Thomas, M., Stansfield, R. F. D., Berneron, M., Filhol, A., Greenwood, G., Jacobe, J., Feltin, D. & Mason, S. A., (1983). *Position Sensitive Detectors of Thermal Neutrons*, edited by P. Convert & J. B. Forsyth, pp. 344–350. London: Academic Press.

Wilkinson, C., Khamis, H. W., Stansfield, R. F. D. & McIntyre, G. J. (198). *J. Appl. Cryst.* **21**, 471–478.

Zeiher, E. H. K., DeWit, D. G. & Caulton, K. G. (1984). *J. Am. Chem. Soc.* **106**, 7006–7011.

Acta Cryst. (1992). **B48**, 444–449

Structural Studies of Oxygen-Bridged Iron Compounds

By I. Vasilevsky† and N. J. Rose

Department of Chemistry, University of Washington, Seattle, Washington 98195, *USA*

and R. E. Stenkamp‡

Department of Biological Structure, University of Washington, Seattle, Washington 98195, *USA*

(*Received* 4 *April* 1991; *accepted* 6 *January* 1992)

Abstract

Compound (I): *cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2 –)-*O*:*O*′]]dihydroxodiphenyldiborato](3 –)]-μ-methoxydiiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_2(CH_3O)$], M_r = 804.9, monoclinic, Cc, a = 21.228 (6), b = 8.020 (2), c = 20.865 (5) Å, β = 105.2 (1)°, V = 3428 (2) Å^3, Z = 4, D_x = 1.56 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 10.6 cm^{-1}, $F(000)$ = 1648, T = 275 K, R = 0.055 for 3018 unique reflections. Compound (I) contains a pseudo-twofold axis relating the two pyridine dioxime groups bound to the Fe atoms. In addition, two O atoms from the phenylborate moieties bridge the iron atoms, as does a methoxide. The two Cl atoms are bound to the seven coordinate metals axial to the methoxide. Compound (II): *cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2 –)-*O*:*O*′]]dihydroxodiphenyldiborato](3 –)]-μ-hydroxodiiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_2(OH)$].$H_2O$.$2C_2H_3N$, M_r = 891.0, monoclinic, $P2_1/n$, a = 11.860 (2), b = 20.911 (5), c = 16.175 (3) Å, β = 92.88 (1)°, V = 4006 (3) Å^3, Z = 4, D_x = 1.48 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 9.1 cm^{-1}, $F(000)$ = 1832, T = 275 K, R = 0.051 for 7034 unique reflections. Compound (II) contains a hydroxide group replacing the methoxide in compound (I). The crystals also contain two acetonitriles of solvation. The bond lengths in the complex and the hydrogen-bonding pattern in the crystals are consistent with one of the bridging borate O atoms being protonated. Compound (III): μ-chloro-*cis*-dichloro[μ-[bis[μ-[[2,6-diacetylpyridine dioximato](2 –)-*O*:*O*′]]dihydroxodiphenyldiborato](3 –)]-diiron, [$Fe_2(C_{30}H_{29}B_2N_6O_6)Cl_3$].$2C_4H_8O$, M_r = 953.5, triclinic, $P\bar{1}$, a = 10.535 (13), b = 13.908 (22), c = 15.175 (21) Å, α = 91.67 (12), β = 106.45 (11), γ = 94.53 (12)°, V = 2123 (7) Å^3, Z = 2, D_x = 1.49 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 9.3 cm^{-1}, $F(000)$ = 984, T = 275 K, R = 0.077 for 5536 unique reflections. Compound (III) contains a bridging chloride in place of the bridging methoxide found in compound (I). There are also two tetrahydrofuran molecules in the asymmetric unit of crystals of compound (III).

Introduction

In exploring the chemistry of binuclear iron complexes, some related to metalloproteins such as hemerythrin and ribonucleotide reductase, we have synthesized several members of a new class of compounds containing two seven-coordinate Fe atoms bridged by two O atoms and another ligand (CH_3O^-, OH^-, Cl^-). We report here the crystal structures of three of these compounds.

Experimental

Crystals of compound (I) were obtained from a self-assembly reaction involving phenylboric acid, sodium methoxide, 2,6-diacetylpyridine dioxime and ferric chloride hydrate, all in methanol solution. Compound (II) was generated by dissolving compound (I) in pyridine, drying the solution and recrystallizing the material from water/acetonitrile solutions. Evaporation of the red–brown filtrate obtained from a mixture of phenylboric acid, 2,6-diacetylpyridine dioxime, ferric chloride and sodium hydroxide in water yielded a solid which was extracted with chloroform. Crystals from the chloro-

---

† Deceased 30 April 1989.

‡ Author for correspondence.

0108-7681/92/040444-06$06.00

Table 1. *Experimental data*

	(I)	(II)	(III)
Crystal size (mm)	0.17 × 0.17 × 0.04	0.20 × 0.30 × 0.40	0.11 × 0.07 × 0.16
Number of centering reflections[a]	25		25
θ range of centering reflections[a] ( )	2.7–11.8		2.0 13.7
Maximum empirical absorption correction[b]	0.9955	0.9987	-
Minimum empirical absorption correction[b]	0.9246	0.8506	-
Maximum $\sin\theta/\lambda$ (Å^{-1})	0.595	0.595	0.538
Range of h collected	0→25	0→14	0→11
Range of k collected	0→9	0→24	−14→14
Range of l collected	−24→24	−19→19	−16→15
Number of standards	4	4	4
Variation in standards	1.008	1.059	1.003
Number of measurements	3112	7626	6194
Number of unique reflections	3018	7034	5536
$R_{\rm int} = \sum(F - \langle F\rangle)/\sum\langle F\rangle$	0.045	0.039	0.032
Number of unobserved reflections	775	1227	2051
Criteria for unobserved reflections	$2\sigma(I)$	$2\sigma(I)$	$2\sigma(I)$
Number of parameters refined	449	505	532
R value	0.055	0.051	0.077
wR	0.033	0.048	0.033
S	1.45	4.43	0.95
Maximum shift/e.s.d.	0.030	0.007	0.006
Maximum residual difference density (e Å^{-3})	0.5	0.7	0.8
Minimum residual difference density (e Å^{-3})	−0.5	−0.7	−0.9

Notes: (*a*) For (II) information is no longer available due to lost computer output. (*b*) No empirical absorption correction applied to compound (III).

form solution were recrystallized from tetrahydrofuran and were used in the structure determination of compound (III).

