Volume 29
Number 7
April 4, 1990

Inorganic Chemistry

Communications

Synthesis, Structure, and Properties of a Novel Heterobimetallic Fe^{III}Mn^{II} Complex Containing a Septadentate Polyimidazole Ligand

There has been much interest recently in the structure and properties of redox-active non-heme μ-oxo iron proteins.[1,2] The oxygen carrier protein, hemerythrin (Hr), is known to have a μ-oxo–bis(μ-carboxylato)-bridged active site structure,[3] which has been proposed for other diiron proteins[1,2] such as ribonucleotide reductase (RR),[4] purple acid phosphatase (PAP),[5] and methane monooxygenase (MMO).[6] Since each of the μ-oxo iron proteins perform very different chemical functions, it is thought that the auxillary ligands coordinated to the iron centers regulate the redox properties of the active site.[1,2] Histidine is known to be a ligand in Hr[3] and is thought to be present in RR,[7] PAP,[8] and MMO.[6b] The phenolate ion of tyrosine also is thought to be a ligand in PAP and uteroferrin.[8]

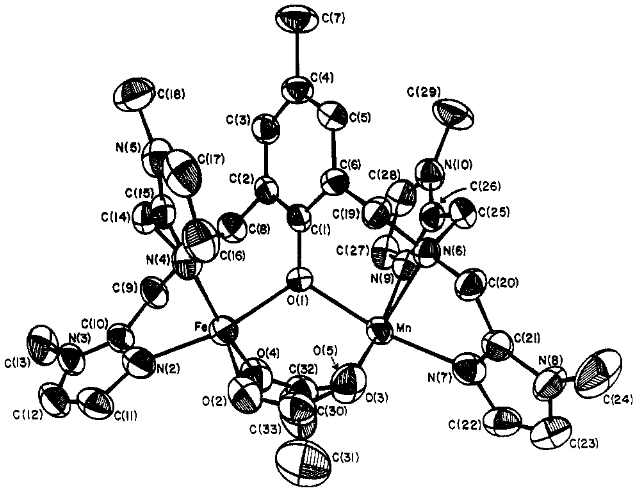

Figure 1. Structure of the cation [Fe^{III}Mn^{II}(bimp)(μ-MeCO$_2$)$_2$]$^{2+}$, showing the atom-labeling scheme. Selected bond distances and angle: Fe···Mn, 3.472 (1) Å; Fe–O(1), 2.035 (3) Å; Fe–N(2), 2.131 (6) Å; Fe–N(4), 2.142 (5) Å; Fe–N(1), 2.308 (5) Å; Fe–O(2), 2.002 (5) Å; Fe–O(4), 2.035 (4) Å; Mn–O(1), 2.092 (3) Å; Mn–N(7), 2.159 (5) Å; Mn–N(9), 2.169 (5) Å; Mn–N(6), 2.316 (5) Å; Mn–O(3), 2.116 (4) Å; Mn–O(5), 2.025 (5) Å; Fe–O(1)–Mn, 114.5 (2)°.

Recently, Averill[8b] and Zerner et al.[9] have shown that purple acid phosphatase and uteroferrin (U$_f$) can be modified to form a novel class of heterobimetallic compounds (Fe^{III}Zn^{II} and Fe^{III}Hg^{II}), in which the Fe^{II} center has been replaced with various divalent metal ions. There is good evidence for the presence of an Fe^{III}Zn^{II} center in red kidney bean phosphatase[10a] and a similar center also may be present in calcineurin[10b] from bovine brain. Recent Mössbauer studies on mixed-metal forms of PAP show that the intrinsic properties of each iron center can be studied without the interference often encountered in exchange-coupled clusters. Therefore, μ-oxo–μ-carboxylato mixed-metal compounds containing imidazole and phenolate ligands are of interest as models of the heterobimetallic centers isolated from PAP and U$_f$.

Recently, we[11a] and others[11b,c] have found that phenol-containing polydentate ligands can be used to stabilize heterobimetallic complexes. While examining the coordination chemistry of a new septadentate polyimidazole ligand, 2,6-bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (H-bimp) (**1**),[12,13] we found that Fe^{III} complexes of **1**, containing either Mn^{II},

---

(1) (a) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195. (b) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (c) Reichard, P.; Ehrenberg, A. *Science* (*Washington, D.C.*) **1983**, *221*, 514. (d) Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111. Sanders-Loehr, J.; Loehr, T. M. *Adv. Inorg. Biochem.* **1979**, *1*, 235. (e) Kurtz, D. M., Jr.; Shriver, D.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 145.

