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Ammonium dichlorobis(dimethylglyoximato-*N*,*N*′)iridate(III)

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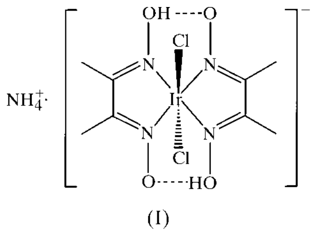
In the title compound, $(NH_4)[IrCl_2(C_4H_7N_2O_2)_2]$, (I), the Ir atom is octahedrally coordinated by two *trans* Cl^- and two dimethylglyoximate chelate ligands in the equatorial plane. A two-dimensional hydrogen-bond network between ammonium cations NH_4^+ and anionic $[IrCl_2(C_4H_7N_2O_2)_2]^-$ complexes is extended along the *bc* plane.

Comment

Among compounds of the elements in Group 9 with dimethylglyoxime (H_2dmg), cobalt complexes, the so-called cobaloximes, have been well studied from the bioinorganic aspects as useful vitamin B_{12} models (Randaccio *et al.*, 1989). Some rhodium complexes are known, but have not been often applied to biological investigation in comparison with the cobalt complexes. The cobaloximes and rhodoximes commonly have octahedral geometry with equatorial coordination of two $Hdmg^-$ anions. As for the iridium complex, more inert than the rhodium, the structure of $[IrCl_2(Hdmg)(H_2dmg)]$, (II), was only reported (Simonov *et al.*, 1996); the geometry about iridium is octahedral, similar to the cobaloximes and rhodoximes. Its properties remain unexplored owing to the low solubility in solvents. We attempted to derive salts by replacement of onium ions such as NH_4^+, NBu_4^+ *etc.* in order to examine chemical and physical properties in solutions. Single crystals of the ammonium salt, $(NH_4)[IrCl_2(Hdmg)_2]$, (I), were obtained from ethanol solution.



(I)

The crystal structure of (I) is constructed of NH_4^+ cations and octahedral $[IrCl_2(Hdmg)_2]^-$ anions. The iridium atom on the inversion center is coordinated by two Cl atoms in *trans* and two $Hdmg^-$ chelate ligands in the equatorial plane, similarly to (II). A pair of the $Hdmg^-$ are planar with a maximum deviation of 0.138 (5) Å of C4 and linked with each other by the O1···H7—O2 intramolecular hydrogen bonds to form a 14-membered macrocycle. The intermolecular hydrogen bonds between the oxime groups of the $[IrCl_2(Hdmg)_2]$ moieties are observed in (II) but not in (I). Insteadly, two-dimensional hydrogen-bond network along the *bc* plane is formed between NH_4^+ and, Cl and O1 atoms of $[IrCl_2(Hdmg)_2]^-$ moieties.

The notable difference between (II) and (I) is found in the O—N distances of the Hdmg moieties. In (I), the O1—N1 distance [1.323 (3) Å] is distinctly shorter than the O2—N2 distance [1.380 (3) Å], while the O—N distances of the two independent molecules in (II) are within a small range (1.36–1.37 Å). The discrepancy of the O—N distances in (I) shows that the H atom is strongly bonded to the O2 atom; such a phenomenon has been found in the cobaloximes or rhodoximes, *e.g.* $[Rh(Hdmg)_2(H_2O)_2](ClO_4)$ (Moszner *et al.*, 1997). In (I), the O—N distances seem quite close to each other owing to the delocalized distribution of the protonated oxime groups. Other bond distances and angles are reasonable within the standard deviations.

Experimental

The protonated iridoxime, $[IrCl_2(Hdmg)(H_2dmg)]$, (II), was prepared according to the procedure reported by Simonov *et al.* (1996). To the suspended aqueous solution of (II), ammoniac water was added to precipitate fine crystals of $(NH_4)[IrCl_2(Hdmg)_2]$, (I). By replacing ammoniac water with 10% methanol solution of NBu_4OH, precipitate of $(NBu_4)[IrCl_2(Hdmg)_2]$, (III), soluble in organic solvents such as CH_2Cl_2, CH_3CN *etc.*, was obtained. Attempts to substitute the axial Cl^- ligands with AgCl or $NaBH_4$ have been unsuccessful.

The single crystals of (I) were obtained from ethanol solution of the precipitate by absorbing vaporized ether. Analysis found: C 18.52, H 3.50, N 13.86%; calculated for $C_8H_{18}Cl_2IrN_5O_4$: C 18.79, H 3.55, N 13.69%.

^{1}H NMR of (III) [$CDCl_3$, 300 MHz, δ p.p.m.) 5.36 (*s*, 2 H, OH), 2.40 (*s*, 12 H, CH_3), 3.18 (*t*, 8 H, $CH_2(NBu_4)$], 1.58 [quintet, 8 H, $CH_2(NBu_4)$], 1.40 [sextet, 8 H, $CH_2(NBu_4)$], 0.99 [t, 12 H, $CH_3(NBu_4)$]. The spectrum is consistent with the octahedral geometry of anionic complex of (I).

Crystal data

$(NH_4)[IrCl_2(C_4H_7N_2O_2)_2]$
$M_r = 511.37$
Monoclinic, $C2/c$
$a = 18.3948\ (13)$ Å
$b = 7.4649\ (14)$ Å
$c = 13.2477\ (16)$ Å
$\beta = 124.752\ (4)^\circ$
$V = 1494.6\ (3)$ Å^3
$Z = 4$
$D_x = 2.273$ Mg m^{-3}
$D_m = 2.27$ Mg m^{-3}
D_m measured by flotation in CCl_4/CBr_4
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.655–14.965^\circ$
$\mu = 9.310$ mm^{-1}
$T = 296\ (2)$ K
Prism, intense green
0.15 × 0.15 × 0.11 mm

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Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.282$, $T_{\max} = 0.359$
2266 measured reflections
2177 independent reflections
1686 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.014$
$\theta_{\max} = 30.0°$
$h = -21 \rightarrow 25$
$k = 0 \rightarrow 10$
$l = -18 \rightarrow 0$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0139$
$wR(F^2) = 0.0345$
$S = 1.049$
2177 reflections
130 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 1.0240P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00299 (8)

Table 1
Selected geometric parameters (Å, °).

Ir—N1	2.005 (2)	O2—N2	1.380 (3)
Ir—N2	1.992 (2)	N1—C2	1.310 (3)
Ir—Cl	2.3437 (6)	N2—C3	1.290 (3)
O1—N1	1.323 (3)	C2—C3	1.468 (3)
N1—Ir—N2	77.48 (8)	N2—Ir—Cl	91.55 (6)
N1—Ir—Cl	90.38 (6)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H7···O1$^{\rm i}$	0.85 (4)	1.92 (4)	2.755 (3)	170 (4)
N3—H8···O1	0.96 (4)	1.83 (4)	2.781 (3)	172 (4)
N3—H9···Cl$^{\rm ii}$	0.85 (4)	2.56 (5)	3.294 (4)	144 (4)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, y-1, z$.

Refined C—H distances are in the range 0.91 (4)–0.96 (4) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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