Metal-to-metal charge-transfer transitions in Prussian blue hexacyanochromate analogues

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ABSTRACT

Time-dependent density functional theory (TD-DFT) calculations are presented for a series of Prussian blue analogues (PBAs) based on hexacyanochromate in order to investigate optical metal-to-metal charge-transfer (MMCT) transitions. PBE0 hybrid DFT calculations at fixed geometry were carried out on binuclear units of $(CN)_5$-M_A-NC-Cr^{III}-$(CN)_5$, with $M_A = V^{II}$, V^{III}, and Cr^{II}. The MMCT transitions occurred at 743 nm for the V^{II}-Cr^{III} PBA and at 780 nm for the V^{III}-Cr^{III} PBA. The ordering of the transition energy and strength for these analogues agreed with data available in the literature. The transition for the Cr^{II}-Cr^{III} MMCT was found to occur at 284 nm. This study shows that TD-DFT is a powerful method to study optical properties of PBAs and that the results for the relatively simple binuclear cluster are comparable to solid PBAs, where MMCT transitions are typically the dominant feature in the visible part of the absorption spectrum.

1. Introduction

Switching functional molecular materials to metastable states using external perturbations is of great interest for future electronics and information storage technologies. A promising class of materials for this purpose are Prussian blue and its analogues (PBAs), which are co-ordination polymers comprising transition metal ions linked by cyanide ligands in a rock-salt structure [1]. The general formula is $C_cA_a[B(CN)_6]_b \cdot nH_2O$ (C = alkali cation, A,B = transition metal ions). The PBAs typically display bright colours due to strong metal-to-metal charge-transfer (MMCT) transitions in the visible spectrum. The charge-transfer (CT) occurs between ions A and B, and can approximately be represented as

$$M_A^n\text{-}NC\text{-}M_B^m \xrightarrow{h\nu} M_A^{(n-1)}\text{-}NC\text{-}M_B^{(m+1)}, \tag{1}$$

where n and m are the corresponding formal oxidation states. In this example, the A ion is reduced as a result of CT from the B ion. The MMCT transition can be very important in controlling the physical properties of PBAs as a means of external optical stimulus. For example, MMCT can lead to meta-stable states that affect the magnetic properties, producing interesting photomagnetic effects [2,3]. On the other hand, it is also possible to turn off the MMCT transition electrically making use of the electrochromic properties of some PBAs. For example, the bright blue colour of Prussian blue itself (containing Fe^{III}-Fe^{II}) can be completely switched off by applying a small potential [4,5].

It is also possible to combine magnetic and electrochromic properties, as is the case for the V-Cr PBA [6–8]. These examples demonstrate one of the many fascinating aspect of PBAs, namely their multifunctional nature. With the capabilities of modern quantum chemistry [9–11], it is becoming possible to quickly screen the properties that control MMCT transitions in complex materials and molecules. Here, we present results of a TD-DFT computational study of the MMCT of a series of PBAs.

Robin and Day have classified mixed-valence compounds into three types, where PBAs typically fall into Class II [12]. This means that the valence electrons are not fully localised on the metal ion sites at elevated temperatures. In fact, the intensity of MMCT transitions can be shown to be proportional to the degree of delocalisation α between the metal ions A and B. The total wavefunction Ψ_0 can be written as a superposition of the fully localised wavefunction Ψ_0' and a wavefunction Ψ_l where the optical electron is fully localised on the other metal ion [12], according to

$$\Psi_0 = \sqrt{1-\alpha^2}\,\Psi_0' + \alpha\Psi_l.$$

For Prussian blue, the value of α is on the order of 1%. It can be shown that the transition dipole moment is proportional to the delocalisation factor α [12,13], which in turn depends on the mixing and energy difference between the fully localised state and the transferred-electron state. This has been thoroughly described by several authors based on symmetry arguments [12–14]. However, with the emerging field of functional materials and the important role of MMCT in their optical properties, it is interesting to revisit the MMCT of PBAs using

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TD-DFT methods.

