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The vibronic structure in the emission spectra of some thienylpyridine complexes

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Contents

Abstract

The compounds $PtCl(Et_2S)(thpy)$, $Pt(Et_2S)I(thpy)$, and $Pt(phpz)(thpy)$, where thpy denotes the 2-(2′-thienyl)pyridine anion and phpz the (1-phenyl)pyrazole anion, were investigated by optical spectroscopy. Solid state emission down to $T=1.3$ K and low temperature luminescence of the Shpol'skii system Pt(phpz)(thpy)/*n*-octane are presented. Thereby, electronic origins and vibronic structure with high resolution were detected. These essentially involve the Pt(II) coordinated $thpy^-$ ligand ([Pt(thpy)]-unit) of the heteroleptic compounds. A detailed comparison with the sharp emission lines of related compounds is performed. The characteristics of zero field splitting and vibronic structure give new criteria for the assignment of the lowest excited states. Weak exchange coupling within the ML π-system, including phase coupling of vibronic interactions, is proposed to explain the spectroscopic peculiarities in

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connection with the specific coordination properties of the title compounds.

Keywords: Thienylpyridine complexes; Heteroleptic compounds; Emission spectra

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1. Introduction

Cyclometallated compounds have been prepared and studied for their photochemical and photophysical aspects over recent years [1], experiments in the optical range being of special interest [2,3]. Specifically, the analysis of the lowest excited states permits the connection of molecular properties and the electronic structure of these molecules, because of the detailed "fingerprint" of electronic and vibronic states that can be observed in high resolution spectra.

Chemical variations have turned out to be a powerful tool for assigning states. Series of transition metal complexes with different metals or ligands [4] reveal varying metal and ligand contributions to the optical spectra, resulting from the specific molecular composition [5]. An important improvement in these data is obtained by investigation of mixed ligand compounds [6].

The detailed information from low temperature emission spectroscopy is accessible for heteroleptic compounds in the same way as for their homoleptic analogues by, for example, the following techniques [7]: luminescence line narrowing, and solid state emission from X- and Y-traps. Investigations using the Shpol'skii technique also lead to high resolution spectra [8], if the guest molecules fit into the host lattice in the required way [9,10].

The results from studies of several chemical variations of the cyclometallated 2-(2′-thienyl)pyridine anion with different kinds of high resolution optical spectroscopy [8] are summarized in this contribution. These investigations are based on a systematic experimental series of cyclometallated Pt(II)-compounds [11]. In this context, it was shown that solid state emission spectra of complexes with a tendency for strong intermolecular interactions consist of broad, almost unstructured bands [12], whereas larger distances between the complexes allowed the observation of highly structured bands — due to X-traps — in the single crystal spectra [13]. Very intense X-trap spectra were found for the homoleptic Pt(II) and Pd(II) $thpy^-$ compounds [14]. In that case, matrix isolation spectroscopy (Shpol'skii) of the molecules was also possible [10]. Therefore, it could be demonstrated that the structured spectra of homoleptic $thpy^-$ complexes in both cases are due to the emission of single molecules. The comparison of these results with data from the corresponding heteroleptic compounds gives new criteria for the identification of the emitting states. Therefore, it is possible to discuss the influence of the specific coordination properties of the molecules in connection with their electronic structure.

2. General molecular and optical properties of [Pt(thpy)]-compounds

The Pt(II) complexes with different ligands, $PtCl(Et_2S)(thpy)$, $Pt(Et_2S)I(thpy)$, Pt(phpz)(thpy), as well as the hompleptic $Pt(thpy)_2$, are members of the large family of cyclometallated compounds with aromatic C, N coordinating π-systems. Fig. 1 shows the different complexes in a schematic way.

Characteristic molecular properties are found, if the geometric data resulting from X-ray structure analysis of $PtCl(Et_2S)(thpy)$ [15] are discussed.

The 2-(2′-thienyl)pyridine anion coordinates to Pt(II) as a strong σ-donor; the Pt–C bond (1.98 Å) is regarded to be covalent, whereas the Pt–N interaction (2.07 Å) is much weaker and provides the possibility of π-acceptance. The five- and six-membered rings are directly connected in such a way that the π-electrons form a conjugated system. This ligand has good coordination properties, if noble metal ions are used for complex formation. In the case of Pt-compounds, "π-back bonding" is indicated by chemical shifts from ^{1}H NMR [16]. The unsymmetric coordination sphere of Pt(II) is shown in Fig. 2. The Pt–S and Pt–Cl distances differ greatly, being 2.27 Å and 2.40 Å, respectively. The 81.83° bite angle of the cyclometallated ligand indicates, in addition to the angles N–Pt–S (173.61°) and C–Pt–Cl (175.26°), deviations from a planar arrangement of the nearest-neighbour atoms. Also, the Ortep plot shows that the Et_2S group is rotated with respect to the coordination plane by nearly 90°. This molecule is located in the unit cell ($P2_1/n$) in such a way that all atoms take general positions *x*,*y*,*z*. The aromatic systems are well separated from each other and shielded by the Et_2S groups of neighbouring molecules. A minimum distance between Pt atoms of 7.27 Å has been calculated. Because of these

