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Large Pressure-Induced Increase in Luminescence Intensity for the $[Pd(SCN)_4]^{2-}$ Complex

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Broad-band luminescence in the red to near-infrared wavelength range from transition metal complexes is usually weak at room temperature.[1,2] The luminescence intensity of $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ single crystals[3] at room temperature shows an unprecedented pressure-induced increase by several orders of magnitude. Other square planar d^8 complexes, such as the well-studied $[Pt(CN)_4]^{2-}$, do not show comparable increases,[4] and compounds, such as $[Ru(bpy)_3]^{2+}$ [5] or *trans*-$[ReO_2(tmen)_2]^+$,[6] show an intensity decrease with pressure. A recent study[7] on manganese(II) ions doped into $Ca_{0.25}Sr_{0.75}F_2$ documents an increase of the luminescence lifetime by a factor of 4 at 40 kbar. This effect is lower by orders of magnitude than the effect described here.

Figure 1 illustrates the variation of the luminescence intensities of $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ as a function of pressure and temperature.[8] The room-temperature luminescence at the lowest pressure shown is very weak. At higher pressures, the luminescence intensities increase rapidly and become up to 3 orders of magnitude larger at 29 kbar than at ambient pressure. Band maxima show a significant blue-shift of 29 cm^{-1}/kbar. The luminescence intensity also varies strongly with temperature, increasing by a factor of 5 between 70 and 10 K. Vibronic progressions involving both the totally symmetric Pd−S stretching mode (a_{1g}, D_{4h}) and the nontotally symmetric in-plane Pd−SCN bending mode (b_{2g}, D_{4h}) are resolved as indicated in Figure 1b. The vibrational assignments are based on a normal coordinate analysis, and the frequencies of these modes are 274 and 147 cm^{-1}.[3] Pressure-dependent Raman spectra show monotonic frequency increases of 0.7 cm^{-1}/kbar for both modes. The absence of any abrupt changes in the pressure-dependent Raman and luminescence spectra indicates that there are no drastic structural changes of the title complex in the pressure range shown in Figure 1a.

Figure 2 shows luminescence lifetimes and integrated band intensities as a function of pressure. The most intense spectrum, observed at 29 kbar, is more intense by a factor of 1500 than the spectrum at 1 kbar. The luminescence lifetimes increase from 330 ns at ambient pressure to 53 μs at 29 kbar, an increase by a factor of 160. By comparison, luminescence lifetimes for complexes with a pressure-induced change of the emitting state, such as $[VCl_6]^{3-}$,[9] or many chromium(III) compounds,[10] show an increase that is smaller by at least an order of magnitude than that for the title complex over the pressure range in Figure 2. Pressure-dependent measurements were also performed on $[Pt(SCN)_4](n\text{-}Bu_4N)_2$, and we observe a lifetime increase from 750 ns at atmospheric pressure to 17 μs at 27 kbar and an intensity increase by almost 2 orders of magnitude (data not shown). All luminescence intensities begin to decrease steadily at pressures above 30 kbar, an effect that is well-established when energy transfer between molecules becomes more efficient at higher pressures.[11]

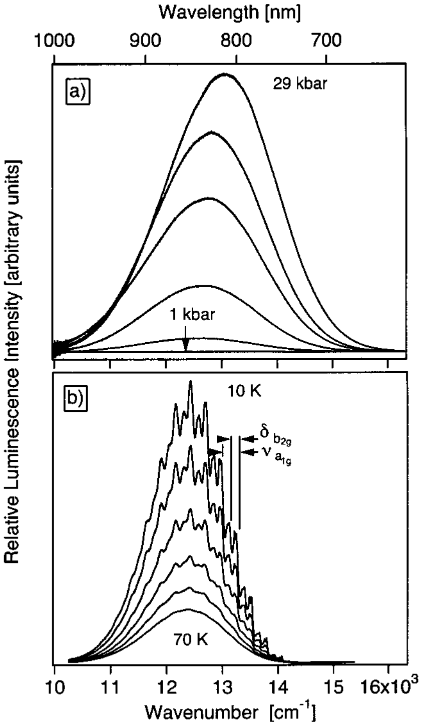

Figure 1. (a) Pressure-dependent luminescence spectra of $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ at 300 K and 1 (bottom trace), 2, 5, 13, 17, and 29 kbar (top trace). (b) Temperature-dependent luminescence of $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ at 70 K (bottom trace), 50, 40, 30, 20, and 10 K (top trace). Modes defining vibronic progression intervals are identified by labels in the D_{4h} idealized point group.

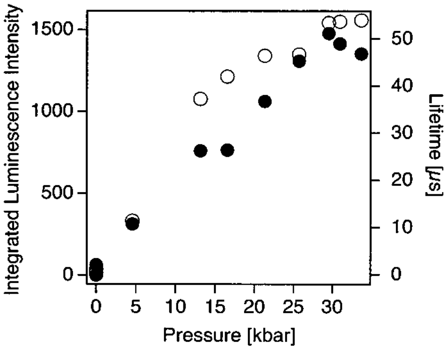

Figure 2. Pressure-dependent luminescence lifetimes (○) and intensities (●) for $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ at 300 K. The integrated intensity at 1 kbar was scaled to 1, and the same scaling factor has been applied to integrated intensities at other pressures.

