Novel HEXOL-type cyclometallated iridium(III) complexes: stereoselective synthesis and structure elucidation†

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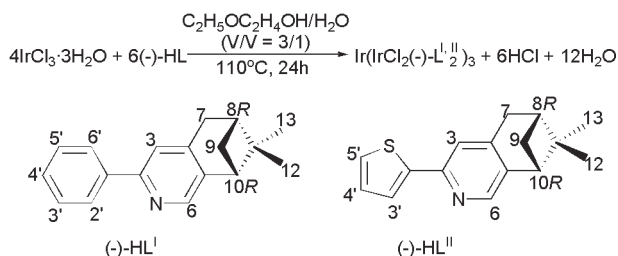**Two diastereoisomers of tetranuclear cyclometallated iridium complexes, either having an inner core of HEXOL-type $[Ir(IrCl_2)_3]^{6+}$ unit and a surface of six chiral, didentate, cyclometallated ligands, are stereoselectively synthesized from an enantiopure pinenopyridine derivative.**

The motif of an octahedral coordination center surrounded by three didentate "ligands", which constitute themselves octahedral coordination entities (HEXOL-type), has been of interest since the classical work of Alfred Werner,[1] mainly due to the inherently chiral nature of such structures.[2] In the present communication we describe tetranuclear iridium(III) complexes of the HEXOL-type, which have some remarkable structural features.

The reaction of iridium trichloride hydrate with enantiopure 2-phenyl-4,5-pinenopyridine derivative (−)-HL^I,[3] in a refluxing mixture of 2-ethoxyethanol and water, leads to the formation of a yellow precipitate (Scheme 1). Flash chromatography on silica column gives two diastereoisomers **1** and **2**.‡ Crystals of **1** and **2** were obtained from CH_2Cl_2/*n*-hexane and $CH_3COOC_2H_5$/diethyl ether, respectively. X-Ray crystallography[4,5] revealed the formation of the HEXOL-type tetranuclear iridium complexes, as shown in Fig. 2.

The inner core of either molecule is a HEXOL-type $[Ir(IrCl_2)_3]^{6+}$ tetranuclear unit, which by itself has D_3-symmetry. The "surface" of these coordination species is formed by six chiral, didentate, cyclometallated ligands, which results in uncharged molecular complexes. These complexes are highly soluble in CH_2Cl_2,

$CH_3COOC_2H_5$ and many other low polar organic solvents due to the nearly complete coverage of the molecular surface by the phenyl-pinenopyridine groups.

Of particular interest is the stereochemistry of these tetranuclear species. Each of the three peripheral iridium atoms, are bound to two C, N-coordinating phenyl-pinenopyridine ligands, adopting a N,N-*trans*, C,C-*cis* arrangement. Thus, all the four iridium atoms can have either Δ-, or Λ-configuration and there are eight possible stereoisomers of the tetranuclear HEXOL-type complex $[Ir(IrCl_2(−)-L^I_2)_3]$. Four kinds of D_3-symmetric species will occur when all the three peripheral iridium atoms have the same configuration (Scheme 2, I), while another four kinds of C_2-symmetric species can be formed when one of the three peripheral iridium atoms has an opposite configuration and breaks the D_3-symmetry (Scheme 2, II). Using enantiopure organic ligands, the stereoselectivity of the formation of such complexes can be investigated.

An NMR investigation of all products formed in Scheme 1 revealed that only two diastereoisomers, were formed and the ratio of **1** to **2** was determined to be 5 : 3. Fig. 3 illustrates the aromatic region of the ^{1}H NMR spectra of complexes **1** and **2**. These spectra, as well as the ^{13}C NMR spectra, show, in each case, the presence of three sets of ligands. Therefore, both complexes are C_2-symmetric species, according to the occurrence of three types of magnetically non-equivalent ligands L^I, L$^{I'}$ and L$^{I''}$ in C_2-symmetric configuration (scheme 2, II). None of the highest possible D_3-symmetric molecules is formed, since in this case, all six ligands would be magnetically equivalent.

