Polarized Low Temperature Luminescence of Single Crystal Pentacarbonylpyridinotungsten(O)-Complexes

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Polarized luminescence spectra of single crystal $W(CO)_5$-X (with X = pyridine, 4-methylpyridine, 4-t-butylpyridine, 3,4-dimethylpyridine, 4-aminopyridine, 3-acetylpyridine, 3,5-dibromopyridine, 3-benzoylpyridine, 4-formylpyridine) at low temperatures ($1.9\text{ K} \leqq T \leqq 80\text{ K}$) are reported.

Depending on the nature of the pyridine substituent the emitting state is either a ligand field (LF) state or a metal to ligand charge transfer (CT) state. This results in drastic differences in both bandshape and temperature behaviour of the luminescence spectra. The CT-luminescence is structureless and is not influenced by temperature variation, whereas the LF-luminescence spectra exhibit in most cases a distinct vibrational fine structure at low temperatures and show a remarkable temperature dependence.

The emission spectra of single crystal $W(CO)_5$-3,4-dimethylpyridine and $W(CO)_5$-pyridine can be strongly influenced by magnetic fields ($H \leqq 6$ T).

The results are explained within a model assuming molecular C_{4v} symmetry and regarding spin orbit coupling.

Introduction

Several efforts have been made to understand the photochemistry and the spectroscopy of metal carbonyls of the type $W(CO)_5$-X [1 – 3], particularly of systems with X = n-electron donor [4 – 8]. These investigations were mostly restricted to solutions. Relatively little information is available on the optical properties of the crystalline complexes. Recently we have reported on the polarized low temperature luminescence of $W(CO)_5$-pyridine single crystals [9], which shows a distinct vibrational fine structure. Based on the results of measurements of the luminescence spectra at low temperatures ($1.9\text{ K} \leqq T \leqq 20\text{ K}$) and at high magnetic fields ($H_{max} = 6$ T) an energy level diagram had been developed assuming molecular C_{4v} symmetry and regarding spin orbit coupling.

In this paper we want to present the results of investigations of the polarized luminescence of single crystal $W(CO)_5$-X as a function of temperature and of magnetic field strength. X stands for pyridine or substituted pyridine. With regard to their emission behaviour these complexes can be divided into two main types:

Type A:	*Type B:*
X = pyridine (A 1)	X = 3-acetylpyridine (B 1)
X = 4-methylpyridine (A 2)	X = 3,5-dibromopyridine (B 2)
X = 4-t-butylpyridine (A 3)	X = 3-benzoylpyridine (B 3)
X = 3,4-dimethylpyridine (A 4)	X = 4-formylpyridine (B 4)
X = 4-aminopyridine (A 5)	

Depending on the nature of the pyridine substituent, the emitting state is either a ligand field (LF) state ("type A" complexes with less electron withdrawing pyridine-substituents) or a metal to ligand charge transfer (CT) state ("type B" complexes with more electron withdrawing pyridine-substituents). A comprehensive discussion of this topic is given in [8]. Although the luminescence of different complexes varies partly drastically in bandshape, energetic position, and emission lifetime, it is intended to explain their emission behaviour by the same energy level diagram. This diagram is based on that developed for $W(CO)_5$-pyridine [9], and considers structural characteristics and especially the energetic position of the CT-state relative to the LF-states.

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Experimental

$W(CO)_5$-X complexes were synthesized by a slightly modified procedure described by Strohmeier [10–12], and recrystallized from benzene/isooctane (1:1, v/v). Purity was established spectroscopically and by elementary analysis.

The spectroscopic measurements were done in the liquid helium bath cryostat of a superconducting magnet system (Oxford Instruments SM 4). The 364 nm line of a Coherent argon ion laser was used for excitation. The emitted light was selected by a Spex double grating monochromator (Czerny-Turner mounting, 0.2 nm resolving power at 500 nm), detected by an EMI S 20 photomultiplier, and processed by a personal computer.

The emission lifetimes were measured by time-to-amplitude-conversion. The apparatus is described in [13].