Diffraction data for all three compounds were measured using an Enraf–Nonius CAD-4 diffractometer. ω–2θ scans were used for the intensity measurements with ω-scan ranges of $(0.6 + 0.35\tan\theta)^\circ$, $(1.0 + 0.35\tan\theta)^\circ$ and $(0.7 + 0.35\tan\theta)^\circ$ for compounds, (I), (II), and (III) respectively. Other experimental details for each structure are listed in Table 1. The initial data reduction was carried out using the *SDP* package (Frenz, 1978), but the *RANTAN*80 (Xing, 1983), *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *XTAL*3.0 (Hall & Stewart, 1990) systems were used for the structure solution, refinement and analysis. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) including anomalous-scattering corrections (Cromer, 1965).

Direct methods were used to locate the Fe atoms in each compound. The structure of compound (I) was solved using partial models, and the model was completed using Fourier methods. The structure was initially solved in space group *C*2/*c*, but disorder in the phenyl rings suggested a model in space group *Cc* which made more structural sense and refined to lower *R* values. For compounds (II) and (III), initial models were obtained by locating the Fe atoms and the bridging atoms using direct methods and then superposing the entire complex from compound (I)

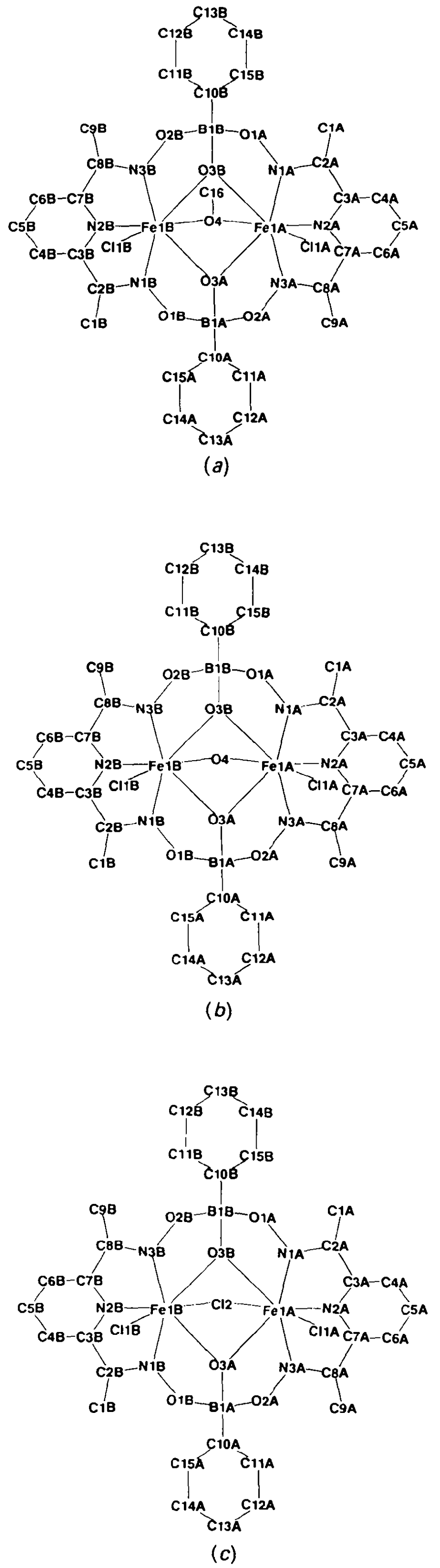


Fig. 1. Atom-labelling scheme for (*a*) compound (I), (*b*) compound (II) and (*c*) compound (III).