Indeed, a close inspection of the X-ray structures in Fig. 2 shows that C_2-symmetry is present and in both cases, the central iridium atoms show Δ-configuration. In complexes **1** and **2**, the three
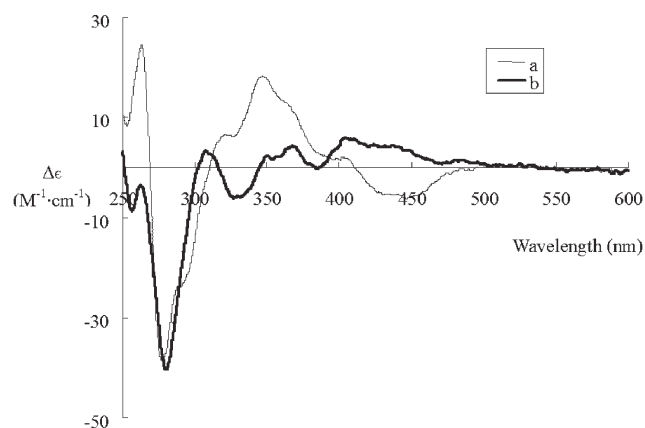
$$4IrCl_3 \cdot 3H_2O + 6(\text{-})\text{-HL} \xrightarrow[\substack{C_2H_5OC_2H_4OH/H_2O \\ (V/V = 3/1) \\ 110°C, 24h}]{} Ir(IrCl_2(\text{-})\text{-}L^{I,\,II}_2)_3 + 6HCl + 12H_2O$$

Scheme 1 Synthesis of the complexes and their numbering scheme for NMR.

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† Electronic supplementary information (ESI) available: X-Ray crystal structure of complex **3** and spectral properties of complexes **1–4**. See http://dx.doi.org/10.1039/b507769a

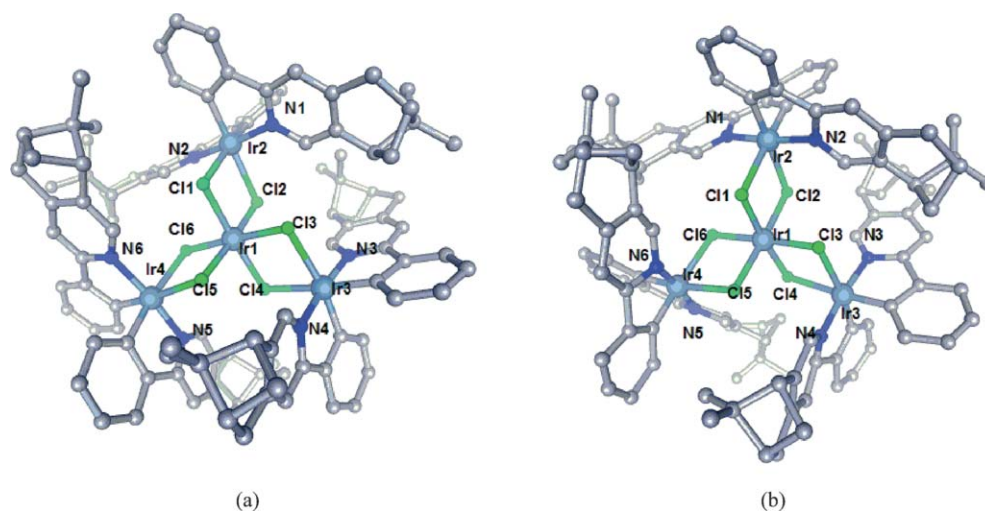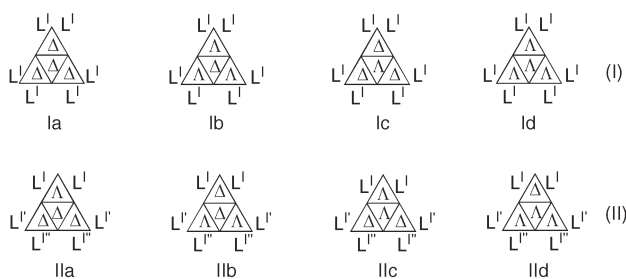**Fig. 1** CD spectra of complexes **1** (a) and **2** (b) (RT, in CH_2Cl_2).

Fig. 2 X-Ray crystal structures of complexes **1** (a) and **2** (b).

