5512 *Inorg. Chem.* **1997,** *36,* 5512−5517

Synthesis, Crystal Structure, High-Resolution Optical Spectroscopy, and Extended Hückel Calculations for [Re(CO)$_4$(thpy)] (thpy$^-$ = 2-(2-Thienyl)pyridinate). Comparison with Related Cyclometalated Complexes

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Received April 9, 1997[⊗]

We have synthesized the new cyclometalated complex [Re(CO)$_4$(thpy)] (thpy$^-$ = 2-(2-thienyl)pyridinate) and determined the crystal and molecular structure by X-ray diffraction. By application of high-resolution optical spectroscopy to single crystals and glasses at cryogenic temperatures, the first excited state is identified as a nominally ligand-centered $^3\pi-\pi^*$ state with some ^{1}MLCT character mixed in by spin−orbit coupling. The coefficient α describing the charge-transfer character in the wave function of the first excited state has a value of 0.019. This admixture leads to a reduced luminescence lifetime (258 μs at 10 K) and the occurrence of sidebands in the absorption and luminescence spectra which are due to metal−ligand vibrations. The parameters characterizing the first excited state are compared with the corresponding parameters of related cyclometalated and noncyclometalated complexes of Rh(III), Ir(III), and Re(I). An extended Hückel calculation was performed to identify the relevant one-electron excitations.

1. Introduction

The photophysical and spectroscopic properties of 4d^6 and 5d^6 complexes with π-accepting ligands continue to be of interest for various reasons. There is a potential application of such complexes as photocatalyst and as photosensitizers in solar energy conversion devices.[1,2] The substitution of chelating ligands such as 2,2′-bipyridine (bpy) by ligands like 2-phenylpyridine (ppy) and 2-(2-thienyl)pyridine (thpy) which are capable of cyclometalation affects the metal−ligand bonding characteristics.[3] We are interested in the effects of such substitutions on the photophysical and spectroscopic properties. The majority of these complexes are luminescent both in the crystalline state and in solution. The nature of the luminescent first excited state is either a ligand-centered $^3\pi-\pi^*$ (^{3}LC) or a metal-to-ligand charge transfer (^{3}MLCT) state.

High-resolution optical spectroscopy of crystals at cryogenic temperatures is a very powerful technique to investigate the properties of the first excited state. It provides information about vibronic couplings and energy splittings not available from low-resolution spectra of solutions and glasses. By the additional application of the luminescence line-narrowing (LLN) technique, high-resolution spectra of diluted samples in glasses can also be obtained.

In the past we have investigated complexes of the type [Rh(C-N)$_2$(N-N)]$^+$ and [Ir(C-N)$_2$(N-N)]$^+$, where (C-N) stands for ppy$^-$ or thpy$^-$ and (N-N) for bpy or en (=ethylenediamine).[4,5] The lowest energy excited state of all these complexes is a ^{3}LC state with some charge transfer character mixed in through spin−orbit coupling. This was deduced from the reduced luminescence lifetime compared to that of the free ligand and the orientation and the magnitude of the transition moment in single-crystal absorption spectra as well as the presence of vibrational sidebands in the highly resolved absorption and emission spectra which are due to metal−ligand vibrations. In a complex of the type [Re(CO)$_4$(C-N)] presented here, the situation is simplified by the presence of only one chelating ligand. The properties of [Re(CO)$_4$(ppy)] and [Re(CO)$_4$(bpy)]$^+$ have been described in refs 6 and 7.

In the present paper, we describe the synthesis, the crystal structure determined by X-ray diffraction, and the excited-state properties of [Re(CO)$_4$(thpy)]. The latter were determined by high-resolution crystal absorption spectroscopy and luminescence spectroscopy, including LLN, as well as lifetime measurements. The relevant one-electron excitations can be identified by an extended Hückel calculation. The excited-state properties are finally compared with those of other cyclometalated 4d^6 and 5d^6 complexes.

2. Experimental Section

2.1. Synthesis and Characterization. The crystals of [Re(CO)$_4$(thpy)] were prepared by a method analogous to the synthesis and crystallization of [Re(CO)$_4$(ppy)] described in ref 6 with a small

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

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S0020-1669(97)00415-1 CCC: $14.00

Table 1. Crystallographic Data for [Re(CO)$_4$(thpy)]

empirical formula	$C_{13}H_6NO_4$ ReS
a (Å)	10.64(7)
b (Å)	11.70(13)
c (Å)	12.23(6)
α (deg)	90
β (deg)	110.33(4)
γ (deg)	90
V (Å^3)	1430(20)
Z	4
M_r	458.45
space group	$P2_1/c$
T (K)	293(2)
λ(Mo Kα) (Å)	0.710 69
density (g cm^{-3})	2.132
max and min transm	0.9995 and 0.6991
F(000)	856
R1[a] [$I > 2\sigma(I)$]	0.0260
wR2[b] [$I > 2\sigma(I)$]	0.0534
R1[a] (all data)	0.0600
wR2[b] (all data)	0.0611

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

modification: the washing solution was 1 M HCl instead of 0.35 M. The two largest faces of the orange crystals have a triangular shape. They were used for the crystal absorption spectra. The overall yield was 27%. The elemental analysis performed by Ciba-Geigy gave the following results. Anal. Calcd: C 34.06; H, 1.32; N, 3.06; S, 6.99; O, 13.96. Found: C, 35.07; H, 1.71; N, 3.13; S, 6.76; O, 13.8.

