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Large Pressure-Induced Red Shift of the Luminescence Band Originating from Nonstacked Square-Planar $[Pt(SCN)_4]^{2-}$ in a Novel Trimetallic Complex

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Luminescence of the novel trimetallic complex $\{Pt(SCN)_2[(\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$ originates from a d–d transition of the square-planar $[Pt(SCN)_4]^{2-}$ moiety. The band maximum shows a red shift of –99 cm^{-1} $kbar^{-1}$ under external pressure up to 32 kbar at room temperature. This red shift is comparable to values for crystals where Pt–Pt interaction between stacked complexes is enhanced by pressure, but the crystal structure for the trimetallic complex shows that no metal–metal interaction can occur.

Luminescence of square-planar complexes of platinum(II) and palladium(II) with simple ligands such as thiocyanate is often observed in the red spectral region, but it is usually weak at ambient temperature and pressure because of the spin-forbidden nature of the d−d transition and efficient nonradiative processes.[1−4] With the application of an external pressure, a blue shift of the luminescence band maximum has been reported for several of these compounds, caused by stronger destabilization of the σ^* lowest unoccupied molecular orbital (LUMO) than the π^* highest occupied MO (HOMO) as a consequence of the reduction of the metal−ligand distances. A typical range of +10 to +24 cm^{-1} $kbar^{-1}$ is reported for $[Pt(SCN)_4]^{2-}$ complexes with different counterions.[4,5] Some of these compounds show an increase of the room-temperature luminescence intensity by 2−3 orders of magnitude with pressure.[3,4]

For a few square-planar complexes of platinum(II) forming column structures, pressure-induced red shifts of absorption or luminescence bands have been observed.[6−14] Typical values vary between −115 and −320 cm^{-1} $kbar^{-1}$ and are a consequence of Pt−Pt interactions. The close stacking of the square-planar complexes, where metal centers are separated by 3 Å or less, leads to an overlap of the d_{z^2} HOMO orbitals from all platinum(II) centers, creating a valence band.[14] With increasing pressure, this valence band is destabilized. The vacant p_z orbitals of adjacent platinum(II) centers start to overlap and form a conduction band, which is stabilized, leading to the drastic decrease in the luminescence energy.

Here we report a new compound[15] that shows a strong red shift of its luminescence maximum under external pressure. In contrast to the red shifts in the literature, its crystallographic structure[16] clearly indicates that no Pt−Pt interactions can occur. The most likely reason for this unusual

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(1) Tuszynski, W.; Gliemann, G. *Z. Naturforsch.* **1979**, *84a*, 211.

(2) Pelletier, Y.; Reber, C. *Inorg. Chem.* **2000**, *39*, 4535.

(3) Grey, J. K.; Butler, I. S.; Reber, C. *J. Am. Chem. Soc.* **2002**, *124*, 9384.

(4) Grey, J. K.; Butler, I. S.; Reber, C. *Inorg. Chem.* **2003**, *42*, 6503.

(5) Hidvegi, I.; Tuszynski, W.; Gliemann, G. *Chem. Phys. Lett.* **1981**, *77*, 517.

(6) Zahner, J. C.; Drickamer, H. G. *J. Chem. Phys.* **1960**, *33*, 1625.

(7) Yersin, H.; Hidvegi, I.; Gliemann, G.; Stock, M. *Phys. Rev. B* **1979**, *19*, 177.

(8) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87.

(9) Yersin, H.; Riedl, U. *Inorg. Chem.* **1995**, *34*, 1642.

(10) Wenger, O. S.; García-Revilla, S.; Güdel, H. U.; Gray, H. B.; Valiente, R. *Chem. Phys. Lett.* **2004**, *384*, 190.

(11) Shirotani, I. *Solid State Commun.* **1986**, *59*, 533.

(12) Konno, M.; Okamoto, T.; Shirotani, I. *Acta Crystallogr.* **1989**, *B45*, 142.