Results

Typ A-Complexes

Figure 1 shows the polarized emission spectra of type A complexes $W(CO)_5$-X with X = pyridine ($\boldsymbol{E} \perp \boldsymbol{L}$, $\boldsymbol{L}$ stands for the longitudinal axis of the needle-shaped crystals), 4-methylpyridine ($\boldsymbol{E} \perp \boldsymbol{L}$), 4-t-butylpyridine ($\boldsymbol{E} \parallel \boldsymbol{L}$), 3,4-dimethylpyridine ($\boldsymbol{E} \perp \boldsymbol{L}$), and 4-aminopyridine ($\boldsymbol{E} \perp \boldsymbol{L}$), at $T = 1.9$ K. The corresponding 1.9 K-spectra for the opposite polarization are similar to these in respect to bandshape and spectral position, but less intensive (by a factor 3–5). To demonstrate the details of the vibrational structure Fig. 2 shows the stretched high energy region of the low temperature emission of $W(CO)_5$-pyridine (A 1), $W(CO)_5$-4-methylpyridine (A 2), and $W(CO)_5$-4-t-butylpyridine (A 3). The half widths of the fine structure lines increase in the sequence A 1, A 2, A 3.

The emission spectra of the type A complexes depend on temperature. As an example Fig. 3 shows the $\boldsymbol{E} \perp \boldsymbol{L}$-spectrum of $W(CO)_5$-pyridine at different temperatures $1.9\text{ K} \leqq T \leqq 50\text{ K}$. Fig. 4 summarizes the temperature dependence of the wavenumber of the emission maximum* for the compounds A 1, A 2, A 3, and A 4. The results belong to that polarization, which is the more intense at low temperature.

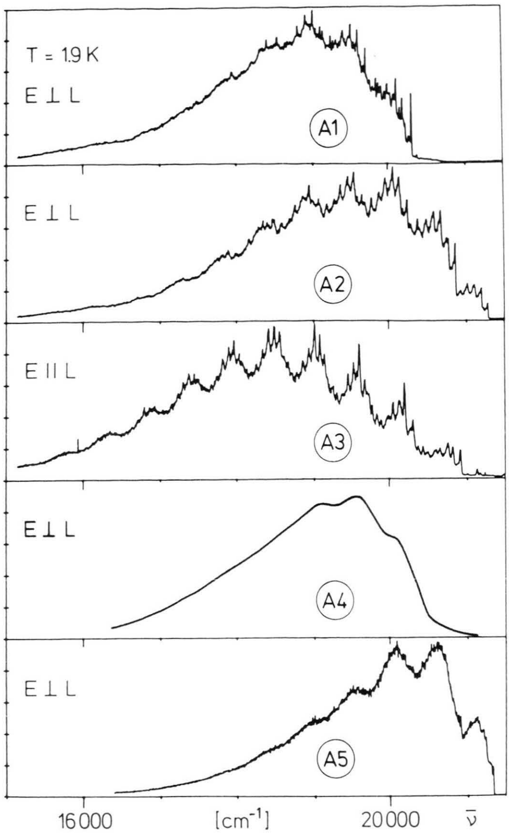

Fig. 1. Polarized emission spectra of type A complexes $W(CO)_5$-X at $T = 1.9$ K. A 1: X = pyridine; A 2: X = 4-methylpyridine; A 3: X = 4-t-butylpyridine; A 4: X = 3,4-dimethylpyridine; A 5: X = 4-aminopyridine; $\lambda_{ex} = 364$ nm.

Figure 5 demonstrates the ratio of the emission intensities $I_\perp / I_\parallel$ for A1 and A2 and $I_\parallel / I_\perp$ for A3, respectively.

The lifetimes at $T \approx 1.9$ K could not be determined by the available apparatus. They were too long for the application of the time-to-amplitude-conversion ($\tau > 50$ μs). The measurement by box car integration fails because of the low emission intensity. Figure 6 shows for $T \geqq 4.3$ K a logarithmic plot of the lifetime of the unpolarized emission as a function of temperature for A 1, A 2, and A 4.

Individual properties of the emission of the type A complexes are described below.

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* For spectra showing pronounced structure the positions of the emission maxima have been determined approximately. They were taken from the graphs, which connect the points of gravity of the coarse fine structure bands, lying above the basic line through the minima of the spectral curve.