2.2. Crystal Structure Determination. The crystal used for the X-ray structure determination had the dimensions 0.6 × 0.5 × 0.4 mm. An Enraf-Nonius CAD4-diffractometer was used for the data collection. Three standard reflections were measured every 2 h. No intensity decay was observed during the measuring period. An empirical absorption correction was applied. The Patterson interpretation routine of SHELXS86[8a] was used for solving the structure. Hydrogen atoms were fixed at idealized positions (C−H distance = 0.93 Å) with an overall refined isotropic displacement parameter. Non-hydrogen atoms were refined by full-matrix least-squares procedures using the program SHELXL93.[8b]

2.3. Optical and IR Absorption Spectra. Infrared spectra of a 10^{-4} M solution of [Re(CO)$_4$(thpy)] in CH_2Cl_2 and of crystalline [Re(CO)$_4$(thpy)] in a KBr matrix were measured on a Perkin-Elmer 1720X FTIR spectrophotometer.

The polarized optical absorption spectra of a 10^{-4} M CH_2Cl_2 solution and of a single crystal were measured on a Cary 5E spectrophotometer with fixed spectral bandwidths of 2 and 0.07 nm, respectively. The light propagation was perpendicular to the largest crystal face (110). The crystal was cooled in a closed-cycle helium cryostat which has been described before.[7]

2.4. Luminescence Spectra. Luminescence experiments were carried out on polycrystalline samples sealed under He in a quartz capillary and on a 10^{-3} mol/L poly(methyl methacrylate) (PMMA) sample. The samples were cooled in a double-wall helium gas flow tube. The samples were excited by the light from a 150 W Oriel Xe lamp, filtered with a Schott UG11 filter to cut off all visible light from the excitation source, with the 514.5 nm line from a Spectra Physics 2045 argon ion laser for the luminescence line-narrowed spectra or with a PRA LN250 nitrogen laser for the measurement of the luminescence lifetime. The experimental setup has been described in ref 4.

3. Results

3.1. Crystal Structure. Crystallographic data for [Re(CO)$_4$(thpy)] are presented in Table 1 and in the X-ray crystallographic file (see Supporting Information). The large triangular face which was used for the optical absorption experiments is the (110) plane, and the longest edge of the triangle coincides with the crystallographic c axis. The unit cell constants are almost the same as the constants for [Re(CO)$_4$(ppy)]:[6] $a = 10.559(3)$ Å, $b = 11.571(3)$ Å, $c = 12.449(4)$ Å, $\beta = 104.11(3)°$, $Z = 4$.

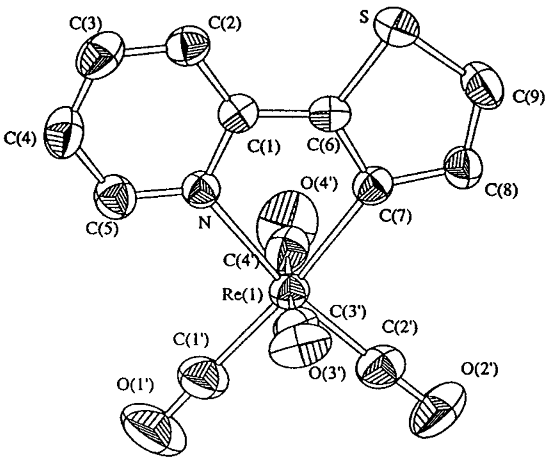

Figure 1. ORTEP plot of a [Re(CO)$_4$(thpy)] molecule (50% probability level for the thermal ellipsoids) with the atomic numbering scheme used for the tables.

The molecular structure is shown in Figure 1. The atomic positional parameters, bond distances and angles, and the anisotropic displacement parameters for all non-hydrogen atoms are given in the X-ray crystallographic file (Supporting Information). The Re−N distance is 0.05 Å longer than the Re−C$^-$ bond. This bond length difference is only 0.024 Å in [Re(CO)$_4$(ppy)],[6] whereas it is 0.071 Å in [Rh(thpy)$_2$(bpy)]Cl•$2^1/_8$$H_2O$[9] and 0.129 Å in [Ir(thpy)$_3$].[10] The bite angle of the title complex is 76.1(5)°, compared to 76.2(2)° for [Re(CO)$_4$(ppy)]. The CO ligands have C−Re−C angles ranging from 90.0 to 92.4°. These angles range from 89.4 to 94.7° for [Re(CO)$_4$(ppy)]. The out-of-plane CO ligands have longer Re−C distances than the in-plane CO ligands (1.907 and 1.954 Å for the in-plane vs 1.98 and 1.99 Å for the out-of-plane). This was also found for [Re(CO)$_4$(ppy)] (1.914 and 1.941 Å vs 1.976 and 1.981 Å). [Re(CO)$_4$(thpy)] is isostructural with [Re(CO)$_4$(ppy)], and mixed crystals can be made.

