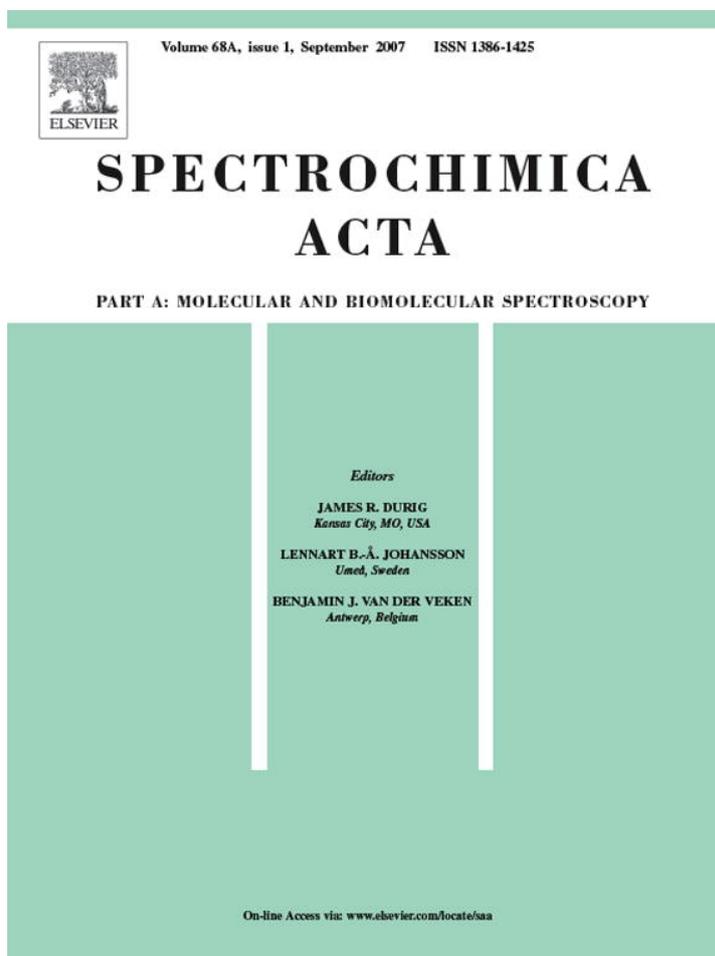


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Photo-induced charge transfer in Prussian blue analogues as detected by photoacoustic spectroscopy

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Abstract

The photo-induced charge transfer in four series of Prussian blue (PB) analogues was studied from photoacoustic spectra. In cobaltcyanides the observed signals were assigned to a metal-to-ligand charge transfer, which appears as a shoulder below 450 nm, and to d–d transitions for Co(II), Ni(II) and Cu(II) complex salts. No evidence of metal-to-metal charge transfer was observed for this series, which is probably due to the high stability of low spin cobalt(III) in the hexacyanide complex. Photoacoustic spectra for ferricyanides are broad bands, which result particularly intense up to 750 nm. Such features were attributed to the overlapping of contributions from metal-to-ligand (<600 nm) and metal-to-metal charge transfer transitions, with probably also a minor contribution from d–d transitions in the outer metal. The spectra for the ferrocyanides series are dominated by the metal-to-ligand charge transfer band below 550 nm, approximately 100 nm above this transition in cobaltcyanides. Within the studied solids, the most intense and broad metal-to-metal charge transfer bands were found for a series of low spin Co(III) high spin Co(II) hexacyanoferrates(II,III) and with similar features also for ferric ferrocyanide (Prussian blue), assigned to Fe(II) → Co(III) and Fe(II) → Fe(III) photo-induced transition, respectively. The first of these transitions requires of more energetic photons to be observed, its maximum falls at 580 nm while for Prussian blue it is found at 670 nm. Prussian blue analogues are usually obtained as nanometric size particles and many of them have a microporous structure. The role of surface atoms on the observed charge transfer bands in the studied series of compounds is also discussed.

