexes

no.	complex[a]	$-J_{calc}$, cm^{-1}	$-J_{obs}$, cm^{-1}	P_{calc}, Å	P_{obs}, Å
1	$[Fe_4O_2(BICOH)_2(BICO)_2(O_2CPh)_4]^{2+}$ [a]	27			1.91 (1)
		21			1.93 (1)
2	$[Fe_4O_2(O_2CCF_3)_8(H_2O)_6]$ [b]	36			1.889 (4)
		30			1.902 (4)
3	$[Fe_4O_2L_2(CO_3)_2]^{6-}$ [c]	77	63	1.844	1.829 (4)
		5	11.2	1.981	2.053 (4)
4	$[Fe_4O_2L_2(OH)_2]^{4-}$ [d]	124			1.791 (3)
		10			1.989 (2)
5	$[Fe_2O(OAc)_2(tpbn)]_2{}^{4+}$ [e]	119			1.794 (3)
6	$[Fe_2O(OAc)_2(tptn)]_2{}^{4+}$ [f]		120	1.794	
7	$[Fe_4O_2(OH)_4(TACN)_4]I_4 \cdot 3H_2O$ [g]	9.1	15.1	1.957	1.997 (6)
		90	106.3	1.803	1.816 (6)
8	$[Fe_4O_2(BTACN)_2(OAc)_4](PF_6)_4$ [h]	148			1.777 (3)

[a] BICOH = bis(*N*-methylimidazol-2-yl)carbinol; ref 52. [b] Reference 53. [c] LH_5 = (2-hydroxy-1,3-propanediyl)diiminetetraacetic acid; ref 19a. [d] See footnote *e*, Table I; ref 27. [e] tpbn = tetrakis(2-pyridylmethyl)-1,4-butanediamine; ref 54. [f] tptn = tetrakis(2-pyridylmethyl)-1,3-propanediamine; ref 54. [g] Reference 19b. [h] BTACN = 1,4-bis(1,4,7-triaza-1-cyclononyl)butane; ref 61.

Table IV. Metalloenzymes Known or Believed To Contain Dinuclear Oxo–Iron Centers

no.	enzyme	$-J_{calc}$ cm^{-1}	$-J_{obs}$, cm^{-1}	P_{calc}, Å	P_{obs}, Å
1	methemerythrin[a]		134	1.785	
2A	oxyhemerythrin[b]		77	1.829	
2B	oxyhemerythrin[c]	86			1.82
3A	azidomethemerythrin[d]	142			1.78 (2)
3B	azidomethemerythrine[e]		62–122	1.79–1.85	
4	azidometmyohemerythrin[f]	125			1.79 (2)
5	ribonucleotide reductase[g]	142	108^{+25}_{-20}	1.80 ± 0.02	1.78[a,j]
6	uteroferrin[h]	15	≥ 40	≤ 1.88	1.96
7	beef spleen phosphatase[i]	11	≥ 150	≤ 1.776	1.98[j]

[a] References 8b and 44a. [b] Reference 44a. [c] Reference 44b. [d] Reference 8. [e] NMR data; ref 41b. [f] Reference 8c. [g] References 9b and 55. [h] Reference 10a,b,e. [i] Reference 10c–e. [j] EXAFS data.

of the ligands are reflected by the parameter P, which correlates with J. The Fe–O–Fe angle seems to have a second-order effect upon J. Angular variation is important only when P is constant or large.[16] This observation may explain the larger spread of the experimental values observed for $|J| < 15$ cm^{-1} (see Figure 1).

Table II lists diiron(III) complexes for which only structural data are reported or those that present a problem. P_{obs} and J_{obs} are the experimentally observed values while J_{calc} and P_{calc} are the values calculated by using eq 2. For the first entry, the agreement between observed and calculated values is very good. For entry 2 no crystal structure has been reported yet but the structure of the perchlorate salt, which has a similar diiron center, is known[37] (see entry 26, Table I). The -95-cm^{-1} value reported initially by using a limited data set measured above liquid nitrogen temperature could be in error. Entry 3, for which low-temperature measurements have not been performed, represents a problem; the differences between calculated and observed values are outside the acceptable errors. Considering that entries 2a and 3 are structurally similar, it seems warranted to repeat the magnetic measurements on entry 3 down to liquid helium temperatures. Entry 7 is discussed below.

