

Extreme Pressure-Induced Shifts of Emission Energies in $M[\text{Au}(\text{CN})_2]$ and $M_2[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$. Compounds with Low-Dimensional Metal–Metal Interactions

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Emission properties of dicyanoaurates(I) and tetracyanoplatinates(II) are investigated under high hydrostatic pressure up to ≈ 20 kbar and ≈ 40 kbar, respectively, at $T = 295$ K. One observes pressure-induced red shifts of the emission energies, which are the largest values known for solid state compounds: $\Delta\bar{\nu}/\Delta p$ ($\text{cm}^{-1}/\text{kbar}$) = -120 ($\text{Cs}_2\text{Na}[\text{Au}(\text{CN})_2]_3$); -150 ($\text{Cs}[\text{Au}(\text{CN})_2]$); -200 ($\text{K}[\text{Au}(\text{CN})_2]$); -300 ($\bar{E} \parallel \bar{c}$) and -250 ($\bar{E} \perp \bar{c}$) ($\text{Li}_2[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$). In the investigated pressure range the energy shifts are linear and no phase transition is observed. Interestingly, $\text{Li}_2[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ is a very particular compound of the series of tetracyanoplatinates(II). Using this material it is possible to tune the emission in the visible energy range continuously over more than 6000 cm^{-1} by high pressure application up to 20 kbar. For both types of compounds, the reported large values of pressure induced shifts are related to low-dimensional metal–metal interactions. These interactions lead to the formation of electronic energy bands, delocalized free exciton states, and self-trapped states. The importance of such states for the emission properties of these compounds is also discussed.

1. Introduction

$M[\text{Au}(\text{CN})_2]$ compounds (e.g. with $M = \text{K}, \text{Cs}, \frac{1}{2}\text{Ca}, \frac{1}{2}\text{Ba}$ etc.) have found an increasing interest during the past decades due to their layered structures,^{1–10} where the $[\text{Au}(\text{CN})_2]^-$ complexes and thus the gold atoms form *two-dimensional* networks with relatively short Au–Au distances within a layer (e.g. $\text{Cs}[\text{Au}(\text{CN})_2]$: 3.11, 3.14, and 3.72 Å)^{2,4,6} and with large distances between the layers ($\text{Cs}[\text{Au}(\text{CN})_2]$: 8.15 Å).^{2,4} This specific structure type leads to a series of very unusual emission properties,^{5–10} which are strongly reminiscent of the properties of $M_2[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$ compounds.^{5–9,11–14} These form quasi *one-dimensional* structures with short in-chain distances (e.g. $\text{Mg}[\text{Pt}(\text{CN})_4] \cdot 7\text{H}_2\text{O}$: 3.155 Å)^{15,16} and large separations between the platinum atoms of different chains ($\text{Mg}[\text{Pt}(\text{CN})_4] \cdot 7\text{H}_2\text{O}$: 10.28 Å).^{15,16} Both the dicyanoaurates(I) and the tetracyanoplatinates(II) exhibit distinct metal–metal interactions, which lead to the formation of electronic energy bands. This has been

predicted for the dicyanoaurates(I)^{6,8,9} and already shown for the tetracyanoplatinates(II).^{14,17} The corresponding band widths and the resulting energy gaps, respectively, determine many optical properties and, in particular, the emission energy. (Note that the emission energy is generally not equal to the band gap energy.^{14,18,19}) Thus, the in-chain or the in-plane metal–metal distances control sensitively the low energy transitions. It is expected that application of high hydrostatic pressure reduces these distances and thus leads to pronounced red shifts of the emission energies. Indeed, this effect has been found for the tetracyanoplatinates(II). Interestingly, the observed pressure induced red shifts are—to our knowledge—the largest values found for solid state compounds and they range from -130 to -400 $\text{cm}^{-1}/\text{kbar}$.^{20–23} On the other hand, dicyanoaurates(I) have not yet been studied under high pressure, although one expects to find—and indeed finds as is shown in this contribution—comparably large energy shifts. Therefore, the subject of this contribution is the investigation of several $M[\text{Au}(\text{CN})_2]$ compounds under high pressure. Further, it is intended to present some new data for an interesting compound of the tetracyanoplatinates(II). An additional aspect of this paper is to point to a series of similarities between the compounds with quasi one- and quasi two-dimensional metal–metal interactions.

