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Observation of back-donation in 3d metal cyanide complexes through N K absorption spectra

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Abstract

N K and 3d atom $L_{2,3}$ absorption spectra of hexacyano complexes in solid $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$, $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, and $K_3Co(CN)_6$ have been measured by detecting the total electron yield. The N K spectra of the complexes are very similar and differ only in intensity of the lowest-energy absorption band. The intensity of this feature systematically decreases and its energy position systematically shifts to lower energies along the $[Cr(CN)_6]^{3-}$ – $[Mn(CN)_6]^{3-}$ – $[Fe(CN)_6]^{3-}$ series. In the spectra of $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ this band is lacking. A similar lowest-energy band is also observed in the 3d metal $L_{2,3}$ absorption spectra of the complexes. These findings were qualitatively explained in terms of π -back-bonding in the formation of lower-energy unfilled electronic states in the 3d metal cyanide complexes. It was found that the lowest-energy band has a common origin in the N K and metal $L_{2,3}$ spectra and it is associated with core electron transitions to the partly filled $2t_{2g}$ MO of these complexes. The occurrence of this band in the N K absorption spectra can be treated as a direct experimental evidence for the appreciable π -back-bonding in the 3d metal cyanide complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Soft X-ray absorption spectra; 3d Metal cyanide complexes; π -Back-bonding

1. Introduction

Octahedral cyanide complexes of 3d metal atoms are of fundamental importance in coordination chemistry for obtaining a detailed understanding of the transition metal–ligand bonding [1,2]. The 3d π –

$2\pi(\pi^*)$ charge transfer (π -back-donation) between the 3d atom and ligands (CN^- , CO, NO, etc.) with low-lying unfilled antibonding $2\pi(\pi^*)$ molecular orbitals (MOs) is a characteristic feature of chemical bonding in these and similar compounds [3]. Electronic structure of cyano complexes was extensively studied by X-ray absorption, but only the spectra of 3d atoms at the K and $L_{2,3}$ edges are known in the literature [4–7], while no investigations of ligand core excitations are available. The recent X-ray absorption study of $K_4Fe(CN)_6$ [8] has shown that

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the ligand N K and C K absorption spectra can provide a wealth of information on the local electronic structure of the complex. Furthermore, the chemical state of CN^- anion and the electronic structure of complexes are strongly influenced by the back-donation effect and thus it should be reflected in ligand core excitations. The present study is aimed to investigate and compare X-ray absorption spectra of ligand (nitrogen) and 3d-metal (Cr, Mn, Fe, Co) atoms for a series of hexacyano complexes in order to obtain information on their empty lower-energy electronic states and the π -back-donation effect in the 3d atom–ligand bonding.

2. Experimental

The X-ray absorption measurements on hexacyano complexes in solid $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Cr}(\text{CN})_6$, $\text{K}_3\text{Mn}(\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_3\text{Co}(\text{CN})_6$ were performed at the PM-1 beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY I) [9]. The samples were prepared by rubbing of the powder in a scratched copper plate. N K and 3d metal $L_{2,3}$ absorption spectra were recorded in the total electron yield (TEY) mode. The photon-energy resolution ΔE was set to 0.4 and 0.7–1.0 eV for the N K and metal (Cr, Mn, Fe, Co) $L_{2,3}$ absorption spectra, respectively. The photon energy was calibrated using the energy of the $1s \rightarrow \pi^*2p$ resonance in the N K spectrum of $\text{K}_4\text{Fe}(\text{CN})_6$ (399.6 eV [8]) with an accuracy of ± 0.3 eV. The spectra were normalized to the incident photon flux, which was recorded by measuring TEY of a clean Cu(110) surface.

3. Results and discussion

Fig. 1a shows N K absorption spectra of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ that contain a stable octahedral $[\text{Fe}(\text{CN})_6]^{n-}$ complex for two formal charge states of the iron atom: Fe(II), $n=4$ and Fe(III), $n=3$, respectively. It should be noted that the spectrum of $[\text{Fe}(\text{CN})_6]^{4-}$ is not sensitive within experimental accuracy to the substitution of the external potassium cation by the sodium one in accordance with the popular opinion about a