The correlation of eq 2 applies not only to dinuclear but also to complexes of higher nuclearity. We have shown previously[23] how an unsymmetric, (μ_3-oxo)triiron(III) center containing an isosceles triangle of metals can be formally decomposed geometrically and magnetically into interacting mononuclear Fe^{3+} and dinuclear $\{Fe_2O\}^{4+}$ centers. For this particular compound, $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$, entries 5 and 18 in Table I represent, respectively, the interaction of a mononuclear and a dinuclear center (defined as an "inter" type interaction) and the interaction of the two metals within the dinuclear center (defined as an "intra" type interaction). The presence of the third, more distant mononuclear Fe^{3+} has the effect of lengthening the two iron–oxo bonds in the $\{Fe_2O\}^{4+}$ center to 1.865 Å; the exchange coupling decreases from approximately -110 cm^{-1}, a value typical for (μ-oxo)diiron(III) species, to -55 cm^{-1}. As the mononuclear Fe^{3+}, situated at 2.067 (6) Å, moves toward the dinuclear center and the iron–oxo distances further increase, the $\{Fe_3O\}^{7+}$ isosceles triangle transforms into an equilateral triangle with three equal μ_3-oxo–Fe distances, P, of 1.92 Å. As a consequence, J "inter" increases from -8 to -31 cm^{-1} while J "intra" decreases from -55 to -31 cm^{-1}. The -31-cm^{-1} value was determined for $[Fe_3O(alanine)_6(H_2O)_3](ClO_4)_7$, the $\{Fe_3O\}^{2+}$ core of which is taken as the prototype for basic iron carboxylates. Similarly, for entry 15, P is 1.924 Å and $J = -26$ cm^{-1}. Entry 7, Table II, may represent another situation similar to entry 5, Table I. The Mg^{2+} ion should lengthen the Fe–O bonds (as compared to a (μ-oxo)diiron complex) upon binding to the Fe–O–Fe unit. Consequently J decreases to -62 cm^{-1} from a typical -100 cm^{-1}.

Like metalation, alkylation or protonation of the μ-oxo oxygen atom also reduces the exchange-coupling interaction; for the μ-alkoxo and μ-hydroxo complexes J ranges from -7 to -17 cm^{-1}. Thus, removal of a proton from a μ-OH bridge will result in the gradual increase of J up to the values known for μ-oxo complexes, going through intermediate stages that correspond to various degrees of hydrogen bonding.

Table III lists tetranuclear iron(III) oxo complexes, which can be formally decomposed into dinuclear units according to geometric criteria described previously.[51] Since the "intradimer" P's are smaller than the "interdimer" ones, the exchange-coupling interactions are expected to differ in accord with eq 2. The first and second lines corresponding to each compound listed in Table III represent the "intra-" and "interdimer" values, respectively. The agreement between the calculated and observed values for entry 3 is considered to be acceptable, especially since the molecular field approximation was used to derive J values and because of the difficulties in establishing the exact chemical composition of the sample used for magnetic measurements.[19] The formal assembly of tetranuclear aggregates by condensing two dinuclear species[19,51,52] converts the μ_2-oxo into μ_3-oxo bridges. As a consequence, the magnetic couplings are expected to approach values encountered for $\{Fe_3O\}^{7+}$ and $\{Fe_2(OH)\}^{5+}$ centers.

On the basis of the above results, we suggest that, for aggregates of higher nuclearity that can be magnetically decomposed into

---

(60) Nishida, Y.; Nasu, Miyuki; Tokii, T. *Inorg. Chim. Acta* **1990**, *169*, 143.

(61) Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1990**, *29*, 4143.

subfragments,[51c] exchange-coupling interactions will also follow the magnetostructural relationship described by eq 2. This type of "magnetic dissection" using the HDVV formalism has been proposed previously for oxo-bridged trinuclear $Fe^{III}{}_2Mn^{II}$ complexes, but only recently have inelastic neutron scattering studies confirmed its validity.[31b]

The remaining entries in Table III are predictions based on structural data for planar $\{Fe_4O_2\}$ cores (entries 1 and 2), an adamantane-like arrangement of a $\{Fe_4O_4\}$ core (entry 4), and three $\{Fe_2O\}_2$ cores that are so far apart that the "interdimer" interactions are negligible (entries 5, 6, and 8). The calculated *P* and *J* values are also listed for these incompletely characterized complexes. For entry 7 the agreement is also reasonable, especially for the shorter *P*. It will be interesting to determine the highest degree of nuclearity of iron oxo aggregates for which the magnetostructural correlation is valid. The answer may shed light on the problem of determining the borderline between a molecular structure, described by localized, pairwise magnetic interactions, and a solid-state structure, described by extended, long-range interactions.

Data on metalloenzymes known or believed to contain dinuclear iron(III) oxo centers are presented in Table IV. Exchange-coupling constants of -150 and -120 cm^{-1}, are predicted for azidomethemerythrin and azidometmyohemerythrin, respectively. These values are in good agreement with those determined for hemerythrin models.

The -77-cm^{-1} value of oxyhemerythrin approaches the -55-cm^{-1} value obtained for the "intradimer" coupling in $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$. In this complex the Fe–O–Fe unit is "metalated" but the third Fe^{3+} is not as close to the μ_2-oxo atom as it is in basic iron carboxylates and sulfates, $-J = 26$–31 cm^{-1}. A hydrogen bond to the μ-oxo atom of oxyhemerythrin is therefore reasonable since it will lengthen the Fe–O distance, thus making it intermediate between a μ-oxo and a μ-hydroxo bond ($J = 7$–11 cm^{-1} for hydroxo-bridged complexes). The presence of a hydrogen-bonded hydroperoxide group[8c] at the active site of oxyhemerythrin is thus entirely consistent with the magnetic results, and the iron–oxo bond is predicted to be 1.829 Å long. This value is in excellent agreement with the 1.82-Å Fe–O bond length measured by EXAFS.[44b]

