Orthorhombic
Pbca
$a = 9.714\,(2)$ Å
$b = 16.742\,(2)$ Å
$c = 16.540\,(2)$ Å
$V = 2689.9\,(7)$ Å^3
$Z = 8$
$D_x = 1.673$ Mg m^{-3}
D_m not measured

Cell parameters from 25
    reflections
$\theta = 10.4–15.1°$
$\mu = 2.195$ mm^{-1}
$T = 293\,(1)$ K
Plate
$0.70 \times 0.50 \times 0.06$ mm
Light brown

Data collection

Enraf–Nonius CAD-4-MACH*S*
    diffractometer
$\omega/2\theta$ scans
Absorption correction:
    Gaussian (Sheldrick,
    1976)
    $T_{min} = 0.343$, $T_{max} = 0.876$
3371 measured reflections
2636 independent reflections
2158 reflections with
    $I > 2\sigma(I)$

$R_{int} = 0.016$
$\theta_{max} = 25.98°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 20$
$l = -1 \rightarrow 20$
3 standard reflections
    frequency: 160 min
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.074$
$S = 1.031$
2636 reflections
180 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2$
$\quad + 1.7223P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}
Extinction correction: none
Scattering factors from
    International Tables for
    Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Te—C14	2.120 (4)	N—C8	1.416 (4)
Te—C1	2.122 (3)	C2—C7	1.488 (4)
O—C7	1.230 (3)	C8—C13	1.376 (5)
N—C7	1.341 (4)	C8—C9	1.392 (4)
C14—Te—C1	96.66 (16)	O—C7—C2	120.1 (3)
C7—N—C8	129.0 (3)	N—C7—C2	117.5 (2)
C3—C2—C1	119.6 (3)	C13—C8—C9	119.1 (3)
C3—C2—C7	121.1 (3)	C13—C8—N	117.8 (3)
C1—C2—C7	119.3 (2)	C9—C8—N	123.0 (3)
O—C7—N	122.4 (3)		
C14—Te—C1—C6	19.2 (3)	C1—C2—C7—O	-32.0 (4)
C14—Te—C1—C2	-162.1 (3)	C3—C2—C7—N	-34.4 (4)
C8—N—C7—O	-5.8 (5)	C1—C2—C7—N	147.7 (3)
C8—N—C7—C2	174.5 (3)	C7—N—C8—C13	167.2 (3)
C3—C2—C7—O	145.9 (3)	C7—N—C8—C9	-15.4 (5)

The coordinates of the H atom attached to N were refined [N—H = 0.72 (3) Å]; other H atoms were treated as riding. U_{iso} values of all H atoms were refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *PRO-CESS_DATA* (Gable *et al.*, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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The biologically active iron chelators 2-pyridylcarboxaldehyde isonicotinoyl-hydrazone, 2-pyridylcarboxaldehyde benzoylhydrazone monohydrate and 2-furaldehyde isonicotinoylhydrazone

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Abstract

In the crystal structures of the respective title compounds, $C_{12}H_{10}N_4O$, $C_{13}H_{11}N_3O\cdot H_2O$ and $C_{11}H_9N_3O_2$, variations in the torsion angles of the aromatic pyridyl

and benzoyl groups are observed, and the disposition of the heterocyclic aldehyde is shown to be influenced by the ring size of this group.

Comment

Aroylhydrazone ligands continue to attract interest as potential chelators for the treatment of iron-overload disease and also as agents with considerable anti-tumour activity (Johnson *et al.*, 1982; Baker *et al.*, 1992; Richardson *et al.*, 1995; Richardson & Milnes, 1997). As part of our research programme examining the development of clinically useful iron chelators, we have synthesized and determined the crystal structures of three aroylhydrazones, namely 2-pyridylcarboxal-dehyde isonicotinoylhydrazone, (1), 2-pyridylcarboxal-dehyde benzoylhydrazone monohydrate, (2)·H_2O, and 2-furaldehyde (2-furfural) isonicotinoylhydrazone, (3). These chelators were designed to improve upon the aqueous solubility and iron-chelation efficacy of the pyridoxal isonicotinoylhydrazone analogues that were examined previously. Studies assessing the biological activity of compounds (1)–(3) have been completed and will be described elsewhere (Becker & Richardson, 1999). The title compounds have been known for some time [(1), Beyerman *et al.* (1954); (2), Grammaticakis (1956); (3), Fox & Gibas (1953)], but no crystal structures of this series have been published.

