

Facial Tris Cyclometalated Rh³⁺ and Ir³⁺ Complexes: Their Synthesis, Structure, and Optical Spectroscopic Properties

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The synthesis of the facial tris cyclometalated complexes *fac*-[Rh(ppy)₃] (ppyH = 2-phenylpyridine), *fac*-[Ir(ppy)₃], and *fac*-[Ir(thpy)₃] (thpyH = 2-(2-thienyl)pyridine) by a generalized method is described. The conformation of the complexes is discussed on the basis of the ¹H NMR spectra, and for *fac*-[Ir(thpy)₃] the room-temperature crystal structure is presented: chemical formula C₂₇H₁₈N₃S₃Ir, cubic, space group *Pa* $\bar{3}$, *Z* = 8, *a* = 16.872(4) Å, *V* = 4803(3) Å³. The excited-state properties are investigated by absorption, luminescence, and luminescence line-narrowing spectroscopy in different media. The lowest excited states of *fac*-[Rh(ppy)₃] and *fac*-[Ir(thpy)₃] embedded in poly(methyl methacrylate) (PMMA) correspond to ligand-centered ³π-π* transitions at 21 500 and 18 340 cm⁻¹, respectively, whereas for *fac*-[Ir(ppy)₃] a metal to ligand charge-transfer (³MLCT) lowest excited state is found. Evidence for a mixing of charge-transfer character into the ³π-π* lowest excited states is provided by the short luminescence decay times.

1. Introduction

Cyclometalated 4d⁶ and 5d⁶ transition metal complexes with aromatic ligands are considered to be suitable systems for photoreduction processes, because the σ-donor and π-acceptor properties of the ligands give rise to low-lying metal to ligand charge-transfer (MLCT) states. The MLCT character of the lowest excited state is supposed to be highest with the maximum number of metal–C σ-bonds;¹ therefore, the preparation of complexes with a maximum number of coordinating C atoms is aimed for. With chelating aromatic ligands Rh³⁺ and Ir³⁺ preferentially form bis cyclometalated complexes.^{1–13} A number of tris cyclometalated Rh³⁺ and Ir³⁺ complexes with phosphine ligands were prepared quite some time ago,¹⁴ but the π-back-bonding to the phosphine ligands moves the MLCT states up in energy.¹⁵ Therefore, for a long time *fac*-[Ir(ppy)₃] (ppyH = 2-phenylpyridine), which was obtained as a side product in the synthesis of [Ir(ppy)₂Cl]₂, was the only member of the class of tris cyclometalated compounds with a promising photoactivity.^{1,15}

Subsequently a new synthetic route resulted in tris cyclometalated Ir³⁺ complexes with substituted 2-phenylpyridine in high yield.¹⁶ Unfortunately this preparative method failed for Rh³⁺ and for other cyclometalating ligands. Only very recently the first synthesis of *mer*-[Rh(ppy)₃] and *mer*-[Ir(ppy)₃] as well as some other tris cyclometalated complexes was reported.¹⁷

In the following we present a general preparative method for facial tris cyclometalated Rh³⁺ and Ir³⁺ complexes, which enabled us to synthesize the facial isomers *fac*-[Rh(ppy)₃] and *fac*-[Ir(ppy)₃] and also the novel tris cyclometalated compound *fac*-[Ir(thpy)₃] (thpyH = 2-(2-thienyl)pyridine). The molecular structure of these complexes is discussed on the basis of ¹H NMR spectra, and their excited states are characterized with the aid of absorption, luminescence, and luminescence line-narrowing spectra. The crystal structure of *fac*-[Ir(thpy)₃] is determined and compared with the structures of related complexes.

2. Experimental Section

2.1. Synthesis and Sample Preparation. *fac*-[Ir(ppy)₃] (ppyH = 2-Phenylpyridine). The synthesis of this complex has been described in the literature,^{1,15,16} but the complex can also be obtained in a 75% yield with respect to [Ir(ppy)₂Cl]₂ by following the method given below for *fac*-[Ir(thpy)₃]. Single crystals were grown by dissolving the complex in acetonitrile (Merck, pa) followed by vapor-phase solvent exchange of acetonitrile by methanol (Merck, pa) in a desiccator.

fac-[Ir(thpy)₃] (Hthpy = 2-(2-thienyl)pyridine). The pulverized starting materials [Ir(thpy)₂Cl]₂ (110 mg ▲ 0.1 mmol; synthesized as described in ref 12), AgCF₃SO₃ (53 mg ▲ 0.2 mmol; Fluka, purum) and thpyH (1.5 g ▲ 30 times molar excess; Lancaster Synthesis) were combined in a 25-mL bulb. The reaction mixture was slowly heated in an argon atmosphere to 110 °C and refluxed at this temperature under permanent stirring for 24 h. After the mixture was cooled to room temperature, excess ligand was extracted with degassed ethanol (Merck, pa) and the residual was collected on a porcelain filter frit, redissolved in degassed

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dichloromethane (Merck, pa), and flash chromatographed over silica gel. The solvent was evaporated under reduced pressure, and the resulting raw product was chromatographed over Sephadex LH 20 (Pharmacia) with an 1:1 v/v mixture of degassed tetrahydrofuran/dichloromethane as eluent. The progress of the chromatography was monitored by absorption spectroscopy. The tris cyclometalated complex is found in the early fractions, whereas the later fractions consist of nonreacted dimer. Fractions with identical absorption spectra were combined, the solvent was removed by distillation under reduced pressure, and the product was dried under vacuum to yield 80 mg (58% with respect to $[\text{Ir}(\text{thpy})_2\text{Cl}]_2$) of $\text{fac-}[\text{Ir}(\text{thpy})_3]$ as an orange powder. Single crystals were grown by dissolving the complex in tetrahydrofuran (Merck, pa) followed by vapor-phase solvent exchange with methanol. $\text{fac-}[\text{Ir}(\text{thpy})_3]$ crystallizes as orange-red octahedra.