Table 2. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Compound (I)				
Fe1*A*	0.03285	0.0798 (3)	0.19722	0.054 (1)
Fe1*B*	−0.03287 (6)	0.0790 (3)	0.30307 (6)	0.056 (1)
Cl1*A*	0.0596 (3)	0.3085 (6)	0.1422 (2)	0.074 (2)
Cl1*B*	−0.0672 (3)	0.3059 (6)	0.3498 (2)	0.072 (2)
O1*A*	0.1621 (4)	0.087 (1)	0.3054 (5)	0.054 (4)
O2*A*	−0.1118 (5)	0.062 (1)	0.1038 (5)	0.063 (4)
O3*A*	−0.0597 (5)	0.201 (1)	0.2052 (4)	0.049 (3)
O1*B*	−0.1656 (5)	0.091 (1)	0.1883 (5)	0.072 (5)
O2*B*	0.1051 (5)	0.070 (1)	0.3951 (5)	0.077 (5)
O3*B*	0.0471 (4)	0.191 (1)	0.2894 (4)	0.050 (3)
O4	−0.0013 (6)	−0.0960 (5)	0.2524 (6)	0.051 (2)
N1*A*	0.1318 (6)	0.023 (2)	0.2478 (6)	0.067 (6)
N2*A*	0.0708 (6)	−0.103 (2)	0.1424 (6)	0.055 (5)
N3*A*	−0.0497 (7)	0.011 (2)	0.1140 (6)	0.075 (6)
N1*B*	−0.1331 (6)	0.014 (1)	0.2501 (6)	0.055 (5)
N2*B*	0.0665 (6)	−0.097 (2)	0.3646 (6)	0.054 (5)
N3*B*	0.0436 (6)	0.007 (2)	0.3891 (6)	0.047 (5)
B1*A*	0.1206 (7)	0.178 (2)	0.1557 (8)	0.043 (6)
B1*B*	0.1118 (9)	0.187 (2)	0.3367 (9)	0.064 (8)
C1*A*	0.2374 (8)	0.109 (2)	0.2553 (8)	0.078 (7)
C2*A*	0.1667 (7)	0.086 (2)	0.2187 (8)	0.048 (6)
C3*A*	0.1324 (8)	−0.153 (2)	0.1601 (9)	0.066 (8)
C4*A*	0.156 (1)	−0.266 (2)	0.118 (1)	0.093 (9)
C5*A*	0.1121 (9)	−0.302 (2)	0.0549 (9)	0.088 (8)
C6*A*	0.0505 (8)	−0.275 (2)	0.0405 (8)	0.063 (7)
C7*A*	0.0310 (6)	−0.165 (2)	0.0827 (8)	0.055 (6)
C8*A*	−0.0390 (8)	0.097 (2)	0.0739 (8)	0.064 (6)
C9*A*	−0.0949 (7)	−0.165 (2)	0.0135 (7)	0.079 (7)
C10*A*	0.1555 (6)	0.346 (2)	0.1240 (7)	0.053 (5)
C11*A*	−0.2038 (7)	0.331 (2)	0.0621 (7)	0.083 (6)
C12*A*	−0.2370 (7)	0.472 (2)	0.0313 (6)	0.092 (6)
C13*A*	−0.225 (1)	0.610 (2)	0.0699 (9)	0.112 (9)
C14*A*	−0.190 (1)	0.627 (3)	0.1254 (9)	0.14 (1)
C15*A*	−0.1491 (9)	0.490 (2)	0.1579 (9)	0.104 (8)
C1*B*	−0.2438 (8)	−0.112 (2)	0.2501 (9)	0.088 (8)
C2*B*	−0.172 (1)	−0.065 (2)	0.2740 (8)	0.076 (8)
C3*B*	−0.1310 (8)	−0.146 (2)	0.3427 (8)	0.060 (7)
C4*B*	−0.1594 (6)	−0.253 (2)	0.3786 (8)	0.068 (7)
C5*B*	−0.1193 (8)	0.330 (2)	0.4319 (8)	0.072 (6)
C6*B*	−0.0516 (9)	−0.259 (2)	0.4555 (8)	0.084 (8)
C7*B*	−0.0245 (9)	−0.152 (2)	0.4176 (8)	0.066 (7)
C8*B*	0.0395 (8)	−0.099 (2)	0.4358 (7)	0.054 (6)
C9*B*	0.0880 (8)	0.155 (2)	0.4910 (9)	0.084 (7)
C10*B*	0.1396 (8)	0.339 (3)	0.3612 (8)	0.078 (7)
C11*B*	0.1905 (8)	0.380 (2)	0.413 (1)	0.086 (8)
C12*B*	0.2259 (8)	0.539 (3)	0.4373 (8)	0.11 (1)
C13*B*	0.1950 (9)	0.663 (2)	0.399 (1)	0.095 (9)
C14*B*	0.1433 (8)	0.658 (2)	0.3492 (7)	0.110 (8)
C15*B*	0.1169 (9)	0.492 (3)	0.3346 (8)	0.108 (8)
C16	−0.0271 (5)	−0.250 (1)	0.2299 (5)	0.080 (6)
Compound (II)				
Fe1*A*	0.67514 (4)	0.16202 (2)	0.84516 (3)	0.0268 (2)
Fe1*B*	0.61064 (4)	0.15290 (2)	0.67211 (3)	0.0279 (2)
Cl1*A*	0.59180 (8)	0.20866 (5)	0.95521 (6)	0.0486 (4)
Cl1*B*	0.44878 (8)	0.18185 (5)	0.59699 (6)	0.0456 (4)