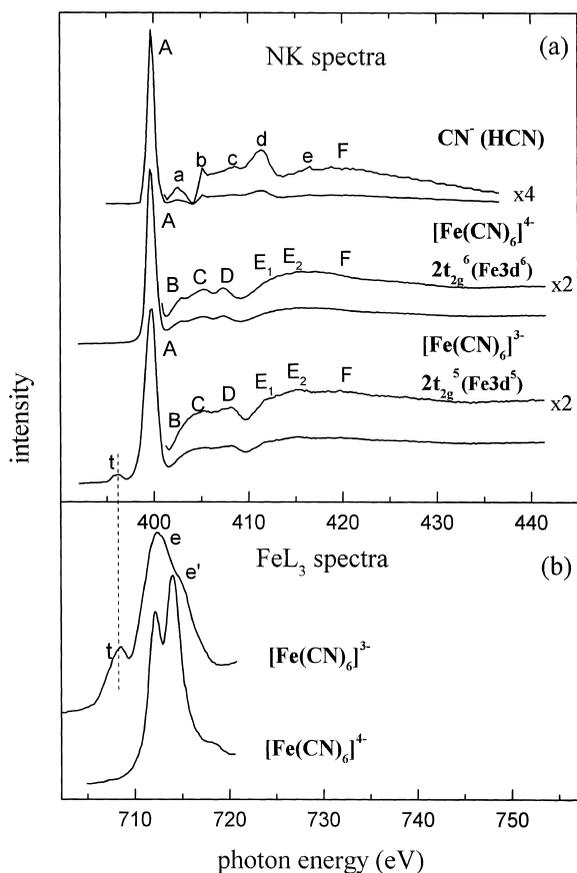


Fig. 1. X-ray absorption spectra of Fe(II) and Fe(III) hexacyano complexes in solid $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. (a) N K spectra of complexes compared to that of the cyanide anion in gas-phase HCN [10]. The spectra of complexes are normalized to the intensity of the peak A. (b) Fe L_3 spectra of complexes. The energy scales for N K and Fe L_3 spectra are aligned in energy using XPS data [13] on energy separation (312.1 eV) between the iron $2p_{3/2}$ and nitrogen $1s$ core levels of $\text{K}_3\text{Fe}(\text{CN})_6$.

quasimolecular nature of the X-ray photoabsorption in similar polyatomic systems [4–8]. One can see from this figure that both spectra are dominated by the strong low-energy peak A, which is followed at higher energies by weak bands B–F. The only essential difference between the spectra under comparison is the lowest-energy feature t in the spectrum of the Fe(III) complex, which is absent in the spectrum of the Fe(II) complex.

From the comparison of N K absorption spectra for iron complexes and the cyanide anion CN^- in HCN [10] (Fig. 1a) one can see that the counterparts

of the main π^*2p and σ^*2p resonances of CN^- (bands A and F) are present in the N K spectra of ligands at similar energies. This experimental fact indicates obviously that the CN^- anion is weakly affected by the 3d atom–ligand bonding. Thus, it can be considered as a stable fragment (a quasimolecule) interacting with the central 3d atom. In the vicinity of the π^*2p resonance (additional band t) and in the region between the π^*2p and σ^*2p resonances (new bands B–E₂) the spectra of the complexes and of HCN differ significantly.

The nature of the metal–CN bonding in transition metal cyanides is usually described in terms of σ electron donation from the highest filled, ‘lone-pair’ MO of CN^- ($\text{CN} \rightarrow \text{metal}$) and π -back-donation of metal 3d electrons into the first unfilled antibonding $2\pi(\pi^*)$ orbital of the ligand ($\text{metal} \rightarrow \text{CN}$) [1–3]. The first band t is thus representative of the 3d π –2p π^* bonding effects while the other new absorption bands B–E₂ correspond to transitions of the N K electrons to unoccupied σ MOs of the complexes. In the present paper we restrict ourselves to a consideration of empty π -states that are responsible for lower core excitations in X-ray absorption spectra of complexes; a complete analysis of the spectra obtained will be performed elsewhere. In $[\text{M}(\text{CN})_6]^{n-}$ the metal (valence) 3d orbitals are split by the octahedral ligand field into a higher energy doubly degenerate $3d_{e_g}$ orbital and a lower energy triply degenerate $3d_{t_{2g}}$ orbital (Fig. 2). As the $\pi 2p$ MOs of the ligands