$\text{fac-}[\text{Rh}(\text{ppy})_3]$. The starting materials $[\text{Rh}(\text{ppy})_2\text{Cl}]_2$ (100 mg), AgCF_3SO_3 (58 mg), and ppyH (1.2 g, Lancaster Synthesis) were reacted as described above for $\text{fac-}[\text{Ir}(\text{thpy})_3]$. After completion of the reaction excess ligand was removed by vacuum distillation ($p \approx 10^{-2}$ mbar). The residuals were dissolved in dichloromethane and flash chromatographed over silica gel. The chromatographed solution was concentrated by evaporation of the solvent under reduced pressure to a total volume of a few milliliters, and then 5 mL of degassed methanol was added to initiate precipitation. After evaporation of the solvent the raw product was purified as described for $\text{fac-}[\text{Ir}(\text{thpy})_3]$ to yield 5.1 mg (4%) of $\text{fac-}[\text{Rh}(\text{ppy})_3]$ as a yellowish powder.

The complexes were embedded in poly(methyl methacrylate) (PMMA) by dissolving the compounds in dichloromethane and adding this solution to a solution of 8% PMMA in dichloromethane. Glasses were obtained by slow evaporation of the solvent. Doped crystals were prepared by dissolving the host and guest complex together in tetrahydrofuran followed by cocrystallization of the complexes by slow solvent exchange with methanol.

2.2. NMR Measurements and X-ray Structure Determination. All products were characterized by ^1H NMR spectroscopy and powder X-ray diffraction. ^1H NMR spectra were obtained on a Bruker AC-300 FT NMR spectrometer with dichloromethane- d_2 (99.7%, Chemische Fabrik Uetikon) as solvent.

For the structure determination of $\text{fac-}[\text{Ir}(\text{thpy})_3]$ a single crystal with dimensions of $0.45 \times 0.35 \times 0.45$ mm was chosen. Preliminary precession photographs served to determine the space group. Intensity parameters were measured at room temperature on an Enraf-Nonius CAD-4 diffractometer. The stability of the crystal was monitored during data collection by measuring the intensities of three standard reflexions every 120 min. During data collection an intensity variation of 0.01%/h was noted. Intensities were corrected for extinction and absorption, but no decay correction was applied. Absorption coefficients were determined empirically based on ψ -scans, and transition factors ranging from 81.36% to 99.86% with an average of 91.82% were calculated with the SDP package.¹⁸ The cell parameters were calculated from 25 reflections in the range $9.3^\circ < \theta < 14.6^\circ$. Details of the X-ray structure determination are listed in Table 1.

The structure was solved by heavy-atom methods using the SHELX76¹⁹ program system. Hydrogen atoms were fixed at idealized positions ($d(\text{C}-\text{H}) = 0.95 \text{ \AA}$) with an overall refined isotropic displacement parameter. Non-hydrogen atoms were refined by full-matrix least squares. The Ir parameters were restrained to $x = y = z$, $U_{11} = U_{22} = U_{33}$, and $U_{12} = U_{13} = U_{23}$ due to the special position on a 3-fold axis. The refinement converged by minimizing $\sum w(|F_o| - |F_c|)^2$. No unusual bond distances, angles, or displacement parameters were found. Experimental details of the structure determination as well as bond lengths, bond angles, and thermal parameters are available as supplementary material.

2.3. Optical Spectroscopy. Absorption spectra of solutions were recorded in a fused silica cell on a Hewlett Packard 8452A diode array spectrophotometer. Room-temperature luminescence spectra were measured on a commercial spectrofluorometer (Spex FluoroMax) which was equipped with a Hamamatsu R928 side window photomultiplier (PM) tube. For low-temperature measurements the samples were cooled with the helium gas flow tube technique.²⁰ For the low-temperature luminescence spectra the samples were generally excited with suitable lines

Table 1. Crystallographic Parameters and Refinement Results for $\text{fac-}[\text{Ir}(\text{thpy})_3]$

formula	$\text{C}_{27}\text{H}_{18}\text{N}_3\text{S}_3\text{Ir}$
fw	672.88
space group	$P\bar{a}3$
a (Å)	16.872(4)
V (Å ³)	4803(3)
Z	8
ρ_{calc} (g/cm ³)	1.861
ρ_{obs} (g/cm ³)	1.8 (pycnometric method)
data colln temp (K)	295
radiation (λ , Å)	Mo $K\alpha$ (0.710 69)
monochromator	graphite
μ (cm ⁻¹)	56.03
R^a	0.0212
R_w^a	0.0255