O1*A*	0.5448 (2)	0.0374 (1)	0.8667 (1)	0.0419 (9)
O2*A*	0.8062 (2)	0.2810 (1)	0.7837 (1)	0.0393 (9)
O3*A*	0.6167 (2)	0.2418 (1)	0.7628 (1)	0.0313 (8)
O1*B*	0.7080 (2)	0.2942 (1)	0.6509 (1)	0.0410 (9)
O2*B*	0.5258 (2)	0.0214 (1)	0.7192 (1)	0.0407 (9)
O3*B*	0.5400 (2)	0.1299 (1)	0.7761 (1)	0.0284 (8)
O4	0.7418 (2)	0.1336 (1)	0.7418 (1)	0.0326 (8)
O5	0.3946 (2)	0.2625 (1)	0.7732 (2)	0.086 (1)
N1*A*	0.6427 (2)	0.0674 (1)	0.8912 (2)	0.035 (1)
N2*A*	0.8152 (2)	0.1334 (1)	0.9280 (2)	0.031 (1)
N3*A*	0.8085 (2)	0.2342 (1)	0.8423 (2)	0.031 (1)
N1*B*	0.7044 (2)	0.2330 (1)	0.6181 (2)	0.036 (1)
N2*B*	0.6870 (2)	0.1192 (2)	0.5625 (2)	0.036 (1)
N3*B*	0.5799 (2)	0.0523 (1)	0.6590 (2)	0.036 (1)
N4	−0.0364 (3)	0.1722 (2)	0.6678 (3)	0.099 (2)
N5	0.2095 (5)	0.3379 (3)	0.7145 (4)	0.147 (3)
B1*A*	0.6912 (3)	0.2945 (2)	0.7422 (3)	0.034 (2)
B1*B*	0.4928 (4)	0.0680 (2)	0.7877 (2)	0.033 (2)
C1*A*	0.6786 (4)	0.0203 (2)	0.9906 (2)	0.062 (2)
C2*A*	0.7050 (3)	0.0416 (2)	0.9498 (2)	0.038 (1)
C3*A*	0.8045 (3)	0.0801 (2)	0.9724 (2)	0.038 (1)
C4*A*	0.8851 (4)	0.0647 (2)	1.0357 (2)	0.056 (2)
C5*A*	0.9730 (4)	0.1071 (2)	1.0523 (3)	0.064 (2)
C6*A*	0.9820 (3)	0.1620 (2)	1.0065 (2)	0.049 (2)
C7*A*	0.8999 (3)	0.1738 (2)	0.9428 (2)	0.035 (1)
C8*A*	0.9007 (3)	0.2296 (2)	0.8875 (2)	0.033 (1)
C9*A*	0.9960 (3)	0.2740 (2)	0.8829 (3)	0.052 (2)
C10*A*	0.6549 (3)	0.3642 (2)	0.7694 (2)	0.037 (1)
C11*A*	0.5996 (3)	0.3739 (2)	0.8421 (3)	0.052 (2)
C12*A*	0.5769 (4)	0.4355 (2)	0.8710 (3)	0.063 (2)
C13*A*	0.6093 (4)	0.4879 (2)	0.8272 (3)	0.063 (2)
C14*A*	0.6643 (4)	0.4798 (2)	0.7561 (3)	0.060 (2)
C15*A*	0.6866 (3)	0.4189 (2)	0.7269 (2)	0.047 (2)
C1*B*	0.8059 (3)	0.2782 (2)	0.5042 (3)	0.065 (2)
C2*B*	0.7497 (3)	0.2263 (2)	0.5487 (2)	0.038 (1)
C3*B*	0.7427 (3)	0.1614 (2)	0.5159 (2)	0.042 (1)
C4*B*	0.7917 (3)	0.1410 (3)	0.4441 (2)	0.062 (2)
C5*B*	0.7784 (4)	0.0779 (3)	0.4203 (3)	0.073 (2)
C6*B*	0.7207 (4)	0.0354 (2)	0.4675 (3)	0.060 (2)
C7*B*	0.6759 (3)	0.0580 (2)	0.5411 (2)	0.042 (2)
C8*B*	0.6142 (3)	0.0187 (2)	0.5987 (2)	0.040 (1)
C9*B*	0.5986 (3)	−0.0519 (2)	0.5905 (3)	0.059 (2)
C10*B*	0.3588 (3)	0.0661 (2)	0.7935 (2)	0.030 (1)
C11*B*	0.2911 (3)	0.0156 (2)	0.7656 (2)	0.048 (2)
C12*B*	0.1745 (3)	0.0165 (2)	0.7728 (3)	0.059 (2)
C13*B*	0.1229 (3)	0.0673 (2)	0.8070 (3)	0.053 (2)
C14*B*	0.1872 (4)	0.1172 (2)	0.8354 (3)	0.058 (2)
C15*B*	0.3035 (3)	0.1165 (2)	0.8291 (2)	0.047 (2)
C16	0.0466 (4)	0.1686 (2)	0.6413 (3)	0.067 (2)
C17	0.1598 (5)	0.1629 (3)	0.6104 (4)	0.118 (3)
C18	0.1262 (6)	0.3529 (3)	0.6912 (4)	0.094 (3)
C19	0.0121 (5)	0.3700 (3)	0.6588 (4)	0.109 (3)
Compound (III)				
Fe1*A*	−0.3309 (1)	0.21341 (8)	−0.61110 (8)	0.0323 (6)
Fe1*B*	−0.4270 (1)	−0.20516 (8)	0.81523 (8)	0.0326 (6)
Cl1*A*	0.1451 (2)	0.2611 (2)	0.5151 (2)	0.055 (1)
Cl1*B*	−0.3308 (2)	−0.2385 (1)	−0.9271 (1)	0.047 (1)