3.2. IR and Vis Absorption Spectra. The IR spectra of [Re(CO)$_4$(thpy)] in solution and in a KBr pellet in the region of the CO stretch vibrations are shown in Supporting Information Figure 1. The four peaks of the solution spectrum are split in the solid state spectrum in the same way as for [Re(CO)$_4$(ppy)].[6] The reason for this splitting is the same for both compounds, since they are isostructural, with four formula units per unit cell. Two of these are converted into the other two by a glide plane or a screw axis in the space group $P2_1/c$. The spectroscopically relevant unit is thus a dimer of [Re(CO)$_4$(thpy)] molecules. This leads to a doubling of the vibrational transitions, a so-called correlation field splitting.[11] The solid state spectrum of [Re(CO)$_4$(bpy)]PF_6 does not show this splitting (see Supporting Information Figure 1, top) since this complex has a different crystal packing, with only two complexes per unit cell.[7] These are interconverted by an inversion center.

The solution spectrum of [Re(CO)$_4$(thpy)] in the visible and UV part is very similar to the spectra of [Rh(thpy)$_2$(bpy)]$^+$, [Rh(thpy)$_2$(en)]$^+$, [Ir(thpy)$_2$(bpy)]$^+$, and [Ir(thpy)$_2$(en)]$^+$.[5c] It shows

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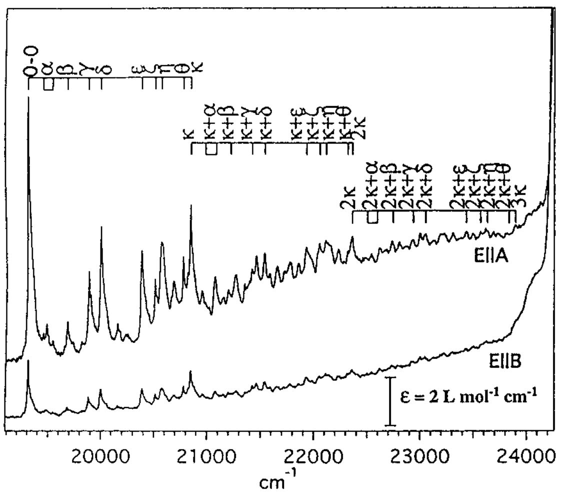

Figure 2. Polarized single-crystal absorption spectra of [Re(CO)$_4$(thpy)] at 10 K. The light propagation is perpendicular to the largest crystal face (110). *A* and *B* are the optical extinction directions of the crystal. Fundamental vibrational sidebands and their combination bands for the $\kappa = 1545$ cm^{-1} mode are indicated.

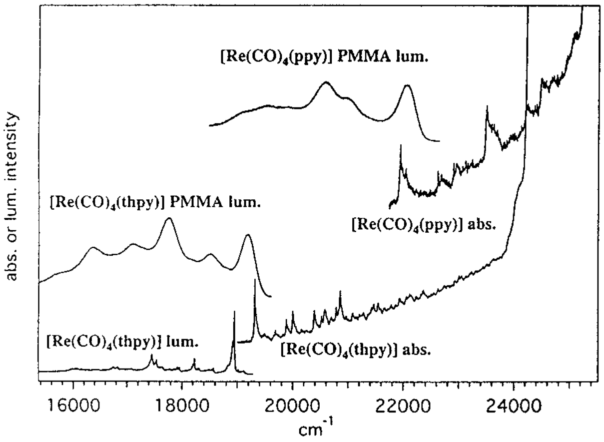

Figure 3. Luminescence spectra of crystalline [Re(CO)$_4$(thpy)] (bottom), of [Re(CO)$_4$(thpy)] dissolved in a PMMA glass (10^{-3} M, middle), and of [Re(CO)$_4$(ppy)] dissolved in a PMMA glass (10^{-3}M, top). The single-crystal absorption spectra (*E*||*B*) of both complexes are given for comparison. The vertical scales are arbitrary. All spectra were measured at 10 K.

band maxima at 26 800 and 34 500 cm^{-1} and a shoulder at 32 500 cm^{-1}.

The polarized single-crystal optical absorption spectrum of [Re(CO)$_4$(thpy)] at 10 K is shown in Figure 2. The light propagation is perpendicular to the (110) plane, and *A* and *B* are the optical extinction directions within this plane. The *B* direction makes an angle of 20° with the crystallographic *c* axis. The intensity ratio *I*(*A*)/*I*(*B*) is around 4.5 throughout the spectrum.

The very rich fine structure originates from vibrational sidebands, overtones, and combination bands of the electronic origin at 19 302 cm^{-1}. The fundamental vibrations ($\alpha-\kappa$) together with the combination bands with κ and 2κ are indicated in Figure 2.

3.3. Luminescence. The luminescence spectra of polycrystalline [Re(CO)$_4$(thpy)] at 10 K is shown in the lowest trace of Figure 3. The spectrum is red-shifted by about 360 cm^{-1} with respect to the absorption origin which is included in Figure 3. The fine structure disappears, the band shape changes, and the luminescence intensity drops dramatically on raising the temperature. This luminescence clearly originates from traps.

