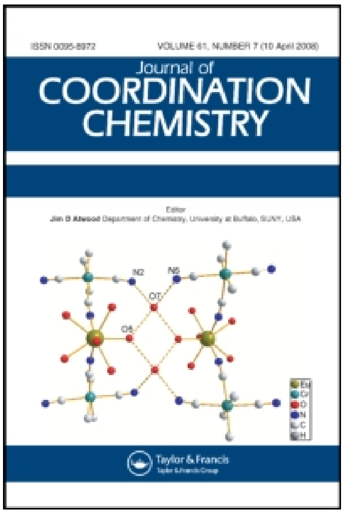

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THE STRUCTURE OF A LOW-TEMPERATURE FORM OF *TRANS*-$[Ir(PYRIDINE)_4Cl_2]Cl. 6H_2O$

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THE STRUCTURE OF A LOW-TEMPERATURE FORM OF *TRANS*-$[Ir(PYRIDINE)_4Cl_2]Cl.6H_2O$

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Trans-$[Ir(pyridine)_4Cl_2]Cl.6H_2O$ exists in at least two forms. A high temperature form, crystallized from water at room temperature, is disordered in the solid state. A low temperature form, crystallized from aqueous solution at 2°, has been structurally characterized using x-ray crystallographic methods. It is monoclinic, space group $P2_1/c$, $a = 12.595(2)$, $b = 10.498(3)$, $c = 21.243(5)$Å, $\beta = 98.26(2)°$, Z = 4. The structure was refined to $R = 0.034$, for 3998 reflexions for which $I > 3\sigma(I)$. The cation has regular octahedral geometry with the Ir-Cl bond lengths equal to 2.35 and the Ir-N bond lengths equal to 2.06 Å. The water molecules, together with the chloride anion lie in hydrogen-bonded sheets at 0.5*a*.

INTRODUCTION

The degree of hydration of the complex *trans*-dichlorotetrakispyridineiridium(III) chloride, *trans*-$[Ir(py)_4Cl_2]Cl.nH_2O$, has been variously reported to be n = 5, 5.5 or 6.[1-4] We have been carrying out a series of investigations aimed at resolving these conflicting reports and those for analogous complexes of Rh(III).

We report here our finding that the hexahydrate *trans*-$(Ir(py)_4Cl_2]Cl.6H_2O$ is dimorphous. The crystal and molecular structure of the low-temperature form, obtained by crystallization from aqueous solution at 2°, has been determined, and is presented below. The dimorph crystallizing at high temperatures appears to crystallize with some disorder in its packing mode.[1]

EXPERIMENTAL

To a solution of $K_3IrCl_6.3H_2O$ (0.521g) in water (18 cm^3) was added pyridine (6.5 cm^3), then ethanol (3 cm^3). The reaction mixture was heated on the steam bath for 15 min to yield a yellow solution. The solution was concentrated to 5 cm^3 on the bath and cooled in ice, whereupon yellow leaflets of the high-temperature form crystallized. [*Anal.* Found: C, 33.2; H, 4.4; N, 7.9; H_2O, 15.0%. Calc. for $C_{20}H_{32}N_4O_6IrCl_3$: C, 33.2; H, 4.5; N, 7.8; H_2O, 15.0%]. The low-temperature form was obtained by dissolving the above product in water, and evaporating the solution at 2°. Stout yellow prisms of the low-temperature form of the complex slowly crystallized, and these were collected at the pump, washed with ice-cold water and air dried. [*Anal.* Found: C, 32.8; H, 4.4; N, 8.5; H_2O, 14.5%. Calc. for $C_{20}H_{32}N_4O_6IrCl_3$: C, 33.2; H, 4.5; N, 7.8; H_2O, 15.0%]. Water of hydration was determined thermogravimetrically using a Stanton Redcroft TG 750 thermobalance.

