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One-Dimensional Migration of ^{3}MLCT Excitation Energy in Pd^{II}(phbpy)Cl (phbpy = 6-Phenyl-2,2′-bipyridine)

Cyclometalated complexes of d^6 and d^8 transition-metal ions have received a great deal of attention in recent years.[1-5] The synthesis and the crystal structure of the title compound have been described only recently.[3,4] The structure is characterized by a one-dimensional stacking of the molecular units. Pd^{II}(phbpy)Cl (phbpy = 6-phenyl-2,2′-bipyridine) exhibits very unusual luminescence properties below 80 K, which will be reported and interpreted in this communication. The nature of the luminescent state is triplet metal-to-ligand charge transfer (^{3}MLCT) as in Ru(bpy)$_3^{2+}$. Very efficient energy migration with an estimated hopping rate of 10^{11} s^{-1} occurs at 41 K. From an analysis of the decay curves this migration is shown to be highly one-dimensional (1-D), as can be expected from the crystal structure. Pd^{II}(phbpy)Cl was prepared by stirring a solution of 350 mg (1.02 mmol) of Na$_2$PdCl$_4$ and 302 mg (1.3 mmol) Hphbpy in 50 mL of methanol for 24 h at room temperature. The yellow solid was filtered out and washed with hexane, water, acetone, and diethyl ether (yield 86%). The analytical and NMR data were consistent with the above formula. Needlelike crystals were grown from a saturated solution in DMF by slow evaporation (3 weeks).

At the top of Figure 1 the 8 K luminescence spectrum of a crystal of Pd^{II}(phbpy)Cl is shown in comparison with the 77 K spectrum of Ru(bpy)$_3^{2+}$ in a 4:1 ethanol/methanol glass.[5] There is a striking similarity of the two spectra with the ~1500-cm^{-1} progression as a dominant feature. The first strong peak in Pd^{II}(phbpy)Cl is an ~500-cm^{-1} vibronic origin, as can be deduced from a comparison with the absorption spectra (not illustrated here).[6] This energy is in the range of the Pd–Cl vibration. In Ru(bpy)$_3^{2+}$ the enabling modes are about 200 cm^{-1}.[7] It is thus safe to assume that the nature of the luminescent states is the same for both complexes, i.e. ^{3}MLCT.

Figure 1 also illustrates the temperature dependence of the Pd^{II}(phbpy)Cl luminescence. At 8 K most of the luminescence is intrinsic. Raising the temperature leads to luminescence from a trap with the first strong luminescence peak shifted by ~1400 cm^{-1} to lower energy. At 80 K the intrinsic luminescence can no longer be observed. Thus, excitation energy migration from the originally excited Pd^{II}(phbpy)Cl molecules is transferred to traps, and this excitation energy transfer is thermally activated.

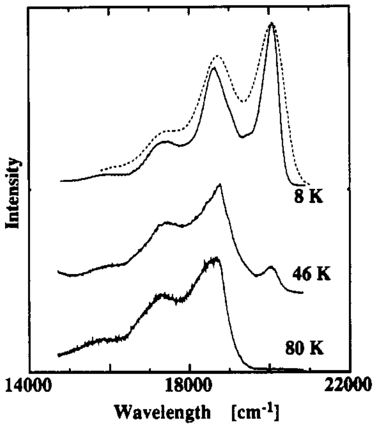

Figure 1. Temperature dependence of the Pd^{II}(phbpy)Cl single-crystal luminescence. The integral of the spectra has been normalized. The broken line is the Ru(bpy)$_3^{2+}$ luminescence in a 4:1 ethanol/methanol glass at 77 K shifted by 2720 cm^{-1} to higher energy.

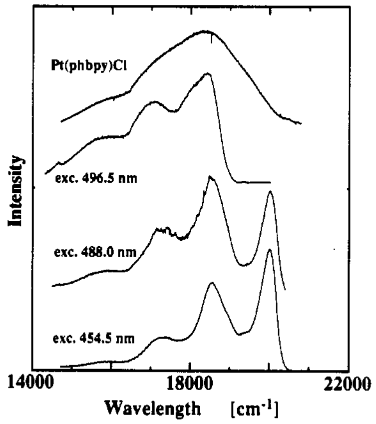

Figure 2. 8 K luminescence of a Pd^{II}(phbpy)Cl crystal excited at various wavelengths. The spectra have been normalized. The top trace depicts the 11 K luminescence of Pt^{II}(phbpy)Cl in PMMA.

Figure 2 shows the dependence of the luminescence spectrum of Pd^{II}(phbpy)Cl on the wavelength of excitation at 8 K. The 496.5-nm Ar$^+$ ion laser line—by which the Pd(II) complex is not excited—leads to selective excitation of the trap luminescence, as can be seen by comparison with the 80 K spectrum in Figure 1. A good guess as to the nature of the trap is obtained from a comparison with the corresponding Pt^{II}(phbpy)Cl. A spectrum of this complex imbedded in PMMA (poly(methyl methacrylate)) is included in Figure 2. It is not as well resolved as in the crystal, but we can safely assign the trap to this complex, which easily substitutes for a host molecule in the crystal. The Na$_2$PdCl$_4$

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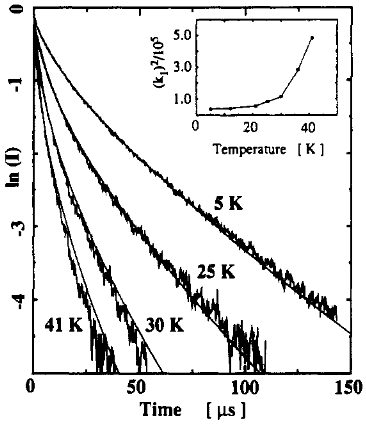