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|. R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}; w = 1.686 / [\sigma^2(F + 0.000074F^2)].$$

of a Spectra Physics 2045 argon ion laser. Selective excitation was achieved with a Spectra Physics 375 jet dye laser, operating with coumarine 6 (Radiant Dyes) in ethylene glycol and pumped by the 488-nm line of the argon ion laser. The wavelength of the dye laser output was measured with a Burleigh jr wavemeter and tuned with an intracavity three-plate birefringent filter. The luminescence was dispersed in a 0.85-m Czerny-Turner double monochromator (Spex 1402), using gratings blazed at 500 nm with 1200 grooves/mm, and detected by a cooled RCA 31034 end window PM tube connected to a Stanford Research SR 400 photon-counting system. Luminescence lifetimes were determined by chopping the exciting light with a Coherent 305D digital modulation system driven by a Wavetek 802 pulse generator and recording the luminescence decay curves with the RCA 31034 end window PM tube connected via a Stanford Research SR 440 preamplifier to a Stanford Research SR430 multichannel scaler. For monochromator control and data acquisition a 286 DOS computer was used. With this set-up a resolution of 2 cm⁻¹, an accuracy of about ± 3 cm⁻¹ in energy, and a time resolution of typically 0.1 μs could be achieved.

3. Results

3.1. Crystal and Molecular Structure. The ^1H NMR spectra of the three complexes are displayed in Figure 1. The spectrum of $[\text{Rh}(\text{ppy})_3]$ shows two single resonances at 7.58 and 7.95 ppm vs tetramethylsilane (TMS) and two groups of resonances, one between 6.75 and 7 ppm and one at 7.7 ppm, which correspond to a subset of four and two coupled spins, respectively. Therefore the overall spectrum can be assigned to a set of eight coupled spins. The spectrum of $[\text{Ir}(\text{ppy})_3]$ is very similar, and the resonance frequencies almost coincide. The resonance feature at highest field has now split into two groups of two spins, but the overall spectrum still agrees with a set of eight coupled spins. The resonance pattern of $\text{fac-}[\text{Ir}(\text{thpy})_3]$ is distinctively different. There are three single resonances observed at 6.34, 6.78, and 7.21 ppm vs TMS and a set of three spins around 7.5 ppm vs TMS, which accounts for a total of six coupled spins.

$\text{fac-}[\text{Ir}(\text{thpy})_3]$ crystallizes in the cubic space group $P\bar{a}3$, $Z = 8$, and $a = 16.872(4) \text{ \AA}$. Additional crystallographic parameters are included in Table 1, and the atomic positional parameters are listed in Table 2. The molecular structure of the complex with the atomic numbering is shown in Figure 2. Hydrogen atoms are omitted for clarity. The ligands are found in a facial arrangement, leading to a 3-fold symmetry axis of the complex. This molecular symmetry axis is maintained in the crystal. All eight Ir atoms of the unit cell are crystallographically equivalent (Wyckoff position 8c), and the same holds for the 24 thpy⁻ ligands. Therefore only one type of Ir-C bond length (2.006 Å) and one type of Ir-N distance (2.135 Å) are observed.

Powder X-ray diffraction patterns show that $\text{fac-}[\text{Rh}(\text{ppy})_3]$ and $\text{fac-}[\text{Ir}(\text{ppy})_3]$ crystallize in an isomorphous structure, which, however, is different from the structure of $\text{fac-}[\text{Ir}(\text{thpy})_3]$. Single crystals of $\text{fac-}[\text{Ir}(\text{ppy})_3]$ show between crossed polarizers always extinctions for light traveling along one of the three crystal axes, indicating that the crystal system is uniaxial.

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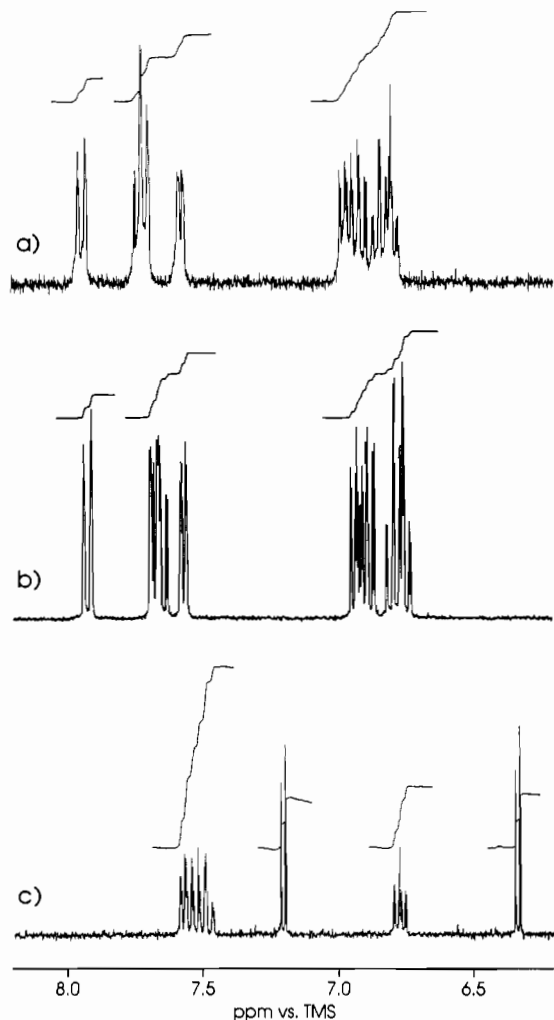


Figure 1. ¹H NMR spectra of *fac*-[Rh(ppy)₃] (a), *fac*-[Ir(ppy)₃] (b), and *fac*-[Ir(thpy)₃] (c) in CD₂Cl₂, displayed in ppm vs tetramethylsilane (TMS).

