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A Theoretical Rationale for the Formation, Structure and Spin State of Pentacyanochromate(II)

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The pentacyanochromate(II) complex is unusual in two respects. Firstly, it is one of the few homoleptic cyanide species with a high-spin ground state. Secondly, it was synthesised during an attempt to make the hexacoordinate complex. A combination of qualitative ligand field theory and quantitative density functional theory including solvation effects is applied to rationalise these observations. The spin state depends on the d orbital energy differences and how the promotion energy, PE, associated with a change in spin state compares to the d–d spin pairing energy, SPE. The calculations show that PE > SPE for octahedral $[Cr^{II}(CN)_6]^{4-}$, hence it has a spin triplet $S = 1$ ground state, while PE < SPE for $[Cr^{II}(CN)_5]^{3-}$, hence it is high spin with $S = 2$. The hexacyanide is stabilised in aqueous solution by solvation. In less polar solvents such as acetonitrile, the unfavourable electrostatic interactions dominate and the reaction stops at the pentacyano complex. In both complexes, the cyanide behaves as a strong-field ligand and is both a good σ donor and π acceptor.

Introduction

Ligand Field Theory (LFT)[1] classifies the cyanide ligand as strong field and, therefore, the normal expectation is for homoleptic complexes to exhibit low-spin configurations. Octahedral cyanide complexes are invariably low spin, but there are some interesting exceptions for other coordination numbers. For example, low-spin (i.e. $S = 1$) $[Cr(CN)_6]^{4-}$ can be synthesised from aqueous solution providing excess cyanide is present but in acetonitrile, pentacyanochromate(II) is produced with magnetic properties consistent with a high-spin $S = 2$ d^4 configuration. Both the higher spin state and lower coordination number were not anticipated.[2]

An explanation of this behaviour is amenable to computation. This communication describes the first detailed computational study of $[Cr(CN)_5]^{3-}$ and $[Cr(CN)_6]^{4-}$ using both qualitative ligand field theory (LFT) and quantitative density functional theory (DFT) calculations. Theory successfully explains not only why $[Cr(CN)_5]^{3-}$ is high spin, but also why the change in medium from aqueous solution to acetonitrile causes the reaction to stop at coordination number five.

Results and Discussion

Hexacyanochromate(II) is extremely air sensitive[3] which goes some way to explain the relative lack of experimental data. However, the crystal structure of $Na_4[Cr(CN)_6]\cdot(H_2O)_{10}$ has been reported some years ago[4] and $[Cr(CN)_6]^{4-}$ remains of interest in the context of molecular magnets.[2,5] Indeed, it was in the search for new molecular magnetic materials that Nelson et al.[2] attempted a non-aqueous route to $[Cr^{II}(CN)_6]^{4-}$ which resulted in the unexpected preparation of the very interesting pentacyanochromate(II) anion. Their work highlighted two intriguing aspects of the chemistry of $[Cr(CN)_5]^{3-}$. Firstly, why does the system display a high-spin $S = 2$ state given that high-field ligands such as cyanide are conventionally associated with low-spin configurations? Secondly, why is a pentacyano complex isolated from the non-aqueous synthetic procedure rather than the expected hexacoordinate complex, which can be made in aqueous solution provided an excess of cyanide is present?

In principle, modern computational chemistry should be able to address these issues quantitatively although, apart from an early Xα study,[6] there appears to be no other computational work on either $[Cr^{II}(CN)_6]^{4-}$ nor $[Cr^{II}(CN)_5]^{3-}$.

The spin state is a balance between one-electron (orbital) and two-electron (interelectronic repulsion) effects. The d–d interelectron repulsion term favours a high-spin configuration (maximum quantum mechanical exchange, minimal spin pairing energy, SPE) while the one-electron term relates to d orbital splittings and favours low-spin configurations (minimum electronic promotion energy, PE). Note that, depending on the symmetry, low spin need not necessarily imply diamagnetic properties. For example, the low-spin configuration for octahedral d^4 species is t_{2g}^4 which still has two unpaired electrons. Critically, the d orbital

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splittings are ligand- and geometry-dependent while, to a first approximation, the spin-pairing energy is not.

