



Review

Topological analysis of the metal-metal bond: A tutorial review

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ABSTRACT

This contribution explains how the topological methods of analysis of the electron density and related functions such as the electron localization function (ELF) and the electron localizability indicator (ELI-D) enable the theoretical characterization of various metal-metal (M–M) bonds (multiple M–M bonds, dative M–M bonds). Examples are taken in both bulk metals, alloys and molecular complexes. Metallic bonds as well as weak partially covalent M–M interactions, are described and characterized unambiguously combining AIM (atoms in molecules) and ELF/ELI-D topological analysis.

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1. Introduction

Among the 88 metallic elements, 20 belong to the main groups, 40 to the transition periods, 14 to the lanthanides and 14 to the actinides offering a potentially large panel of metal-metal (M–M) bonding situations. M–M bonding is encountered in a wide variety of molecular compounds or crystalline systems such as bulk metals, alloys, superconducting materials, Zintl-Klemm phases. Although compounds featuring M–M bonds are known for many decades, the chemistry of M–M bonds is still a hot topic as attested by several reviews dedicated to recent advances in both main group and transition element chemistry [1–5]. Compounds with homometallic or heterometallic extended metal atom chains (EMACs) are considered as potential molecular wires [3,6–9].

For a given metal, the M–M interatomic distance can be modulated by a suitable choice of the number and the nature of the ligands which implies specific synthesis approaches. The evidence by X-ray crystallography of a very short Re–Re distance in the $[\text{ReCl}_8]^{2-}$ dianion [5,10,11] identified later as a quadruple bond [12] is a significant landmark in inorganic chemistry. It opened the way of a rich chemistry of multiple M–M bonding in bimetallic complexes [10–12] as illustrated by the Cr–Cr distances ranging from 1.706 Å [13] to 2.498 Å in the bulk metal and even to 2.612 Å [14]. The wealth and diversity of M–M bonding across the transition element series has no equivalent in rare-earth metals, but recent compounds involving heavy main group elements such as Sn, Pb, Sb or Bi complexes [15–17] challenges the long-held assumption that multiple bonds are stable only between first-row elements.

The interpretation of the bonding requires at least pieces of information concerning the geometry, the charge density, the spin state of the metallic centres and the curvature of the energy hypersurface at the equilibrium. These data can be either obtained by experimental techniques such as single-crystal X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), vibrational, Nuclear Magnetic Resonance (NMR), Electron Spin Resonance (ESR), Electron Spectroscopy for Chemical Analysis (ESCA), electronic spectroscopies [14,18] or by quantum mechanical calcula-

tions. Which are the pieces of information available by experiment?

1. M–M distance from XRD analysis;
2. Electron density maps: X-ray scattering, incorrectly termed as “experimental densities” fit of promolecular density;
3. Number of interacting metal atoms from NMR coupling constants or ESR hyperfine structures;
4. Bond strength from Raman M–M force constants, from $\delta \rightarrow \delta^*$ electronic transitions or from X-ray photoelectron spectroscopy XPS (δ bond only [19]);
5. Oxidation state from NMR and XPS [20,21] or from electrochemical measurements;
6. Enhanced photoluminescence because of Ligand to Metal-Metal Charge Transfer (LMMCT) excited states (electronic spectroscopy).

Molecular M–M bonding is primarily characterized by the intermetallic distance in the crystal structure. A M–M interaction is anticipated when the intermetallic distance is shorter than the sum of van der Waals radii (and comparable to the sum of covalent radii) of the metal atoms. Pt(II)–Pt(II) bonding was indeed assumed in switchable platinum tweezers on the basis of intermolecular Pt–Pt distances of 3.21 Å shorter than twice the van der Waals radii of Pt, namely 3.44 Å (covalent radii of Pt 1.4 Å) [22]. The intermetallic distance criterion should however be taken with care, because molecular charge, bridging ligands, symmetry or crystal packing forces may significantly influence the M–M contacts and rule out any quantitative relationship between the M–M distance and bond strength [23].

Besides short intermetallic distances, M–M bonding exhibit unique spectroscopic signatures.

1. Nuclear magnetic resonance signatures of M–M bonding are:
 - (i) A downfield shift of the NMR signal of either the metal nuclei or a proximal nuclei of the ligands with non-zero nuclear spin, that are strongly affected by the M–M bonding [24]. A strongly deshielded resonance of $\delta = 1142.3$ ppm in

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