Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 384 (2004) 190–192

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Pressure dependence of Pt(2,2′-bipyridine)Cl_2 luminescence. The red complex converts to a yellow form at 17.5 kbar

Oliver S. Wenger [a], Sara García-Revilla [b], Hans U. Güdel [c], Harry B. Gray [a], Rafael Valiente [b,*]

[a] Beckman Institute, California Institute of Technology, Pasadena, CA 91125, USA
[b] Dept. de Física Aplicada, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain
[c] Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, 3000 Bern 9, Switzerland

Received 22 August 2003

Abstract

The luminescence of the red (linear-chain) form of Pt(bpy)Cl_2 (bpy = 2,2′-bipyridine) has been measured as a function of hydrostatic pressure up to 30 kbar. The luminescence band maximum is red-shifted (158 cm^{-1}/kbar), and the intrachain Pt(II)–Pt(II) distance decreases from 3.45 to 3.25 Å, between ambient pressure and 17.5 kbar. Strong discontinuities in the emission energy, bandwidth, and intensity at 17.5 kbar are interpreted in terms of a crystallographic phase transition from the red to a yellow form of Pt(bpy)Cl_2.

The luminescence properties of linear-chain Pt(II) systems depend strongly on the intrachain metal–metal separation [1,2]. In the red form of Pt(bpy)Cl_2 (bpy = 2,2′-bipyridine), the intrachain distance decreases by 0.08 Å upon cooling from room temperature to 20 K, a decrease that is accompanied by a 950 cm^{-1} red-shift of the emission band maximum [3]. In the course of our work on the effects of hydrostatic pressure on Pt(II) luminescence properties, we have found that red Pt(bpy)Cl_2 undergoes a pressure-induced crystallographic phase transition at 17.5 kbar. Our results suggest that this phase transition is associated with the conversion of the red complex to a denser yellow form.

The room temperature luminescence of a microcrystalline sample of red Pt(bpy)Cl_2 at ambient pressure (Fig. 1a) originates from a ^{3}MLCT state [4], where the HOMO (dσ^*) is built from Pt(II) dz^2 orbitals of the stacked complexes, and the LUMO (π^*) is localized on the bpy ligand [3,5]. In contrast, the LUMO of tetracyanoplatinates is a predominantly metal-centered pσ orbital [1]. Increasing the pressure to 12 kbar red-shifts the ^{3}MLCT luminescence, as shown in Fig. 1 (spectrum b) [6]. The 1800 cm^{-1} luminescence maximum (ν_{max}) red-shift is accompanied by a 350 cm^{-1} bandwidth decrease (full width at half maximum, FWHM). As illustrated in Fig. 2, ν_{max} decreases linearly with increasing pressure in the 1 bar–17.5 kbar pressure range. The shift rate dν_{max}/dp of −158 cm^{-1}/kbar is roughly a factor of five higher than the shift rates typically found for emission bands associated with a variety of d–d excited states of transition metal complexes [7], but rather modest when compared to those previously reported for some tetracyanoplatinates [1]: $Ba[Pt(CN)_4] \cdot 4H_2O$, for example, exhibits a pressure-induced ν_{max}-shift of –270 cm^{-1}/kbar (Table 1) [8]. Temperature-dependent luminescence and X-ray measurements on red Pt(bpy)Cl_2 have revealed the following relation between ν_{max} and the Pt(II)–Pt(II) distance R (ν_{max} and R are in units of cm^{-1} and Å, respectively) [3]

$$\nu_{max} = 29500 - 5.4 \times 10^5\ R^{-3}. \qquad (1)$$

For each pressure p between 1 bar and 17.5 kbar, the Pt(II)–Pt(II) distance $R(p)$ can be calculated from the respective $\nu_{max}(p)$. Eq. (1) predicts a decrease in R from 3.45 Å at ambient pressure to 3.25 Å at 17.5 kbar, and

---

[*] Corresponding author. Fax: +34-942-20-14-02.
E-mail address: valientr@unican.es (R. Valiente).

0009-2614/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2003.11.102

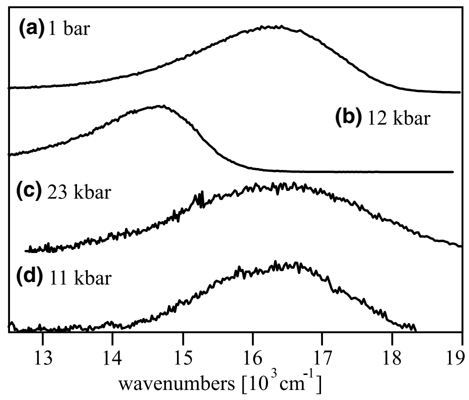

Fig. 1. Luminescence spectra of red Pt(bpy)Cl_2 as a function of increasing pressure: (a) 1 bar; (b) 12 kbar; and (c) 23 kbar. (d) is the spectrum after decreasing the pressure from 23 to 11 kbar.

