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Crystal Structure
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$[Fe(C_{12}H_8N_3O_2)Cl_2(ROH)]$, with R = Me and Et

Takashi Kajiwara and Tasuku Ito*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
Correspondence e-mail: ito@agnus.chem.tohoku.ac.jp

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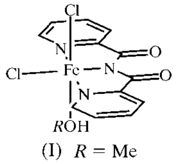
The title octahedral complexes, [bis(pyridine-2-carbonyl)aminate]dichloro(methanol)iron(III), $[Fe(C_{12}H_8N_3O_2)Cl_2(CH_4O)]$, and [bis(pyridine-2-carbonyl)aminate]dichloro(ethanol)iron(III), $[Fe(C_{12}H_8N_3O_2)Cl_2(C_2H_6O)]$, both crystallize in space group $P\overline{1}$ and have similar structures. Monoanionic bpca$^-$ [bis(pyridine-2-carbonyl)aminate] acts as a planar tridentate ligand in both cases. Coordination bond distances are in the range typical of high-spin Fe^{III} complexes. Carbon–oxygen distances are typical of a C═O double bond suggesting the negative charge of the bpca$^-$ ligand is localized on the central N atom.

Comment

It is known that bpca$^-$ [bis(pyridine-2-carbonyl)aminate], formed upon deprotonation of Hbpca, acts as a tridentate N-donor rigid ligand and coordinates to transition metal ions such as Fe^{II} and Fe^{III} (Wocadlo *et al.*, 1993), Mn^{II} (Marcos *et al.*, 1990), Cu^{II} and Zn^{II} (Marcos *et al.*, 1989), and Rh^{III} (Paul *et al.*, 1998). The resulting complex $[M(\text{bpca})_2]^{n+}$ contains two sets of free β-diketone groups which can coordinate to other metal ions in a chelating mode. We demonstrated that this type of complex acts as a bridging complex ligand to give multi-metal-centered complexes (Kajiwara & Ito, 1998). With Cu^{II} and Fe^{III} ions, this ligand also forms other types of complexes formulated as $[Cu(\text{bpca})X(H_2O)_n]$ (Folgado *et al.*, 1988, 1989) and $[Fe(\text{bpca})Cl_2(H_2O)]$ (Wocadlo *et al.*, 1993). The latter contains high-spin Fe^{III}, whereas the Fe^{III} ions in $[Fe(\text{bpca})_2]X$ are in a low-spin or medium-spin state depending on X. Such high-spin complexes can be excellent complex ligands in the construction of multi-metal complexes with a large high-spin ground state. We report here two novel Fe^{III} complexes, namely [bis(pyridine-2-carbonyl)aminate]dichloro(methanol)iron(III), (I), and [bis(pyridine-2-carbonyl)aminate]dichloro(ethanol)iron(III), (II), which are promising high-spin complexing ligands.



(I) R = Me
(II) R = Et

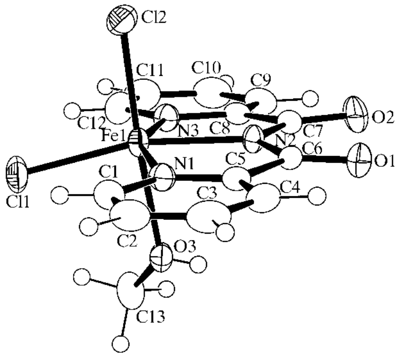


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

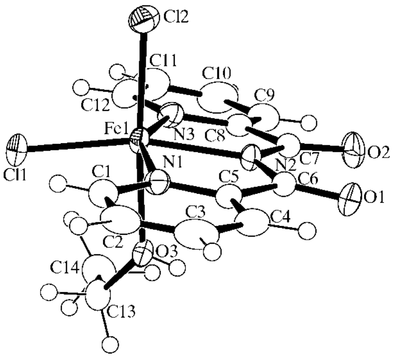


Figure 2
The molecular structure of (II) showing 50% probability displacement ellipsoids.

The reaction of Hbpca in nitromethane with $FeCl_3$ in methanol or ethanol affords yellow crystals of (I) and (II), respectively. The molecular structures of (I) and (II) are very similar to each other except for the coordinating alcohol molecules. The hexacoordination of the Fe^{III} ion in each compound is achieved by three N atoms from the planar bpca$^-$ ligand, two Cl ligands *cis* to each other and the O atom of the alcohol. Iron–ligand distances are all in the range expected for high-spin Fe^{III} complexes (Wocadlo *et al.*, 1993). The O3—Fe—L angles (L = N1, N2 and N3) are significantly smaller than 90°. Atoms N1, N2, N3 and Cl1 are practically coplanar, and the Fe atom deviates by 0.203 (1) and 0.1979 (7) Å from their best mean planes in (I) and (II) respectively. The C═O distances [1.223 (3) and 1.218 (3) Å in (I), and 1.222 (2) and 1.214 (2) Å in (II)] are in the usual range for a C═O double bond (Etter & Reutzel, 1991), suggesting that the negative charge of bpca$^-$ is localized mainly on the amide N atom of the O—C—N—C—O moiety.