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Keywords: Charge transfer; Molecular magnets; Photoacoustic; Photo-induced; Porous materials; Prussian blue

1. Introduction

Prussian blue (PB) analogues or hexacyanometallates form a family of coordination compounds that has received a notable attention as prototype of molecular materials in the last decade. The CN group is a strong bridge ligand that allows a pronounced charge overlapping between the metal centers linked at its C and N ends. From this fact, PB analogues show interesting properties as molecular magnets, among them, high temperature of magnetic ordering [1,2], pole-inversion magnets [3], spin-glass behavior [4] and photo-induced magnetism [5]. This last effect is related to the photo-induced charge transfer between the metal centers changing the available population of electrons with unpaired spins and, in consequence the material magnetic properties. This is a typical metal-to-metal charge transfer (MM'CT)

but with a relatively large stability for the excited state to attain magnetic ordering below certain critical temperature (T_c). The MM'CT transitions in PB analogues have also been studied for potential applications of these compounds as electrochromic materials, e.g. smart windows and electrochromic displays [6], since the charge transfer transition leads to a color change. The MM'CT effect in hexacyanometallates is closely related to the nature of the CN ligand. It has a low energy π -antibonding orbital at the C end which overlaps with the t_{2g} orbitals of the inner metal (M'), providing a low energy route for the electron movement between the metal centers. The deep blue color of ferric ferrocyanide (Prussian blue) has been ascribed to a MM'CT transition among iron atoms [7]. The existence of that low energy π^* -orbitals also allows the occurrence of metal-to-ligand charge transfer (M'LCT) in this family of compounds. The optical absorption spectra of hexacyanometallates are mainly related to these two charge transfer mechanisms together with the possibility of d–d transitions in the involved transition metals. Such spectra are usually recorded by UV–vis spectroscopy.

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Photoacoustic spectroscopy (PAS) is a versatile technique with increasing applications to Chemistry and Physics. The photoacoustic spectrum results from acoustic waves generated by the sample heating during the absorption of intensity modulated light [8,9]. From this fact, this technique appears ideally suited for the study of opaque objects, such as many PB analogues. However, the available information on applications of PAS to this family of compounds is scarce [10,11]. In order to shed light on the scope of PAS for the study of PB analogues, spectra for ferrocyanides, ferricyanides and cobalticyanides, were obtained and evaluated. For cobalt hexacyanoferrates, compounds closely related to the above mentioned photo-induced magnetization, a series of mixed valence states (MVS) of high spin Co(II) low spin Co(III) hexacyanoferrates(II,III) were generated by a partial heat induced charge transfer in Co(II) ferricyanide(Co(II) \rightarrow Fe(III)) [12] and the resulting compositions included in this study (the fourth series). The obtained results indicate that from photoacoustic spectra valuable information on the photo-induced charge transfer transitions in PB analogues can be derived.

2. Experimental

The studied complex salts were obtained mixing 0.01 mol/L aqueous solutions of potassium hexacyanometallates and of the appropriate metal (M) sulfate, with M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The formed precipitates were then isolated by filtration, followed by successive washing to obtain a filtrate free of the accompanying anions and cations. The reagents used were analytical grade from Sigma and Merck. The resulting solids were air-dried until constant weight. By the same procedure, a PB sample (M = Fe(III)) was prepared. The nature and chemical composition of the obtained samples were established from infrared (IR) spectra, energy dispersed X-ray spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetry (TG).

The studied samples of MVS were obtained heating cobalt ferricyanide under a N₂ flow (200 mL/min) during one hour at 80, 100, 120, 140 and 160 °C, and then allowing the sample cooling until room temperature within the used furnace. The following samples will be labeled MVS80, MVS100, MVS120, MVS140 and MVS160, respectively. The characterization of these MVS compositions according to their crystal and electronic structures is reported elsewhere [12].

IR spectra were recorded using the KBr pressed disk technique except for ferricyanides. Ferricyanides reduce to ferrocyanide, through a mechanochemical reaction, during the disk preparation for IR spectroscopy [13]. XRD powder patterns were obtained in the Bragg-Brentano geometry using Cu K α radiation. The TG curves were recorded under a nitrogen flow (800 mL/min) using a TA Instrument thermo-balance (2950 model) operated in the high-resolution mode. PAS spectra were recorded in the absorption mode using a conventional cell and pressed disk-shaped samples. The light coming from a halogen lamp (operated at 700 W) was modulated at a fixed frequency of 17 Hz with a mechanical chopper after it passes through a monochromator with 1200 lines/mm diffraction grating in order to obtain monochromatic light in the 400–1000 nm

spectral range. PAS spectra were normalized using carbon black as reference sample in the usual way. More details about PAS can be found elsewhere [8,9].