2. Experimental Section

$\text{K}[\text{Au}(\text{CN})_2]$ (Alfa, p. a.) was purified through ion exchange of K^+ by H^+ in an aqueous solution and subsequently neutralized with K_2CO_3 . After evaporation a white precipitate of microcrystalline $\text{K}[\text{Au}(\text{CN})_2]$ was obtained. $\text{Cs}[\text{Au}(\text{CN})_2]$ was prepared according to the method of Schubert.⁴ $\text{Cs}_2\text{Na}[\text{Au}(\text{CN})_2]_3$ was synthesized by slow addition of an aqueous solution of $\text{Cs}[\text{Au}(\text{CN})_2]$ to a stoichiometric

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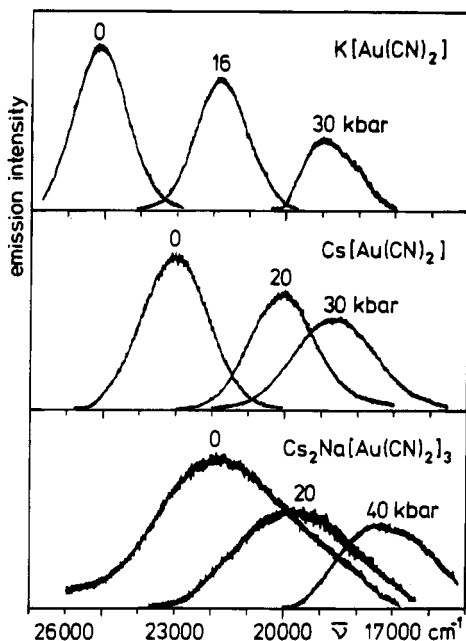


Figure 1. Emission spectra of different $M[Au(CN)_2]$ single crystals for various pressures at 295 K. Excitation wavelength: 325 nm. The intensities are not comparable, but with increasing pressure one observes an intensity decrease.

solution of $Na[Au(CN)_2]$. ($Na[Au(CN)_2]$ was prepared analogously to $Cs[Au(CN)_2]$.) After concentrating the solution at 40 °C the precipitate was washed with cold water. The dicyanoaurates(I) were purified by repeated recrystallization. Single crystals were grown from aqueous solution by slow evaporation at 35 °C.

$Li_2[Pt(CN)_4] \cdot 4H_2O$ was prepared according to the methods described in ref 24. Slow evaporation of an aqueous solution at room temperature yielded single crystals. Only crystals were used which had been purified by repeated recrystallizations.

For spectroscopic measurements single crystals of high optical quality were selected. The high pressure cell was a modified sapphire cell of Bridgman's opposed anvil type. The pressure was determined by the red shift of the emission of small pieces of ruby placed near to the sample. Details of the high pressure cell and the emission spectrophotometer are described elsewhere.²⁰

3. Results and Discussion

Figure 1 shows the emission spectra of $K[Au(CN)_2]$, $Cs[Au(CN)_2]$, and $Cs_2Na[Au(CN)_2]_3$ at different hydrostatic pressures measured at 295 K and in Figure 2 the energies of the peak maxima are plotted versus pressure. One observes a linear red shift for the three compounds partly up to 40 kbar. Table 1 summarizes the values of the pressure induced red shifts. The value for the potassium salt is about 70% larger than the one for the cesium-sodium compound. This may be explained by a larger compressibility within the two-dimensional $[Au(CN)_2]^-$ network of the potassium compound. The pressure-induced changes of the interplane distances do not seem to be relevant for the energy shifts, since these distances are still too large for an important interaction or change of interaction.