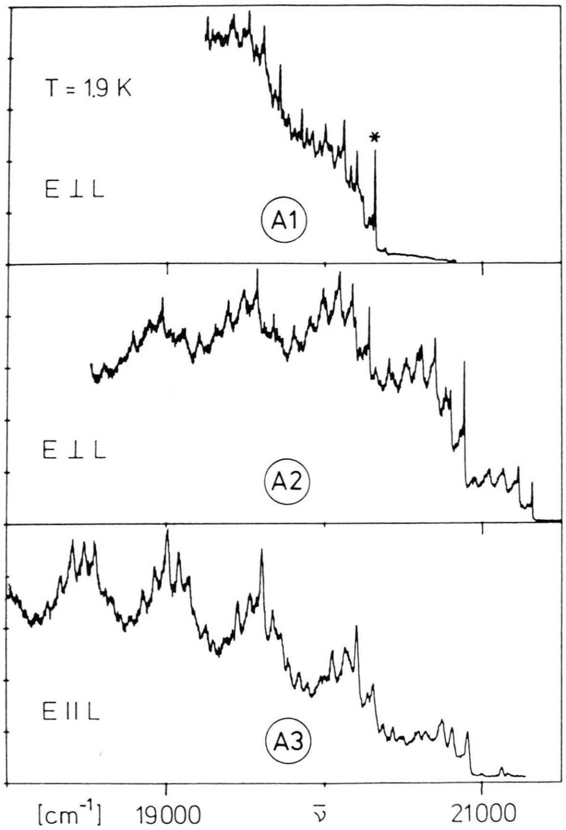

Fig. 2. Stretched high energy region of the polarized emission of type A complexes $W(CO)_5$-X at $T = 1.9$ K. A1: X = pyridine; A2: X = 4-methylpyridine; A3: X = 4-t-butylpyridine; $\lambda_{ex} = 364$ nm.

$W(CO)_5$-pyridine (A1)

The $E \perp L$ emission spectrum of $W(CO)_5$-pyridine at $T = 1.9$ K (cf. Fig. 1) shows a coarse structure with equidistant bands ($\Delta E = 550\ cm^{-1}$). This coarse structure exhibits a distinct intense, sharp lined fine structure, cf. Fig. 2 [9, 14]. The emission has its maximum at about $19000\ cm^{-1}$ and a half width of about $3000\ cm^{-1}$.

Temperature increase yields the following effects (cf. Figures 3 and 4). Between $T = 1.9$ K and $T = 30$ K the maximum of the $E \perp L$ emission is blue-shifted by about $500\ cm^{-1}$. Further temperature increase induces no additional energetic shift of the emission maximum.

At $T > 5$ K an additional emission appears at higher energy, showing a similar line pattern as the high energy region of the low temperature emission, cf. Figure 3. The energetic difference between corresponding fine structure peaks is $453\ cm^{-1}$ [9, 14].

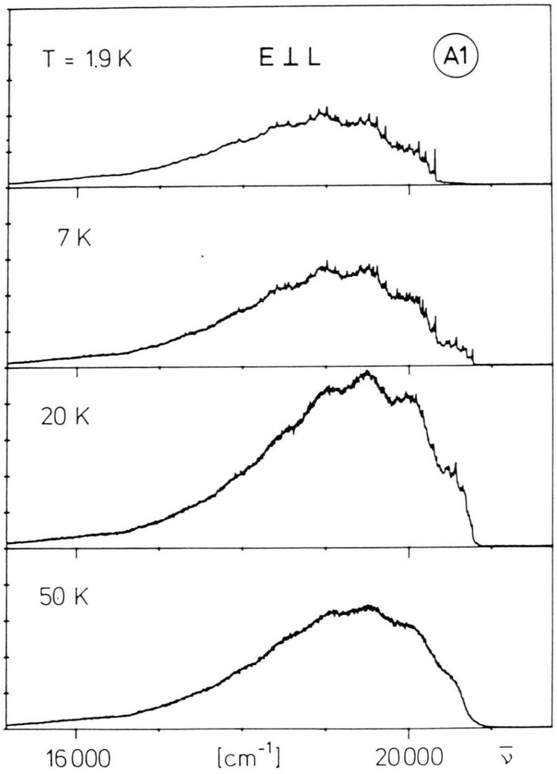

Fig. 3. $E \perp L$-emission of $W(CO)_5$-pyridine at different temperatures $1.9\ K \leqq T \leqq 50$ K. $\lambda_{ex} = 364$ nm.

Between $T = 1.9$ K and $T \approx 30$ K the $E \perp L$ emission intensity grows, above $T = 30$ K it declines. The intensity ratio $I_\perp / I_\parallel$, however, increases up to $T = 15$ K and decreases above this temperature, cf. Figure 5.

The emission lifetime remains constant between $T = 4.3$ K and $T = 10$ K ($\tau = 5.5\ \mu s$), at further temperature increase it falls off exponentially, as shown by Figure 6.

By application of a homogeneous magnetic field $H \perp L$ ($H \leqq 6$ T) an additional $E \perp L$ emission at higher energy appears [9]. Its fine structure is similar to that of the $H = 0$ spectrum but blue shifted by $431\ cm^{-1}$. The intensity of the fine structure lines of the magnetic-field-induced emission is proportional to the square of the magnetic field strength.