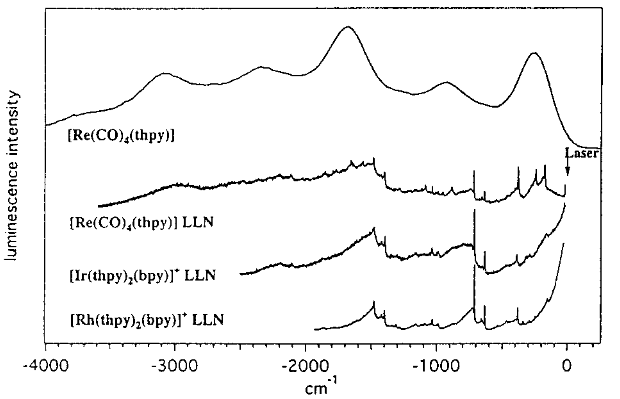

Figure 4. Luminescence line-narrowed (LLN) spectra of [Rh(thpy)$_2$(bpy)]$^+$, [Ir(thpy)$_2$(bpy)]$^+$, and [Re(CO)$_4$(thpy)] in a PMMA glass excited at 18831 cm^{-1} (Rh and Ir) and at 19436 cm^{-1} (Re). The LLN spectra are displayed relative to the exciting laser line. The unnarrowed luminescence spectrum of [Re(CO)$_4$(thpy)] in the PMMA glass, excited with a Xe lamp, is given for comparison. All spectra were measured at 10 K.

The luminescence of a 10^{-3} M [Re(CO)$_4$(thpy)] PMMA glass at 10 K is shown in the middle of Figure 3. It is structured but inhomogeneously broadened in the glass. The single-crystal absorption spectrum of [Re(CO)$_4$(ppy)] and the luminescence of a 10^{-3} M [Re(CO)$_4$(ppy)] PMMA glass at 10 K are displayed for comparison in Figure 3 (top). The electronic origin is moved by about 2600 cm^{-1} to lower energy on going from [Re(CO)$_4$(ppy)] to [Re(CO)$_4$(thpy)].

Laser excitation in the electronic origin sharpens the luminescence of the PMMA sample extremely. This technique is known as luminescence line narrowing (LLN),[12] and the result is shown in Figure 4. The LLN spectra of [Rh(thpy)$_2$(bpy)]$^+$ and [Ir(thpy)$_2$(bpy)]$^{+\ 5c}$ are shown for comparison in the two lowest traces of Figure 4. All three LLN spectra are presented relative to the exciting laser line. They show a remarkable resemblance. The sharp sidebands above 300 cm^{-1} occur at the same energies for the three complexes. The title complex exhibits two additional lines at 173 and 241 cm^{-1} which are not present in the spectra of [Rh(thpy)$_2$(bpy)]$^+$ and [Ir(thpy)$_2$(bpy)]$^+$.

The luminescence decay under pulsed excitation of the PMMA sample is monoexponential and temperature independent in the range between 10 and 100 K with a value $\tau = 258 \pm 5$ μs. When the temperature is raised to 250 K, the lifetime decreases to 144 μs. The luminescence intensity shows a very similar drop between 100 and 250 K. Nonradiative decay processes are obviously responsible for the drop in both intensity and lifetime.

3.4. Extended Hückel Calculations. To obtain some insight into the nature of the spectroscopically relevant orbitals, we carried out an extended Hückel calculation on [Re(CO)$_4$(thpy)]. We made use of the CACAO program by Mealli and Proserpio.[13] The calculation was performed on the basis of the atomic positions found in the crystal structure determination (see section 3.1) with a small modification: the thpy$^-$ ligand was chosen to be completely planar, thus ensuring C_s molecular symmetry.[14] The results of this calculation are shown on the right side of Figure 5. Only the energy level scheme and a pictorial

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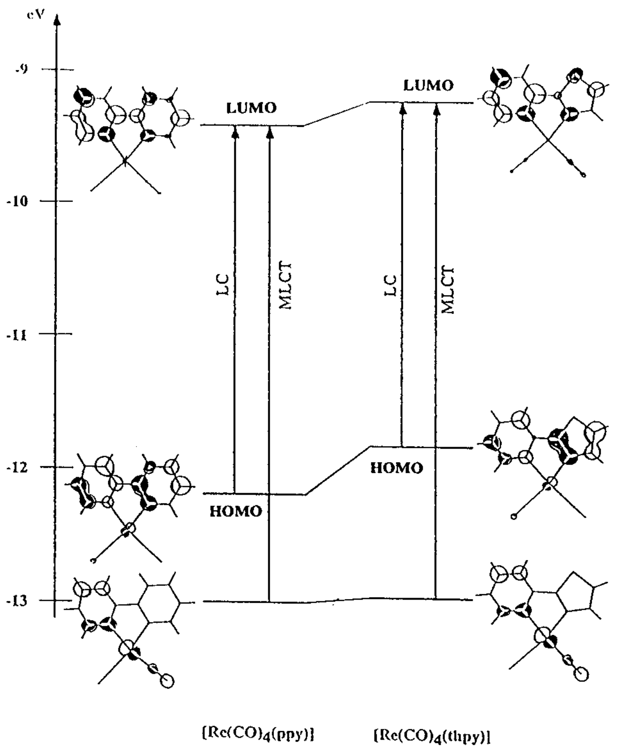