Cl2	0.5584 (2)	−0.1764 (1)	0.7080 (1)	0.043 (1)
O1*A*	−0.2121 (5)	−0.0081 (4)	−0.6077 (4)	0.044 (3)
O2*A*	0.4929 (5)	0.4190 (4)	−0.6598 (4)	0.041 (3)
O3*A*	−0.3412 (4)	−0.3209 (3)	0.7225 (3)	0.027 (2)
O1*B*	−0.5193 (5)	−0.4276 (4)	−0.8237 (4)	0.048 (3)
O2*B*	−0.3356 (5)	−0.0075 (3)	−0.7651 (4)	0.039 (3)
O3*B*	−0.2753 (4)	−0.1499 (3)	0.7118 (3)	0.030 (2)
O4	−0.1042 (6)	−0.3378 (4)	−0.7414 (5)	0.061 (3)
O5	0.0859 (9)	0.3690 (7)	0.1420 (9)	0.142 (6)
N1*A*	−0.2845 (6)	−0.0640 (5)	−0.5651 (5)	0.036 (3)
N2*A*	0.4128 (7)	0.1849 (6)	0.4997 (4)	0.037 (4)
N3*A*	−0.4619 (6)	−0.3424 (5)	−0.5999 (5)	0.035 (3)
N1*B*	−0.5582 (7)	−0.3412 (5)	−0.8586 (5)	0.038 (3)
N2*B*	−0.6050 (6)	−0.1760 (6)	−0.9191 (4)	0.037 (3)
N3*B*	−0.4297 (7)	−0.0502 (5)	−0.8279 (4)	0.034 (3)
B1*A*	−0.416 (1)	−0.4157 (7)	−0.7339 (7)	0.036 (5)
B1*B*	−0.227 (1)	−0.0507 (7)	−0.7013 (7)	0.037 (5)
C1*A*	−0.2426 (8)	−0.0659 (5)	−0.4460 (5)	0.053 (4)
C2*A*	−0.2992 (8)	−0.0305 (6)	0.4900 (6)	0.036 (4)
C3*A*	−0.3838 (8)	−0.0973 (6)	−0.4521 (6)	0.034 (4)
C4*A*	−0.4406 (8)	−0.0776 (6)	−0.3823 (6)	0.041 (4)
C5*A*	−0.5284 (9)	−0.1473 (8)	−0.3629 (6)	0.054 (5)
C6*A*	−0.5520 (8)	−0.2380 (6)	−0.4084 (6)	0.047 (5)
C7*A*	−0.4938 (9)	−0.2539 (7)	−0.4773 (6)	0.036 (4)
C8*A*	−0.5229 (8)	−0.3433 (6)	−0.5371 (6)	0.034 (4)
C9*A*	0.6258 (8)	−0.4205 (6)	−0.5316 (6)	0.059 (5)
C10*A*	−0.331 (1)	0.5085 (6)	−0.7211 (7)	0.044 (5)
C11*A*	−0.3613 (9)	−0.5861 (8)	0.7873 (7)	0.071 (6)
C12*A*	−0.283 (1)	−0.6658 (9)	−0.771 (1)	0.100 (9)
C13*A*	−0.177 (1)	0.666 (1)	0.693 (1)	0.11 (1)
C14*A*	−0.147 (1)	−0.5931 (8)	−0.6282 (9)	0.090 (7)
C15*A*	−0.221 (1)	−0.5137 (6)	−0.6433 (7)	0.059 (5)
C1*B*	−0.7275 (9)	−0.4371 (6)	0.9750 (6)	0.081 (5)
C2*B*	−0.6582 (8)	−0.3452 (7)	−0.9307 (6)	0.042 (5)
C3*B*	−0.6919 (9)	−0.2488 (7)	−0.9638 (6)	0.038 (4)
C4*B*	0.8014 (9)	0.2318 (7)	1.0330 (6)	0.057 (5)
C5*B*	−0.8221 (9)	−0.1381 (8)	−1.0579 (6)	0.066 (5)
C6*B*	−0.7340 (9)	−0.0636 (6)	1.0106 (6)	0.051 (5)
C7*B*	0.6256 (8)	−0.0852 (7)	−0.9420 (6)	0.036 (4)
C8*B*	−0.5253 (9)	−0.0109 (7)	−0.8849 (6)	0.041 (4)
C9*B*	−0.5331 (7)	0.0942 (5)	−0.8870 (5)	0.053 (4)
C10*B*	−0.0937 (8)	−0.0195 (6)	−0.7298 (6)	0.037 (4)
C11*B*	−0.0156 (9)	0.0684 (7)	−0.6915 (6)	0.048 (5)
C12*B*	0.094 (1)	0.0979 (6)	−0.7201 (7)	0.060 (5)
C13*B*	0.1317 (9)	0.0424 (8)	−0.7856 (7)	0.069 (6)
C14*B*	0.057 (1)	−0.0434 (7)	−0.8213 (7)	0.067 (5)
C15*B*	0.0537 (9)	−0.0737 (6)	−0.7937 (7)	0.054 (5)
C16	−0.093 (1)	−0.3967 (7)	−0.8171 (7)	0.074 (6)
C17	0.027 (1)	−0.3536 (9)	−0.841 (1)	0.128 (9)
C18	0.116 (1)	−0.3145 (9)	−0.746 (1)	0.128 (9)
C19	0.024 (1)	−0.3029 (8)	0.6843 (8)	0.103 (7)
C20	−0.164 (2)	0.308 (1)	0.111 (1)	0.115 (9)
C21	−0.294 (1)	−0.3108 (9)	−0.186 (1)	0.122 (9)
C22	−0.275 (2)	−0.3680 (9)	−0.264 (1)	0.117 (9)
C23	0.138 (2)	0.390 (1)	0.237 (1)	0.16 (1)