$W(CO)_5$-4-methylpyridine (A2)

The $E \perp L$ emission spectrum of $W(CO)_5$-4-methylpyridine at $T = 1.9$ K (emission maximum

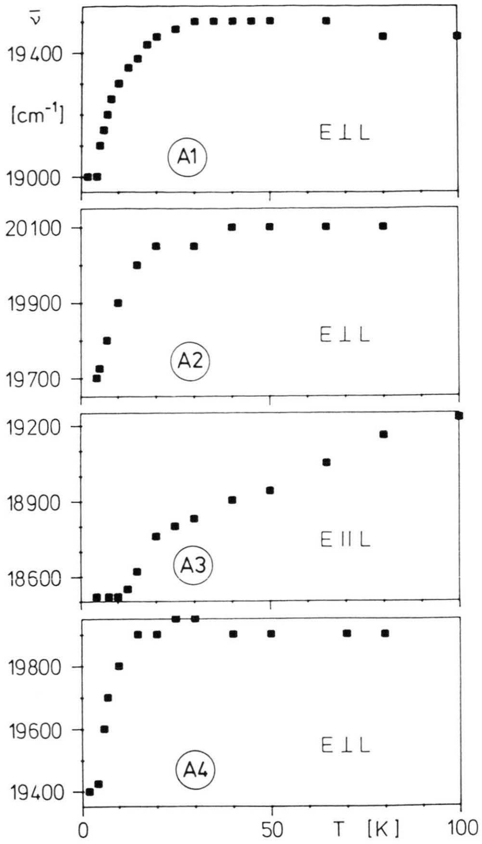

Fig. 4. Temperature dependence of the wavenumber of the emission maximum of type A complexes $W(CO)_5$-X. A1: X = pyridine; A2: X = 4-methylpyridine; A3: X = 4-t-butylpyridine; A4: X = 3,4-dimethylpyridine; $\lambda_{ex} = 364$ nm.

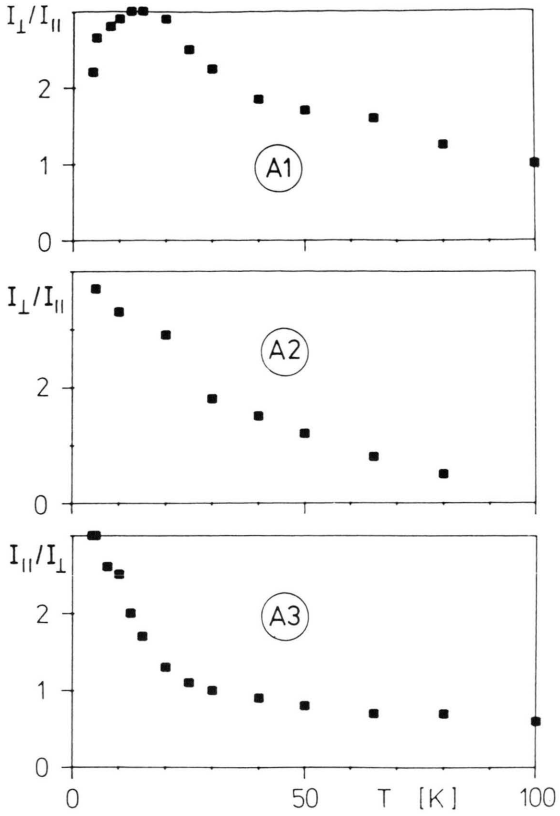

Fig. 5. Temperature dependence of the intensity ratio of the perpendicularly polarized emissions of type A complexes $W(CO)_5$-X. A1: X = pyridine; A2: X = 4-methylpyridine; A3: X = 4-t-butylpyridine; $\lambda_{ex} = 364$ nm.

at about 19800 cm^{-1}) also shows a coarse structure with a 550 cm^{-1}-progression (cf. Fig. 1) and a distinct vibrational fine structure (cf. Figure 2). The additional high energy emission, however, which appears in the emission of $W(CO)_5$-pyridine only at higher temperatures, is for A2 apparent already at $T = 1.9$ K. (The energetic difference of corresponding fine structure lines of the two high energy bands is 440 cm^{-1}, but not 550 cm^{-1}.)

The temperature dependence of the $\boldsymbol{E} \perp \boldsymbol{L}$ emission maximum is given in Figure 4. With increasing temperature a blue shift of the emission is observed with a saturation value of ≈ 400 cm^{-1} at $T \gtrsim 20$ K.

The intensity of the $\boldsymbol{E} \perp \boldsymbol{L}$ emission and the intensity ratio $I_\perp/I_\parallel$ steadily decline with increasing temperature (cf. Figure 5).

