High-Pressure, Low-Temperature Emission Studies of a Metal−Organic Platinum(II) Compound in a Shpol'skii Matrix

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The emission of Pt(2-thpy)$_2$ (2-thpy$^-$ = 2-(2-thienylpyridinate)) doped into an *n*-decane Shpol'skii matrix has been studied at $T = 4.2$ K (0 kbar) and at different pressures up to 14 kbar at $T \approx 5$ K. This type of matrix is used for the first time for high-pressure investigations of transition metal complexes. The emitting state of Pt(2-thpy)$_2$ is of $^3\pi\pi^*$ character with a significant MLCT admixture, and the ground state is a singlet. The spectra are well resolved and thus show the electronic origin (0−0 transition) of the most intensively emitting triplet sublevel as well as a number of vibrational Franck−Condon satellites. The corresponding pressure-induced shifts are determined. In particular, the value for the electronic origin is with $\Delta\bar{\nu}/\Delta p = -(3 \pm 1)$ cm^{-1}/kbar^{-1} relatively small, due to an apparently small inherent shift of the singlet−triplet transition. In addition, the smallness of this value seems to be related to the very weak interaction between the chromophore and the environment for this Shpol'skii matrix, whereby this interaction does not strongly change with pressure. The intensity distribution of the vibrational satellite structure shows that the equilibrium positions of the potential hypersurfaces of ground and excited states are very similar at ambient pressure. Apparently this situation is not changed up to 14 kbar.

1. Introduction

Platinum(II) complexes have attracted an increasing interest in recent years as—depending on the coordinated ligands—the lowest excited states may result from completely different types of electronic HOMO−LUMO transitions. Consequently, the different compounds exhibit very different photophysical and photochemical properties. For example, the lowest states can be metal-centered of dd* character like in [PtCl$_4$]$^{2-}$,[1,2] of metal-to-ligand charge-transfer (MLCT) character like in [Pt(CN)$_4$]$^{2-}$,[3−6] of intraligand-charge-transfer character like in Pt(qol)$_2$ (qol$^-$ = quinolinate),[7,8] of ligand-centered (LC) $\pi\pi^*$ character like in [Pt(bpy)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine),[9] or of ligand-to-ligand charge-transfer character like in Pt(tdt)(bpy) (tdt^{2-} = 3,4-toluene-dithiolate).[10,11] Of special interest is the possibility that different electronic contributions to the low-lying excited states may be chemically adjusted, as for the series of the orthometalated Pt(II) compounds.[12−14] For these it is possible to vary the MLCT contribution to the lowest states of LC character by changing the ligands.[14−16] The most intensively and successfully studied representative of this class is Pt(2-thpy)$_2$ (2-thpy$^-$ = 2-(2-thienylpyridinate), see inset of Figure 1). A deep insight into the electronic and vibronic properties of this compound could be achieved, since it was possible to obtain highly spectrally- and time-resolved emission and excitation spectra, when Pt(2-thpy)$_2$ was dissolved (doped) in an *n*-alkane matrix (Shpol'skii matrix).[16−19] However, until now, no investigations have been carried out, how an external, physical distortion—such as high pressure—influences the low-lying electronic transitions. Such an investigation is also of a more general interest, since, to our knowledge, no low-temperature studies of transition metal compounds dissolved in Shpol'skii matrices have ever been carried out at different high pressures. Therefore, it is the subject of this contribution to investigate the relatively well-resolved emission of Pt(2-thpy)$_2$ in an *n*-decane matrix under application of different hydrostatic high pressures.

2. Experimental Section

The preparation of Pt(2-thpy)$_2$[12] and the application of the Shpol'skii matrix technique[17] are described elsewhere. According to the final concentration of Pt(2-thpy)$_2$ in the matrix of about 10^{-5} mol/L, the chromophores are well isolated from each other. The measurements at