The X-ray crystallographic study of $(NEt_4)_3[Cr^{II}(CN)_5]$·MeCN·1/8THF reveals four chromium complexes in the unit cell displaying geometries which are distorted to varying degrees away from either ideal square-pyramidal (SPY) or trigonal-bipyramidal (TBP) structures.[2] The question then is how the promotion energy for pentacoordinate systems compares to Δ_{oct}.

The d orbital energies can be conveniently expressed in terms of the Angular Overlap Model (AOM).[7] For an octahedral complex of "linear ligator" ligands like cyanide, $\Delta_{oct} = 3e_\sigma - 4e_\pi$, where e_σ and e_π are respectively the AOM parameters describing M–CN σ and π bonding. The expressions for individual d orbital energies are given in Equations (1), (2), (3) and (4) for SPY and (5), (6) and (7) for TBP and include group theory labels appropriate to C_{4v} and D_{3h} symmetry, respectively. In Equations (1)–(4), α refers to the angle between the apical and equatorial ligands.

$$E(d_{x^2-y^2}) = E(b_1) = 3/4(1 - \cos 2\alpha)^2 \cdot e_\sigma(eq) + (\sin^2 2\alpha) \cdot e_\pi(eq) \quad (1)$$

$$E(d_{z^2}) = E(a_1) = 1/4(1 + 3\cos 2\alpha)^2 \cdot e_\sigma(eq) + e_\sigma(ax) + 3(\sin^2 2\alpha) \cdot e_\pi(eq) \quad (2)$$

$$E(d_{xy}) = E(b_2) = 4(\cos^2 2\alpha) \cdot e_\pi(eq) \quad (3)$$

$$E(d_{xz}, d_{yz}) = E(e) = 3/2(\sin^2 2\alpha) \cdot e_\sigma(eq) + 2(\cos^2 2\alpha) \cdot e_\pi(eq) + e_\pi(ax) \quad (4)$$

$$E(d_{z^2}) = E(a_1) = 3/4e_\sigma(eq) + 2e_\sigma(ax) \quad (5)$$

$$E(d_{x^2-y^2}, d_{xy}) = E(e') = 9/8e_\sigma(eq) + 3/2e_\pi(ax) \quad (6)$$

$$E(d_{xz}, d_{yz}) = E(e'') = 1/2e_\pi(eq) + 2e_\pi(ax) \quad (7)$$

The relevant orbital energy differences corresponding to the promotion energy which must be overcome for a high-spin d^4 configuration are shown in Figure 1.

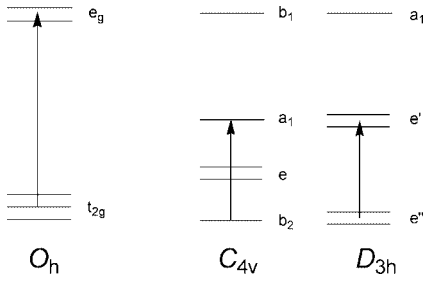

Figure 1. Qualitative d orbital energy level diagrams for octahedral (O_h), SPY (C_{4v}) and TBP (D_{3h}) symmetries illustrating the high-spin promotion energy for a d^4 configuration.

Figure 1 is not drawn to scale. A numerical comparison can be based on Equations 1–7. Hence, the promotion energies, PE, are Equations (8), (9), and (10).

$$PE(O_h) = 3e_\sigma - 4e_\pi \quad (8)$$

$$PE(C_{4v}) = 0.83e_\sigma(eq) + e_\sigma(ax) + 0.35e_\pi(eq) - 3.53e_\pi(eq) = 0.65e_\sigma(eq) + e_\sigma(ax) - 3.18e_\pi(eq) \quad (9)$$

$$PE(D_{3h}) = 9/8e_\sigma(eq) - 1/2\{e_\pi(eq) + e_\pi(ax)\} \quad (10)$$

In arriving at these expressions, the angle α between apical and equatorial cyanides in the SPY structure has been taken as 100° and cyanide was assumed to be a π acceptor (i.e. $e_\pi < 0$). We return to the latter issue below.