Crystal Data for the Low-Temperature Form

$C_{20}H_{32}N_4O_6IrCl_3$, $M_r = 723.1$, Monoclinic, $a = 12.595(2)$, $b = 10.498(3)$, $c = 21.243(5)$ Å, $\beta = 98.26(2)°$, $U = 2779.7$ Å^3, $D_m = 1.71$ g cm^{-3}, $Z = 4$, $D_c = 1.73$ g cm^{-3}. Systematic absences: *OkO* for *k* odd and *hOl* for *l* odd. Space group $P2_1/c$ (No. 14).

Accurate unit cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractor using Mo-K$_\alpha$ radiation by Dr. M.B. Hursthouse at Queen Mary College, London. Of the 5175 reflexions recorded, 3998 had $I > 3\sigma(I)$ and these were used for the structure analysis after correction for Lorenz polarization and absorption effects. The structure was solved by the heavy atom method and refined using full-matrix least-squares calculations. Unit weights were used throughout. Hydrogen atomic positions were not included and the refinement process was terminated when the change in the minimization function ($\Sigma\Delta^2$) was less than 0.5% and when the maximum shift in the parameters for the atoms was $< 0.3\sigma$. The final value for *R* based on 3998 reflexions was 0.034. All calculations were carreid out on an ICL 2980 computer using the XRAY package[5] of programmes. Scattering factors were taken from the usual source[6] with corrections being applied for anomalous dispersion. Final atomic positioned parameters are given in Table I. Lists of anisotropic temperature factors and observed and calculated structure factors have been deposited with the Editor and are available upon request.

TABLE I
Final atomic coordinates (x 10^4) with estimated standard deviations in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Ir	181.7(3)	2235.6(3)	3817.3(2)
Cl(1)	−11(2)	28(2)	3940(1)
Cl(2)	362(2)	4445(2)	3686(1)
Cl(3)	5016(2)	739(3)	1198(1)
O(1)	3980(6)	1177(8)	9732(4)
O(2)	4993(7)	1405(7)	6737(3)
O(3)	4990(6)	1546(7)	4644(3)
O(4)	3829(6)	5587(8)	9230(4)
O(5)	3968(6)	6117(7)	1425(3)
O(6)	4043(6)	6433(7)	7022(3)
N(1)	1497(5)	1949(6)	3356(3)
C(11)	2358(7)	2707(10)	3468(4)
C(12)	3261(8)	2550(10)	3155(5)
C(13)	3276(8)	1549(11)	2723(5)
C(14)	2381(8)	753(10)	2616(5)
C(15)	1502(7)	975(9)	2925(4)
N(2)	−1116(5)	2543(6)	4282(3)
C(21)	−1239(7)	1866(8)	4817(4)
C(22)	−2064(7)	2133(10)	5165(4)
C(23)	−2761(7)	3114(10)	4990(4)
C(24)	−2655(7)	3806(9)	4437(4)
C(25)	−1820(7)	3500(8)	4106(4)
N(3)	1193(5)	2294(7)	4683(3)
C(31)	1007(7)	3131(9)	5141(4)
C(32)	1572(8)	3079(10)	5750(5)
C(33)	2371(8)	2161(11)	5887(5)
C(34)	2587(7)	1328(10)	5415(5)
C(35)	1965(6)	1412(9)	4807(4)
N(4)	−847(5)	2104(7)	2967(3)
C(41)	−1763(7)	1423(9)	2940(4)
C(42)	−2457(8)	1279(10)	2373(5)
C(43)	−2188(9)	1831(11)	1821(5)
C(44)	−1240(8)	2532(10)	1853(4)
C(45)	−581(7)	2659(9)	2432(4)

Crystal Data for the High-Temperature Form

Single crystal data were collected photographically using a Weissenberg camera and Cu-K$_\alpha$ radiation. The complex is orthorhombic, a = 25.96(2), b = 15.07(3), c = 7.35(1) Å. For Z = 4, D_c = 1.67 g cm^{-3}. Powder X-ray data were collected using a Guinier camera with Cu-K$_\alpha$ radiation, and d-spacings were calibrated against α-Al$_2$O$_3$.