Scheme 2 Eight possible stereoisomers of the tetranuclear HEXOL-type complex [Ir(IrCl$_2$(−)–L$^I_2$)$_3$].
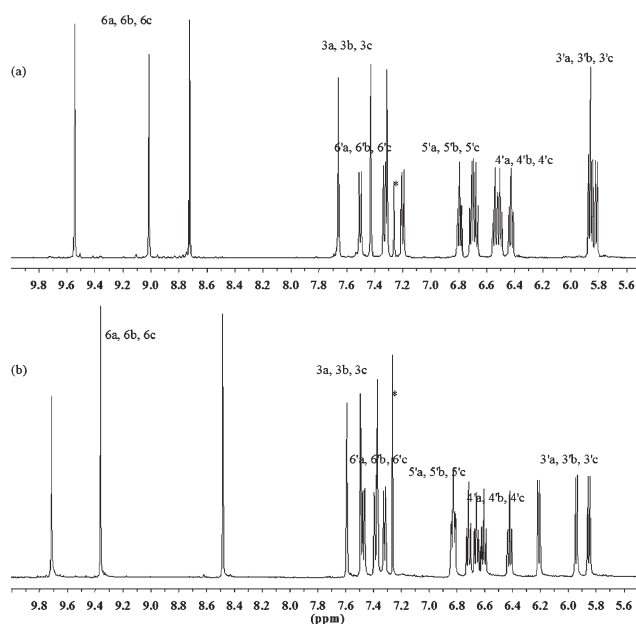

Fig. 3 Aromatic region of the ^{1}H NMR spectra of complexes **1** (a) and **2** (b) (500 MHz, CDCl$_3$(*), RT).

peripheral iridium atoms, Ir2, Ir3 and Ir4, have Δ-, Λ-, Λ- and Δ-, Λ-, Δ-configurations, respectively. Thus, the products obtained from the reaction of ligand (−)-HL^I are stereoisomers Δ-Ir(Δ-IrCl$_2$({C,C-*cis*-N,N-*trans*}(−)-L^I)$_2$)(Λ-IrCl$_2$({C,C-*cis*-N,N-*trans*}(−)-L^I)$_2$)$_2$), **1** (Scheme 2, IIb), and Δ-Ir(Δ-IrCl$_2$({C,C-*cis*-N,N-*trans*}(−)-L^I)$_2$)$_2$(Λ-IrCl$_2$({C,C-*cis*-N,N-*trans*}(−)-L^I)$_2$), **2** (Scheme 2, IIa), respectively.

A related ligand, (−)-HL$^{II},$[6] (Scheme 1) yielded analogous complexes **3** and **4**. The ratio of the two isomers is somewhat different in this case (1 : 5).

Thus, stereoselectivity is complete as far as the configuration of the central iridium is concerned. It appears only in the Δ-configuration, using the (−)-HL$^{I, II}$ ligands. The occurrence of mixed configurations, Δ-, Λ-, Λ-, and Δ-, Λ-, Δ-, respectively, of the peripheral iridium atoms is rather surprising. Under the same conditions, the reaction of iridium trichloride hydrate with unsubstituted phenylpyridine (HPhPy) yields a Cl-bridged dinuclear cyclometallated compound [Ir(PhPy)$_2$Cl]$_2$.[7] Thus, the formation of the tetranuclear species with phenyl pinenopyridine derivatives is caused by the pinene group annelated to the pyridine ring.