Assuming $e_\lambda(ax) = e_\lambda(eq)$, λ = σ, π, Equations (8)–(10) collapse to Equations (11), (12), and (13)].

$$PE(O_h) = 3e_\sigma - 4e_\pi \quad (11)$$

$$PE(C_{4v}) = 1.65e_\sigma - 3.18e_\pi \quad (12)$$

$$PE(D_{3h}) = 1.13e_\sigma - e_\pi \quad (13)$$

This is a very crude assumption because the AOM parameters will vary strongly with distance. Nevertheless, the difference between O_h and C_{4v} or D_{3h} promotion-energies expressions is so great that the assertion that the promotion energies for pentacoordinate symmetries would be substantially less than for an octahedral complex seems secure. The observation of high-spin $[Cr(CN)_5]^{3-}$ is thus simply a function of the coordination number and symmetry. Cyanide may continue to be a strong-field ligand in the sense that the AOM parameter values could be identical in all symmetries. That is, strong-field ligands do not necessarily have to be associated with low-spin electronic configurations – e.g. the tetrahedral complex $[Mn(CN)_4]^{2-}$ is high spin consistent with the well-known result that the tetrahedral splitting $\Delta_{tet} \approx 1/2\ \Delta_{oct}$.

However, while LFT can easily rationalise why $[Cr(CN)_5]^{3-}$ is high spin, it cannot address the issue of why is forms in the first place. For this we require a more sophisticated quantum mechanical approach like DFT.

DFT has effectively revolutionised the application of quantum chemistry to transition-metal systems,[8] but it is by no means a perfect model. In particular, current functionals may not give a good description of spin state energy differences.[9–13] Our experience with Fe^{II} and Fe^{III} complexes shows that although there can be large numerical differences, most pure functionals give the correct qualitative trend.[9] Others have focussed on tuning the amount of exact exchange in the B3LYP functional to give more accurate results for spin-crossover systems.[11,13] The present problem is less delicate, which probably means that almost any gradient corrected functional will be at least qualitatively reasonable. To test this, the DFT protocol was first validated against $[Cr(CN)_6]^{4-}$, which is known to be a low-spin, t_{2g}^4 $S = 1$ system (see Table 1).

In octahedral symmetry, high-spin $[Cr(CN)_6]^{4-}$ has a ^5E_g state, which is expected to display a strong Jahn–Teller distortion hence the second optimisation in D_{4h} symmetry which allows for an orbitally-nondegenerate state leading to the expected elongated octahedral structure. Similarly, the

Table 1. Optimised Cr–CN distances and relative total energies (including solvation) for $[Cr(CN)_6]^{4-}$ in O_h symmetry unless otherwise stated. E_{tot} is total DFT energy and equals the sum of the electronic energy, E_{el}, and the COSMO solvation energy, E_{sol}. ΔE is the energy difference between E_{tot} for that entry and E_{tot} for the octahedral, $S = 1$ state.

S	Cr–CN [Å]	E_{tot} [kJ·mol^{-1}]	ΔE [kJ·mol^{-1}]	E_{el} [kJ·mol^{-1}]	E_{sol} [kJ·mol^{-1}]
2	2.23	–11797.09	+169	–9164.82	–2632.27
2	2.11, 2.61[a]	–11832.87[a]	+90[a]	–9217.93[a]	–2614.94[a]
1	2.04	–11957.43	0	–9234.30	–2723.13
1	2.03, 2.03, 2.07[b]	–11966.56	–9[b]	–9241.16[b]	–2725.40[b]
0	2.02	–11890.43	+73	–9160.40	–2730.03

[a] D_{4h} Symmetry, axial elongation. [b] D_{2h} symmetry.

spin triplet state in octahedral symmetry is $^3T_{2g}$ and is also formally Jahn–Teller active. However, compared to the ^5E_g case, the Jahn–Teller effect for the $^3T_{2g}$ state is much more complicated but since it is dominated by π effects, it is also much weaker. A complete analysis has not been attempted. Instead, the geometry was reoptimised in D_{2h} symmetry as an example of one possible distortion mode. Finally, the spin singlet state is clearly going to be higher than the $S = 1$ state and, although in O_h symmetry, this too is formally orbitally degenerate, only the octahedral geometry has been computed.

The DFT results in Table 1 are in good agreement with experiment. They correctly predict the spin-triplet $S = 1$ ground state with an optimised Cr–CN bond length (in O_h symmetry) only about 0.03 Å longer than the average Cr–CN distance reported for $Na_4[Cr(CN)_6]\cdot 10H_2O$.[4] Note that in the absence of solvation, the optimised Cr–C distance for octahedral, $S = 1$ hexacyanochromate(II) extends 0.08 Å to 2.12 Å. In the gas phase, many occupied orbitals have physically unreasonable positive energies. This leads to an expansion of the Cr–C bond. The solvation field stabilises the anionic charge, lowers the orbital energies and generates a better optimal structure.