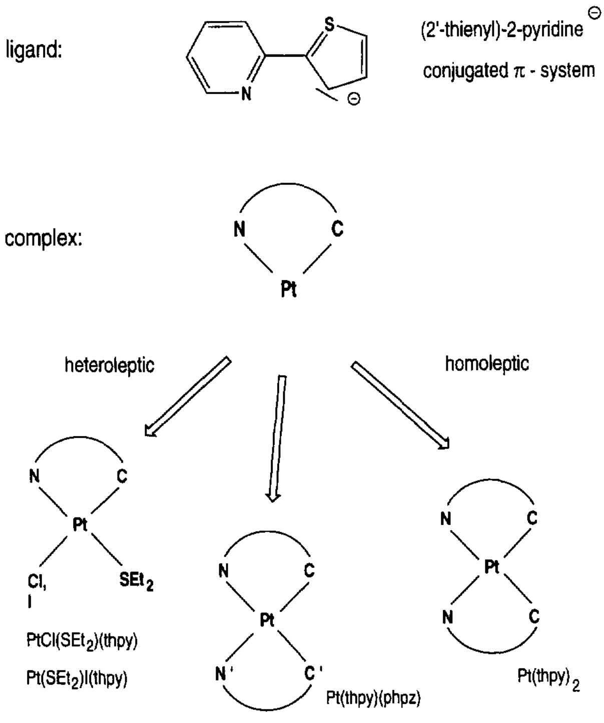


Fig. 1. The 2-(2′-thienyl)pyridine anion and some of its Pt(II)-complexes.

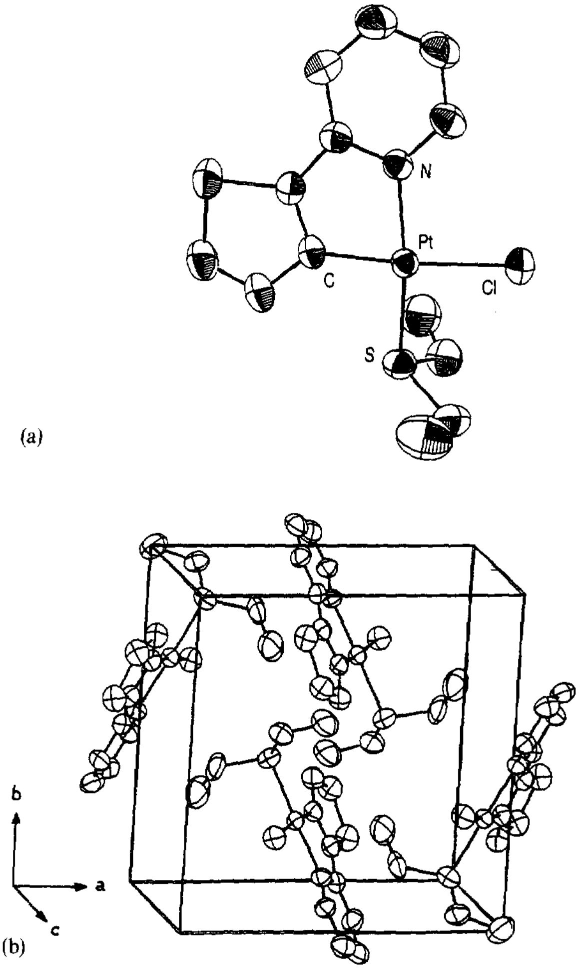


Fig. 2. Molecular structure (a) and unit cell (b) of $PtCl(Et_2S)(thpy)$ (Ortep plots).

results, neither π-stacking interactions nor strong intermetallic contacts need to be discussed, the molecules being regarded as "quasi-isolated" in the solid state.

Comparing the characteristic data of the compounds, such as the reported [17] absorption bands at low energies in solution (Table 1) or the luminescence maxima that were measured [18] in butyronitrile at $T = 77$ K, very similar optical properties were found.

The broad, almost unstructured absorption bands of $PtCl(Et_2S)(thpy)$ and Pt(phpz)(thpy) have comparable energetic positions in the visible spectral region and seem to be characteristic of charge transfer. At these low energies, $Pt(thpy)_2$ also absorbs. Deuschel-Cornioley et al. [17] point out this analogy and discuss the common maximum at $\bar{\nu} = 23\,800$ cm^{-1} as MLCT from Pt to $thpy^-$. The second

Table 1
Absorption bands in the visible spectral region: maxima and extinction coefficients ($CHCl_3$ solutions, measured at room temperature; data from Ref. [17])

Compound	$\bar{\nu}$ (cm^{-1})	ϵ (M^{-1} cm^{-1})
$PtCl(Et_2S)(thpy)$	23810	4140
	24510	4410
	30300	14110
Pt(phpz)(thpy)	23810	3180
	26320	8640
	29240	10600
$Pt(thpy)_2$	21740	1900
	23810	10700
	25510	4970
	28570	14140

aromatic ligand of Pt(phpz)(thpy), $phpz^-$, absorbs at higher energies than $thpy^-$ ($\Delta\bar{\nu}=6300$ cm^{-1}). This is also reflected after coordination: the first absorption maximum of $Pt(phpz)_2$ [16] is found at $\bar{\nu}=29\,400$ cm^{-1} and for Pt(phpz)(thpy) the band at $\bar{\nu}=26\,320$ cm^{-1} is assumed to be due to this absorption.

The study of the luminescence properties leads to the same trends. At $T=77$ K, the spectral positions and intensity distributions of the emission bands are similar to the spectrum of $Pt(thpy)_2$. As in the luminescence of the two protonated ligand molecules, the maxima in the emission spectra of both homoleptic complexes are separated by about $\bar{\nu}=5700$ cm^{-1}. Therefore, it can be assumed that the emission bands of Pt(phpz)(thpy) with their maximum at $\bar{\nu}=18\,000$ cm^{-1} involve $thpy^-$, in accordance with the conclusions of Sandrini et al. [18].