(1)

(2)

(3)
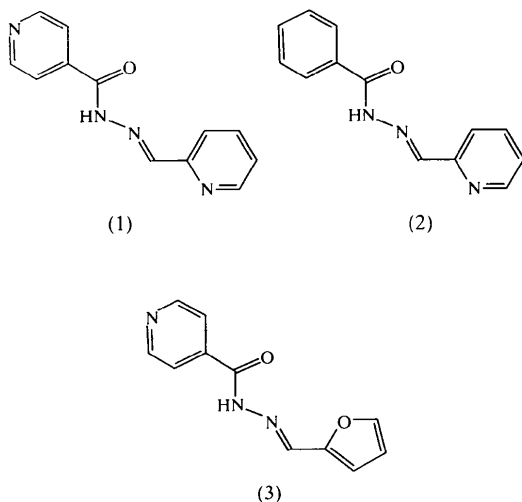
In the crystal structure of (1) (Fig. 1), the 2- and 4-pyridyl rings are each twisted slightly about their connecting C—C bonds, defined by the respective C3—C2—C1—N1 and C9—C8—C7—N2 torsion angles of 3.9 (9) and 9.7 (7)°. The 2-pyridyl N atom (N3) is *anti* with respect to the imine N atom (N1), which avoids repulsion between the H atoms attached to C1 and C3. As a consequence, the molecule is unfavourably disposed

to chelate a metal ion in a tridentate configuration. In order for this ligand to bind meridionally (through the donor atoms O1, N1 and N3), the pyridyl group would have to rotate by *ca* 180° about C1—C2.
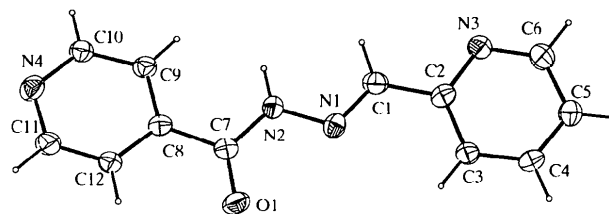

Fig. 1. View of (1) showing 30% probability ellipsoids.

The crystal structure of the benzoyl analogue (2)·-H_2O (Fig. 2) found the hydrazone and a water of crystallization each located on a general site. The bond lengths are similar to those found in (1). The phenyl ring is somewhat more twisted about the connecting C—C bond [N2—C7—C8—C9 torsion angle 22.6 (3)°] than its 4-pyridyl analogue in (1). The disposition of the 2-pyridyl ring again finds N3 *anti* to N1. Hydrogen bonding with the water O atom (O2) was also identified. The most significant contacts are O2—H2B···N3^i of 1.97 Å [O2···N3^i 2.875 (2) Å] and N2—H2N···O2^{ii} of 2.00 Å [N2···O2^{ii} 2.852 (2) Å] [symmetry codes: (i) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$; (ii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, z].
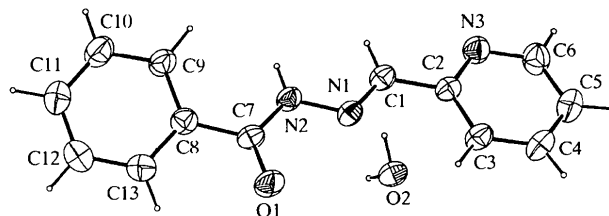

Fig. 2. View of (2)·H_2O showing 30% probability ellipsoids.

The furfural hydrazone (3) (Fig. 3) crystallizes with two independent molecules ($n = A$ and B) in the asymmetric unit, but the structural differences between these molecules are negligible. The furyl O atom (O1n) is *syn* with respect to the imine N atom (N1n), in contrast to the structures of (1) and (2) where the heteroatoms were *anti*. In this case, the *ca* 10° more obtuse C1n—C2n—C3n angle enforced by the planar five-membered furyl ring (*ca* 130°) relieves the C1n—H···H—C3n repulsion which led to the corresponding *anti* conformers (1) and (2). In (3), the 4-pyridyl ring is twisted significantly about its connecting C—C bond (C8n—C7n—C6n—N2n *ca* 33°), whereas the furyl ring torsion is relatively small (*ca* 4°).
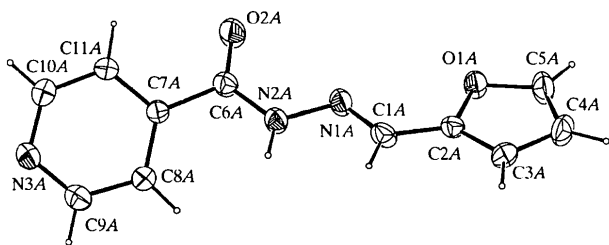
Fig. 3. View of (3) (one independent molecule) showing 30% probability ellipsoids.

We are currently exploring the coordination chemistry and biological activity of these three potential ligands and their analogues.

Experimental

The title compounds were prepared in good yield by Schiff base condensation between the corresponding aldehyde [2-pyridylcarboxaldehyde for (1) and (2), and 2-furfural for (3)] and acid hydrazide [isonicotinic acid hydrazide for (1) and (3), and benzoic acid hydrazide for (2)] in refluxing ethanol. The ^{1}H NMR and microanalytical results are consistent with their formulation. Crystals of each compound were grown from saturated ethanolic solutions.