Figure 5. Results of extended Hückel calculations for [Re(CO)$_4$(ppy)] and [Re(CO)$_4$(thpy)]. The LUMO as well as the relevant occupied orbitals with their corresponding one-electron excitations are shown for both complexes. The Re–C bond points to the right in both pictures. The contributions of the out-of-plane CO's are omitted to prevent confusion with the contribution of Re.

representation of the LUMO, HOMO, and highest occupied orbital with substantial metal character are presented. Both the HOMO and LUMO are almost pure ligand-centered π orbitals with admixtures of 2% and 0% metal d character, respectively. The "metal" orbital has 46% metal d character, and it involves only the pyridine part of the thienylpyridine ligand. The corresponding picture for the closely related complex [Re(CO)$_4$(ppy)][6] is shown on the left side of Figure 5. The orbitals are equivalent to those in [Re(CO)$_4$(thpy)]. The MLCT one-electron excitation is at higher energy in [Re(CO)$_4$(thpy)] whereas the $\pi-\pi^*$ excitation on the ligand is at lower energy.

4. Discussion

4.1. Assignment of Excited States. It is possible to assign the bands in the near-UV solution absorption spectrum of [Re(CO)$_4$(thpy)] by comparison with the corresponding spectra of [Rh(thpy)$_2$(bpy)]$^+$, [Rh(thpy)$_2$(en)]$^+$, [Ir(thpy)$_2$(bpy)]$^+$, and [Ir(thpy)$_2$(en)]$^+$.[5c] The band with maximum at 26 800 cm^{-1} is assigned to a ^{1}MLCT transition. The bands above 30 000 cm^{-1} correspond to ligand-centered singlet $\pi-\pi^*$ excitations. The shoulder at 24 100 cm^{-1} in the single-crystal absorption spectrum ($E \| B$; see Figure 2) is assigned as a ^{3}MLCT transition.

The lowest-energy absorption transition is only observable in the crystal spectrum. As shown in Figure 2 at 10 K, it consists of an electronic origin and fundamental vibrational sidebands as well as their combination bands and overtones. The modes designated $\beta-\kappa$ in Figure 2 are assigned to fundamental thpy$^-$ vibrations, since the same sideband energies were also found in the excitation spectra of [Rh(thpy)$_2$(bpy)]$^+$, [Ir(thpy)$_2$(bpy)]$^+$, and [Pd(thpy)$_2$].[5,15] In all these complexes, the lowest energy transition has been assigned to a ^{3}LC excitation, and we make this assignment also for the title complex. The α modes which are unique to the present system are discussed in the next section. It is remarkable that the vibrational fine structure can be observed over a range of more than 4500 cm^{-1}.

The ^{3}LC assignment of this transition is in good correspondence with the total oscillator strength $f_{^3\mathrm{LC}} = 2.0 \times 10^{-5}$ derived from the crystal spectrum and the luminescence lifetime $\tau_{77\mathrm{K}} = 258\ \mu$s. For [Os(bpy)$_3$]$^{2+}$, in which the first excitation is due to a ^{3}MLCT transition, the corresponding values are $f_{^3\mathrm{MLCT}} = 4\ 10^{-4}$[16] and $\tau_{77\mathrm{K}} = 1.8\ \mu$s.[17]

The sideband structures of [Re(CO)$_4$(thpy)] are very similar in absorption and emission. This is best seen in the spectra of the crystalline material; see bottom traces in Figure 3. In the PMMA matrix, the same structure can still be recognized despite the considerable inhomogeneous broadening; see Figures 3 and 4. In the LLN experiment (Figure 4), a small part of the sideband intensity is narrowed into very sharp lines which form again the same energy pattern as in the absorption spectrum. Figure 4 shows that, above 300 cm^{-1}, this energy pattern is exactly the same for the three complexes [Re(CO)$_4$(thpy)], [Rh(thpy)$_2$(bpy)]$^+$, and [Ir(thpy)$_2$(bpy)]$^+$. These sidebands are obviously due to normal modes of the thpy$^-$ ligand, which is common to all three complexes. We observe no evidence of coupling to C–O modes in [Re(CO)$_4$(thpy)]. It is therefore a good approximation to assign the luminescent first excited state to a thpy$^-$-centered $^3\pi-\pi^*$ state.

This conclusion is confirmed by the results of the extended Hückel calculation. The lowest energy one-electron excitation is essentially a thpy$^-$-centered $\pi-\pi^*$ transition; see Figure 5. The first nominal d → π^* one-electron excitation is calculated 0.870 eV higher in energy. For a comparison with the experiment, we also have to consider the singlet–triplet splitting of these one-electron excitations. This singlet–triplet splitting is always significantly larger for a ligand-centered $\pi-\pi^*$ excitation than for a d → π^* charge-transfer excitation. Thus the calculation predicts a lowest ^{3}LC state.