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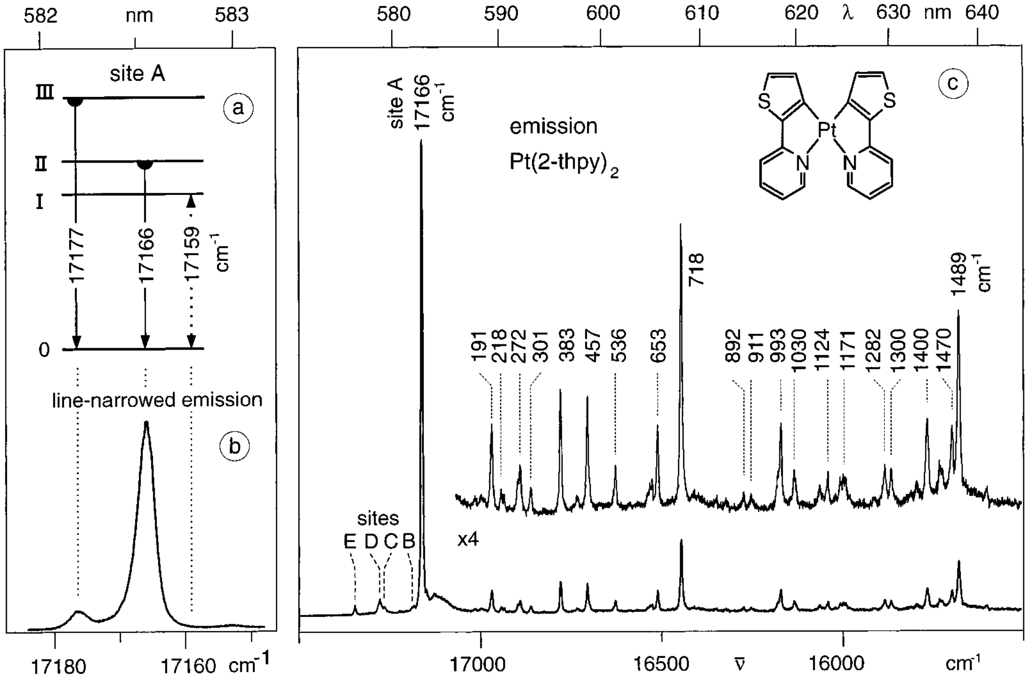

Figure 1. Emission spectra at $T = 4.2$ K and $p = 0$ kbar of Pt(2-thpy)$_2$ dissolved in *n*-decane (Shpol'skii matrix) (b, c) and energy level diagram for the lowest triplet (a). The spectra are recorded with the sample in a quartz glass tube immersed into liquid He. Spectrum (c) is excited at 457.9 nm (≙21 289 cm^{-1}), while spectrum (b) is line-narrowed according to an excitation at 17 874 cm^{-1} (vibrational satellite to origin II).

$p = 0$ kbar were performed at $T = 4.2$ K with samples in a quartz glass cell, which was positioned into the liquid He, while the high-pressure cell was immersed in superfluid, thermally highly conducting He with a nominal temperature of $T = 1.7$ K obtained by pumping off He. However, this temperature was not reached within the pressure chamber under optical excitation, despite the fact that the laser power chosen was as weak as possible. An estimate, using the known temperature dependence of emission spectra,[17] gave a sample temperature of about 5 K.

As high-pressure cell, a modified Bridgman's sapphire cell was used, as described in refs 20 and 21. A metal gasket consisting of Inconel 718 with a small round hole (diameter 0.4 mm) lies between two sapphire pistons and thus forms the high-pressure chamber. The pressure was applied via the *n*-decane matrix itself. The pressure was determined to an accuracy of about ±1 kbar[22] from the pressure-induced red-shift of the R$_1$ line of small ruby crystals,[23] which were also brought into the pressure chamber. The pressure could be adjusted from outside the cryostat by a 1:100 force transmitting differential gear.

The samples were excited with a focused, but strongly attenuated beam of an argon ion laser with a wavelength of 457.9 nm. The emission spectra were recorded with an optical setup, which essentially corresponds to the one described elsewhere.[20]

3. Results and Discussion

3.1. Electronic Transitions and Vibrational Satellites. The spectroscopic properties of Pt(2-thpy)$_2$ doped into *n*-octane have been discussed in detail in refs 16−18. These properties change only slightly, when the chromophore is dissolved in *n*-decane. Thus, one may essentially perform the same assignments as given in these references. Hence, only a short summary is presented here. The lowest excited state is a triplet of ligand centered $\pi\pi^*$ character with a significant MLCT admixture, which involves Pt(II) 5d orbitals and thus, via spin−orbit coupling, causes a zero-field splitting of 18 cm^{-1} of the three sublevels (Figure 1a). The transition between the lowest sublevel I and the singlet ground state 0 is strongly forbidden. Hence the emission lifetime is with $\tau_I = 105$ μs,[24] relatively long at $T = 1.3$ K, and the electronic origin (0−0 transition) lying at 17 159 cm^{-1} is hard to detect, but can easily be determined by application of a magnetic field of about $B = 1$ T (compare ref 15). With temperature increase sublevel II is increasingly populated. Thus, due to the larger probability of transition II ↔ 0 by some orders of magnitude as compared to I ↔ 0, the emission spectrum at $T = 4.2$ K is strongly dominated by the emission from state II (0−0 transition at 17 166 cm^{-1}). At this temperature, one can also observe the electronic origin (0−0 transition) corresponding to the triplet sublevel III (at 17 177 cm^{-1}) (Figure 1b).