(2) Que, L., Jr.; Scarrow, R. C. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 159–178.

(3) (a) Stenkamp, R. E.; Siekler, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273.

(4) (a) Sjöberg, B.-M.; Loehr, T. M.; Sanders-Loehr, J. *Biochemistry* **1982**, *21*, 96. (b) Joelson, T.; Uhlin, U.; Eklund, H.; Sjöberg, B.-M.; Hahne, S.; Karlson, M. *J. Biol. Chem.* **1984**, *259*, 9076. (c) Petersson, L.; Gräslund, A.; Ehrenberg, A.; Sjöberg, B.-M.; Reichard, P. *J. Biol. Chem.* **1980**, *255*, 6706.

(5) (a) 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. (b) Antanaitis, B. C.; Strekos, T.; Aisen, P. *J. Biol. Chem.* **1982**, *257*, 3766.

(6) (a) Dalton, H. *Adv. Appl. Microbiol.* **1980**, *26*, 71. (b) Ericson, A.; Hedman, B.; Hodgson, K. O.; Green, J.; Dalton, H.; Bentsen, J. G.; Beer, S. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2330. (c) Fox, B. G.; Surerus, K. K.; Munck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553.

(7) Sahlin, M.; Ehrenberg, A.; Gräslund, A.; Sjöberg, B.-M. *J. Biol. Chem.* **1986**, *261*, 2778.

(8) (a) Lauffer, R. B.; Antanaitis, B. C.; Aisen, P.; Que, L., Jr. *J. Biol. Chem.* **1984**, *258*, 14212. (b) Davis, J. C.; Averill, B. A. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 4623.

(9) (a) Keough, D. T.; Dionysius, D. A.; de Jersey, J.; Zerner, B. *Biochim. Biophys. Res. Commun.* **1980**, *94*, 600. (b) Beck, J. L.; Keough, D. T.; de Jersey, J.; Zerner, B. *Biochim. Biophys. Acta* **1984**, *791*, 357. (c) Beck, J. L.; McConachie, L. M.; Summors, A. C.; Arnold, W. N.; de Jersey, J.; Zerner, B. *Biochim. Biophys. Acta* **1986**, *869*, 61. (d) Sage, J. T.; Xia, Y.-M.; Debrunner, P. G.; Keough, D. T.; de Jersey, J.; Zerner, B. *J. Am. Chem. Soc.* **1989**, *111*, 7239.

(10) (a) Beck, J. L.; de Jersey, J.; Zerner, B. *J. Am. Chem. Soc.* **1988**, *110*, 3317. (b) King, M. M.; Huang, C. Y. *J. Biol. Chem.* **1984**, *259*, 8847.

(11) (a) Preliminary account of mixed-metal complexes: Buchanan, R. M.; Oberhausen, K. J.; Richardson, J. F. Presented at the 195th National Meeting of the American Chemical Society, Toronto, June 1988; paper INORG 530. (b) Suzuki, M.; Uehara, A.; Oshio, H.; Endo, K.; Yanaga, M.; Kida, S.; Saito, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3547. (c) Borovik, A. S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1986. (d) Borovik, A. S.; Papaefthmiou, V.; Taylor, L. F.; Anderson, O. P.; Que, L., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6183.

(12) Buchanan, R. M.; Oberhausen, K. J.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 971.

0020-1669/90/1329-1299$02.50/0 © 1990 American Chemical Society

Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II} ions, can be prepared in reasonable yields. We wish to report herein the synthesis and properties of a novel $Fe^{III}Mn^{II}$ complex of **1**.

The heterobimetallic complex $[Fe^{III}Mn^{II}(bimp)(\mu\text{-}O_2CCH_3)_2](ClO_4)_2$ (**2**) has been prepared by several methods. The easiest procedure involves addition of stoichiometric quantities of $Fe(ClO_4)_3\cdot 9H_2O$ and $Mn(CH_3CO_2)_2\cdot 4H_2O$ to a methanol solution containing 1 equiv of H-bimp and 2 equiv of sodium acetate. Addition of 2.5 equiv of $NaClO_4$ affords a black precipitate, which after crystallization from a CH_2Cl_2/CH_3CN solution gives crystals adequate for structure determination. Recently, Que et al.[11c] have reported an alternative procedure for preparing heterobimetallic complexes. Following their method, $Fe(NO_3)_3$ is added to a stirred solution of H-bimp and 2 equiv of sodium acetate, affording a monometalated intermediate of **1** that reacts cleanly with $Mn(CH_3CO_2)_2$, giving **2**. Sequential metalation procedures have been employed successfully in preparing other mixed-metal complexes;[14] however, the present H-bimp ligand is unusual in that it forms heterometallic complexes directly.

