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Ab Initio Investigation of Spectroscopic Parameters for CrX_6^{3-}: The Unexpected Role of Bond Length Variation – Size Really Matters

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Ligand field states were calculated in the CrX_6^{3-} series with X = F, Cl, Br, and I from first principles, and the ligand field parameter, *Δ*, was deduced. The decrease in *Δ* follows the spectrochemical series; π effects are usually invoked to justify this trend. It is shown that while the covalence increases, the π effect decreases and that the key role in the decrease in *Δ* is played by the increase in bond length in the halide series.

Introduction

Knowledge of the excited states of a molecule is essential for the study of luminescence and optical spectroscopy. Excited states play a key role in excited state dynamics and energy transfer processes. In transition metal complexes, the ligand field spectrum is largely determined by the ligand field parameter, *Δ*. This parameter can be crucial for ground-state properties when spin-orbit coupling is involved, as is the case for the zero-field splitting in single-molecule magnets. In order to tune the properties of molecules, it is of prime importance to know the effect of the nature of the ligands on the parameters. Ligand field theory is an efficient tool, widely used in the inorganic chemistry community. For a given nature of the metal center, ligands are classified by following the spectrochemical series. Molecular orbital arguments are used to justify this series; the increase in π donation down the series destabilizes the metallic t_{2g} orbital and lowers the ligand field gap. But the effect of the bond length has, to the best of our knowledge, never been analyzed. In this work, we fill in this gap by considering simultaneously the effects of the bond length and the nature of the ligand on *Δ*. The CrX_6^{3-} series with X = F, Cl, Br, and I is considered as an example.

Results and Discussion

The computed bond lengths are listed in Table 1. They increase within the series from 1.96 to 2.73 Å and agree satisfactorily with the two available experimental values: 1.90 Å for CrF_6^{3-}[1] and 2.36 Å for $CrCl_6^{3-}$.[2] The entire ligand field spectra of these $3d^3$ complexes are calculated. For CrF_6^{3-}, experimental bands are known. A comparison of experimental[3] and calculated (in parentheses) absorption bands, $^4T_2$ 14900 (13200), $^4T_1$ 22700 (19300) and 34400 (31400), ^4E 15700 (14900), $^2T_1$ 16400 (15800), $^2T_2$ 22 0000 (21400) cm^{-1}, shows that the experimental spectrum is reasonably reproduced by the calculations. These transitions have previously been calculated by CI and DFT methods.[4,5] This agreement illustrates that the level of computation is sufficiently accurate to draw reliable conclusions. The ligand field parameter, *Δ*, and the two Racah interelectron repulsion parameters, *B* and *C*, are extracted from the spectrum and summarized in Table 1. The standard deviation, *σ*, is small, showing that the spectrum calculated from first principles is well reproduced by the ligand field model. The ligand field parameter, *Δ*, decreases upon going from fluoride to bromide in accordance with the spectrochemical series and increases slightly for iodide, while both *B* and *C* decrease in the column in accordance with the nephelauxetic series, reflecting an increase in covalence.

A crude measure of the covalent character of a bond is the amount of charge transfer in the molecule as compared to the ionic fragments. As shown in Table 1, the Mulliken population analysis indicates that the charge transfer from ligand to metal increases in the series, for all types of orbitals s, p, and d, indicating an increase in covalent effects. It should be noticed that the change in population of orbital type do not sum to give the total charge change, *Q*, due to charge in polarizing f orbitals. The energy gap, $\Delta\varepsilon$, between the nonbonding t_{1g} ligand orbitals and the t_{2g} metal orbitals decreases in the column, as expected from electronegativity criteria, and, combined with an increase in the diffuse character of the ligand p orbitals, leads to an increase in the covalence. The weight of antibonding t_{2g} and e_g orbitals on ligands is used to quantify π and σ interactions, respectively, while this weight decreases from 3.5 to 2.3% for π bonding, it increases from 17.6 to 27.6% for σ bonding.

