

# Synthesis, structure and electrochemical properties of tris-picolinate complexes of rhodium and iridium

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## Abstract

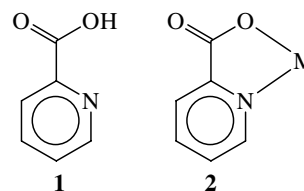
Reaction of picolinic acid (Hpic) with rhodium trichloride or iridium trichloride affords tris-picolinate complexes of the type  $[M(\text{pic})_3]$  ( $M = \text{Rh}, \text{Ir}$ ). The crystal structures of both complexes have been determined by X-ray diffraction. In both complexes, the picolinate ligands are coordinated to the metal center as bidentate N,O-donors forming five-membered chelate rings. There is one molecule of water of crystallization per molecule of each  $[M(\text{pic})_3]$  complex. The water molecule is hydrogen bonded to the carboxylate fragments of two adjacent  $[M(\text{pic})_3]$  molecules and thus acts as a bridge between the individual complex molecules. The complexes are diamagnetic (low-spin  $d^6$ ,  $S = 0$ ) and show intense MLCT transitions in the visible region. Cyclic voltammetry on the  $[M(\text{pic})_3]$  complexes shows a M(III)–M(IV) oxidation near 1.0 V versus SCE and a ligand-centered reductive response near  $-1.0$  V versus SCE. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Rhodium and iridium tris-picolinate complexes; Crystal structures; Electronic spectra; Electrochemical properties

## 1. Introduction

The chemistry of rhodium and iridium has been receiving considerable current attention [1], largely because of the interesting properties exhibited by the complexes of these two metals. As the properties of the complexes are dictated primarily by the coordination environment around the metal center, complexation of these metals by ligands of selected types has been of significant importance, and the present work has originated from our interest in this area [2]. For the complexation of rhodium and iridium, picolinic acid (**1**) has been chosen as the ligand in the present study. Picolinic acid (abbreviated as Hpic, where H stands for the dissociable carboxylic proton) is known to bind to metal ions as a bidentate N,O-donor forming a stable five-membered

chelate ring (**2**) [3]. It is interesting to note that the two donor sites of the picolinate ligand are of significantly different nature.



The pyridine nitrogen is a soft donor and a recognized stabilizer of the lower oxidation states of transition metals, whereas the carboxylate oxygen is a hard donor and is known to stabilize transition metals in their higher oxidation states. Hence, coordination of rhodium and iridium by the picolinate ligand may be expected to have an interesting effect on the redox properties of the complexes. The main objective of the present work has been to synthesize the tris-picolinate complexes of rhodium

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and iridium, and to study their physicochemical properties. It may be mentioned here that though tris-picolinate complexes of many transition metals have been studied well [4], those of rhodium and iridium appear to have remained unexplored. It may also be mentioned here that the tris-picolinate complexes of several transition metals have important applications in the biological field [4c,4e–4g]. Reaction of picolinic acid with the trichlorides of rhodium and iridium has afforded the targeted  $[M(pic)_3]$  ( $M = Rh, Ir$ ) complexes and the chemistry of these two complexes is reported in this paper with special reference to their synthesis, structure and, spectroscopic and electrochemical properties.

## 2. Experimental

### 2.1. Materials and measurements

Rhodium trichloride and iridium trichloride were obtained from Arora Matthey, Kolkata, India. Picolinic acid was purchased from Merck, India. All other chemicals and solvents were reagent grade commercial materials and were used as received. Purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [5]. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample

magnetometer fitted with a Walker Scientific L75FBAL magnet.  $^1H$  NMR spectra were obtained on a Bruker AV300 NMR spectrometer using TMS as the internal standard. Thermogravimetric analyses were carried out on a Shimadzu DT-30 thermal analyzer. IR spectra were obtained on a Perkin–Elmer spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were made using a CH Instruments Model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

### 2.2. Synthesis

#### 2.2.1. $[Rh(pic)_3] \cdot H_2O$

Picolinic acid (0.4 g, 3.25 mmol) was dissolved in ethanol (40 ml) and to it was added triethylamine (0.1 g, 0.99 mmol) followed by  $RhCl_3 \cdot 3H_2O$  (0.1 g, 0.38 mmol). The solution was heated at reflux for 4 h to produce a bright yellow solution. Upon cooling the solution to room temperature, a white precipitate separated, which was removed by filtration. Upon partial evaporation of the filtrate, yellow crystals of  $[Rh(pic)_3] \cdot H_2O$  separated,