on that set of core atoms. Subsequent Fourier calculations allowed development of more complete models. H atoms were included at calculated and observed positions. Each structure was refined using full-matrix least squares on F with weights of $1/\sigma^2(F_o)$. Anisotropic temperature factors were included for the non-H atoms.

Table 3. *Selected interatomic distances* (Å) *and angles* (°)

	(I)	(II)	(III)
Fe1*A*—Fe1*B*	2.905 (2)	2.8708 (8)	2.983 (4)
Fe1*A*—Cl1*A*	2.312 (5)	2.296 (1)	2.246 (3)
Fe1*B*—Cl1*B*	2.273 (5)	2.301 (1)	2.264 (4)
Fe1*A*—N1*A*	2.14 (1)	2.155 (3)	2.146 (7)
Fe1*B*—N1*B*	2.19 (1)	2.214 (3)	2.219 (7)
Fe1*A*—N2*A*	2.14 (1)	2.165 (3)	2.145 (8)
Fe1*B*—N2*B*	2.15 (1)	2.149 (3)	2.156 (6)
Fe1*A*—N3*A*	2.19 (1)	2.189 (3)	2.216 (7)
Fe1*B*—N3*B*	2.16 (1)	2.144 (3)	2.171 (7)
Fe1*A*—O3*A*	2.24 (1)	2.224 (2)	2.197 (5)
Fe1*B*—O3*A*	2.199 (9)	2.367 (2)	2.242 (5)
Fe1*A*—O3*B*	2.067 (9)	2.022 (2)	1.990 (5)
Fe1*B*—O3*B*	2.00 (1)	1.976 (2)	1.981 (4)
Fe1*A*—O4	2.07 (1)	2.011 (2)	
Fe1*A*—Cl2			2.532 (3)
Fe1*B*—O4	1.98 (1)	1.976 (2)	
Fe1*B*—Cl2			2.459 (4)
Cl1*A*—Fe1*A*—N1*A*	94.4 (4)	91.75 (8)	94.3 (2)
Cl1*B*—Fe1*B*—N1*B*	91.6 (3)	90.87 (8)	88.7 (2)
Cl1*A*—Fe1*A*—N2*A*	95.9 (4)	89.10 (8)	91.9 (2)
Cl1*B*—Fe1*B*—N2*B*	94.3 (4)	91.47 (8)	89.6 (2)
Cl1*A*—Fe1*A*—N3*A*	93.1 (4)	93.63 (8)	95.8 (2)
Cl1*B*—Fe1*B*—N3*B*	96.5 (4)	94.18 (8)	98.5 (2)
Cl1*A*—Fe1*A*—O3*A*	91.6 (3)	90.72 (6)	95.2 (2)
Cl1*B*—Fe1*B*—O3*A*	90.5 (3)	96.83 (6)	96.7 (2)
Cl1*A*—Fe1*A*—O3*B*	97.2 (3)	102.07 (7)	106.0 (2)
Cl1*B*—Fe1*B*—O3*B*	94.7 (3)	97.77 (7)	103.3 (2)
Cl1*A*—Fe1*A*—O4	170.0 (3)	171.91 (7)	
Cl1*A*—Fe1*A*—Cl2			171.7 (1)
Cl1*B*—Fe1*B*—O4	171.7 (3)	175.79 (7)	
Cl1*B*—Fe1*B*—Cl2			172.72 (8)
N1*A*—Fe1*A*—N2*A*	70.1 (5)	71.2 (1)	70.5 (3)
N1*B*—Fe1*B*—N2*B*	73.4 (4)	71.4 (1)	70.7 (3)
N1*A*—Fe1*A*—N3*A*	144.7 (6)	141.4 (1)	141.3 (3)
N1*B*—Fe1*B*—N3*B*	140.9 (5)	142.1 (1)	140.8 (2)
N1*A*—Fe1*A*—O3*A*	145.5 (4)	147.12 (9)	145.3 (3)
N1*B*—Fe1*B*—O3*B*	141.4 (4)	139.7 (1)	139.8 (2)
N1*A*—Fe1*A*—O3*B*	75.4 (4)	74.68 (9)	75.1 (3)
N1*B*—Fe1*B*—O3*A*	69.9 (4)	69.51 (9)	71.3 (2)
N2*A*—Fe1*A*—N3*A*	74.9 (5)	70.8 (1)	71.9 (3)
N2*B*—Fe1*B*—N3*B*	67.9 (5)	70.9 (1)	70.8 (3)
N2*A*—Fe1*A*—O3*A*	142.8 (4)	141.67 (9)	142.2 (2)
N2*B*—Fe1*B*—O3*B*	143.5 (4)	146.8 (1)	145.8 (3)
N2*A*—Fe1*A*—O3*B*	143.8 (4)	144.3 (1)	142.3 (3)
N2*B*—Fe1*B*—O3*A*	143.1 (4)	140.1 (1)	141.3 (2)
N3*A*—Fe1*A*—O3*A*	68.4 (5)	70.98 (9)	70.5 (2)
N3*B*—Fe1*B*—O3*B*	76.0 (4)	76.6 (1)	76.0 (2)
N3*A*—Fe1*A*—O3*B*	137.5 (5)	140.5 (1)	136.2 (2)
N3*B*—Fe1*B*—O3*A*	147.7 (4)	146.3 (1)	144.4 (2)
O3*A*—Fe1*A*—O3*B*	70.2 (3)	72.75 (8)	70.1 (2)
O3*B*—Fe1*B*—O3*A*	72.1 (3)	70.40 (8)	69.3 (2)
O4—Fe1*A*—N1*A*	91.2 (5)	96.2 (1)	
Cl2—Fe1*A*—N1*A*			90.0 (2)
O4—Fe1*B*—N1*B*	89.0 (5)	87.9 (1)	
Cl2—Fe1*B*—N1*B*			85.8 (2)
O4—Fe1*A*—N2*A*	93.8 (5)	94.8 (1)	
Cl2—Fe1*A*—N2*A*			82.9 (2)
O4—Fe1*B*—N2*B*	93.8 (5)	91.9 (1)	
Cl2—Fe1*B*—N2*B*			84.1 (2)
O4—Fe1*A*—N3*A*	86.9 (5)	81.0 (1)	
Cl2—Fe1*A*—N3*A*			76.5 (2)
O4—Fe1*B*—N3*B*	88.2 (5)	89.3 (1)	
Cl2—Fe1*B*—N3*B*			82.9 (2)
O4—Fe1*A*—O3*A*	79.1 (4)	81.81 (8)	
Cl2—Fe1*A*—O3*A*			85.2 (2)
O4—Fe1*A*—O3*B*	76.2 (4)	78.75 (9)	
Cl2—Fe1*A*—O3*B*			81.9 (2)
O4—Fe1*B*—O3*A*	81.9 (4)	78.96 (8)	
Cl2—Fe1*B*—O3*A*			86.0 (2)
O4—Fe1*B*—O3*B*	79.7 (4)	80.69 (9)	
Cl2—Fe1*B*—O3*B*			84.0 (2)
Fe1*A*—*O3A*—Fe1*B*	81.9 (3)	77.34 (7)	84.4 (2)
Fe1*A*—*O3B*—Fe1*B*	91.0 (3)	91.78 (9)	97.4 (2)
Fe1*A*—*O4*—Fe1*B*	91.8 (2)	92.10 (9)	
Fe1*A*—Cl2—Fe1*B*			73.4 (1)
B1*A*—O3*A*—Fe1*A*	122.3 (9)	121.9 (2)	123.8 (6)
B1*B*—O3*B*—Fe1*B*	125 (1)	121.3 (2)	123.4 (5)
B1*A*—O3*A*—Fe1*B*	125.1 (9)	116.8 (2)	118.5 (4)
B1*B*—O3*B*—Fe1*A*	120 (1)	122.2 (2)	120.2 (6)
Fe1*A*—O4—C16	125.8 (9)		
Fe1*B*—O4—C16	131 (1)		

Fig. 1 illustrates the atom-numbering scheme for these three compounds and is based on that used in previous iron complexes of this dioxime (Vasilevsky, Stenkamp, Lingafelter & Rose, 1988). The halves of each molecule are labelled *A* and *B*. The bridging methoxide (O4—C16) in compound (I) becomes a hydroxide bridge (O4) in compound (II) and a chloride (Cl2) in (III). The asymmetric unit for compound (II) also contains two acetonitrile molecules (N4—C16—C17; N5—C18—C19) and a water molecule (O5) as well as the metal complex. The two tetrahydrofuran molecules found in compound (III) are made up of atoms O4—C16—C17—C18—C19 and O5—C20—C21—C22—C23.