For the present investigation it is of interest to recall shortly the assignments of the highly resolved emission spectrum, measured at $T = 4.2$ K (Figure 1c), since the measurements under high pressure were carried out at about this temperature. In *n*-decane the emission occurs mainly from one site (site A), for which the very intense electronic origin II lies at 17 166 cm^{-1}. Further several less important sites exhibiting corresponding electronic origins at 17 188 (B), 17 269 (C), 17 283 (D), and 17 354 cm^{-1} (E) are also marked in Figure 1c. But these may be disregarded in the context of the following discussions.

At the low-energy side of the electronic origin of site A one finds a large number of much weaker emission peaks, which correspond to transitions from the electronic state II to phonon or vibrationally excited states of the ground state 0. These satellites below about 100 cm^{-1} from the purely electronic transition at 17 166 cm^{-1} are assigned to be mainly of lattice/phonon character. Up to about 500 cm^{-1} one finds the vibrational metal−ligand modes, and at higher energy separation from the electronic origin vibrational ligand modes appear. Due to the fact that the transition at the electronic origin II is by far

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the most intense one, it may be concluded, that the Franck–Condon activity—involving totally symmetric modes—is very small.[25–27] Only for the most intense vibrational satellites at 718 and 1489 cm^{-1}, respectively, one finds the second members of the Franck–Condon progressions. The corresponding Huang–Rhys factors S (compare refs 25–27) are smaller than 0.2 and 0.1, respectively. This result demonstrates the small shifts of the equilibrium positions between ground state 0 and excited state II. Presumably most of the other satellites occurring in the emission spectrum (Figure 1c), at least the more intense ones, may also be assigned to Franck–Condon active and totally symmetric modes with similar or even smaller Huang–Rhys factors. In particular, the modes corresponding to the satellites at 191, 383, 457, 653, 1030, 1124, and 1400 cm^{-1} have also been assigned to Franck–Condon active modes for Pt(2-thpy)$_2$ dissolved in *n*-octane.[17,18]

3.2. Emission Spectra at High Pressure. Figure 2 shows the emission spectra at different pressures normalized to the energy position of the electronic origin. Because of the low emission intensity due to the very small sample volume in the pressure cell, the spectral resolution obtained was somewhat reduced compared to the experiments carried out at zero pressure (Figure 2a and b). From Figure 2 it is obvious that with application of high pressure the peaks observed are further broadened due to inhomogeneities over the sample volume. This effect is more pronounced than found for samples of single crystals immersed in a pressure transmitting medium.[28,29] Possibly, the broadening is additionally increased due to the fact that the matrix for Pt(2-thpy)$_2$ acts equally as pressure medium in the present investigation. Nevertheless, the fine structure of the spectrum is maintained. Thus, one can determine the shift of the electronic origin II (Figure 3) and the relative shifts of several vibrational satellites (Figure 4) with application of high pressure.

The electronic transition between the triplet sublevel II and the ground state 0 exhibits a red shift of $\Delta\bar{\nu}/\Delta p = -(3 \pm 1)$ cm^{-1} kbar^{-1} (Figure 3). This value is caused by the shift of the LC–$\pi\pi^*$ transition upon compression, but it is also influenced by the shift of the d orbitals due to the MLCT admixtures.[17] A comparison with other compounds shows that the shift observed is relatively small (Table 1). For example, for pentacene,[30] the singlet–singlet transition of $\pi\pi^*$ character is shifted by −16 cm^{-1} kbar^{-1} and for $[Ru(bpy)_3]^{2+}$ in $[Zn(bpy)_3](ClO_4)_2$ or $[Os(bpy)_3]^{2+}$ in $[Ru(bpy)_3](ClO_4)_2$ the lowest sublevels of ^{3}MLCT character exhibit pressure-induced shifts of −12.5 and −13 cm^{-1} kbar^{-1}, respectively.[31] Often, in highly diluted systems the shifts under application of high pressure are explained only on the basis of electronic effects due to an inherent intramolecular compression, while the chromophore–matrix interactions are not taken into account (but see, for example, the reports by Offen et al.[32]). Changes of such interactions under application of high pressure may easily result in a significant contribution to the total pressure-induced shift. The importance of the matrix is manifested by the fact that the energy positions of the electronic transitions depend mostly significantly on the matrix material and/or on the individual environment. This is displayed, for example, by the occurrence of sites with different energies and can directly be observed in highly resolved spectra (e.g. see Figure 1c). Moreover, the changes of the chromophore–matrix interactions under application of high pressure will—besides other effects such as symmetry changes—also depend on the type of the intermolecular interaction, which is characteristic for the matrix material. For example, matrices with long-range electrostatic forces, like ionic materials, will obviously be connected to different shifts compared to matrices with short-