(13) Shirotani, I.; Inagaki, Y.; Utsumi, W.; Yagi, T. *J. Mater. Chem.* **1991**, *1*, 1041.

(14) Takeda, K.; Shirotani, I.; Yakushi, K. *Chem. Mater.* **2000**, *12*, 912.

(15) Synthesis of $\{Pt(SCN)B_2B[(\mu\text{-}SCN)Mn(NCS)(bipy)B_2B]B_2B\}$ (**3**): $Mn(NCS)_2(py)_4$ (**1**) and $Mn(NCS)_2(bipy)_2$ (**2**) were synthesized in a way similar to that reported for the iron(II) analogues. (Kauffman, G. B.; Albers, R. A.; Harlan, F. L. In *Inorganic Synthesis*; John Wiley & Sons Inc.: New York, 1982; Vol. 12, pp 251. Gallois, B.; Real, J.-A.; Hauw, C.; Zarembowitch, J. *Inorg. Chem.* **1990**, *29*, 1152. Real, J.-A.; Gallois, B.; Granier, T.; Suez-Panama, F.; Zarembovitch, J. *Inorg. Chem.* **1992**, *31*, 4972.) Synthesis of **1**: An aqueous mixture containing NH_4SCN was added to an aqueous mixture containing $MnCl_2$ and pyridine. The resulting white precipitate was obtained and washed with an aqueous mixture of pyridine (9:1), yield 81%. Synthesis of **2**: A solution of 2,2′-bipyridine in methanol was added to a solution of **1** in methanol. The resulting yellow precipitate was isolated upon filtration and then washed with methanol, yield 92%. Anal. Calcd for $MnC_{22}N_6S_2H_{16}$: C, 54.5; H, 3.57; N, 17.3; S, 13.2. Found: C, 54.5; H, 3.53; N, 17.2; S, 13.7. Synthesis of **3**: A suspension of $PtCl_2$ in acetone was added to a solution of **2** under reflux in acetone. After stirring, methanol was added to the suspension, and the mixture turned limpid yellow after 20 min. The solution was cooled to room temperature, and slow evaporation led to the formation of orange crystals. Anal. Calcd for $Pt_1Mn_2C_{46}N_{14}S_6H_{32}$: C, 43.2; H, 2.52; N, 15.3; S, 15.1. Found: C, 43.1; H, 2.55; N, 15.3; S, 14.8.

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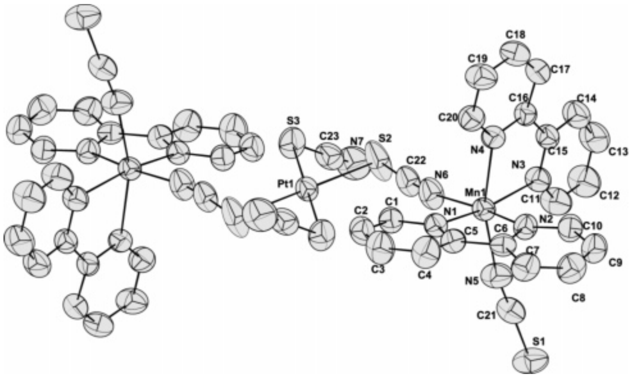

Figure 1. Representation of the complex $\{Pt(SCN)_2[(\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$. The hydrogen atoms have been omitted for clarity. Ellipsoids are represented at the 30% probability level.