Further vindication that DFT (with solvation) describes these systems well can be seen in Table 2 where DFT data for $[Cr(CN)_5]^{3-}$ are presented.

For both symmetries, the spin state energies increase quintet < triplet < singlet. The $^5B_1$ state in C_{4v} and the $^5A_1$ state in D_{3h} are orbitally non-degenerate, and thus Jahn–Teller inactive as is the $^3A_1$ state in C_{4v} derived from the $b_2^2e^2$ configuration. The remaining triplet and the two singlet states are much higher in energy and, even though some are orbitally degenerate, the effect is not large enough to alter the overall conclusion that the predicted DFT ground state of $[Cr(CN)_5]^{3-}$ is a spin quintet.

The computed structures are also reasonable, although compared to $[Cr(CN)_6]^{4-}$ DFT now gives somewhat shorter Cr–C distances than observed for $[Cr(CN)_5]^{3-}$. Both SPY and TBP structures are predicted to have virtually identical energies consistent with the somewhat distorted structures observed in the crystal structure and with the general notion that five-coordinate systems are not rigid.

DFT can also be applied to explain the relative stabilities of $[Cr^{II}(CN)_6]^{4-}$ vs. $[Cr^{II}(CN)_5]^{3-}$. The data in Table 1 and Table 2 clearly demonstrate the critical importance of the environment of the complex. Thus, the reaction energy for the process

$$[Cr(CN)_5]^{3-} + CN^- \rightarrow [Cr(CN)_6]^{4-}$$

is –87 kJ·mol^{-1} when the COSMO solvation energies are included, but an enormous +794 kJ·mol^{-1} from just the electronic energies alone. Obviously, there is a strong repulsive interaction when trying to bring a monoanion like cyanide up to a complex which already carries three negative charges, but because the solvation energy is proportional to Z^2, the additional solvation energy of a tetraanion vs. a trianion amounts to an extra 1100–1200 kJ·mol^{-1}, which is sufficient to overcome this repulsive term. Because the solvation energy depends on $(1 - 1/\varepsilon)$, where ε is the dielectric constant, large solvation energies are associated with a high dielectric constant. Acetonitrile is simply not polar enough to support the reaction hence the hexacyano complex cannot form.

Having established that the relative spin states are well described (with and without solvation energies) and seen that the complex formed depends strongly on the solvent,

Table 2. DFT results for $[Cr(CN)_5]^{3-}$ for different spin states (S) and symmetries – C_{4v} for SPY and D_{3h} for TBP. Bond lengths in Å, energies in kJ·mol^{-1}. E_{tot} is total DFT energy and equals the sum of the electronic energy, E_{el}, and the COSMO solvation energy, E_{sol}. ΔE is the energy difference between E_{tot} for that entry and the lowest E_{tot} overall. Experimental data[2] in parentheses.

Symmetry	S	Cr–C_{ax}	Cr–C_{eq}	C_{ax}–Cr–C_{eq}	E_{tot}	ΔE	E_{el}	E_{sol}
C_{4v}	2	2.14	2.08	101	–9980.87	3	–8442.11	–1538.76
	2	(2.23)	(2.12)	(100)				
C_{4v}	1	1.98	2.02	95.2	–9943.53	41	–8363.30	–1580.23
C_{4v}	0	1.94	2.00	97.7	–9854.66	130	–8275.92	–1578.74
D_{3h}	2	2.07	2.09	–	–9984.20	0	–8445.02	–1539.18
D_{3h}	1	2.01	2.01	–	–9880.40	104	–8319.32	–1561.08
D_{3h}	0	1.97	1.96	–	–9857.02	127	–8275.47	–1581.55
$C_{\infty v}$[a]	–	–	–	–	–1886.33	–	–1583.47	–302.86

[a] Data for isolated CN^-.

the issue of whether cyanide is always a "strong-field" ligand requires an assessment of whether the fundamental nature of the Cr–CN bonding changes radically with coordination number. In the spirit of LFT, let us use the DFT structures and orbital energies as the basis of a ligand-field analysis.