are transformed as the irreducible representations t_{1g} , t_{1u} , t_{2g} , and t_{2u} [11], the π -bonding in $[\text{M}(\text{CN})_6]^{n-}$ can be generated only through the interaction of the metal $3d_{t_{2g}}$ orbital and the ligand $\pi 2p_{t_{2g}}$ MOs. With consideration for the π -back-donation into the $2\pi(\pi^*)$ MO, there are three t_{2g} MOs for $[\text{M}(\text{CN})_6]^{n-}$ that are formed from mixing the metal $3d_{t_{2g}}$ and the ligand bonding $1\pi_{t_{2g}}$ and antibonding $2\pi_{t_{2g}}$ orbitals [3] (Fig. 2). According to the calculations [12], the $1t_{2g}$ ($3t_{2g}$) orbital is always filled (unfilled) while the $2t_{2g}$ orbital is gradually populated in going from $[\text{Cr}(\text{CN})_6]^{3-}$ to $[\text{Co}(\text{CN})_6]^{3-}$ with increasing 3d electron number of the metal atom. From these calculations it is also known that the $2t_{2g}$ orbital is fully occupied in $[\text{Fe}(\text{CN})_6]^{4-}$ and has one hole in $[\text{Fe}(\text{CN})_6]^{3-}$ resulting in ground-state electronic configurations $\dots(2t_{2g})^6, {}^1A_{1g}$ and $\dots(2t_{2g})^5, {}^2T_{2g}$ for the Fe(II) and Fe(III) complexes, respectively. Thus, the extra lowest-energy band t in N K absorption spectrum of $[\text{Fe}(\text{CN})_6]^{3-}$ complex can be associated with the nitrogen core electron transition to the partly occupied $2t_{2g}$ MO of this complex. Although the $2t_{2g}$ MO is mainly localized on the metal atom, the $\text{N}1s \rightarrow 2t_{2g}$ transition is observed because of the ligand $2\pi_{t_{2g}}$ contribution to this MO.

This assignment of the extra band t is in good agreement with the identification of a similar structure t in the Fe L₃ absorption spectra (Fig. 1b) of $[\text{Fe}(\text{CN})_6]^{3-}$ performed in Ref. [14]. After alignment

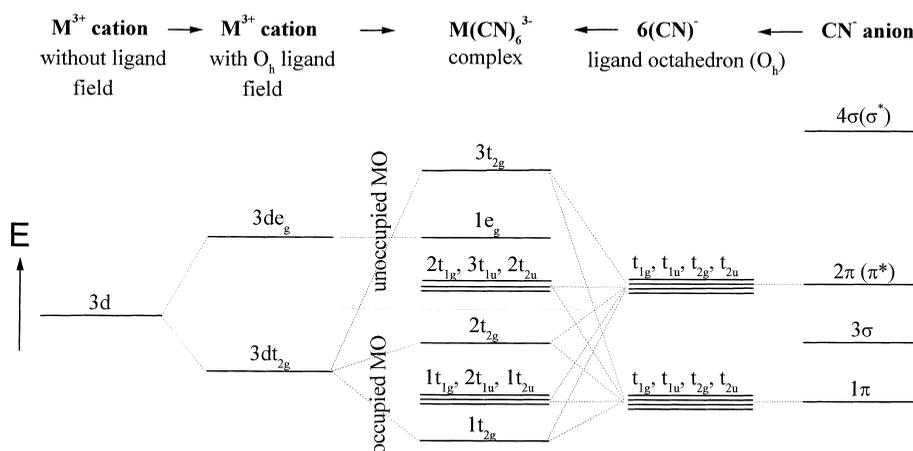


Fig. 2. Qualitative MO energy level diagram for octahedral $[\text{M}(\text{CN})_6]^{3-}$ complexes ($\text{M}=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$) only with the metal–ligand π -interaction.

in energy using energy separation between the $\text{Fe}2p_{3/2}$ and $\text{N}1s$ core levels (312.1 eV [13]) the band t has the same energy position in the N K and $\text{Fe} L_3$ spectra. This coincidence is indicative of the common origin for this band in both spectra: it can be assigned to the core electron transitions to the unfilled $2t_{2g}$ MO. Furthermore, in the context of the above MO-description we associate the main double absorption band e–e' with transitions of the $\text{Fe}2p_{3/2}$ electrons to the empty $1e_g$ and $3t_{2g}$ MO of the iron complexes.