3. Results and discussion

3.1. On the nature of the studied samples

IR spectra of all the studied samples show only the absorption bands reported for hexacyanometallates [14]. The frequency values found for these bands are available as [Supplementary data](#). According to the EDS analyses, the M:Fe and M:Co atomic ratios obtained for ferricyanides and cobalticyanides were close to 3:2. Such atomic ratio corresponds to complex salts with the unit formula, M₃[M'(CN)₆]₂·xH₂O, with M' = Fe, Co. In what follows, we will denote these compounds as M₃M'₂. For ferrocyanides, mixed salts containing potassium were formed, with unit formula, MK₂[Fe(CN)₆]₂·xH₂O, except for Zn. For this last metal, the Zn:Fe:K ratio (3:2:2) indicates formation of Zn₃K₂[Fe(CN)₆]₂·xH₂O. The prepared PB reference sample was found to be practically free of K, which corresponds to the insoluble modification (IPB), Fe₄[Fe(CN)₆]₃·xH₂O.

XRD powder patterns of the studied M₃M'₂ solids, including those resulting from the annealing of Co₃Fe₂ (MVS series), correspond to a cubic unit cell. PB analogues usually crystallize in the *Fm-3m* space group (cubic) [15]. In this structure both metal centers remain octahedrally coordinated and the unit cell edge corresponds to the M–N≡C–M'–C≡N–M chain length. The charge balance (stoichiometry) forces the existence of 1/3 of vacant sites for the molecular octahedral block, [M'(CN)₆], in ferricyanides and cobalticyanides and of 1/4 in IPB. These vacant sites lead to a network of pores of about 8.5 Å (diameter) which, in the as-synthesized samples, remain filled of coordinated and zeolitic water molecules. The outer metal (M), always found at the pore surface, has a mixed coordination sphere, M(NC)₄(H₂O)₂ for M₃M'₂ and Fe(NC)_{4.5}(H₂O)_{1.5} for IPB. These coordinated waters stabilize the zeolitic ones through hydrogen bonding bridges. The hydration degree for the studied samples, as derived from the TG curves (not shown), is relatively high, from 10 to 16 water molecules per unit formula, depending on the polarizing power of the metal (M) [16]. Ferrocyanides were found to be orthorhombic (Mn, Co, Ni, Cu and Cd) and rhombohedral (Zn). These results agree with the reported crystal structures for these compounds [17–20]. Their structures are free of vacancies and potassium is an extra-framework atom, playing the role of a charge balancing cation. Additional structural information on the studied samples is provided as [Supplementary data](#).

The CN group is a very strong ligand and the metal (M') coordinated at its C end is always found in low spin configuration. Hexacyanometallates are only formed for transition metals (M') with a maximum of six electrons in the *nd* shell [21], which in the low spin configuration are accommodated in the metal t_{2g} orbitals. At the N end the CN group behaves as a less covalent ligand and the metal M is found in high spin state except for Co(III). In the MVS series, for instance, Co(III) is found with a low spin configuration, t_{2g}⁶e_g⁰ [12]. The reported photo-induced

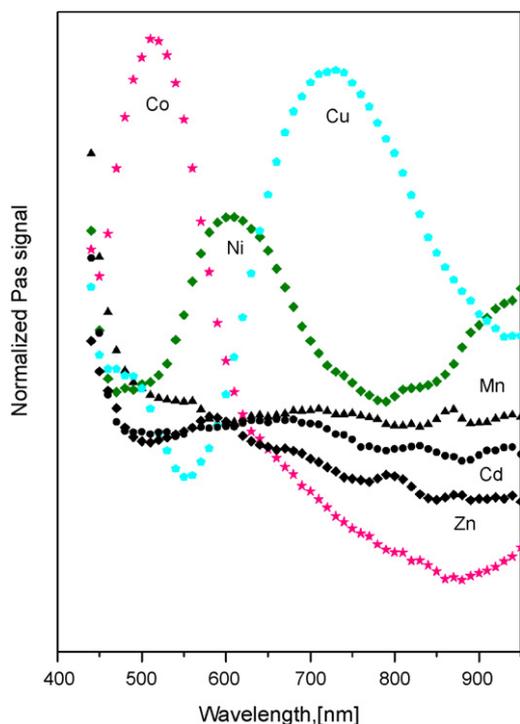


Fig. 1. Photoacoustic spectra of divalent transition metal hexacyanometallate(III). These spectra are composed by a M'LCT transition, observed as a shoulder below 450 nm and d–d transitions for the complex salts of Co(II), Ni(II) and Cu(II).

charge transfer from Co(III) \rightarrow Fe(II) through the CN bridges to form Co(II)–Fe(III) species also involves a spin crossover, from low to high spin, for the cobalt atom [5,22].

