



Review

Metal–metal bonded compounds with uncommon low oxidation state

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ABSTRACT

Over the past decade, the metal–metal bonded compounds with uncommon low oxidation state has tremendously facilitated the development of metal–metal bond chemistry. Herein, we review the syntheses, molecular and electronic structures, important properties and applications of more than one hundred metal–metal bonded compounds with uncommon low oxidation state. These compounds cover both homonuclear metal–metal bonded compounds and heteronuclear ones, as well various metal–metal bonds from localized bi-center to delocalized multi-center systems. Furthermore, theoretical calculations on some compounds systematically analyzed orbital bonding and electron occupancy, further elucidating the intrinsic relationship among the functions, stabilities and structures.

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1. Introduction

Chemical bonding is the cornerstone for building the chemistry edifice [1,2]. Among the various types of chemical bonding, metal–metal bonding exploration has been one of the most important themes in chemistry research, because it is a fertile territory to further understand the nature of electronic structure, orbital bonding, reactivity and properties of corresponding compounds. Since Cotton et al. proposed the theory of metal–metal quadruple bonding based on $[\text{Re}_2\text{Cl}_8]^{2-}$ ion in 1964, lots of metal–metal bonded compounds were reported [3], and the novel and unusual metal–metal bonds are being explored intensively [4–9]. Importantly, the single and multiple metal–metal bonds concept in coordination chemistry was well established. It should be noted that in 2004, the landmark discovery of $[\text{Cp}^*\text{ZnZnCp}^*]$ $\text{Cp}^* = \text{C}_5\text{Me}_5$ reported by Carmona and his coworkers opened the new epoch in metal–metal bonding chemistry [10], and later the multitudinous and excellent works about the synthesis, reactivity and applications of metal–metal bonded compounds witnessed the great progress in the field, such as $\text{Mg}^{\text{I}}\text{--Mg}^{\text{I}}$, $\text{In}^{\text{I}}\text{--In}^{\text{I}}$, $\text{Co}^{\text{I}}\text{--Co}^{\text{I}}$, $\text{Cd}^{\text{I}}\text{--Cd}^{\text{I}}$ and those with quintuple metal–metal bonds between $\text{Cr}^{\text{I}}\text{--Cr}^{\text{I}}$ or $\text{Mo}^{\text{I}}\text{--Mo}^{\text{I}}$ [11–16]. During preparing these metal–metal bonded compounds, metal ions with low oxidation state (LOS) need to be protected by sterically bulky ligands, because they are easy to take place disproportionation reaction into stable metal ions with high oxidation state and metal atoms. Furthermore, most of reported those are $[\text{M}_2]^{2+}$ dimeric species, which are not stable in air or solvent with either spontaneous combustion or decomposition [17]. Therefore, it is necessary and important to improve the stability of metal–metal bonded compounds with LOS to systematically explore the properties, functions and even applications of these compounds.

Considering the well-known bonding model of carbon atoms, two adjacent C atoms can form three kinds of bonds, C–C single bond in sp^3 hybridization, C=C double bond in sp^2 hybridization and C≡C triple bond in sp hybridization. The valence electronic configuration of carbon atom is $2\text{s}^22\text{p}^2$. One s and three p orbitals (p_x , p_y and p_z) can provide four bonding orbitals with adjacent atoms, constructing millions of organic molecules with different structures and functions. Comparably, metal atoms possess complicated d or f orbitals, and five d and/or seven f orbitals can theoretically form more unexpected and complicated bonding orbital and structure types together with s orbitals in the valence electronic configuration of metal atoms.