RESULTS AND DISCUSSION

Low Temperature Form

An ORTEP[7] drawing of the cation in the low temperature form of *trans*-[Ir(py)$_4$Cl$_2$]Cl.6H$_2$O is shown in Figure 1. Bond lengths and angles are given in Table II. The coordination sphere geometry is of a regular octahedral form in the sense that all of the appropriate angles are close to 90°. However some tetragonal distortion is apparent. The average Ir-Cl distance (2.35 Å) is 0.2 Å longer than the average Ir-N distance (2.06 Å). The pyridine ligands are arranged as to describe a four-bladed propellor about the Ir atom although of course, space group $P2_1/c$ requires that both antipodes be present in the unit cell. The pitch angles, between the pyridine rings and the plane described by Ir, N(1), N(2), N(3) and N(4) are 49.5, 51.2, 42.3 and 42.3°, respectively, related to the pyridine rings containing the above nitrogen atoms in turn. This propellor arrangement is quite analogous to others found in related compounds[8,9] containing the *trans*-[Rh(py)$_4$Cl$_2$]$^+$ and *trans*-[Ru(py)$_4$Cl$_2$]$^+$ cations.

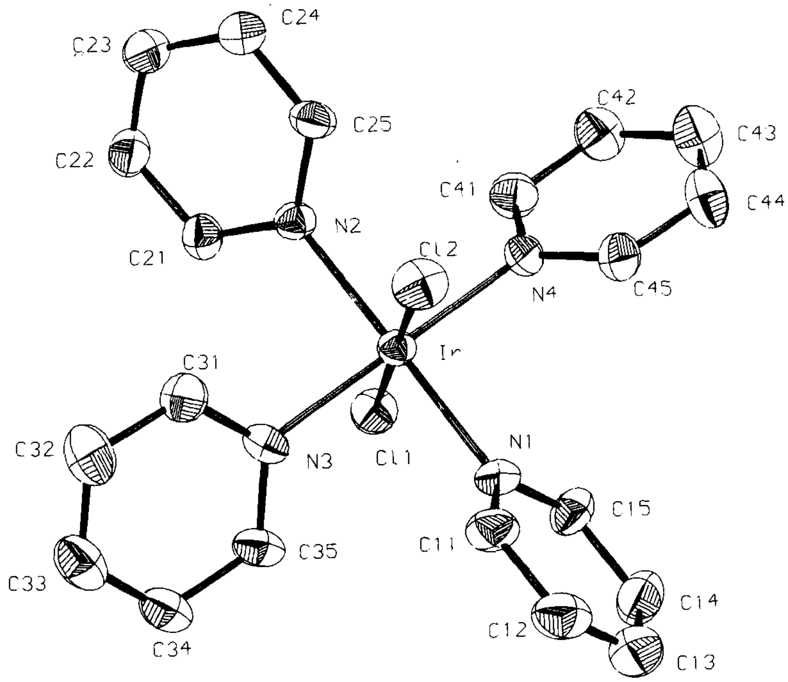

FIGURE 1 ORTEP drawing of the complex cation with thermal ellipsoids represented at 50% probability.

TABLE II
Bondlengths (Å) and angles (degrees) for the complex cation with estimated standard deviations in parentheses.