Table 1  
Selected crystallographic data for  $[Rh(pic)_3] \cdot H_2O$  and  $[Ir(pic)_3] \cdot H_2O$

Compound	$[Rh(pic)_3] \cdot H_2O$	$[Ir(pic)_3] \cdot H_2O$
Empirical formula	$C_{18}H_{14}N_3O_7Rh$	$C_{18}H_{14}N_3O_7Ir$
Formula weight	487.23	576.52
$T$ (K)	295(2)	295(2)
$\lambda$ (Mo $K\alpha$ ) (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
<i>Unit cell dimensions</i>		
$a$ (Å)	30.3514(11)	30.4463(13)
$b$ (Å)	8.5072(3)	8.4725(4)
$c$ (Å)	13.9537(5)	13.9589(6)
$\beta$ (°)	95.311(1)	95.0621(11)
$V$ (Å <sup>3</sup> )	3587.5(2)	3586.7(3)
$Z$	8	8
$D_{calc}$ (Mg m <sup>-3</sup> )	1.804	2.135
Absorption coefficient (mm <sup>-1</sup> )	1.002	7.495
$F(000)$	1952	2208
Crystal size (mm)	0.20 × 0.10 × 0.03	0.30 × 0.14 × 0.03
$\theta$ Range for data collection (°)	1.35–27.50	1.34–27.50
Index ranges	$-39 \leq h \leq 39, -11 \leq k \leq 11, -18 \leq l \leq 18$	$-39 \leq h \leq 39, -11 \leq k \leq 10, -18 \leq l \leq 16$
Number of reflections collected ( $R_{int}$ )	20525 (0.0583)	17398 (0.0442)
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0544, wR_2 = 0.1138$	$R_1 = 0.0320, wR_2 = 0.0772$
Number of parameters refined	270	262
Maximum and minimum transmission	0.9706 and 0.8248	0.8064 and 0.2120
Goodness-of-fit on $F^2$	1.289	1.174
Largest difference peak and hole (e Å <sup>-3</sup> )	0.887 and -0.984	1.480 and -0.789

which were collected by filtration, washed with water and dried in vacuo over  $P_4O_{10}$ . (~70% yield). *Anal. Calc.* for  $C_{18}H_{14}N_3O_7Rh$ : C, 44.35; H, 2.87; N, 8.62. Found: C, 45.01; H, 2.83; N, 8.64%. FT-IR (KBr phase),  $cm^{-1}$ : 3522m, 1676s, 1604s, 1472m, 1329s, 1285m, 1149m, 1098w, 1057m, 862m, 766m, 716m, 689m, 475m (s, strong; m, medium; w, weak).

### 2.2.2. $[Ir(pic)_3] \cdot H_2O$

Sodium acetate (1 g, 12.2 mmol) and  $IrCl_3 \cdot 3H_2O$  (0.1 g, 0.28 mmol) were taken in glacial acetic acid (40 ml). The solution was warmed and picolinic acid (0.4 g, 3.25 mmol) was added to it. The solution was heated at reflux for 4 h to produce a bright yellow solution. Upon partial evaporation of this solution, yellow crystals of  $[Ir(pic)_3] \cdot H_2O$  separated, which were collected by filtration, washed with water and dried in vacuo over  $P_4O_{10}$  (~75% yield). *Anal. Calc.* for  $C_{18}H_{14}N_3O_7Ir$ : C, 37.50; H, 2.43; N, 7.29; Found: C, 37.83; H, 2.37; N, 7.28%. FT-IR (KBr phase),  $cm^{-1}$ : 3529m, 1684s, 1608s, 1472m, 1326s, 1282m, 1148m, 1099w, 1059m, 864m, 770m, 718m, 688m, 471m (s, strong; m, medium; w, weak).

### 2.3. X-ray crystallography

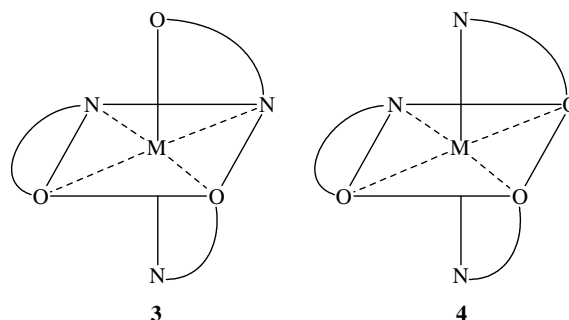
Single crystals of both  $[Rh(pic)_3] \cdot H_2O$  and  $[Ir(pic)_3] \cdot H_2O$  were obtained directly from the synthetic reactions. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by  $\omega$  scans. X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [6,7]. The structures were solved by direct methods.

