An Ab Initio Study of the Ligand Field and Charge-Transfer Transitions of $Cr(CN)_6^{3-}$ and $Mo(CN)_6^{3-}$

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Currently, high-nuclearity metal-cyanide clusters are intensively studied due to the interest in designing single molecule magnets (SMM).[1–4] An important class of such clusters are the discrete Prussian blue analogues containing octahedral $[M(CN)_6]^{m-}$ hexa-cyanometalates of the first-row transition metal ions. By varying the structure and the chemical composition, their magentic properties can easily be tuned.[5] Thus, high magnetic ordering temperatures were obtained in compounds containing $[Cr(CN)_6]^{3-}$ complexes as building blocks.[6–9] However, not only strong exchange interactions between metal centers, but also a pronounced magnetic anisotropy, are required to obtain good SMM characteristics. In this context, the substitution of Cr^{3+} by second- and third-row transition metal ions with more diffuse and high-energy d orbitals and considerably larger spin−orbit interactions is very promising.

Recently, several cyano-bridged compounds containing the octahedral $[Mo(CN)_6]^{3-}$ high-spin complex as a building block were synthesized and characterized.[7–9] It has been shown that the use of Mo^{3+} instead of Cr^{3+} gives rise to a considerable increase in the exchange parameters and zero-field splittings. The strength of the magnetic coupling in the $[Mo_2(CN)_{11}]^{5-}$ bioctahedral dimer holds the record for cyano bridged binuclear complexes.[7] For the understanding of the magnetic properties of the polynuclear complexes, a detailed analysis of the electronic structure of these individual building blocks as obtained from elaborated ab initio calculations can be quite useful. Experimental information concerning the electronic structure is mainly inferred from spectroscopic data of the mononuclear complexes, and therefore a correct interpretation of these data with the aid of theoretical considerations is of paramount importance. Although the ligand field part of the spectrum of $Cr(CN)_6^{3-}$ is well understood, the nature of the charge-transfer transition is still unclear. For $Mo(CN)_6^{3-}$, an experimental spectrum and a possible interpretation have been published recently.[7]

With the aim of elucidating the electronic spectra, a high-level comparative ab initio study of the two d^3 complexes $Cr(CN)_6^{3-}$ and $Mo(CN)_6^{3-}$ was carried out. For the sake of obtaining an idea about the accuracy of the theoretical model used, the spectra[10,25] of $MoCl_6^{3-}$ and $Mo(CN)_8^{4-}$ were also calculated. The chromium complex has been intensively investigated in the past.[11–13] In particular, the ligand field spectrum has been calculated quite accurately by the CASPT2 method,[14] and therefore we will apply the same computational method again, using the MOLCAS.5.2 software.[15] Computational details concerning the active spaces, basis sets,[16] and geometries[7,17,18,24] used in the calculations can be found as Supporting Information. As could be expected, our calculated excitation energies for the $Cr(CN)_6^{3-}$ and $MoCl_6^{3-}$ complexes reproduce quite well the experimental spectra, the differences averaging about 1500 cm⁻¹ (Table 1). For the chromium complex,

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Table 1. Comparison of Calculated CASPT2 Excitation Energies with Experimental Band Positions (All Values Given in Wavenumbers)

transition	$Cr(CN)_6^{3-}$ exp[11,12]	ref 14	this work	$Mo(CN)_6^{3-}$ this work	ligand field fit	$MoCl_6^{3-}$ this work	exp[10]
$^4A_{2g}$	0	0	0	0		0	
^2E_g ($t_{2g} \rightarrow t_{2g}$)	12 460	14 276	14 138	9430	8953	11 702	9650
$^2T_{1g}$ ($t_{2g} \rightarrow t_{2g}$)	13 070	14 921	15 362	9761	9107	12 071	
$^2T_{2g}$ ($t_{2g} \rightarrow t_{2g}$)	18 370	20 648	20 770	13 924	14 634	16 520	14 800
$^4T_{2g}$ ($t_{2g} \rightarrow e_g$)	26 700	29 358	27 564	42 647	42 000	20 859	19 200
$^4T_{1g}$ ($t_{2g} \rightarrow e_g$)	32 680	34 682	31 967	45 851	46 313	25 014	24 000
$^4T_{1u}$ ($t_{2u} \rightarrow t_{2g}$)			39 851	33 481			
$^4T_{2u}$ ($t_{2u} \rightarrow t_{2g}$)	38 600		40 324	33 847			
$^4T_{1u}$ ($t_{2g} \rightarrow t_{1u}$)			63 028	49 597			
$^4T_{2u}$ ($t_{2g} \rightarrow t_{1u}$)			63 461	50 886			