The temperature dependence of the emission lifetime is similar to that of $W(CO)_5$-pyridine (vide infra). The lifetime at low temperatures ($4.3\ \text{K} \lesssim T \lesssim 10$ K) is 10 μs.

$W(CO)_5$-4-t-butylpyridine (A3)

For the compound A3 the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission at low temperatures is more intensive than the $\boldsymbol{E} \perp \boldsymbol{L}$ emission. Like the $\boldsymbol{E} \perp \boldsymbol{L}$ emission of the compounds A1 and A2, the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission of A3 exhibits both a coarse 550 cm^{-1}-progression (cf. Fig. 1) and a distinct vibrational fine structure (cf. Fig. 2) at $T = 1.9$ K. The wavenumber of the emission maximum and the half width are about 18500 cm^{-1} and 3000 cm^{-1}, respectively.

The dependence of the spectral position of the emission maximum on temperature is shown in Figure 4. Up to $T \approx 10$ K the position of the maximum remains constant, at higher temperatures it

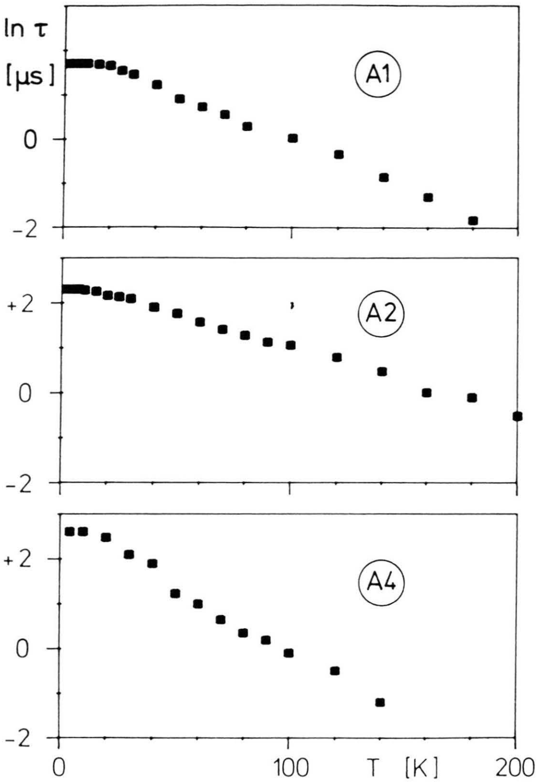

Fig. 6. Temperature dependence of the emission lifetime of type A complexes $W(CO)_5$-X (logarithmic scale). A1: X = pyridine; A2: X = 4-methylpyridine; A4: X = 3,4-dimethylpyridine; $\lambda_{ex} = 364$ nm.

becomes blue-shifted. The total amount of this blue-shift within the temperature range between 1.9 K and 80 K is $600-700\ \text{cm}^{-1}$. This value is distinctly larger than that for the complexes considered above.

The intensity of the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission remains nearly constant within the temperature range $1.9\ \text{K} < T \leqq 80$ K, the intensity ratio $\boldsymbol{I}_{\parallel}/\boldsymbol{I}_{\perp}$, however, decreases from about 3 at $T = 1.9$ K to about 0.5 at $T = 80$ K, as is shown in Figure 5.

$W(CO)_5$-3,4-dimethylpyridine (A4)

The $\boldsymbol{E} \perp \boldsymbol{L}$ emission spectrum of A4 at $T = 1.9$ K is presented in Figure 1. It shows only a weak coarse structure ($550\ \text{cm}^{-1}$ progression), and there is no indication of an additional fine structure. The wave number of the emission maximum and the half width are about $19400\ \text{cm}^{-1}$ and $3000\ \text{cm}^{-1}$, respectively.

The temperature dependence of the spectral position of the emission maximum (cf. Fig. 4) is qualitatively the same as that found for A1. Starting from $19400\ \text{cm}^{-1}$ at $T = 1.9$ K it gets blue-shifted up to $T \approx 20$ K by $\Delta\bar{\nu} \approx 500\ \text{cm}^{-1}$. At $T > 20$ K no further blue-shift is observed.

The emission lifetime at low temperatures is about 13.5 μs. Above $T \approx 10$ K it decreases exponentially with increasing temperature (cf. Figure 6).

By application of a homogeneous magnetic field the maximum of the $\boldsymbol{E} \perp \boldsymbol{L}$ emission is blue-shifted and the total emission intensity increases quadratically with the magnetic field strength H. Between $H = 0$ and $H = 6$ T the shift is $\approx 300\ \text{cm}^{-1}$ and the intensity grows by a factor of about 2. Both processes are expected to continue at higher field strengths. These effects show a close analogy to the magnetic field dependence of the $W(CO)_5$-pyridine emission [9].

