Periodic trends in metal–metal bonding in edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems

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Abstract

Periodic trends in metal–metal interactions in edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems, involving the transition metals from groups 4 through 8 and electronic configurations ranging from d^1d^1 through d^5d^5 , have been investigated by calculating metal–metal bonding and spin-polarization (exchange) effects using density functional theory. The trends found in this study are compared with those for the analogous face-shared $[\text{M}_2\text{Cl}_9]^{3-}$ systems reported in earlier work. Strong linear correlations between the metal–metal bonding and spin-polarization terms have been obtained for all groups considered. In general, spin polarization and electron localization are predominant in 3d–3d species whereas electron delocalization and metal–metal bonding are favoured in 5d–5d species, with more variable results observed for 4d–4d systems. As previously found for face-shared $[\text{M}_2\text{Cl}_9]^{3-}$ systems, the strong correlations between the metal–metal bonding and spin polarization energy terms can be related to the fact that both properties appear to be similarly affected by the changes in the metal orbital properties and electron density occurring within the $d^n d^n$ groups. A significant difference between the face-shared and edge-shared systems is that while the 4d metals in the former show a strong tendency for delocalized metal–metal bonded structures, the edge-shared counterparts display much greater variation with both metal–metal bonded and weakly coupled complexes observed. The tendency for weaker metal–metal interactions can be traced to the inability of the edge-shared bridging structure to accommodate the smaller metal–metal distances required for strong metal–metal bonding.

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1. Introduction

Dinuclear and polynuclear transition metal complexes exhibit great diversity in metal–metal interactions, ranging from weak magnetic coupling through to multiple metal–metal bonding [1]. Such interactions are intrinsically interesting for fundamental reasons, but are also important due to their potential applications in a variety of fields spanning metal surfaces, electronic and magnetic devices, catalysis, and bioinorganic chemistry [2–4].

The extent of the interaction between the metal centres is clearly dependent on the electronic properties of the con-

stituent metals but the nature of the bridging ligand framework, if present, can also play a significant role. Among the species displaying metal–metal interactions, the dinuclear compounds represented by the face-shared $[\text{M}_2\text{X}_9]^{2-}$ and edge-shared $[\text{M}_2\text{X}_{10}]^{2-}$ (dimer) species are particularly noteworthy as they are formed by many transition metals and exhibit considerable variation in structural, electronic, and magnetic properties due to the competing effects of the metal–metal and metal–bridge interactions.

Although from a computational perspective, dinuclear face-shared $[\text{M}_2\text{X}_9]^{2-}$ and edge-shared $[\text{M}_2\text{X}_{10}]^{2-}$ systems are amenable to reasonably high-level calculations due to their relatively small size and high symmetry, the large range of metal–metal interactions makes the theoretical treatment of these complexes particularly challenging. Nevertheless, we have shown in our previous work that density

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functional theory in combination with the broken-symmetry approach of Noodleman and coworkers [5,6] can accurately describe the entire range of metal–metal interactions, from weak antiferromagnetic coupling through to multiple metal–metal bonds, as well as encompassing both high-spin and low-spin metal configurations. The success of this procedure can be exemplified by noting that our broken-symmetry density functional calculations have accurately reproduced experimentally observed properties in a large number of $[\text{M}_2\text{X}_9]^{z-}$ dimers with electronic configurations ranging from d^1d^1 through to d^5d^5 [7–14] as well as mixed-valence d^1d^2 , d^2d^3 , d^3d^4 and d^4d^5 configurations [15,16]. We have also used this methodology to successfully investigate metal–metal interactions in a variety of other dimer systems, including edge-shared $[\text{M}_2\text{X}_{10}]^{z-}$ and phosphine-bridged $[\text{M}_2\text{X}_6(\text{P}-\text{P})_4]^{z-}$ systems [17,18], indicating that this theoretical approach is broadly applicable across many dinuclear transition metal complexes.

