EQUILIBRIA IN COMPLEXES OF N-HETEROCYCLIC MOLECULES—XLVIII.* DIMORPHS OF FACIAL– TRICHLORO-TRIS-PYRIDINE-IRIDIUM(III)

R. D. GILLARD[†] and S. H. MITCHELL

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, Wales, U.K.

(Received 30 January 1989; accepted 26 April 1989)

Abstract—Crystalline dimorphs of fac-[Ir(py)₃Cl₃] are described and characterized. They give identical solutions and one converts irreversibly to the other.

Even in single solid phases containing individual uncharged molecules (including octahedral compounds—for example,² fac-Ir(CH₃)₃(PMe₂ Ph)₃)—there are many examples of differing geometry for such molecules at inequivalent positions within the unit cell.

The existence of distinct crystalline forms of such molecular structures seems likely to be common. Though not so commonly noticed, there are in fact plenty of cases. For example,³ [Pt(bipy)Cl₂] molecules may pack in the common yellow form and a less common red form.

We describe here a new case, that of fac-[Ir(py)₃Cl₃], ostensibly a well known compound, in the sense that many properties have been reported (such as far-IR and Raman, and its electronic spectrum). However, all such reports seem (so far as we can see) to relate to measurements on samples actually provided by Delepine or his associates, so we describe our preparations in detail.

Delepine first synthesized⁴ fac- and mer-[Ir(py)₃Cl₃], both via extensive heating of chloroor pyridinechloro-precursors (IrCl₃·3H₂O, K₃IrCl₆, *cis*- or *trans*-[Ir(py)₂Cl₄]⁻ and others) with pyridine. Some picoline (i.e. methylpyridine) analogues have also been described, by his students : fac- and⁵ mer-[Ir(3-pic)₃Cl₃], and⁶ [Ir(2-pic)₃Cl₃] (probably the mer-isomer).

The *fac*-isomer was isolated here as a by-product in the synthesis of the *trans*- $[Ir(py)_4Cl_2]^+$ cation: we recently reported⁷ the structure of one dimorph of the chloride hexahydrate of this. A more recent report⁸ of the analogous dibromorhodium compound is of an isostructural lattice.

EXPERIMENTAL

$fac-[Ir(py)_{3}Cl_{3}]$ (Form A)

 $K_3IrCl_6 \cdot 3H_2O$ (0.521 g) dissolved in water (18 cm³) and heated (steam bath) was treated with a mixture of pyridine (6.5 cm³) and ethanol (3 cm³). Reaction to a yellow solution was complete after ~ 15 min; the solution was evaporated to ~ 20 cm³ (to remove ethanol and some pyridine), and allowed to cool. Yellow crystals (Form A) slowly formed; these were collected. The filtrate was concentrated to ~ 10 cm³ giving a second crop. Contaminating *trans*-[Ir(py)₄Cl₂]Cl · *n*H₂O in this second crop was extracted with hot water. Total yield of A = 0.065 g (13.5%). Other similar preparations, and one using IrCl₃ · 3H₂O gave yields in the range 12–18%. With propan-2-ol (instead of ethanol) as catalyst/solvent the yield improved to 29%.

Form **B**

 K_3 IrCl₆· 3H₂O (0.104 g) dissolved in water (1.5 cm³), pyridine (0.1 cm³), propan-2-ol (0.5 cm³) and chloroform (2.0 cm³) was set to reflux very slowly in a 5 cm³ foil-covered flask. After 8 h, yellow crystals had formed in the chloroform layer. The reflux was continued overnight, then the yellow crystals were removed by filtration and washed with chloroform. Yield = 0.026 g (27%).

Properties

Form **B** differs from Form **A** in the vibrational spectrum, X-ray diffraction and thermogravimetric analysis, although both show the same solubility properties: they dissolve (giving

^{*} For part XLIX, see ref. 1.

[†]Author to whom correspondence should be addressed.

identical solutions) only very slowly in cold solvents: CH_2Cl_2 , $CHCl_3$, pyridine, H_3CCN and 50:50 H_2O -pyridine; although both are insoluble in water. Both are slightly soluble in propan-2-one (acetone) and hardly soluble (if at all) in CS_2 .

Form A was dissolved in 50% v/v aqueous pyridine, passed through an anion exchange resin (Sephadex A25) and recovered by steam distilling pyridine (i.e. evaporating the solution to remove pyridine vapour but keeping the volume constant by adding water): 95% of the original mass of complex was recovered as long needles entirely of Form **B**.

Form A can be recrystallized from 20-50% v/v aqueous pyridine with varying degrees of success (0-100%). However, in no instance was it possible to obtain Form A from Form **B**.

Both forms were neutral, since (dissolved in 50% v/v aqueous pyridine) they pass through anion and

cation (Sephadex A25 and C25, respectively) exchange resins; if the solutions are allowed to age, then the *anion* exchange resin retains some complex, suggesting slow base hydrolysis to $[Ir(py)_2Cl_3 (OH)]^-$. Analyses are given in Table 1.