The octahedral complex is our starting point. Although the electronic spectrum of $[Cr(CN)_6]^{4-}$ has been reported,[3] no assignments were offered due to the broad nature of the diffuse reflectance bands. The DFT estimate of ca. 32000 cm^{-1} may be compared to the values in Table 3, which also include computed results for other hexacyanides.

Table 3. Experimental[14] and calculated Δ_{oct} values [cm^{-1}] for hexacyanometallate complexes.

Complex	Δ_{oct}	Δ_{oct} (calcd.)
$[Cr(CN)_6]^{3-}$	26600	29815
$[Cr(CN)_6]^{4-}$	–	31989
$[Mn(CN)_6]^{3-}$	34000	32400
$[Mn(CN)_6]^{4-}$	30000	33777
$[Fe(CN)_6]^{3-}$	34950	35614
$[Fe(CN)_6]^{4-}$	33800	36426

It appears that the DFT spherical configuration orbital energy differences (see Computational Details section) generally overestimate Δ_{oct}. Experimentally, one normally sees larger values for higher metal oxidation states. Hence, given an experimental value for $[Cr^{III}(CN)_6]^{3-}$ of 26600 cm^{-1} and a threshold value at which a first-row octahedral d^4 species switches from quintet to triplet spin of about 23500 cm^{-1},[15] Δ_{oct} for $[Cr(CN)_6]^{4-}$ should lie between 23500 and 26600 cm^{-1}. The DFT estimate is ca. 32000 cm^{-1}.

For the Cr(II) complex Δ_{oct} is probably quite close to that for Cr^{III}. Because both are low spin, the lower oxidation state, which has more d electrons, has a larger ligand field stabilisation energy (LFSE) at least in terms of Δ_{oct} values. Hence, the M^{II}–C bond lengths are actually shorter than the M^{III}–C distances despite the latter's higher formal oxidation state and smaller ionic radius. The relative change in LFSE increases from 20% for the d^5/d^6 Fe^{III}/Fe^{II} couple to 25% for d^4/d^5 Mn^{III}/Mn^{II} to 33% for the d^3/d^4 Cr^{III}/Cr^{II}, which correlates reasonably well with bond–length contractions of 0.02, 0.05 and 0.05 Å, respectively. Given the large percentage change in Δ_{oct}, the decrease in Cr–C distance and the DFT prediction that Δ_{oct} for M^{II} gets larger relative to that for M^{III} in the series Fe < Mn < Cr, the assertion that Δ_{oct} for $[Cr^{II}(CN)_6]^{4-}$ and $[Cr^{III}(CN)_6]^{3-}$ are about the same seems reasonable.

While a better theoretical treatment along the lines of, say, ligand field DFT,[16] time-dependent DFT[17] or CASPT2[18] may provide better quantitative agreement with experiment, the precise value of Δ_{oct} is not important for the present analysis because the errors seems to be propagated more or less systematically between $[Cr^{II}(CN)_6]^{4-}$ and $[Cr^{II}(CN)_5]^{3-}$. The aim is to see whether the AOM parameter values deduced from the DFT orbital energies of $[Cr(CN)_6]^{4-}$ generate AOM d orbital energies for $[Cr(CN)_5]^{3-}$, which in turn agree with the DFT equivalents. If so, then the ligand-field strength is essentially the same in both complexes.

Of course, as $\Delta_{oct} = 3e_\sigma - 4e_\pi$, unique values for both AOM parameters cannot be extracted from a single value of Δ_{oct}. By applying a small tetragonal distortion to the molecule, the "d" orbitals will split, which will provide three degrees of freedom but now there are four parameters, e_σ(eq), e_σ(ax), e_π(eq) and e_π(ax). The number of free variables can be halved if the distance dependence is established. Lengthening the Cr–C bonds, r, from 2.038 to 2.078 Å lowers the computed Δ_{oct} from 31989 to 29233 cm^{-1}. Assuming all AOM parameters depend on r^{-m} yields m = 4.6, which is close enough to the electrostatic theory value of m = 5. Applying an axial elongation to the two ligands on the z axis (r_{ax} = 2.078, r_{eq} = 2.038 Å) gives a "d" orbital sequence of $b_{2g} < e_g < a_{1g} < b_{1g}$ and because in the AOM $E(b_{2g}) = e_\pi(eq)$, $E(e_g) = 2e_\pi(eq) + 2e_\pi(ax)$, and $|e_\pi(eq)| > |e_\pi(ax)|$ because r_{eq} is shorter, the DFT calculations are consistent with $e_\pi < 0$ – i.e. cyanide is behaving as a π acceptor. Assuming m = 5, the $e_g - b_{2g}$ and $b_{1g} - a_{1g}$ DFT orbital energy differences equate to effective AOM parameter values of e_σ = 8767 and e_π = –1398 cm^{-1} at the octahedral geometry.

