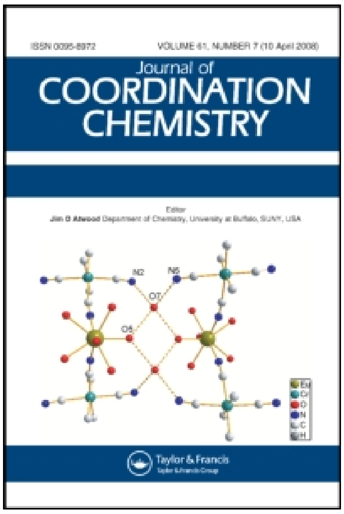

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An Fe(III) Complex with the Dianionic form of 2,6-Diacetylpyridine Bis(Acylhydrazone). The Crystal Structure of [Diaqua-2',2'''-(2,6-PyridinediyldiEthylidyne)Dioxamohydrazide]Iron(III) Perchlorate Trihydrate, [Fe(dapsox)$(H_2O)_2$]$ClO_4\cdot 3H_2O$

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AN Fe(III) COMPLEX WITH THE DIANIONIC FORM OF 2,6-DIACETYLPYRIDINE BIS(ACYLHYDRAZONE). THE CRYSTAL STRUCTURE OF [DIAQUA-2′,2‴-(2,6-PYRIDINEDIYLDIETHYLIDYNE)DIOXAMOHYDRAZIDE]IRON(III) PERCHLORATE TRIHYDRATE, [Fe(DAPSOX)$(H_2O)_2$]$ClO_4 \cdot 3H_2O$

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The title compound was prepared by a template synthesis from 2,6-diacetylpyridine, dioxamohydrazide and $Fe(ClO_4)_3 \cdot 6H_2O$ (mol ratio 1 : 2 : 1) in MeOH/H_2O (3 : 1) solution and its structure determined by single-crystal X-ray diffraction; triclinic, space group $P\bar{1}$, $a = 7.5186(7)$, $b = 10.9730(9)$, $c = 14.6110(10)$ Å, $\alpha = 95.866(1)$, $\beta = 100.252(1)$, $\gamma = 92.895(1)$, $z = 2$. The polydentate ligand is coordinated as a dianionic pentadentate while water molecules occupy apical positions in the structure. This is the first example of a monomeric, pentagonal bipyramidal structure of an Fe(III) complex with a dianionic bis(acylhydrazone) derivative of 2,6-diacetylpyridine.

Keywords: Fe(III); Bis(acylhydrazone); X-ray structure

INTRODUCTION

Our studies have concentrated for a long period on the influence of ligand charge and properties of the central metal ion in the structures of transition metal complexes with bis(acylhydrazones) of 2,6-diacetylpyridine (dap) [1–8]. Although the stability of pentagonal bipyramidal (PBP) complexes can be expected to be great in the case of ions with spherically symmetrical electron distributions [9,10], only a few Fe(III) complexes of this geometry have been synthesized and characterized.

Among Fe(III) complexes of this geometry with bis(acylhydrazones) of dap, only the three following complexes have been structurally characterized: [Fe(H_2dapsc)Cl_2]

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$Cl \cdot 2H_2O$ [9], $[Fe_2(daps)Cl_2(EtOH)_2]$ [11] and $[Fe(dapoamh)_2(H_2O)_2 \cdot 3H_2O$ [7][1]. The first represents a monomeric complex with a neutral pentadentate and the second a binuclear complex with tetradeprotonated $daps^{4-}$ as a heptadentate. As far as this structure is concerned, it is interesting to note the presence of two non-equivalent Fe(III) ions bridged by two hydrazide oxygen atoms, one in PBP and the other in octahedral surroundings. The third abovementioned complex of this type represents a dimer with both Fe(III) ions located in PBP surroundings with double deprotonation of the coordinated pentadentate (dapoamh). Since the synthesis of $[Fe(dapoamh)_2(H_2O)_2] \cdot 3H_2O$ complex in aqueous solution is accompanied by a series of hydrolytic processes and the appearance of monomeric PBP complexes of Fe(III), we have found it of interest to isolate and characterize some of these intermediates. This was important not only in order to confirm the mechanism of low-spin $[Fe(dapoamh)_2(H_2O)_2] \cdot 3H_2O$ formation, but also because these intermediates represent the first example of monomeric Fe(III) structures with an anionic pentadentate in the coordination sphere. Knowledge of the influence of the ligand deprotonation on coordination number and geometry of thus formed complexes can be of great help in studies of electron-transfer processes in biological redox systems [12,13].

