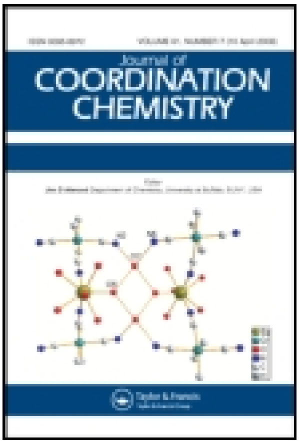

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Ligand field strengths of carbon monoxide and cyanide in octahedral coordination†

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Ligand field splittings were extracted from absorption spectra of metal hexacarbonyl and hexacyano complexes over 35 years ago by Gray and coworkers (*J. Am. Chem. Soc.*, **85**, 2922 (1963); *ibid.* **90**, 4260, 5713 (1968)). Recent time-dependent density functional theory calculations by Baerends and coworkers (*J. Am. Chem. Soc.*, **121**, 10356 (1999)) on $M(CO)_6$ with $M = Cr, Mo, W$ raised questions about the magnitudes of these ligand field splittings. In order to reexamine such effects systematically, we report here the splittings for a series of $3d^6$ metal hexacarbonyl, hexaisocyano and hexacyano complexes: $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$ and $Fe(CO)_6^{2+}$; $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$; and $V(CNH)_6^-$, $Cr(CNH)_6$, $Mn(CNH)_6^+$ and $Fe(CNH)_6^{2+}$. This work demonstrates that the 3d splittings induced by the ligands in question generally fall in the order $CO > CNH > CN^-$. We agree with Baerends and colleagues that CO exerts a much stronger ligand field than was originally thought.

Keywords: Density functional theory; Ligand field strength; Carbon monoxide; Cyanide; Isocyanide

1. Introduction

It is well known that carbon monoxide gives rise to some of the largest splittings of ligand field (LF) energy levels of transition metal complexes. It would be interesting to determine exactly how carbon monoxide compares in LF strength with other ligands known to induce large splittings. To the best of our knowledge, no computational study comparing the LF strengths of carbon monoxide with other strong field ligands has ever been performed.

Over 35 years ago, one of us (Gray), along with Beach and Alexander, assigned the absorption spectra of metal hexacarbonyl and hexacyano complexes [1–3]. In all cases the intense absorptions were assigned to allowed metal-to-ligand charge transfer (MLCT) transitions and the weaker, lower energy features to LF excitations.

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From these assignments of the spectra, corresponding values for the LF splitting parameter, Δ, were estimated for each of the metal hexacyano and hexacarbonyl complexes in question. Typical values were $\sim 35\,000\,\mathrm{cm}^{-1}$ for cyanide [1,2] and $\sim 34\,000\,\mathrm{cm}^{-1}$ for carbon monoxide [1,3], suggesting that CN^- is a stronger field ligand than CO.

Recent calculations by Baerends and coworkers [4] indicate that the original assignment of the weak bands [3] in the spectra of metal hexacarbonyl complexes was incorrect. Using time-dependent density functional theory (DFT) they calculated excitation energies for various MLCT and LF transitions for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. For each of the complexes they considered, they found that the energies of the orbitally-forbidden MLCT transitions are lower than the energies of the LF transitions. This would suggest that the Δ parameters estimated earlier for carbon monoxide [3] may be too low, leaving open the question of whether CN^- or CO is the stronger field ligand.

Here we resolve this issue by using DFT to calculate the ground-state orbital energies of the t_{2g} and e_g orbitals for an isoelectronic series of complexes: $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$, $Fe(CO)_6^{2+}$, $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$. For further comparison we have also calculated the LF splitting induced by CNH for the complexes $V(CNH)_6^-$, $Cr(CNH)_6$, $Mn(CNH)_6^+$ and $Fe(CNH)_6^{2+}$. These calculations have elucidated the relative LF strengths of CNH, CO and CN^-.