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Table 1. Optimized Cr–X distances in Å, model parameters Δ, B, and C, standard deviation σ in cm^{-1}, $A = \Delta R^5$ in 10^6 cm^{-1} Å^5, Mulliken population on the chromium atom (total Q_{Cr} and per orbital type relative to the free ion), metal–ligand orbital energy gap in eV, and weights of antibonding t_{2g} and e_g orbitals on ligand orbitals.

	r_{eq}	Δ	B	C	σ	A	Q_{Cr}	Δs_{Cr}	Δp_{Cr}	Δd_{Cr}	$\Delta\varepsilon$	$p_X^{t_{2g}}$	$p_X^{e_g}$	$s_X^{e_g}$
CrF_6^{3-}	1.96	13300	880	2970	210	0.39	2.08	0.10	0.15	0.54	10.0	0.035	0.133	0.043
$CrCl_6^{3-}$	2.40	12010	780	2430	309	0.96	1.04	0.35	0.66	0.85	4.59	0.028	0.179	0.038
$CrBr_6^{3-}$	2.54	11800	770	2170	342	1.25	1.21	0.28	0.59	0.87	3.43	0.026	0.194	0.028
CrI_6^{3-}	2.73	11950	720	1790	290	1.81	0.64	0.40	0.82	1.07	2.25	0.023	0.276	0.000

Table 2. Values of the parameters described in Table 1 at $R = 2.4$ Å.

	Δ	B	C	σ	A	Q_{Cr}	Δs_{Cr}	Δp_{Cr}	Δd_{Cr}	$\Delta\varepsilon$	$p_X^{t_{2g}}$	$p_X^{e_g}$	$s_X^{e_g}$
CrF_6^{3-}	5590	890	3160	177	0.44	2.15	0.18	0.25	0.37	4.80	0.008	0.057	0.004
$CrCl_6^{3-}$	12010	780	2430	309	0.96	1.04	0.35	0.66	0.85	4.59	0.028	0.179	0.038
$CrBr_6^{3-}$	14370	700	1850	310	1.17	1.19	0.21	0.55	0.97	4.13	0.039	0.273	0.140
CrI_6^{3-}	23160	520	1780	520	1.84	0.33	0.27	0.82	1.50	3.20	0.060	0.448	0.150

This latter interaction is partly due to the interaction with the *n*s orbitals of the ligands at the bottom, but this effect disappears down the series. The covalence, mainly due to σ interactions, increases in the series, but the energetic destabilization of the antibonding orbital decreases; π interactions decrease and can not be invoked to justify the series. When forming molecular orbitals from two fragments, two parameters play a role: the difference of energy $\Delta\varepsilon$ between the fragments and the overlap, which is governed by the distance, R, between the centers and the extent of the diffuse character of the orbitals.

In order to separate the effects of bond length extension from changes in electronegativity, a new set of calculations was performed by using a common bond length of 2.4 Å, namely the bond length of Cr–Cl (see Table 2). While the Racah parameters B and C and the charge transfers into the metallic s and p orbitals are not greatly affected by the change in bond length, the charge transfers into the d orbitals and Δ are significantly modified. When the bond length decreases, $\Delta\varepsilon$ increases; the metal orbitals are destabilized by electrostatic repulsion between the metal electrons and the negatively charged ligands, and the ligand orbitals are also destabilized due to the repulsion between the ligands, but this latter effect is partly compensated by the attraction by the positively charged metal. However, the increase in $\Delta\varepsilon$ with shorter bond length is more than compensated by the concomitant increased overlap between metal and ligand orbitals, and it thus leads to an increased covalent character and thereby increased Δ down the series. According to the weights of antibonding t_{2g} and e_g orbitals, both σ and π interactions increase with shortening bond length.

