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fac-Ir(ppy)$_3$: Structures in the Gas-Phase and of a New Solid Modification

Raphael J. F. Berger,*[a] Hans-Georg Stammler,[a] Beate Neumann,[a] and Norbert W. Mitzel*[a]

Dedicated to Professor Wolf-Walther du Mont on the occasion of his 65th birthday

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The structure of *fac*-Ir(ppy)$_3$ has been determined in the gas phase by means of electron diffraction. A new modification (space group $P\bar{4}2_1c$) has been obtained by sublimation of the compound at 385 °C and its structure been determined by X-ray diffraction. Concerning the importance of *fac*-Ir(ppy)$_3$ as triplet emitter in OLED devices, and the fact that the relevant layers most of these are generated via gas phase deposition techniques the new structures are of high relevance. They mark an improvement to an earlier solid-state structure determination of a monoclinic modification yielded by crystallisation from solution. Selected structural parameters are (gas/solid): Ir1–C8 2.033(6)/2.016(2) Å, Ir1–N2 2.158(7)/2.130(2) Å; N2–Ir1–N2b 98(1)°/94(2)°, C8–Ir1–C8b 93(1)°/94(2)°.

Introduction

The use of organometallic complexes of iridium and platinum, like *fac*-tris(2-phenylpyridine) iridium(III) [*fac*-Ir(ppy)$_3$, **1**] as a prime example, marks a breakthrough in OLED (organic light-emitting device) research and application.[1] Mainly their ability to act as exciton traps and to emit light with high efficiency from the three times more probably populated triplet states than singlet states are responsible for their success in OLED applications.[2] The high efficiency of **1** as a triplet emitter is generally explained with strong spin-orbit coupling (SOC) at the Ir atom leading to a fast inter system crossing and a high probability for a radiative $T_1 \rightarrow S_0$ transition.[2c] Clearly a core issue for rapid progress in OLED research is a solid understanding of these properties. A detailed theoretical study from 2007 provides good quantitative agreement between observed phosphorescence parameters of interest, although vibronic couplings effects have not yet been considered.[3]

However, a principal problem which the authors of this contribution and others face is the lack of reliable experimental structural data of **1**, helping to assess and validate the employed theoretical methods. This is in particular so due to the non-trivial electronic ground state structure[4] and substantial contributions of relativistic effects (like SOC). As late as in 2005 a solid-state structure of **1** has been determined by single-crystal X-ray diffraction (XRD). However, this structure determination was "severely hampered by systematic twinning and pseudo-symmetry", which means that the Ir-bonded C and N positions were found to be superimposed.[5] In the light of the classical text book example of the solid-state structure determination of the $[Ir(bipy)_3]^{3+}$ trication (bipy = bipyridyl),[6] in which C and N atoms have been wrongly assigned by overlooking possible isomerisation, this structure of **1** does not allow the extraction of highly accurate structure parameters. Moreover the structure determination was on a modification obtained by crystallisation from solution, whereas the gross of **1**-based OLED devices are obtained by using gas-phase processes. The determination of an accurate structure of a possibly different modification obtained by sublimation or even of the free molecules (gas-phase) to allow direct comparison with the theoretical data remained therefore highly desirable to foster further development in this important field. For this reason we undertook both types of structural investigations and report these within this contribution.

Results and Discussion

Single crystals of **1** were obtained by sublimation at about 658 K and 10^{-6} mbar pressure with exclusion of light. An IR spectrum of the crystalline material showed no signs of a hydro-pyridinonium stretching frequency. Consequently, the above mentioned C–N bond isomerism problem was absent. In contrast to the earlier reported $P\bar{3}$ modification[5] the compound crystallizes under these conditions

[a] Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany
Fax: +49-521-1066026
E-mail: raphael.berger@uni-bielefeld.de
mitzel@uni-bielefeld.de

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in the acentric tetragonal space group $P\bar{4}2_1c$. The molecular $Ir(ppy)_3$ units possess no crystallographically imposed symmetry higher than C_1. π-Stacking motifs, as well as weak C–H···π type hydrogen bridges[7] are detected between the hydrogen atoms H14b and H18b and a pyridylen ring fragment in an opposing molecule (Figure 1).