Let us now consider N K absorption spectra of $[\text{M}(\text{CN})_6]^{3-}$ complexes with $\text{M}=\text{Cr}, \text{Mn}, \text{Fe},$ and Co (Fig. 3) taking into account the above considerations regarding the nature of lower-energy empty elec-

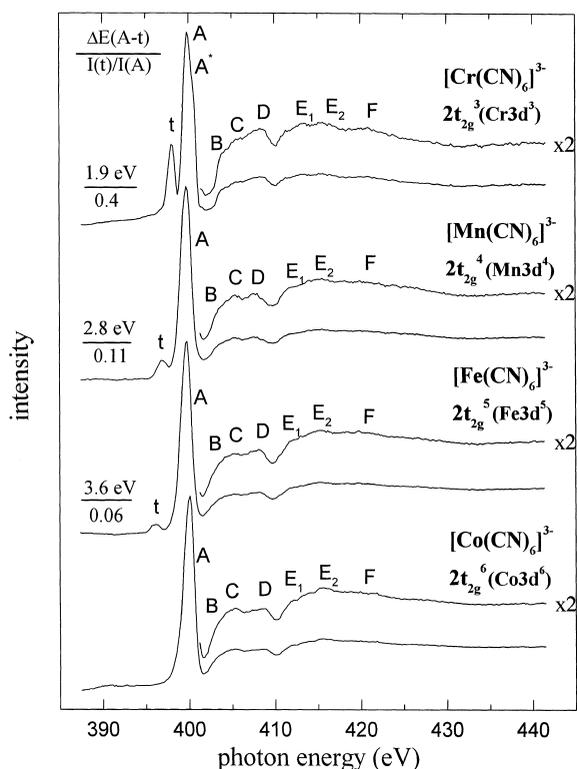


Fig. 3. N K absorption spectra of hexacyano complexes in solid $\text{K}_3\text{M}(\text{CN})_6$ with the metal atom $\text{M}=\text{Cr}(\text{III}), \text{Mn}(\text{III}), \text{Fe}(\text{III}),$ and $\text{Co}(\text{III})$. The spectra were normalized to the intensity of the peak A. The extra band t is characterized by its energy position $\Delta(\text{A}-\text{t})$ and relative intensity $I(\text{t})/I(\text{A})$ in reference to the main peak A.

tronic states in these complexes. From the figure we notice that only the band t undergoes an appreciable decrease in its intensity and a low-energy shift in its position along the $[\text{Cr}(\text{CN})_6]^{3-}-[\text{Mn}(\text{CN})_6]^{3-}-[\text{Fe}(\text{CN})_6]^{3-}$ series (it is absent in the spectrum of $[\text{Co}(\text{CN})_6]^{3-}$) whereas the other structures A–F are very similar in all the spectra except that the peak A has a shoulder A* in the case of $[\text{Cr}(\text{CN})_6]^{3-}$. Because the peak A reflects ligand 2π -states ($t_{1g}, t_{1u},$ and t_{2u}) that are not involved in the metal–ligand π -bonding, it is convenient to use it as a reference for examination of the observed changes of the band t. Thus, in the order $\text{Cr}-\text{Mn}-\text{Fe}$, the intensity of the band t relative to that of the peak A, $I(\text{t})/I(\text{A})$, decreases systematically and becomes equal to zero in $[\text{Co}(\text{CN})_6]^{3-}$, while the energy separation between the peak A and the band t, $\Delta(\text{A}-\text{t})$, increases gradually. In the light of the above electronic structure consideration for $[\text{M}(\text{CN})_6]^{3-}$, it is clear that the observed intensity change of the band t is due to successive filling of the $2t_{2g}$ MO in going from $[\text{Cr}(\text{CN})_6]^{3-}$ ($2t_{2g}^3$) to $[\text{Fe}(\text{CN})_6]^{3-}$ ($2t_{2g}^5$) as a result of the increasing 3d electron number of the metal atom. In $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ this MO is fully occupied ($2t_{2g}^6$) and the band t is absent. Since the $2t_{2g}$ MO is localized mainly on the metal atom, the $\text{N}1s \rightarrow 2t_{2g}$ transitions can be observed because of the mixing of the metal $3d_{2g}$ and ligand $2\pi_{2g}$ orbitals due to the π -back-bonding between the 3d atom and ligands. Thus, the observation of the band t in the N K absorption spectra of $[\text{M}(\text{CN})_6]^{3-}$ with the partially filled upper valence $2t_{2g}$ MO is a direct experimental evidence for the π -back-bonding in these complexes. The spectral characteristics $I(\text{t})/I(\text{A})$ and $\Delta(\text{A}-\text{t})$ may be used for a quantitative evaluation of the π -back-bonding in these complexes.