3.2. Photoacoustic spectra

3.2.1. Cobalticyanides

Fig. 1 shows the obtained spectra for this series of hexacyanometallates. For Mn, Zn and Cd no evidence of photo-absorption in the visible spectral region was obtained, except below 450 nm, an expected result since these compounds are white powders. Zn and Cd have $3d^{10}$ and $4d^{10}$ as electronic configuration, respectively, without possibilities of d–d transitions. Mn(II) has five unpaired electrons ($3d^5: t_{2g}^3 e_g^2$) but this result suggests that a d–d transition involving spin pairing has a low probability of occurrence. A d–d transition at the cobalt(III) atom is practically forbidden due to the nature of the CN ligand. The observed shoulder below 450 nm was attributed to a M'LCT transition from the cobalt(III) atom towards the CN group. These transitions in hexacyanometallates are usually observed at short wavelength, close to the ultraviolet region [23].

For Co, Ni and Cu spectra in addition to the M'LCT shoulder, signals assigned to d–d transitions were observed. These samples are pink, greenish and pale blue (cyan) powders, respectively, and their photoacoustic maxima were found to be at 512 nm (Co), 606 nm (Ni) and 722 nm (Cu) (Fig. 1). These are the colors observed for many hydrated salts of these metals, e.g. sulfates and chlorides. As mentioned above, in the studied materials these metals are sited at the pore surface with two

water molecules in their coordination sphere, as average. The assignment of these signals as d–d transitions is supported by the reported optical transitions for these metals in an octahedral ligand field. The reported PAS spectrum for nickel chloride shows two sharp peaks at 605 and 640 nm assigned to a ${}^3A_{2g} \leftarrow {}^3T_{1g}(F)$ transition for Ni(II) [24]. For Co(II) the optical transitions have been calculated to be at 503, 529 and 562 nm ascribed to a ${}^4T_1(F) \leftarrow {}^4T_1(P)$ transition [25] and for Cu(II) a triplet around 670 nm (${}^2E_g \leftarrow {}^2T_{2g}$) has been reported [26]. However, in Co(II), Ni(II) and Cu(II) cobalticyanides the observed transitions appear as a broad band and not as resolved sharp peaks. Such behavior was attributed to the random distribution of the $[Co(CN)_6]$ vacancies within the material structure. This leads to different local configurations of ligands for the metal at the pore surface, $M(CN)_{6-x}(H_2O)_x$, and also to certain shift for the corresponding optical transitions. The net effect is the observed broad peak.

3.2.2. Ferricyanides

Fig. 2 shows the recorded spectra for the studied ferricyanides. For Zn and Cd two possible transitions are expected, a d–d transition within the low spin iron(III) atom and a M'LCT band from that last one towards the CN groups. According to the Mössbauer spectroscopy results [16,27], the energetic separation between t_{2g} orbitals in ferricyanides is of the order of kT (at room temperature). From this fact, the d–d transition in the iron(III) atom falls in the IR region. The pronounced shoulder observed below 600 nm was interpreted as due to the M'LCT band. Zn and Cd ferricyanides, and also potassium ferricyanide,

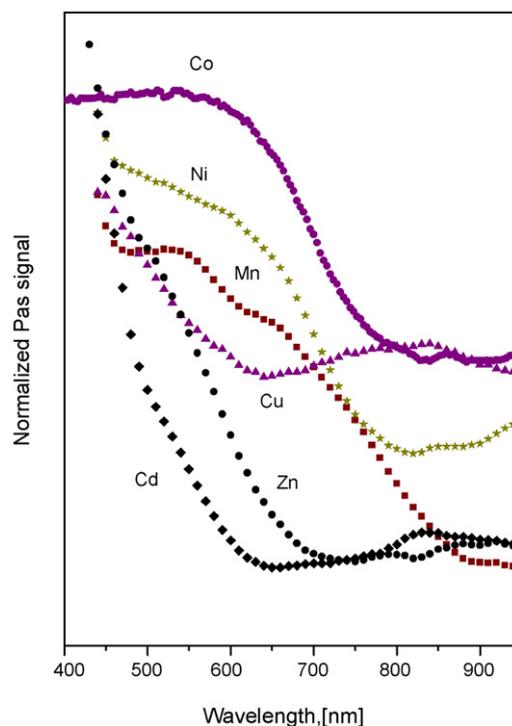


Fig. 2. Photoacoustic spectra of divalent transition metal hexacyanoferrates(III). These spectra are composed by a M'LCT transition, observed as a shoulder below 600 nm, and MM'CT bands overlapped with d–d transitions for the complex salts of Co(II), Ni(II) and Cu(II).

are yellow solids, in correspondence with the absorption of light from the blue spectral region.