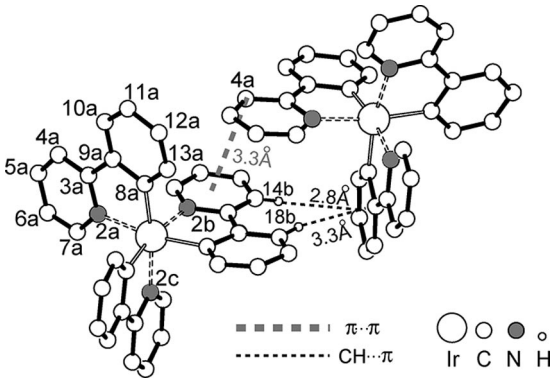

Figure 1. C–H···π (black dotted lines) and π···π contacts (gray dotted line) in the solid-state structure of **1**. The atom labelling scheme using *a*, *b* and *c* should not imply symmetry relation, but was chosen in order to simplify comparisons with the C_3 symmetric gas-phase structure. The distances attributed to the C–H···π contact refer to the distance from the hydrogen atoms to py ring centroid. The distance attributed to the π···π contact refers to the orthogonal distance of atom C4a to a mean plane defined by the opposing py ring.

The new solid-state structure of **1** can be described as close packing of weakly associated tetrameric subunits (Figure 2). The dipole moments are roughly parallel or antiparallel to the *c*-axis, and due to the $\bar{4}$ symmetry operation, they alternate in direction within the tetramers as well as the chirality of the molecules does.

According to quantum chemical calculations this ensures efficient packing and maximises attractive dispersion interactions in this type of C_3 (in our case close-to C_3) symmetric propeller shaped molecules.[8] Figure 3 shows four unit cells as seen along the crystallographic *c*-axis. No special types of interactions exist between the tetrameric units. The homochiral molecules are organised in strictly alternating layers parallel to the (1,0,0) planes.

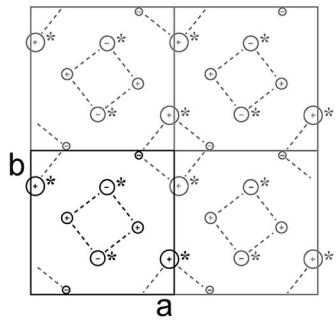

Figure 3. Schematic scaled representation of four unit cells in the tetragonal modification of **1** viewed along the *c* axis. Each circle stands for an individual molecule. The large circles correspond to a larger *c* coordinate (higher position in the unit cell) while the smaller circles correspond to deeper lying molecules in the same unit cell. The signs ("+","–") mark the orientation of the dipole moment vectors of the molecules, which are all approximately either parallel or antiparallel to the *c* axis. The molecules with an asterisk are the enantiomers of the molecules without one. Molecules connected with a dotted line belong to one tetramer (shown in Figure 2).

The gas-phase structure determination by means of electron diffraction (GED) was undertaken with the diffractometer at the University of Bielefeld using a newly constructed high-temperature nozzle.[9] Nozzle and sample temperature were held at about 658 K. The molecular intensity curves are shown in Figure 4 and their Fourier transform, the radial distribution curve is shown in Figure 5. As the gas-phase structure of **1** is of utmost interest as a reference for accurate theoretical descriptions of its molecular and electronic structure in the context of OLED research, we decided to refine an r_{h1} structure type. This is an approximation to the computationally accessible equilibrium structures r_e.[10]

For the gas-phase structure refinement of **1**, C_3 symmetry and planarity of the pyridylene (py) and phenylene (ph) rings were assumed (Figure 6). These were allowed to deviate from a predefined ppy ligand plane by a torsion angle τ (C8–C9–C3–N2) in a way that the py ring adopts 2/3 of positive τ and the ph ring 1/3 of negative τ. This takes into account the different chemical binding strengths of polar

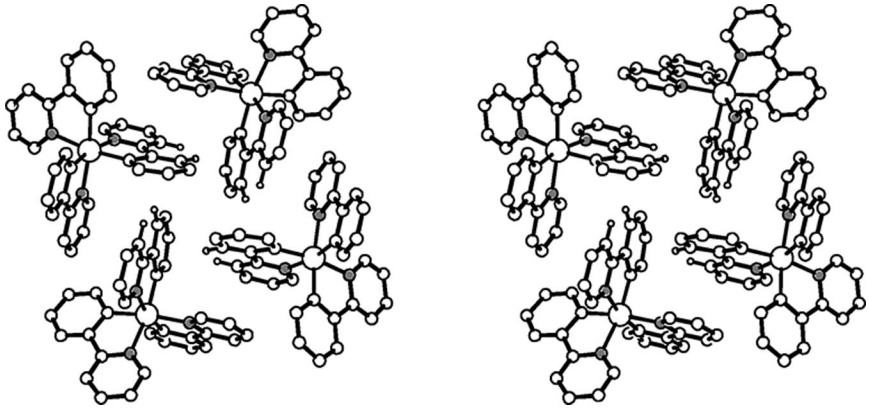

Figure 2. Stereographic projection displaying the tetrameric subunits found in the solid-state structure of the $P\bar{4}2_1c$ modification of **1**.