The crystal structure of **2**[15] is shown in Figure 1. No crystallographic symmetry is imposed on the cation, and assignments of the high-spin Fe^{III} ($S = {}^5/_2$) and high-spin Mn^{II} ($S = {}^5/_2$) atomic positions are based on the overall shortening of the metal–ligand bond distances associated with the Fe^{III} ion. A possible problem arises in differentiating the positions assigned to the Fe^{III} and Mn^{II} ions, due to their identical $S = {}^5/_2$ spin configurations. The longer Mn^{II}–O and Mn^{II}–N distances, however, are consistent with lengths reported recently for the mixed-valence $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}O_2CCH_3)_2]^{2+}$ ion[12] and other[16] isostructural μ-phenoxo–bis(μ-carboxylato)-bridged Mn compounds. The Fe^{III}–O and Fe^{III}–N distances are slightly longer than the distances reported for $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CC_6H_5)_2]^{2+}$ [13] and related compounds but are consistent with lengths reported for other phenolate-bridged Fe^{III} complexes.[17] The Fe···Mn distance in **2** is 3.445 (3) Å.

Presence of a high-spin Fe^{III} ion in **2** has been confirmed by the 100 K ^{57}Fe Mössbauer spectrum, which shows a single quadrupole-split doublet with a splitting of 0.646 (3) mm/s and isomer shift of 0.355 mm/s vs iron foil at room temperature. The electronic spectrum of **2** consists of a broad band centered at 559 nm (ϵ = 674 M^{-1} cm^{-1}) and a shoulder at 329 nm (ϵ = 1343 M^{-1} cm^{-1}). A similar spectrum has been reported for $[Fe^{II}Zn^{III}(bpmp)(\mu\text{-}OPr)_2]^{2+}$ [11d] and $Fe^{II}Fe^{III}(bimp)(\mu\text{-}OAc)_2]^{2+}$.[13] Comparison of the spectrum of **2** with those of $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}OAc)_2]^{2+}$ [13] (523 nm, ϵ = 606 M^{-1} cm^{-1}) and $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}OAc)_2]^{2+}$ [12] (606 nm, ϵ = 430 M^{-1} cm^{-1}) allows us to understand the nature of these transitions. The absorption at 559 nm is due to the phenolate-to-Fe^{III} charge-transfer transition. The intensity of the band is similar to that observed for $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}OAc)_2]^{2+}$, which indicates that the phenolate-to-Fe^{III} charge-transfer transition is not appreciably affected by the presence of the divalent cation. The intense band at 329 nm obscures the weak ${}^6A_1 \rightarrow {}^4T_2({}^4D)$ ligand field transition expected for a high-spin ferric ion and is likely due to ligand π–π^* transitions and metal–ligand charge-transfer transitions.[18] No intervalence charge-transfer band is observed in the near-IR region; therefore, the data appear consistent with the $Fe^{III}Mn^{II}$ bridged structure observed in the crystal structure.

