Formation of some 2-Pyridone Hg/M [M = Mn(II), Fe(III) and Cu(II)] Heterometallic Complexes and Crystal Structure of Hexakis(2-pyridone)iron(III) Nitrate

DAVID M. L. GOODGAME*, DAVID J. WILLIAMS
and RICHARD E. P. WINPENNY

*Chemistry Department, Imperial College of Science,
Technology and Medicine, London SW7 2AY (U.K.)*

(Received August 25, 1989)

We have recently described a series of hetero-metallic complexes in which the anion of 2-pyrrolidone links mercury to a wide range of other metal ions [1–3]. In view of the variety of unusual structures adopted by these compounds, we were interested to explore the use of a related ligand, 2-pyridone (pyOH), as homobimetallic complexes containing bridges based on this ring type are well known. We report here the synthesis of the compounds $Hg_3Mn(pyO)_6(NO_3)_2$ (1), $Hg_2Cu(pyO)_4$-$(NO_3)_2$ (2) and $Hg_3Fe(pyO)_6(NO_3)_3$ (3) and the crystal structure of $Fe(pyOH)_6(NO_3)_3$ (4).

Experimental

Preparations

Compounds **1–3** were prepared from mercury(II) acetate, 2-pyridone and the appropriate, hydrated metal nitrate using the method adopted [4] for the Hg/M complexes of 2-pyrrolidone. Use of methanol or ethanol as solvent resulted in immediate precipitation of the complexes. Compound 1: white; IR ν(C=O) 1615 cm^{-1}. *Anal.* Found: C, 26.4; H, 1.7; N, 8.1. Calc.: C, 26.4; H, 1.9; N, 8.2%. Compound 2: green; IR ν(C=O) 1620 cm^{-1}. *Anal.* Found: C, 24.8; H, 2.0; N, 9.4. Calc.: C, 24.9; H, 1.7; N, 8.7%. Compound 3: yellow–brown; IR ν(C=O) 1610 cm^{-1}. *Anal.* Found: C, 26.6; H, 2.0; N, 9.4. Calc.: C, 25.6; H, 1.7; N, 9.0%.

Compound 4 was first isolated from an attempt to prepare a Cu(II)/Fe(III) heterometallic complex, as follows. Copper(II) hydroxide (2 mmol) and 2-pyridone (16 mmol) were refluxed in methanol (70 cm^3). Addition of iron(III) nitrate (2 mmol) caused the colour to change from green to deep red. After overnight reflux, the solution was allowed to evaporate to a red paste. Addition of ethanol (10 cm^3) redissolved the majority of this paste leaving large, dark-red crystals of 4 suitable for X-ray study. *Anal.* Found: C, 43.5; H, 3.6; N, 15.2. Calc.: C, 44.3;

H, 3.7; N, 15.5%. Crystals of the compound can be more conveniently prepared by slow evaporation of a methanolic solution of iron(III) nitrate and a large excess of 2-pyridone.

Physical Measurements

These were made as in ref. 4.

X-ray Studies

Compound 4: $FeC_{30}H_{30}N_9O_{15}$, $M = 812.5$; triclinic, $a = 14.182(4)$, $b = 14.493(3)$, $c = 19.964(5)$ Å; $\alpha = 73.12(2)$, $\beta = 71.08(2)$, $\gamma = 89.26(2)°$, $U = 3699$ Å^3, space group $P\bar{1}$, $Z = 4$ (comprising one and two half, crystallographically independent formula units), $D_c = 1.46$ g cm^{-3}, μ(Cu Kα) = 40 cm^{-1}, $F(000) = 1675$. A total of 7606 independent reflections ($\theta \leqslant 50°$) were measured on a Nicolet R3m diffractometer with Cu Kα radiation (graphite monochromator) using ω scans. Of these, 5795 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors, but not for absorption effects. The structure was solved by the heavy-atom method which revealed the position of the iron atom, Fe(3), in a general position. The other two independent, special-position iron sites and the other non-hydrogen atoms were located from subsequent ΔF maps and were refined aniso-tropically. The pyridone rings were idealised and refined as rigid bodies. The position of the nitrogen atom within each pyridone ring was established both by its scattering relative to the other ring atoms and by an analysis of inter- and intramolecular hydrogen bonding interactions. All hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. Refinement was by block-cascade full-matrix least-squares and converged to give $R = 0.088$, $R_w = 0.089$ [$w^{-1} = \sigma^2(F) + 0.00115F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 1.12 and -0.43 e Å^{-3} respectively. The mean and maximum shift/errors in the final refinement were 0.040 and 0.171 respectively. The rather high final value for R was due to the presence of diffuse residual electron density produced by disordered unresolvable solvent present in the crystals. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [5]. Salient bond lengths and angles are listed in Table 1 (see also Supplementary Material).