in particular, our results and the calculated LF transitions in ref 14 are in close agreement: the small variations are the result of the difference in active space. Comparison with the corresponding transitions for the $Mo(CN)_6^{3-}$ complex leads to two observations: (i) The intraconfigurational transitions are smaller in the molybdenum complex. This is not only the case within the $(t_{2g})^3$ configuration but can also be observed in a smaller splitting of the $^4T_{2g}$ and $^4T_{1g}$ states, which both belong to the $(t_{2g})^2(e_g)^1$ configuration. Fitting the transition energies to ligand field expressions gives Racah parameters for $Cr(CN)_6^{3-}$ (B = 620 cm⁻¹, C = 2985 cm⁻¹) that are larger than those for the molybdenum complex (B = 370 cm⁻¹, C = 1950 cm⁻¹). All of these results can be ascribed to the more diffuse d orbitals of the latter complex. (ii) Our fitted 10 Dq parameter for the $Cr(CN)_6^{3-}$ equals 27 500 cm⁻¹ and corresponds quite well with the experimental value of 26 600 cm⁻¹. This illustrates that the level of computation is sufficiently accurate to draw reliable conclusions. The quartet transitions of the molybdenum complex are located at much higher energies, resulting in a calculated 10 Dq parameter of 42 000 cm⁻¹. The more diffuse orbitals of the molybdenum overlap better with ligand orbitals and cause a larger ligand field splitting of the 4d shell. This is a generally observed fact in transition metal complexes. For instance, the substitution of Co(III) in its hexacyano complex by Rh(III) enlarges the 10 Dq value from 34 500 to 44 000 cm⁻¹.[11] Additional proof can be found in Jorgensen's empirical formula[19,20] for calculating the ligand field splitting parameter as a product of a ligand factor and a metal factor:

$$10 \text{ Dq} = f(\text{ligands}) \cdot g(\text{metal ion})$$

Applying this formula for $Cr(CN)_6^{3-}$ and its mobydenum analogue yields values of 26 690 and 41 820 cm⁻¹, respectively. All of these facts unequivocally predict that $t_{2g} \rightarrow e_g$ transitions lie above 40 000 cm⁻¹ for $Mo(CN)_6^{3-}$ and not in the region of 25 000 cm⁻¹ as mentioned in ref 7.

With the aim to further substantiate the accuracy of our computational model, we extended our study to the electronic spectrum of the octa-coordinated $Mo(CN)_8^{4-}$. Although this d^2 complex has been known for a long time,[25] there is still some controversy about the nature of the excitations responsible for the experimental bands.[26,27] The consensus, however, is that the low-lying excitations are due to ligand field transitions: the lowest-lying very weak ($\epsilon = 2.7$) band at 19 600 cm^{-1} corresponds to a spin-forbidden ligand field excitation, whereas the high-lying very intense ($\epsilon = 15\,540$) band at 41 670 cm^{-1} corresponds to a charge-transfer transition. Our calculations confirm these conclusions very well. The lowest excitation is indeed predicted as a transition from the $^1A_1$ $((x^2 - y^2)^2)$ ground state to the $^3B_1$ $((x^2 - y^2)^1(z^2)^1)$ state at 19 413 cm^{-1}. By calculating oscillator strengths, we found very intense charge-transfer bands of the metal-to-ligand type (CTML) at excitation energies of 40 360 and 44 146 cm^{-1}. Fitting the ligand field expressions to the CASPT2 energies yields $e_\sigma = 25\,850$ cm^{-1} and $e_\pi = 9100$ cm^{-1} and hence a hypothetical 10 Dq value of 41 150 cm^{-1}, which compares excellently with our proposed value for $Mo(CN)_6^{3-}$.

To determine what kind of transition in $Mo(CN)_6^{3-}$ is responsible for the bands in the 25000 cm^{-1} region, we performed calculations on charge-transfer states. The results show that for both complexes the CTLM transitions are calculated at lower energies than the CTML excitations. For $Cr(CN)_6^{3-}$, this contradicts the conclusions of Alexander and Gray of 1968 but affirms the assignment made by Wasielewska.[21] It should be mentioned, however, that these former assignments were based on simple semiempirical molecular orbital calculations, so that more elaborated calculations are needed to decide the matter. Carrying out CASPT2 calculations with different active spaces always places CTLM transitions below the CTML excitations. The correspondence between the experimental excitation energy of 38 600 and the theoretical value of 40 324 cm^{-1} demonstrates that charge-transfer states are computable with accuracies similar to those of ligand field states. Our assignment as CTLM concurs with the photochemical behavior of $Cr(CN)_6^{3-}$ when irradiated at 38 600 cm^{-1}.[22,23] For $Mo(CN)_6^{3-}$, the CASPT2 method situates CTML transitions around 50 000 cm^{-1}; the CTLM transitions are much lower at about 34 000 cm^{-1}. Our CASPT2 calculations do not predict any transitions between 25 000 and 30 000 cm^{-1}.

In summary, we can state that our theoretical treatment of the ligand field spectra of $Mo(CN)_6^{3-}$ predicts a rather large 10 Dq value of about 42 000 cm^{-1}, as opposed to the small value of 24 800 cm^{-1} as was recently put forward. The lowest lying charge-transfer transition is calculated for both hexacyano complexes to be CTLM. Both of these theoretical conclusions concerning the ligand field and charge-transfer transitions are substantiated by experimental evidence.

Supporting Information Available: Computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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