Stereoselective synthesis of cyclometalated iridium(III) complexes: Characterization and photophysical properties

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The stereoselective synthesis of a highly luminescent neutral Ir(III) complex comprising two bidentate chiral, cyclometalating phenylpyridine derivatives, and one acetylacetonate as ligands is described. The final complex and some intermediates were characterized by X-ray structural analysis, NMR-, CD-, and CPL-spectroscopy.

Current interest in stereoselective synthesis and in emissive metal complexes has motivated the synthesis of chiral luminescent materials. Before, we reported the fabrication of C2-symmetric complexes of Ru(II) and Ir(III), and C3-symmetric species of Pt(II), with chiral enantiopure bipyridine- or cyclometalating phenylpyridine-derivatives [1]. Two types of chiral pinene-phenylpyridine ligands have been synthesized as precursors for the tripod ligands, having the pinene moiety annellated in 4,5-position (HL1) or in 5,6-position (HL2) (Scheme 1) [2]. As reported recently, HL1 yields with IrCl3 · 3H2O a HEXOL-type tetrancular species Ir4Cl6L12, which shows an interesting stereochemistry [3]. In the present communication, we report on the fabrication of a dinuclear complex Ir2Cl2L12 and derivatives thereof. Of special interest is the stereoselective synthesis of a mononuclear molecular complex Ir(L2)(acac), which has interesting properties, especially with regard to its luminescence behavior.

As shown in Scheme 2, the reaction of iridium trichloride hydrate with enantiopure 2-phenyl-5,6-pineneypyridine derivative (−)-HL2, in a refluxing mixture of 2-ethoxyethanol and water, leads to the formation of a red precipitate. Flash chromatography on a short silica column gives complex 1 Ir(L1)2(μ − Cl)2 as a red powder. Reaction of complex 1 with 2,4-pentanedione (Hacac) and sodium carbonate in refluxing 2-ethoxyethanol under inert gas atmosphere, followed by chromatography, gives the mononuclear molecular complex 2, Ir(L1)2(acac). Attempts to crystallize complex 1 from various solvents result in the formation of a solvolysis product of 1, namely Ir(L2)2(CH3CN)Cl. The molecular structure of the latter was determined by X-ray crystallography. Crystals of 2 were obtained from CH2Cl2/n-hexane.

Fig. 1 illustrates the aromatic region of the 1H NMR spectra of complexes 1 and 2. These spectra, as well as the 13C NMR spectra, show the presence of two sets of magnetically non-equivalent cyclometalating ligands in complex 1, while only one set of magnetically equivalent cyclometalating ligands in complex 2. Comparison of the NMR spectra of dissolved crystals from complex 1 and the powder obtained from chromatography, an additional signal attributed to CH3CN appears. Therefore, the μ-chloro bridge was broken by CH3CN during the process of crystallization, yielding the acetonitrile coordinated complexes shown in Fig. 2.

The ORTEP plots [4] in Fig. 2 show that there are two independent mononuclear molecules of the complex per asymmetric unit. It shows that the formation of complex 1 is completely regioselective, i.e. only C,C-cis-N,N-trans isomers are obtained. Metal atoms Ir1 and Ir2 have ∆- and ∆- configuration, respectively. It has already been reported that in the formation of [Ir(phenpy)2(μ − Cl)]2, structural models suggest that interligand steric interactions in the meso form favor formation of the racemate [5]. In the formation of complex 1, the two diastereoisomers [Δ − Ir(L1)2(μ − Cl)]2 and [∆ − Ir(L1)2(μ − Cl)]2, which can be designated as pseudoenantiomers, occur in a 1:1 ratio,
causing the appearance of the two sets of magnetically non-equivalent cyclometalating ligands in the NMR spectra.

The X-ray structure [6] in Fig. 3 shows clearly that in complex 2, the metal center Ir1 atom has \( \Delta \)-configuration and thus it explains the difference between the NMR spectra of complex 1 and 2. During the reaction of complex 1 with 2,4-pentanedione (Hacac), only \( \Delta - Ir(LII)_{2}(acac) \) is stereoselectively formed.

Neither the chiral didentate ligand nor complex 1 show detectable CD activities in the range 250–600 nm, whereas upon formation of the mononuclear Ir\((LII)_{2}(acac)\), a strong Cotton effect is observed in the 250–400 nm region. The absence of signals in the CD spectrum of complex 1 is undoubtedly due to the opposite configurational of the two Ir-centers. Fig. 4 shows the CD spectrum of complex 2 in CH\(_2\)Cl\(_2\) at RT.

Complex 2 exhibits intense emission spectra similar to the achiral analogous [7], displaying a maxima around 507 nm and a shoulder around 542 nm. The luminescence quantum yield, \( \phi \), was determined using the following equation:

\[
\phi = \frac{Q_x}{Q_r} = \frac{A_x(i_x)}{A_r(i_r)} \times \frac{I_x(i_x) \times n_x^2}{I_r(i_r) \times n_r^2} \times \frac{D_x}{D_r}
\]

(Scheme 1. Chiral pinene-phenylpyridine ligands and their numbering scheme for NMR in the cyclometalated complexes.