Results and Discussion

The reactions between mercury(II) acetate, 2-pyridone and the nitrates of Mn(II), Fe(III) and Cu(II) under the same conditions employed [4] for

---

*Author to whom correspondence should be addressed.

TABLE 1. Bond lengths and angles for compound **4**

Bond lengths (Å)

Fe(1)–O(1)	1.980(6)	Fe(1)–O(2)	1.987(6)
Fe(1)–O(9)	1.995(7)	Fe(2)–O(3)	1.997(6)
Fe(2)–O(4)	2.004(5)	Fe(2)–O(5)	2.011(8)
Fe(3)–O(6)	1.992(5)	Fe(3)–O(7)	2.037(7)
Fe(3)–O(8)	1.986(7)	Fe(3)–O(10)	1.985(5)
Fe(3)–O(11)	1.979(7)	Fe(3)–O(12)	1.998(7)

Bond angles (°)

O(1)–Fe(1)–O(2)	91.8(2)	O(1)–Fe(1)–O(9)	88.6(3)
O(2)–Fe(1)–O(9)	92.3(3)	O(1)–Fe(1)–O(1')	180.0
O(1)–Fe(1)–O(2')	88.2(2)	O(2)–Fe(1)–O(2')	180.0
O(1)–Fe(1)–O(9')	91.4(3)	O(2)–Fe(1)–O(9')	87.8(3)
O(9)–Fe(1)–O(9')	180.0	O(3)–Fe(2)–O(4)	87.4(2)
O(3)–Fe(2)–O(5)	93.2(3)	O(4)–Fe(2)–O(5)	90.9(3)
O(3)–Fe(2)–O(3')	180.0	O(3)–Fe(2)–O(4')	92.6(2)
O(4)–Fe(2)–O(4')	180.0	O(3)–Fe(2)–O(5')	86.8(3)
O(4)–Fe(2)–O(5')	89.1(3)	O(5)–Fe(2)–O(5')	180.0
O(6)–Fe(3)–O(7)	89.9(3)	O(6)–Fe(3)–O(8)	89.2(3)
O(7)–Fe(3)–O(8)	89.9(3)	O(6)–Fe(3)–O(10)	178.4(3)
O(7)–Fe(3)–O(10)	88.7(3)	O(8)–Fe(3)–O(10)	90.2(3)
O(6)–Fe(3)–O(11)	87.9(3)	O(7)–Fe(3)–O(11)	175.9(3)
O(8)–Fe(3)–O(11)	93.6(3)	O(10)–Fe(3)–O(11)	93.6(3)
O(6)–Fe(3)–O(12)	93.4(3)	O(7)–Fe(3)–O(12)	88.2(3)
O(8)–Fe(3)–O(12)	176.8(2)	O(10)–Fe(3)–O(12)	87.2(3)
O(11)–Fe(3)–O(12)	88.4(3)		

the synthesis of 2-pyrrolidone Hg/M compounds gave compounds 1–3 as powders not amenable to full structural characterisation by X-ray diffraction. The compounds were too insoluble for recrystallisation from appropriate organic solvents, nor could crystallinity be improved by varying the solvent employed in the synthesis.

The ν(C=O) band of the pyridone ligands in the IR spectra of all three compounds was at appreciably lower frequency (1610–1620 cm^{-1}) than in complexes [6] in which pyridone binds to transition metal ions in simple unidentate fashion via oxygen. A similar reduction in ν(C=O) was found [1, 4] for the 2-pyrrolidone bridges between Hg and other metal ions.