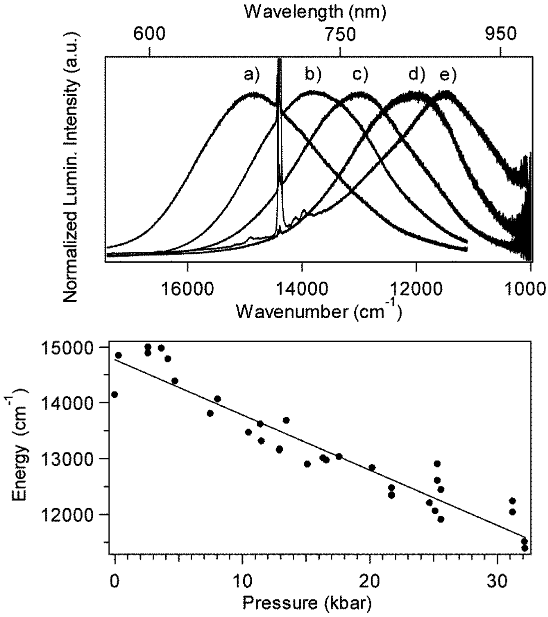

Figure 2. Top: Pressure-dependent luminescence spectra for crystalline $\{Pt(SCN)_2[\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$ at (a) 0.3, (b) 8, (c) 16, (d) 25, and (e) 32 kbar. Spectra are corrected for instrument response and normalized to identical intensities. The intense peak at 14 400 cm^{-1} is the ruby R line. Bottom: The luminescence maximum as a function of the pressure shows a red shift of −99 cm^{-1} kbar^{-1}.

spectroscopic behavior is the existence of interactions with neighboring organic ligands along the *z* axis.

The trimetallic complex $\{Pt(SCN)_2[(\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$ crystallizes in the monoclinic $P2_1/n$ space group. It is centrosymmetric at the platinum(II) ion, as shown in Figure 1, and contains two manganese(II) ions linked by SCN^- ligands to the platinum(II) center. The coordination geometry of the manganese(II) ions is pseudo-octahedral with two bidentate bipyridine and two thiocyanate ligands in the cis position coordinated by nitrogen atoms. The platinum(II) ion is coordinated by four sulfur atoms of the thiocyanate ligands in an almost perfect square-planar arrangement, and the bridging ligands toward the manganese(II) centers are in the trans position. The S−C−N axes of the nonbridging thiocyanate ligands are out of the PtS_4 plane. The platinum(II) centers are separated by at least 8.2 Å and the bipyridine ligands of neighboring complexes are π-stacked, forming a three-dimensional network, as shown in the Supporting Information.

Luminescence spectra were obtained by focusing the 488- and 514.5-nm lines of argon ion lasers on the crystals using a Renishaw 3000 microscope equipped with a cooled CCD detector. All spectrometers and correction procedures have been described before.[4,17] The Raman spectra of crystalline samples presented in the Supporting Information were measured with the 782-nm line of a diode laser as the excitation source. For pressure-dependent measurements, a diamond-anvil cell was used to apply a hydrostatic pressure on a crystalline sample in a Nujol medium, and the pressure was calibrated with the ruby R line. Luminescence decay curves of the crystals as shown in the Supporting Information were measured using the 532-nm line of a pulsed Nd:YAG laser, with the emitted light dispersed through a 0.5-m monochromator (Spex 500M; 600 lines mm^{-1}grating), detected by a photomultiplier tube (Hamamatsu R928) and a digital oscilloscope.

The temperature-dependent luminescence spectra show a broad, symmetrical band with a full width at half-height of 1900 cm^{-1}. The band maximum is at 14 190 cm^{-1} at 143 K. The width and energy of the band are very close to those reported for $(n\text{-}Bu_4N)_2Pt(SCN)_4$ (maximum at 14 440 cm^{-1} at 150 K; full width at half-height of 2500 cm^{-1}).[4] These similarities confirm the platinum(II)-centered d−d nature of the transition. The absorption spectrum in methanol solution shows a weak band at 410 nm with a molar absorptivity of 225 M^{-1} cm^{-1} corresponding to the lowest-energy spin-allowed d−d transition and an even weaker shoulder at 500 nm with a molar absorptivity of less than 100 M^{-1} cm^{-1}, arising from the transitions to triplet excited states similar to bands reported for $K_2Pt(SCN)_4$ and $(n\text{-}Bu_4N)_2Pt(SCN)_4$.[1,4]