EXPERIMENTAL

Physical Measurements

IR spectra were recorded on a Perkin-Elmer FTIR 1726X spectrophotometer with the KBr technique. The molar conductivity of a DMF solution of the complex (1×10^{-3} mol dm^{-3}) was measured at room temperature on a Jenway-4009 digital conductivity meter. The magnetic moment was determined (291 K) with an MSB MK1 magnetic susceptibility balance and corrected for diamagnetic contributions.

Template Synthesis of $[Fe(dapsox)(H_2O)_2]ClO_4 \cdot H_2O$

To a suspension containing 0.12 g (1.12 mmol) of semioxamazide (sox) and 0.10 g (0.56 mmol) of 2,6-diacetylpyridine in 45 cm^3 of methanol–water mixture (75 : 25) in a round-bottomed flask, 0.26 g (0.56 mmol) of $Fe(ClO_4)_3 \cdot 6H_2O$ was added. The mixture was refluxed for 45 min, filtered and left for 24 h at ambient temperatures. After that time, the dark brown product in a crystalline form was obtained with a yield of 52%. *Anal.* Calcd. for $C_{13}H_{23}ClFeN_7O_{13}$(%); C, 26.95; H, 4.10; N, 16.82. Found: C, 27.07; H, 4.03; N, 16.99. IR spectrum (KBr; ν/cm^{-1}): 3372(s), 1701 (vs), 1613 (s), 1551 (vs), 1513 (m), 1321 (s), 1146 (s), 1118 (s), 1088 (s), 690 (m), 628 (m), 532 (m), 458 (m). Values of molar conductivity demonstrates that the complex is a 1 : 1 electrolyte ($\Lambda_m = 84.5\ \Omega^{-1}$ cm^2 mol^{-2}), while the magnetic susceptibility of $\mu_{eff} = 5.26$ BM confirm that the complex is high-spin.

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[1] H_2dapsc = 2,6-diacetylpyridinebis(semicarbazone); H_2daps = 2,6-diacetylpyridinebis(salicyloylhydrazone); $H_2dapoamh$ = dioxo-2,6-pyridinediylbis(ethylidyne-1-hydrazinyl-2-iliden)diacetic acid.

TABLE I Crystal data and structure refinement details for $[Fe(dapsox)(H_2O)_{1.6}(MeOH)_{0.4}]ClO_4 \cdot 2.6H_2O$

Empirical formula	$C_{13.40}H_{23}Cl\ Fe\ N_7O_{12.60}$
Formula weight	575.09
Temperature (K)	293 (2)
Wavelength (Å)	0.71069
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	$a = 7.5186(7)$ $\alpha = 95.866(1)$
	$b = 10.9730(9)$ $\beta = 100.252(1)$
	$c = 14.6110(10)$ $\gamma = 92.895(1)$
Volume (Å^3)	1177.1(2)
Z, Calculated density (Mg/m^3)	2, 1.623
Absorption coefficient (mm^{-1})	0.830
Reflections collected/unique	9713/3402 [R(int) = 0.0316]
Data/restraints/parameters	3402/18/406
Goodness-of-fit on F^2	1.004
Final R indices* [$I > 2\sigma(I)$]	$R1 = 0.0472$, $wR2 = 0.1280$
R indices* (all data)	$R1 = 0.0632$, $wR2 = 0.1363$
Largest ΔF maximum/minimum (e/Å^3)	1.036/− 0.350

*$R1 = \sum ||Fo|^2 - |Fc|^2| / \sum |Fo|^2$; $wR2 = \{\sum[w(Fo^2 - Fc^2)^2] / \sum[w(Fo^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (0.965P)^2]$, $P = [2Fc^2 + \mathrm{Max}(Fo^2, 0)]/3$.