## 3. Results and discussion

### 3.1. Syntheses and crystal structures

Reaction of picolinic acid with rhodium trichloride proceeds smoothly in refluxing ethanol in the presence of triethylamine to afford the targeted tris-picolinate rhodium(III) complex,  $[Rh(pic)_3]$ , in a decent yield. The analogous iridium complex,  $[Ir(pic)_3]$ , has been obtained in a similar yield from the reaction of picolinic acid with iridium trichloride using slightly different experimental conditions. Such differences in experimental procedure is often required for the synthesis of analogous complexes of rhodium and iridium [8]. An excess of picolinic acid has been used in both synthetic reactions to optimize the yield of the  $[M(pic)_3]$  ( $M = Rh, Ir$ ) complexes. The observed elemental (C, H, N) analytical data of the two complexes agree well with their com-

positions. As the picolinate anion is an unsymmetrical bidentate ligand, the tris-picolinate complexes of rhodium and iridium may exist, in principle, in two different isomeric forms, viz. facial (3) and meridional (4). Chromatographic experiments have shown that these  $[M(pic)_3]$  complexes are isomerically pure.



To find out the stereochemistry of these complexes, structure of both the complexes has been determined by X-ray crystallography. Both the structures have been found to be very similar. The structure of the  $[Rh(pic)_3]$  complex is shown in Fig. 1 and structure of the  $[Ir(pic)_3]$  complex is deposited as Fig. S1. Some selected bond parameters are listed in Table 2. In each complex the picolinate ligands are coordinated to the metal center in the usual fashion (2), with a bite angle of  $\sim 81^\circ$ . In both complexes, the central metal ion is thus sitting in an  $N_3O_3$  coordination sphere, which is distorted from an ideal octahedral geometry as reflected in all the bond parameters around the metal centers. The relative

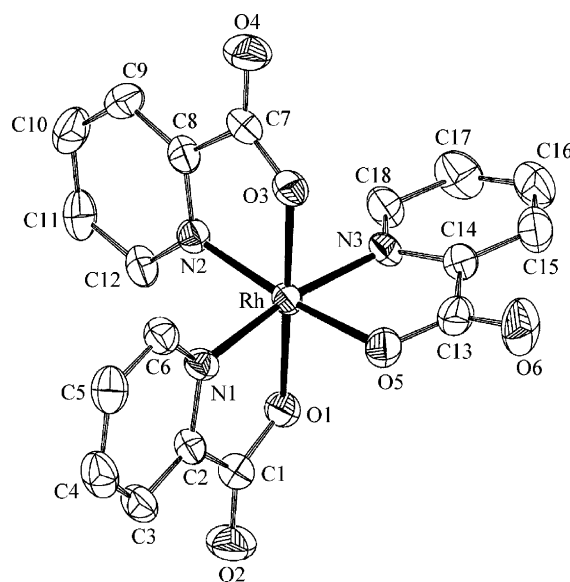


Fig. 1. View of the  $[Rh(pic)_3]$  complex. The  $[Ir(pic)_3]$  complex is visually identical to the  $[Rh(pic)_3]$  complex and the same atom numbering scheme has been used for both structures.

Table 2  
Selected bond distances (Å) and angles (°) for [Rh(pic)<sub>3</sub>]·H<sub>2</sub>O and [Ir(pic)<sub>3</sub>]·H<sub>2</sub>O