However, some interesting differences should be remarked upon. The absorption spectra of the heteroleptic compounds Pt(thpy)(X,Y) show that the extinction coefficients of the MLCT bands have about half the value determined for $Pt(thpy)_2$. From emission lifetime measurements [18], it was found that τ of Pt(phpz)(thpy) is increased to 160% of the value for the homoleptic analogue. This difference grows even larger in the case of measurements at room temperature in fluid solutions, where $\tau(\text{heteroleptic})\approx 3\tau(\text{homoleptic})$.

Having suitable properties, the compounds Pt(thpy)(X,Y) were investigated by low temperature spectroscopy in a way similar to the investigations [10,19] of $Pt(thpy)_2$, to obtain more information about the heteroleptic compounds in comparison to their homoleptic analogues with respect to the coordination properties of [Pt(thpy)]-complexes.

3. Low temperature emission of heteroleptic [Pt(thpy)]-complexes

Detailed information concerning the electronic structure of the described compounds is obtained by analysis of the low temperature optical spectra. The experimental conditions are given in Ref. [8].

First, the results of luminescence measurements of crystalline Pt(phpz)(thpy), PtCl(Et_2S)(thpy), and Pt(Et_2S)I(thpy) are presented (Fig. 3). The spectra were recorded at the temperature $T=4.2$ K of the sample. Lowering the temperature to

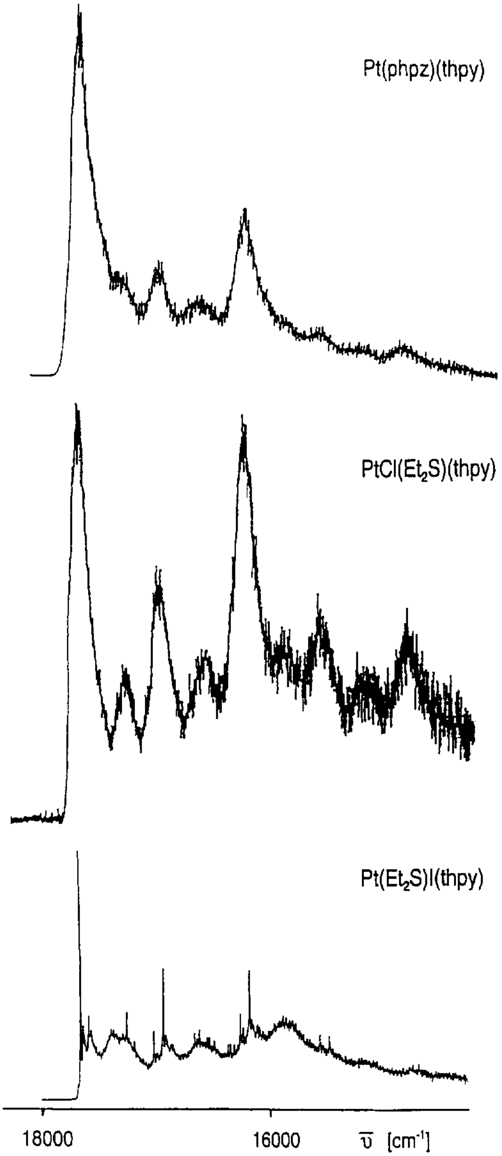


Fig. 3. Luminescence of microcrystalline Pt(phpz)(thpy), PtCl(Et_2S)(thpy) ($T=4.2$ K), and single crystal Pt(Et_2S)I(thpy) ($T=1.3$ K); $\lambda_{exc}=457.9$ nm. (For this comparison, the emission spectra of Pt(phpz)(thpy) and PtCl(Et_2S)(thpy) have been shifted to the position of the intensity maximum of the R(Et_2S)(thpy) emission; the original spectral onsets are given in Table 2, respectively.)

$T = 1.3$ K improved only the resolution of the spectral bands obtained from single crystal Pt(Et_2S)I(thpy) (halfwidth: $\Delta\bar{\nu} \approx 5$ cm^{-1}). For all three samples, the intensity distribution showed no significant changes within this temperature range.

Similar general emission properties are found. The emission maxima at high energies correspond to the peaks with the highest intensities in all three cases. At lower energies, several more or less resolved bands follow, leading to comparable intensity distributions in the spectra. The energetic positions of the spectral onset and the energetic distances between the different emission maxima are given in Table 2. The distinct onset values at $\bar{\nu} = 17\,250$ cm^{-1} (Pt(phpz)(thpy)), $\bar{\nu} = 17\,760$ cm^{-1} (PtCl(Et_2S)(thpy)), and $\bar{\nu} = 17\,650$ cm^{-1} (Pt(Et_2S)I(thpy)) are found at energies similar to the X−trap emission of Pt(thpy)$_2$ crystals ($\bar{\nu} = 17\,000$ cm^{-1}, $T = 1.9$ K; [19]).