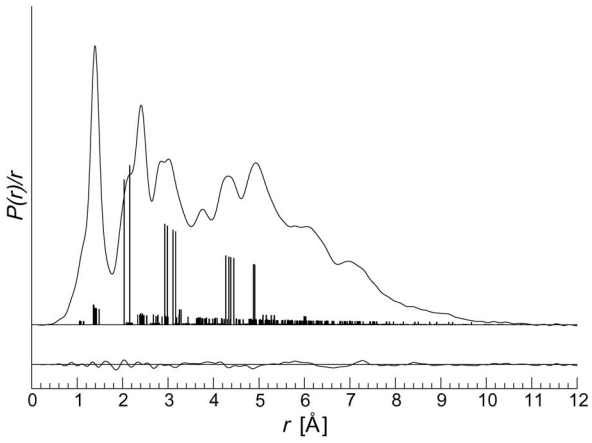

Figure 4. Experimental and difference (experimental minus theoretical) molecular-intensity curves for **1**.

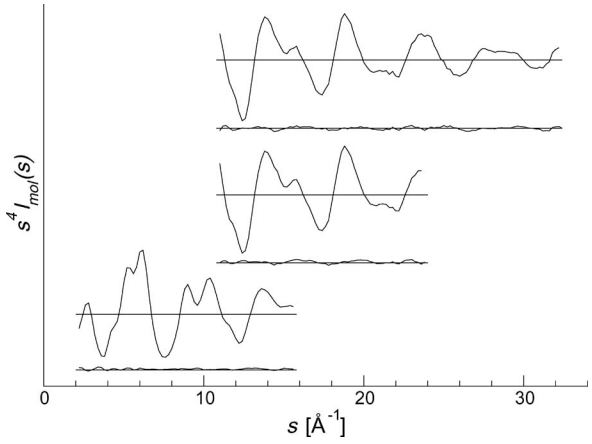

Figure 5. The radial distribution curve, bond length stick diagram and difference curve (experimental minus theoretical) from the gas-phase structure refinement of **1**.

covalent Ir–C and dative Ir–N bonds and the fact that the total of τ is small anyway. The position of this predefined ppy ligand plane with respect to the C_3 axis is defined uniquely by the angles N2–Ir1–N2b and C8–Ir1–C8b. These two parameters the bonded Ir1–C8 and Ir1–N2 distances and τ were freely refined.

The distance parameters for all C–C and C–N bonds (printed in bold, see Figure 6) were tied together by the ratios derived from the means of the three ligand geometries determined crystallographically and using one common "scaling factor" (f_{CC}) as an independent parameter. In addition, the corresponding bond angles between these atoms were fixed. We decided to apply such a procedure since there is a) no reliable *first-principles* calculation available or feasible, yet (see above) and therefore the quality of calculated parameters, which could be used as restraints,[11] are at least in doubt; b) it is to be expected, that the solid-state parameters concerning only the ligand geometry are in good agreement with the corresponding gas-phase parameters, as this is frequently found to be the case; c) due to the limited information contained in the GED data regarding these individual distances or the differences between

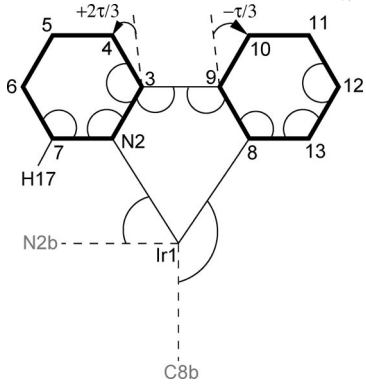

Figure 6. Geometric model and labelling scheme for the gas-phase structure refinement of **1**. Each continuous line or arc represents a parameter used to define the structure (for simplicity only one hydrogen atom is shown).

them it will not be possible to refine them independently solely based on GED data. An overall scaling of the ring sizes, while refining the rest of the molecular geometry is thus a good compromise to get most information out of the experimental data.