We have recently completed a detailed investigation of periodic trends in metal–metal interactions across an extensive series of $[\text{M}_2\text{Cl}_9]^{z-}$ species [19]. In this study, the periodic trends were investigated by means of density functional calculations on a large number of even-electron (same-valence) $[\text{M}_2\text{Cl}_9]^{3-}$ and $[\text{M}'\text{M}''\text{Cl}_9]^{3-}$ and odd-electron (mixed-valence) $[\text{M}_2\text{Cl}_9]^{2-}$ dimers involving the transition metals of groups 4 through 8. The degree of metal–metal bonding in these systems is determined by the relative magnitudes of two opposing terms, namely the spin polarization (exchange stabilization) energy which favours localization of the metal-based electrons and weak magnetic coupling, and the metal–metal bonding energy which favours delocalization of the metal-based electrons and thus (strong) metal–metal bonding. Remarkable linear correlations between the metal–metal bonding and spin polarization energy terms were obtained for all group and period series considered, and were rationalized on the basis that both properties appear to be similarly affected by changes in the metal orbital properties and electron density occurring within groups and across periods.

In the present work, the investigations of periodic trends in metal–metal interactions, using the concepts of metal–metal bonding energy and spin polarization energy, are extended to edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems. Computational studies of $[\text{M}_2\text{L}_{10}]^{z-}$ species have been reported previously, and include the work by Cotton and Feng [20] on Mo complexes ($[\text{Mo}_2\text{Cl}_6(\text{PH}_3)_4]$, $[\text{Mo}_2\text{Cl}_6(\text{PH}_2\text{CH}_2\text{PH}_2)_2]$, $[\text{Mo}_2\text{Cl}_6(\text{CHO}_2)_2(\text{PH}_3)_2]$, $[\text{Mo}_2\text{Cl}_6(\text{NHCHNH})_2(\text{PH}_3)_2]$) using configuration interaction techniques, and our density functional investigations of Cr, Mo, and W complexes ($[\text{M}_2\text{Cl}_{10}]^{4-}$, $[\text{M}_2\text{Cl}_6(\text{PH}_3)_4]$, $[\text{M}_2\text{Cl}_6(\text{PH}_2\text{CH}_2\text{PH}_2)_2]$) [17,18]. However, all of these studies have focused on species with a formal d^3d^3 metal-based configuration, whereas in this work we consider $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems involving all transition metals from group 4 through 8 and electronic configurations ranging from d^1d^1 through d^5d^5 . Although both edge-shared and face-shared systems can in principle accommodate metal–metal bonds, the different bridging architectures give

rise to fundamentally different orbital interactions. In the edge-shared system σ , π and δ bonds are possible, whereas in the face-shared complexes only σ and δ_π ($2/3\delta + 1/3\pi$) interactions are feasible. Due to the inherent differences in metal–metal interactions compared to the previously investigated face-shared complexes, the present study involving an extensive series of edge-shared dimers, provides an additional and useful check on the applicability of our approach to the analysis of periodic trends in metal–metal bonding across various classes of dinuclear systems.

2. Calculation details

All density-functional calculations reported in this article were carried out with the Amsterdam Density Functional (2004) package [21–23]. Functionals based on the Volko–Wilk–Nusair (VWN) form [24] of the local density approximation (LDA) [25] were utilized, and no gradient corrections or relativistic effects were included, as previous work has shown that these normally result in poorer agreement with experimental structural data [8,26]. Basis sets of triple-zeta quality and one polarization function (TZP or type IV), incorporating frozen cores (Cl.2p, and M.2p, M.3d, M.4f for the first, second, and third transition series, respectively), were employed [21–23].

3. Results and discussion

The molecular structure of edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems (shown in Fig. 1) is characterized by D_{2h} symmetry, with the metal sites lying in a distorted octahedral environment corresponding to C_{2v} local symmetry. This distorted environment implies that the metal-based octahedral t_{2g} d-type orbitals relevant to metal–metal bonding possess a_1 , b_2 , and a_2 (C_{2v}) symmetry and generate, respectively, bonding [σ , π , δ] and antibonding [σ^* , π^* , δ^*] molecular orbitals that transform as the a_g , b_{2u} , b_{3g} , b_{3u} , b_{1g} , and a_u irreducible representations in the full D_{2h} symmetry of the $[\text{M}_2\text{Cl}_{10}]^{4-}$ systems. The correlation between the C_{2v}

Fig. 1. Molecular structure of edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ dimers.

Fig. 2. Correlation between the metal-based molecular orbitals in C_{2v} and D_{2h} descriptions of edge-shared $[M_2Cl_{10}]^{4-}$ dimers.

and D_{2h} orbital descriptions is shown in Fig. 2 and plots of the metal–metal bonding and antibonding molecular orbitals obtained from calculations on (d^3d^3) $[W_2Cl_{10}]^{4-}$ are given in Fig. 3.