Comparing the differences $\Delta\bar{\nu}$ between the intensity maxima and the maxima at lower energies in each spectrum of the heteroleptic compounds, remarkable similarities are seen. For example, two maxima in the spectrum of Pt(phpz)(thpy), located at $\Delta\bar{\nu} = 690$ cm^{-1} and 1460 cm^{-1}, are comparable with the values 689 cm^{-1} and 1444 cm^{-1} of PtCl(Et_2S)(thpy), or with 715 cm^{-1} and 1482 cm^{-1}

Table 2
Solid state emission of heteroleptic [Pt(thpy)]-compounds

	Compound		
	Pt(phpz)(thpz)	PtCl(Et_2S)(thpy)	Pt(Et_2S)I(thpy)
Electronic origin: $\bar{\nu}$ (cm^{-1})	17250	17760	17650
Vibronic bands: $\Delta\bar{\nu}$ (cm^{-1})	200	100	24
			74
	400	390	390
			460 w
			630
	690	689	715
		740 w	740 w
		792 w	787 w
	1045		1033
		1090	1100 w
			1123 w
		1226	1280 w
			1307 w
			1395
			1427 w
	1460	1444	1482
			1505 w
			1556 w
		1832	1785 b
			2116 w
	2140 w	2132	2195
		2521	2440 b
	3090 w	2888	2880 b

(Pt(Et_2S)I(thpy)). Schwarz et al. measured the most intense maxima in the spectrum of Pt$(thpy)_2$ at $\Delta\bar{\nu} = 708$ cm^{-1} and 1480 cm^{-1} [19]. Similarly, the emission of the solid butyronitrile solutions [18] showed roughly the same intensity distribution.

It can therefore be concluded that the luminescence behaviour of the presented heteroleptic compounds in the solid state is mainly due to the Pt(II)-coordinated $thpy^-$ ligand ([Pt(thpy)]-unit) of the complex molecules. Thereby, the energy range of the electronic origins could be determined. The structured intensity distributions at lower energies are caused by vibrational bands, accompanying the purely electronic transitions.

It was then possible to obtain high resolution spectra for Pt(phpz)(thpy) using the Shpol'skii technique. In the polycrystalline matrix of a saturated organic compound, the electronic π-system of the complex molecule cannot interact significantly with the σ-framework of the host molecule [20]. It can, therefore, be regarded as isolated.

Low temperature emission spectra were recorded at temperatures of $T = 1.3$ K and 4.2 K (Fig. 4). The intense sharp line at $\bar{\nu} = 17\,625$ cm^{-1} dominates the spectrum (Figs. 5(a) and (b)) and does not change its position upon variation of the temperature. A shoulder of low intensity appears at $T = 4.2$ K with $\Delta\bar{\nu} = 5$ cm^{-1} (blue shift). Experiments applying external magnetic fields clearly show the characteristics of a manifold of electronic origins for these lines with a total zero field splitting (ZFS) of $\Delta\bar{\nu} = 8$ cm^{-1} (Fig. 5(c) and Fig. 5(d)).

The rich vibrational structure consists of lines with a halfwidth of $\Delta\bar{\nu} \geq 5$ cm^{-1}. Some minor changes are observed in varying the temperature. The intensity grows larger for all bands, and e.g. at $\Delta\bar{\nu} = 1433$ cm^{-1} or 1568 cm^{-1} the spectrum shows distinct maxima in comparison with the data at $T = 1.3$ K. Additionally, some vibrational peaks shift their positions under the influence of a magnetic field, according to the pattern of electronic transitions.

In contrast to Pt(phpz)(thpy), no Shpol'skii system was formed with e.g. Pt(Et_2S)I(thpy) because of the strong deviation from planarity which has already

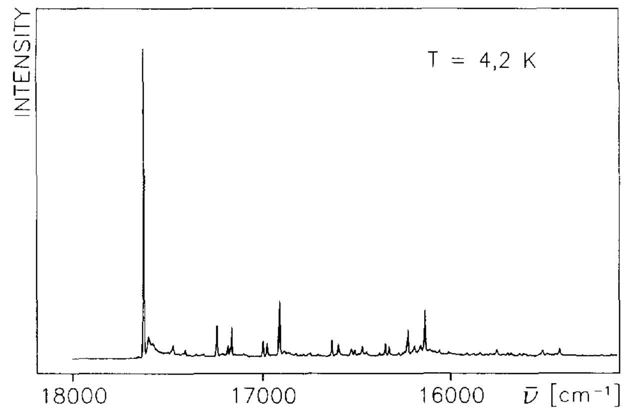


Fig. 4. Low temperature emission of the Shpol'skii system Pt(phpz)(thpy)/*n*-octane; $\lambda_{exc} = 457.9$ nm.

