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Chemical bonding in complexes with high coordination numbers: a charge density study

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The topological analysis of an experimental charge-density distribution in crystalline tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) revealed that the metal–ligand bonds occupy nearly the same place in the energetic scale as the hydrogen bonds do, thus being extremely sensitive to steric and crystal-packing effects.

What is a coordinate bond? According to IUPAC, the coordinate link is a description of covalent bonding between two atoms in which both electrons shared in the bond come from the same atom.[1] However, this definition is not precise: once such a bond has been formed, it cannot be distinguished from other polar covalent bonds, *e.g.*, those in the M_2Cl_2 fragment. In general, the term *coordinate bond* denotes the interaction between a metal atom and a ligand in a complex compound. Most of the coordinate bonds are labile: the influence of neighboring ligands, the coordination number and the spin state of a metal atom leads to variations in coordinate bond lengths and energies over a wide range. Upon the analysis of a particular compound, it is difficult to distinguish the inherent features of a complex due to, *e.g.*, a structural *trans*-effect,[2–4] and those governed by specific interactions between ligands[5] and a crystal environment.[6] It is, in particular, the case of complexes containing a metal center with a high coordination number.

To elucidate the influence of different factors on molecular geometry, it is desirable to have an approach that can give direct estimates for the energetic parameters of M–ligand bonds, specific intramolecular interactions, and crystal packing effects. An appropriate solution could be the topological analysis of an electron-density distribution function $\rho(r)$, derived from high-resolution X-ray diffraction (XRD) data, within Bader's Atoms in Molecules (AIM) theory.[7] First attempts to apply this to the case of coordination complexes were made as early as the late 1980s, but they were limited by technical capabilities of X-ray diffraction equipment of that time.[8] Since then, great progress has been reached in using conventional sealed-tube X-ray[9] and powerful synchrotron sources.[10] Still, little is done for the direct estimation of the energy of coordinate bonds. To the best of our knowledge, the application of a correlation proposed by Espinosa *et al.*[11] (CEML), which interconnects the energy of an interaction (E_{int}) with the potential energy density [$v(r)$] in its bond critical point (BCP), allows estimating the values of E_{int} for various interactions;[12] the examples are Mg···C and Ca···C coordinate bonds in zeolites[13] (DFT studies), Si–N bonds in hypervalent silicon compounds,[14] Gd–OH_2, Gd–N(phenanthroline), Gd–Cl[15] and Au–P[16] bonds [XRD analysis of $\rho(r)$ topology].

Here, we report the results of a study for tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) **1** complex [Figure 1(*a*),(*b*)].[†]

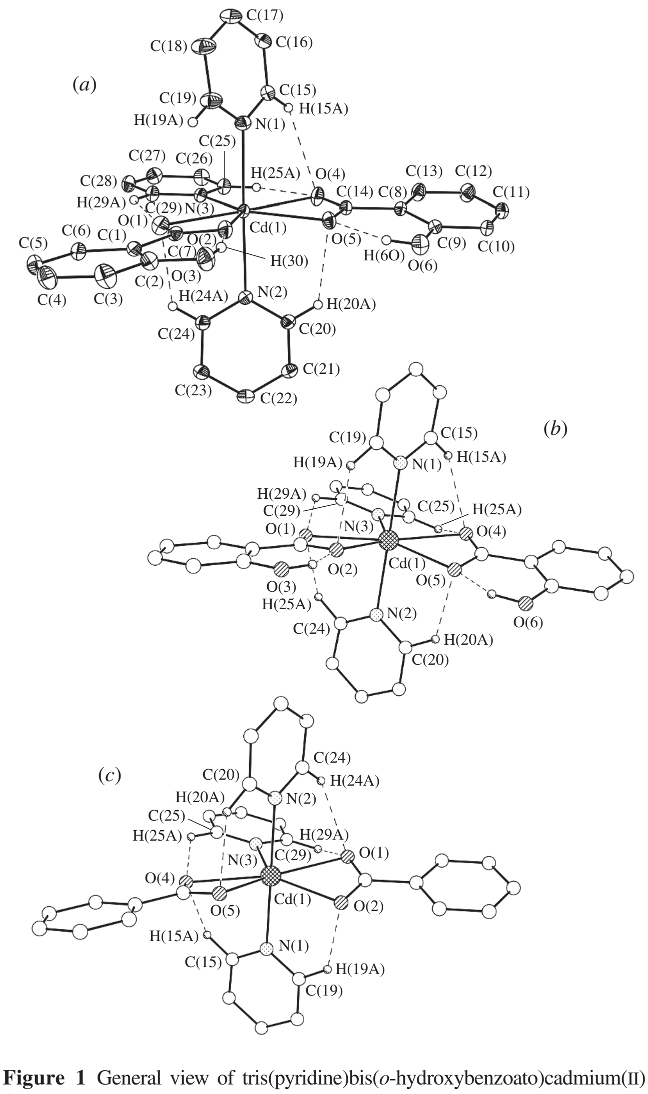

Figure 1 General view of tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) **1** [(*a*) X-ray and (*b*) DFT data] and tris(pyridine)bis(benzoato)cadmium(II) **2** [(*c*) DFT data]. Hydrogen atoms not involved in C–H···O interactions are omitted for clarity.