3.1. General results

In previous studies [19], periodic trends in metal–metal interactions have been described and analyzed in terms of two factors, namely, the metal–metal bonding (ΔE_{mbe}) energy and the spin-polarization (ΔE_{spe}) energy.

The metal–metal bonding term can be defined as the stabilization energy arising from bond formation between opposite metal centres, whereas the spin-polarization term represents the exchange stabilization energy associated with the presence of unpaired electron density on the metal centres. Significant bonding interaction between the metal atoms favours electron delocalization over both metal sites, whereas the spin-polarization effects favour electron localization on the opposite metal centres. The difference between the two terms (denoted $\Delta E_{spe} - \Delta E_{mbe}$) measures the tendency of the metal-based electrons to delocalize and thus determines the degree of metal–metal bonding.

Three separate calculations are required to determine the metal–metal bonding and spin-polarization terms (Fig. 4). These correspond to the $S = 0$ state, where complete delocalization of the metal-based electrons in metal–metal bonds occurs, the $S = S_{max}$ state, in which all metal-based electrons are unpaired and therefore weakly coupled, and the reference state (RS), which is defined so that the contributions from metal–metal bonding and spin polarization cancel. The energy of the reference state can be obtained from a spin-restricted calculation on an electronic configuration where the metal–metal bonding and antibonding orbitals are evenly occupied.

The metal–metal bonding energy and the spin-polarization energy are defined in terms of these three states as follows

Fig. 3. Plots of the molecular orbitals representing the metal–metal interactions in $[W_2Cl_{10}]^{4-}$.

$$\Delta E_{mbe} = E(S = 0) - E(RS) \quad (1)$$

$$\Delta E_{spe} = E(S = S_{max}) - E(RS) \quad (2)$$

The occupancy of the metal-based orbitals in the metal–metal bonded $S = 0$ state for the five $d^n d^n$ configurations can be schematically described as follows

Fig. 4. Schematic definition of the metal–metal bonding (ΔE_{mbe}) energy and spin polarization (ΔE_{spe}) energy in relation to the $S = 0$, $S = S_{\text{max}}$, and reference states of $d^n d^n$ systems.

$$d^1 d^1 \quad (\sigma)^2 (\pi)^0 (\delta)^0 (\delta^*)^0 (\pi^*)^0 (\sigma^*)^0$$

$$d^2 d^2 \quad (\sigma)^2 (\pi)^2 (\delta)^0 (\delta^*)^0 (\pi^*)^0 (\sigma^*)^0$$

$$d^3 d^3 \quad (\sigma)^2 (\pi)^2 (\delta)^2 (\delta^*)^0 (\pi^*)^0 (\sigma^*)^0$$

$$d^4 d^4 \quad (\sigma)^2 (\pi)^2 (\delta)^2 (\delta^*)^2 (\pi^*)^0 (\sigma^*)^0$$

$$d^5 d^5 \quad (\sigma)^2 (\pi)^2 (\delta)^2 (\delta^*)^2 (\pi^*)^2 (\sigma^*)^0$$

where it should be noted that, for $d^3 d^3$ systems, the most favourable occupation corresponds to an inversion of the δ and δ^* orbitals [17,18].

For the “completely localized” $S = S_{\text{max}}$ states, the occupancy of the metal-based orbitals corresponds to the configurations

$$d^1 d^1 \quad (\sigma)^1 (\pi)^0 (\delta)^0 (\delta^*)^0 (\pi^*)^0 (\sigma^*)^1 \quad (S = 1)$$

$$d^2 d^2 \quad (\sigma)^1 (\pi)^1 (\delta)^0 (\delta^*)^0 (\pi^*)^1 (\sigma^*)^1 \quad (S = 2)$$

$$d^3 d^3 \quad (\sigma)^1 (\pi)^1 (\delta)^1 (\delta^*)^1 (\pi^*)^1 (\sigma^*)^1 \quad (S = 3)$$

$$d^4 d^4 \quad (\sigma)^1 (\pi)^1 (\delta)^2 (\delta^*)^2 (\pi^*)^1 (\sigma^*)^1 \quad (S = 2)$$

$$d^5 d^5 \quad (\sigma)^1 (\pi)^2 (\delta)^2 (\delta^*)^2 (\pi^*)^2 (\sigma^*)^1 \quad (S = 1)$$