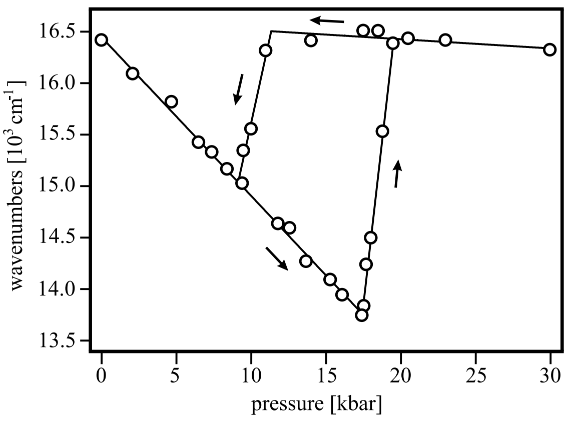

Fig. 2. Energy of the luminescence band maximum (ν_{max}) of Pt(bpy)Cl_2 as a function of pressure (open circles; lines are guides).

Table 1
Values for the pressure-induced ν_{max}-shift rate ($d\nu_{max}/dp$), linear compressibility along the crystallographic *c*-axis (χ_c), and intrachain Pt(II)–Pt(II) distance r_0 at ambient pressure for red Pt(bpy)Cl_2 and Ba[Pt(CN)$_4$]·$4H_2O$ at room temperature

	Red Pt(bpy)Cl_2	Ba[Pt(CN)$_4$]·$4H_2O$
Luminescence transition	$d\sigma^* \leftarrow \pi^*$ (bpy)	$d\sigma^* \leftarrow p\sigma$
$d\nu_{max}/dp$ (cm^{-1}/kbar)	−158	−270
χ_c (kbar)	3.6×10^{-3}	4.2×10^{-3}
r_0 (Å)	3.45	3.32

this translates to a linear compressibility (along the crystallographic *c*-axis) χ_c of 3.6×10^{-3} kbar^{-1} [9]. In Ba[Pt(CN)$_4$]·$4H_2O$ χ_c is 17% larger (Table 1). The ν_{max}-shift rate, on the other hand, is 71% larger for Ba[Pt(CN)$_4$]·$4H_2O$ relative to red Pt(bpy)Cl_2, thereby indicating that the $d\sigma^*$–π^* energy gap in the latter has a significantly weaker dependence on the Pt(II)–Pt(II) distance than the $d\sigma^*$–$p\sigma$ energy gap in the tetracyanoplatinate. In both systems increasing pressure destabilizes the $d\sigma^*$ HOMO, and it appears reasonable to assume that this effect is of comparable magnitude in red Pt(bpy)Cl_2 and Ba[Pt(CN)$_4$]·$4H_2O$. However, whereas the energy of the bpy π^* LUMO in the former is only relatively weakly pressure dependent [10], the tetracyanoplatinate $p\sigma$ LUMO is stabilized significantly with increasing pressure [11,12].

As pressure is increased above 17.5 kbar, three dramatic effects are observed within a very narrow pressure range: First, ν_{max} increases by about 2500 cm^{-1}(Fig. 2); second, the emission bandwidth increases by almost 70% (compare spectra b and c in Fig. 1); and third, the luminescence intensity decreases by at least an order of magnitude. These abrupt changes in emission properties clearly signal a structural phase transition. Pressure-induced phase transitions have previously been reported for several tetracyanoplatinates, typically occurring between 5 and 15 kbar [1]. However, only compounds of the stoichiometry $M_2[Pt(CN)_4]_3 \cdot nH_2O$ exhibit similarly strong discontinuities in their emission properties, and these are compounds that typically also undergo a first-order phase transition upon cooling to cryogenic temperatures. Red Pt(bpy)Cl_2 does not undergo any phase transition even when cooled to 20 K [3]. However, Pt(bpy)Cl_2 occurs in both red and yellow forms at room temperature and ambient pressure. Under these standard conditions, the densities of the two forms are 2.55 and 2.65 g/cm^3, respectively, i.e., red Pt(bpy)Cl_2 is 4% less dense than its yellow counterpart [13]. Thus, a pressure-induced red to yellow phase transition is reasonable. The spectroscopic changes occurring around 17.5 kbar are consistent with this proposal; in particular, they all are indicative of a switch from ^{3}MLCT to ^{3}LF luminescence, and yellow Pt(bpy)Cl_2 is a ^{3}LF emitter [14]. The emission maxima of Pt(II) ^{3}LF states exhibit comparatively weak pressure dependences, with typical shift rates on the order of 10–40 cm^{-1}/kbar [15]. Between 20.5 and 30 kbar, ν_{max} shifts –13 cm^{-1}/kbar (Fig. 2). The bandwidth of spectrum c in Fig. 1 is 3100 cm^{-1} (FWHM), and this compares to 4000 cm^{-1} in yellow Pt(bpy)Cl_2 at ambient pressure and 250 K [5]. A narrower luminescence bandwidth at elevated pressures is to be expected, owing to diminished relative distortions of the emissive and ground states [16,17]. The same effect accounts for the narrower bandwidth associated with the 12 kbar luminescence of red Pt(bpy)Cl_2 (Fig. 1b) relative to that observed in the ambient pressure spectrum (Fig. 1a). Finally, the order-of-magnitude decrease in luminescence intensity accompanying the phase transition at 17.5 kbar also is consistent with a change from red to yellow Pt(bpy)Cl_2. The room temperature ambient pressure luminescence quantum yields of microcrystalline samples of these two compounds are known to differ by more than an order of magnitude [14]. Pressure-dependent excitation spectra (data not shown) confirm our interpretation of the crystallographic phase transition at 17.5 kbar: between 12 and