Table 2. Atomic Positional Coordinates and Isotropic Equivalent Displacement Parameters for *fac*-[Ir(thpy)₃]

atom ^a	x/a	y/b	z/c	U _{eq} ^b (Å ²)
Ir	0.37518(1)	0.37518(1)	0.37518(1)	0.03521(6)
S	0.4147(1)	0.4344(1)	0.1199(1)	0.0567(5)
N	0.3930(3)	0.4974(3)	0.3476(3)	0.036(1)
C ₁	0.4074(4)	0.5133(4)	0.2689(4)	0.036(1)
C ₂	0.4182(4)	0.5900(4)	0.2434(4)	0.047(1)
C ₃	0.4157(4)	0.6515(4)	0.2948(5)	0.056(3)
C ₄	0.4009(4)	0.6370(4)	0.3730(4)	0.054(1)
C ₅	0.3894(4)	0.5604(4)	0.3977(4)	0.044(1)
C ₆	0.4051(4)	0.4417(4)	0.2219(4)	0.038(1)
C ₇	0.3909(3)	0.3688(4)	0.2575(3)	0.037(1)
C ₈	0.3864(4)	0.3067(4)	0.1998(4)	0.048(1)
C ₉	0.3992(4)	0.3326(5)	0.1255(4)	0.062(3)
H ₂	0.4277	0.6000	0.1888	0.055(9)
H ₃	0.4241	0.7041	0.2767	0.055(9)
H ₄	0.3986	0.6795	0.4099	0.055(9)
H ₅	0.3785	0.5510	0.4521	0.055(9)
H ₈	0.3758	0.2529	0.2127	0.055(9)
H ₉	0.3995	0.2987	0.0805	0.055(9)

^a The atoms are numbered as shown in Figure 1. The hydrogen atoms are numbered as the carbon atoms to which they are bonded. ^b Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

3.2. Absorption and Luminescence Spectra. The absorption spectra of the three complexes in CH₂Cl₂ at room temperature are shown in Figure 4. All spectra show essentially the same features: an intense band in the UV and a broad band reaching into the visible region. The spectra of *fac*-[Rh(ppy)₃] and *fac*-

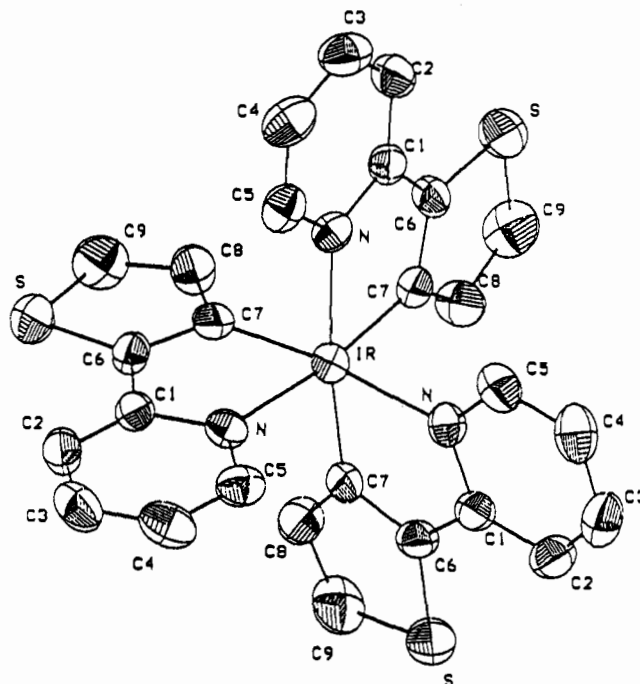


Figure 2. View of the molecular structure of *fac*-[Ir(thpy)₃] along the 3-fold axis with atomic numbering and thermal ellipsoids representing a 50% probability density (295 K).

[Ir(ppy)₃] are almost identical. In both spectra the intense band ($\epsilon \approx 29\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) is centered at $35\,200 \text{ cm}^{-1}$, and the absorption maxima of the broad bands ($\epsilon \approx 8\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) at $27\,300 \text{ cm}^{-1}$ (Rh³⁺) and $26\,500 \text{ cm}^{-1}$ (Ir³⁺) are quite close in energy. A distinguishing feature between the two spectra is the onset of the low-energy absorption. The broad band of *fac*-[Rh(ppy)₃] starts at about $23\,500 \text{ cm}^{-1}$, whereas in *fac*-[Ir(ppy)₃] there are some features down to $20\,000 \text{ cm}^{-1}$. The spectrum of *fac*-[Ir(thpy)₃] can be easily distinguished from the spectra of the complexes with ppy⁻ ligands. All the bands are more intense, and the band in the UV ($\epsilon = 40\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) has red shifted to $33\,300 \text{ cm}^{-1}$. However, the low energy band at $26\,000 \text{ cm}^{-1}$ ($\epsilon \approx 16\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) is found at a similar energy as in the other two complexes, and it also extends into the visible region, accounting for the orange-red color of the crystals.