Coordinates for the compounds are presented in Table 2,* and selected interatomic distances and angles for the three compounds are included in Table 3.

Discussion

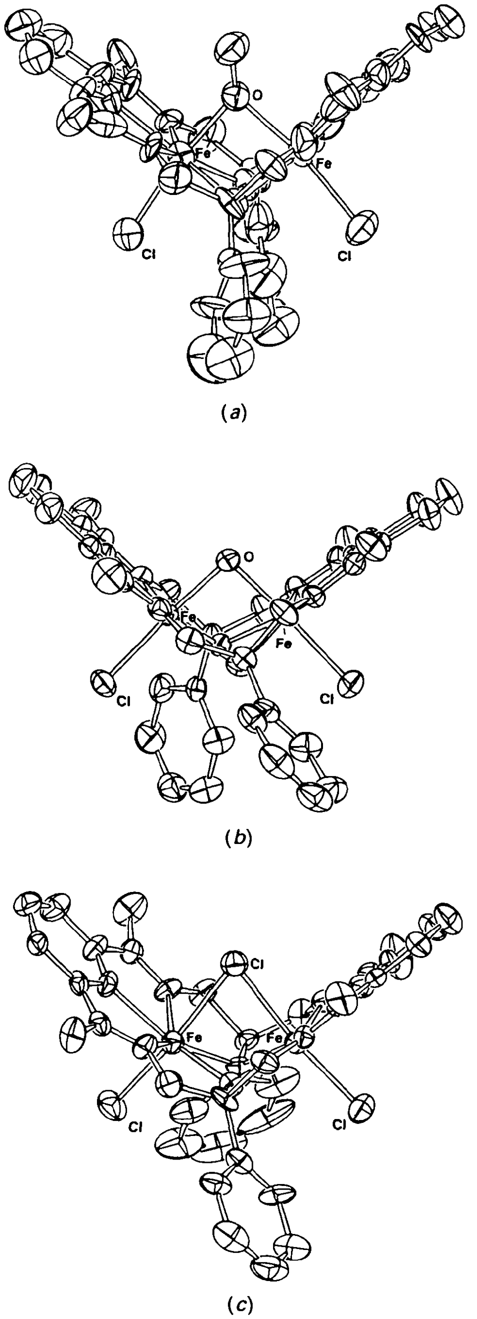
Compound (I), see Figs. 2 and 3, is the initial member of this class of molecules and is a methoxide derivative of the fundamental metal complex. Each iron is seven-coordinate (pentagonal bipyramidal coordination) and shares three bridging atoms with the other iron. Three N atoms from the dioxime and two bridging O atoms make up the pentagonal equatorial plane about each metal. Cl atoms and the other bridging group [methoxide in compound (I), hydroxide in compound (II), chloride in compound (III)] serve as axial ligands for the metal. This arrangement of coordinating atoms causes the macrocycle to take on a characteristic 'butterfly' shape with the axial bridging site above the hinge connecting the 'wings'. The dihedral angles between the planes containing the equatorial ligands are 104.6 (3), 102.16 (6), and 105.0 (1)° for compounds (I), (II) and (III) respectively. O4 is nearly trigonal and thus unlikely to be protonated. Accordingly, we have interpreted the bridging ligand to be methoxide rather than methanol.

The bond lengths and angles for the central part of the molecule are consistent with protonation of one

---

* Lists of structure factors, anisotropic temperature factors, H-atom coordinates, and additional bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54939 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0523]

of the bridging oxygens (O3*A*). Stronger evidence for this can be found in the crystal structure of compound (II) (see below), but even in compound (I), the bond lengths for O3*A* are significantly longer than those for O3*B*, suggesting that O3*A* is bound to four other atoms (the two Fe atoms, *B*1*A*, and presumably an H atom). This protonation is consistent with the Fe atoms being in the ferric oxidation state.



(*a*)

(*b*)

(*c*)

Fig. 2. *ORTEP* drawings (Johnson, 1965) of (*a*) compound (I), (*b*) compound (II) and (*c*) compound (III).

Compound (II) contains an OH^- group replacing the bridging CH_3O^-, see Figs. 1 and 2. The hydroxyl H atom was located in a difference electron density map and is involved in a hydrogen bond to one of the acetonitrile solvent molecules [O4···N4 = 2.986 (5) Å]. Likewise, O3*A* is protonated, and electron density for the H atom was observed. This atom is involved in hydrogen bonding to solvent molecules in the lattice [O3*A*···O5 = 2.683 (3) Å] providing additional evidence for the protonation of O3*A*. In fact, these results prompted us to look for the bond-length differences noted above for compound (I).

To investigate the chemistry of the binuclear iron complex, we have synthesized a chloride derivative of the molecule [compound (III)] and determined its structure, see Fig. 2. The larger bridging atom appears to be accommodated mainly by changes in the Fe–bridge bond lengths and Fe–bridge–Fe bond angles. As can be seen in Table 3, the distance between the Fe atoms and Cl2 is about 0.5 Å longer than those between the Fe atoms and O4. Also, the Fe—Cl2—Fe bond angle is about 20° smaller than those in compounds (I) and (II). If the rest of the molecule is rigid, these structural changes should result in a smaller Cl2—Fe*x*—N2*x* bond angle ($x = A$ or *B*). Such an effect is seen in compound (III) where the angles drop to 82.9 (2) and 84.1 (2)°.