The lowest-energy band t that changes its relative intensity and energy position in a similar manner along the series of the $[\text{M}(\text{CN})_6]^{3-}$ complexes is also observed in the L_3 absorption spectra of 3d atoms for cyano complexes (Fig. 4). This experimental result agrees well with the $2t_{2g}$ -origin of the lowest-energy partly filled electronic state in the hexacyano complexes of $\text{Cr}(\text{III}), \text{Mn}(\text{III}),$ and $\text{Fe}(\text{III})$.

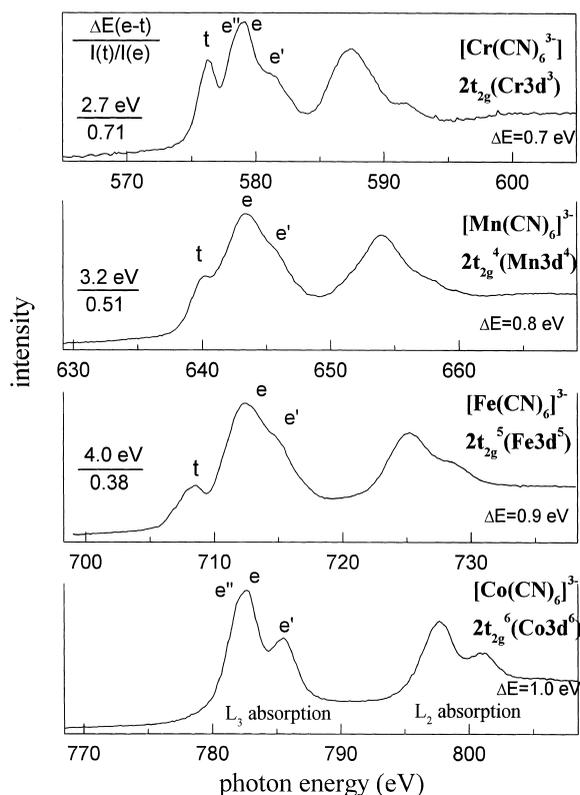


Fig. 4. Metal atom $L_{2,3}$ absorption spectra of hexacyano complexes in solid $K_3M(CN)_6$ with the metal atom $M=Cr(III)$, $Mn(III)$, $Fe(III)$, and $Co(III)$. The spectra were matched at the energy position of the band e and normalized to its intensity. The extra band t is characterized by its energy position $\Delta(e-t)$ and relative intensity $I(t)/I(e)$ in reference to the band e.

4. Conclusions

The N K and metal $L_{2,3}$ absorption spectra of hexacyano complexes in solid $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$, $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, and $K_3Co(CN)_6$ give information about the π -back-bonding and the nature of lower-energy empty electronic states in these complexes. The obtained N K spectra show very similar structures involving the main π^*2p and σ^*2p core excitations of the cyanide anion CN^- . The principal difference between them consists in the occurrence of an additional lowest-energy absorption band t in the spectra of

$[Cr(CN)_6]^{3-}$ – $[Mn(CN)_6]^{3-}$ – $[Fe(CN)_6]^{3-}$. This band undergoes an appreciable decrease in its intensity and a gradual shift in its energy position along the $[Cr(CN)_6]^{3-}$ – $[Mn(CN)_6]^{3-}$ – $[Fe(CN)_6]^{3-}$ series and disappears in $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. A similar lowest-energy band is also observed in the 3d metal $L_{2,3}$ absorption spectra of the complexes. These findings were qualitatively explained in terms of a key role of the π -back-bonding in the formation of lower-energy unfilled electronic states in the 3d metal cyanide complexes. It was found that the lowest-energy band has a common origin in the N K and metal $L_{2,3}$ spectra and it is associated with core electron transitions to the partly filled $2t_{2g}$ MO of these complexes. The occurrence of this band in N K absorption spectra can be treated as direct experimental evidence for an appreciable π -back-bonding in the 3d metal cyanide complexes.

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