The luminescence spectra of the complexes in PMMA are displayed in Figure 5. At room temperature *fac*-[Rh(ppy)₃] shows a structured band. The first and second maximum at $21\,400$ and $20\,100 \text{ cm}^{-1}$, respectively, are roughly equally intense. At 9 K the structure is much more pronounced, and the first maximum, which is now clearly more intense than the other maxima, has slightly shifted up in energy to $21\,530 \text{ cm}^{-1}$.

The luminescence spectrum of *fac*-[Ir(ppy)₃] at room temperature consists of a broad, asymmetric band with its intensity maximum at $19\,600 \text{ cm}^{-1}$. Lowering the temperature to 9 K leads to the appearance of a new band at $22\,000 \text{ cm}^{-1}$, whereas the shape and energy of the broad band are hardly affected by the decrease in temperature.

The structured luminescence band of *fac*-[Ir(thpy)₃] is red shifted by about 3000 cm^{-1} with respect to the ppy⁻ samples, and the first maximum at $18\,340 \text{ cm}^{-1}$ carries most of the intensity, both at room temperature and at 9 K . Temperature variation has the least effect on this band. At low temperature the structure is better resolved, but no change in the band energy or band shape could be observed.

fac-[Ir(thpy)₃] has also been doped in low concentration (1%) into the crystal lattice of *fac*-[Ir(ppy)₃]. The resulting spectrum with excitation in the UV is essentially the same as the one in PMMA at low temperature. The bands are just a little narrower, and the dominant band carries a larger amount of the total intensity.

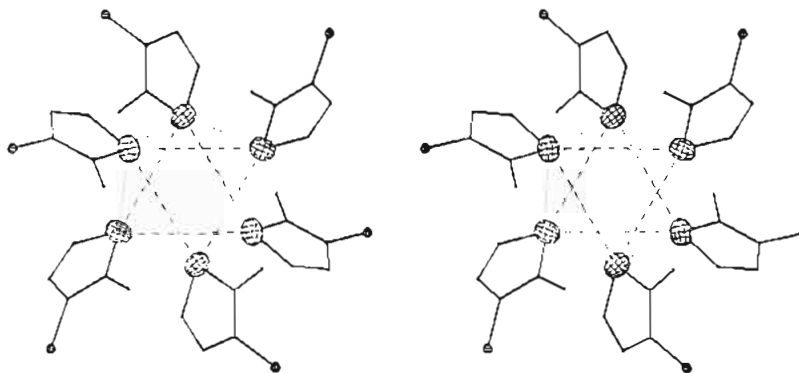


Figure 3. Clustering of six thienyl rings around a point of $\bar{3}$ symmetry. Nonbonded distances in the S_6 -hexagon (---) are 3.596(3) Å. C6-S...S angles are 169.3° (compare Figure 2). Nonbonded distances in the two S_3 -triangles (- - -) are 4.075(3) Å. Sulfur atoms are shown as large ellipsoids, and iridium atoms as small ones.

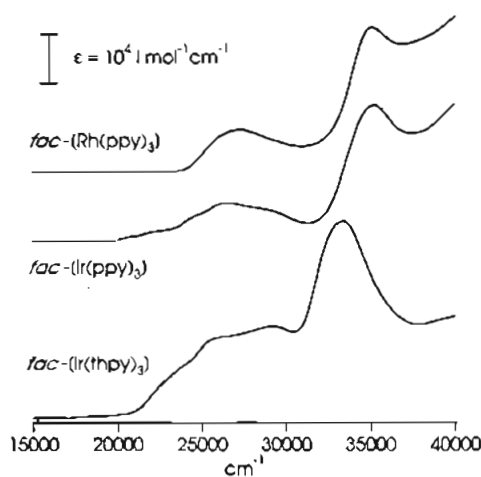


Figure 4. Absorption spectra of *fac*-[Rh(ppy)₃], *fac*-[Ir(ppy)₃], and *fac*-[Ir(thpy)₃] in CH₂Cl₂ at ambient temperature.

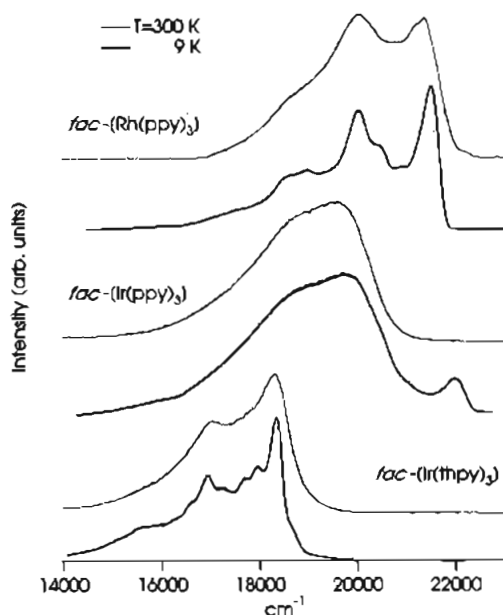


Figure 5. Luminescence spectra of *fac*-[Rh(ppy)₃], *fac*-[Ir(ppy)₃], and *fac*-[Ir(thpy)₃] in poly(methyl methacrylate) (PMMA) at $T = 9$ K (—) and at ambient temperature (---).