The metal–ligand distance, R, has a crucial effect on the Δ parameter. At $R = 2.4$ Å, the ligand field parameter of the iodide complex is four times larger than that for the fluoride complex, as expected from electronegativity criteria. It therefore appears clearly that there are two opposing effects: if all the halogen atoms had the same radius, the trend would be opposite. The increase in bond length is related to the increase in ionic radius. With the definition proposed by Shannon,[6] fluoride, chloride, bromide, and iodide ions have ionic radii of 1.19, 1.67, 1.82, and 2.06 Å, respectively. It has been shown that the variation of Δ with the bond length is well described by a power law given by Equation (1).[7]

$$\Delta = \frac{A}{R^5} \tag{1}$$

Thus, when Δ is calculated from first principles, one recovers the variation obtained with crystal field theory,[8] but with another parameter, A. This variation is borne out by the present calculations, since the product ΔR^5 varies only slightly with R (Table 1 and Table 2). However, this product depends strongly on the nature of the ligand in contrast to the formula proposed by crystal field theory, where A depends only on the charge of the ligand. A is taken as an empirical parameter that depends on the chemical nature of the ligand; from Equation (1) and Tables 1 and 2, one finds $A = 0.4$, 1.0, 1.2, and 1.8×10^6 cm^{-1} Å^5 for fluoride, chloride, bromide, and iodide complexes, respectively. In Figure 1, Equation (1) is plotted for the four complexes. This plot enables one to visualize the two opposing effects: considering electronic effects, A increases from fluoride to iodide and consequently Δ increases at a fixed distance; considering ionic radii, R increases, which lowers Δ. It is not possible to determine a priori which effect will be dominant. Figure 1 shows that Δ is actually almost constant in

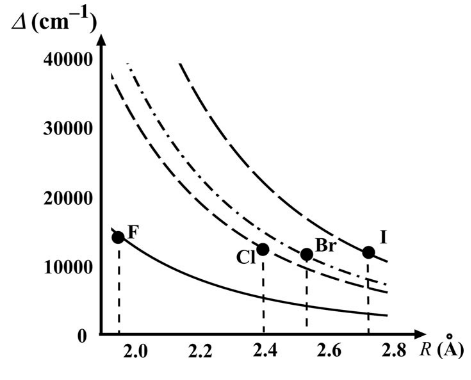

Figure 1. $\Delta = A/R^5$ curves with $A = 0.4$, 1.0, 1.2, and 1.8×10^6 cm^{-1} Å^5.

the series; there is a slight decrease from fluoride to chloride because of the variation of bond length and then a weak increase because of the large variation of *A* from bromide to iodide due to electronic effects. Both *A* and *R* vary almost linearly with the ionic radius.

Conclusion

The spectrochemical series is presented in all the textbooks of inorganic chemistry and is interpreted as dominated by π effects. For instance, in ref.[9] we read "The overall order of the spectrochemical series may be interpreted in broad terms as dominated by π effects". No argument is given why π effects should be more important than σ effects. In addition, while the spectrochemical series is similar in hexahalide actinide complexes,[10,11] π effects have the opposite effect in f complexes as compared to d complexes. In these complexes, the ligand field gap is between a nonbonding and a π antibonding orbital; increasing π donation increases *Δ*. In this article, we have considered the halide series of transition metal complexes, in which there is a large variation of the metal–ligand distance. Down the column, the electronegativity decreases, which favors both σ and π interactions. But, simultaneously, the ionic radius and consequently the bond length increase. Despite of this bond lengthening, the covalence of the bond increases in the series in the sense that the global charge transfer from ligand to metal increases. But π interactions decrease, because they are more sensible to distance than σ interactions, and the destabilization of the antibonding orbitals decreases because ligand orbitals are more and more diffuse down the column; with diffuse orbitals, the charge transfer is made easier but does not contribute as much to a gain of energy.

