

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

Liangru Yang<sup>a,b</sup>, Alex von Zelewsky<sup>b,\*</sup>, Huong P. Nguyen<sup>c</sup>, Gilles Muller<sup>c</sup>, Gaël Labat<sup>d</sup>, Helen Stoeckli-Evans<sup>d</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, He'nan University of Technology, 450001 He'nan, P.R. China

<sup>b</sup> Department of Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland

<sup>c</sup> Department of Chemistry, San José State University, One Washington Square, San José, CA 95192-0101, United States

<sup>d</sup> Institute of Microtechnology, University of Neuchâtel, 2002 Neuchâtel, Switzerland

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  $C_3$ -symmetric complexes of Ru(II) and Ir(III), and  $C_2$ -symmetric species of Pt(II), with chiral enantiopure bipyridine- or cyclometalating phenylpyridine-derivatives [1]. Two types of chiral pinene-phenylpyridine ligands, having the pinene moiety annellated in 4,5-position ( $HL^I$ ) or in 5,6-position ( $HL^{II}$ ) (Scheme 1) [2]. As reported recently,  $HL^I$  yields with  $IrCl_3 \cdot 3H_2O$  a HEXOL-type tetranuclear species  $Ir_4Cl_6L_6^I$ , which shows an interesting stereochemistry [3]. In the present communication, we report on the fabrication of a dinuclear complex  $Ir_2Cl_2L_4^{II}$  and derivatives thereof. Of special interest is the stereoselective synthesis of a mononuclear molecular complex  $Ir(L^{II})_2(acac)$ , 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-pinenepyridine derivative ( $-$ )- $HL^I$ , 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**  $Ir(L^{II})_2(\mu-Cl)_2$  as a red powder. Reaction of complex **1** with 2,4-pentanedione (Hacac) and sodium carbonate in refluxing 2-ethoxyethanol under inert gas

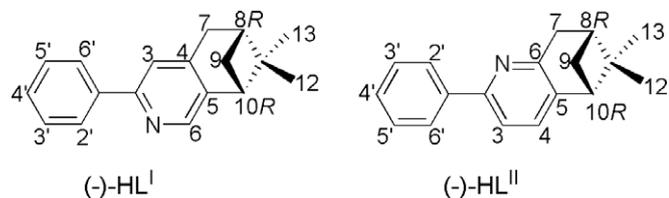
atmosphere, followed by chromatography, gives the mononuclear molecular complex **2**,  $Ir(L^{II})_2(acac)$ . Attempts to crystallize complex **1** from various solvents resulted finally in the formation of a solvolysis product of **1**, namely  $Ir(L^{II})_2(CH_3CN)Cl$ . The molecular structure of the latter was determined by X-ray crystallography. Crystals of **2** were obtained from  $CH_2Cl_2/n$ -hexane.

Fig. 1 illustrates the aromatic region of the  $^1H$  NMR spectra of complexes **1** and **2**. These spectra, as well as the  $^{13}C$  NMR spectra, show the presence of two sets of magnetically non-equivalent cyclometalating ligands in complex **1**, while 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  $CH_3CN$  appears. Therefore, the  $\mu$ -chloro bridge was broken by  $CH_3CN$  during the process of crystallization, yielding the acetonitrile coordinated complexes shown in Fig. 2.

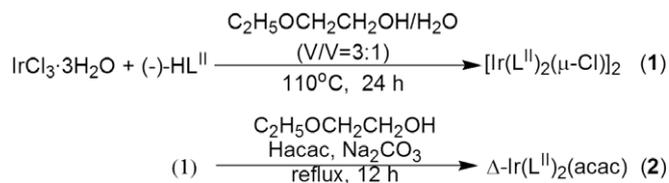
The ORTEP plots [4] in Fig. 2 show that there are two independent mononuclear molecules of the complex per asymmetric unit. It shows that the formation of complex **1** is completely regioselective, i.e. only  $C,C$ -*cis*- $N,N$ -*trans* isomers are obtained. Metal atoms Ir1 and Ir2 have  $\Lambda$ - and  $\Delta$ - configuration, respectively. It has already been reported that in the formation of  $[Ir(phpy)_2(\mu-Cl)]_2$ , 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  $[\Lambda - Ir(L^{II})_2(\mu-Cl)]_2$  and  $[\Delta - Ir(L^{II})_2(\mu-Cl)]_2$ , which can be designated as pseudoenantiomers, occur in a 1:1 ratio,

\* Corresponding author.