Notes and references

‡ Iridium trichloride hydrate (0.3 mmol) was combined with HL^I, dissolved in a mixture of 2-ethoxyethanol (15 mL) and water (5 mL), and heated at 110 °C for 24 h. The solution was cooled to RT. The yellow precipitate formed was collected and washed with ethanol to give a mixture of **1** and **2** in the ratio of 5 : 3. The mixture was then separated by flash chromatography on silica column using CH$_2$Cl$_2$/*n*-hexane 1 : 1 as eluent to yield two diastereoisomers **1** (70 mg, 38%) and **2** (42 mg, 23%). The relative R_f value of complexes **1** and **2** are 0.52 and 0.40, respectively. Fig. 1 displays the CD spectra of complexes **1** and **2**.
§ CCDC 269178. See http://dx.doi.org/10.1039/b507769a for crystallographic data in CIF or other electronic format.
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4 X-Ray data for **1·2 (CH$_2$Cl$_2$)**: C$_{110}$H$_{112}$Cl$_{10}$Ir$_4$N$_6$, M_r = 2641.36, yellow rod, 0.34 × 0.11 × 0.09 mm^3, $F(000)$ = 5168. Orthorhombic, space group $P2_12_12_1$, a = 18.7702(8), b = 21.6033(11), c = 28.1507(12) Å, $\alpha = \beta = \gamma = 90°$, V = 11415.1(9) Å^3, Z = 4, ρ_{calcd} = 1.537 g cm^{-3}. Data collection at 173 K on a Stoe Image Plate Diffraction System, by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Image plate distance: 70 mm, ϕ oscillation scans 0–200°, step $\Delta\phi$ = 0.8°, 2θ = 3.27–52.1°, d_{min}/d_{max} = 12.45/0.81 Å. A total of 38417 reflections collected of which 18654 reflections were independent and used to refine 1129 parameters. 13655 observed reflections with $I > 2\sigma(I)$. R_1 = 0.0314, wR_2 = 0.0544 (observed); R_1 = 0.0490, wR_2 = 0.0574 (all data). The structure was solved by direct methods (SHELXS-97) and refined anisotropically, using weighted full-matrix least-squares on F^2 (SHELXL-97). The H-atoms were included in calculated positions and treated as riding atoms. Max./min. residue electron density +0.556/−0.887 e Å^{-3}. An empirical absorption correction was applied using the DELrefABS routine in PLATON (A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13); transmission factors: T_{min}/T_{max} = 0.507/0.844. A region of disordered electron density was removed using the SQUEEZE routine in PLATON; 290 electrons for a volume of 3009 Å^3. This was assumed to be equivalent to 2 molecules of dichloromethane per molecule of complex. Certain C-atoms on the exterior of the molecule undergo higher thermal motion than those at the interior of the molecule. The atomic coordinates correspond to the absolute structure of the molecule in the crystal. § Flack parameter x = −0.018(5).

5 X-Ray data for **2·3 (CH$_3$COOC$_2$H$_5$)**: C$_{120}$H$_{132}$Cl$_6$Ir$_4$N$_6$O$_6$, M_r = 2735.82, yellow block, 0.30 × 0.15 × 0.10 mm^3, $F(000)$ = 5408. Orthorhombic, space group $P2_12_12_1$, a = 18.5074(13), b = 21.1473(16), c = 28.8458(17) Å, $\alpha = \beta = \gamma = 90°$, V = 11289.7(13) Å^3, Z = 4, ρ_{calcd} = 1.610 g cm^{-3}. Data collection at 173 K on a Stoe Mark II-Image Plate Diffraction System equipped with a two-circle goniometer, by using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å). Image plate distance: 135 mm, ω rotation scans 0–180° at ϕ 0°, step $\Delta\phi$ = 1.0°, with an exposure time of 8 min per image, 2θ range 1.70–51.55°, d_{min}/d_{max} = 23.995/0.817 Å. A total of 54825 reflections of which 20065 reflections were independent and used to refine 577 parameters. 8345 observed reflections with $I > 2\sigma(I)$. R_1 = 0.0710, wR_2 = 0.1457 (observed); R_1 = 0.1353, wR_2 = 0.1738 (all data). The structure was solved by direct methods (SHELXS-97) and only the Ir, Cl and N atoms were refined anisotropically, while the C atoms were refined isotropically, using weighted full-matrix least-squares on F^2 (SHELXL-97). The H-atoms were included in calculated positions and treated as riding atoms. Max./min. residue electron density +0.843/−1.443 e Å^{-3}. An empirical absorption correction was applied using the DELrefABS routine in PLATON (A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13); transmission factors: T_{min}/T_{max} = 0.033/0.426. A region of disordered electron density was removed using the SQUEEZE routine in PLATON; 658 electrons for a volume of 2819 Å^3. This was assumed to be equivalent to 3 molecules of CH$_3$COOCH$_2$CH$_3$ per molecule of complex. Attempts to refine the C atoms anisotropically were unsuccessful. The crystal diffracted weakly beyond 40° in 2θ and only 42% of the data can be considered to be observed $I > 2\sigma(I)$. The atomic coordinates correspond to the absolute structure of the molecule in the crystal. ¶ Flack parameter x = 0.013(15).

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