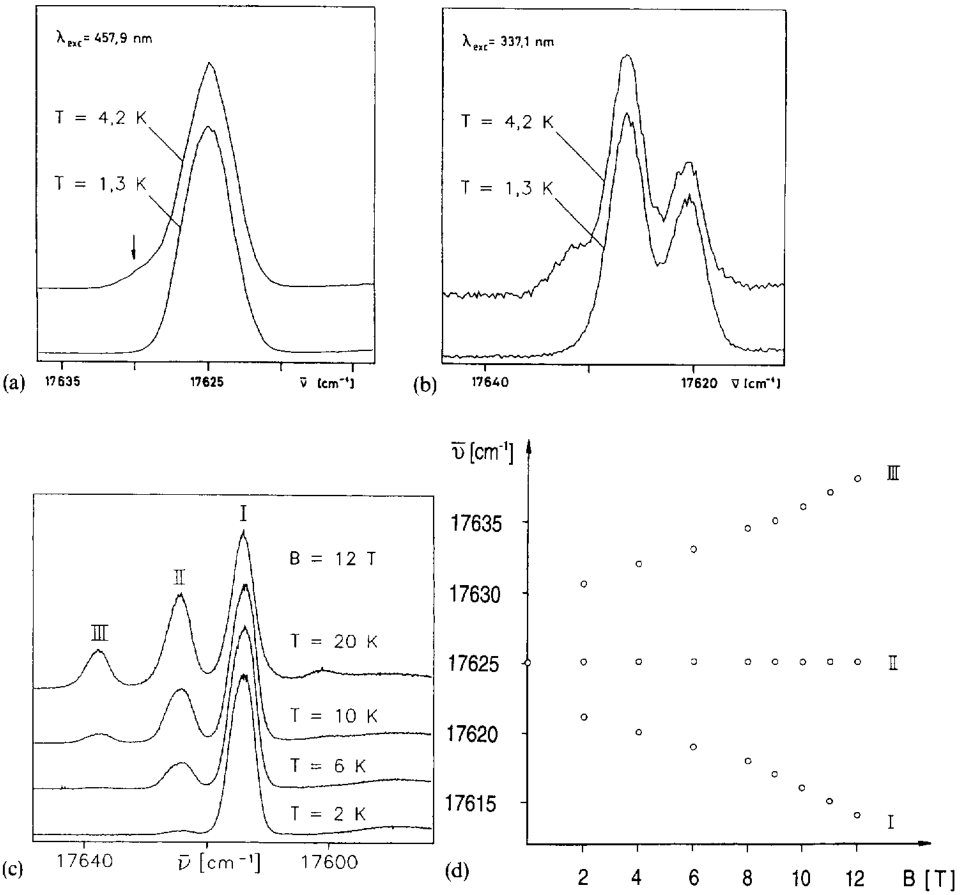


Fig. 5. Pt(phpz)(thpy)/*n*-octane: the extended region of the electronic transitions: (a) with excitation $\lambda_{exc}=457.9$ nm; temperature dependence; (b) with excitation $\lambda_{exc}=337.2$ nm; temperature dependence; (c) with excitation $\lambda_{exc}=457.9$ nm; temperature dependence, applied external magnetic field $B=12$ T; (d) change in ZFS applying magnetic fields up to $B=12$ T.

been mentioned above. The observed fine structure of the Shpol'skii system is therefore compared with the structure of the highly resolved solid state spectrum of Pt(Et_2S)I(thpy), whereby striking similarities are found. This again indicates the great influence of thpy$^-$, coordinated to Pt, on the total emission behaviour of the heteroleptic complexes.

Interesting results are found when the excitation wavelength is changed. Excitation of the emission using $\lambda_{exc}=337.2$ nm (N_2-laser), 324.6 nm (He/Cd-laser), or 363.8 nm (Ar^+-laser) gave for the lines of the electronic origins a smaller halfwidth and larger distances from each other. Therefore, I and III are already found without the influence by magnetic fields, at least as shoulders (I). Additionally, a second intense peak, red-shifted from II ($\Delta\bar{\nu}\approx 6$ cm^{-1}), is observed. At the same time, the position of II is slightly shifted (17 626 cm^{-1}) (Fig. 5(b)). Origin lines I, II, and III show, with respect to temperature and magnetic fields using high energy excitation, behaviour similar to the results for $\lambda_{exc}=457.9$ nm (or 476.2 nm, Ar^+-laser). The peak at $\bar{\nu}=17\,620$ cm^{-1} shows comparable properties to II and is assigned as II′.

The vibronic bands follow this change of behaviour. At $T=1.3$ K, for example, some bands show an increased intensity, others splitting and doubling, and new bands are observed, while others remain unchanged (for a more detailed comparison, see below).

These results are in contrast with those of the homoleptic $Pt(thpy)_2$, where no significant changes were detected on switching λ_{exc} from 337.2 to 457.9 nm [10]. Therefore, the question should be posed as to whether the possible excitation of an electronic transition involving the [Pt(phpz)]-unit of the complex, could be responsible for the changes in the emission spectrum.

4. Vibronic coupling

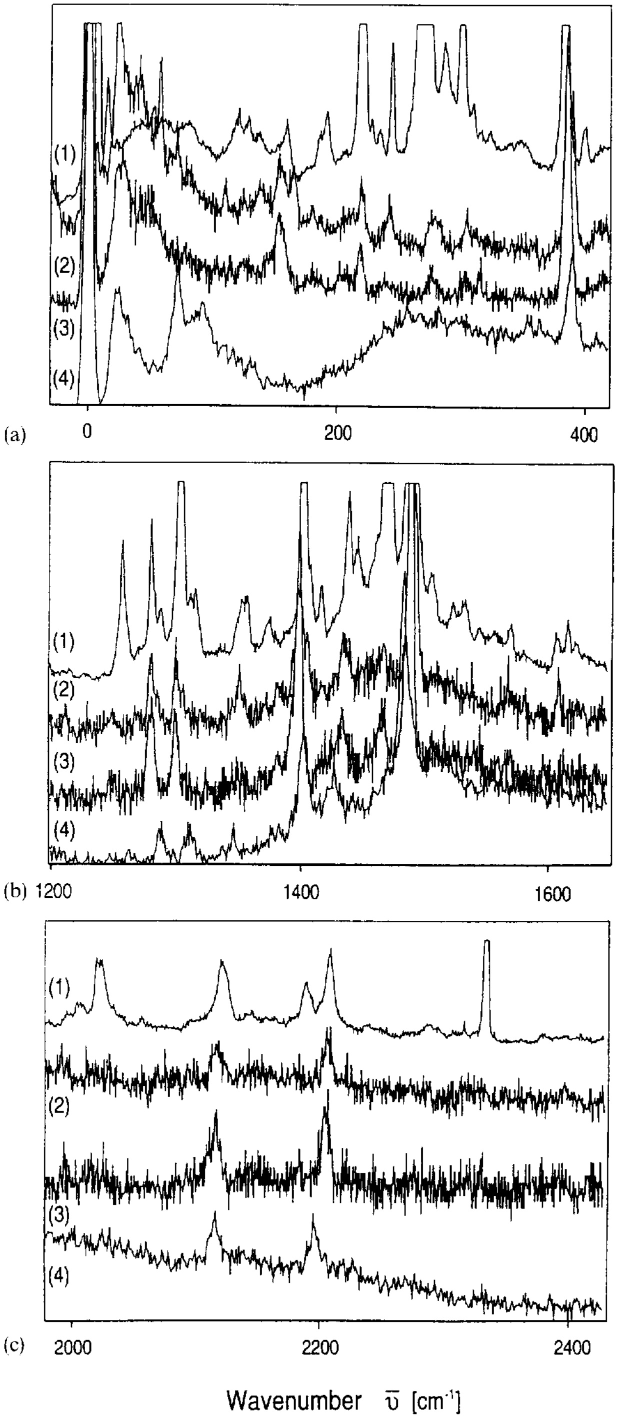
4.1. $Pt(Et_2S)I(thpy)$–$Pt(phpz)(thpy)$–$Pt(thpy)_2$