$W(CO)_5$-4-aminopyridine (A5)

The $\boldsymbol{E} \perp \boldsymbol{L}$ emission of $W(CO)_5$-4-aminopyridine at $T = 1.9$ K (cf. Fig. 1) exhibits a distinct coarse structure ($430\ \text{cm}^{-1}$ progression), and in the high energy region a weakly pronounced fine structure is indicated. The wave number of the emission maximum and the half width are about $20500\ \text{cm}^{-1}$ and $2500\ \text{cm}^{-1}$, respectively.

Temperature increase causes no change of the spectral position of the emission maximum, but the structure of the emission spectrum disappears more and more, and at temperatures $T > 20$ K the emission is structureless.

Type B-Complexes

The emission spectra of the type B complexes $W(CO)_5$-X with X = 3-acetylpyridine, 3,5-dibromopyridine, 3-benzoylpyridine, 4-formylpyridine, at $T = 4.3$ K are shown in Figure 7. In all cases the emission does not exhibit any fine structure, the halfwidth is $2500-3000\ \text{cm}^{-1}$, and the emission lifetime is about 30 μs. The wave numbers of the emission maxima are $17900\ \text{cm}^{-1}$ (3-acetylpyridine), $17600\ \text{cm}^{-1}$ (3,5-dibromopyridine), $17000\ \text{cm}^{-1}$ (3-benzoylpyridine), and $15800\ \text{cm}^{-1}$ (4-formylpyridine), respectively. Neither the bandshape and the spectral position nor the emission lifetime are affected by temperature increase between 4.3 K and 80 K and by magnetic fields up to $H = 6$ T.

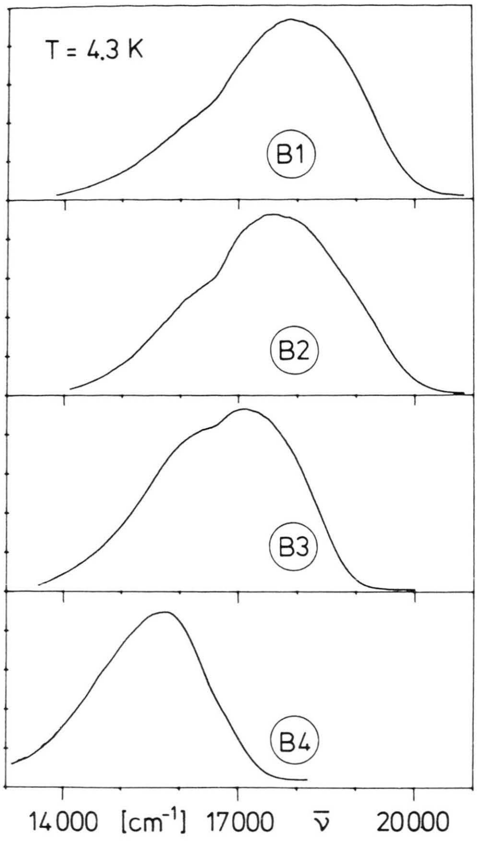

Fig. 7. Emission spectra (unpolarized) of type B complexes $W(CO)_5$-X at $T = 4.3$ K. B1: X = 3-acetylpyridine; B2: X = 3,5-dibromopyridine; B3: X = 3-benzoylpyridine; B4: X = 4-formylpyridine; $\lambda_{ex} = 364$ nm.

Discussion

The experimental results can be explained by a model of oriented, mutually uncoupled complexes, whose point symmetry is (approximately) characterized by the double group C_{4v}'. The metal-nitrogen direction defines the intramolecular z axis.

For type A complexes an energy level diagram is appropriate, which has been recently developed for $W(CO)_5$-pyridine on the basis of the temperature- and magnetic field-dependence of its single crystal emission [9]. This diagram with the ligand field term ^3E, respectively with its spin-orbit components A_2', $2A_1'$, and E' as the energetically lowest excited states of the complex, is shown at the left-hand side of Figure 8. (The higher-energetic spin-orbit components B_1' and B_2' of ^3E are omitted.) The energies of these LF states are expected to depend only insignificantly on the nature of the pyridine substituent (cf. [1–8]).