The distance C3–C9 for the bond between the py and ph units was refined independently (i.e. not effected by the scaling parameter f_{CC}). The remaining degrees of freedom for the structural description of the ppy ligand geometry were designated to the eight angles shown in Figure 6. These values were refined using the corresponding average values from the solid-state structure of **1** as restraints, each with an uncertainty of 0.5° in the sense of a SARACEN refinement.[11] The hydrogen atoms were positioned exactly on the bisectors of the respective C–C–C/N fragments and one common C–H distance was refined.

A selection of gas-phase structure parameters and the respective values from the crystal structure determination and two ab initio methods is listed in Table 1.

In the earlier crystal structure determination of the $P\bar{3}$ modification of **1**,[5] which was hampered by systematic twinning, Ir–C distances of 2.034(9), 2.032(9) and 2.060(10) Å and Ir–N distances of 2.086(8), 2.095(9) and 2.071(10) Å were reported. Here in particular the Ir–N distances appear to be extremely short in this structure, compared to the values of the $P\bar{4}2_1c$ modification of **1** described in this contribution at 2.126(2), 2.128(2) and 2.137(2) Å.

For our new data the difference between the distances Ir1–N2 and the Ir1–C8 is 0.125(7) Å in the gas-phase and 0.114(2) Å for the solid-state. Both values are significantly larger than the respective value of 0.04(1) Å (in average) determined for the $P\bar{3}$ modifycation.[5] This difference increases slightly from the crystal to the gas-phase. The increase in the Ir1–N2 distance is accompanied by an increase in the N2–Ir1–N2b angle, suggesting a weaker Ir–N interaction in the gas-phase than in the solid state. A possible reason for this might be the well known trend of donor-acceptor interactions to be weaker in the gas-phase and show longer donor-acceptor distances, than in condensed phases.[12] Another explanation is that the anharmonic con-

Table 1. Selection of structure parameters of **1** determined by GED, XRD and ab initio calculations.

Parameter	GED[a] (Å, deg)	XRD[b] (Å, deg)	HF[c] (Å, deg)	MP2[c] (Å, deg)
Ir1–C8	2.033(6)	2.016(2)	2.052	1.970
Ir1–N2	2.158(7)	2.130(2)	2.201	2.079
N2–Ir1–N2b	98(1)	94(1)	97	97
C8–Ir1–C8b	93(1)	94(1)	97	94
f_{CC}	1.0072(6)	1.0	–	–
N2–C7	1.357[d]	1.347(1)	1.324	1.346
C7–C6	1.388[d]	1.378(2)	1.370	1.387
C6–C5	1.396[d]	1.387(4)	1.385	1.393
C5–C4	1.392[d]	1.381(4)	1.370	1.388
C4–C3	1.404[d]	1.394(4)	1.395	1.398
C3–N2	1.374[d]	1.365(6)	1.333	1.363
C9–C10	1.412[d]	1.402(2)	1.394	1.402
C10–C11	1.392[d]	1.382(7)	1.373	1.390
C11–C12	1.399[d]	1.389(5)	1.387	1.397
C12–C13	1.397[d]	1.387(5)	1.377	1.395
C13–C8	1.415[d]	1.405(4)	1.398	1.406
C8–C9	1.429[d]	1.417(4)	1.403	1.422
C3–C9	1.458(9)	1.470(4)	1.474	1.456
C–H_{av}	1.128(8)	0.92(4)	1.072	1.083
τ(C8–C9–C3–N2)	–5(3)	–5(2)	–2	–3

[a] r_{h1} structure, 658 K. [b] Tetragonal modification, 100 K, average values for the three independent sites, standard deviation of the three values. [c] def2-TZVPP basis set.[11] [d] Mean XRD value multiplied by the scaling factor f_{CC}.

tribution to the thermal average of the Ir1–N2 distance becomes larger at elevated temperatures causing an increase of the r_{h1} Ir1–N2 distance compared to the desired r_e value;[13] the temperature difference between gas-phase and crystal structure determination were 558 K (XRD at 100 K, GED at 658 K).

A more definite interpretation of the observed Ir1–N2 distance will require additional information from high-level quantum chemical calculations in order to describe the multi-reference character, non-scalar relativistic effects (like SOC) and presumably also core electron correlation or spectroscopic information (e.g. MW).