E-mail address: alexander.vonzewelsky@unifr.ch (A.von Zelewsky).



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

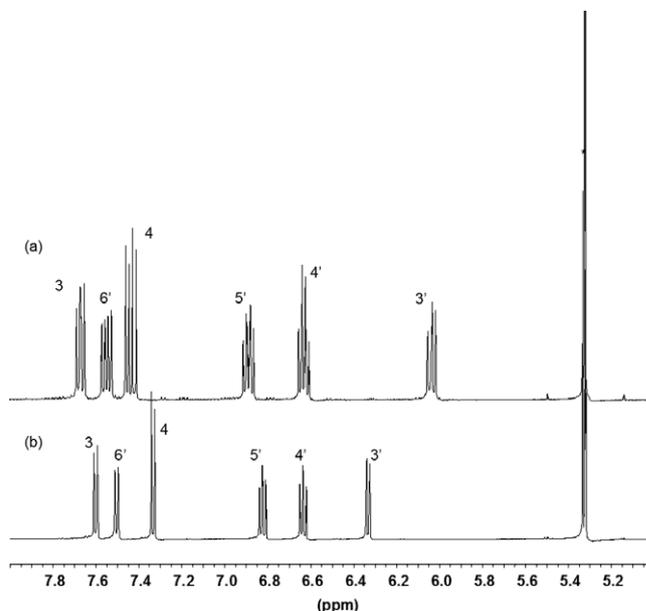


**Scheme 2.** Synthesis of complexes **1** and **2**.

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(L<sup>II</sup>)<sub>2</sub>(acac) is stereoselectively formed.

Neither the chiral didentate ligand nor complex **1** show detectible CD activities in the range 250–600 nm, whereas upon formation of the mononuclear Ir(L<sup>II</sup>)<sub>2</sub>(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 con-