For Mn, Co, Ni and Cu the photoacoustic signal covers a wide spectral range for the visible region. The peak shape profiles assigned to d–d transitions in Co, Ni and Cu cobalticyanides are not clearly observed for ferricyanides. These broad signals (bands) were interpreted as resulting from the overlapping of M'LCT, MM'CT and d–d transitions. For Mn the curve appears as two partially resolved contributions, at 537 and 659 nm (Fig. 2), probably due to the M'LCT band and to the Mn(II) → Fe(III) charge transfer, respectively. In the second band also certain contribution from a d–d transition in the temporally formed Mn(III) species could be present. The existence of Mn(III) hexacyanoferrates, with sufficient stability to be observed by IR and Mössbauer spectroscopies, have been reported for ozonized Mn(II) hexacyanoferrates(II,III) samples [28].

Cu(II) atoms linked at the N end of CN groups in hexacyanometallates show unique bonding properties. The CN group has certain ability to donate electron at its N end through a 5σ orbital which has a slight anti-bonding character and the copper(II) atom is able to receive charge at its e_g hole to favor an electronic configuration close to $3d^{10}$. This results in a particularly strong interaction of the copper atom with the CN groups. Such strong interaction leads to a short M–N≡C–M'–C≡N–M chain length for copper hexacyanometallates, to a low hydration degree for these copper salts, and also to the lowest Mössbauer isomer shift value for copper within transition metal ferricyanides [29]. These unique bonding properties for copper(II) in hexacyanometallates could explain the existence of a MM'CT in copper ferricyanide. The effective charge on the copper atom is close to that expected for Cu(I) and this allows the Cu → Fe electron transfer by photon absorption.

Co(III) ferrocyanide can be obtained as a stable species, which through light absorption transforms into Co(II) ferricyanide [5]. The inverse process in Co(II) ferricyanide, but induced by heating, leads to formation of Co(III) ferrocyanide [12]. These two processes suggest that in cobalt hexacyanoferrates the Co(II)–Fe(III) and Co(III)–Fe(II) electronic configurations remain separated by a relatively low energetic barrier. The observed photoacoustic curve for the cobalt(II) ferricyanide sample (Fig. 2) indicates that in this compound certain degree of Fe(II) → Co(III) charge transfer is taking place by light absorption, particularly around the blue spectral region. During the wet synthesis of Co(II) ferricyanide always a small fraction of Co(III) ferrocyanide is formed [12], probably favored by the reducing effect of the ferricyanide anion in solution. That fraction of Co(III) ferrocyanide could be the responsible for that MM'CT band in the sample of Co(II) ferricyanide. Such MM'CT band has been reported at 510 nm for Co(III) ferrocyanide clusters [23]. For Ni the photoacoustic curve suggests the occurrence of a MM'CT transition (Ni → Fe). Ni(III) ferrocyanide has not been reported as a stable species; its formation is not detected even under ozonization of Ni(II) hexacyanoferrates [30]. However, this last fact does not discard the occurrence of a MM'CT tran-

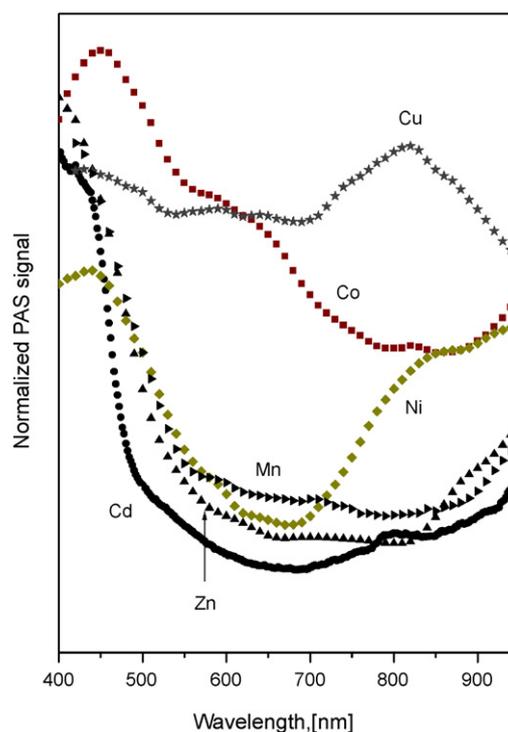


Fig. 3. Photoacoustic spectra of divalent transition metal hexacyanoferrates(II). These spectra are composed by a M'LCT transition, observed as a shoulder below 550 nm, MM'CT bands overlapped with d–d transitions (Co,Cu). For these last two metals a strong absorption in the near infrared region is observed.