[Rh(pic) <sub>3</sub> ]·H <sub>2</sub> O		[Ir(pic) <sub>3</sub> ]·H <sub>2</sub> O	
<i>Bond distances</i>			
Rh–N(1)	2.011(4)	Ir–N(1)	2.014(4)
Rh–N(2)	2.017(4)	Ir–N(2)	2.026(5)
Rh–N(3)	2.028(4)	Ir–N(3)	2.039(4)
Rh–O(1)	2.022(3)	Ir–O(1)	2.033(4)
Rh–O(3)	2.013(3)	Ir–O(3)	2.042(4)
Rh–O(5)	2.025(3)	Ir–O(5)	2.037(4)
C(1)–O(1)	1.306(6)	C(1)–O(1)	1.309(6)
C(1)–O(2)	1.203(6)	C(1)–O(2)	1.207(7)
C(7)–O(3)	1.303(6)	C(7)–O(3)	1.289(7)
C(7)–O(4)	1.208(6)	C(7)–O(4)	1.206(7)
C(13)–O(5)	1.267(6)	C(13)–O(5)	1.286(7)
C(13)–O(6)	1.222(6)	C(13)–O(6)	1.220(7)
<i>Bond angles</i>			
N(1)–Rh–O(1)	81.15(14)	N(1)–Ir–O(1)	80.44(15)
N(2)–Rh–O(3)	81.90(14)	N(2)–Ir–O(3)	81.27(17)
N(3)–Rh–O(5)	81.75(15)	N(3)–Ir–O(5)	80.72(16)
N(1)–Rh–N(3)	170.73(16)	N(1)–Ir–N(3)	170.95(17)
N(2)–Rh–O(5)	172.48(15)	N(2)–Ir–O(5)	172.52(18)
O(1)–Rh–O(3)	179.07(14)	O(1)–Ir–O(3)	179.46(15)

disposition of the nitrogen and oxygen atoms shows that both [M(pic)<sub>3</sub>] (M = Rh, Ir) complexes have the meridional stereochemistry (4), which is quite common in trischelates of rhodium and iridium [1]. The M–N and M–O distances are all quite normal and so are the C–O distances in the carboxylate fragments [2,3]. There is one molecule of water of crystallization per molecule of both [M(pic)<sub>3</sub>] complexes. A closer look at the packing pattern of the crystals reveals that the water molecule is hydrogen bonded to the carboxylate fragments of two adjacent [M(pic)<sub>3</sub>] molecules, which is illustrated in

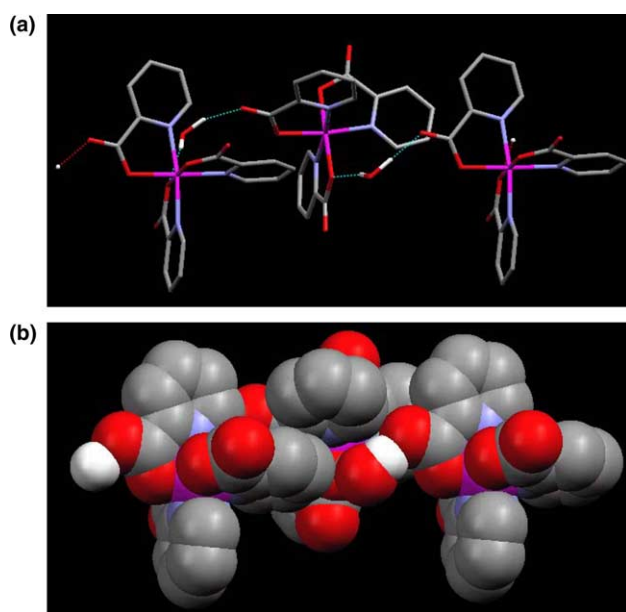


Fig. 2. Chain structure of [Rh(pic)<sub>3</sub>]·H<sub>2</sub>O through intermolecular hydrogen-bonding in (a) the stick style and (b) the space-filling model.

Fig. 2. One hydrogen of the water molecule is hydrogen-bonded to a carboxylate oxygen, which is coordinated to the metal center. The other hydrogen of the same water molecule is hydrogen-bonded to another carboxylate oxygen of an adjacent [M(pic)<sub>3</sub>] molecule, which is not coordinated to the metal center. The water molecule thus acts as a bridge between individual complex molecules. The [M(pic)<sub>3</sub>]·H<sub>2</sub>O complex molecules, when viewed along the *b*-axis, exhibit an extended spiral of M(pic)<sub>3</sub>·H<sub>2</sub>O chains, which run along the *c*-axis and thus the [M(pic)<sub>3</sub>] complexes have acquired a chain supramolecular structure (Fig. 2). This extended intermolecular hydrogen-bonding has resulted in poor solubility of these [M(pic)<sub>3</sub>] complexes (vide infra). To assess the strength of the observed hydrogen-bonding, both the [M(pic)<sub>3</sub>]·H<sub>2</sub>O complexes have been subjected to thermogravimetric analysis. Within 120–150 °C each complex shows a mass loss, which corresponds well with the loss of one molecule of water per molecule of the [M(pic)<sub>3</sub>]·H<sub>2</sub>O complexes. This shows that the water molecule is held fairly tightly in the crystal lattice of both the complexes through hydrogen bonding.