The essence of metal–metal bonds can be explained by the example of atomic d orbitals of the transition metal elements in M_2 molecules. Just as mentioned above, the AOs of the metal elements in d block have five d orbitals, and the combination of the d-AOs in M_2 configuration molecules gives five bonding MOs components (1σ , 2π , 2δ) and five the antibonding MOs components ($1\sigma^*$, $2\pi^*$, $2\delta^*$) (Fig. 1) [18]. Along the symmetric axis direction of orbital, the d_z^2 -AOs in atom A overlaps in “head to head” way with that in atom B, forming σ bonding. Whilst d_{xz} and d_{xz} , d_{yz} and d_{yz} AOs will overlap sideways in “shoulder to shoulder” way, constituting π bonding, so the π bonding energy usually is higher than homologous σ bonding. And the d_{xy} and d_{xy} , $d_{x^2-y^2}$ and $d_{x^2-y^2}$ AOs overlap in “face to face” way, building δ bonding, which has the same symmetry as the d orbitals. Therefore, the energy of δ bonding locates at the highest level in five bonding orbitals. The corresponding five antibonds molecular orbitals ($1\sigma^*$, $2\pi^*$, $2\delta^*$) between two atoms own higher energy level. Under the given conditions, two adjacent transition metal atoms can form up to nine bonds by the participation of all the valence s, p and d orbitals [19], which provides the possibility of constructing the complicated multiple metal–metal bonds. For example, the group 6 metal atoms with the valence electronic configuration $n\text{s}^1(n-1)\text{d}^5$ can

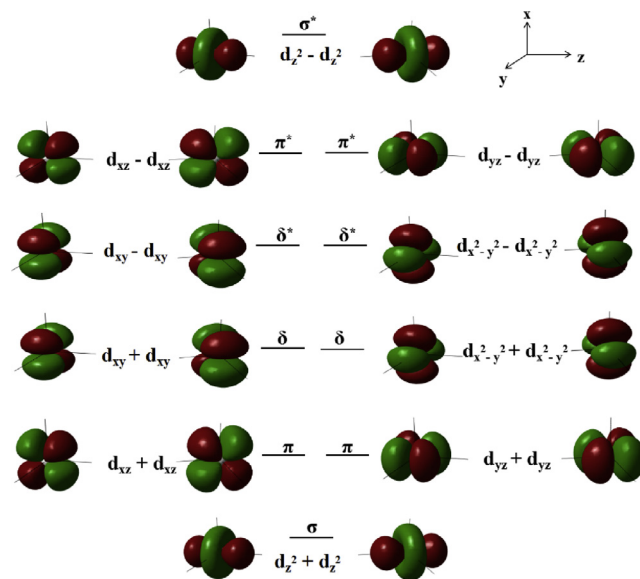


Fig. 1. Schematic representation of the chemical bonding between transition metals that is possible with five atomic d orbitals.

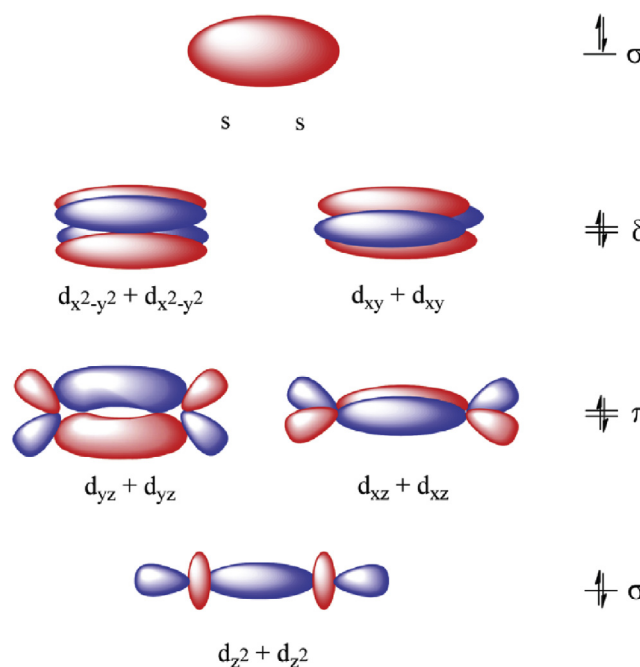


Fig. 2. The bonding molecular orbitals of the group 6 diatomic Cr_2 molecules. Copyright 2014 The Royal Society of Chemistry.

provide potentially sixfold metal–metal bonds in diatomic Cr_2 molecules, namely 2σ , 2π and 2δ , as shown in Fig. 2.

Similarly to carbon atom in the benzene molecule, the metal atoms can also construct the multicentered metal–metal bonds, such as tri, tetra, penta-nuclear or other high-nuclear compounds with different geometry configuration from planar to polyhedron. The electron configuration will be more multifarious to ensure the stability of the metal–metal bonding compounds. To our knowledge, the multicentered metal–metal bonding based on LOS metal ions was rarely reported, and such type of bonding can be extensively delocalized rather than localized bonding in bicentered metal–metal bonds. The case implies the kinds of

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