The electronic configurations for the reference states are obtained by evenly distributing the metal-based electrons over the six relevant orbitals, as follows:

$$d^1 d^1 \quad (\sigma)^{1/3} (\pi)^{1/3} (\delta)^{1/3} (\delta^*)^{1/3} (\pi^*)^{1/3} (\sigma^*)^{1/3}$$

$$d^2 d^2 \quad (\sigma)^{2/3} (\pi)^{2/3} (\delta)^{2/3} (\delta^*)^{2/3} (\pi^*)^{2/3} (\sigma^*)^{2/3}$$

$$d^3 d^3 \quad (\sigma)^1 (\pi)^1 (\delta)^1 (\delta^*)^1 (\pi^*)^1 (\sigma^*)^1$$

$$d^4 d^4 \quad (\sigma)^{4/3} (\pi)^{4/3} (\delta)^{4/3} (\delta^*)^{4/3} (\pi^*)^{4/3} (\sigma^*)^{4/3}$$

$$d^5 d^5 \quad (\sigma)^{5/3} (\pi)^{5/3} (\delta)^{5/3} (\delta^*)^{5/3} (\pi^*)^{5/3} (\sigma^*)^{5/3}$$

Geometrical parameters for the reference, $S = 0$, and $S = S_{\text{max}}$ states, and the calculated values of the ΔE_{mbe} , ΔE_{spe} , and $\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$ terms for all species studied in the present work are given in Tables 1 and 2, respectively.

Table 1

Optimized metal–metal bond distance (Å) for the reference (RS), $S = 0$, and $S = S_{\text{max}}$ states of $d^n d^n$ [M_2Cl_{10}] $^{4-}$ systems

configuration	molecule	RS	$S = 0$	$S = S_{\text{max}}$
$d^1 d^1$	[Ti ₂ Cl ₁₀] $^{4-}$	3.976	3.214	3.926
	[Zr ₂ Cl ₁₀] $^{4-}$	4.263	3.295	4.261
	[Hf ₂ Cl ₁₀] $^{4-}$	4.271	3.296	4.271
$d^2 d^2$	[V ₂ Cl ₁₀] $^{4-}$	3.846	2.897	3.844
	[Nb ₂ Cl ₁₀] $^{4-}$	4.084	2.801	4.097
	[Ta ₂ Cl ₁₀] $^{4-}$	4.096	2.801	4.098
$d^3 d^3$	[Cr ₂ Cl ₁₀] $^{4-}$	3.755	2.791	3.762
	[Mo ₂ Cl ₁₀] $^{4-}$	3.941	2.798	3.956
	[W ₂ Cl ₁₀] $^{4-}$	4.000	2.800	4.000
$d^4 d^4$	[Mn ₂ Cl ₁₀] $^{4-}$	3.651	2.820	3.698
	[Tc ₂ Cl ₁₀] $^{4-}$	3.842	2.711	3.894
	[Re ₂ Cl ₁₀] $^{4-}$	3.885	2.767	3.931
$d^5 d^5$	[Fe ₂ Cl ₁₀] $^{4-}$	3.580	3.435	3.695
	[Ru ₂ Cl ₁₀] $^{4-}$	3.753	3.035	3.815
	[Os ₂ Cl ₁₀] $^{4-}$	3.824	3.106	3.898

Table 2

Metal–metal bonding (ΔE_{mbe}) energy (eV) and spin-polarization (ΔE_{spe}) energy (eV) for $d^n d^n$ [M_2Cl_{10}] $^{4-}$ systems

Configuration	Molecule	ΔE_{mbe}	ΔE_{spe}	$\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$
$d^1 d^1$	[Ti ₂ Cl ₁₀] $^{4-}$	0.25	0.54	+0.29
	[Zr ₂ Cl ₁₀] $^{4-}$	1.01	0.49	−0.52
	[Hf ₂ Cl ₁₀] $^{4-}$	1.11	0.48	−0.63
$d^2 d^2$	[V ₂ Cl ₁₀] $^{4-}$	0.37	1.63	+1.26
	[Nb ₂ Cl ₁₀] $^{4-}$	1.79	1.08	−0.71
	[Ta ₂ Cl ₁₀] $^{4-}$	2.05	1.00	−1.05
$d^3 d^3$	[Cr ₂ Cl ₁₀] $^{4-}$	0.57	3.62	+3.05
	[Mo ₂ Cl ₁₀] $^{4-}$	1.84	2.21	+0.37
	[W ₂ Cl ₁₀] $^{4-}$	2.15	1.98	−0.17
$d^4 d^4$	[Mn ₂ Cl ₁₀] $^{4-}$	−0.34	1.44	+1.78
	[Tc ₂ Cl ₁₀] $^{4-}$	0.73	0.69	−0.04
	[Re ₂ Cl ₁₀] $^{4-}$	1.05	0.56	−0.49
$d^5 d^5$	[Fe ₂ Cl ₁₀] $^{4-}$	−0.87	0.00	+0.87
	[Ru ₂ Cl ₁₀] $^{4-}$	−0.51	−0.29	+0.22
	[Os ₂ Cl ₁₀] $^{4-}$	−0.35	−0.36	−0.01