The luminescence bands are inhomogeneously broadened due to a distribution of sites in the PMMA or to disorder phenomena in the crystalline sample. By application of the luminescence line-narrowing (LLN) technique,²¹ the bandwidth can be drastically reduced and the vibrational sidebands can be resolved. After selective excitation into the origin at 21 345 cm⁻¹ the spectrum

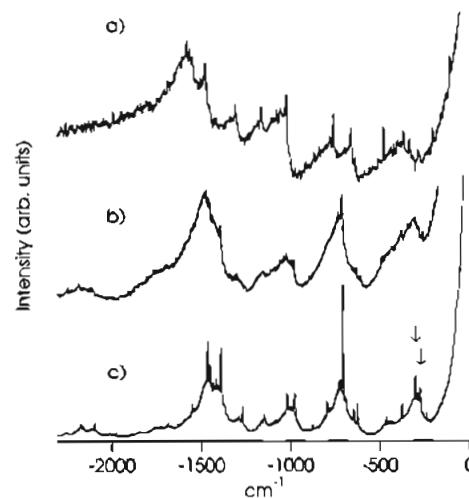


Figure 6. Luminescence line-narrowing spectra at $T = 8$ K of *fac*-[Rh(ppy)₃] in PMMA (a), *fac*-[Ir(thpy)₃] in PMMA (b), and *fac*-[Ir(thpy)₃] doped into the crystal lattice of *fac*-[Ir(ppy)₃] (c). The arrows in spectrum c mark metal–ligand vibrations.

of *fac*-[Rh(ppy)₃] at 8 K is partially narrowed to sharp lines (Figure 6, top trace), the vibrational pattern of which is similar to the one of the LLN spectra of the bis cyclometalated complexes [Rh(ppy)₂bpy]⁺ and [Rh(ppy)₂cn]⁺.^{22,23} The luminescence spectrum of *fac*-[Ir(ppy)₃] shows no narrowing after selective excitation into the origin at 21 833 cm⁻¹, but the spectra of *fac*-[Ir(thpy)₃], imbedded in PMMA and doped into *fac*-[Ir(ppy)₃], respectively, both show resolved vibrational structure after laser excitation at 18 345 and 18 208 cm⁻¹, respectively (Figure 6, bottom traces). The main sharp features of both spectra are very similar and match again the LLN patterns of the bis cyclometalated Rh³⁺ and Ir³⁺ complexes [M(thpy)₂bpy]⁺ and [M(thpy)₂en]⁺, M = Rh³⁺ and Ir³⁺.^{12,22–24} The narrowing effect in the crystalline sample is much more pronounced than in PMMA. The arrows in the LLN spectrum of *fac*-[Ir(thpy)₃] doped into *fac*-[Ir(ppy)₃] shown in Figure 6 mark metal–ligand vibrations.

The luminescence decay curves of all three complexes show small deviations from single exponential behavior in crystalline as well as glassy media. By fitting them with single exponentials, one can obtain average luminescence lifetimes. For *fac*-[Rh(ppy)₃] a luminescence lifetime of 46 μs at 77 K results. The luminescence lifetimes of the Ir³⁺ complexes are strongly

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Table 3. Comparison of the Metal–Carbon and the Metal–Nitrogen Bond Lengths (Å) of *fac*-[Ir(thpy)₃] and Related Ir³⁺ and Rh³⁺ Complexes

compd	coord sphere	M–C	M–N _{cis}	M–N _{trans}	ref
[Ir(bpy) ₃](ClO ₄) ₃ ·2 ¹ / ₃ H ₂ O	IrN ₆		2.021(5) ^a		25
[Ir(bpy) ₂ (bpy)-C ³ ,N ⁵](ClO ₄) ₂ · ¹ / ₃ H ₂ O	IrN ₅ C	1.980(6)	2.054(5) ^a	2.131(5)	26
<i>fac</i> -[Ir(4-CH ₃ -ppy) ₃]	IrN ₃ C ₃	2.024		2.132	15
<i>fac</i> -[Ir(thpy) ₃]	IrN ₃ C ₃	2.006(6) ^a		2.135(5) ^a	
[Rh(bpy) ₃]Cl ₃	RhN ₆		2.036(1) ^a		27
[Rh(phpy)(bpy) ₂](PF ₆) ₂	RhN ₅ C		2.043(3) ^b		28
[Rh(phpy) ₂ (bpy)]PF ₆	RhN ₄ C ₂	1.992(3) ^a	2.039(2) ^a	2.142(2) ^a	29
[Rh(thpy) ₂ (bpy)]Cl·2 ¹ / ₈ H ₂ O	RhN ₄ C ₂	1.989(5) ^a	2.060(5) ^a	2.142(4) ^a	11

^a Mean values with their estimated deviations, $\sigma(d) = \{[\sum(d_i - \langle d \rangle)^2] / m(m - 1)\}^{1/2}$, in parentheses. ^b The structure of [Rh(phpy)(bpy)₂](PF₆)₂ is disordered. Therefore, only a mean value for the Rh–X (X = C, N) bond length is given.

temperature dependent. They increase from 5 μs at 77 K to 90 μs at 5 K for *fac*-[Ir(ppy)₃] and from 5 μs at 50 K to 22 μs at 10 K for *fac*-[Ir(thpy)₃].