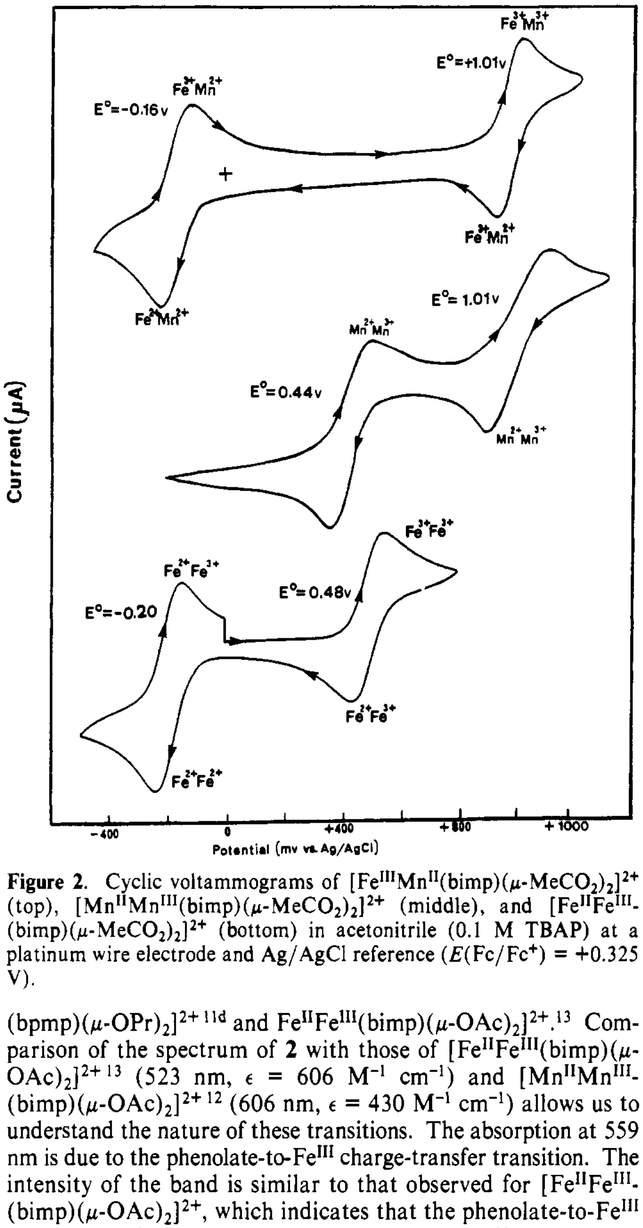

Figure 2. Cyclic voltammograms of $[Fe^{III}Mn^{II}(bimp)(\mu\text{-}MeCO_2)_2]^{2+}$ (top), $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}MeCO_2)_2]^{2+}$ (middle), and $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}MeCO_2)_2]^{2+}$ (bottom) in acetonitrile (0.1 M TBAP) at a platinum wire electrode and Ag/AgCl reference ($E(Fc/Fc^+)$ = +0.325 V).

A cyclic voltammogram of complex **2** in acetonitrile is displayed in Figure 2, along with the voltammograms of $[Fe^{II}Fe^{III}(bimp)(\mu\text{-}O_2CCH_3)_2]^{2+}$ [13] and $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}O_2CCH_3)_2]^{2+}$.[12] Two quasireversible redox processes are observed for each complex corresponding to successive one-electron-transfer steps. The redox steps at −0.16 and +1.01 V vs Ag/AgCl ($E(Fc/Fc^+)$ = 0.325 V) for **2** correspond to the $Fe^{II}Mn^{II}/Fe^{III}Mn^{II}$ and $Fe^{III}Mn^{II}/Fe^{III}Mn^{III}$ couples, respectively. These values are in close agreement with the first and last redox steps observed for the Fe_2 and Mn_2 homologues, respectively. The 565-mV shift in the Mn^{II}/Mn^{III} redox couple in **2**, relative to the second Mn^{II}/Mn^{III} redox step in $[Mn^{II}Mn^{III}(bimp)(\mu\text{-}OAc)_2]^{2+}$, is a result of the close proximity of the manganous and ferric ions and simple coulombic interactions.

---

(13) Mashuta, M. S.; Webb, R. J.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 2745.

(14) (a) Brewer, G. A.; Sinn, E. *Inorg. Chem.* **1987**, *26*, 1529. (b) Costello, U.; Vigato, P. A.; Viladi, M. *Coord. Chem. Rev.* **1977**, *23*, 31. (c) Chandhuri, P.; Winter, M.; Kuppers, H.-J.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1987**, *26*, 3302. (d) Bencini, A.; Caneschi, A.; Dei, A.; Gatteschi, D.; Zanchini, C.; Kahn, O. *Inorg. Chem.* **1986**, *25*, 1374. (e) Mikuriya, M.; Okawa, H.; Kida, S.; Veda, I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2920. (f) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1979**, *23*, 2225. (g) Lintvedt, M. D.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. D. *Inorg. Chem.* **1976**, *15*, 1646. (h) Lambert, S. L.; Spiro, C. L.; Gagné, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1982**, *21*, 68. (i) Costes, J.-P.; Serra, J.-F.; Dahan, F.; Laurent, J.-P. *Inorg. Chem.* **1986**, *25*, 2790.