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We qualitatively consider four effects that contribute to the large and unexpected increase in luminescence intensity of the $[Pd(SCN)_4]^{2-}$ complex with increasing pressure shown in Figures 1 and 2. This large increase occurs because radiative and nonradiative relaxation rate constants are competitive in magnitude.

The point-group symmetry of the PdS_4 fragment is D_{4h}.[3] External pressure can break the inversion symmetry, for example by slightly bending some of the SCN^- ligands out of the plane of the complex, leading to a more allowed luminescence transition in a lower symmetry and to shorter luminescence lifetimes. The fact that both lifetimes and intensities *increase* with increasing pressure suggests that the nonradiative rate constant decreases significantly.

The blue-shift of the luminescence band indicates that the gap between the ground and emitting states increases with pressure. The number of vibrational quanta needed to bridge this energy gap also increases, and the nonradiative rate constant is expected to decrease according to the energy gap law.[12] For the title complex, the number of 2100 cm^{-1} CN stretching quanta increases from 6.0 to 6.2 between ambient pressure and 29 kbar, leading to a decrease of the nonradiative rate constant at high pressure by less than a factor of 2. This reveals that the blue-shift is a likely contribution to the observed increase of lifetimes and intensities in Figure 2, but not sufficient to fully account for the effect.

The luminescence spectra of $[Pd(SCN)_4]^{2-}$ in Figure 1b show that the offsets between the ground-state and emitting potential energy surfaces along several metal−ligand normal coordinates are large.[1] The activation energy for nonradiative relaxation increases when pressure reduces these large displacements. Literature reports indicate that pressure effects on bending modes of four-coordinate complexes lead to larger changes in the electronic spectra[13] than effects on stretching modes, and we therefore expect that the offset along the b_{2g} bending coordinate decreases most with pressure and leads to a much higher activation energy for nonradiative relaxation. This is corroborated by preliminary pressure-dependent luminescence spectra of $K_2[PdBr_4]$ where the published analysis of the low-temperature spectra shows that the only nonzero offsets occur for stretching normal coordinates.[2] A very small pressure-induced luminescence intensity increase by a factor of 4 is observed for $[PdBr_4]^{2-}$, followed by a rapid decrease at higher pressures. These results imply that the nature of the ligands and the emitting-state distortions that they induce play an important role in the increase of luminescence intensities with pressure. In the title complex, the spatial arrangement of the thiocyanate ligands appears to be significantly altered by intermolecular effects, in which these ligands act as efficient levers that pressure-tune the metal-centered luminescence transition. This characteristic is a major contribution to the pressure effects in Figures 1 and 2.

Previous work on D_{4h} *trans*-dioxo rhenium(V) complexes has demonstrated that pressure can change the shape of the ground-state potential energy surface by "pushing up" areas at larger values along the coordinates with nonzero offsets.[6] This effect is a manifestation of an avoided crossing between coupled electronic states and depends strongly on the energies and normal coordinate offsets of the potential energy minima. Electronic states can be coupled through spin−orbit and configuration interactions, which are strong for second- and third-row transition metal complexes. Coupling amplifies the effect of pressure on the potential energy surfaces beyond the simple shifts discussed in the preceding paragraph, resulting in even higher activation energies for nonradiative transitions. This effect is most important for lower-energy transitions, as illustrated by the comparison with $[Pt(SCN)_4]^{2-}$, where we observe a luminescence maximum higher in energy by approximately 2000 cm^{-1} than that for the title complex and, consequently, less dramatic pressure effects on luminescence intensities and lifetimes.

It is likely that all four effects described above contribute to the surprising pressure-induced luminescence properties of the title complex. The large enhancement, at relatively modest pressures, of the near-infrared luminescence properties of the $[Pd(SCN)_4]^{2-}$ complex is unprecedented and may lead to new applications as a remote sensor for pressure.

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Supporting Information Available: Selected pressure-dependent Raman spectra, luminescence decay curves, with single-exponential fits, and temperature-dependent luminescence intensities and lifetimes for $[Pd(SCN)_4]^{2-}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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(8) $[Pd(SCN)_4](n\text{-}Bu_4N)_2$ was prepared following ref 3. The spectrometers and correction procedures used have been described before.[6] Microscope optics (Renishaw 3000) allowed us to verify and adjust the sample position and obtain reliable intensities as pressure is varied. Pd−S Raman bands were used as internal intensity standards leading to estimated errors of less than ±40 units on the intensity scale of Figure 2. Luminescence lifetimes as a function of pressure were measured using the 532 nm output of a pulsed Nd: YAG laser, a photomultiplier tube (Hamamatsu R928) and a digital oscilloscope. All pressure-induced phenomena presented here are reversible.
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