There are several PBAs reported in the literature with the corresponding MMCT occurring at different spectral positions in the visible spectrum. For example, in electrochemically deposited thin films of $(Fe_x^{II}Cr_{1-x}^{II})_{1.5}[Cr^{III}(CN_6)]$ PBAs, where x ranges from 0 to 1, the colour of the films could be tuned by the stoichiometry producing films that were either colourless (x = 0), violet (x = 0.2), red (x = 0.4), or orange (x = 1) [15]. A more attractive system to investigate in a computational study, is the ternary $K_a^I V_x^{II/III} Cr_{1-x}^{II}[Cr^{III}CN_6]_b$ PBA [16] due to the relatively small number of electrons of the d^3 ions Cr(III) and V(II), and the d^2 ion V(III). For the case when x = 1, the MMCT occurs either at 660 nm (Cr^{III}-V^{III}) or 540 nm (Cr^{III}-V^{II}) [8,17,18] and provides an interesting case to study the MMCT as a function of vanadium oxidation state. In the case when x = 0, the MMCT has been assigned to occur at 510 and 610 nm [15]. These transitions are not fully understood since the peaks that have been assigned as MMCT in the visible are rather weak and, furthermore, in another study the MMCT was assigned to occur in the UV at around 380 nm [19].

We recently carried out TD-DFT computations to support the assignment of the optical spectrum of the V-Cr PBA [20]. We used a simplified model of the PBA by carrying out quantum chemical calculations on a binuclear unit. In this model, both metal ions are surrounded by cyanide ligands, giving the formula $(CN)_5$-M_A-NC-Cr^{III}-$(CN)_5$ with $M_A = V^{II}$, V^{III}, and Cr^{II}. This approach worked surprisingly well considering its simplicity. In this paper, we have expanded the range of variable inputs in the calculations and studied the effects of initial geometry and spin state of the open-shell system. We found that the TD-DFT calculations could reproduce the relative energy and oscillator strengths of the MMCT of $V^{II/III}$-Cr^{III} PBA in good agreement with previously published experimental work. The larger oscillator strength for the MMCT of V^{II}-Cr^{III} vs V^{III}-Cr^{III} was explained by the larger degree of delocalisation of the optically active orbitals in the V^{II}-Cr^{III} PBA. We found that the MMCT for Cr^{II}-Cr^{III} occurred in the UV involving the HOMO − 2 orbitals, which are more localised than the HOMO (which in turn is responsible for the magnetic properties). Interestingly, in Cr^{II}-Cr^{III} PBAs, the delocalised HOMO gives rise to a relatively high magnetic ordering temperature ($T_c \approx 240$ K [21–25]) whereas the more localised HOMO − 2 gives rise to a weak oscillator strength for the MMCT.

2. Method

To study PBAs using "Gaussian-based" quantum chemical techniques we chose a single binuclear unit with, initially, a fixed geometry, comprising one V with five CN^- ligands (with N pointing toward V), one Cr with five CN^- ligands (with C pointing toward Cr) and one bridging CN^- ligand (with N toward V and C toward V). This model has been adapted previously in DFT studies of the magnetic properties of a number of different PBAs [22–25]. This monomeric unit possesses C_{4v} symmetry. The charge of the cluster is given by the sum of the oxidation states of the metal ions and the 11 negatively-charged cyanide ligands. The bond lengths chosen for the model monomeric unit are those as determined by Garde et al. using X-ray absorption data [17]. The same bond length was also used for the Cr^{II}-Cr^{III} calculations. The bonds N−C, C−Cr and N−V have lengths of 1.15, 2.06 and 2.12 Å, respectively. This corresponds to a V−Cr distance of 5.33 Å. For the V part of the monomeric unit, the C ends of the cyano ligands were uncapped. Fig. 1 depicts the binuclear unit of V−Cr PBA used to perform the calculations. In addition, a 'stretched' geometry where the V−Cr distance is 5.75 Å was considered by having the bridging bond lengths for V−N, N−C and C−Cr of 2.33, 1.15 and 2.27 Å, respectively. In the calculations for Cr^{II}-Cr^{III} PBA, we chose Cr^{II} in the N site and Cr^{III} in the carbon site. Experimentally, the oxidation states of the Cr−Cr PBA can be quite difficult to determine [19,26] and so whenever we refer to experimental data published in the literature we do not give the oxidation state.
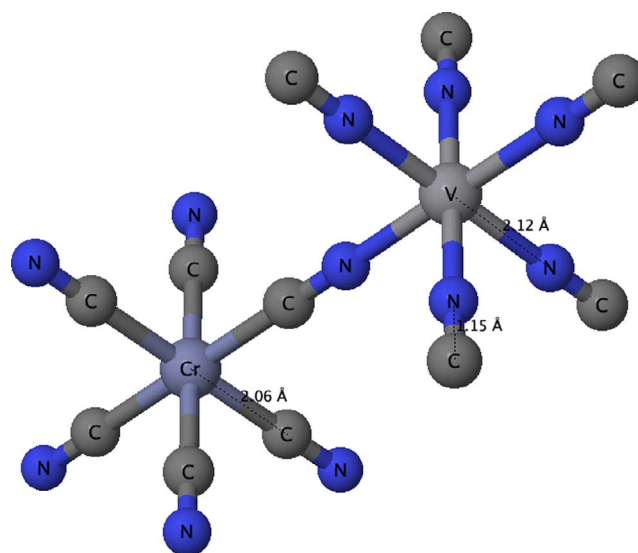