(15) The compound analyzes correctly for C, H, N, Cl, Fe, and Mn. Crystallographic data at 298 K: monoclinic space group $P2_1/n$; a = 13.411 (3), b = 21.680 (3), c = 15.573 (3) Å; β = 95.03 (1)°; V = 4510.5 $Å^3$; Z = 4; R = 6.3%, R_w = 7.9%; d_{obsd} = 1.50 (1), d_{calcd} = 1.49 g/cm^3. Data were collected on a blue-brown 0.4 × 0.4 × 0.35 mm crystal coated with epoxy at 298 K with Mo Kα radiation (λ = 0.71073 Å, 2θ = 45° on an Enraf-Nonius CAD-4 diffractometer). The structure was solved and refined (SDP package) by using 5158 unique reflections ($I > 3\sigma(I)$). One counterion and the CH_3CN solvate were disordered but reasonably modeled. (*Caution!* As with all perchlorates salts, samples should be handled with care.)

(16) (a) Diril, H.; Chang, H.-R.; Zhang, X.; Larsen, S. K.; Potenza, J. A.; Pierport, C. G.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6207. (b) Chang, H.-R.; Diril, H.; Nilges, M. J.; Zhang, X.; Potenza, J. A.; Schugar, H. J.; Hendrickson, D. N.; Isied, S. S. *J. Am. Chem. Soc.* **1988**, *110*, 625.

(17) (a) Borovik, A. S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2345. (b) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 2444. (c) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M.; McPartlin, M.; Tasker, P. A. *Inorg. Chim. Acta* **1977**, *25*, L137. (d) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1900.

(18) The compound $[Mn_2(bimp)(\mu\text{-}OAc)_2](ClO_4)$ has been prepared. The electronic spectrum shows an intense band at 309 nm (ϵ = 3730 M^{-1} cm^{-1}) that is most likely due to a ligand π–π^* transition. No ligand field or charge-transfer transitions are observed in the visible region.

Magnetic susceptibility measurements on powdered crystals of **2** between 299.7 and 5.2 K indicate that the metal ions are weakly coupled antiferromagnetically. The magnetic moment of the sample drops from 7.18 μ_B/complex at 299.7 K to 0.872 μ_B/complex at 5.2 K. Susceptibility data were least-squares fitted by using the Hamiltonian for an isotropic exchange interaction, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ (S_1 and $S_2 = {}^5/_2$). The exchange-coupling constant J was determined to be -7.7 cm^{-1} with $g = 1.9$ and TIP fixed at 800×10^{-6} cgsu. The powder EPR spectrum of **2** at 4.2 K is consistent with an $S = 5$ coupled binuclear system.[19]

In summary, the bimp$^-$ ligand appears capable of stabilizing heterobimetallic complexes containing discrete trivalent and divalent metal ion binding sites, similar to PAP and U$_f$. A complete discussion of the structure and properties of **2** and related complexes (Fe^{III}M^{II}, where M^{II} = Co, Ni, Cu, and Zn) will be reported later. These complexes should be useful in evaluating the electronic properties of isolated iron centers in the presence or absence of exchange coupling.

Acknowledgment. We are thankful for support from the National Science Foundation (Grant No. RII-8610671), the Commonwealth of Kentucky through the Kentucky EPSCoR Program (R.M.B.) and the National Institutes of Health (Grant No. HL13652) (D.N.H.).

Supplementary Material Available: Figures displaying magnetic, Mössbauer, and EPR data and tables including atomic coordinates, isotropic and anisotropic thermal parameters, hydrogen coordinates, and bond lengths and bond angles (16 pages); a listing of structure factor amplitudes (F_o, F_c) (29 pages). Ordering information is given on any current masthead page.

---

(19) Mathur, P.; Crowder, M.; Dismukes, G. C. *J. Am. Chem. Soc.* **1987**, *109*, 5227.

(20) Part of this research done at the University of Illinois.

Department of Chemistry
University of Louisville
Louisville, Kentucky 40292

Robert M. Buchanan*
Mark S. Mashuta
John F. Richardson
Kenneth J. Oberhausen

Department of Chemistry
University of California at San Diego, D-006
La Jolla, California 92093

David N. Hendrickson*,[20]

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Robert J. Webb
Mark A. Nanny

Received June 7, 1989

Molecular Mechanics of Single Bonds in Tetrakis(carboxylato)dirhodium Systems

In a previous analysis[1] of dirhodium centers by molecular mechanics, a harmonic force constant of 0.88 mdyn Å^{-1}, calculated from a measured[2] Rh-Rh vibration frequency of 170 cm^{-1}, was used in the force field for Rh-Rh single bonds. More recent, more detailed electronic, infrared, Raman, and resonance Raman studies[3,4] have shown that $\nu(\mathrm{Rh_2})$ should rather be assigned to the band at 289 cm^{-1}. It is of interest to see if this assignment could be sustained by molecular mechanics simulation of the known dirhodium systems, using the corresponding harmonic force constant of 2.73 mdyn Å^{-1} (N cm^{-1}).