The pressure-dependent luminescence spectra in Figure 2 show a large red shift of −99 cm^{-1} kbar^{-1} for the band maximum with increasing pressure, for a total shift of −3300 cm^{-1} between 0.3 and 32 kbar. The similar shape of the band in low- and high-pressure spectra indicates that the luminescence originates from the same transition at all pressures. In contrast to other crystalline $[Pt(SCN)_4]^{2-}$ complexes, the intensity increases only slightly at low pressures and decreases at pressures higher than 15−20 kbar, as shown in the Supporting Information. All pressure effects are reversible, indicating a nondestructive process. The bandwidth, large at any pressure, decreases by 300 cm^{-1} between 0.3 and 25 kbar, as predicted on the basis of potential energy surfaces,[18−20] where the external pressure reduces the offset

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(16) Empirical formula, $C_{46}H_{32}Mn_2N_{14}Pt_1S_6$; fw = 1246; $\lambda = 0.710\ 69$ Å; cryst syst, monoclinic; space group, $P2_1/n$; $Z = 2$; $a = 8.215(5)$ Å; $b = 24.546(5)$ Å; $c = 12.543(5)$ Å; $\alpha = 90°$; $\beta = 94.157(5)°$; $\gamma = 90°$; $V = 2522.6(19)$ Å^3; $\rho_{calcd} = 1.640$ g cm^{-3}; $\mu = 3.555$ mm^{-1}; $F(000) = 1182$; cryst size = 0.1 × 0.1 × 0.1 mm; Θ range = 1.659−28.274°; limiting indices, $0 \leq h \leq 10°$, $0 \leq k \leq 32°$, $-16 \leq l \leq 16°$; reflections collected, 6060; independent reflections, 5909 [R(int) = 0.000], absorption correction, none; max and min transmission, 1.0000 and 1.0000; refinement method, full-matrix least squares on F^2; data = 3965; restraints = 0; parameters = 313; GOF on $F^2 = 1.0109$; final R indices [$I > 3\sigma(I)$], $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.0335$, $wR(F^2) = \sum[w((F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2} = 0.0393$; R indices (all data): $R(F) = 0.0589$, $wR(F^2) = 0.0519$; residual electron density, 0.86 and −0.68 e Å^{-3}.

(17) Davis, M. J.; Reber, C. *Inorg. Chem.* **1995**, *34*, 4585.

(representing structural differences) between the ground- and excited-state potential energy minima.

The red shift is comparable in magnitude to values obtained for crystalline $[Pt(CN)_4]^{2-}$ [7-10] and $[Pt(dmg)_2]$,[6,11-14] where the square-planar complexes are stacked in linear columns. Pressure-dependent Raman spectra are given in the Supporting Information. They show smooth shifts to higher frequency for all metal−ligand vibrational bands, with no evidence of a phase transition. As an example, the Pt−S stretching band at 309 cm^{-1} shifts by $+0.54$ cm^{-1} $kbar^{-1}$, which is very similar to the value of $+0.60$ cm^{-1} $kbar^{-1}$ obtained for the Pt−S breathing mode (303 cm^{-1}) in $(n\text{-}Bu_4N)_2Pt(SCN)_4$.[4] This indicates that the structural deformation under pressure for the PtS_4 moiety is similar in both cases and is therefore not the cause of the luminescence shift observed for the trimetallic complex. The pressure-induced shortening of the Pt−S bonds tends to shift luminescence bands toward slightly higher energies, but a different effect, leading to the surprising red shift shown in Figure 2, must dominate for the title complex.