2. Computational methods

All calculations reported herein were performed with the TURBOMOLE program package for *ab initio* electronic structure calculations [5]. We used the QZVP basis set [6] for all atoms in calculating the properties of these complexes. We performed four different DFT calculations for each complex, each using a different exchange-correlation functional selected from B3LYP, PBE, BP86 and BLYP [7–15]. Each calculation assumed octahedral symmetry and was performed with an m3 gridsize [16]. The geometry of each complex was optimized using TURBOMOLE's JOBEX program with generalized internal coordinates [17]. The energies of the molecular orbitals in the ground state were then calculated with the DSCF module for semi-direct self-consistent field evaluation.

3. Results

We have calculated the bond lengths and the octahedral field splittings for all complexes in question with each of the exchange-correlation functionals. The calculated bond lengths are given in tables 1–3 and the corresponding octahedral field splittings are given in table 4.

4. Discussion

For both $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, the LF splitting parameter has been determined experimentally to be $\sim 4.3\,\mathrm{eV}$ [2]. We find that B3LYP overestimates this value by 40%,

Table 1. Calculated M–C bond distances (Å) using various density functionals.

	B3LYP	PBE	BP86	BLYP
$\mathrm{V(CNH)_6^-}$	1.985	1.970	1.973	2.000
$\mathrm{Cr(CNH)_6}$	1.934	1.913	1.916	1.943
$\mathrm{Mn(CNH)_6^+}$	1.918	1.886	1.890	1.917
$\mathrm{Fe(CNH)_6^{2+}}$	1.928	1.883	1.887	1.917
$\mathrm{V(CO)_6^-}$	1.972	1.957	1.960	1.987
$\mathrm{Cr(CO)_6}$	1.927	1.905	1.908	1.935
$\mathrm{Mn(CO)_6^+}$	1.921	1.885	1.889	1.918
$\mathrm{Fe(CO)_6^{2+}}$	1.950	1.895	1.900	1.932
$\mathrm{Co(CN)_6^{3-}}$	1.956	1.919	1.923	1.956
$\mathrm{Fe(CN)_6^{4-}}$	2.033	1.955	1.960	2.002

Table 2. Calculated C–X (X = O or N) bond distances (Å) using various density functionals.

	B3LYP	PBE	BP86	B-LYP
$\mathrm{V(CNH)_6^-}$	1.197	1.210	1.208	1.209
$\mathrm{Cr(CNH)_6}$	1.178	1.190	1.190	1.190
$\mathrm{Mn(CNH)_6^+}$	1.162	1.174	1.174	1.174
$\mathrm{Fe(CNH)_6^{2+}}$	1.149	1.161	1.161	1.161
$\mathrm{V(CO)_6^-}$	1.155	1.168	1.167	1.169
$\mathrm{Cr(CO)_6}$	1.138	1.151	1.151	1.152
$\mathrm{Mn(CO)_6^+}$	1.124	1.138	1.138	1.138
$\mathrm{Fe(CO)_6^{2+}}$	1.113	1.128	1.128	1.128
$\mathrm{Co(CN)_6^{3-}}$	1.163	1.177	1.176	1.175
$\mathrm{Fe(CN)_6^{4-}}$	1.174	1.189	1.189	1.187

Table 3. Calculated N–H bond distances (Å) using various density functionals.

	B3LYP	PBE	BP86	BLYP
$\mathrm{V(CNH)_6^-}$	0.986	0.994	0.994	0.994
$\mathrm{Cr(CNH)_6}$	0.990	0.997	0.997	0.997
$\mathrm{Mn(CNH)_6^+}$	0.996	1.003	1.003	1.002
$\mathrm{Fe(CNH)_6^{2+}}$	1.004	1.011	1.011	1.011

Table 4. Calculated octahedral field splittings (eV), $\Delta = E[\mathrm{e_g}] - E[\mathrm{t_{2g}}]$, using various density functionals.