The solution electronic spectra from both forms indicate that the basic structural unit is the same (Table 2): the band positions of Jorgensen are in good agreement with ours; the figures¹⁰ of Rio and Lareze for absorption wavelengths of the *fac*-isomer differ slightly; they included extinction coefficients.

Vibrational spectra are presented in Table 3, and in Figs 1 and 2. IR spectra were measured using Perkin–Elmer 557 and Pye Unicam SP3-200 spectrometers (calibrated with polystyrene) on NaCl or CsI plates for mulls in Nujol or fluorolube.

X-ray diffraction: there is a small difference

	Form A	Form B	Calc. for [Ir(C5H5N)3Cl3]
C (%)	33.8	32.7	33.6
H (%)	3.1	3.1	2.8
N(%)	8.4	8.6	7.8
Cl (%)	20.0	21.9	19.9
Ir (%)	36.1	35.9	35.9
Total	101.4	102.2	
$T(^{\circ}C)^{a}$	275	280	
Loss (% mass)	3.7	3.4	3.7 (¹ / ₄ py)
T	340	330	
Loss	24.5	25.3	25.8 (1 ³ ₄ py)
Т	630	460 and 610	
Loss	36.6	35.1	34.6 (py + 3Cl)

Table 1. Analytical results for solid fac-[Ir(py)₂Cl₂]

^a Thermogravimetric analysis with a Stanton Redcroft TG750 thermobalance in nitrogen flowing at 25 cm³ min⁻¹: heating rate was 2° C min⁻¹.

	λ (nm)	$\epsilon \pmod{dm^{-2}} \times 10^{-2}$	λ	з	λ	Е	λ	3	λ	3	Reference
Form A	325	822	275.5	1248	265.5	1200					This work
Form B	325	825	276	1248	266.5	1200					This work
fac	330	600	282	920	267	970					10
-	326.5		276		265						9(a)
fac	324										9(b)
mer	319	~ 547	274		267	1319	262		250		This work
	319ª	1600			265						9(a)
mer	314										a

Table 2. Electronic spectra of the various forms of monomeric [Ir(py)₃Cl₃]

^a Reference 9(a) also describes a weak singlet-triplet band at 432 nm.

	fa	c-A	fa	ıc-B		mer-
v	IR	R ^a	IR	\mathbf{R}^{a}	IR	R ^a
4	1600m		1607m		1611m	
5	1482m 1471m		1485m 1473m		1486m 1478m	
14	1450s		1452m 1447s		1452s	
15	1338w		1 340 w		1347w	
16	1236m		1236vw		1237m	
6	1217m 1210s		1220m 1211s		1215s	
17			1153m		1157w	
7	1072w 1064m		1069m ^b		1076sh 1067m	
8	1052w				1050w	
9		1026vs		1024vs		1030vs 1021vs
	1015m 983w 974w		1015m 985w 973w		1016w 982w 970w	
23 or 24	953w 944w		848w		953w	
	878w		871w		871w 857w 785s	
25	771s 763s		768s ^b		767s 760s	
26	700s 696s		703s 692w		699s 693s	
10	656w 653w 644m		647w		648w	
27	465w		471w		481w 477w 471w	
c	325m	328m,sh 322s	329m 324sh	328s 323m	331s	
	316s 313w,sh 302sh	318m,sh	313m 304sh	317m 312w,sh	320m 310sh 307sh	318s 310s
	270m 265sh	274w	270m	273w	273w 263m 256sh	276w 266w
		242w 225w,br		241w 223w,br	246sh	232w,br

Table 3. IR and Raman (R) spectra for solid monomeric [Ir(py)₃Cl₃]

"Selected bands only (see text).

^b Bands with structure.

Bands arising from Mpy and M-Cl vibrations.



Fig. 1. IR spectra of ligand modes (600–950 cm⁻¹) in the forms of *fac*-[Ir(py)₃Cl₃].



Fig. 2. Patterns of C—H stretching modes in the IR spectra of the forms of *fac*-[Ir(py)₃Cl₃].



Fig. 3. X-ray diffraction patterns for the powdered dimorphic forms of *fac*-[Ir(py)₃Cl₃].

between the two powder patterns, illustrated in Fig. 3. The diffraction patterns have not been previously reported, nor are any crystallographic details yet known: crystal morphology is so far poor.

RESULTS AND DISCUSSION

The distinguishing differences between the spectra of the two *fac* forms are : a slight difference in a number of band positions, especially M—L/M—Cl bands; the change in activity of two bands (ligand modes): v_{16} has medium intensity in Form **A**, but is almost absent in Form **B**, and vice versa for v_{17} ; a distinctive difference in the splitting of ligand modes v_{10} , v_{25} and v_{26} (Fig. 1) and a different structure in the C—H stretching region (Fig. 2: A at *3144, 3116, 3084, 3071, 3048, 3032 and 3009; **B** at 3115, 3083, 3074, *3058, *3045, 3023 and 2001 cm⁻¹. The bands marked * have no counterpart in the spectrum of the other dimorph).