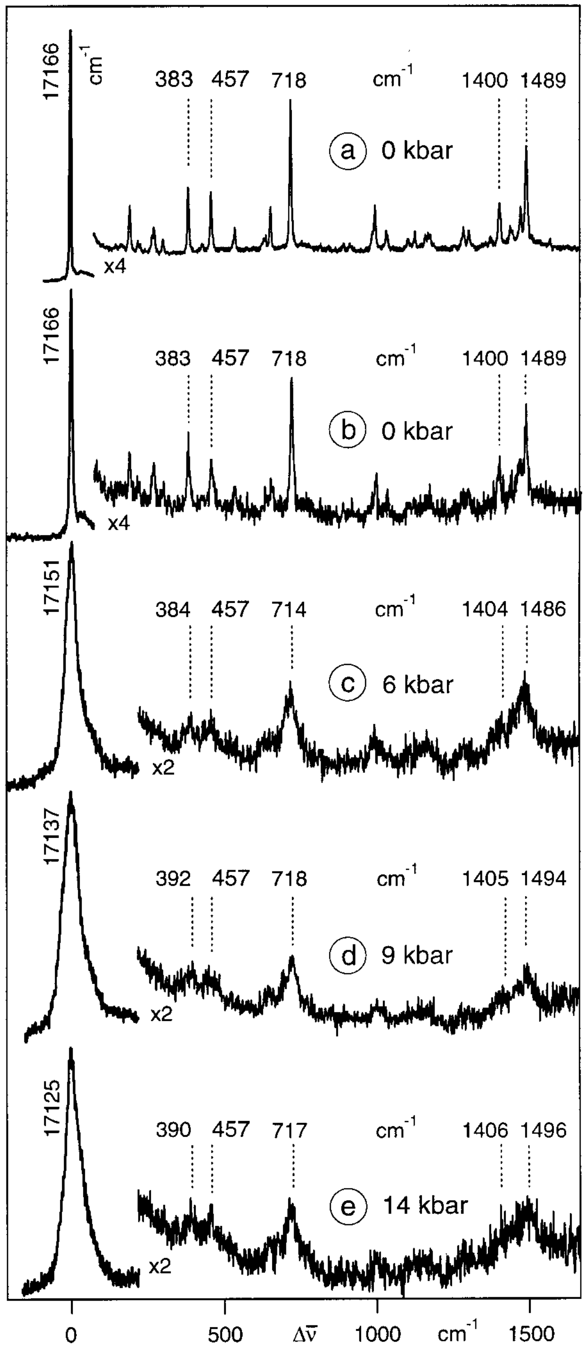

Figure 2. Emission spectra of Pt(2-thpy)$_2$ in *n*-decane (Shpol'skii matrix) at different pressures ($T \approx 5$ K) (b–e). For comparison the $p = 0$ kbar spectrum recorded at $T = 4.2$ K with a higher resolution is also reproduced (a) (same spectrum as shown in Figure 1c). The spectra are normalized to the energy positions and the peak heights of the electronic origins. For $p \geq 6$ kbar the matrix becomes transparent.