Expectedly the scalar-relativistic (relativistic ECP for Ir) single reference ab initio calculations provide an insufficient quantitative description of the Ir-to-ligand structure parameters (Ir1–C8, Ir1–N2).[4] Note also the large variation between HF and MP2 values and the mismatch of both with the experimental gas-phase results (GED). In contrast, there is already a good agreement between the HF calculations and the experimental gas-phase structure for the structure of the ligand itself and this is even improving upon applying the MP2 level of theory.

The overall quality of the gas-phase structure refinement (see Exp. Sect.) confirms the model assumption of a close similarity of py and ph unit structures in both, gas phase and solid state. Moreover, the good agreement of the ligand ring structures calculated by single reference ab initio methods with the experimentally determined ones suggests that the influence of a multi-reference character and the non-scalar relativistic SOC on the ligand structure can be expected to be small. In this sense such effects will only be of importance for a proper description of the proximate surrounding of the iridium atom, i.e. the parameters Ir1–N2, Ir1–C8, N2–Ir1–N2b and C8–Ir1–C8b. This interpretation also supports the validity of the basic assumption of SOC effects being perturbations of the orbitals located largely at the iridium atom, like in the recently suggested extension of the ligand field model by Yersin et al.,[2c] explaining SOC effects on the electronic structure of related Ir^{III} organometallic coordination compounds.

Conclusions

With experimental structure determinations in both, gas-phase and crystalline state, our results lay a new and accurate experimental structural basis for further investigations of the important OLED basis compound Ir(ppy)$_3$ (**1**). Our own calculations and those of others show, that there is still no reliable theoretical description of this comparatively simple compound. The often neglected differences between gas-phase and solid-state structures, which can reliably be derived only from experimental work in both phases, point the way for further theoretical research. Such work is now under way in our laboratories.

Experimental Section

GED Experiment: Compound **1** was obtained from Aldrich Chemicals in 98% sample purity and used without further purification prior to the GED experiment. At about 385 °C sufficient sample vapour pressure was built up to give well detectable diffraction patterns with 30–60 seconds of exposure time and 100 nA primary beam current. Diffraction patterns were recorded at nozzle-to-plate distances of about 250 and 500 mm and at about 60 kV of electron acceleration voltage. Reduction of the data and their treatment by our usual procedures[10] led to the experimental intensity curves shown in Figure 2.

GED Refinement: Structure type r_{h1}, data sets [1, 2, 3], R_g (%) [6.41, 24.15, 17.36], R_d (%) [4.56, 16.51, 11.18], $R_{g\,tot}$(%) 9.07, $R_{d\,tot}$(%) 8.05, scale factors (k) [0.783(8), 0.760(28), 0.745(29)], corr. par. [0.342, 0.479, 0.490], Δs (nm^{-1}) 0.2, s_{min} (nm^{-1}) [22.0, 110.0, 110.0], s_{max} (nm^{-1}) [42.0, 322.0, 236.0], nozzle-to-plate dist. (mm) [496.95, 247.63, 247.63], λ (pm) [4.8700, 4.8700, 4.8700], nozzle temperatures (°C) [388(1), 375(1), 392(1)]. Further details on the GED refinement can be found in the supplementary material section.

Crystal Structure Determination: Single crystals of **1** were yielded by sublimation at 385 °C and 10^{-6} mbar pressure and under exclusion of light. *Crystal data for* ***1****:* $C_{33}H_{24}IrN_3$, tetragonal, $P\bar{4}2_1c$, a = 23.1064(3), c = 9.1159(1) Å, V = 4867.03(11) Å^3, Z = 8, $\rho_{ber.}$ = 1.787 g cm^{-3}, λ = 0.71073 Å, $2\theta_{max.}$ = 60.0°, T = 100(2) K, μ = 5.515 mm^{-1}. 104437 measured, 7096 independent refl. (R_{int} = 0.0464). 431 parameters, hydrogen atoms were refined isotropically, all other atoms anisotropically, R_1 = 0.0182 for 6470 refl. with $I>4\sigma(I)$ and wR_2 = 0.0326 for all 7096 data. Max./min. residual peaks 0.453/–0.370 e Å^{-3}. Programs: G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

CCDC-747921 contains 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.

Supporting Information (see also the footnote on the first page of this article): Complete listing of experimental and refinement parameters for the gas electron-diffraction experiment.

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