The EPR spectrum of 1 showed only a broad band in the g_{eff} = 2 region with no evidence of zero-field splitting. This is consistent with a polymeric structure and consequent loss of magnetic dilution at the manganese centres [7] but, unfortunately, provides no information about the geometry at the Mn sites.

The EPR spectrum of the Hg/Cu(II) complex 2 was rather unusual as at Q-band frequency it showed four sharp bands at g_{eff} = 2.389, 2.150, 2.068 and 2.038 (the last two bands were unresolved at X-band frequency). It was quite unlike either the S = 1 spectra reported [8] for the dimeric copper(II) pyridone-bridged complexes or a normal spectrum for a single S = 1/2 Cu(II) site (e.g. ref. 4). The electronic

spectrum of the solid had two bands (9165 and 11 950 cm^{-1}).

Dark-red crystals of compound 4 were initially obtained from an attempt to prepare heterometallic pyridone complexes containing Cu(II)$_4$/Fe(III)$_2$ arrays analogous to the Cu(II)$_4$/Ln(III)$_2$ (Ln = Dy or Gd) arrays recently described [9]. X-ray analysis showed that 4 had the stoichiometry Fe(pyOH)$_6$-(NO$_3$)$_3$.

There are three independent iron sites in the asymmetric unit; two of them [Fe(1) and Fe(2)] lie on centres of symmetry, the third is in a general position. In each cation the iron atom is octahedrally coordinated, being bound to six oxygen atoms of 2-pyridone ligands (Fig. 1). Distortion from regular octahedral geometry is, in each case, small (Fe–O bond lengths 1.98–2.04 Å, O–Fe–O bond angles 87–94 and 176–180°).

There are, however, marked differences in the geometries of the three independent cations. Although they all apparently approach S_6 symmetry, this symmetry is broken. This is due, principally, to the positions of the nitrogen atoms within the pyridone rings. In the cation containing Fe(1) (Fig. 1(a)) two diametrically opposite nitrogen atoms are disposed in the opposite sense to the other four. This is also true of the other centrosymmetric cation (Fig. 1(c)). In the third cation, however, only one nitrogen atom, N(10), is out of phase (Fig. 1(e)). In
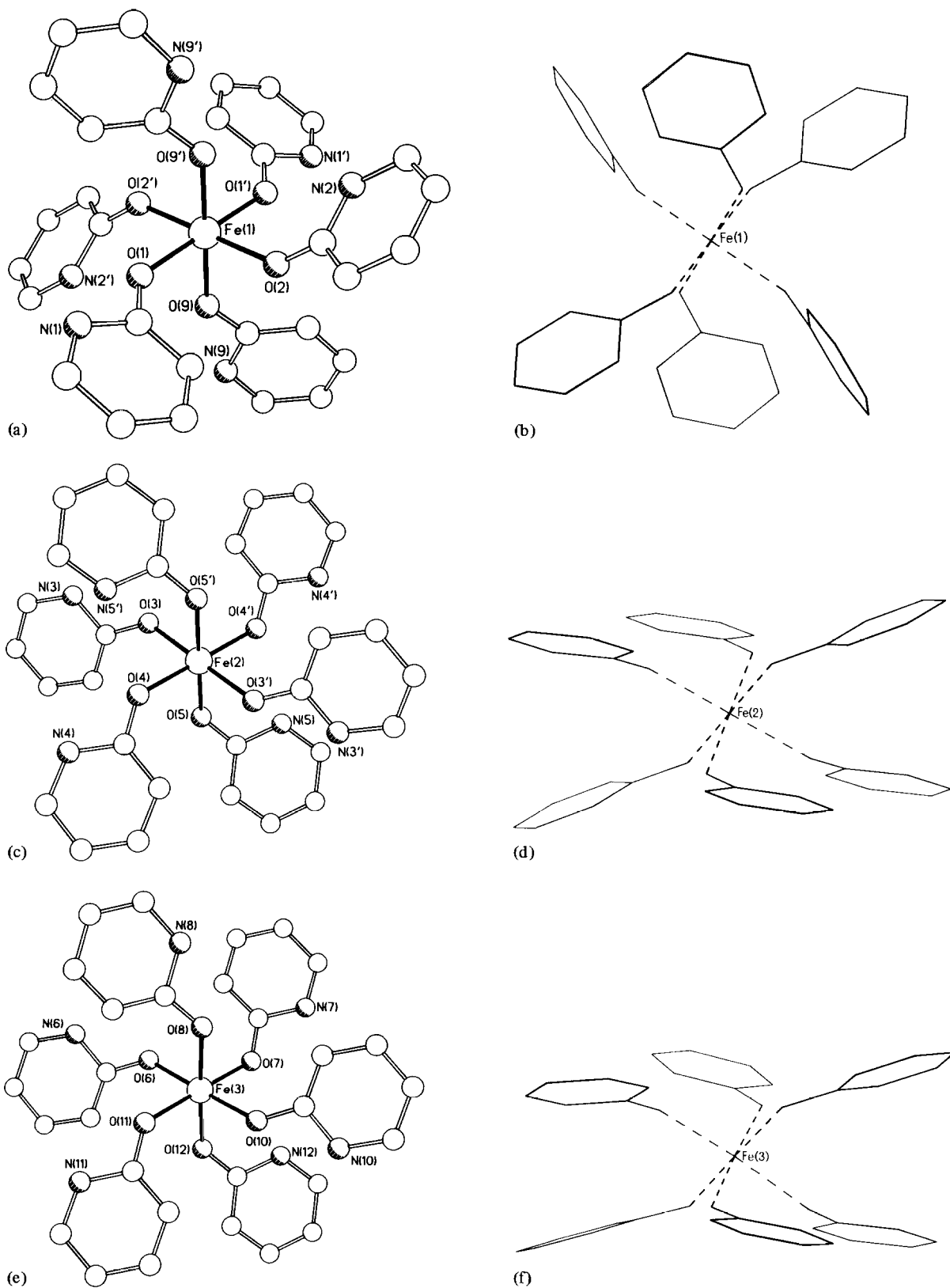
Fig. 1. The three crystallographically independent iron sites in **4** giving the relevant atom numbering schemes, and also their comparative elevations illustrating the differing degrees of flattening.

