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EQUILIBRIA IN COMPLEXES OF N-HETEROCYCLIC COMPOUNDS—LI.* SYNERGIC SOLUBILITY AND X-RAY CRYSTAL STRUCTURE ANALYSIS OF *MER*-CHLORO-OXALATO-TRIS-PYRIDINE-IRIDIUM(III), $[IrCl(py)_3(C_2O_4)]$

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Abstract—The title compound, *mer*-$[IrCl(py)_3(C_2O_4)]$, has been made by the reaction of the known *trans*-dichloro-tetrapyridine-iridium(III) chloride with ethanedioate ion(oxalate) in aqueous ethanol. A non-electrolyte, it resembles its rhodium eutrope in showing extraordinary synergic solubility in water : pyridine. An X-ray structure determination has confirmed the *mer* geometry.

Complex ions of rhodium (and to an extent iridium) with pyridine and with chelating dicarboxylates such as ethane-1,2-dioate (oxalate) have been well studied. A few mixed species, such as $[RhCl(py)_3(C_2O_4)]$ (**A**) are known. The unusual synergic solubility of this compound had been known for many years and we are trying to understand its molecular origin. We therefore synthesized the new iridium(III) mixed compound *mer*-$[IrCl(py)_3(C_2O_4)]$ (**B**) and report here some of its properties, including its structure. The known bromo-rhodium compound $[RhBr(py)_3(C_2O_4)]$ (**C**) is also further described with a convenient synthesis.

EXPERIMENTAL

Preparation of complexes

Mer-*Chlorotrispyridineoxalatoiridium*(*III*) (**B**). *Trans*-$[IrCl_2(py)_4]Cl \cdot 6H_2O$[2] (0.444 g, 0.614 mmol) and potassium oxalate (0.113 g, 0.614 mmol) were refluxed for 7 days in 50% ethanol solution (100 cm^3). Yellow needles (0.08 g) formed on cooling: these were collected by filtration. The filtrate was treated with an excess of ethanol to precipitate unreacted potassium oxalate. After filtration, the volume was reduced on a rotary evaporator when a further crop of crystals of the desired product was obtained (0.116 g). Yield: 58%. Found: C, 36.8; H, 2.8; N, 7.5. Calc. for $C_{17}ClH_{15}N_3O_4Ir$: C, 36.9; H, 2.7; N, 7.6%. IR: 1700m, 1670m, 1610m, 1245w, 1160w, 1072m-w, 1020w, 880w, 805w, 762m-w, 700s, 655w, 560w, 485w, 465w, 365w, 345s, 310w, 290w, 265m, 235w cm^{-1}.

A measurement of conductance (*ca* 10^{-3} M in aqueous pyridine) gave $\Lambda_m = 6.82$ S $mol^{-1}dm^3$. Complex **B** dissolves in boiling concentrated hydrochloric acid and on cooling, the solution yields the known complex $[IrCl_3(py)_3]$ as its *mer* isomer,[3] identified by its electronic spectrum in chloroform. Three bands were observed in the UV region at 320–317 shoulder, 266 and 238 nm. A visible absorption was also observed at 421–436 nm. These are in accordance with the electronic spectrum of the *mer*-$[IrCl_3(py)_3]$[4] isomer.

Mer-*bromotrispyridineoxalatorhodium*(*III*) (**C**). *Trans*-$[RhBr_2(py)_4]Br$ was prepared by boiling *trans*-$[RhCl_2(py)_4]\cdot 6H_2O$ with an excess of aqueous potassium bromide. After approximately 2 h the desired orange solid formed. This was collected by filtration, washed with ice-cold water and recrystallized from hot water; **C** was synthesized from it, ***mutatis mutandis***, as with **A**.[2] Found: C, 40.3; H, 3.0; N, 8.3. Calc. for $C_{17}BrH_{15}N_3O_4Rh$: C, 40.18; H, 2.98: N, 8.27%. IR: 1703m, 1668m,

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*See ref. 1.

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1605m, 1242w, 1212m, 1153w, 1068m, 1015w, 881w, 796w, 775m, 761m, 708s, 697s, 686m, 651s, 553s, 480m, 470s, 412m, 360s, 350s, 275m, 251w cm^{-1}.

Electronic spectra were measured using a Kontron–Uvikon 930 UV–vis spectrophotometer. IR spectra were measured using a Perkin–Elmer 577 IR grating spectrophotometer, as Nujol mulls on caesium iodide plates; wave numbers are quoted to $\pm 2\ cm^{-1}$.

Crystallography

Data for compound **B** were collected on a FAST TV Area Detector diffractometer following previously described procedures.[5] The structure was solved and developed via the heavy-atom method and refined by full-matrix least-squares techniques. A correction for absorption was made using DIFABS.[6] All hydrogens were placed in idealized positions. Crystal data and details of the structure refinement are given in Table 1. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited as supplementary material with the Editor. Atomic coordinates have also been deposited at the Cambridge Crystallographic Data Centre.