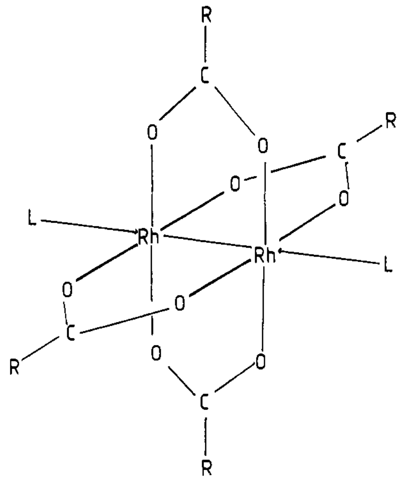

Figure 1. Schematic drawing of the bridged $\mathrm{Rh_2(O_2CR)_4L_2}$.

Table I. Calculated and Observed Rh-Rh Distances (k = 2.73 mdyn Å^{-1}) Together with the Tabulated Values of r_0

axial donor, L	R	r(obs)/Å	ref	r(calc)/Å	r_0/Å
H_2O (planar)	CH_3	2.3855 (5)	4	2.385	2.42
H_2O (tetr)	CH_3	2.3855 (5)	4	2.385	2.43
Me_2OS	CH_3	2.406 (1)	5	2.406	2.44
Me_2OS	C_2H_5	2.407 (1)	6	2.407	2.43
Me_2SO	CF_3	2.419 (1)	6	2.420	2.45
H_2O (planar)	$C(CH_3)_3$	2.371 (1)	5	2.371	2.41
H_2O (tetr)	$C(CH_3)_3$	2.371 (1)	5	2.371	2.42

Table II. Improved Force—Field Parameters for Bond Stretching (k/mdyn Å^{-1}, r_0/Å) and Angle Bonding (k/mdyn Å rad^{-1}, θ_0/rad)

	k	r_0 or θ_0
Rh—S(ax)	0.80	2.35
H—O(ax)	5.00	0.96
C—S(ax)	3.50	1.80
O═S(ax)	3.50	1.45
O=-C(br)	3.00	1.26
C—F	0.40	1.32
Rh—Rh—O,S(ax)	0.3	3.1416
O—Rh—O,S(br)	0.8	1.571
Rh—O—Lp(br)	0.4	2.094
Rh—O=-C(br)	0.2	2.094
Lp—O=-C(br)	0.6	2.094
O=-C=-O(br)	1.5	2.094
O=-C(br)—C	1.0	2.094
F—C—C(br)	0.65	1.911
F—C—F	0.52	1.911
Rh—O—H,Lp(ax)	0.4	2.094, 1.911
Rh—S—C(ax)	1.0	1.911

Torsional Parameters (U/J mol^{-1}, ϕ_0/deg)

	U	ϕ_0
X—O=-C—X	0.63	0
X—Rh—O—X(ax)	0.42	90

Calculations were done on a series of $\mathrm{Rh_2(O_2CR)_4L_2}$ systems,[5,6] shown in Figure 1, by using a Newton-Raphson minimization procedure coded by Boyd.[7] The series of compounds considered allowed for the variation of both the carboxyl group and the axial ligands. In each case the parameter r_0 in the expression for bond strain, $V = {}^1/_2k(r - r_0)^2$, was varied for constant k = 2.73 mdyn Å^{-1} until the observed bond length was reproduced. The results

---

(1) Boeyens, J. C. A.; Cotton, F. A.; Han, S. *Inorg. Chem.* **1985**, *24*, 1750.

(2) Miskowski, V. M.; Schaeffer, W. P.; Sadeghi, B.; Santarsiero, B. D.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 1154.

(3) Clark, R. J. H.; Hempleman, A. J. *Inorg. Chem.* **1988**, *27*, 2225.

(4) Clark, R. J. H.; Hempleman, A. J.; Flint, C. D. *J. Am. Chem. soc.* **1986**, *108*, 518.

(5) Cotton, F. A.; De Boer, B. G.; La Prada, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr.* **1971**, *B27*, 1664.

(6) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323, 2347.

(7) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.