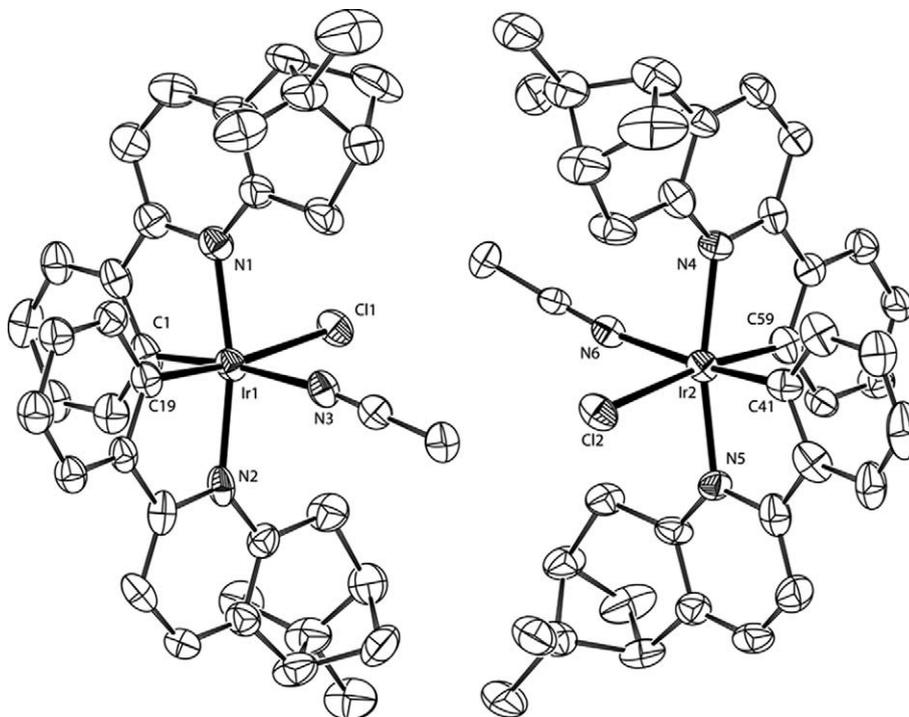


**Fig. 1.** Aromatic region of the <sup>1</sup>H NMR spectra of complexes **1** (a) and **2** (b) (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>( ), RT).

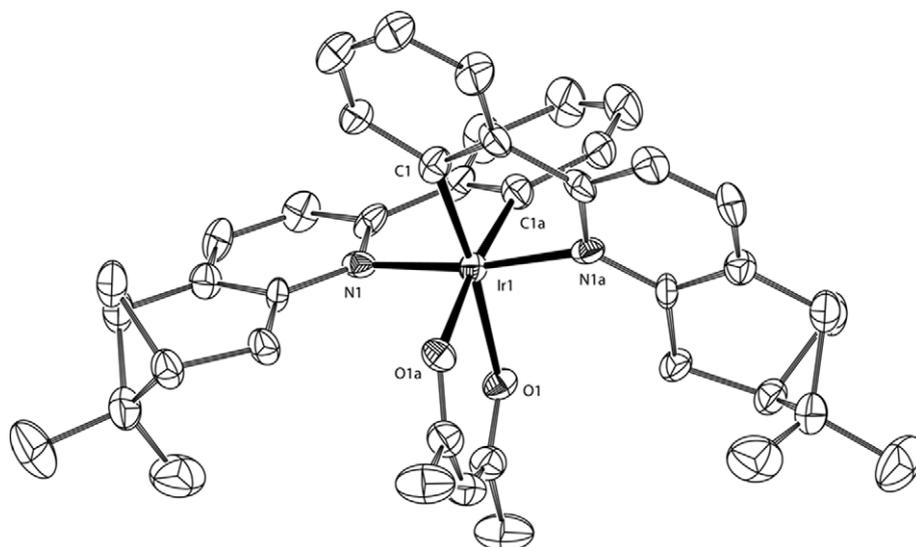
figuration of the two Ir-centers. Fig. 4 shows the CD spectrum of complex **2** in CH<sub>2</sub>Cl<sub>2</sub> at RT.

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:

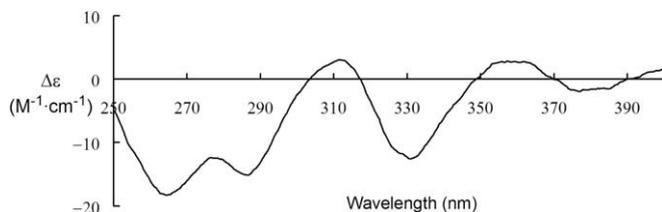
$$\phi = \frac{Q_x}{Q_r} = \frac{A_r(\lambda_r)}{A_x(\lambda_x)} \times \frac{I_r(\lambda_r)}{I_x(\lambda_x)} \times \frac{n_x^2}{n_r^2} \times \frac{D_x}{D_r} \quad (1)$$