In a first comparison (Fig. 6), four different emission spectra, exemplary of the series of [Pt(thpy)]-compounds, are depicted: the Shpol'skii system $Pt(thpy)_2$ (1) ($\lambda_{exc}=337.2$ nm; adapted from a spectrum published in Ref. [21]), the Shpol'skii system Pt(phpz)(thpy) with $\lambda_{exc}=337.2$ nm (2) and 457.9 nm (3), and the solid state emission of $Pt(Et_2S)I(thpy)$ (4) at $T=1.3$ K.

Spectrum (1) has the greatest variety of vibrational sidebands. The emission intensity is remarkably high in comparison to that of the heteroleptic compounds. In spectrum (4), however, several peaks are observed, which retain either their characteristics or show only minor changes in all examples. In spectra (3) and (2), the number of vibronic peaks, relative to (4), is gradually increased. These spectra are therefore regarded to display their function as a "mediator" between the significant differences in (1) and (4).

In the region of ML vibrations (Fig. 6(a)), for example, the band at $\Delta\bar{\nu}=390$ cm^{-1} (4) (385 cm^{-1} (3),(2); 383 cm^{-1} (1)) shifts to lower frequencies and splits ($\Delta\bar{\nu}\approx 5$ cm^{-1} (2); 16 cm^{-1} (1)). The peak at $\Delta\bar{\nu}=218$ cm^{-1} e.g. is not found in (4), and gains significant intensity in (1) in comparison to (2) and (3). Some bands are particular for each complex, e.g. $\Delta\bar{\nu}=70$–90 cm^{-1} (4); $\bar{\nu}(Pt\text{–}SEt_2)$), 153 cm^{-1} (3), 164 cm^{-1} (2) and 190 cm^{-1} (1), and are assigned to complex vibrations. Fig. 6(b) expands the frequencies between 1200 and 1600 cm^{-1} ("fingerprint" for aromatic compounds). The frequency difference from $\Delta\bar{\nu}=1403$ to 1427 cm^{-1} (4) increases (1398, 1433 cm^{-1} (3); 1400, 1437 cm^{-1} (2)), and larger splitting and intensity

Fig. 6. Vibronic bands in the spectra of different [Pt(thpy)]-complexes at $T=1.3$ K in the frequency regions (a) 0–400 cm^{-1}, (b) 1200–1600 cm^{-1}, and (c) 2000–2400 cm^{-1}: (1) $Pt(thpy)_2$(Shpol'skii system, $\lambda_{exc}=337.2$ nm; see text); (2) Pt(phpz)(thpy) (Shpol'skii system, $\lambda_{exc}=337.2$ nm); (3) Pt(phpz)(thpy) (Shpol'skii system, $\lambda_{exc}=457.9$ nm); (4) $Pt(Et_2S)I(thpy)$ (solid state emission, $\lambda_{exc}=457.9$ nm). The intensities of the electronic origins II are set to the same value; the low intensity range of the spectra is shown.


(1)
(2)
(3)
(4)
(a)
0
200
400
(1)
(2)
(3)
(4)
(b) 1200
1400
1600
(1)
(2)
(3)
(4)
(c)
2000
2200
2400
Wavenumber ῡ [cm⁻¹]

enhancement from (2) to (1) are significant here. The same features are shown in Fig. 6(c). The bands at $\Delta\bar{\nu}=2122$ and $2195\ \mathrm{cm}^{-1}$ (4) are present in all examples, and their positions remain nearly unchanged.

It can be deduced from these results that an extension of the coordination from one bidentate system in the heteroleptic complexes to a second equal ligand in the homoleptic compound leads to significant changes in the vibronic sidebands of the emission spectra. These changes follow the remarkable differences in the ZFS pattern. In particular, origin I becomes more intense and the Raman active modes grow larger in the case of $Pt(thpy)_2$. This fact is demonstrated if a second, but not equal, π-system coordinates to Pt(II) in a similar way.