3.2. Periodic trends

Periodic trends in the metal–metal bonding (ΔE_{mbe}) and spin polarization (ΔE_{spe}) energy terms in all [M_2Cl_{10}] $^{4-}$ systems studied are schematically represented in the plots shown in Fig. 5.

For all five transition metal groups investigated, qualitatively similar trends in the variation of the metal–metal bonding and spin-polarization terms are observed. On descending each group, the calculated values of the metal–metal bonding energy increase while those of the spin polarization energy decrease, with the most significant differences found between 3d–3d and 4d–4d species.

An explanation for these qualitative trends can be given in terms of how the changes in the metal properties affect the two energetic factors [19]. As a group is descended,

Fig. 5. Periodic variation of the spin-polarization and metal–metal bonding energy terms.

the greater size of the metal atoms and the more diffuse nature of the metal orbitals lead to an enhancement of the metal–metal bonding interactions, but to a reduction in spin polarization as a consequence of the increased average interelectronic separation.

Across a period, the changes in the spin-polarization energy reflect its dependence on the number of like-spin electrons, the calculated values increasing from d^1d^1 through to d^3d^3 configurations, and subsequently decreasing from d^3d^3 through to d^5d^5 configurations. For $[M_2Cl_9]^{3-}$ systems, the variation of the spin-polarization energy across a period is mirrored around the values for group 6, and an explanation for this result has been proposed [19] in terms of the electron–hole equivalence of the d^1d^1 – d^5d^5 and d^2d^2 – d^4d^4 configurations, and the relationship between the spin-polarization energy and the number (n) of like-spin electrons, represented by the expression

$$\Delta E_{\text{spe}} \propto (n!/2) \quad (3)$$

Unlike the $[M_2Cl_9]^{3-}$ systems, the variation in the spin-polarization energy is not symmetrical across the $[M_2Cl_{10}]^{4-}$ series. Although the results are similar for (d^2d^2) $[V_2Cl_{10}]^{4-}$ and (d^4d^4) $[Mn_2Cl_{10}]^{4-}$, in general, the

values for d^4d^4 and d^5d^5 species are significantly smaller than those for d^2d^2 and d^1d^1 systems, respectively. A comparison of the structural data in Table 1 for the reference and $S = S_{\text{max}}$ states reveals structural differences between the $[M_2Cl_9]^{3-}$ and $[M_2Cl_{10}]^{4-}$ dimers that may account for the different trends observed in the spin-polarization energy results. In the former, the optimized metal–metal distances in the reference and $S = S_{\text{max}}$ states are almost identical, whereas in the latter, this pattern generally holds for d^1d^1 and d^2d^2 dimers, but not for d^4d^4 and d^5d^5 dimers, which exhibit shorter metal–metal bond lengths in the reference state than in the $S = S_{\text{max}}$ state.

In the case of the metal–metal bonding energy, the greater values obtained for d^2d^2 and d^4d^4 species relative to d^1d^1 and d^5d^5 systems, respectively, correlate with the increase in formal metal–metal bond order from 1.0 to 2.0. For d^3d^3 dimers, the δ – δ^* orbital inversion implies that there is no formal triple bond despite the presence of six metal-based electrons, and the metal–metal interaction is more appropriately described as a formal double bond [20]. Accordingly, a comparative examination of the results for d^2d^2 and d^3d^3 species, in both the 4d–4d and 5d–5d series, reveals that the metal–metal bonding energy and the optimized bond lengths in the $S = 0$ state are largely similar. The metal–metal interaction appears somewhat stronger in $[Cr_2Cl_{10}]^{4-}$ than $[V_2Cl_{10}]^{4-}$, but a more significant change in the metal–metal distances is observed in this case. Analogous to the $[M_2Cl_9]^{3-}$ systems, the values of the metal–metal bonding energy for d^4d^4 and d^5d^5 dimers are smaller than those obtained for d^2d^2 and d^1d^1 dimers, respectively, and this result can be attributed to the influence of factors such as the occupation of antibonding orbitals and the expected contraction of the metal-based orbitals across a period.

