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A computational thermochemical vale for Cr-Cu dissociation energy: Using Crystal field theory to understand the chemical bond in metal clusters

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Abstract Semi-empirical (PM6) approach was employed to modelling Cr-Cu dimmer. The obtained bond dissociation energy for such specie agrees very well with experimental/reference values. It was verified that in the Cr-Cu dimmer, chromium has only one unpaired electron, meaning that copper behaves, in such dimmer, as a strong field ligand. Such results strongly suggest that 1:1 Cr-Cu bronzes must behave as a one unpaired electron compound and not a five unpaired electrons one, with, of course, remarkable influences on their magnetic properties.

Keywords: Chromium, copper, clusters, bond dissociation energy, crystal field theory.

INTRODUCTION

Formation enthalpies as well as bond dissociation energies were calculates to Cr, Cu and the dimmer Cr-Cu.

Chromium has the valence configuration $3d^5 4s^1$ and copper is $3d^{10} 4s^1$. In the dimmer Cr-Cu can be supposed that both atoms are pairing their *s* electrons forming a single bond. The question is: chromium retain its five unpaired electrons (as in a weak field ligand complex: $t_{2g}^3\ e_g^2$) or, on the other hand, it is has only one unpaired electron (as in a strong filed ligand complexes: $t_{2g}^5\ e_g^o$) ? Hence, the dimmer Cr-Cu was modelled as both: five unpaired electrons and one unpaired electron.

METHODOLOGY

All computations were performed by using semi-empirical (PM6) method. The SE-PM6 approach was chose taking into account its minor computation time consuming and its reliability, as verified for PtF_6 [1]. The results obtained in the present work also illustrate the reliability of such approach for other inorganic systems.

RESULTS AND DISCUSSION

The bond dissociation energy for the studied dimmer was calculated as:

$$D^o = \Delta_f H_m^{\ o}{}_{(dimmer)} - \Sigma\, \Delta_f H_m^{\ o}{}_{(atoms)} \qquad (1)$$

The obtained results are summarized in Table 1. As can be verified, the calculated formation enthalpies for the investigated atoms are in very good agreement with the experimental/reference values [2], showing that the chose approach was a reliable one to study such inorganic systems.

As can be also verified, the calculated bond dissociation energy to the Cr-Cu dimmer agrees very well with the experimental/reference value [2] only to the one unpaired electron system. That is, in the Cr-Cu dimmer,

chromium has only one unpaired electron, meaning that copper behaves, in such dimmer, as a strong filed ligand.

Such results strongly suggest that Cr-Cu bronzes must behave as a one unpaired electron compound and not as a five unpaired electrons one, with, of course, remarkable influences on their magnetic properties.

Table 1. Calculated formation enthalpies and bond dissociation energies (kJ mol^{-1}) for Cr, Cu and Cr-Cu.

Element /dimmer	$\Delta_f H_m^o$ (ref.)	$\Delta_f H_m^o$ (calc.)	D^o (ref.)	D^o (calc.)
Cr	397.5 ± 4.2	397.5	_	-
Cu	337.4 ±1.2	337.7	_	-
Cr-Cu	-	_	154.4 ± 14.5	
Cr-Cu[a]	-	890.29	-	155.2
Cr-Cu[b]	-	800.07	-	64.9

[a]With one unpaired electron (from Cr); [b]With five unpaired electrons (from Cr);

The obtained results prove that the Cr-Cu cluster exhibits a single (σ) bond (in contrast with Cr_2 with a sextuple bond). Furthermore, the obtained results also illustrates that crystal field theory can also be successfully applied to understand and predict the electron distributions on metal clusters and (possibly) alloys.

The calculated spin density map for the modelled dimmer in shown in Figure 1.

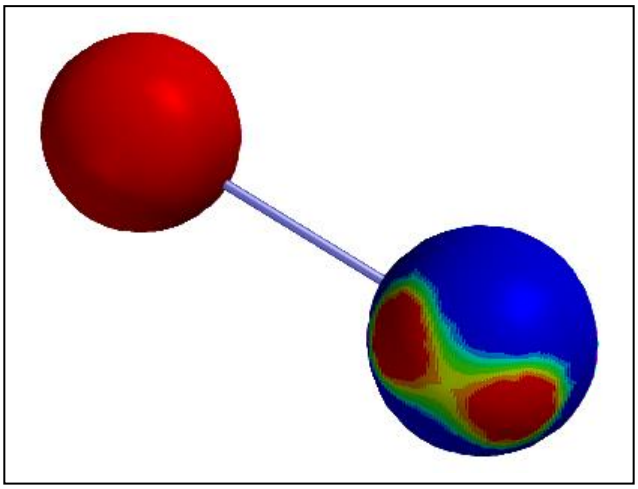

Fig. 1. Spin density map for Cr-Cu (Cu: red; Cr: blue).

REFERENCES

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