Table 1. Crystal data and details of structure refinement for *mer*-$[IrCl(py)_3(C_2O_4)]$

Formula	$C_{17}H_{15}N_3O_4ClIr$
Mol. wt	552.997
Crystal system	Orthorhombic
a (Å)	10.016(1)
b (Å)	12.059(3)
c (Å)	14.950(3)
V (Å^3)	1805.8(6)
θ range for cell (°)	1.5–25
Space group	$P2_12_12_1$
Z	4
D_c (g cm^{-3})	2.0341
$F(000)$	1056
μ (cm^{-1})	75.410
T (K)	298
θ range for data (°)	2.170–29.610
h_{min}, h_{max}	−12, 13
k_{min}, k_{max}	−15, 10
l_{min}, l_{max}	−14, 19
Total data measured	7717
Total unique	3677
R_{merge}	0.045
Total observed	3359
Significance test	$F_0 > 3\sigma F_0$
Absorption correction factors: min, max	0.884, 1.198
No. of parameters	250
ρ_{min}–ρ_{max} (e Å^{-3})	−1.53, 1.88
$(\Delta/\sigma)_{max}$	0.001
Weighting scheme	Unit weights
R	0.0420
ωR	0.0420

RESULTS AND DISCUSSION

The three compounds, $[MX(py)_3(C_2O_4)]$ (**A**: M = Rh, X = Cl; **B**: M = Ir, X = Cl; **C**: M = Rh, X = Br) show synergic solubility in aqueous pyridine, as depicted in Fig. 1. The property was discovered[7] for the chloro-rhodium species and Reichardt[8] singled out this case in his discussion of solvent effects in organic systems. Chloro-oxalato-tris-pyridine-iridium(III) forms only slowly, even with ethanol present. Such a substitution at rhodium(III) centres is often strongly catalysed by the 2e-reductant ethanol, but that is not obvious here. Powder patterns show that compounds **A** and **B** are clearly isostructural (powder data have been deposited). The crystalline form which we have is isostructural with the well-known rhodium(III) eutrope. Our structure, therefore, confirms both that the rhodium compound is indeed the *mer* isomer and that its reaction [eq. (1)] with hydrochloric acid is, like many such acid displacements of oxalate in acid, stereoretentive: the product with an absorption at 428 nm was already known from spectroscopy to be the *mer* isomer.

$$mer\text{-}[RhCl(py)_3(C_2O_4)] + 2HCl \rightarrow mer\text{-}[RhCl_3(py)_3] + H_2C_2O_4 \quad (1)$$

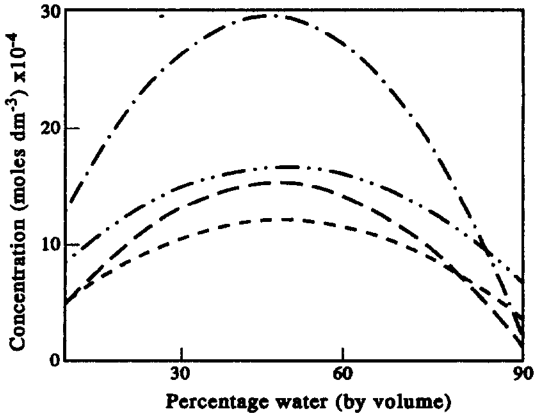

Fig. 1. Solubilities (given as concentrations of saturated solutions at 30° C) in water/pyridine of *mer*-$[MX(py)_3(C_2O_4)]$: ----, A(M = Rh, X = Cl^-); -------, B(M = Ir, X = Cl^-); ------, C(M = Rh, X = Br^-). The curve ---- is that reported[7] for A, *mer*-$[RhCl(py)_3(C_2O_4)]$, measured at 15° C.

Table 2. Selected bond lengths (Å) and angles (°) for **B**

Ir—Cl	2.341(6)	Ir—O(1)	2.040(11)
Ir—O(2)	2.033(11)	Ir—N(11)	2.045(14)
Ir—N(21)	2.045(13)	Ir—N(31)	2.061(11)
O(1)—Ir—Cl	174.0(3)	O(1)—Ir—O(2)	83.0(5)
O(2)—Ir—Cl	91.1(4)	N(11)—Ir—Cl	89.9(5)
N(11)—Ir—O(2)	87.6(5)	N(11)—Ir—O(1)	90.0(5)
N(21)—Ir—Cl	91.3(4)	N(21)—Ir—O(1)	88.5(5)
N(21)—Ir—O(2)	88.5(5)	N(21)—Ir—N(11)	176.0(5)
N(31)—Ir—Cl	92.8(4)	N(31)—Ir—O(1)	93.2(5)
N(31)—Ir—O(2)	176.0(5)	N(31)—Ir—N(11)	93.4(6)
N(31)—Ir—N(21)	90.4(5)		

We have also shown this stereoretention for eq. (2):

$$mer\text{-}[IrCl(py)_3(C_2O_4)] + 2HCl \rightarrow mer\text{-}[IrCl_3(py)_3] + H_2C_2O_4 \quad (2)$$

Our crystals of the product from eq. (1) indeed have the well-known spectroscopic properties of *mer*-$[RhCl_3(py)_3]$ (e.g. *d–d* absorption at 428 nm). They have the same space group and unit cell as those studied in crystallographic detail elsewhere.[9] The available[9] crystal and molecular structure of *mer*-$[RhCl_3(py)_3]$, determined for a compound of unknown spectroscopic properties and provenance, is that of the isomer absorbing at 428 nm.