Plots showing the variation of the metal–metal bonding energy as a function of the spin-polarization energy are shown in Fig. 6. Strong linear correlations have been obtained for all groups considered, as previously observed for face-shared $[M_2X_9]^{z-}$ series involving a variety of metals and ligands [19,27]. The dashed line corresponds to

$$\Delta E_{\text{mbe}} = \Delta E_{\text{spe}} \quad (4)$$

and thus separates the systems exhibiting a preference for electron delocalization and metal–metal bonding ($\Delta E_{\text{mbe}} > \Delta E_{\text{spe}}$) from those where electron localization and weak magnetic coupling is more favourable ($\Delta E_{\text{mbe}} < \Delta E_{\text{spe}}$). In general, delocalization and metal–metal bonding preferably occur in 5d–5d species whereas localization and weaker coupling between the metal atoms are favoured in 3d–3d species, with the results being more variable across 4d–4d systems. Although the general trends for the 3d–3d and 5d–5d series are similar to those described previously for $[M_2Cl_9]^{3-}$ systems [19], the behaviour of the 4d–4d dimers is rather different, as evidenced by the fact that metal–metal bonding is clearly preferred by all 4d–4d face-shared $[M_2Cl_9]^{3-}$ species whereas only the $[Zr_2Cl_{10}]^{4-}$ and $[Nb_2Cl_{10}]^{4-}$ edge-shared systems exhibit a definitive tendency

Fig. 6. Variation of the metal–metal bonding energy as a function of the spin-polarization energy.

towards electron delocalization and metal–metal bond formation. As previously noted [17], this result is related to the apparent inability of the edge-shared bridging structure to support the short metal–metal separations required for strong metal–metal bonding.

The strong correlation between the metal–metal bonding and spin polarization energy terms has been previously [19] rationalized on the basis that both properties appear to be similarly affected by changes in the metal orbital properties and electron density within each group. As found for the $[\text{M}_2\text{Cl}_9]^{3-}$ systems, a connection between the two energy terms and the electron density is also observed for the $[\text{M}_2\text{Cl}_{10}]^{4-}$ species, as revealed by the strong linear correlations between the $\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$ values and the square of the metal spin density (ρ_s^2) obtained from a Mulliken population analysis for the $S = S_{\text{max}}$ state (Fig. 7).

For all $d^n d^n$ groups, the importance of metal–metal bonding relative to spin polarization is found to increase as the spin density decreases. Thus, the tendency towards metal–metal bond formation becomes stronger upon descending a given group, as indicated by the diminishing values of the $\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$ term, and can be correlated

Fig. 7. Representation of the difference ($\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$) between the spin polarization and metal–metal bonding terms as a function of the square of the spin density (ρ_s^2) in the $S = S_{\text{max}}$ state.

with the decrease in the spin density on the metal centres in the $S = S_{\text{max}}$ state.

Across the 3d–3d series, spin polarization effects become increasingly important as the number of unpaired electrons in the $S = S_{\text{max}}$ state and, consequently, the spin density on the metal centres, increases from $d^1 d^1$ (Ti) and $d^5 d^5$ (Fe), through $d^2 d^2$ (V) and $d^4 d^4$ (Mn), to $d^3 d^3$ (Cr) systems. As observed in Fig. 5, the spin polarization and metal–metal bonding energy terms exhibit similar trends across the 3d–3d series, but the steeper variation displayed by the former leads to its increasingly dominant role across the $[d^1 d^1, d^2 d^2, d^3 d^3]$ and $[d^5 d^5, d^4 d^4, d^3 d^3]$ sets of systems within this period.