X-ray Methods

Dark-red, prism-shaped, single crystals suitable for X-ray diffraction were obtained from methanol. X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 diffractometer equipped with a CCD detector using graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). Data collection details: crystal to detector distance 5.0 cm; 1321 frames (hemisphere mode); time per frame 30 s; oscillation $\Delta\omega = 0.300°$. The last 50 frames were used to monitor crystal decay, which was negligible. Data reduction was performed by the SAINT package [14] and data were corrected for absorption effects by SADABS [15]. The structure was solved by direct methods [16] and refined by full-matrix least-squares on F^2 [17]: Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were located in Fourier maps and refined isotropically, except for those of methyl groups which were introduced in calculated positions. The coordination environment is characterized by disorder involving the substitution of a water molecule by a methanol molecule. The occupancy factors of the two ligands were refined to 60% and 40%, respectively. Final maps showed a residual electronic density modelled as a partially disordered water molecule. Data collection and refinement results, and final atomic coordinates for all non-hydrogen atoms are summarized in Tables I and II, respectively.

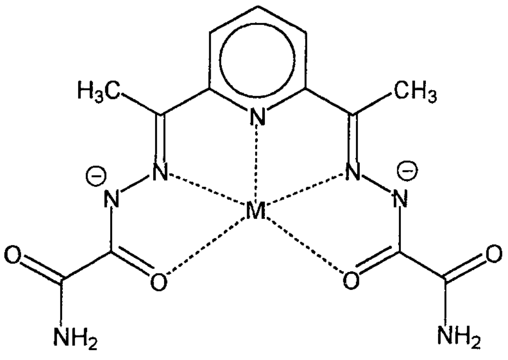
RESULTS AND DISCUSSION

Starting from $Fe(ClO_4)_3 \cdot 6H_2O$, template synthesis performed in the presence of dap and sox (1 : 1 : 2) in methanol–water solution (75 : 25) afforded $[Fe(dapsox)(H_2O)_2]\ ClO_4 \cdot 3H_2O$ with PBP geometry with the planar pentacoordinate dapsox ligand as its dianionic form. The same complex was produced by dissolving $[Fe(Hdapsox)Cl_2] \cdot 1/2H_2O$ and addition of a water–methanol solution of $NaClO_4$.

Symmetry of the side chains in the dapsox ligand (Scheme 1) is concluded from the IR spectrum of the complex. In comparison with $[Fe(Hdapsox)Cl_2]$ where in the