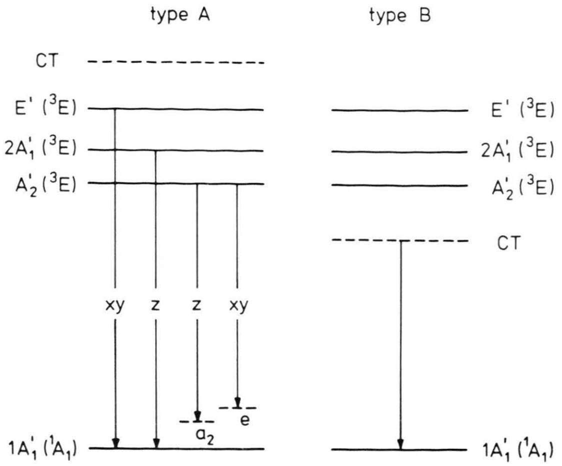

Fig. 8. Proposed energy level diagrams of the lowest states of type A complexes (left-hand side) and of type B complexes (right-hand side), schematic. (Symmetry C_{4v}', the z axis is defined by the direction metal-nitrogen.)

A group theoretical analysis predicts electrical dipole allowed transitions between the ground state $1A_1'$ and the excited states $2A_1'$ and E' with z- and xy-polarization, respectively. The transition between the ground state $1A_1'$ and the excited state A_2' is symmetry forbidden. Due to vibronic coupling, however, weak emission transitions $A_2' \rightarrow 1A_1' + a_2$-vibration ($z$-polarization) and $A_2' \rightarrow 1A_1' +$ e-vibration (xy-polarization) can appear.

From a structure determination [14] we know for $W(CO)_5$-pyridine, that all molecular z-axes lie perpendicular to the crystallographic c-axis, which is parallel to the needle axis $\boldsymbol{L}$ of the crystals. For $W(CO)_5$-4-methylpyridine and the other complexes such a simple assignment of the crystal axes relative to the molecular axis cannot be made. Therefore, in the following only for the system A1 a definite polarization assignment can be given: $\boldsymbol{E} \parallel \boldsymbol{L}$ is xy-polarized, whereas $\boldsymbol{E} \perp \boldsymbol{L}$ contains the z-polarization.

Besides the ligand field states there are also energetically low lying metal to ligand charge transfer states. The energetical position of these CT states strongly depends on the nature of the pyridine substituent, as mentioned above. In the case of type A complexes the lowest CT state lies energetically higher than the lowest LF states. For type B complexes, however, the lowest excited state is a CT state, cf. the right-hand side of Figure 8. We cannot give a definitive symmetry asignment of the lowest CT state but there are some indications for E-symmetry of this state [14].

Type A-Complexes

$W(CO)_5$-pyridine (A1)

At low temperatures ($T \leqq 4.3$ K) the luminescence with $\boldsymbol{E} \perp \boldsymbol{L}$ is due to the vibronic transition $A_2' \rightarrow 1A_1' + a_2 + \Sigma\, n\, a_1$ ($n = 1, 2, \ldots$), where a_1 and a_2 represent the symmetries of vibrational quanta [9]. The sharp intense fine structure peak at 20312 cm^{-1} ($*$ in Fig. 2) can be assigned to the false origin $\bar{\nu}(0,0) + \bar{\nu}(a_2)$ of the vibronic transition. The expression $\Sigma\, n\, a_1$ stands for progressions of totally symmetric vibrations built up on the false origin. For an interpretation of the vibrational fine structure of the luminescence confer [9, 14]. The coarse structure with equidistant bands ($\Delta E = 550$ cm^{-1}) can be explained by the "missing mode effect", MIME [15, 16].

With increasing temperature thermal repopulation of the $2A_1'$ term from the lowest excited term A_2' arises and, thus, the electric dipole allowed transition $2A_1' \rightarrow 1A_1' + \Sigma\, n\, a_1$ becomes more and more effective. The energetic difference between this transition and the $T \leqq 4.3$ K transition equals the energetic difference of corresponding fine structure lines in both spectra: $[\bar{\nu}(2A_1') - \bar{\nu}(A_2')] + \bar{\nu}(a_2) = 453$ cm^{-1}. The overall emission spectrum at $T > 5$ K is a superposition of both transitions. Thus, with increasing temperature a blue shift of this spectrum is observed.

Moreover, at temperatures $T > 20$ K a thermal repopulation of the E' state occurs. The emission from this state is $\boldsymbol{E} \parallel \boldsymbol{L}$ polarized. This fact explains the temperature dependence of the intensity ratio $I_{\perp}/I_{\parallel}$. At low temperatures the $\boldsymbol{E} \perp \boldsymbol{L}$ transition dominates, but with increasing temperature the $\boldsymbol{E} \parallel \boldsymbol{L}$ transition "steals" more and more of the $\boldsymbol{E} \perp \boldsymbol{L}$ intensity.