Scheme 2. Synthesis of complexes 1 and 2.)
where the subscript $r$ and $x$ denote reference and sample, respectively; $A$ is the absorbance at the exciting wavelength, $I$ is the intensity of the excitation light at the same wavelength, $n$ is the refractive index of the solution ($n = 1.343$ in CH$_3$CN and $n = 1.424$ in CH$_2$Cl$_2$), and $D$ is the measured integrated luminescence intensity.

The luminescence quantum yield of complex 2 was determined to be 6.1% by reference to the [Ru(bpy)$_3$]$^{2+}$ complex (absolute quantum yield: 6.2% [8]) in deoxygenated CH$_2$Cl$_2$ and CH$_3$CN solutions at concentrations of $1.3 \times 10^{-5}$ and $3.6-6.7 \times 10^{-5}$ M at 295 K, respectively. The luminescence quantum yield was determined at excitation wavelengths at which (i) the Lambert–Beer law is obeyed and (ii) the absorption of the reference closely matches that of the sample.

The circularly polarized luminescence ($\Delta I$) and total luminescence ($I$) spectra measured for complex 2 in CH$_2$Cl$_2$ solution (at 295 K) are shown in Fig. 5. The degree of circularly polarized luminescence is given by the luminescence dissymmetry ratio:

$$g_{\text{sum}} = \frac{\Delta I}{2I} = \frac{I_L - I_R}{2(I_L + I_R)}$$

where $I_L$ and $I_R$ refer, respectively, to the intensity of left and right circularly polarized emissions. The total luminescence of complex 2 is remarkably high, while as is usual for most chiral organic chromophores and transition metal complexes [9], the $g_{\text{sum}}$ obtained for complex 2 is small: $+0.0019 \pm 0.0004$ as determined at the maximum emission wavelength. Although the $g_{\text{sum}}$ values are very small (a value equal to $\sim 0.002$ corresponding to light that is only 0.2% circularly polarized) and the signals here are weak [1], they are measurable.

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Appendix A. Supplementary material

CCDC 282956 and 282957 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jica.2008.10.011.

References

[4] X-ray data for crystals from complex 1: C24H15Cl5N9O3, M = 806.83, yellow-orange plate, 0.27 × 0.19 × 0.08 mm2, obtained from dichloromethane by the diffusion of hexane, f(0 0 0) = 3216. Monoclinic, space group C2, α = 35.163(3), β = 13.2940(11), γ = 23.990(3) Å, V = 8211.6(14) Å3, Z = 8, ρcalc = 1.305 g cm−3. Data collection at 173 K on a Stoe Image Plate Diffraction System, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Image plate distance: 70 mm, ϕ oscillation scans 0–200°, step Δϕ = 1.0°, exposure time 5 min, 2θ = 3.27–52.1°, dmin/dmax = 12.45/0.81 Å. A total of 32,629 reflections were collected of which 14,629 reflections were independent and used to refine 212 parameters. 3009 observed reflections with I > 2σ(I) were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULscanABS in PLATON, transmission factors: Tmin/Tmax = 0.346/0.422. CCDC-282957.
[6] X-ray data for complex 2: C44H44IrN2O2(H2O), M = 807.00, yellow cube, 0.30 × 0.30 × 0.25 mm3, obtained from dichloromethane by the diffusion of hexane, f(0 0 0) = 1221. Trigonal, space group P321, α = 13.5401(8), β = 13.5401(8), γ = 18.8922(12) Å, V = 2999.6(3) Å3, Z = 3, ρcalc = 1.340 g cm−3. A yellow crystal of complex 2 was mounted on a Stoe Imaging Plate Diffraction System (Stoe & Cie. 1995) equipped with a one-circle ϕ goniometer and a graphite-monochromator. Data collection was performed at −100 °C using Mo Kα radiation (λ = 0.71073 Å). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with 0 < ϕ < 200° and the crystal oscillating through 1° in ϕ. The resolution was dmax = 12.45/0.81 Å. A total of 10,477 reflections were collected of which 3844 reflections were independent and used to refine 212 parameters. 3009 observed reflections with I > 2σ(I), R1 = 0.0301, wR2 = 0.0598 (observed), R1 = 0.0431, wR2 = 0.0614 (all data). Flack Parameter x = 0.001(11). The molecular formula of this complex is [(Ir(C18H18N)2(C5H8O2))(H2O)]. The SQUEEZE instruction in PLATON [Spek, A. L. J. Appl. Cryst. 36 (2003) 7.] was used to calculate the remaining potential solvent accessible area in the unit cell; 31 electrons for a volume of 550.3 Å3; estimated to be equivalent to one water molecule per molecule of the complex. The structure was solved by direct methods using the program SHELX-97 and refined by full-matrix least-squares on F2 with SHELXL-97. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using MULscanABS in PLATON, transmission factors: Tmin/Tmax = 0.346/0.422. CCDC-282957.

PLATON [Spek, A. L. J. Appl. Cryst. 36 (2003) 7]: transmission factors: Tmin/Tmax = 0.265/0.718. A region of dosed electron density was squeezed out using the SQUEEZE routine in PLATON: 167 electrons for a volume of 2305.6 Å3, and assumed to be equivalent to 0.5 CH2Cl2 per molecule of the complex. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing, Fig. 2. CCDC-282956.