Figure 2 shows also the shifts of the emission maxima versus pressure of $Li_2[Pt(CN)_4] \cdot 4H_2O$,²⁵ investigated for the first time. Obviously, no phase transition occurs up to ≈ 20 kbar. Although, this compound does not exhibit the largest value observed for pressure-induced shifts²² (Table 1), it represents a compound of particular interest of the series of tetracyanoplatinates(II) investigated up to now, since it allows to tune the

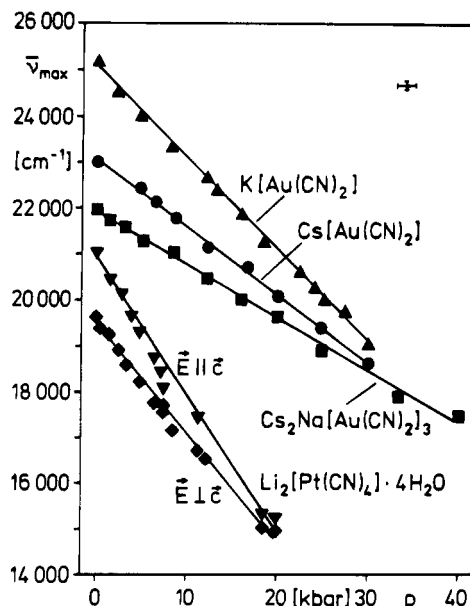


Figure 2. Pressure-induced shifts of the emission peak maxima at $T = 295$ K for different single-crystal $M[Au(CN)_2]$ compounds and for $Li_2[Pt(CN)_4] \cdot 4H_2O$ single crystals (\vec{E} : electric field vector, \vec{c} : chain axis).

emission energy continuously in the visible energy range from $21\,050\text{ cm}^{-1}$ (475 nm) to $\approx 15\,000\text{ cm}^{-1}$ (666 nm) by high pressure application of ≈ 20 kbar. The $\Delta\bar{\nu}/\Delta p$ values of most of the platينات are larger than those of the aurates. This behavior may be ascribed to the larger in-chain linear compressibility ($Li[Pt(CN)_4] \cdot 4H_2O$: $\kappa_c = 5.0 \times 10^{-3}\text{ kbar}^{-1}$)¹³ and to the higher pressure sensitivity of the band gap energy at this low metal-metal distance compared to the corresponding properties of the aurates which, however, are still unknown. (For an explanation of the different polarization properties shown in Figure 2, see below.)

3.1. Electronic Properties of Tetracyanoplatinates(II)

The electronic properties of the tetracyanoplatinates(II) were mainly discussed in original publications.^{11,14,17-19} Thus, it seems to be important to shortly summarize these relatively complicated properties. The electronic transitions being responsible for the discussed emission may be traced back to the 5d, 6s-HOMO and the 6p, $CN\pi^*$ -LUMO of $[Pt(CN)_4]^{2-}$. In the quasi one-dimensional structure these molecular orbitals overlap and form electronic energy bands. The HOMOs and the LUMOs give the valence band and the conduction band, respectively. For the tetracyanoplatinates(II) the corresponding band widths have been calculated.^{14,17,18} They strongly depend on the Pt-Pt distances and are several eVs broad (1 eV = 8067 cm^{-1}). It could further be shown that the resulting band gap energies may very roughly be correlated to the optical transition energies.¹⁷ However, photoconductivity measurements¹⁹ revealed that the absorption and emission peak energies are not given directly by the band gap energies. Obviously, the excited electron in the conduction band interacts with the hole created in the valence band. Thus, the two particles lead to a stabilized situation with respect to the band gap energy. These so-called excitons are not confined to a specific complex unit but are strongly delocalized along the chains due to the translational symmetry. Such a situation may be described by (a ground state and) an energetically relatively broad exciton band. For $Ba[Pt(CN)_4] \cdot 4H_2O$ (exhibiting the same Pt-Pt distance like $Li_2[Pt(CN)_4] \cdot 4H_2O$) the (delocalized) exciton of lowest energy is stabilized with respect to the discussed band gap energy by $\approx 0.5\text{ eV}$.¹⁹ It has been shown that the very short-lived emission and the corresponding very strong absorption both polarized