[†] Details of crystal structure refinement, multipole refinement, quantum chemical calculations and CSD search, the table of topological parameters, the tables of atomic coordinates according to DFT optimization, monopole, dipole, quadrupole and hexadecapole populations, atomic volumes and charges and residual electron density maps as well as molecular graph of **1** reconstructed from the high-resolution XRD data are available as Online Supplementary Materials (Figures S1–S7, Tables S1–S12). Results of CSD searches are summarized in a histogram therein.

CCDC 798772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

According to XRD data,[17] this system seems an ideal candidate for distinguishing the role of different factors in complex stabilization: (i) the coordination number of the cadmium ion is 7; (ii) the Cd–O bond lengths vary in a wide range [2.3869(9)–2.5191(9) Å]; (iii) there are strong intramolecular O–H···O bonds [O···O 2.544(1)–2.572(1) Å] and a plethora of shortened C–H···O contacts (H···O *ca.* 2.3–2.5 Å) between *o*-hydroxybenzoate and pyridine ligands. The topological analysis of $\rho(r)$ for this complex was carried out based on high-resolution XRD data and DFT calculations. To elucidate the role of intramolecular H-bonding, we performed the DFT calculation of model tris(pyridine)-bis(benzoato)cadmium(II) species **2** [Figure 1(*c*)].

The pentagonal pyramidal environment of the cadmium atom consists of four oxygen atoms in its equatorial plane and three nitrogen atoms: one of them occupies equatorial (almost coplanar with CdO_4) plane and two of them are axial ones (Figure 1). It seems that the variation of Cd–O bond lengths in the crystal and the gas phase (hereinafter denoted as **1** and **1a**, respectively) is mainly governed by the presence of strong intramolecular H-bonds. Indeed, in the gas phase (**1a**), the smallest Cd–O distances (2.386–2.393 Å) are observed for H-bonded atoms O(2) and O(5) (O···O 2.566 Å). Although in the crystal two of the Cd–O bonds [2.3490(8)–2.3869(9) Å] are also shorter than others (*ca.* 2.51 Å), this shortening is observed for another pair, namely, the O(1) and O(5) atoms. Therefore, the observed distribution of the Cd–O bond lengths cannot be directly attributed to the intramolecular H-bonds. This conclusion is consistent with the DFT data for **2** displaying the shortening of Cd–O bonds for the O(2) and O(5) atoms (2.368 *vs.* 2.512 Å), exactly as in **1a**, although the O–H···O bonds are *a priori* absent from **2**. The Cd–N bonds are less labile [2.3488(8)–2.3677(8) Å], and we can presume them to be stronger than the Cd–O ones. Finally, the C–O bonds in **1** and **1a** are significantly affected by these H-bonds, while their perturbation by the Cd–O interactions is almost negligible (Table S1†).

Based on the DFT data for **1a** and **2**, we can propose that the elongation of Cd–O bonds can result from the steric repulsion between the C–O carboxylic bonds and the pyridine ligand lying in the equatorial plane [Figure 1(*b*),(*c*)]. Indeed, the atoms O(1) and O(4) in **1a** and **2** are involved in the shortest C–H···O contacts with the C(29)–H(29) and C(25)–H(25) bonds (the H···O distance is ~2.30 Å). However, this assumption cannot explain the distribution of the bond lengths in the crystal of **1**, in which the C–H bonds of the pyridine moiety participate in the formation of similar C–H···O contacts (the H···O distance is ~2.5 Å) and thus should affect the Cd(1)–O(1) and Cd(1)–O(4) bonds to the same extent.

The analysis of available structural data for compounds containing the $CdPy_3(COO)_2$ fragment within the Cambridge Structural Database (CSD)[18] also allowed us to exclude such a factor as the structural *trans*-effect (Figure S1†). In a series of similar compounds, the distribution of the Cd–O bond lengths is rather chaotic with no definite trends, and neither the presence of hydrogen bonds nor the ligand structural *trans*-effect can explain the disposition of two longer Cd–O bonds in the above coordination polyhedron.

To quantify the perturbation level of all the factors influencing the metal-ligand bonding and to generalize the scale of all the interactions present, we analysed the chemical bonding pattern in the crystal of **1** by means of the deformation electron density (DED) distribution, atomic charges and topological parameters in BCPs.