**Fig. 2.** X-ray structures of the two independent molecules from complex **1**, with thermal ellipsoids at the 30% probability level. Configurations, selected bond lengths (Å) and bond angles (°) are: (left)  $\Delta$ -configuration; Ir1–C1, 1.995(9); Ir1–C19, 2.040(10); Ir1–N2, 2.092(9); Ir1–N1, 2.095(7); Ir1–N3, 2.141(8); Ir1–Cl1, 2.491(2); C1–Ir1–N1, 80.5(3); C19–Ir1–N2, 79.8(3); N3–Ir1–Cl1, 85.42(18); C1–Ir1–C19, 87.8(4); N2–Ir1–N1, 168.3(3); (right)  $\Delta$ -configuration; Ir2–C41, 1.980(8); Ir2–C59, 2.044(11); Ir2–N5, 2.098(7); Ir2–N4, 2.099(8); Ir2–N6, 2.140(7); Ir2–Cl2, 2.503(2); C41–Ir2–N5, 81.4(3); C59–Ir2–N4, 78.9(4); N6–Ir2–Cl2, 84.02(19); C41–Ir2–C59, 88.6(4); N5–Ir2–N4, 167.5(3).



**Fig. 3.** X-ray molecular structure of complex **2**, with thermal ellipsoids at the 50% probability level [Symmetry code (i)  $x - y, -y, 5/3 - z$ ]. Configuration, selected bond lengths (Å) and bond angles ( $^\circ$ ) are:  $\Delta$ -configuration; C1–Ir1, 1.972(6); N1–Ir1, 2.089(5); O1–Ir1, 2.168(4); Ir1–C1a, 1.972(6); Ir1–N1a, 2.089(5); Ir1–O1a, 2.168(4); C1–Ir1–N1a, 81.6(2); C1a–Ir1–N1, 81.6(2); O1a–Ir1–O1, 87.7(2); C1–Ir1–C1a, 92.3(3); N1–Ir1–N1a, 171.5(3).



**Fig. 4.** CD spectrum of complex **2** (298 K, in  $\text{CH}_2\text{Cl}_2$ ).

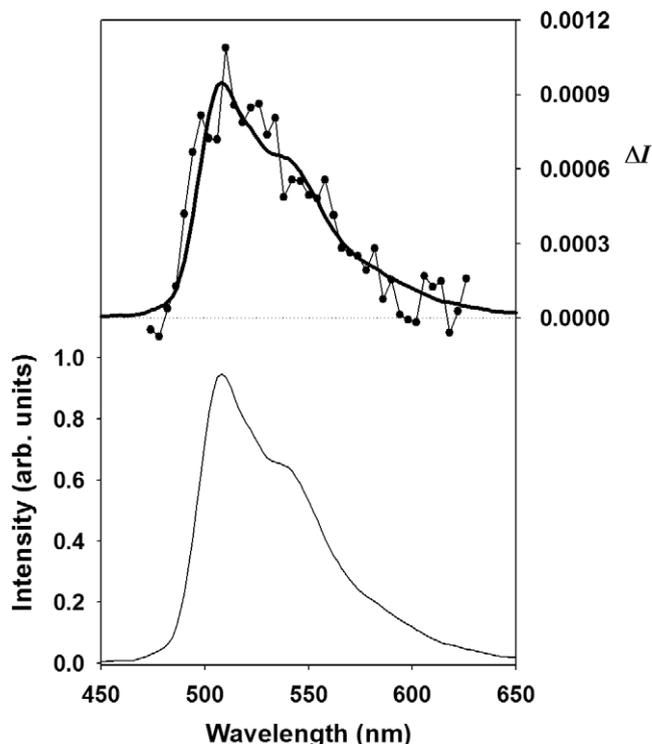
where the subscript  $r$  and  $x$  denote reference and sample, respectively;  $A$  is the absorbance at the exciting wavelength,  $I$  is the intensity of the excitation light at the same wavelength,  $n$  is the refractive index of the solution ( $n = 1.343$  in  $\text{CH}_3\text{CN}$  and  $n = 1.424$  in  $\text{CH}_2\text{Cl}_2$ ), 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  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex (absolute quantum yield: 6.2% [8]) in deoxygenated  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  solutions at concentrations of  $1.3 \times 10^{-5}$  and  $3.6\text{--}6.7 \times 10^{-6}$  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  $\text{CH}_2\text{Cl}_2$  solution (at 295 K) are shown in Fig. 5. The degree of circularly polarized luminescence is given by the luminescence dissymmetry ratio:

$$g_{lum} = \frac{\Delta I}{I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)} \quad (2)$$

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  $g_{lum}$  obtained for complex **2** is small:  $+0.0019 \pm 0.0004$  as determined at the maximum emission wavelength. Although the  $g_{lum}$  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.