4. Discussion

4.1. Structural Considerations. The ¹H NMR spectra of our complexes indicating a set of eight coupled spins in the case of *fac*-[Rh(ppy)₃] and *fac*-[Ir(ppy)₃] and a set of six coupled spins in the case of *fac*-[Ir(thpy)₃], respectively, are only compatible with a facial arrangement of the ligands, in which the three ligands are magnetically equivalent due to the 3-fold symmetry axis of the molecule. In a meridional configuration of the ligands their protons would be magnetically inequivalent, which would lead to a set of 24 coupled spins or 18 coupled spins for the ppy⁻ or thpy⁻ complexes, respectively.

The crystal structure determination of [Ir(thpy)₃] confirms the facial arrangement of the three ligands as derived from NMR spectra. All nitrogen atoms are therefore trans to carbon atoms. It is remarkable that starting from a dimer in which the coordinating carbons are trans to the chloro bridge, a facial tris cyclometalated complex is obtained. Intuitively the formation of the meridional isomer would be expected in such a reaction.¹⁵ Due to the trans influence of the cyclometalating carbons the metal–nitrogen distance of 2.135(5) Å is about 0.1 Å longer than the metal–nitrogen bond length for IrN₆ coordination.²⁵ A trans influence of the same order is generally observed for related compounds (Table 3).^{11,15,26–29} The molecular packing shows six thienyl rings clustered around a point with $\bar{3}$ symmetry. The sulfur π-electrons of each thienyl ring are oriented in the direction of the S–C bond (σ*-orbital) of the neighboring thienyl ring (Figure 3), a favorable orientation for nucleophile–electrophile contacts between the S atoms.³⁰ The S···S distance is 3.596(3) Å, and the S···S–C angle is 169.3°. This has to be compared to the second set of distances and angles, which do not show this orientation preference, S···S distance = 4.075(3) Å and S···S–C angles = 93.3 or 110.5°, respectively.

4.2. Nature of the Lowest Excited States. On the basis of their intensity and spectral positions, which correspond approximately to the ones of the free protonated ligands, the intense absorption bands around 35 000 cm⁻¹ can be assigned to spin-allowed ¹π–π* transitions on the cyclometalating ligands. The broad absorption bands at lower energy are typical for spin-allowed metal to ligand charge-transfer (¹MLCT) transitions, as has been extensively discussed for analogous bis cyclometalated complexes.^{7,12,24,31,32} The weaker absorption features reaching

into the visible region and only observed for the Ir³⁺ complexes are assigned to the corresponding formally spin-forbidden ³MLCT transitions. They get intensity by mixing with higher lying spin-allowed transitions through spin–orbit coupling. Because of the larger spin–orbit coupling constant of Ir³⁺ the corresponding ³MLCT bands are more intense for Ir³⁺ than for Rh³⁺. Of course *fac*-[Rh(ppy)₃] also shows ³MLCT as well as ³π–π* states in the spectral gap between the ¹MLCT band at 27 300 cm⁻¹ and the luminescence band at 21 400 cm⁻¹, but the transitions to these states are very weak and inhomogeneously broadened, so that they are barely observable in the solution absorption spectra.

Despite the similarity of their absorption spectra the luminescence band shapes and energies of the three complexes are quite different. This indicates that their lowest excited states are of a different nature. The structured luminescence band of *fac*-[Ir(thpy)₃] occurs at a comparable spectral position and has a similar shape to the luminescence bands of [Ir(thpy)₂bpy]⁺¹² and [Ir(thpy)₂en]⁺,²⁴ which have been attributed to ³π–π* transitions on the thpy⁻ ligand. In analogy we assign the lowest excited state of *fac*-[Ir(thpy)₃] to a ³π–π* transition on the thpy⁻. An analogous argument can be used to assign the bands of the luminescence spectrum of *fac*-[Ir(ppy)₃]. The dominant broad band with its maximum at 19 600 cm⁻¹ matches nicely the one of [Ir(ppy)₂en]⁺ in CH₂Cl₂ solution,²⁴ which was ascribed to an Ir → ppy⁻ ³MLCT transition. Therefore the lowest excited state of *fac*-[Ir(ppy)₃] in PMMA at room temperature may be identified as ³MLCT excitation to the ppy⁻. The occurrence of an additional, somewhat more narrow band at 22 000 cm⁻¹ in the low-temperature spectrum indicates that at low temperature there are two different luminescent states. The same phenomenon was observed for [Ir(ppy)₂bpy]⁺³² and [Ir(ppy)₂en]⁺²⁴ and was explained by two excited states lying close to each other, one ³π–π* and one ³MLCT in nature. The energy of the latter is much more dependent on the viscosity of the surrounding than the former. By a lowering of the temperature, the rigidity of the medium is increased and the ³MLCT moves up in energy. This can be nicely followed by the rigidochromic band shifts. At some stage the ³MLCT state will cross the ³π–π* state, which will then become the emitting state at 10 K. Due to the broad inhomogeneous distribution of sites in the glass, there are complexes on either side of the crossing point. As a result, a superposition of the two types of luminescences is observed. With this argument we may assign the band at 22 000 cm⁻¹ to a ³π–π* (ppy⁻) luminescence, which lies close to the origin of the corresponding ³MLCT luminescence.