23 kbar the absorption edge shifts discontinuously from 15 000 to 20 300 cm^{-1}.

Upon decreasing the pressure the ^{3}LF-emissive high-pressure form of Pt(bpy)Cl$_2$ persists down to 11 kbar (Fig. 2). The occurrence of a yellow to red phase transition at 11 kbar might indicate that the high-pressure yellow form differs structurally somewhat from the known ambient pressure yellow form. Notably, there is a hysteresis in the luminescence properties with a bistable region extending from 11 to 17.5 kbar. In this range, either ^{3}MLCT (Fig. 1b) or ^{3}LF emission (Fig. 1d) is observed, depending on the history of the sample. A similar pressure hysteresis loop has been reported recently for $[(C_2H_5)_2NH_2]_4[Pt_2(P_2O_5H_2)]$ [18].

Acknowledgements

This work was supported by the Swiss National Science Foundation and the Spanish MCyT under project no. BFM2001-0695. Work at Caltech was supported by the US National Science Foundation.

References

[1] G. Gliemann, H. Yersin, Struct. Bond. 62 (1985) 87.

[2] M. Kato, C. Kosuge, K. Morii, J.S. Ahn, H. Kitagawa, T. Mitani, M. Matsushita, T. Kato, S. Yano, M. Kimura, Inorg. Chem. 38 (1999) 1638.

[3] W.B. Connick, L.M. Henling, R.E. Marsh, H.B. Gray, Inorg. Chem. 35 (1996) 6261.

[4] Red Pt(bpy)Cl$_2$ was prepared as described in [3]. Luminescence measurements: sample excitation at 488 nm using an Ar$^+$ laser; detection employed a photomultiplier tube (RCA 31034) connected to a Spex 1402 3/4-m monochromator. All measurements were performed at room temperature.

[5] V.M. Miskowski, V.H. Houlding, C.-M. Che, Y. Wang, Inorg. Chem. 32 (1993) 2518.

[6] Pressure-dependent luminescence and excitation spectra were recorded using sapphire and diamond anvil cells as described in O.S. Wenger, G.M. Salley, R. Valiente, H.U. Güdel, Phys. Rev. B 65 (2002) 212108; S. García-Revilla, F. Rodríguez, R. Valiente, M. Pollnau, J. Phys.: Condens. Matter 14 (2002) 447.

[7] K.L Bray, Top. Curr. Chem. 213 (2001) 1.

[8] M. Stock, H. Yersin, Chem. Phys. Lett. 40 (1976) 423.

[9] Linear compressibility values for a series of tetracyanoplatinates have been calculated in an analogous manner [1]; the calculated χ_c values are in good agreement with those extracted from pressure-dependent X-ray measurements.

[10] D.C. Fisher, H.G. Drickamer, J. Chem. Phys. 54 (1971) 4825.

[11] M.-H. Whangbo, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 6093.

[12] J.C. Zahner, H.G. Drickamer, J. Chem. Phys. 33 (1960) 1625.

[13] M. Textor, H.R. Oswald, Z. Anorg. Allg. Chem. 407 (1974) 244.

[14] V.H. Houlding, V.M. Miskowski, Coord. Chem. Rev. 111 (1991) 145.

[15] M.A. Stroud, H.G. Drickamer, M.H. Zietlow, H.B. Gray, B.I. Swanson, J. Am. Chem. Soc. 111 (1989) 66.

[16] O.S. Wenger, R. Valiente, H.U. Güdel, J. Chem. Phys. 115 (2001) 3819.

[17] J.K. Grey, M. Triest, I.S. Butler, C. Reber, J. Phys. Chem. A 105 (2001) 6269.

[18] H. Matsuzaki, H. Kishida, K. Takizawa, H. Okamoto, Synthetic Met. 135 (2003) 607.