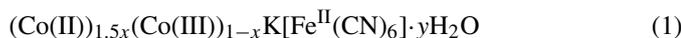
sition in Ni(II) ferricyanide. The occurrence of MM'CT in ferric ferrocyanide (PB) is a well known and an accepted fact [6], even when ferrous ferricyanide only exist is an unstable species [31].

3.2.3. Ferrocyanides

Fig. 3 shows the photoacoustic spectra obtained for the ferrocyanides series. The pronounced shoulder below 550 nm appears to be independent of the involved M metal and was attributed to the M'LCT transition in the iron atom environment. For the cobalticyanides series, with also a $3d^6e^0$ electronic configuration for the inner metal (M'), that shoulder was observed to be below 450 nm. Such difference of 50 nm corresponds to a lower energy barrier, by about 0.2 eV, between the ground and excited states for the iron complex.

For Mn, Zn and Cd only the M'LCT shoulder was observed. That behavior for these three metals is consistent with the results discussed above for their cobalt(III) analogues. Cobalt(II) ferrocyanide shows a broad peak at 450 nm, probably resulting from the overlapping of the highly probable d–d transition in the cobalt(II) atom and the M'LCT band. The photoacoustic band observed for this compound around 612 nm was ascribed to a MM'CT band of Fe(II) → Co(III) resulting from the existence of a small fraction of Co(III) ferrocyanide in the studied sample. Such band is similar to that found in the Co(II) ferricyanide sample, which was attributed to the Fe(II) → Co(III) transition. The formation of at least a fraction of mixed Co(III)Co(II) ferrocyanide during wet synthesis of Co(II) hexacyanoferrates(II,III) is an expected result due to the relatively high stability of that

species. Such mixed ferrocyanide has the following unit formula [18]:

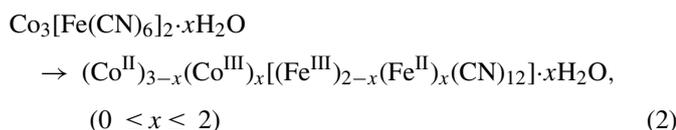


The Fe(II) → Co(III) MM'/CT transition in that mixed ferrocyanide has been intensively studied related to the photo-induced magnetic ordering [32]. In the spectral region where the d–d transitions for Ni(II) and Cu(II) are expected, only weak signals were observed. Unlike to the cobalticyanide analogues, where the outer metal is found with a mixed coordination sphere, $\text{M}(\text{NC})_4(\text{H}_2\text{O})_2$, in the studied ferrocyanides series it remains linked to six N ends of CN groups (see Supplementary data). In this last coordination environment, a higher fraction of electrons from the CN groups populates the e_g orbitals of nickel(II) and copper(II) atoms and probably this fact reduces the probability of transition for the expected d–d transitions and their relative intensity.

According to the obtained photoacoustic spectra for ferrocyanides and also from those for ferricyanides, the studied materials show an intense light absorption in the near infrared spectral region (Figs. 2 and 3). For Ni(II) and Cu(II) ferrocyanides such absorption begins at relatively low wavelength, about 750 nm. From our point of view, the available spectral and structural information is insufficient to provide an unequivocal explanation to that behavior.

3.2.4. Mixed valence state compounds

By heating a MM'/CT can also be induced in certain coordination compounds. Such effect is observed, for instance, in cobalt(II) ferricyanide to form the mixed valence states compounds Co(II)Co(III) hexacyanoferrates(II,III), according to [12]:



The inverse MM'/CT process corresponds to that discussed above by photon absorption.

Fig. 4 shows the photoacoustic spectra for the studied MVS series. For comparison, the spectrum of the IPB sample has been included in that figure. For all these compounds a broad band in the 450–850 nm spectral range is observed, ascribed to Fe(II) → Co(III) and Fe(II) → Fe(III) MM'/CT transitions in Co(II)Co(III) hexacyanoferrates(II,III) and ferric ferrocyanide (PB), respectively.