More variable results are observed across the 4d–4d and 5d–5d series but, in all cases, the smallest values of the $\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$ term, and therefore the most delocalized structures, have been obtained for the species with $d^2 d^2$ and $d^4 d^4$ configurations. Within their respective $[d^1 d^1, d^2 d^2, d^3 d^3]$ series, the $d^3 d^3$ $[\text{Mo}_2\text{Cl}_{10}]^{4-}$ and $[\text{W}_2\text{Cl}_{10}]^{4-}$ dimers exhibit the largest $\Delta E_{\text{spe}} - \Delta E_{\text{mbe}}$ values, in accord with the observation that these systems have the highest number of unpaired electrons and metal spin density values

in the $S = S_{\max}$ state, and the fact that their capacity for metal–metal bonding seems to be somewhat unfavourably affected by the δ – δ^* orbital inversion. The Zr, Hf, Nb, and Ta dimers all show a preference for metal–metal bonding over electron localization, but a greater tendency towards delocalization is predicted for the d^2d^2 species ($[\text{Nb}_2\text{Cl}_{10}]^{4-}$ and $[\text{Ta}_2\text{Cl}_{10}]^{4-}$) than the d^1d^1 species ($[\text{Zr}_2\text{Cl}_{10}]^{4-}$ and $[\text{Hf}_2\text{Cl}_{10}]^{4-}$), respectively, due to fact that the greater strength of the metal–metal bonds in the former appears to dominate over the increased spin polarization resulting from a higher number of unpaired electrons and metal spin density in the $S = S_{\max}$ state. These observations also apply to the 4d–4d species within the $[d^5d^5, d^4d^4, d^3d^3]$ series, with the d^3d^3 dimer ($[\text{Mo}_2\text{Cl}_{10}]^{4-}$) displaying the greatest preference for electron localization while metal–metal bonding is more favourable in the d^4d^4 dimer ($[\text{Tc}_2\text{Cl}_{10}]^{4-}$) than the d^5d^5 dimer ($[\text{Ru}_2\text{Cl}_{10}]^{4-}$). In the case of the 5d–5d analogues, the greatest tendency towards delocalization and metal–metal bond formation is also predicted for the d^4d^4 dimer ($[\text{Re}_2\text{Cl}_{10}]^{4-}$), but in contrast with the trends for the 3d–3d and 4d–4d species, the d^5d^5 dimer ($[\text{Os}_2\text{Cl}_{10}]^{4-}$) is calculated to be the most localized system, rather than the d^3d^3 dimer ($[\text{W}_2\text{Cl}_{10}]^{4-}$).

4. Conclusion

Periodic trends in metal–metal interactions have been investigated by means of density functional calculations on a large number of edge-shared $[\text{M}_2\text{Cl}_{10}]^{4-}$ dimer systems, involving the transition metals from groups 4 through 8 and electronic configurations ranging from d^1d^1 through d^5d^5 .

The tendency for metal–metal bond formation or electron localization has been analyzed in terms of periodic trends in metal–metal bonding and spin polarization effects. As found in a previous study of face-shared $[\text{M}_2\text{Cl}_9]^{2-}$ systems, remarkably strong linear correlations between these two energy terms have been obtained for all $d^n d^n$ groups considered, and can be traced to a similar dependence of both factors on the radial dilation of the metal d orbitals and electron density within a given group.

Strong linear correlations are also observed, within all groups, between the square of the spin density on the metal centres (obtained from calculations on the $S = S_{\max}$ state) and both the metal–metal bonding and spin polarization terms. However, unlike the $[\text{M}_2\text{Cl}_9]^{3-}$ systems, across the nd–nd series, the relationship between the two terms, and the dependence of both terms on the electron density, are, in general, not characterized by (similarly strong) linear correlations, possibly due to the influence of the δ – δ^* orbital inversion in the $[\text{M}_2\text{Cl}_{10}]^{4-}$ dimers.

Not unexpectedly, the relative magnitudes of the metal–metal bonding and spin polarization terms indicate that delocalization and metal–metal bond formation are most favourable in the 5d–5d species whereas localization and weaker coupling between the metal atoms are preferred

in the 3d–3d species. The results are more variable across the 4d–4d systems with the Zr and Nb dimers showing a tendency towards metal–metal bonding, but electron localization being favoured in the Ru and Mo dimers. This contrasts with the analogous face-shared systems where all 4d–4d dimers are predicted to be delocalized.

Overall, the $[\text{M}_2\text{Cl}_{10}]^{4-}$ dimers exhibit less delocalized structures than their face-shared $[\text{M}_2\text{Cl}_9]^{3-}$ counterparts, and this tendency can be attributed to the more inflexible nature of the edge-shared bridging structure, which is less able to accommodate the shorter metal–metal separations required for strong metal–metal bonding.

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