On the basis of its low-temperature luminescence band shape and band energy, an assignment of the lowest excited state of *fac*-[Rh(ppy)₃] to a ³π–π* excitation on the ppy⁻ seems most probable. At room temperature the intensity distribution is different, and a contribution from a weak broad ³MLCT band cannot be excluded. The assignment of the lowest excited states of *fac*-[Rh(ppy)₃] and *fac*-[Ir(thpy)₃] to ³π–π* excitations is supported by the luminescence line-narrowing spectra. Only π–π* transitions can be substantially narrowed by site-selective excitation, whereas the selectivity of the excitation process is reduced in the case of ³MLCT transitions.²⁴ The vibrational sideband

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pattern of the luminescence line-narrowing spectra is very characteristic for each type of ligand. In mixed-ligand complexes this fact has been used to identify the active ligand, i.e. the ligand on which the excitation is localized.^{22,23} Additionally, the mixing of charge-transfer character into the $^3\pi-\pi^*$ states is reflected in the observation of metal–ligand vibrations in the sideband pattern.^{12,32} In the narrowed luminescence spectrum of *fac*-[Ir(thpy)₃] doped into *fac*-[Ir(ppy)₃] these metal–ligand sidebands are readily observed. Evidence for a considerable mixing of the $^3\pi-\pi^*$ states with close-lying MLCT states is also provided by the luminescence lifetimes. For *fac*-[Ir(ppy)₃] a near-unity luminescence quantum yield at 77 K has been estimated,¹⁵ and the study of similar bis cyclometalated complexes confirmed the high quantum yields of these systems at low temperatures.^{12,24} Therefore, the lifetimes are essentially radiative, and the mixing between $^3\pi-\pi^*$ and MLCT states is directly reflected in a decrease of the luminescence lifetimes. The lifetime of *fac*-[Ir(thpy)₃] doped into *fac*-[Ir(ppy)₃] at 10 K is 22 μ s, i.e. the same order of magnitude as in [Ir(thpy)₂bpy]⁺¹² and [Ir(thpy)₂en]⁺,²⁴ where a strong mixing between the states has been reported. The lifetime of 45 μ s at 77 K of *fac*-[Rh(ppy)₃] in PMMA is the shortest radiative lifetime reported for a $^3\pi-\pi^*$ transition of a Rh³⁺ complex so far. At the same temperature [Rh(ppy)₂bpy]⁺ has a lifetime of 170 μ s.³¹ Since the degree of mixing between a ¹MLCT and a $^3\pi-\pi^*$ state depends upon their energy separation, this can be taken as a confirmation of the rule that the MLCT transitions are lowered in energy with an increasing number of carbon atoms bonded to the metal. However, when this rule is applied to mixed-ligand complexes, a combination of the donor–acceptor properties and singlet–triplet splittings of the individual ligands has to be considered. [Ir(thpy)₂bpy]⁺, for example, with only two coordinating carbons has a Ir \rightarrow bpy ³MLCT lowest excited state in CH₂Cl₂ solution at room temperature, whereas *fac*-[Ir(thpy)₃] with its three coordinating carbons still shows a $^3\pi-\pi^*$ emission under these conditions.

The lowering of approximately 3000 cm⁻¹ of the first $^3\pi-\pi^*$ excited states in *fac*-[Ir(thpy)₃] compared to *fac*-[Rh(ppy)₃] is ascribed to two factors. First we note that the ¹ $\pi-\pi^*$ absorption band of *fac*-[Ir(thpy)₃] is also lowered, by approximately 2000 cm⁻¹ (Figure 4). The remaining difference must be due to a

larger singlet–triplet splitting of the $\pi-\pi^*$ excitation in *fac*-[Ir(thpy)₃]. This splitting is determined by electron exchange integrals in the excited $\pi-\pi^*$ configuration. The observed behavior for *fac*-[Ir(thpy)₃] and *fac*-[Rh(ppy)₃] is very similar to the behavior observed for [Ir(ppy)₂bpy]⁺ and [Ir(thpy)₂bpy]⁺, respectively.²⁴

5. Conclusions

The spectroscopic investigation of the tris cyclometalated complexes, which were prepared by a new synthetic method, provides a deeper insight into the nature of the lowest excited state of this class of compounds. The concepts which have been developed previously for the description of the photophysical properties of charged bis cyclometalated complexes are found to be also valid for the neutral tris cyclometalated analogs. With the use of optical spectroscopic methods the $^3\pi-\pi^*$ and ³MLCT excited states lying close in energy can be identified. The short luminescence decay times of the $^3\pi-\pi^*$ lowest excited states as compared to the ones of the free ligands reflect a considerable mixing of charge-transfer character into the nominally $^3\pi-\pi^*$ states. The degree of mixing is determined by the separation of the states involved. Therefore, the significantly shorter lifetimes of the tris cyclometalated Rh³⁺ complex as compared to the ones of similar bis cyclometalated Rh³⁺ complexes support the idea that with an increasing number of coordinating C- atoms the energy of the MLCT states is lowered. The nucleophile–electrophile S...S contacts appear to be an important structural element in *fac*-[Ir(thpy)₃]. The low sublimation points of the title compound predestine them for molecular beam spectroscopy.

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Supplementary Material Available: Experimental details of the structure determination, Tables giving bond distances, bond angles, and anisotropic displacements parameters for non-hydrogen atoms (3 pages). Ordering information is given on any current masthead page.