The optimised C_{4v} structure for $[Cr(CN)_5]^{3-}$ has r_{ax} = 2.14 and r_{eq} = 2.08 Å corresponding to e_σ(ax) = 6869, e_π(ax) = –1095, e_σ(eq) = 7918 and e_π(eq) = –1263 cm^{-1}. Substituting these values into Equations (1)–(4) with α = 101° gives the energy difference between the highest and lowest energy d functions, $d_{x^2-y^2}(b_1)$ and d_{xy}, of 26222 cm^{-1} vs. the DFT spherical configuration estimate of 28136 cm^{-1}. Hence, the assumption that cyanide remains a strong ligand generates quite good agreement with the DFT electronic structure.

Moreover, using the AOM parameter values for r = 2.038 Å in Equations (11)–(13) yields rough promotion energies of ca. 32000, 19000 and 11000 cm^{-1} for O_h, C_{4v} and D_{3h} symmetries, respectively, the former clearly being more than, while the latter two are clearly less than the spin crossover threshold of 23500 cm^{-1}.

Conclusions

A combination of AOM and DFT arguments and calculations provides a simple explanation for the high-spin quintet ground state of $[Cr(CN)_5]^{3-}$ – the cost of promoting an electron to give an S = 2 state is less than the cost of spin pairing. The reverse applies in octahedral symmetry and a triplet S = 1 configuration results. In both cases, the combination of the BP86 functional and COSMO solvation provides a DFT protocol which successfully predicts good structures and the correct order of spin state energies. COSMO is critical for obtaining good structural data but does not alter the predicted lowest energy spin state. Spin contamination is minimal.

Given the highly charged species involved, the COSMO aqueous solvation energies are large and predict that the

formation of hexacyanochromate(II) from the pentacyanide precursor is favourable by 79 kJ·mol^{-1}. However, the "raw" electronic energies show that the powerful electrostatic interactions disfavour the process by over 700 kJ·mol^{-1} and hence in less polar media such as acetonitrile, there is insufficient solvation energy to form the tetraanionic species.

An AOM ligand-field analysis based on DFT orbital energies for $[Cr(CN)_6]^{4-}$ suggests that cyanide is both a strong σ donor and reasonably strong π acceptor with typical e_σ and e_π values around 8500 and –1400 cm^{-1}, respectively. Assuming that cyanide remains a strong-field ligand for pentacyanochromate(II) yields AOM-derived d orbital energies in good agreement with their DFT counterparts. However, due to the change in coordination number and symmetry, even a strong-field ligand cannot force the ground state to a lower spin degeneracy.

Strong M–CN binding results in relatively large changes in energy as a function of coordination number and/or symmetry. Hence, the theoretical predictions tolerate larger errors and are more robust. In particular, DFT, in conjunction with a treatment of the environment, provides a reasonable basis for describing the chemistry of Cr(II)–cyanide complexes and, most likely, metallocyanides in general.