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Table 1. Emission Peak Energies and Pressure-Induced Shifts of $M[Au(CN)_2]$ and $M_2[Pt(CN)_4]_nH_2O$ Compounds at $T = 295$ K

compound	unpolarized		shortest metal-metal dist (Å)	ref
	$\bar{\nu}_{em}^a$ (cm ⁻¹)	$\Delta\bar{\nu}_{em}/\Delta p^b$ (cm ⁻¹ /kbar)		
K[Au(CN) ₂]	25 200	-200	3.65 ¹	this work
Cs[Au(CN) ₂]	23 000	-150	3.11, 3.14, 3.72 ^{2,4}	this work
Cs ₂ Na[Au(CN) ₂] ₃	21 900	-120	3.45, 3.62 ^{3,4}	this work

compound	$\bar{\nu}_{em}^a$ (cm ⁻¹)		$\Delta\bar{\nu}_{em}/\Delta p^b$ (cm ⁻¹ /kbar)		shortest metal-metal dist (Å)	ref
	$\vec{E} \parallel \vec{c}^c$	$\vec{E} \perp \vec{c}$	$\vec{E} \parallel \vec{c}$	$\vec{E} \perp \vec{c}$		
Ba[Pt(CN) ₄] ₄ H ₂ O	21 000	19 500	-280	-195	3.32 ¹⁶	20, 22
Li ₂ [Pt(CN) ₄] ₄ H ₂ O	21 050	19 600	-300	-250	3.32 ¹²	this work
Mg[Pt(CN) ₄] ₇ H ₂ O	17 550	16 800	-320	-270	3.155 ¹⁵	21

^a Emission energies at $p = 1$ bar. ^b Experimental error: $\pm 5\%$. ^c Electric field vector \vec{E} polarized parallel or perpendicularly to the chain axis.

parallel to the chains ($\vec{E} \parallel \vec{c}$, see Figure 2) have to be assigned to transitions between the ground state and these delocalized exciton states.^{11,14,18}

On the other hand, the lowest excited states of the tetracyanoplatinates(II) could not be detected in absorption but they lead to a very strong, perpendicularly polarized emission ($\vec{E} \perp \vec{c}$, see Figure 2). Interestingly, these states display distinctly localized properties, which strongly resemble to those of molecular units (relatively large zero field splittings of the triplets, long emission lifetimes, strong vibrational couplings to the surroundings, etc.).¹¹⁻¹⁴ Indeed, it could be shown that these states are localized onto a small number of $[Pt(CN)_4]^{2-}$ complexes.^{11,26-28} Further, these localized states are separated by an activation barrier from the delocalized exciton.¹¹⁻¹⁴ The localized states could be classified as *self-trapped excitons*.^{11,14,26} The localization process occurs since the delocalized exciton interacts with in-chain vibrational lattice modes and thus can lead to energetically stabilized states.^{14,18} According to this exciton-lattice interaction the exciton becomes very massive and traps itself by partly reducing the inchain metal-metal distances. A similar excited state distortion has also been observed for $[Pt_2(P_2O_5H_2)_4]^{4-}$.²⁹⁻³¹

According to this model one expects that with an increase of the force constants of the relevant vibrational lattice modes (by high pressure application) the process of selftrapping will become more and more difficult and finally will no longer be possible. Indeed, this happens, as has been shown to occur for $Mg[Pt(CN)_4]_7H_2O$ near 15 kbar^{14,21} and should also become manifested near 26 kbar for $Li_2[Pt(CN)_4]_4H_2O$. At this pressure the energy gain by the process of selftrapping becomes zero (formal crossing of the $\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ plots in Figure 2).

3.2. Electronic Properties of the Dicyanoaurates(I). The spectroscopic behavior of the dicyanoaurates(I) are in many respects very similar to the properties of the tetracyanoplatinates(II), as recognized long ago.⁵⁻⁹ The electronic transitions being responsible for the discussed emission may also be traced back to the 5d, 6s-HOMO and the 6p, $CN\pi^*-LUMO$ of the $[Au(CN)_2]^-$ complex.^{9,32,33} The similarly large high pressure-induced shifts (Table 1) support further the idea of developing a comparably detailed model as exists for the tetracyanoplati-