Figure 3. Normalized logarithmic plot of the emission decay curves of Pd^{II}(phbpy)Cl measured at 20 000 cm^{-1} for several temperatures. The full lines correspond to fits of the decay curves by eq 1 with k_e = 14 050 s^{-1}. The insert shows the temperature dependence of the square of k_1.

compound supplied by Fluka had a nominal Pt impurity level of 120 ppm. From an X-ray fluorescence analysis of our samples we conclude that the synthesis and crystallization of Pd^{II}(phbpy)Cl leads to an accumulation of Pt(II) up to an order of magnitude of 0.1%.

In Figure 3 the decay curves of the intrinsic luminescence measured at 20 000 cm^{-1} are illustrated for four temperatures. We notice a considerable increase of the decay rate between 5 and 41 K, and we attribute this to nonradiative excitation energy migration through the Pd^{II}(phbpy)Cl lattice to the traps. The decay curves are nonsingle exponentials down to 5 K. This can have several reasons, and in the present system it is most likely due to a pronounced anisotropy of the energy migration. We have one of the very rare examples of a system in which the transfer rate in one dimension significantly exceeds the rates in the other directions, thus leading to a "slowing down" in the course of the luminescence decay process. The archetype 1-D transition-metal compound is tetramethylammonium manganese(II) chloride (TMMC), in which the luminescence decay curves show a very similar behavior and to which various theoretical models of exciton migration have been applied.[8,9] The decay curves in Figure 3 can reasonably be fitted by the function[10]

$$I = I_0 \exp(-k_e t - k_1 t^{1/2}) \qquad (1)$$

This function has been derived for 1-D energy migration in a lattice with an ordered distribution of impurities.[10] This assumption is likely to be incorrect in our case, but it has been shown that experimental data usually do not significantly discriminate between this equation (eq 1) and treatments that assume random distributions of the impurity.[8,9] In eq 1 k_1 is the rate constant for exciton trapping along the chain and k_e is the sum of the intrinsic decay rate k_i and a rate constant k_3, which takes into account three-dimensional energy migration to traps ($k_e = k_i + k_3$). The curves were fitted by a least-squares procedure before taking the logarithm of the intensity. For the 5 K curve both parameters k_e and k_1 were optimized whereas for all the other curves k_e was kept at its 5 K value. The 5 K values of k_e and k_1 are 14 050 s^{-1} and 193 $s^{-1/2}$, respectively. The insert in Figure 3 shows the temperature dependence of the square of k_1, which is directly proportional to the 1-D hopping rate ν_1 as given by eq 2, where X_{trap} corresponds to the mole fraction of trap sites to

$$\nu_1 = \pi(k_1)^2/[8(X_{trap})^2] \qquad (2)$$

Pd(II) sites.[10] With a trap concentration of around 0.1% we thus get a 1-D hopping rate of approximately 10^{11} s^{-1} at 41 K. This rate is about 10 times slower than the on-chain hopping rate in tetramethylammonium manganese(II) chloride at room temperature.[8,9] Recalling the one-dimensional stacked structure of the present compound, with a Pd–Pd separation of about 5.06 Å,[11] we find that the deduced order of magnitude of the transfer rate seems reasonable. The obtained 1-D hopping rate represents an upper limit, since k_e was kept at its 5 K value for fitting the curves at higher temperatures. Fits in which k_e was floated as well were not significantly better. For a more rigorous analysis of the decay curves a measurement of the intrinsic decay rate k_i in a dilute medium would be necessary. However, we have failed to find a suitable glass. All the glasses examined showed very large red shifts of the spectra, indicating that some changes occur in the first coordination sphere.

Nevertheless, we can get a lower limit of the one- to three-dimensional hopping rate ratio on the basis of the present results. The three-dimensional hopping rate, ν_3, can be approximated by[8]

$$\nu_3 \approx -\nu_1/2 + (\nu_1^2/4 + 0.8k_3^2/X_{trap}^2)^{1/2} \qquad (3)$$

Taking into account that $k_3 \leq k_e$, we obtain an upper limit for ν_3 of 1 × 10^4 s^{-1} and a lower limit for the ν_1:ν_3 ratio of 1 × 10^6 *at 5 K*. A pronounced one-dimensionality of the energy migration is therefore established.

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Bond Angle of CaF_2 in Several Host Matrices

In 1989, we published a note[1] indicating that infrared measurements of central metal atom isotope shifts for TiF_2 isolated in an argon matrix, which had been used to calculate an FTiF bond angle of ca. 120°, were in error. In addition, we questioned "how many of the results on high temperature molecules lead to *unambiguous* determination of the shape of the free molecule". Since that paper, we have shown[2] that, in a nitrogen matrix, $NiCl_2$ has a bond angle of ca. 130° using infrared isotope shift data and the harmonic approximation. This is in contrast to an argon matrix[2] where "The isotopic shift method ... cannot reliably detect any non-linearity". It is also known that the shapes of $ThCl_4$,[3] $CsUF_6$,[4] $CsNbF_6$,[5] and some pentachlorides[6] are martrix dependent.

For the group IIa dihalides, the heavier metals in combination with the more electronegative halogens appear to give the more strongly bent structures. The experimental techniques that have

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