addition there is a significant flattening of the cation geometry around Fe(2) and Fe(3) (Figs. 1(d) and (f)) in contrast to that about Fe(1) (Fig. 1(b)).

All the ring nitrogen atoms are involved in hydrogen bonding. In two of the cations there are intramolecular hydrogen bonds of *c.* 2.84 Å, between N(5) and O(4′) and between N(12) and O(7). It is the two cations containing these intramolecular hydrogen bonds in which the geometry is appreciably flattened. All other hydrogen-bonding interactions are to the nitrate ions; the contacts ranging between 2.68 and 2.96 Å. These give rise to a continuous network of hydrogen-bonding-mediated cation–anion interactions involving all three iron centres.

It is interesting that the combination of hydrogen-bonding patterns, both intra- and intermolecular, and cation–anion packing requirements, gives rise to the observed diversity of conformation at the iron centres for a molecule of such potentially high symmetry.

Supplementary Material

A list of fractional atomic coordinates and isotropic thermal parameters is available from the authors on request.

References

1 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Polyhedron, 7* (1988) 1807, and refs. therein.
2 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.,* (1989) 1439.
3 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Polyhedron, 8* (1989) 1913.
4 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl., 26* (1987) 1044.
5 G. M. Sheldrick, *SHELXTL,* an integrated system for solving, refining, and displaying crystal structures from diffraction data, Revision 4.1, University of Gottingen, F.R.G., 1983.
6 C. C. Houk and K. Emerson, *J. Inorg. Nucl. Chem., 30* (1968) 1493.
7 R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *Nature (London), 219* (1968) 1037.
8 D. M. L. Goodgame, Y. Nishida and R. E. P. Winpenny, *Bull. Chem. Soc. Jpn., 59* (1986) 344.
9 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Polyhedron, 8* (1989) 1531.