Bondlengths			
Ir-Cl(1)	2.348(1)	Ir-Cl(2)	2.351(1)
Ir-N(1)	2.064(16)	Ir-N(2)	2.053(16)
Ir-N(3)	2.082(23)	Ir-N(4)	2.070(23)
N(1)-C(11)	1.338(4)	N(3)-C(31)	1.356(3)
N(1)-C(15)	1.374(1)	N(3)-C(35)	1.342(4)
C(11)-C(12)	1.406(11)	C(31)-C(32)	1.385(13)
C(12)-C(13)	1.398(1)	C(32)-C(33)	1.394(4)
C(13)-C(14)	1.396(4)	C(33)-C(34)	1.387(4)
C(14)-C(15)	1.385(11)	C(34)-CC(35)	1.414(14)
N(2)-C(21)	1.369(3)	N(4)-C(41)	1.351(1)
N(2)-C(25)	1.356(5)	N(4)-C(45)	1.362(6)
C(21)-C(22)	1.387(11)	C(41)-C(42)	1.392(15)
C(22)-C(23)	1.369(5)	C(42)-C(43)	1.394(6)
C(23)-C(24)	1.405(2)	C(43)-C(44)	1.396(1)
C(24)-C(25)	1.384(11)	C(44)-C(45)	1.387(15)
Angles			
Cl(1)-Ir-Cl(2)	179.42(92)	Cl(2)-Ir-N(4)	91.22(1)
Cl(1)-Ir-N(1)	90.67(1)	N(1)-Ir-N(2)	179.19(30)
Cl(1)-Ir-N(2)	89.98(1)	N(3)-Ir-N(4)	177.60(28)
Cl(1)-Ir-N(3)	89.49(1)	N(1)-Ir-N(3)	89.56(1)
Cl(1)-Ir-N(4)	88.23(1)	N(1)-Ir-N(4)	91.23(1)
Cl(2)-Ir-N(1)	89.43(1)	N(2)-Ir-N(3)	89.96(2)
Cl(2)-Ir-N(2)	89.93(1)	N(2)-Ir-N(4)	89.28(2)
Cl(2)-Ir-N(3)	91.05(1)		
Ir-N(1)-C(11)	121.00(1)	Ir-N(3)-C(31)	120.40(1)
Ir-N(1)-C(15)	120.37(1)	Ir-N(3)-C(35)	119.16(1)
C(11)-N(1)-C(15)	118.63(1)	C(31)-N(3)-C(35)	120.12(1)
N(1)-C(11)-C(12)	122.45(1)	N(3)-C(31)-C(32)	121.74(1)
C(11)-C(12)-C(13)	119.12(1)	C(31)-C(32)-C(33)	118.78(1)
C(12)-C(13)-C(14)	118.04(1)	C(32)-C(33)-C(34)	119.66(1)
C(13)-C(14)-C(15)	120.27(1)	C(33)-C(34)-C(35)	118.80(1)
C(14)-C(15)-N(1)	121.45(1)	C(34)-C(35)-N(3)	120.84(1)
Ir-N(2)-C(21)	120.73(1)	Ir-N(4)-C(41)	119.75(1)
Ir-N(2)-C(25)	121.22(2)	Ir-N(4)-C(45)	120.10(2)
C(21)-N(2)-C(25)	117.76(1)	C(41)-N(4)-C(45)	120.09(1)
N(2)-C(21)-C(22)	121.37(2)	N(4)-C(41)-C(42)	121.40(1)
C(21)-C(22)-C(23)	120.48(1)	C(41)-C(42)-C(43)	119.02(1)
C(22)-C(23)-C(24)	118.83(1)	C(42)-C(43)-C(44)	119.15(2)
C(23)-C(24)-C(25)	118.37(1)	C(43)-C(44)-C(45)	119.57(1)
C(24)-C(25)-N(2)	123.12(1)	C(44-C(45)-N(4)	120.75(2)

The six water molecules, together with other symmetry-related ones are contained in a hydrogen-bonded sheet lying at approximately 0.5*a*. A view of this arrangement of the water molecule is shown in Figure 2, and the dimensions of the proposed hydrogen bonds are given in Table III. The uncoordinated chloride ions lie in holes in these sheets, as shown in the Figure. No Cl^{-}–OH_2 contacts are closer than 3 Å. The space between the sheets of water molecules and chloride ions are occupied in turn by other sheets of complex cations. No hydrogen bonds between the coordinated chloride ligands and the water molecules are observed.