### 3.2. Spectral and electrochemical properties

Magnetic susceptibility measurements show that the [M(pic)<sub>3</sub>] complexes are diamagnetic, which corresponds to the +3 state of rhodium and iridium (low-spin d<sup>6</sup>, *S* = 0) in these complexes. <sup>1</sup>H NMR spectra of both the complexes have been recorded in DMSO-d<sub>6</sub> solution. Each complex shows several overlapping signals within 7.7–8.6 ppm. The spectra clearly show the absence of any C<sub>3</sub> symmetry in the complex molecules and thus indicate that the meridional stereochemistry (4) also prevails in solution for both the complexes. The infrared spectra of both the [M(pic)<sub>3</sub>] complexes are very similar. Each complex shows a broad band around 3520 cm<sup>-1</sup> due to the water of crystallization and several bands of different intensities in the 1700–400 cm<sup>-1</sup> region. Assignment of each individual band to a specific vibration has not been attempted. However, a broad and strong band observed at 1676 cm<sup>-1</sup> in [Rh(pic)<sub>3</sub>] and at 1684 cm<sup>-1</sup> in [Ir(pic)<sub>3</sub>] is attributable to the coordinated carboxylate fragment [9].

The [M(pic)<sub>3</sub>] complexes are poorly soluble in methanol, ethanol and acetonitrile, and moderately soluble in dimethylformamide and dimethylsulfoxide, producing light yellow solutions. Electronic spectra of these complexes have been recorded in acetonitrile solution. Each complex shows several intense absorptions below 400 nm (Table 3). The lowest energy absorption, displayed near 370 nm by both the complexes, is probably due to a metal-to-ligand charge-transfer transition. The other absorptions at higher energies are believed to be due to transitions within the ligand orbitals. To have a better in-

Table 3  
Electronic spectral<sup>a</sup> and cyclic voltammetric<sup>b</sup> data

Compound	$\lambda_{\max}/\text{nm}$ ( $\epsilon/M^{-1} \text{ cm}^{-1}$ )	$E/V$	
		Oxidation <sup>d</sup>	Reduction <sup>e</sup>
[Rh(pic) <sub>3</sub> ]	366 <sup>c</sup> (2100), 328 <sup>c</sup> (9000), 266 (9900), 218 <sup>c</sup> (22200)	1.06	-1.03
[Ir(pic) <sub>3</sub> ]	378 <sup>c</sup> (1900), 296 (9200), 270 (9800), 236 (20700)	1.13	-1.07

<sup>a</sup> In acetonitrile.

<sup>b</sup> Solvent, acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s<sup>-1</sup>.

<sup>c</sup> Shoulder.

<sup>d</sup> Anodic peak potential ( $E_{\text{pa}}$ ).

<sup>e</sup> Cathodic peak potential ( $E_{\text{pc}}$ ).

sight into the nature of the absorption near 370 nm, qualitative EHMO calculations have been performed [10] on computer generated models of both [M(pic)<sub>3</sub>] complexes. Results of these calculations have been found to be similar for both the complexes. A partial MO diagram of the [Rh(pic)<sub>3</sub>] complex is shown in Fig. 3, and that of the [Ir(pic)<sub>3</sub>] complex is deposited as supporting information (Fig. S2). Compositions of some selected molecular orbitals are given in Table 4. The highest occupied molecular orbital (HOMO) and the next two filled orbitals (HOMO - 1 and HOMO - 2) are relatively close and have major ( $\geq 74\%$ ) contributions from the metal  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals, and hence they may be regarded as the metal  $t_2$  orbitals. The lowest unoccupied molecular orbital (LUMO) and next two vacant orbitals

(LUMO + 1 and LUMO + 2) are also close in energy and they are delocalized almost entirely ( $\geq 95\%$ ) on the picolinate ligands. The intense absorption near 370 nm may therefore be assigned to the charge-transfer transition taking place from the filled metal  $t_2$ -orbital (HOMO) to the vacant  $\pi^*$ -orbital (LUMO) of the picolinate ligand.