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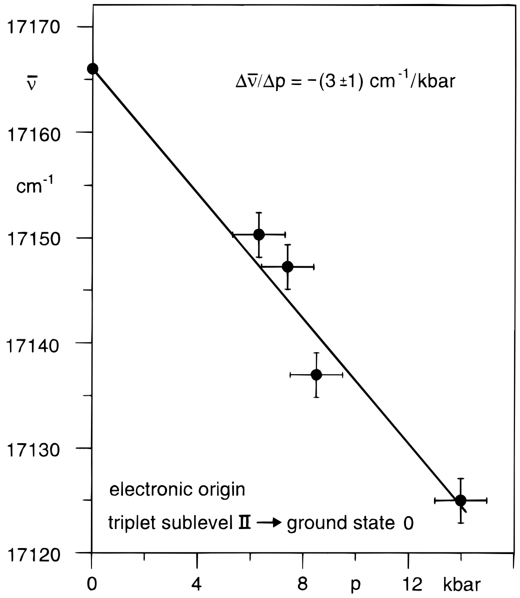

Figure 3. Pressure-induced shift at $T \approx 5$ K of the electronic origin (0−0 transition) corresponding to the transition of the triplet sublevel II to the electronic ground state 0 of Pt(2-thpy)$_2$ dissolved in *n*-decane (Shpol'skii matrix).

range dispersion forces such as Shpol'skii matrices (if equal compressibilities are assumed). Thus, the smallness of the pressure-induced shift for Pt(2-thpy)$_2$ in *n*-decane seems to be connected to the relatively inert alkane matrix in combination with a small intramolecular electronic effect. Interestingly, a comparatively small pressure-induced shift of -4.8 cm^{-1} kbar^{-1} has also been found for the singlet−singlet transition of $\pi\pi^*$ character of dihydroporphine dissolved in an *n*-octane Shpol'skii matrix,[33] which seems to support the model discussed above.

Figure 2 shows that several vibrational satellites may still be resolved up to 14 kbar. In particular, those satellites that exhibit relatively high intensities in regions of spectrally nonoverlapping satellites may be used to determine the pressure-induced shifts of the vibrational energies relative to the purely electronic transition. Figure 4 reproduces shifts for several vibrations. The values observed are rather different and range from zero to $+0.85$ cm^{-1}/kbar. Shifts of similar amounts have often been determined from pressure-dependent emission and IR/Raman investigations.[28,31,34−39] Shifts to higher energies result from strengthening of the force constants of the corresponding vibrations. Large pressure-induced blue shifts are found for vibrations of metal−ligand (M−L) character (383 cm^{-1} mode) as well as for modes of nearly pure ligand character (1489 cm^{-1}), while the unshifted vibration (457 cm^{-1}) has been assigned to be an M−L vibration. This tells us that a simple correlation between pressure-induced shifts and the energy or the coarse assignment of the character of the vibration does not exist. A more detailed assignment is currently not possible, since in particular, a normal coordinate analysis is not yet available for Pt(2-thpy)$_2$.

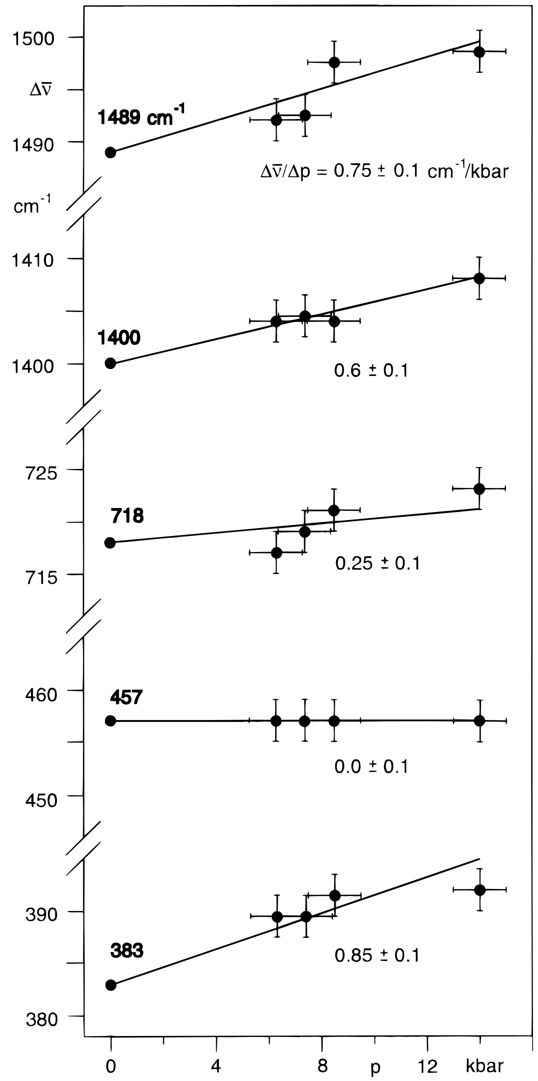

Figure 4. Pressure-induced shifts at $T \approx 5$ K of several vibrational modes, which occur as satellites to the electronic origin II → 0 in the emission of Pt(2-thpy)$_2$ dissolved in *n*-decane.