4.2. MLCT Character in the Lowest ^{3}LC State. There is multiple evidence, however, for some charge-transfer character mixed into this nominal ^{3}LC state. The vibrational sidebands at 173 and 241 cm^{-1} in the LLN spectrum and the α modes (146, 176, and 235 cm^{-1}) in the single-crystal absorption spectrum are assigned to metal–ligand bending and stretch vibrations. They clearly indicate that the electronic transition is not purely ligand-centered. Their intensity is a measure of the changes in the metal–ligand angles and distances occurring with the excitation. There is no reliable technique for a quantitative analysis, however, and for an estimate of the MLCT character in the first excited state, we rely on the luminescence lifetime and the absorption intensity of the first transition.

The luminescence lifetime of [Re(CO)$_4$(thpy)] at 10 K is 258 μs, whereas the lifetime of the free ligand thpyH is 35 ms.[18] We can obtain an estimate of the radiative lifetime of the first

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(14) The following valence orbital ionization energies were used in the calculation. C: 2s, −21.4 eV; 2p, −11.4 eV. H: 1s, −13.6 eV. N: 2s, −26.0 eV; 2p, −13.4 eV. O: 2s, −32.3 eV; 2p, −14.8 eV (Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397). Re: 6s, −9.36 eV; 6p, −5.96 eV; 5d, −12.66 eV (Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141). S: 3s, −20.0 eV (Chen, M. M. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1647); 3p, −13.3 eV (Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654).

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Table 2. Excited-State Parameters for the Title Complex and Related Complexes[a]

	$[Rh(thpy)_2(bpy)]^+$	$[Rh(ppy)_2(bpy)]^+$	$[Ir(thpy)_2(bpy)]^+$	$[Ir(ppy)_2(bpy)]^+$	$[Re(CO)_4(thpy)]$	$[Re(CO)_4(ppy)]$	$[Re(CO)_4(bpy)]^+$
$f_{^3LC}$	$8.1 \times 10^{-6\,b}$	1.69×10^{-5} 2.37×10^{-5}	2.06×10^{-4} 1.53×10^{-4}	3.82×10^{-4} 1.06×10^{-3}	2.0×10^{-5}	4.2×10^{-5}	7×10^{-5}
$f_{^1MLCT}$	2.5×10^{-2}	2.9×10^{-2}	2.6×10^{-2}	3.6×10^{-2}	2.3×10^{-2}	5.7×10^{-2}	$4.0 \times 10^{-1\,g}$
$\tilde{\nu}_{^3LC(origin)}$ (cm^{-1})	19 110	22 140	18 860	21 459	19 302	21 938	22 510
$\tilde{\nu}_{^2MLCT(max)}$ (cm^{-1})	25 000^c	25 550^c	23 300^c	23 000^c	24 100	25 700	28 000
$\tilde{\nu}_{^1MLCT(max)}{}^d$ (cm^{-1})	26 000^c	26 000^c	25 000^c	25 000^c	26 800	28 500	31 570^g
$\Delta E_{max}{}^d$ (cm^{-1})	5230	2060	4480	1741	5838	4762	7260
$\langle ^3LC\|H_{so}\|^1MLCT\rangle$ (cm^{-1})	61	32	237	147	112	81	63
τ_{exp} (μs)	500	170	17	4.8	258	89	32
ZFS (^{3}LC) (cm^{-1})	0.144	0.14^e	5	10	1.9^e	2.0^e	0.57^e
α^f	0.012	0.016	0.053	0.085	0.019	0.017	0.009

[a] The values for the Rh(III) and Ir(III) complexes were taken from ref 5c, those for $[Re(CO)_4(ppy)]$ from ref 6, and those for $[Re(CO)_4(bpy)]^+$ from ref 7. [b] Calculated from the 77 K lifetime using formula 1 and $n = 1.5$ (see ref 5a). [c] Estimated value (see ref 5c). [d] It is important to use the maxima of the overall absorption bands for the calculation of ΔE. [e] Calculated from the spin−orbit matrix element and the energies found in the absorption spectra using formula 5. [f] As defined in formula 3. [g] ^{1}MLCT and ^{1}LC are not seperated, and we take the total.

excited state by use of the formula[19]

$$\tau_{rad} = 1.5 \times 10^4\left(\frac{1}{f}\right)\frac{(c/\nu)^2}{n((n^2+2)/3)^2}\frac{g_e}{g_g} \tag{1}$$

where f is the oscillator strength, c is the velocity of light, ν is the transition frequency, n is the refractive index, and g_e and g_g are the degeneracies of the excited and ground states, respectively. Choosing a value of $n = 1.5$, we calculate $\tau_{rad} = 201$ μs. We conclude that the experimental $\tau_{obs} = 258$ μs is completely radiative. The calculated value may be too low because the value $n = 1.5$ is a rough estimate. Also, the oscillator strength has an uncertainty of up to 30%.

The direction of the transition moment of the lowest energy transition was determined by the method described in ref 4a. It is very similar to that of the isostructural $[Re(CO)_4(ppy)]$.[6] The electronic structures of $[Re(CO)_4(thpy)]$ and $[Re(CO)_4(ppy)]$ are very similar; see Figure 5. We therefore conclude that the intensity of the lowest energy transition in the title complex arises from mixing with the first ^{1}MLCT excitation, as was suggested for $[Re(CO)_4(ppy)]$ in ref 6.