To summarize, covalent effects increase down the column and, consequently, at a common bond length, *Δ increases* strongly in the column. The ligand field parameter is well described by a power law of the metal–ligand bond length, *R*, whose prefactor, *A*, depends on electronic effects; *A* increases when the covalence of the bond increases, decreases by π donation, and increases by π back-donation. Thus, comparing ligands whose bonding atoms have roughly the same ionic radii, the variation of *Δ* is essentially dominated by the variation of *A*, and if the two atoms have roughly the same electronegativity, the variation of *A* is essentially dominated by π effects. But, as shown in this article, bond length effects can become dominant when comparing ligands with very different radii. In this work, we argue that the ordering of the spectrochemical series in the halide column is better explained by the increase in ionic radius.

Computational Details

The calculations were performed by using the MOLCAS-7 suite of programs.[12] Wave functions are generated by the multiconfigurational CASSCF method,[13] and dynamical electron correlation effects are calculated by using the second order perturbative CASPT2 method.[14] Scalar relativistic effects are taken into account by means of the Douglas-Kroll-Hess transformation.[15] The all-electron basis sets ANO-RCC of TZP (Triple Zeta plus Polarization) quality are used.[16] A minimal active space (3/5) is used; it comprises three electrons in the five 3d orbitals of Cr. Equilibrium distances of the $^4A_2$ ground state have been calculated at the CASPT2 level, without breaking O_h symmetry. The entire ligand field spectrum is calculated; four spin quartet states, the ground state $^4A_2$, two $^4T_1$ and $^4T_2$ states, and sixteen spin doublet states, one $^2A_1$, one $^2A_2$, four ^2E, five $^2T_1$, and five $^2T_2$ states. The excitation energies are expressed in terms of the three model parameters *Δ*, *B*, and *C*, by diagonalizing the electrostatic matrices as given by Griffith[8] and are optimized by a least-squares procedure to fit the calculated spectrum. The validity of the model is assessed by calculating the standard deviation:

$$\sigma = \frac{1}{N}\sqrt{\sum_{i=1}^{N} (E_i^{calc} - E_i^{mod})^2}$$

N is the number of transitions considered, E_1^{calc} and E_1^{mod} are the energies of the *i*th transition calculated with the ab initio method and with the model using the optimized values of the parameters, respectively.[7]

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[1] M. R. Silva, A. M. Beja, J. A. Paixao, *Acta Crystallogr., Sect. E* **2005**, *61*, 2459.
[2] O. Filipenko, D. Makilova, O. Krasoclka, V. Ponomarev, L. O. Atovmyan, *Koord. Khim.* **1987**, *13*, 669.
[3] C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, London, **1962**.
[4] K. Pierloot, L. G. Vanquickenborne, *J. Chem. Phys.* **1990**, *93*, 4154.
[5] K. Bellafrouh, C. Daul, H. U. Güdel, F. Gilardoni, J. Weber, *Theor. Chim. Acta* **1995**, *91*, 215.
[6] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
[7] H. Bolvin, *J. Phys. Chem. A* **1998**, *102*, 7525.
[8] J. S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, Cambridge, **1961**.
[9] D. Shriver, P. Atkins, *Inorganic Chemistry*, Oxford University Press, Oxford, **1999**.
[10] N. Edelstein, D. Brown, B. Whittaker, *Inorg. Chem.* **1974**, *13*, 563.
[11] F. P. Notter, H. Bolvin, *J. Chem. Phys.* **2009**, *130*, 184310.
[12] G. Karlström, R. Lindh, P.-A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222.
[13] B. O. Roos, P. R. Taylor, P. E. M. Siegbahn, *Chem. Phys.* **1980**, *48*, 157.
[14] K. Andersson, P.-A. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, *J. Phys. Chem.* **1990**, *94*, 5483.
[15] B. A. Hess, *Phys. Rev. A* **1986**, *33*, 3742.
[16] B. O. Roos, R. Lindh, P. Malmqvist, V. Veryazov, P. O. Widmark, *J. Phys. Chem. A* **2004**, *108*, 2851.

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