The temperature behaviour of the emission lifetime can be interpreted as follows. The lifetime $\tau > 50$ µs at lowest temperatures belongs to the transition $A_2' \rightarrow 1A_1' + a_2$. The constant value $\tau = 5.5$ µs between $T \approx 4.3$ K and 10 K (cf. Fig. 6) is the lifetime of the allowed transition $2A_1' \rightarrow 1A_1'$. Above $T = 10$ K the transition $E' \rightarrow 1A_1'$ becomes more and more important. The logarithmic temperature dependence of its lifetime indicates a strong increase of non radiative decay [17, 18]. This explains also the steady reduction of the emission intensity with increasing temperature, and finally, the disappearance of the emission at $T > 120$ K.

A homogeneous magnetic field $\boldsymbol{H} \parallel z$ reduces the point symmetry to C_4' and mixes the lowest excited states $A'(2A_1')$ and $A'(A_2')$ [9]. The contribution of $2A_1'$ to the first excited state is proportional to the magnetic field strength H. Therefore, a new electric dipole allowed radiative channel $A'(A_2') \rightarrow A'(1A_1') + \Sigma\, n\, a_1$ is opened. The corresponding transition energy differs from the energy of the low temperature transition at $H = 0$ by the quantum 431 cm^{-1} of the a_2 vibration, and the intensity of the magnetic field induced transition is proportional to H^2, in agreement with the experimental results.

$W(CO)_5$-4-methylpyridine (A2)

Even at the lowest attainable temperatures the $\boldsymbol{E} \perp \boldsymbol{L}$ emission of $W(CO)_5$-4-methylpyridine is a mixture of the transitions $A_2' \rightarrow 1A_1' + a_2$ and $2A_1' \rightarrow 1A_1'$, indicating a very small energetical difference between the states A_2' and $2A_1'$. The high energy component, which in the emission of compound A1 appears only by temperature increase, is present in the emission of the compound A2 already at $T = 1.9$ K. By temperature increase the emission occurs more and more from the thermal repopulated $2A_1'$, resulting in a blue shift of the emission maximum.

At low temperatures also the thermal repopulation of the E' state is perceptible, getting more and more effective with increasing temperature, and thus causing a steady decrease of the intensity ratio $I_{\perp}/I_{\parallel}$.

The temperature behaviour of the emission lifetime can be explained as for the compound A1.

$W(CO)_5$-4-t-butylpyridine (A3)

There is some evidence for the presumption, that the low temperature $\boldsymbol{E} \parallel \boldsymbol{L}$ emission of the compound A3 is due to the transition $A_2' \rightarrow 1A_1' + e$. The blue-shift $\Delta\bar{\nu} \approx 600$ cm^{-1} caused by temperature increase is much larger than the a_2-vibration quantum 430 cm^{-1}, but equals approximately the e-vibration quantum 610 cm^{-1} [14]. Based on this facts the temperature behaviour of the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission can be explained as follows.

Between $T = 1.9$ K and $T \approx 10$ K the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission is mainly due to the transition $A'_2 \rightarrow 1A'_1 + e$ and shows no temperature dependence. With increasing temperature the thermal repopulation of the $2A'_1$ term becomes effective, and a $\boldsymbol{E} \perp \boldsymbol{L}$ polarized emission $2A'_1 \rightarrow 1A'_1$ occurs. Due to depolarization effects the $\boldsymbol{E} \parallel \boldsymbol{L}$ emission gets intensity from the $\boldsymbol{E} \perp \boldsymbol{L}$ emission and thus it seems to be blue-shifted. This mechanism also explains the marked temperature dependence of the intensity ratio $I_\parallel / I_\perp$. – In the considered temperature region there is no evidence for thermal repopulation of states of higher energy.

$W(CO)_5$-3,4-dimethylpyridine (A4)

The effects of temperature and magnetic fields on the emission of A4 can be explained analogously to that of A1.

$W(CO)_5$-4-aminopyridine (A5)

The observed temperature dependence of the emission spectrum indicates that the emission of the A5 complex is due to the same transition for all temperatures considered. This can be explained by a very small splitting of the ^3E term (into the states A'_2, $2A'_1$, and E').

Type B-Complexes

In the case of the type B complexes the emitting state is a CT term, independently of the temperature of the crystal. Therefore, the emissions of all type B complexes have comparable spectral bandshapes and lifetimes. The spectral position of the emission depends on the electron-withdrawing-capacity of the pyridine substituent. The larger the capacity the smaller is the transition energy.

Acknowledgement

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