**Fig. 5.** Circularly polarized luminescence (upper curve) and total luminescence (lower curve) spectra of complex **2** in  $\text{CH}_2\text{Cl}_2$  at 295 K, upon excitation at 350 nm. The continuous line in the CPL plot is presented to show the luminescence spectral line shape.

## Acknowledgment

We thank the Swiss National Science Foundation for financially supported to this work. G.M. thanks the National Institute of Health Minority Biomedical Research Support (2 S06 GM008192-27) and Research Corporation Cottrell Science Award CC6624) for their financial support, and Ms. Nicole M. Kosareff for her help in the spectroscopic measurements.

## 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](http://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

- [1] (a) C. Hamann, A. von Zelewsky, A. Neels, H. Stoeckli-Evans, *Dalton Trans.* 3 (2004) 402;  
(b) C. Schaffner-Hamann, A. von Zelewsky, A. Barbieri, F. Barigelletti, G. Muller, J.P. Riehl, A. Neels, *J. Am. Chem. Soc.* 126 (2004) 9339;  
(c) M. Gianini, A. Forster, P. Haag, A. von Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.* 35 (1996) 4889.
- [2] (a) L. Ghizdavu, O. Lentzen, S. Schumm, A. Brodkorb, C. Moucheron, A. Kirsch-De Mesmaeker, *Inorg. Chem.* 42 (2003) 1935;  
(b) A.V. Malkov, M. Bell, M. Vassieu, V. Bugatti, P. Kocovsky, *J. Mol. Catal. A: Chem.* 196 (2003) 179;  
(c) J.P. Djukic, C. Michon, A. Maise-François, R. Allagapen, M. Pfeffer, K.H. Dötz, A. De Cian, J. Fischer, *Chem. Eur. J.* 6 (2000) 1064.
- [3] L. Yang, A. von Zelewsky, H. Stoeckli-Evans, *Chem. Commun.* 33 (2005) 4155.
- [4] X-ray data for crystals from complex 1:  $C_{38}H_{38}ClIrN_3 \cdot 0.5(CH_2Cl_2)$ ,  $M_r = 806.83$ , yellow-orange plate,  $0.27 \times 0.19 \times 0.08 \text{ mm}^3$ , obtained from dichloromethane by the diffusion of hexane,  $F(000) = 3216$ . Monoclinic, space group  $C2$ ,  $a = 35.163(3)$ ,  $b = 13.2940(11)$ ,  $c = 23.990(3) \text{ \AA}$ ,  $\beta = 132.925(7)^\circ$ ,  $V = 8211.6(14) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calcld}} = 1.305 \text{ g cm}^{-3}$ . Data collection at 173 K on a Stoe Image Plate Diffraction System, using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Image plate distance: 70 mm,  $\phi$  oscillation scans  $0-200^\circ$ , step  $\Delta\phi = 1.0^\circ$ , exposure time 5 min,  $2\theta = 3.27-52.1^\circ$ ,  $d_{\text{min}}/d_{\text{max}} = 12.45/0.81 \text{ \AA}$ . A total of 32,629 reflections were collected of which 14629 reflections were independent and used to refine 775 parameters. 9072 observed reflections with  $I > 2\sigma(I)$ .  $R_1 = 0.0351$ ,  $wR_2 = 0.0744$  (observed);  $R_1 = 0.0616$ ,  $wR_2 = 0.0797$  (all data). Flack Parameter  $x = -0.021(7)$ . The structure was solved by direct methods (SHELXS-97). The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H-atoms were refined anisotropically, using weighted full-matrix least-squares  $F^2$ . There are two independent molecules of complex per asymmetric unit ( $Z = 8$ ,  $Z' = 2$ ). An empirical absorption correction was applied using the DELREFABS routine in PLATON [Spek, A. L. *J. Appl. Cryst.