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[Fe(dapsox)(H_2O)_{1.6}(MeOH)_{0.4}]ClO_4 \cdot 2.6H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Fe	509(1)	4773(1)	7829(1)	34(1)
Cl	3681(2)	9806(1)	8219(1)	55(1)
N(1)	−622(5)	6565(3)	7698(2)	34(1)
N(2)	−932(5)	4835(3)	6392(2)	36(1)
N(3)	−1059(5)	3769(3)	5776(2)	37(1)
N(4)	465(6)	847(3)	6214(3)	55(1)
N(5)	1126(5)	5927(3)	9186(2)	35(1)
N(6)	2146(5)	5435(3)	9937(2)	37(1)
N(7)	3964(6)	2522(4)	10028(3)	50(1)
O(1)	613(4)	3100(3)	7089(2)	44(1)
O(2)	−700(6)	1527(3)	4845(2)	69(1)
O(3)	2125(4)	3833(2)	8776(2)	41(1)
O(4)	4269(4)	4154(3)	11128(2)	50(1)
O(5)	2824(4)	5480(3)	7479(2)	41(1)
O(6)	−1815(4)	4134(3)	8180(2)	45(1)
O(7)	2241(6)	10550(4)	8368(3)	85(1)
O(8)	5349(6)	10360(5)	8672(4)	123(2)
O(9)	3445(7)	8641(4)	8545(4)	106(2)
O(10)	3632(8)	9543(5)	7240(3)	111(2)
O(11)	3074(6)	7018(4)	6248(3)	69(1)
O(12)	−4819(10)	3261(9)	6966(7)	180(6)
C(14)	−3550(30)	3350(20)	7657(12)	107(7)
O(13)	−5230(50)	9660(30)	4850(40)	350(20)
O(13)	−5240(40)	8320(40)	4190(50)	750(60)
C(1)	−1535(6)	6816(4)	6864(3)	35(1)
C(2)	−2233(7)	7940(4)	6766(4)	48(1)
C(3)	−1997(7)	8821(4)	7518(3)	51(1)
C(4)	−1083(7)	8560(4)	8372(4)	47(1)
C(5)	−394(6)	7426(4)	8440(3)	37(1)
C(6)	−1726(6)	5776(4)	6125(3)	35(1)
C(7)	−2804(8)	5865(6)	5176(3)	48(1)
C(8)	−199(6)	2954(4)	6230(3)	36(1)
C(9)	−160(6)	1697(4)	5695(3)	42(1)
C(10)	671(6)	7039(4)	9305(3)	36(1)
C(11)	1132(7)	7892(4)	10180(3)	48(1)
C(12)	2577(5)	4344(4)	9616(3)	33(1)
C(13)	3704(6)	3646(4)	10331(3)	38(1)



SCHEME 1.

IR spectrum four intense bands in the region characteristic of the C=O group (from 1712 cm^{-1} to 1608 cm^{-1}) appear as a consequence of side chain asymmetry, the number of characteristic bands in the case of [Fe(dapsox)(H_2O)$_2$]ClO_4 was twice reduced. The first band at 1701 cm^{-1} corresponds to the non-coordinated amide carbonyl group and the second at 1613 cm^{-1} to the coordinated hydrazide group of the deprotonated chain. Shifts from 1712 cm^{-1} to 1701 cm^{-1} point to a weakened bond due to double deprotonation. The appearance of a band at 1551 cm^{-1} is a consequence of C=N vibrations in the deprotonated form of this class of ligands [13]. In the IR spectrum of [Fe(dapsox)(H_2O)$_2$]ClO_4, bands of anionic perchlorate are present (1146 cm^{-1}, 1118 cm^{-1} and 1088 cm^{-1}).

Crystal Structure of [Fe(dapsox)(H_2O)$_2$]$ClO_4 \cdot 3H_2O$

The molecular structure of the cationic [Fe(dapsox)(H_2O)$_2$]$^+$ complex is shown in Fig. 1. In the crystallization process the complex incorporates a significant number (40%) of methanol molecules, which partially displace the apical water O6 in the coordination sphere, and displace one of the hydration waters. The experimental empirical formula of the crystallization product is [Fe(dapsox)(H_2O)$_{1.6}$(MeOH)$_{0.4}$]$ClO_4 \cdot 2.6H_2O$.

The ligand is doubly deprotonated, and coordinates Fe^{3+} through a planar, pentagonal N_3O_2 chelating system. The geometry of the complex cation (Table III) is a highly regular pentagonal bipyramid, with equatorial bond angles ranging from