Fig. 1. The model binuclear unit of V-Cr PBA used to perform the calculations. Bond lengths in Å.

Gaussian 09 [32] was employed to perform TD-DFT calculations using the PBE0 hybrid exchange-correlation functional [33] with the 6-311G(d) basis set [34] for V and Cr ions, and the 6-31G(d) basis set [35,36] for C and N atoms. The unrestricted formalism was used for open shells and for closed-shell V^{II}-Cr^{III}. The unrestricted calculation on V^{II}-Cr^{III} employed the Gaussian 09 keyword "guess = alter" to change the initial guess wave function, where the following pairs of alpha-spin orbitals were switched: 96, 99; 97, 100; 98, 101. Out of curiosity, we also used the restricted formalism for closed electronic shells of the singlet spin V^{II}-Cr^{III} monomeric unit, since the total spin in this system cancel and leaves a singlet state. Of course, magnetic measurements [27] indicate that the spins are mainly localised on either Cr or V in an antiferromagnetic fashion and so the restricted approach, where all electrons are paired up in molecular orbitals, is probably not realistic. We use the conventional nomenclature in quantum chemistry and label the spin up/down projections as alpha and beta. We would like to point out that in the simplified binuclear cluster, the d_{xy} orbital, which lies in the plane perpendicular to the internuclear axis, will have a different energy to the two d orbitals that lie on the axis (d_{xz} and d_{yz}). In the 3D extended network this artefact would not be observed.

3. Results and discussion

One of the most striking results of all the calculations were the relatively few transitions observed and that these were quite "clean" one-electron transitions in specific molecular orbitals (MOs). The results for $V^{II/III}$-Cr^{III}, the stretched geometries of $V^{II/III}$-Cr^{III}, and Cr^{II}-Cr^{III} PBAs are presented below separately and in Tables 1–4.

3.1. $V^{II/III}$-Cr^{III} PBA

Unrestricted V^{II}-Cr^{III}. In the unrestricted calculation on the V^{II}-Cr^{III} binuclear unit, the Cr valence electrons are in the alpha channel with energies of 9.7 eV in MOs 93a and 94a corresponding to d_{xz} and d_{yz} MOs. Both these MOs are partially delocalised over the CN bridging ligand, as expected. MO 91a, corresponding to the d_{xy} orbital, has one electron with an energy of 9.6 eV but is not delocalised over the bridging ligand (because it lies in the xy plane). The slightly lower energy of the d_{xy} orbital is an artefact due to the binuclear model, as discussed in the methods section. There are ligand orbitals (MOs 95a–98a) at 9.9–10.2 eV, close in energy to the Cr MOs, in agreement with density-of-state calculations on the extended V-Cr PBA [28]. The HOMO is in