Due to the fact that the intensities of the vibrational satellites relative to the intensity of the electronic origin (0−0 transition) does not significantly change with application of high pressure up to 14 kbar one can conclude that the radiative mechanisms as well as the very small values of the Huang−Rhys factors are not altered in this pressure range. Further, no indication of a phase transition is seen, as may be deduced from the monotonical shift of the transition energy as is shown in Figure 3. (Compare refs 5b, 6, 20, 34, and 35 for situations with phase transitions.)

4. Conclusion

A high pressure study of the emission spectrum of a metal-organic transition metal compound doped into a Shpol'skii matrix is reported for the first time. Pt(2-thpy)$_2$ is dissolved in *n*-decane and is investigated at $T \approx 5$ K by measuring the emission resulting from one of the low-lying triplet sublevels. The corresponding electronic origin (0−0 transition) lying at

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Table 1. Comparison of Pressure-Induced Shifts of Electronic Transition Energies for Different Compounds

compound	transition energy $\bar{\nu}^a$ [cm^{-1}]	$\Delta\bar{\nu}/\Delta p$ [cm^{-1}/kbar]	T [K]	assignments	ref
Pt(2-thpy)$_2$ in *n*-decane	17 166	−3	5	$^3\pi\pi^*$ + MLCT; II → 0[b]	this work
dihydroporphine in *n*-octane	15 730	−4.8	4.2	$^1\pi\pi^*$ $S_0 \rightarrow S_1$	33
[Cr(urea)$_6$](ClO$_4$)$_2$ single crystal	14 191	−5.5	120	dd* $^2E_g \rightarrow {}^4A_{2g}$	28
[Os(bpy)$_3$]$^{2+}$ in [Ru(bpy)$_3$](ClO$_4$)$_2$	14 169	−13	2	^{3}MLCT; I → 0[b]	31,42
[Ru(bpy)$_3$]$^{2+}$ in [Zn(bpy)$_3$](ClO$_4$)$_2$	17 684	−12.5	2	^{3}MLCT; I → 0[b]	31,42
pentacene in *p*-terphenyl	16 883	−16	15	$^1\pi\pi^*$ $S_0 \rightarrow S_1$	30
KCr(SO$_4$)$_2$·12H$_2$O crystalline	17 700	+17	295	dd* $^4A_{2g} \rightarrow {}^4T_{2g}$	40
[Cr(NH$_3$)$_6$]$^{3+}$ aqueous solution	21 560	+53	295	dd* $^4A_{2g} \rightarrow {}^4T_{2g}$	41
Eu[Au(CN)$_2$]$_3$·3H$_2$O single crystal	23 600	−130	20	two-dimensional semiconductor with tunable energy transfer	29
	16 888	−0.84	20	Eu^{3+} [c] $^5D_0 \rightarrow {}^7F_1$	
K[Au(CN)$_2$] single crystal	25 200	−200	295	two-dimensional semiconductor	43,44
Mg[Pt(CN)$_4$]·7H$_2$O single crystal	17 550	−320	295	one-dimensional semiconductor	5,6,43

[a] $p = 0$ kbar. [b] I, II, and III represent the lowest triplet sublevels, 0 is the singlet ground state. [c] Further shifts of Eu^{3+} lines are given in ref 29.

17 166 cm^{-1} and the related vibrational satellite structure has been spectrally resolved. Interestingly, the pressure-induced shift of the electronic origin of $\Delta\bar{\nu}/\Delta p = -(3 \pm 1)$ cm^{-1} kbar^{-1} is relatively small. Presumably, the occurrence of such a small value is related to the weak chromophore−matrix interaction characteristic for Shpol'skii matrices. This behavior suggests that the interaction with the matrix is more important than usually is assumed, when pressure-induced shifts of electronic transitions of diluted chromophores are interpreted. However, experimentally it will be extremely difficult to conclude on the amount of this matrix induced effect compared to the total shift. The pressure-induced shifts of most of the vibrational energies lie between +0.5 and nearly +1.0 cm^{-1} kbar^{-1} and thus are of the same order as are found usually. Since these shifts occur in an opposite sense as the shift of the electronic origin, it follows that not sufficiently well resolved or broad band spectra could easily give misleading values. This justifies additionally the great efforts to obtain highly resolved spectra.

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