Temperature-dependent Raman spectra show slightly higher frequencies for Pt−S vibrational modes at low temperature, as illustrated in the Supporting Information. The weakening of the bonds at higher temperature should reduce the HOMO−LUMO gap, but we observe a blue shift of $+2.9$ cm^{-1} K^{-1} in the emission spectra, greater than that for $(n\text{-}Bu_4N)_2Pt(SCN)_4$ ($+1.6$ cm^{-1} K^{-1}).[4] This blue shift with increasing temperature is due to more highly allowed vibronic transitions from thermally populated levels. In view of the very similar platinum(II)-thiocyanate frequencies of $(n\text{-}Bu_4N)_2Pt(SCN)_4$ and the trimetallic complex, the larger shift for the latter compound indicates that additional effects influence its luminescence energy. The luminescence lifetimes for $\{Pt(SCN)_2[(\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$ decrease from 1.3 to 0.4 μs between 4 and 250 K and are definitely shorter than those for $(n\text{-}Bu_4N)_2Pt(SCN)_4$ (from 320 to 0.3 μs between 5 and 200 K),[4] indicating more efficient nonradiative relaxation, possibly through interactions on the z axis. The fact that the intensity of the luminescence does not increase by several orders of magnitude under pressure also points toward a quenching through such interactions.

The crystal packing prevents Pt−Pt interactions, even at high pressure, because neighboring complexes cannot move to have the platinum(II) centers stacked similar to crystalline $[Pt(CN)_4]^{2-}$.[7-10] Considering the environment of the platinum(II) center, the hypothesis of an interaction with bipyridine ligands of neighboring complexes is proposed. The structural arrangement created by the out-of-plane thiocyanate ligands and the π-stacked bipyridine ligands leads to cavities above and below the platinum(II) center, with two hydrogen atoms from neighboring bipyridine ligands positioned at 3.4 Å above and below the platinum(II) ion, forming an extremely elongated octahedron. On the basis of these structural features, it is intuitively appealing to consider that external pressure pushes the bipyridine ligands into the cavities, leading to a decrease of the Pt···H distances. The energetic effects of a shorter Pt···H distance have been simulated with density functional theory calculations based on the crystallographic coordinates for the $[Pt(SCN)_4]^{2-}$ moiety and two pyridine rings representing half of the nearby bipyridine ligands. The distance between the platinum(II) center and the pyridine rings was decreased, leading to Pt···H distances similar to those where agostic interactions can occur (ca. 2.9 Å).[21] The resulting HOMO−LUMO gap becomes smaller, qualitatively indicating that this structural change causes the observed red shift of the luminescence band.

Spectroscopic results show that large pressure-induced shifts can be obtained for square-planar complexes that do not stack. Intermolecular interactions with nearby C−H bonds of bipyridine ligands from neighboring complexes appear to be the most likely reason for the observed phenomenon. The pressure-dependent luminescence spectra of the crystalline trimetallic title complex demonstrate that intermolecular effects other than metal−metal interaction can change the electronic structure of square-planar complexes. Such interactions are an attractive area to be explored further because they can be controlled via both the molecular structure of the complex and its three-dimensional packing in a crystalline solid.

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Supporting Information Available: Raman spectra (region of metal−ligand vibrations) as a function of the pressure and temperature, temperature-dependent luminescence spectra and lifetimes, view of the crystal packing and of the platinum(II) environment, calculated HOMO−LUMO gap as a function of the Pt−H distance, selected interatomic distances and angles for the compound, and X-ray crystallographic file in CIF format for $\{Pt(SCN)_2[(\mu\text{-}SCN)Mn(NCS)(bipy)_2]_2\}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Bray, K. L. *Top. Curr. Chem.* **2001**, *213*, 1.

(19) Wenger, O. S.; Valiente, R.; Güdel, H. U. *J. Chem. Phys.* **2001**, *115*, 3819.

(20) Reber, C.; Grey, J. K.; Lanthier, E.; Frantzen, K. A. *Comm. Inorg. Chem.* **2005**, *26*, 233.

(21) Brookhart, M.; Green, M. L.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.