The vibrational spectra of **A** and **B** (as solids) are also very similar. The IR spectrum of **C**, the bromorhodium member, is closely similar, but its crystal lattice is entirely different (data deposited). Despite this (and it may be that a second dimorph crystallizes in this case alone), the solubility properties of all three are alike. The vibrational spectra of these $[MX(py)_3(C_2O_4)]$ complexes are superimposable to 360 cm^{-1}: the vibrations involving metal ions may be compared in **A**(Rh—Cl) and **B**(Ir—Cl), suggesting υ(Rh—Cl) at 318 ± 3 and υ(Ir—Cl) at 290 cm^{-1}. These frequencies are in line with others from the literature.

We interpret the synergism in solubility as representing the specific solvation of the polar meridian (P) by water and the non-polar (NP) meridian by pyridine. Describing the solvation enthalpies $\Sigma\Delta H$ as ΔH_P or ΔH_{NP}, in any solvent mixture we have:

$$\Sigma\Delta H = \Delta H_P + \Delta H_{NP}.$$

Using suffixes W for water and H for heterocycle, we see that:

$$\Delta H_{P(W)} \gg \Delta H_{P(H)}; \quad \Delta H_{NP(H)} \gg \Delta H_{NP(W)}.$$

Denoting the lattice enthalpy by U, dissolution occurs when

$$\Sigma\Delta H > U.$$

We believe that:

$$U > \Sigma\Delta H_W[= \Delta H_{P(W)} + \Delta H_{NP(W)}]$$
$$> \Sigma\Delta H_H[= \Delta H_{P(H)} + \Delta H_{NP(H)}]$$
$$\text{but} < \Sigma\Delta H_M[= \Delta H_{P(W)} + \Delta H_{NP(H)}],$$

where M refers to the mixture.

Our detailed thermodynamic and spectroscopic work on the molecular bases for these variations of ΔH will be published elsewhere.

Figure 2 shows the molecular structure of **B**. Table 2 contains selected bond lengths and angles. The measured iridium–chloride bond length of 2.341(6) Å compares well with those measured for $K_3[IrCl_6]$[10] (2.36 Å) and *trans*-$[IrCl_2(py)_4]Cl \cdot 6H_2O$(2.35 Å). The measured iridium–oxygen bond lengths are slightly longer in *mer*-$[IrCl(py)_3(C_2O_4)]$, at 2.033 and 2.040 Å, than in $K_3[Ir(ox)_3] \cdot 3H_2O$[11] (1.96 Å). In contrast, one of the Ir—N bond lengths in **B** (2.06 Å) is identical to one of the lengths in *trans*-$[IrCl_2(py)_4]Cl \cdot 6H_2O$. The

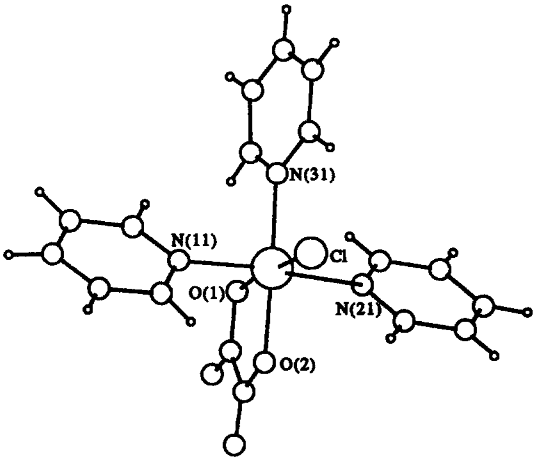

Fig. 2. The molecular structure of **B**.

Table 3. Pyridine ring orientations

	B	E	F	G	H
a*	138.36	130.08	42.48	49.00	65.09
b	79.68	136.20	110.10	43.47	48.58
c*	46.66	125.30	43.31	52.26	119.38

Values given are the dihedral angles between the pyridine ring planes and the meridional py_3MX plane. a* and c* are the outer rings and are interchangeable due to the "chemical" symmetry of the molecule. Similar values correspond to a propeller arrangement, approximate supplementary values correspond to different orientations relative to the meridianal plane.

B = This work; E = *mer*-$[CrCl_3(py)_3]$;[12] F = *mer*-$[InBr_3(py)_3]$;[13] G = *mer*-$[RhCl_3(py)_3]$;[9] H = *mer*-$[TlBr_3(py)_3]$.[14]

other Ir—N bond lengths [2.045(14) Å] are both shorter than those in *trans*-$[IrCl_2(py)_4]Cl \cdot 6H_2O$. A particular feature of this and related structures is the orientation of the pyridine rings with respect to the plane through the iridium and the three nitrogens. A comparison of data for these dihedral angles is given in Table 3.

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