Compound (1)

Crystal data

$C_{12}H_{10}N_4O$
$M_r = 226.24$
Orthorhombic
$Fdd2$
$a = 43.749 (10)$ Å
$b = 20.984 (2)$ Å
$c = 4.5980 (10)$ Å
$V = 4221.1 (14)$ Å^3
$Z = 16$
$D_x = 1.424$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.3 - 14.1°$
$\mu = 0.097$ mm^{-1}
$T = 296 (2)$ K
Prism
$0.50 \times 0.13 \times 0.10$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2163 measured reflections
1060 independent reflections
625 reflections with $I > 2\sigma(I)$

$R_{int} = 0.068$
$\theta_{max} = 24.98°$
$h = -51 \rightarrow 51$
$k = 0 \rightarrow 24$
$l = -2 \rightarrow 5$
3 standard reflections frequency: 120 min intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.122$
$S = 1.034$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none

1060 reflections
154 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Compound (2)

Crystal data

$C_{13}H_{11}N_3O \cdot H_2O$
$M_r = 243.26$
Orthorhombic
$Pbca$
$a = 7.1468 (6)$ Å
$b = 11.994 (7)$ Å
$c = 29.493 (5)$ Å
$V = 2528.1 (16)$ Å^3
$Z = 8$
$D_x = 1.278$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.3 - 13.4°$
$\mu = 0.089$ mm^{-1}
$T = 296 (2)$ K
Prism
$0.60 \times 0.60 \times 0.50$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2250 measured reflections
2220 independent reflections
1548 reflections with $I > 2\sigma(I)$

$R_{int} = 0.008$
$\theta_{max} = 24.97°$
$h = -4 \rightarrow 8$
$k = -4 \rightarrow 14$
$l = -14 \rightarrow 35$
3 standard reflections frequency: 120 min intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.127$
$S = 1.059$
2220 reflections
158 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.2126P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.0039 (9)
Scattering factors from International Tables for Crystallography (Vol. C)

Compound (3)

Crystal data

$C_{11}H_9N_3O_2$
$M_r = 215.21$
Monoclinic
$P2_1/c$
$a = 14.188 (3)$ Å
$b = 5.2850 (3)$ Å
$c = 26.954 (6)$ Å
$\beta = 93.550 (10)°$
$V = 2017.2 (6)$ Å^3
$Z = 8$
$D_x = 1.417$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.6 - 16.0°$
$\mu = 0.101$ mm^{-1}
$T = 296 (2)$ K
Plate
$0.30 \times 0.20 \times 0.07$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{int} = 0.032$
$\theta_{max} = 24.96°$

Scattering factors from International Tables for Crystallography (Vol. C)

ω–2θ scans
Absorption correction: none
3731 measured reflections
3533 independent reflections
1403 reflections with
   $I > 2\sigma(I)$

$h = -1 \rightarrow 16$
$k = -4 \rightarrow 6$
$l = -32 \rightarrow 31$
3 standard reflections
   frequency: 120 min
   intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.143$
$S = 0.971$
3533 reflections
289 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for
   Crystallography (Vol. C)

For (1), the direction of the polar axis could not be determined reliably as the heaviest atom in the structure was oxygen. For structure (3), the presence of a pseudo-*b*-glide plane (perpendicular to **a**) was noted, but no alternative cell could be identified.

For all compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* in *CAD-4 Software*; data reduction: *Xtal3.2* (Hall *et al.*, 1992); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1264). Services for accessing these data are described at the back of the journal.

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4,4'-Bipyridinium diperchlorate

Seik Weng Ng

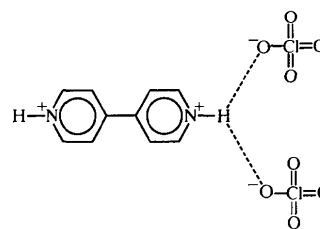*Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: h1nswen@umcsd.um.edu.my*

Abstract

In 4,4'-bipyridinium diperchlorate, $C_{10}H_{10}N_2^{2+}\cdot 2ClO_4^-$, the centrosymmetric dications and the anions are linked by three N$\cdots$O hydrogen bonds [N$\cdots$O = 2.893 (3), 2.915 (3) and 2.972 (3) Å] into a two-dimensional network.

Comment

The two pyridyl moieties of the 4,4'-bipyridinium dication are coplanar in the diiodide (Iyere *et al.*, 1998) and in the monoclinic modification of the dinitrate (Weakley, 1987), but are twisted by 39° in the orthorhombic modification of the dinitrate (Barker *et al.*, 1990). For the dinitrate, the cation lies on a centre-of-inversion in the orthorhombic modification and on a twofold axis in the monoclinic modifications; both modifications display only one N$\cdots$O hydrogen bond [2.77 (1) Å (Weakley, 1987); 2.674 Å (Barker *et al.*, 1990)]. However, C—H$\cdots$X interactions [3.163 (6)–3.239 (4) Å] are present in the two modifications as well as in the centrosymmetric diiodide [C—H$\cdots$I = 3.740 (5)–3.818 (5) Å] (Iyere *et al.*, 1998).

The two rings in the diperchlorate, (I) (Fig. 1), are also exactly coplanar, a feature that is predicted

(I)