As in our earlier studies on 4d^6 and 5d^6 chelate complexes,[5−7] we use the model proposed by Komada et al.[20] for an estimate of the charge-transfer character in the first excited state: the ^{1}MLCT state is mixed into the ^{3}LC state by spin−orbit coupling. The corresponding spin−orbit coupling matrix element is given by

$$\langle ^3LC|H_{so}|^1MLCT\rangle = \sqrt{\frac{1}{3}\frac{f_{^3LC}}{f_{^1MLCT}}\frac{\nu_{^1MLCT}}{\nu_{^3LC}}}\Delta E \tag{2}$$

where $f_{^3LC}$ and $f_{^1MLCT}$ are the oscillator strengths of the ^{3}LC and ^{1}MLCT absorptions, respectively, and $\nu_{^3LC}$ and $\nu_{^1MLCT}$ are the corresponding frequencies. ΔE is their energy difference (expressed in cm^{-1}) and the factor $^1/_3$ accounts for their different spin multiplicities. Using first-order perturbation theory, the charge-transfer character, expressed by the quantity α, in the total wave function Ψ_{exc}

$$\Psi_{exc} = \sqrt{1-\alpha^2}|^3LC\rangle + \alpha|^1MLCT\rangle \tag{3}$$

is given by[21]

$$\alpha = \frac{\langle ^3LC|H_{so}|^1MLCT\rangle}{\Delta E} \tag{4}$$

We obtain a value of $\alpha = 0.019$ for $[Re(CO)_4(thpy)]$.

Komada also correlates the zero-field splitting (ZFS) of the emitting ^{3}LC state with the matrix element of eq 2. It is given by

$$\mathrm{ZFS} = \langle ^3LC|H_{so}|^1MLCT\rangle^2\left(\frac{1}{E_{^3MLCT} - E_{^3LC}} - \frac{1}{E_{^1MLCT} - E_{^3LC}}\right) \tag{5}$$

Inserting the appropriate numbers from the absorption spectrum, we obtain a ZFS = 1.9 cm^{-1} for $[Re(CO)_4(thpy)]$. This is smaller than the width of our zero-phonon line and thus not resolvable.

We have used formulas 2 and 4 before to estimate values of the spin−orbit coupling matrix element and the mixing coefficient in the complexes $[Rh(ppy)_2(bpy)]^+$, $[Ir(ppy)_2(bpy)]^+$, $[Rh(thpy)_2(bpy)]^+$, $[Ir(thpy)_2(bpy)]^+$, $[Re(CO)_4(bpy)]^+$, and $[Re(CO)_4(ppy)]$.[5−7] For the mixed-ligand Rh^{3+} and Ir^{3+} complexes, care is necessary because each ligand contributes to the total intensity and this was not properly considered in each case. Also the values of ΔE were overestimated. We have therefore recalculated all the relevant quantities. The results are collected in Table 2, which will be the basis for a comparative discussion in the next section. The results for $[Re(CO)_4(bpy)]^+$ differ from those in ref 7 because, in this complex, the ^{1}MLCT is superimposed by the first ^{1}LC absorptions, which was not taken into account in ref 7.

4.3. Comparison with Related Complexes. We first compare cyclometalated with corresponding noncyclometalated complexes. For this, the corresponding quantities of $[Re(CO)_4(bpy)]^+$ have to be compared with those of $[Re(CO)_4(ppy)]$ and $[Re(CO)_4(thpy)]$ (see Table 2). The ^{3}MLCT and ^{1}MLCT states are clearly lower in energy for the cyclometalated complexes than for $[Re(CO)_4(bpy)]^+$ (25 700 and 24 100 vs 28 000 cm^{-1} and 28 500 and 26 800 vs 31 570 cm^{-1}, respectively). This is due to the decrease in π-acceptor strength on going from N to C$^-$ and the increased σ-donor character of the anionic ligand. Both effects lower the energy of the MLCT states in the cyclometalated complexes. One expects that this leads to an increase of the MLCT character in the first excited state.[3] This was, for example, observed on going from $[Ir(thpy)_2(bpy)]^+$ to $[Ir(thpy)_3]$.[10]

The same trend is observed for the Re complexes: the α values for $[Re(CO)_4(ppy)]$ and $[Re(CO)_4(thpy)]$ are a factor of 2 larger than that for $[Re(CO)_4(bpy)]^+$. This is due to the

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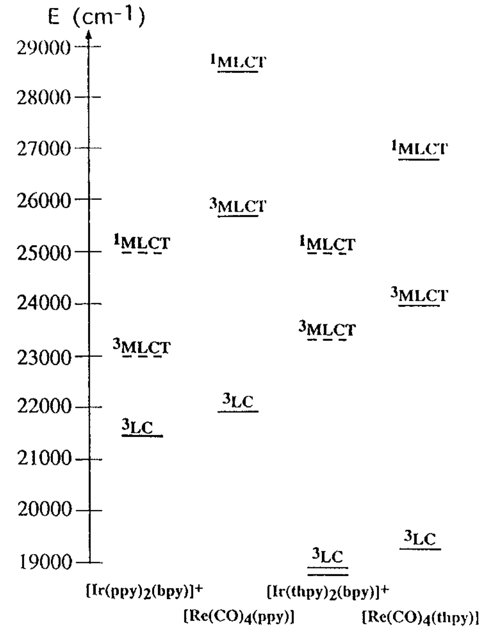