The crystal structure for the MVS series is a 3D network of $\text{Co(II)}-\text{N}\equiv\text{C}-\text{Fe(III)}-\text{C}\equiv\text{N}-\text{Co(II)}$ and $\text{Co(III)}-\text{N}\equiv\text{C}-\text{Fe(II)}-\text{C}\equiv\text{N}-\text{Co(III)}$ chains in the form of a polymeric solid solution. As the annealing temperature increases, a higher amount of $\text{Co(II)}-\text{N}\equiv\text{C}-\text{Fe(III)}$ chains participate in the heat induced $\text{Co(II)} \rightarrow \text{Fe(III)}$ charge transfer [12] and more $\text{Co(III)}-\text{N}\equiv\text{C}-\text{Fe(II)}$ chains are available for the photo-induced inverse process. The obtained spectra for this series show certain sensitivity to the annealing temperature (Fig. 4). As the treatment temperature rises, a progressive signal broadening

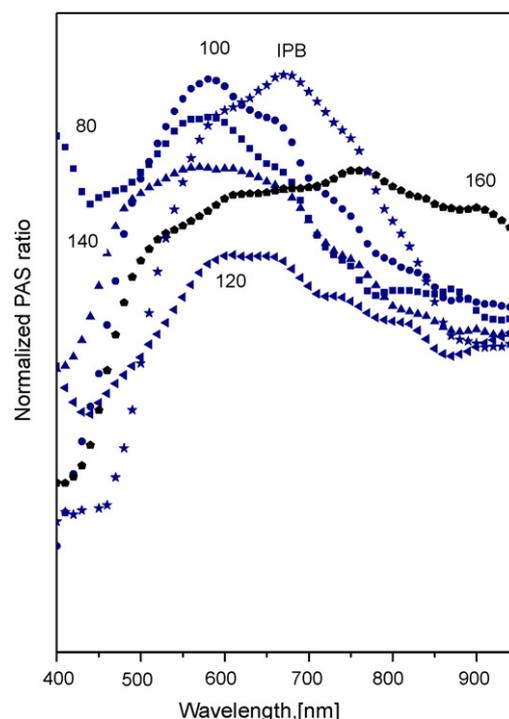


Fig. 4. Photoacoustic spectra of mixed valence state compounds, $(\text{Co(II)})_{3-x}(\text{Co(III)})_x[(\text{Fe(III)})_{2-x}(\text{Fe(II)})_x(\text{CN})_{12}] \cdot x\text{H}_2\text{O}$. Indicated is the temperature used to obtain the MVS samples. For comparison the spectrum of the IPB sample has been included.

is observed. For the MVS samples obtained in the 80–140 °C range of annealing temperature, the maximum light absorption takes place around 580 nm. The reported UV–vis spectrum for the mixed salt $\text{Rb}_{0.66}\text{Co(III)}_{0.84}\text{Co(II)}_{0.41}[\text{Fe}(\text{CN})_6]$ shows the $\text{Co(III)} \rightarrow \text{Fe(II)}$ transition at 550 nm [33]. The sample annealed at 160 °C shows an atypical behavior with a significant contribution from absorption in the red and near infrared spectral region. The heating of Co(II) ferricyanide above 140 °C induces charge transfer but also favors a partial sample decomposition and loss of crystal ordering [12,16]. Probably these structural and compositional changes are responsible for the observed contribution from the region of higher wavelengths in the MVS160 sample spectrum.

The photoacoustic spectrum for ferric ferrocyanide has its maximum around 670 nm, to a difference of about 90 nm related to the MVS series. This is equivalent to a difference of 0.29 eV for the energy barrier among the ground and excited states in Co(III) ferrocyanide and Fe(III) ferrocyanide. Compared to the studied series of MVS complexes, in PB the photo-induced charge transfer requires of light of lower energy.

3.3. Surface atoms and photo-induced charge transfer

The photo-induced charge transfer leads to a change in the electronic configuration for the involved atoms and ligands. For a given atom the crystal radius depends on its electronic configuration [34]. These two facts suggest that the charge transfer transitions are particularly favored for surface atoms where the surface “absorbs” the change in the inter-atomic distances

among the atoms participating in the photon absorption. The energy transferred to the solid during the photons absorption is usually insufficient to produce a cooperative expansion or contraction of its structure. For porous and nanometric size solids a large fraction of the atoms are sited at the surface and for such materials these atoms are able to participate in photo-induced charge transfer processes.