* 36 (2003) 7]; transmission factors:  $T_{\text{min}}/T_{\text{max}} = 0.265/0.718$ . A region of disordered electron density was squeezed out using the SQUEEZE routine in PLATON: 167 electrons for a volume of  $2305.6 \text{ \AA}^3$ , and assumed to be equivalent to  $0.5 \text{ CH}_2\text{Cl}_2$  per molecule of the complex. The molecular structure and crystallographic numbering scheme are illustrated in the PLATON drawing, Fig. 2. CCDC-282956.
- [5] S. Sprouse, K.A. King, P.J. Spellane, R.J. Watts, *J. Am. Chem. Soc.* 106 (1984) 6647.
- [6] X-ray data for complex 2:  $C_{41}H_{44}IrN_2O_2 \cdot (H_2O)$ ,  $M_r = 807.00$ , yellow cube,  $0.30 \times 0.30 \times 0.25 \text{ mm}^3$ , obtained from dichloromethane by the diffusion of hexane,  $F(000) = 1221$ . Trigonal, space group  $P3_121$ ,  $a = 13.5401(8)$ ,  $b = 13.5401(8)$ ,  $c = 18.8928(12) \text{ \AA}$ ,  $V = 2999.6(3) \text{ \AA}^3$ ,  $Z = 3$ ,  $\rho_{\text{calcld}} = 1.340 \text{ g cm}^{-3}$ . A yellow crystal of complex 2 was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle  $\phi$  goniometer and a graphite-monochromator. Data collection was performed at  $-100^\circ \text{C}$  using Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with  $0 < \phi < 200^\circ$  and the crystal oscillating through  $1^\circ$  in  $\phi$ . The resolution was  $d_{\text{min}}/d_{\text{max}} = 12.45/0.81 \text{ \AA}$ . A total of 10 477 reflections were collected of which 3844 reflections were independent and used to refine 212 parameters. 3009 observed reflections with  $I > 2\sigma(I)$ .  $R_1 = 0.0301$ ,  $wR_2 = 0.0598$  (observed);  $R_1 = 0.0431$ ,  $wR_2 = 0.0614$  (all data). Flack Parameter  $x = 0.001(11)$ . The molecular formula of this complex is  $\{[Ir(C_{18}H_{18}N)_2(C_5H_8O_2)](H_2O)\}$ . 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  $550.3 \text{ \AA}^3$ ; estimated to be equivalent to one water molecule per molecule of the complex. The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares on  $F^2$  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. A semi-empirical absorption correction was applied using MULSCANABS in PLATON, transmission factors:  $T_{\text{min}}/T_{\text{max}} = 0.346/0.422$ . CCDC-282957.
- [7] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M.E. Thompson, *Inorg. Chem.* 40 (2001) 1704.
- [8] (a) J.V. Caspar, T.J. Meyer, *Inorg. Chem.* 22 (1983) 2444;  
(b) J.V. Caspar, T.J. Meyer, *J. Am. Chem. Soc.* 105 (1983) 5583.
- [9] (a) J.P. Riehl, G. Muller, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, vol. 34, North-Holland Publishing Company, Amsterdam, 2005, pp. 289-357 (Chapter 220), see also references therein;  
(b) R.D. Peacock, B. Stewart, *J. Chem. Soc., Chem. Commun.* (1982) 295;  
(c) K.E. Gunde, A. Credi, E. Jandrasics, A. von Zelewsky, F.S. Richardson, *Inorg. Chem.* 36 (1997) 426;  
(d) J.E. Field, G. Muller, J.P. Riehl, D. Venkataraman, *J. Am. Chem. Soc.* 125 (2003) 11808.