4.2. *$Pt(Et_2S)I(thpy)$–$[Rh(thpy)_2(bpy)](PF_6)$*

The comparison of the emission spectrum of $Pt(Et_2S)I(thpy)$ with that of $[Rh(thpy)_2(bpy)](PF_6)$ (Fig. 7; adapted from a spectrum published in Ref. [22]) is made to point out a second important property of cyclometallated $thpy^-$ compounds. Despite a total shift of the electronic origins from $\bar{\nu}=17\,625$ to $19\,205\ \mathrm{cm}^{-1}$ (Rh-complex), the frequencies of the vibrational bands are within several wavenumbers almost the same, with the exception of the vibrations at low frequencies. Bands typical of $\bar{\nu}(Pt\text{–}SEt_2)$ are lacking in the spectrum of the Rh-complex, where several new maxima are found (e.g. $114\ \mathrm{cm}^{-1}$, $150\ \mathrm{cm}^{-1}$, $245\ \mathrm{cm}^{-1}$). The first significant band in (1) ($388\ \mathrm{cm}^{-1}$) has a similar shape and intensity to the peak at

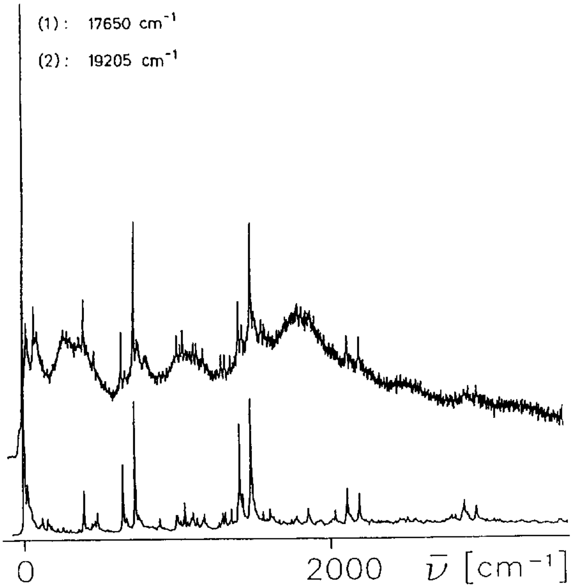


Fig. 7. Emission spectra of $Pt(Et_2S)I(thpy)$ (1) and $[Rh(thpy)_2(bpy)](PF_6)$ (see text) (2): a comparison of the structured bands.

378 cm^{-1} (2). Considering the lines at larger wavenumbers, the spectra are obviously nearly identical.

These comparisons are summarized as follows. Cyclometallation of two $thpy^-$ ligands at the same Rh-complex centre, where the first coordination sphere could be regarded as an octahedron, results in low temperature emission properties similar to those of heteroleptic Pt-complexes with only one coordinated π-system. In contrast, homoleptic π-coordination of Pt(II) — idealized by a planar coordination sphere — leads to strong additional vibronic bands and remarkable intensity enhancement.

5. Coordination sphere and electronic structure

The interesting question remains as to the assignment of these transitions. Based on high resolution spectroscopy and in agreement with conclusions resulting from "chemical, spectroscopic, and electrochemical arguments", Colombo et al. [22] discuss the emission lines of $[Rh(thpy)_2(bpy)](PF_6)$ as involving π–π* transitions of the cyclometallated ligand.

The spectra of $Pt(Et_2S)I(thpy)$ could therefore be interpreted in the same way because of the nearly identical vibronic structure in the emission spectra.

However, this interpretation would not include an explanation of the much larger red shift of the electronic origins in comparison to that of the Rh-complex with respect to the spectrum of the ligand molecule ($\Delta\bar{\nu} \approx 1420$ cm^{-1} (Rh), 2970 cm^{-1} (Pt)) or the very different ZFS patterns (total splitting $\Delta\bar{\nu} = 0.014$ cm^{-1} (Rh), 5 cm^{-1} (Pt)). These facts would indicate a larger metal contribution in the case of the Pt-compound. The energy range of the emission also led to the MLCT assignment [18] of Sandrini et al. for the bands of the heteroleptic complexes. Moreover, the spectral onsets of these compounds are located in the same region as those of $Pt(thpy)_2$ (solid state; Shpol'skii), where significant metal contributions were assumed [10,14]. In the comparison of Pt-compounds, the M–L contributions were additionally reflected by a variable ZFS, different ML vibrational bands, shorter lifetimes and, in some cases, enhanced emission intensities in comparison with the spectra of the free ligand molecules.

To answer to this problem, a more general interpretation model is presented.

5.1. Phase coupling

The π-conjugated $thpy^-$ acts as a bidentate ligand system. Therefore, for the p_π-orbitals two MO types are constructed: the π-system influences the ligand field in the form of in-phase (Ψ-type), or out-of-phase (χ-type) MOs. This model of phase coupled ligators, described by Ceulemans et al. [23], is in contrast with a purely ligand field-based model and with the conventional angular overlap model, where only additive ligand effects are considered.

Extending this model to dπ interactions, another step towards the explanation of the observed phase relationships for vibrational bands can be done.

If one conjugated π-system coordinates to Pt(II), the typical ligand vibrations (in the case of thpy$^-$ the IR active modes, slightly influenced by coordination to the metal) are found in the spectra together with an intense origin line II. On coupling a second conjugated π-system with this ligand, Raman active vibrational modes are also found. If the ligands are equal, they gain intensity. This coupling in terms of the frontier orbital concept is only effective if the metal is sufficiently involved. Spin–orbit coupling thereby supports the overlap between metal d- and ligand p-orbitals in the π-system for known reasons [24].

5.2. Exchange interaction

To retain the main properties of the ligand π–π* transitions, while varying contributions of ML interactions are found, a weak interaction between the metal and ligand π-orbital systems has to be proposed.

In addition, this interaction must be very sensitive to geometric changes in the first coordination sphere of the metal, as was seen on comparing the Rh(III)- and Pt(II)-complexes.