There are two published studies^{11,12} of the IR spectra of *fac*-[Ir(py)₃Cl₃], both on samples supplied by Delepine. The spectrum of Clark and Williams is limited to the far-IR, and agrees closely with the present Form A. Harbelin *et al.* record more of the spectrum (4000–1000 cm⁻¹). While their spectrum agrees better with that of Form A, the detail is poor : it appears to be a hybrid, containing some peaks of Form A and others of Form B. It probably represents chiefly Form A since the authors describe v_{16} as a prominent band (it is almost undetectable in our Form B).

The splitting of the ligand modes in the *fac* form **B** is most similar to that reported for *fac*-[$Rh(py)_3Cl_3$].

The IR spectra and corresponding Raman spectra (Table 3) are very similar in the M-L/M-Cl stretching region.

Isolated molecules of $fac-[Ir(py)_3Cl_3]$ have a three-fold axis of symmetry only if the pyridine ligands are equivalent, i.e. (i) freely rotating with a period less than that of the detection method, (ii) fixed in an orientation where all three planes make equal angles with the axis which passes through the iridium ion and the centre of the triangle defined by the three chloride ligands or (iii) all three rotating in phase through successive conformations like those in (ii). Evidently, the molecules actually possess no such C_3 symmetry in either Form A or **B**, since some pyridine ring vibrations are no longer equivalent and splitting occurs. This probably arises from the site symmetry(ies) of the complex molecules. While this inequivalence is much less pronounced for Form **B**, there is fine structure on many bands.

The earlier suggestion¹³ that the Raman vibration v_9 is insensitive to environment but sen-

sitive to the configuration of the complex molecules seems to be borne out, in that the *mer*-isomer shows two bands of relative intensity, approximately 1:2, corresponding to *cis*- and *trans*-ligands, respectively, while the *fac*-isomer gives only a single band at 1025 cm⁻¹ (Table 3).

Form A seems metastable with respect to **B**, at least in 50% v/v aqueous pyridine as solvent, so may be viewed as a metastable intermediate in the sense of Ostwald's law. The kinetic conditions necessary to produce Form A depend subtly on the original reaction conditions (e.g. temperature or concentration of aqueous pyridine) or on the presence of a trace of some other complex, e.g. *trans*- $[Ir(py)_4Cl_2]^+$, which determines the form by its presence when nucleation begins, or by being incorporated in trace amounts into the crystal lattice.

The present example again demonstrates the frequency of occurrence of various distinct solid forms of individual coordination compounds, and the care needed to identify the particular phase in hand.

REFERENCES

- 1. J. A. Arce Sagues, R. D. Gillard and P. A. Williams, Transition Met. Chem. 1989, 14, 110.
- E. G. Lundquist, K. Folting, J. C. Huffman and K. G. Caulton, *Polyhedron* 1988, 7, 2171.

- 3. E. Bielli, P. M. Gidney, R. D. Gillard and B. T. Heaton, J. Chem. Soc., Dalton Trans. 1974, 2133.
- 4. M. Delepine, Ann. Chim. 1923, 9, 145: a later detailed study (H.-H. Schmidtke and A. Wolf, Inorg. Chim. Acta 1978, 29, 11) of the luminescence spectra of mixed complex compounds containing chloride and pyridine as ligands on iridium(III) was concerned only with ionic species, including only those isomers of composition [Ir(py)₃Cl₃] which were cis- or trans-[Ir(py)₄Cl₂]⁺ salts of cis- or trans-[Ir(py)₂Cl₄]⁻ ions.
- 5. F. Lareze, Compt. Rend. 1964, 259, 3789.
- M. Guillot, Compt. Rend. 1962, 182, 1090; M. Guillot, Bull. Soc. Chim. Fr. 1962, 39, 852.
- R. D. Gillard, S. H. Mitchell, P. A. Williams and R. S. Vagg, J. Coord. Chem. 1984, 13, 325.
- M. M. Muir, G. M. Gomez, J. A. Muir and S. Sanchez, *Acta Cryst.* 1987, C43, 839.
- C. K. Jorgensen, Acta Chem. Scand. 1957, 11, 151;
 C. K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes. p. 191. Pergamon Press, Oxford (1962).
- F. Lareze and G. Rio, Bull. Soc. Chim. Fr. 1975, 2393.
- R. J. H. Clark and C. S. Williams, J. Chem. Soc. 1965, 350.
- 12. F. Herbelin, J. D. Herbelin, J. P. Mathieu and H. Poulet, Spectrochim. Acta 1966, 22, 1515.
- A. W. Addison and R. D. Gillard, J. Chem. Soc., Dalton Trans. 1973, 2002.