Computational Details

All DFT calculations employed ADF version 2005.[19] After some preliminary testing, the Becke Perdew (BP86) functional was chosen in conjunction with triple-ζ plus polarisation basis sets (TZP) and frozen cores[20] up to 2p for the metals and 1s for C and N. Geometries were optimised with full point group symmetry as appropriate in the presence of a COSMO solvation field as implemented in ADF, with atomic radii C: 1.4 Å, N: 1.5 Å[21] and M: 2.58 Å. Where appropriate, all calculations were run spin-unrestricted, and the extent of spin contamination monitored by the calculation of $<S^2>$, which was generally within 0.03 of the ideal value except for $S = 1$, where the worst case was $<S^2> = 2.05$ for Cr systems and 2.08 for $[Mn(CN)_6]^{3-}$, and for $S = 2$, where the worst case was $<S^2> = 6.08$. Orbital energy differences were computed at the relevant optimised geometry using "spherical configurations", which we have used successfully in the past[22,23] and is a modification of the Average Over Configuration approach implemented in ADF and recently described by Atansov and Daul.[24] The five molecular orbitals, which are predominantly d antibonding in character, are identified and then assigned populations of $m/5$ where m is the notional number of d electrons for the idealised metal oxidation state. A spin-restricted single-point calculation is then run to SCF convergence. Angular Overlap Model (AOM) expressions were derived from Figgis and Hitchman.[7]

Acknowledgments

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[1] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, **1962**.
[2] K. J. Nelson, I. D. Giles, W. W. Shum, A. M. Arif, J. S. Miller, *Angew. Chem., Int. Ed.* **2005**, *44*, 3129–3132.
[3] J. P. Eaton, D. Nicholls, *Transition Met. Chem.* **1981**, *6*, 203–208.
[4] E. Ljungstroem, *Acta Chem. Scand.* **1977**, *31*, 104–108.
[5] S. M. Holmes, G. S. Girolami, *Mol. Cryst Liq. Cryst. Sci. Technol., Sect. A* **1997**, *305*, 279–290.
[6] V. A. Nasluzov, A. V. Kondratenko, K. M. Neyman, G. L. Gutsev, *Chem. Phys. Lett.* **1988**, *146*, 253–258.
[7] B. N. Figgis, M. A. Hitchman, *Ligand Field Theory and Its Applications*, John Wiley & Sons Ltd., New York, **2000**.
[8] T. Ziegler, *Can. J. Chem.* **1995**, *73*, 743–761.
[9] R. J. Deeth, N. Fey, *J. Comput. Chem.* **2004**, *25*, 1840–1848.
[10] O. Salomon, M. Reiher, B. A. Hess, *J. Chem. Phys.* **2002**, *117*, 4729–4737.
[11] M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* **2001**, *107*, 48–55.
[12] M. Reiher, *Inorg. Chem.* **2002**, *41*, 6928–6935.
[13] H. Paulsen, A. X. Trautwein, *J. Phys. Chem. Solids* **2004**, *65*, 793–798.
[14] J. J. Alexander, H. B. Gray, *J. Am. Chem. Soc.* **1968**, *90*, 4260–4271.
[15] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, New York, **1984**.
[16] A. Atanasov, C. A. Daul, C. Rauzy, in *Optical Spectra and Chemical Bonding in Inorganic Compounds*, vol. 1, vol. 106, Springer Verlag, Berlin, **2004**, pp. 97–125.
[17] A. Rosa, E. J. Baerends, S. J. A. van Gisbergen, E. van Lenthe, J. A. Groeneveld, J. G. Snijders, *J. Am. Chem. Soc.* **1999**, *121*, 10356–10365.
[18] C. Ribbing, B. Gilliams, K. Pierloot, B. O. Roos, G. Karlstrom, *J. Chem. Phys.* **1998**, *109*, 3145–3152.
[19] E. J. Baerends, A. Bérces, C. Bo, P. M. Boerrigter, L. Cavallo, L. Deng, R. M. Dickson, D. E. Ellis, L. Fan, T. H. Fischer, C. Fonseca Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, F. E. Harris, P. van den Hoek, H. Jacobsen, G. van Kessel, F. Kootstra, E. van Lenthe, V. P. Osinga, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, T. Ziegler, *Scientific Computing and Modelling NV*, Free University, Amsterdam, Amsterdam, **2005**.
[20] E. J. Baerends, D. E. Ellis, P. Ros, *Theor. Chim. Acta* **1972**, *27*, 339.
[21] C. C. Pye, T. Ziegler, *Theor. Chem. Acc.* **1999**, *101*, 396.
[22] R. J. Deeth, *Faraday Discuss.* **2003**, *124*, 379–391.
[23] R. J. Deeth, D. L. Foulis, B. J. Williams-Hubbard, *Dalton Trans.* **2003**, 3949–3955.
[24] M. Atanasov, C. A. Daul, *C. R. Chim.* **2005**, *8*, 1421–1433.

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