In all three compounds, the Fe atoms are displaced away from the axial bridging atom and towards the axial Cl atoms, see Table 4. This displacement is smallest for compound (II) [0.130 (1) Å] and largest for compound (III) [0.249 (2) Å].

Comparison with other iron complexes of just the pyridine dioxime (Vasilevsky, Stenkamp, Lingafelter

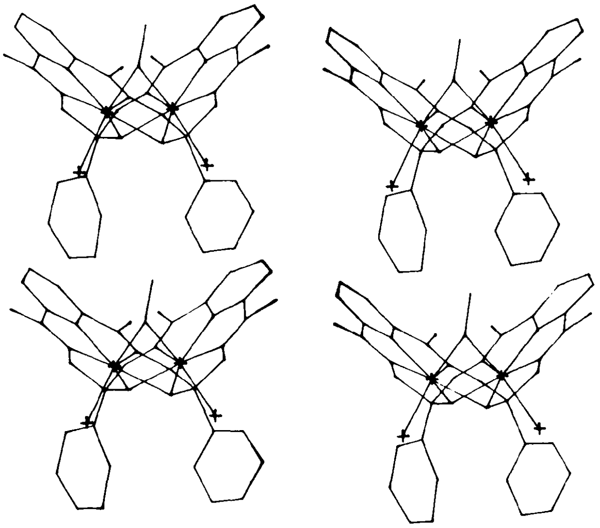


Fig. 3. Stereoview of compound (I) generated with the *FRODO* program (Jones, 1982).

Table 4. *Displacements* (Å) *of the* Fe *atoms from the plane passing through the equatorial ligands*

Molecule	Atom	Displacement
Compound (I)	Fe1*A*	0.166 (3)
	Fe1*B*	0.132 (3)
Compound (II)	Fe1*A*	0.130 (1)
	Fe1*B*	0.161 (1)
Compound (III)	Fe1*A*	0.249 (2)
	Fe1*B*	0.205 (2)

Table 5. *Torsion angles* (°) *about the* B1*x*—C10*x* *bond*

Compound	*x*	O2*x*—B1*x*—C10*x*—C11*x*	O2*x*—B1*x*—C10*x*—C15*x*
(I)	*A*	35 (2)	−156 (2)
	B	44 (3)	−135 (2)
(II)	*A*	−86.6 (4)	86.6 (4)
	B	22.0 (5)	−159.0 (3)
III)	*A*	112 (1)	−70 (1)
	B	82 (1)	−95 (1)

& Rose, 1988) shows that while the ligand does not distort in going from six-coordinate to seven-coordinate complexes, the ligand is roughly 0.3 Å further from the metal atoms in the structures reported here. In four octahedral complexes, the Fe—N bond lengths range from 1.87 to 1.97 Å. Table 3 shows that in compounds (I)–(III), the corresponding bond lengths (Fe*x*—N*xx*) range from 2.14 (1) to 2.219 (7) Å. This increase in metal–ligand distances is consistent with the increase in coordination number for these compounds.

In comparing these compounds, we superposed them to determine how similar they were and discovered that while the metal atoms and pyridine dioxime groups match well, the phenyl rings do not. The torsion angles about the B1*x*—C10*x* bonds are listed in Table 5 and show that the phenyl rings are not all oriented the same relative to the rest of the molecule. We suspect that intermolecular interactions account for the variation in this torsion angle observed in these crystal structures.

This work has been supported by NIH grant 34663 and a grant from Abbott Laboratories. The CAD-4 diffractometer was obtained with funds from the NSF (grant No. CHE8617023). We want to thank Elinor Adman and Lyle Jensen for helpful comments.

References

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

HALL, S. R. & STEWART, J. M. (1990). Editors. *XTAL*3.0 *Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

JONES, T. A. (1982). *Computational Crystallography*, edited by D. SAYRE, pp. 303–317. Oxford Univ. Press.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

VASILEVSKY, I., STENKAMP, R. E., LINGAFELTER, E. C. & ROSE, N. J. (1988). *J. Coord. Chem.* **19**, 171–187.

XING, Y. J. (1983). *Acta Cryst.* A**39**, 35–37.

Acta Cryst. (1992). **B48**, 449–458

Single-Crystal X-ray Diffraction and Variable-Temperature MAS NMR Study on the Heterogeneous Network Clathrate $Na[N(CH_3)_4]_7[Si_8O_{20}].54H_2O$

BY MICHAEL WIEBCKE* AND HUBERT KOLLER†

Fakultät für Chemie, Universität Konstanz, Postfach 5560, *W*-7750 *Konstanz, Germany*

(*Received* 2 *December* 1991; *accepted* 24 *January* 1992)

Abstract

Crystal data: $M_r = 2059.54$, trigonal, $R\bar{3}$, $a = 21.374$ (3), $c = 19.769$ (2) Å, $V = 7821.2$ Å^3, $Z = 3$, $D_x = 1.31$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 0.21$ mm^{-1}, $F(000) = 3372$, $T \simeq 190$ K, $R = 0.078$ for 2534 unique observed reflections. The host–guest compound consists of a three-dimensional four-connected network composed of hydrogen-bonded oligomeric silicate anions with double four-ring structure, $[Si_8O_{20}]^{8-}$, and H_2O molecules. This mixed (heterogeneous) network has the topology of net No. 214 and zeolite-structure type AST. Orientationally disordered cationic guest species NMe_4^+ are enclosed in large $[4^66^{12}]$ octadecahedral cages of

---

* To whom correspondence should be addressed.

† New address: Institut für Technische Chemie I, Universität Stuttgart, Pfaffenwaldring 55, W-7000 Stuttgart 80, Germany.

0108-7681/92/040449-10$06.00