These conditions are combined when exchange coupling of an unpaired electron in the ligand π-system with a single electron located in the metal valence shell is assumed. This coupling is therefore used in a hypothetic model [8] to explain the intensity mechanism, the vibronic structure, and ZFS patterns of different metal complexes with conjugated π-systems as ligands. The idea is that, instead of interpretating the linear combinations of metal and ligand orbitals in terms of electron delocalizing MOs, as required e.g. by π-bonding concepts, the possibility of weak spin coupling within the electronic π-system of the complex molecule should be pointed out. In the case of a direct exchange interaction (Heisenberg), the partial electronic systems "ligand π-orbitals" and "metal valence (d) orbitals" contribute to the common π-system, keeping their individual properties.

An ideal coupling condition is seen for the coupled electrons to be located with high probability in the orbitals directly connecting M and L in both the ground and excited states. Thus, spin delocalization occurs in the sense of a nearest-neighbour interaction [25] leading to the excitation of short spin waves. In this case, high intensities of the electronic transitions are found when compared with the total intensities of the coupled vibrations. By the same argument, only minor changes in the electron distribution are expected upon excitation. The observed high resolution in the emission spectra of the title compounds is therefore due to the good π-coordination properties of thpy$^-$, which remain similar in the ground and first excited states.

The dependence on geometric changes is discussed in the following way (Fig. 8). At first, coupling of the ligand π-orbitals to the metal gives the typical ZFS pattern for that system. Does the second π-system then affect the same metal orbitals? This is the case in "planar" Pt(II)-complexes with an angle of about 180°; the ZFS of the electronic origins is increased (doubled for the homoleptic complex [10,21]), and the accompanying vibrations are phase coupled within the whole system. An angle of 90° in "octahedral" complexes does not favour this kind of vibrational

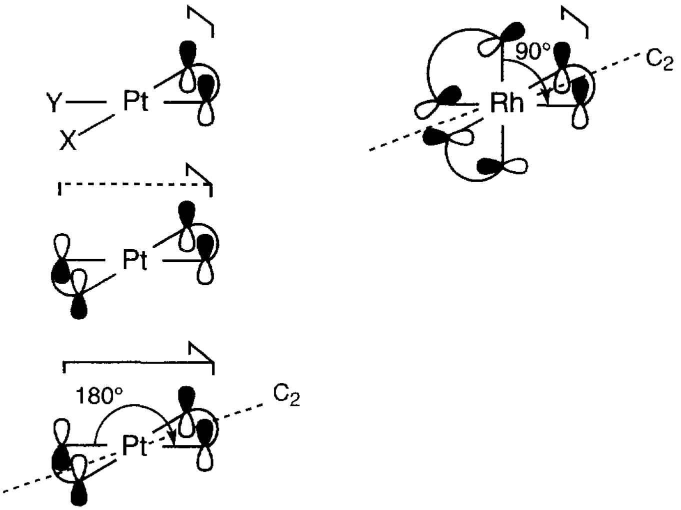


Fig. 8. Ligand vibrations and phase coupling of vibrations in the spectra of (thpy) compounds for the two different coordination types "planar" and "octrahedral". (The C_2-axis defines the ligator orientation of thpy according to Ref. [23]. Intra- and interligand phase coupling is indicated by symbols.)

phase coupling because of the nearly orthogonal arrangement of the dπ linear combinations. Hence, no great additional influence of a second or third equally coordinating ligand on the total ZFS should be found for these complexes. The intensity enhancement, however, can be explained for both coordination types, assuming conservation of the total spin [25] during spin flip excitations (triplet character of the observed transitions) within the M—L π-system.

For the octahedral coordination type, a model discussing excitation exchange coupling of the electrons on the organic ligands was presented by Riesen et al. [26]. This model also explains the negligible changes of ZFS as being dependent on the number of equal ligands for this complex type, as well as the π*-contributions of the ligands to the lowest excited states.

However, only the extension of exchange coupling to the ML interaction allows discussion of the observed highly resolved spectra in the case of the presented series of Pt(II)-complexes.

6. Summary and outlook

Chemical variation allows the preparation of a series of heteroleptic cyclometallated [Pt(thpy)]-compounds suitable for investigations with optical spectroscopy. The emission spectra of crystalline samples of $PtCl(Et_2S)I(thpy)$, $Pt(Et_2S)I(thpy)$, and Pt(phpz)(thpy) at low temperatures are sufficiently resolved to determine the region of electronic origins and vibronic bands. On comparing the vibronic structure of the spectra, clear evidence is found for the main contribution of the [Pt(thpy)]-unit to the emission properties. In addition, the highly resolved emission of the Shpol'skii system Pt(phpz)(thpy)/*n*-octane allows detailed comparison of hompleptic and heteroleptic [Pt(thpy)]-complexes. The spectra of the heteroleptic complexes show much less richness in vibronic structure, systematically depending on the number and type of π-coordinating ligands. In the same way, the sharp lines of X-trap $Pt(Et_2S)I(thpy)$ emission and doped $[Rh(thpy)_2(bpy)](PF_6)$ emission are compared. Despite the different emission energies, the spectra are nearly identical. These results point to a general model for the interpretation of the spectroscopic data, based on direct exchange interactions between metal and ligand π-orbitals, which includes the geometric characteristics of "planar" and "octahedral" π-coordination to the complex centre, as well as the ambiguity of π–π* and MLCT character of the observed transitions. Further experimental results in this field will provide the basis for a more detailed investigation of this type of weak interactions. Also, a quantitative treatment of spin coupling properties in an M–L π-system by ab initio methods should be included to give reliable ZFS values for the discussion of different excitation mechanisms.

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