nates(II) for the dicyanoaurate(I) layers as well. However, this model is not yet available, presumably due to distinct differences. For example, the high energy emission of the $M[Au(CN)_2]$ compounds near 24 000 cm⁻¹ at low temperatures^{5-9,34} is assigned to a transition from an excited singlet to the singlet ground state.⁵⁻⁹ The shoulder found for $Cs_2Na[Au(CN)_2]_3$ near 25 500 cm⁻¹ at 295 K (Figure 1) may correspond to this singlet-singlet transition. (For this correlation one has to take into account that thermal contraction effects lead to a red shift of more than 10³ cm⁻¹, when the temperature is reduced from 295 to 80 K.⁸) However, this transition is not directly related to an absorption.^{34,35} Therefore, an assignment of this shoulder (or peak at low temperature) to a delocalized exciton state is improbable. Moreover, in particular $Cs[Au(CN)_2]$ and $K[Au(CN)_2]$ exhibit emission spectra which consist of at least three peaks spread over the large energy range of ≈ 3000 and ≈ 5000 cm⁻¹, respectively. There is no thermal equilibration among the corresponding states and even at $T = 2$ K also the high energy peaks are still present. Further, metal cryptates of dicyanoaurates(I) with very large Au-Au separations (> 7 Å) also show at $T = 2$ K several emission peaks spread over a similarly large energy range. An explanation for this behavior (proposed in ref 34) is the occurrence of different, from each other spatially isolated $[Au(CN)_2]_n^{n-}$ cluster regions (already in the ground state) with reduced metal-metal distances compared to the regular crystallographic distances. According to this model the corresponding electronic cluster states lie energetically within the band gap of the regular layers. These states are delocalized over the $[Au(CN)_2]_n^{n-}$ cluster units. Until now we have no information about the number n , which determines the cluster size.

For $Cs[Au(CN)_2]$, the observed emission peak at $p = 0$ kbar lies at $T = 295$ K near 23 000 cm⁻¹ (Figure 1). This broad emission peak results from different types of electronic states, since it resolves into two dominating peaks at $T = 5$ K.^{6,7,34} The higher lying one near 24 000 cm⁻¹ corresponds to the discussed delocalized $[Au(CN)_2]_n^{n-}$ cluster state, while the lower lying one near 22 000 cm⁻¹ shows distinct properties of strongly localized states as observed for the tetracyanoplatinates(II) (see Section 3.1). For example, one finds relatively large zero-field splittings,^{7,9} long emission lifetimes,^{7,9,34} and also an energy barrier^{7,9,34} between the delocalized cluster state and these low-lying and localized triplets. Presumably, these low-lying states are connected with a metal-metal shrinkage upon excitation comparable to the self-traps in the tetracyanoplatinates(II)^{11,13,14} and the excited states in the $[Pt_2(P_2O_5H_2)_4]^{4-}$ ²⁹⁻³¹ compound. The region of localization of these low-lying excited states is

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certainly confined to one cluster and many involve only a very small number of $[\text{Au}(\text{CN})_2]^-$ complexes. It is suggested that under high pressure the process of metal-metal shrinkage through excitation becomes energetically unfavorable and may be tuned off like in the tetracyanoplatinates(II).^{11,14,21} Possibly, the decrease of half-widths in the emission spectra (Figure 1) is—apart from a decrease of inhomogeneity³⁶—connected to the proposed process.

Conclusion

The emission properties of the tetracyanoplatinates(II) and the dicyanoaurates(I) depend strongly on the applied hydrostatic pressure. One observes the largest energy shifts found for solid state compounds. This behavior is connected with the quasi one- and quasi two-dimensional, respectively, metal-metal interactions and the formation of electronic energy bands. The band widths increase strongly with pressure, which leads to a reduced band gap energy and to the observed large red shifts of the transition energies. A more detailed description of the

electronic structure has to take into account an electron-hole interaction, giving the delocalized excitons, and an exciton-lattice interaction, leading to a self-localization onto a small number of complex units. This process is also pressure dependent. There are indications that the situation for the dicyanoaurates(I) is additionally complicated by the occurrence of clusters already in the ground state.

Note Added in Proof. Only recently ref 37 came to our attention, in which it is shown by Raman scattering experiments that $\text{K}[\text{Au}(\text{CN})_2]$ exhibits two phase transitions at 6.6 and 10.5 kbar. However, the pressure dependence of the emission spectra did not reveal any indication of structure changes. Possibly, the relatively large half-widths of the emission peaks prevent the detection of these phase transitions.

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