Electrochemical properties of both the complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBAP). Each complex shows an oxidative response on the positive side and one reductive response on the negative side. Voltammetric data are given in Table 3. Keeping the results of the EHMO calculations in view, the oxidation is assigned to the M(III)–M(IV) oxidation and the reduction is attributable to reduction of the coordinated picolinate ligands.

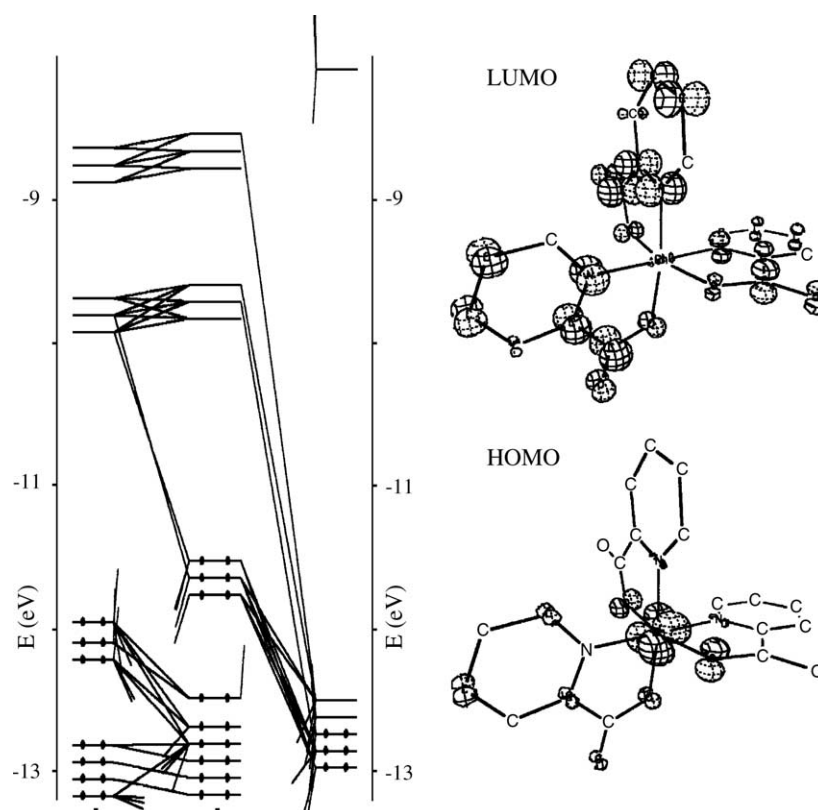


Fig. 3. Partial molecular orbital diagram of [Rh(pic)<sub>3</sub>].



Table 4  
Composition of molecular orbitals

Compound	Contributing fragment	Percentage contribution of fragments to					
		HOMO	HOMO – 1	HOMO – 2	LUMO	LUMO + 1	LUMO + 2
[Rh(pic) <sub>3</sub> ]	Rh	76	74	76	1	3	5
	pic	24	26	24	99	97	95
[Ir(pic) <sub>3</sub> ]	Ir	77	84	88	1	2	4
	pic	23	16	12	99	98	96

Both the redox responses are irreversible in nature, which indicates that the oxidized [M(pic)<sub>3</sub>]<sup>+</sup> and reduced [M(pic)<sub>3</sub>]<sup>–</sup> species are unstable in nature and undergo rapid decomposition.

#### 4. Conclusion

The present study shows that coordination by picolinic acid (**1**), in the usual bidentate fashion (**2**) via dissociation of the carboxylic proton, can stabilize the higher oxidation states of a transition metal. This is manifested in the stabilization of the trivalent state of rhodium and iridium in the [M(pic)<sub>3</sub>] (M = Rh, Ir) complexes. This study also shows that simple water of crystallization may give rise to an interesting supramolecular chain structure through intermolecular hydrogen-bonding.

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#### Appendix A. Supplementary data

Crystallographic data for [Rh(pic)<sub>3</sub>] · H<sub>2</sub>O and [Ir(pic)<sub>3</sub>] · H<sub>2</sub>O complexes in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 248414 and 248413, respectively. A view of the [Ir(pic)<sub>3</sub>] complex has been deposited as Fig. S1 and a partial MO diagram of the [Ir(pic)<sub>3</sub>] complex has been deposited as Fig. S2. Copies of this infor-

mation may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or at www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2004.10.015.

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