Experimental

Solutions of Hbpca (113 mg, 0.5 mmol) in nitromethane (5 ml) and $FeCl_3$ (81 mg, 0.05 mmol) in methyl alcohol or ethyl alcohol (5 ml) were mixed with stirring. From the resulting yellow–orange solutions, yellow compounds crystallized after a few days.

Compound (I)

Crystal data

$[Fe(C_{12}H_8N_3O_2)Cl_2(CH_4O)]$
$M_r = 385.01$
Triclinic, $P\overline{1}$
$a = 8.3695$ (11) Å
$b = 8.5208$ (11) Å
$c = 11.7567$ (16) Å
$\alpha = 101.532$ (2)°
$\beta = 97.517$ (2)°
$\gamma = 109.958$ (3)°
$V = 753.91$ (17) Å^3

$Z = 2$
$D_x = 1.696$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2034 reflections
$\theta = 1.81$–$26.00°$
$\mu = 1.369$ mm^{-1}
$T = 223$ (2) K
Prismatic, yellow
0.25 × 0.24 × 0.18 mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.582$, $T_{max} = 0.801$
3890 measured reflections

2795 independent reflections
2247 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 26°$
$h = -10 \rightarrow 7$
$k = -5 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 0.990$
2795 reflections
247 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Compound (II)

Crystal data

$[Fe(C_{12}H_8N_3O_2)Cl_2(C_2H_6O)]$
$M_r = 399.03$
Triclinic, $P\overline{1}$
$a = 8.5609$ (6) Å
$b = 8.5998$ (6) Å
$c = 12.0245$ (9) Å
$\alpha = 99.744$ (1)°
$\beta = 99.944$ (1)°
$\gamma = 110.483$ (1)°
$V = 791.13$ (10) Å^3

$Z = 2$
$D_x = 1.675$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3161 reflections
$\theta = 1.78$–$26.02°$
$\mu = 1.308$ mm^{-1}
$T = 193$ (2) K
Prismatic, yellow
0.32 × 0.28 × 0.15 mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.688$, $T_{max} = 0.862$
4571 measured reflections

3059 independent reflections
2691 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 26.02°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -9 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.027$
3059 reflections
264 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.2465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1998); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °) for (I).

Fe1—N1	2.122 (2)	Fe1—O3	2.232 (2)
Fe1—N2	2.078 (2)	Fe1—Cl1	2.2554 (8)
Fe1—N3	2.115 (2)	Fe1—Cl2	2.2894 (9)
N2—Fe1—N1	77.24 (8)	N3—Fe1—Cl1	102.95 (7)
N2—Fe1—N3	77.30 (8)	N1—Fe1—Cl2	93.91 (7)
N3—Fe1—N1	153.99 (9)	N2—Fe1—Cl2	95.44 (7)
N1—Fe1—O3	86.84 (8)	N3—Fe1—Cl2	93.69 (7)
N2—Fe1—O3	81.22 (8)	O3—Fe1—Cl1	85.43 (6)
N3—Fe1—O3	84.13 (8)	O3—Fe1—Cl2	176.34 (6)
N1—Fe1—Cl1	100.57 (6)	Cl1—Fe1—Cl2	97.95 (3)
N2—Fe1—Cl1	166.55 (7)		

Table 2
Selected geometric parameters (Å, °) for (II).

Fe1—N1	2.1269 (16)	Fe1—O3	2.2051 (15)
Fe1—N2	2.0767 (15)	Fe1—Cl1	2.2564 (6)
Fe1—N3	2.1187 (16)	Fe1—Cl2	2.2946 (6)
N2—Fe1—N1	77.00 (6)	N3—Fe1—Cl1	102.18 (5)
N2—Fe1—N3	77.37 (6)	O3—Fe1—Cl1	85.83 (4)
N3—Fe1—N1	154.07 (6)	N1—Fe1—Cl2	93.93 (5)
N1—Fe1—O3	86.00 (6)	N2—Fe1—Cl2	96.11 (5)
N2—Fe1—O3	80.23 (6)	N3—Fe1—Cl2	92.62 (5)
N3—Fe1—O3	85.88 (6)	Cl1—Fe1—Cl2	97.84 (2)
N1—Fe1—Cl1	101.72 (5)	O3—Fe1—Cl2	176.26 (4)
N2—Fe1—Cl1	166.05 (5)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1093). Services for accessing these data are described at the back of the journal.

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