Figure 6. Energies of the lowest excited states of four cyclometalated 5d^6 complexes. The broken lines indicate estimated values.

decrease in ΔE mentioned above and an increase in the value of spin−orbit coupling matrix element under cyclometalation: 81 and 112 vs 63 cm^{-1}, respectively. This also leads to an increase of the ZFS: 1.9 and 2.0 vs 0.6 cm^{-1}, respectively. A ZFS < 0.5 cm^{-1} was recently measured for [Re(CO)$_4$(bpy)]$^+$.[22]

Replacing ppy$^-$ by thpy$^-$ as a ligand leads to a drop of 2600−3000 cm^{-1} in the value of $\tilde{\nu}_{^3\mathrm{LC}}$; see Table 2 and Figure 3. This drop in the transition energy is qualitatively reproduced by the extended Hückel calculations; see Figure 5. The calculations predict a reduction in the LUMO−HOMO energy difference of 0.7 eV (=5646 cm^{-1}) on going from [Re(CO)$_4$(ppy)] to [Re(CO)$_4$(thpy)]. We should not expect a quantitative agreement from such a simple one-electron calculation in which the ^{1}LC/^{3}LC splitting is neglected. As seen in Table 2, the ^{1}MLCT/^{3}MLCT splitting is hardly influenced by substituting ppy$^-$ by thpy$^-$: 2700 vs 2800 cm^{-1}, respectively.

Energy level diagrams in the region of the first excited states are shown in Figure 6 for both complexes together with those of [Ir(ppy)$_2$(bpy)]$^+$ and [Ir(thpy)$_2$(bpy)]$^+$. The energy difference Δ*E* between the ^{1}MLCT and ^{3}LC states is larger by 1000−3200 cm^{-1} for all thpy$^-$-containing complexes than for the corresponding ppy$^-$ complexes. This trend is already reflected by the extended Hückel calculation. The energy difference between the highest occupied "metal" orbital and the HOMO is larger for [Re(CO)$_4$(thpy)] than for [Re(CO)$_4$(ppy)]; see Figure 5. The increase in Δ*E* on substitution of ppy$^-$ by thpy$^-$ causes a reduction of the oscillator strength of the lowest energy excitation; see Table 2. This leads to an increase of the luminescence lifetimes by a factor of 3−3.5 under the same substitution.

Δ*E* is also larger for [Re(CO)$_4$(C-N)] complexes than for [Ir(C-N)$_2$(N-N)]$^+$ and [Rh(C-N)$_2$(N-N)]$^+$ complexes; see Figure 6 and Table 2. This can be explained as follows: the metal d orbitals of Re are stabilized by π back-bonding with the CO ligands. The LC transition energies are not affected by this, but the MLCT transitions increase strongly in energy compared to those of complexes having no CO as ligands; see, e.g., [Rh(C-N)$_2$(N-N)]$^+$ and [Ir(C-N)$_2$(N-N)]$^+$ complexes in Figure 6 and Table 2.

The spin orbit coupling matrix element $\langle ^3\mathrm{LC}|H_{\mathrm{so}}|^1\mathrm{MLCT}\rangle$ is about 1.6 times larger for thpy$^-$-containing complexes than for ppy$^-$-containing ones. This is ascribed to the heavy S atom, which enhances the effective spin−orbit coupling parameter. The influence of the central metal ion on the spin−orbit coupling matrix element can also be seen in Table 2. The ratio of values on going from Rh(III) to Re(I) to Ir(III) is about 1:2.2:4.3, which should roughly scale with the spin−orbit coupling parameters of the free ions. No experimental values are known for these free-ion parameters, but they can be estimated as proposed in ref 23. This gives a ratio of 1:1.8:3.3, in reasonable agreement with our matrix elements.

We conclude that the excited-state properties of 4d^6 and 5d^6 chelate complexes can be tuned by chemical variation. Both the variation of the metal ion and its oxidation state and the nature of the chelating ligands have an influence on the relative positions of ^{3}LC and ^{1}MLCT states and their admixture. Electron-withdrawing groups are expected to lower the MLCT excitations and to increase the mixing coefficients, while electron-donating groups should have the opposite effect. We are currently studying the effect of such substitutions on the bpy and ppy$^-$ ligands.

Acknowledgment. We thank Naomi Furrer for help in the synthetic work and Andreas Hauser, Høgni Weihe, Hans Riesen, and Elmars Krausz for fruitful discussions and correspondence. The financial support by the Swiss National Science Foundation is gratefully acknowledged.

Supporting Information Available: IR spectra in the C−O stretching region of crystalline [Re(CO)$_4$(bpy)](PF$_6$), [Re(CO)$_4$(thpy)], and a 10^{-4} M solution of [Re(CO)$_4$(thpy)] in CH$_2$Cl$_2$ (1 page). An X-ray crystallographic file, in CIF format, for [Re(CO)$_4$(thpy)] is available on the Internet only. Ordering and access information is given on any current masthead page.

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