Prussian blue analogues are usually obtained with a nanometric particle size and, in addition, many of them have a porous structure [27,35]. For the studied cobaltcyanides, ferricyanides and MVS series, and also for the IPB sample, always the outer metal (M) is found sited at the pore surface. These two features of Prussian blue analogues and the strong charge overlapping among the metal centers that the CN ligand allows, explain the frequently observed charge transfer bands for this family of molecular materials. For the photo-induced charge transfer in Co(III) ferrocyanide to form Co(II) ferricyanide a variation of 0.2 Å in the Co–N inter-atomic distance has been reported [36,37]. During the annealing of Co(II) ferricyanide to obtain the MVS compositions a progressive cell contraction was observed, which amounts 2% of the cell volume reduction for the sample annealed at 140 °C, where the ferrocyanide fraction formed is close to 50 % of the sample weight [12].

The porosity of a given solid influences its thermal properties, thus affecting the intensity of the corresponding photoacoustic signal. However, it is a very well known fact that one of the advantages of PAS respecting other kinds of optical spectroscopy is that the position of the absorption bands in the signal becomes almost insensitive to light scattering by the sample [38,39], as taking place within porous samples [40], such as our pressed ones. Therefore, the obtained information on the photo-induced charge transfer processes was not affected by the sample's porosity. Moreover, it is worth to notice that all our disk shaped samples were prepared under the same pressure conditions

4. Conclusions

The photoacoustic spectroscopy appears as versatile technique to detect photo-induced charge transfer transitions in molecular materials based on the Prussian blue analogue. Many of these materials are highly opaque solids, which absorb a large fraction of the incident radiation. The absorbed energy is then liberated in the form of heat, which is responsible for an intense photoacoustic signal. For cobaltcyanides, the observed signals correspond to a metal-to-ligand charge transfer at the cobalt atom, detected as a shoulder below 450 nm and d–d transitions in Co(II), Ni(II) and Cu(II). In ferricyanides, the spectra reveal light absorption in practically all the visible region except for Zn and Cd. Such wide absorption region was attributed to the overlapping of M'LCT, MM'CT and d–d transitions. The spectra for the ferrocyanides series are dominated by the M'LCT transition except for cobalt and iron, where also MM'CT bands were observed. The most intense MM'CT bands were found for the MVS series and the IPB sample, attributed to Fe(II) → Co(III) and Fe(II) → Fe(III) photo-induced electron transfer. The M'LCT and MM'CT transitions lead to a change

in the electronic configuration for both metals and ligands, and since such change produces a variation in the inter-atomic distance among the involved atoms, the photo-induced charge transfer transitions must be favored for surface atoms. For such atoms the surface “absorbs” all the local distortions generated in the solid network.

5. Supplementary material

Supplementary Information associated with this article is available from the online version, and includes the IR spectral data, the cell parameters and atomic packing within the unit cell for all the studied samples. The calculated atomic positions, occupation and temperature factors and the estimated inter-atomic distances and bond angles derived from the structural Rietveld refinements have been deposited at ICSD Fachinformationszentrum Karlsruhe (FIZ) (email: crysdta@fiz-karlsruhe.de) with CSD file numbers: 416745: Mn₃[Co(CN)₆]₂·14H₂O; 416742: Co₃[Co(CN)₆]₂·14H₂O; 416746: Ni₃[Co(CN)₆]₂·14H₂O; 416743: Cu₃[Co(CN)₆]₂·10H₂O; 416744: Zn₃[Co(CN)₆]₂·13H₂O; 416741: Cd₃[Co(CN)₆]₂·13H₂O; 416994: Mn₃[Fe(CN)₆]₂·14H₂O; 416993: Co₃[Fe(CN)₆]₂·14H₂O; 416997: Ni₃[Fe(CN)₆]₂·14H₂O; 416995: Cu₃[Fe(CN)₆]₂·10H₂O; 416998: Zn₃[Fe(CN)₆]₂·12H₂O; 416996: Cd₃[Fe(CN)₆]₂·14H₂O; 417021: (Co(II))_{3-x}(Co(III))_x[(Fe(III))_{2-x}(Fe(II))_x(CN)₁₂]₂·12H₂O; 416404: Co(II)K₂[Fe(CN)₆]₂·2H₂O.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2006.11.013.

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