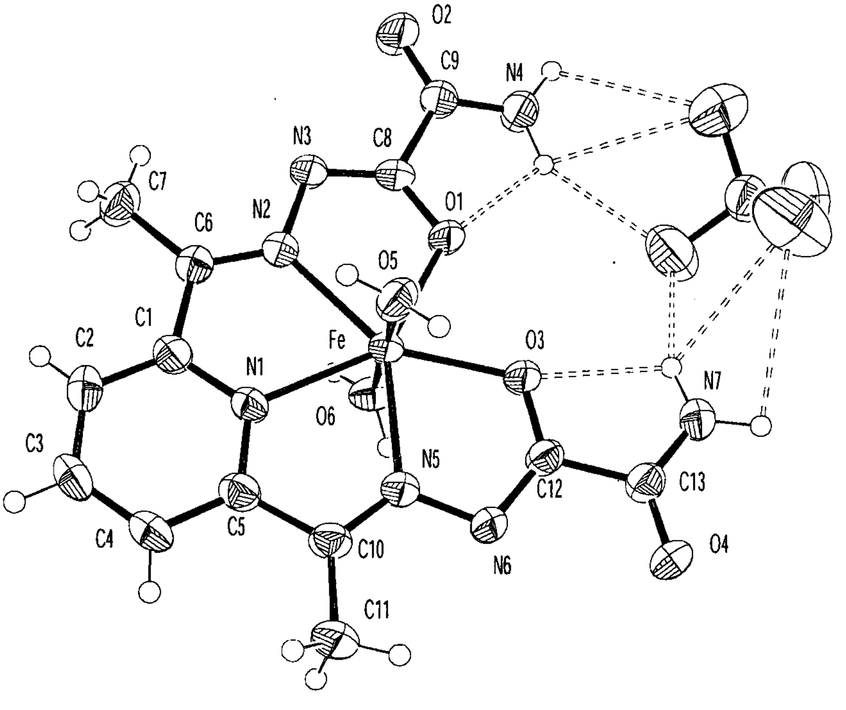


FIGURE 1 Perspective view of [Fe(dapsox)H_2O)$_2$]$^+$. Disorder involving O6 and a methanol molecule is not shown. The outer sphere coordination of the perchlorate anion is also shown and hydrogen bonds involving cation–anion recognition are indicated by dashed lines.

TABLE III Selected bond lengths (Å) and angles (°) for $[Fe(dapsox)(H_2O)_{1.6}(MeOH)_{0.4}]ClO_4 \cdot 2.6H_2O$

Fe–O6	2.019(3)	N3–C8	1.299(5)
Fe–O5	2.038(3)	N4–C9	1.315(6)
Fe–O1	2.046(3)	N5–C10	1.286(5)
Fe–O3	2.066(3)	N5–N6	1.395(5)
Fe–N1	2.195(3)	N6–C12	1.319(5)
Fe–N2	2.195(3)	N7–C13	1.304(6)
Fe–N5	2.202(3)	O1–C8	1.283(5)
N1–C5	1.344(5)	O2–C9	1.229(5)
N1–C1	1.349(5)	O3–C12	1.276(5)
N2–C6	1.278(5)	O4–C13	1.231(5)
N2–N3	1.389(5)		
O6–Fe–O5	177.9(1)	O5–Fe–N2	90.0(1)
O6–Fe–O1	88.5(1)	O1–Fe–N2	71.9(1)
O5–Fe–O1	93.4(1)	O3–Fe–N2	148.4(1)
O6–Fe–O3	93.7(1)	N1–Fe–N2	70.1(1)
O5–Fe–O3	87.7(1)	O6–Fe–N5	88.7(1)
O1–Fe–O3	76.8(1)	O5–Fe–N5	90.2(1)
O6–Fe–N1	89.3(1)	O1–Fe–N5	148.1(1)
O5–Fe–N1	88.6(1)	O3–Fe–N5	71.7(1)
O1–Fe–N1	141.9(1)	N1–Fe–N5	69.8(1)
O3–Fe–N1	141.3(1)	N2–Fe–N5	139.9(1)
O6–Fe–N2	89.6(1)		