High Temperature Form

The high temperature form of the complex crystallizes in the orthorhombic system with $a = 25.96(2)$, $b = 15.07(3)$, $c = 7.35(1)$ Å. These dimensions refer to a super-

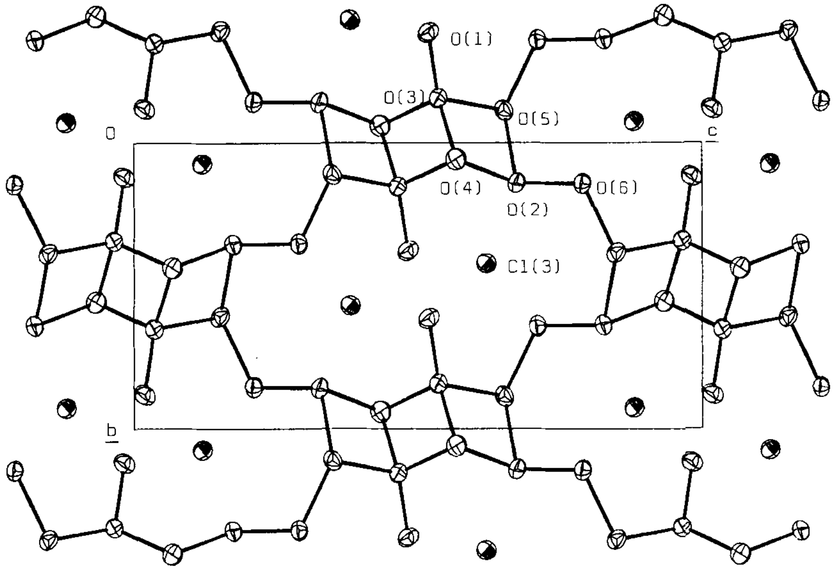

FIGURE 2 ORTEP drawing of the sheet of hydrogen bonded water molecules and uncoordinated chloride ions lying at 0.5*a*. Thermal ellipsoids are represented at 50% probability.

cell with axis doubling in the *b* direction. We have found that for this cell, in photographs of the {*hkl*} zones with *k* odd, all reflexions are comparatively weak, diffuse and streaked. It is, therefore, apparent that some kind of disordering exists in the high temperature dimorph.

Because of this disorder, a single-crystal structure determination of the compound has not been attempted. We have recorded the powder X-ray pattern for the complex for comparison, and these results are tabulated in Table IV. We have also noticed that single crystals of the high temperature form of the complex exhibit considerable decomposition in the X-ray beam. After several hours exposure, the surface of the crystals darken to a deep-orange hue.

ACKNOWLEDGEMENT

We are grateful to the S.E.R.C. crystallographic data collection service for recording the X-ray intensity data for the low temperature form of the complex.

TABLE III
Dimensions of proposed hydrogen bonds (Å) with estimated standard deviations in parentheses.

Donor	Acceptor	Acceptor at relative position			Distance
0(2)	0(4)	1-*x*,	*y*-½	½-*z*	2.835(22)
0(2)	0(6)	1-*x*,	*y*-½	½-*z*	2.739(23)
0(3)	0(4)	1-*x*,	*y*-½,	½-*z*	2.814(25)
0(5)	0(3)	1-*x*,	*y*-½,	1½-*z*	2.817(21)
0(6)	0(5)	*x*,	1½-*y*,	½+*z*	2.863(1)
0(1)	0(3)	*x*,	½-*y*,	½+*z*	2.727(2)
0(4)	0(3)	*x*,	½-*y*,	½+*z*	2.748(9)
0(2)	0(5)	*x*,	½-*y*,	½+*z*	2.978(6)

TABLE IV
Powder X-ray results (Cu-K_α radiation) for the high temperature dimorph.

d_{obs}(Å)	d_{calc}(Å)	*hkl*
12.903	12.981	200
7.499	7.505	310
6.838		
6.510	6.517	220
6.172		
5.556	5.601	301
5.155	5.156	121
4.955	4.932	130
4.495	4.495	321
4.374	4.345	330
4.114	4.147	031
4.022	3.973	430
3.842		
3.692	3.695	521
3.618	3.619	240, 611
3.533	3.535	202
3.446	3.441	212
3.369		
3.290	3.299	312
3.249	3.246	241
3.186		
2.763		
2.625		
2.574		
2.464		
2.432		
2.401		
2.245		

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