	B3LYP	PBE	BP86	B-LYP
$\mathrm{V(CNH)_6^-}$	2.88	2.21	2.43	1.89
$\mathrm{Cr(CNH)_6}$	4.84	3.95	4.12	3.58
$\mathrm{Mn(CNH)_6^+}$	6.66	4.84	4.83	4.51
$\mathrm{Fe(CNH)_6^{2+}}$	6.99	4.59	4.56	4.28
$\mathrm{V(CO)_6^-}$	6.71	5.40	5.45	5.06
$\mathrm{Cr(CO)_6}$	7.26	5.41	5.38	5.04
$\mathrm{Mn(CO)_6^+}$	7.16	5.05	5.01	4.67
$\mathrm{Fe(CO)_6^{2+}}$	6.93	4.53	4.50	4.18
$\mathrm{Co(CN)_6^{3-}}$	6.62	4.03	4.02	3.77
$\mathrm{Fe(CN)_6^{4-}}$	5.68	3.65	3.66	3.34

while the other density functionals underestimate this value by 10% for PBE and BP86, and 20% for BLYP.

For the metal hexacarbonyl complexes, the typical experimental estimate for the octahedral field splitting parameter was ~4.2 eV [3]. However, all the exchange-correlation functionals considered here lead to values anywhere from 20% larger (for BLYP) to 70% larger (for B3LYP). Thus we agree with Baerends and colleagues that the original assignment of the weak bands for the metal hexacarbonyl complexes underestimated the energies of the typical LF splittings, possibly by more than 1 eV.

Comparing metal–carbon bond distances for systems with like oxidation states, we find similar ground-state geometries for the metal hexacarbonyl and hexaisocyano complexes. However, the calculated hexacyano metal–carbon bond distances are much greater. This is reasonable because the net negative charge present on cyanide ligands would be likely to decrease the relative amount of $M \rightarrow \pi^*$ CX backbonding, an important factor in the strength of these metal–carbon bonds. The greater bond distances for metal hexacyano complexes leads to lesser σ-overlap, and the corresponding lower octahedral field splitting noted in table 4. Thus CN^- exerts a weaker LF than either CO or CNH.

The data in table 4 indicate that the induced octahedral field splitting in metal hexacarbonyl complexes has little dependence on metal oxidation state. These data indicate that decreased $M \rightarrow \pi^*$ CO backbonding in the transition from V(−I) to Fe(II) destabilizes the t_{2g} orbital by as much as the e_g orbital is destabilized by the increase in σ-bonding. However, for the metal hexaisocyano complexes, we find a much stronger dependence of LF splitting on metal oxidation state. For Fe(II), the hexacarbonyl and hexaisocyano complexes have comparable octahedral field splittings. But for V(−I), the splitting is much greater in the hexacarbonyl case. This indicates that, on average, CO is a stronger field ligand than CNH, but the exact relative strengths may depend on the metal in question.

We can rationalize the differences among the above complexes as follows. Regardless of the metal to which it is bound, CN^- derives most of its LF strength from strong σ-donation, as there is little $M \rightarrow \pi^*$ CN^- backbonding. On the other hand, CO derives its LF strength from a combination of σ-donation and $M \rightarrow \pi^*$ backbonding. CNH falls between CN^- and CO in terms of its strength as a π-acceptor, so for any given metal, there will be more $M \rightarrow \pi^*$ backbonding for $M(CO)_6$ than for $M(CNH)_6$. For Fe(II), there is very little backbonding, so most of the octahedral field splitting will be due to σ-donation, and the induced splitting will be similar for $Fe(CO)_6^{2+}$ and $Fe(CNH)_6^{2+}$; but for V(−I), backbonding is very important, and as CO is a better π-acceptor than CNH, we expect a larger induced splitting for $V(CO)_6^-$ than for $V(CNH)_6^-$. The observed differences among the induced splittings in the metal hexacarbonyl and hexaisocyano complexes make sense in light of this explanation.

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