69.8(1) to 76.8(1)°. The largest value corresponds to the O1–Fe–O3 bite angle, slightly widened by steric strain caused by divergence of the two symmetrically coordinated ligand arms, an effect already observed for $[Fe(dapoamh)(H_2O)]_2O$ [7]. The equatorial coordination atoms are almost perfectly coplanar (maximum deviation = 0.07 Å) and the entire ligand is planar to within 0.3 Å. The only deviation from planarity of the coordinated ligand is due to the torsion angle of 9.8(6)° of the terminal amide group O2–C9–N4 around the C8–C9 bond. Two apical water molecules, O5 and O6, complete PBP geometry, forming an almost linear angle (O5–Fe–O6 = 177.9(1)°). The coordination mode of $dapsox^{2-}$ is remarkably similar to that observed for $dapoamh^{2-}$ in the above mentioned μ-oxo-Fe(III) complex [7], where deprotonation of the hydrazone system caused a shortening of the N–C (here N3–C8 and N6–C12) bonds as compared with analogous protonated ligands. The crystal organization of $[Fe(dapsox)(H_2O)_{1.6}(MeOH)_{0.4}]ClO_4 \cdot 2.6H_2O$ is based on extensive hydrogen bonding, given the high number of donors and acceptors present in the structure (the cationic complex $[Fe(dapsox)(H_2O)_2]^+$ itself contains 8 donor D–H groups and 8 acceptors. Notably, the perchlorate anions participate in the hydrogen bond network, in spite of their weak acceptor ability. A remarkable feature of the ion pair association in this structure is the capability of the cation to intimately associate with the anion by means of shape recognition, hydrogen bond complementarity, and charge assistance. In fact, the cation acts as a sort of "charged tweezers", due to the shape and orientation of the $C(O)–NH_2$ arms. The two amide tails are held in a pre-organized arrangement by coordination to the metal, and define a cavity of suitable size to host the perchlorate anion, which also fits the charge distribution, as shown in Table IV.

Table IV lists hydrogen bonds responsible for crystal organization. As regards the cation, both terminal $-NH_2$ groups are involved in intramolecular hydrogen bonds with the metal-coordinated carbonyl oxygens (N4–H $\cdots$ O1 and N7–H $\cdots$ O3) and in

TABLE IV Most relevant hydrogen bonds in the crystal organization of $[Fe(dapsox)(H_2O)_{1.6}(MeOH)_{0.4}]\ ClO_4 \cdot 2.6H_2O$

D–H···A	D···A (Å)	D–H···A (°)
Intramolecular		
N4–H1···O1	2.652(5)	107(2)
N7–H2···O3	2.678(5)	104(2)
Intermolecular		
O5–H2···O11	2.613(5)	174(4)
O6–H2···O12	2.678(8)	161(5)
O11–H1···O10	2.967(6)	171(4)
O12–H2···O5(1)	3.19(1)	114.5(5)
O6–H1···N6 (2)	2.801(5)	176(2)
O5–H1···O4(4)	2.691(4)	175(3)
N7–H1···O9(4)	3.020(6)	166(4)
O11–H2···O2(5)	2.842(5)	137(4)
O11–H2···N3(5)	3.089(5)	147(4)
N4–H2···O2(6)	2.920(5)	166(3)
Cation–anion recognition		
N4–H1···O7(3)	3.248(6)	147(2)
N4–H1···O10(3)	3.078(7)	99(2)
N4–H2···O10(3)	3.078(7)	96(2)
N7–H2···O7(3)	3.125(5)	151(3)
N7–H2···O8(3)	3.265(7)	112(2)
N7–H1···O8(3)	3.265(7)	92(2)

Equivalent positions; (1) $x-1$, $+y$, $+z$; (2) $-x$, $-y+1$, $-z+2$; (3) x, $+y-1$, $+z$; (4) $-x+1$, $-y+1$, $-z+2$; (5) $-x$, $-y+1$, $-z+1$; (6) $-x$, $-y$, $-z+1$.

the above described anion chelation, but they are differentiated in other intermolecular contacts; N4 interacts with the carbonyl group O2 atom of an equivalent ($-x$, $-y$, $1-z$) adjacent complex, in a common $R_2^2(8)$ motif, while N7 points towards another perchlorate at ($1-x$, $1-y$, $2-z$). The coordinated water molecules O5 and O6 have also different roles; the former is strongly hydrogen bonded to the crystallization water O11 and to the carbonyl O4 ($1-x$, $1-y$, $2-z$), while the latter is strongly hydrogen bonded to water O12 and to hydrazide N6 ($-x$, $1-y$, $2-z$).

Supplementary Data

Full lists of crystallographic data are available from the authors.

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