For ribonucleotide reductase a *P* value of 1.80 ± 0.02 Å is predicted, in agreement with a recent EXAFS determination.[55] Uteroferrin is listed in Table IV, but crystallographic structural information is not available. EXAFS results for the diiron(III) form of methane monooxygenase have been recently reported,[56b] but more accurate data are needed before any sensible prediction of the value of *J* can be made. The -40-cm^{-1} value for the exchange-coupling interaction in uteroferrin is a lower limit from which an upper limit of $P = 1.88$ Å can be calculated. This value is somewhat at odds with the 1.98-Å value determined from EXAFS measurements. The latter value results in a calculated *J* of only -11 cm^{-1}, suggesting the presence of a hydroxo bridge. A lower limit for *J* of -150 cm^{-1} for bovine spleen purple acid phosphatase has been reported.[10c] The calculated Fe–O(bridging) bond length of 1.776 Å is not comparable with the 1.98-Å EXAFS value. The presence of short, ~1.9-Å, Fe–O(tyrosine) distances, however, makes the EXAFS value less accurate.[10d]

Conclusions

A quantitative relationship between the antiferromagnetic exchange interaction constant, *J*, and a single structural parameter *P*, the length of the shortest superexchange pathway, is presented. This correlation holds for multiply bridged dinuclear iron(III) complexes. It was also found that this relationship is valid for some oligonuclear complexes, thus allowing for their "magnetic dissection" into smaller, dinuclear units. On the basis of this relationship, data in the literature can be critically analyzed and, more importantly, structural and magnetic predictions can be made.

This relationship does not apply to singly bridged dinuclear iron(III) species. Calculations aimed at explaining this phenomenological correlation are in progress.[62]

Acknowledgment. This work received support in part from NIH Research Grant GM 32134 (to S.J.L.) from the National Institute of General Medical Services. We thank Professor Dr. K. Wieghardt for permission to quote data prior to publication and Drs. P. Turowski and R. Beer for reading the manuscript.

Supplementary Material Available: Figures S1–S3, describing correlations between the exchange-coupling interactions and various geometrical parameters for the diiron(III) complexes listed in Table I (3 pages). Ordering information is given on any current masthead page.

---

(62) Hart, J. R.; Rappe, A. K.; Gorun, S. M.; Upton, T. H. Submitted for publication.

Contribution from the Regional Sophisticated Instrumentation Centre,
Indian Institute of Technology, Madras 600 036, India

EPR and Structural Investigations on Single Crystals of $K_2NbO_2F_5 \cdot H_2O$

Ramakrishnan Geetha, Pillutla Sambasiva Rao, Varghese Babu, and Sankaran Subramanian*

Received March 14, 1990

The single-crystal structural investigation of dipotassium pentafluoroperoxoniobate hydrate, $K_2NbO_2F_5 \cdot H_2O$ (DPPN), is reported. The crystals are monoclinic with space group C_2, and the unit cell dimensions are $a = 8.927$ (4) Å, $b = 8.926$ (3) Å, $c = 9.266$ (2) Å, $\beta = 99.93$ (1)°, and $Z = 4$. The least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to an *R* factor of 0.057. The EPR spectra of a γ-irradiated single crystal of DPPN suggest a Nb hole species stable at room temperature. The anomalous behavior in spacing, number, and intensity of Nb hyperfine lines has been successfully explained by including a quadrupolar term in the Hamiltonian. The spin-Hamiltonian parameters for this hole species are as follows: $g_{xx} = 2.039$ (1), $g_{yy} = 2.013$ (1), $g_{zz} = 2.054$ (1); $A_{xx}(^{93}Nb) = 0.62$ (2), $A_{yy}(^{93}Nb) = 0.79$ (2), $A_{zz}(^{93}Nb) = 0.93$ (2) mT; $Q_{xx}(^{93}Nb) = Q_{yy}(^{93}Nb) = 0.065$, $Q_{zz}(^{93}Nb) = -0.130$ mT. The EPR results further indicate that the unpaired electron in the $[NbO_2F_5]^-$ radical occupies the nonbonding orbital of the peroxo oxygen atoms; this is further supported by EHMO calculations done on the precursor.

Introduction

Reports of EPR investigations of the ions and complexes of the first-row transition series ($3d^n$) abound in the literature, while there have been relatively fewer reports on the second- ($4d^n$) and the third-row ($5d^n$) transition series. Only in the last two decades has there been considerable activity in the study of transition-metal complexes of second- and third-row transition-metal ions, especially those of Mo, Nb, Tc, Ru, Rh, Pd, and Pt, some for their biological significance[1] and others for their catalytic activity.[2] Whereas

---

* To whom correspondence should be addressed.

(1) Spiro, T. G., Ed. *Mo Enzymes*; Wiley-Interscience: New York, 1986; see also references therein.

0020-1669/91/1330-1630$02.50/0