Although the peculiarities of DED observed are typical (Figure 2), it should be noted that the Cd–N and Cd–O interactions are characterized by a peak-to-peak arrangement of *d*-orbitals and electron lone pairs instead of the peak-to-hole type, which is more common for bonds involving transition metals.[19] The same peak-to-peak type was recently found in ionic Gd–X bonds.[15]

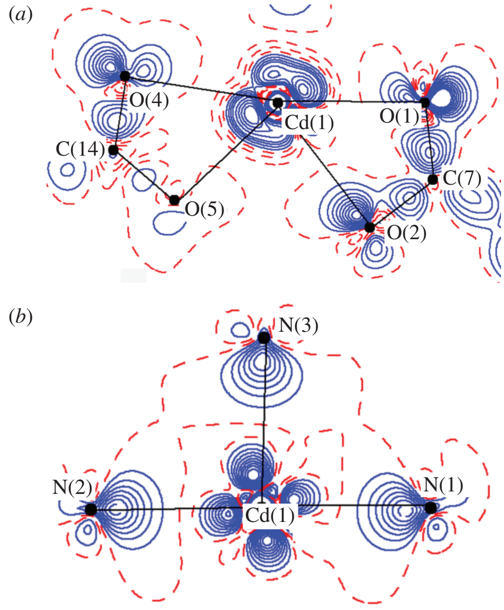

Figure 2 The DED maps in the planes of (*a*) Cd(1)O(1)O(4) and (*b*) Cd(1)N(1)N(3). The contours are drawn with 0.1 eÅ^{-3} step, the positive contours are solid, the negative contours are dashed. The deviations of O(2) and O(5) atoms from the Cd(1)O(1)O(4) plane are 0.14 and 0.44 Å, respectively.

The analysis of atomic charges (Q) obtained by the integration of $\rho(r)$ within the atomic basins[7] (Table S2†) revealed that, in a crystal, the charge of the Cd(1) atom is 1.83 *e*, which is close to the formal oxidation state +2, indicating the high ionicity of Cd–ligand bonds. As expected, the negative charge is mainly located on the benzoate ligands (–0.80 to –0.65 *e*), while the net charges of the pyridines are only from –0.20 to –0.10 *e*. The oxygen charges[7] confirm that the C–O bonds are mainly governed by the intramolecular H-bonds: the H-bonded O(2) and O(5) atoms bear lower charges (–0.88 and –0.87 *e*), as compared to the O(1) and O(4) atoms (–0.98 and –0.93 *e*). The charge of the N(1) atom is slightly lower (–0.91 *e*) than those for the nitrogens N(2) and N(3) (–0.93 *e* each), which is in a good agreement with the Cd–N bond lengths.

A small covalent component of the Cd–O bonding can be further illustrated by the values of $\nabla^2\rho(r)$ and local energy density $h_e(r)$ in the corresponding BCPs. Unlike the most of the transition metal–ligand bonds,[20] which correspond to the intermediate type in the AIM notation [$\nabla^2\rho(r) > 0$ and $h_e(r) < 0$ in BCP], the Cd(1)–O(2) and Cd(1)–O(4) bonds in **1** are of the closed-shell type [$\nabla^2\rho(r) > 0$ and $h_e(r) > 0$, Table S1†]; only the shortest Cd(1)–O(1) and Cd(1)–O(5) bonds are characterized by slightly negative values of $h_e(r)$. In contrast, the Cd–N and O–H···O bonds correspond to the intermediate type of interactions. This allows us to expect that the Cd–O coordinate bonds in complex **1** are weaker than the intramolecular O–H···O hydrogen bonds. Indeed, the energies of the O(3)–H(3O)···O(2) and O(6)–H(6O)···O(5) hydrogen bonds obtained using CEML[11] are high (18.2 and 20.3 kcal mol^{-1}, respectively). These values are typical of strong O–H···O bonds and comparable with *ab initio* and experimental estimations.[21,12(*e*)]

The energy of the Cd–O bonds is as small as 9–14 kcal mol^{-1} (Table S1) with an almost linear correlation between E_{int} and Cd–O bond lengths. The energies observed can be indirectly compared with experimental data. According to thermochemical measurements, the Cd–O bond energies in $CdX_2 \cdot nL$ (X = Cl, Br, I; n = 1, 2, 3; L = organic base containing CO or PO groups) are 42.6±9.8 and 34.0±2.2 kcal mol^{-1} for the complexes with the Cd coordination numbers of 3 and 4, respectively.[22] Assuming the Cd–X bond length to increase as a function of the coordination number (Figure S2†) and the relation between the binding energy and the bond length to be linear, one can predict the Cd–O binding energy for the complexes with a coordination number of 7 to be as small as ~8 kcal mol^{-1}, which is close to our E_{int} values. The Cd–N bonds in **1** are somewhat stronger (17–20 kcal mol^{-1}, see Table S1). As far as we are aware, there was only one charge-density study of cadmium derivatives, namely, the chain polymers $[M(\mu\text{-}X)_2(py)_2]$[23] (M = Cd, Zn; X = Cl, Br; the coordination number of a central atom is 6). The topological parameters of the Cd–N bonds [$\rho(r)$ ~ 0.30 eÅ^{-3}; $\nabla^2\rho(r)$ ~ 6.0 eÅ^{-5}], as well as the reported range of bond lengths (2.35–2.39 Å), are close to those in complex **1**. According to the $v(r)$ value[23] and CEML,[11] the energy of the Cd–N bonds is ~18.2 kcal mol^{-1}, which is similar to those in **1**, **1a** and **2**.

Finally, we have to mention the intramolecular C–H···O interactions, which were located based on the BCP search (see Figure S3†) and were found to be of the closed-shell type. The strongest C–H···O interactions C(29)–H(29A)···O(1) and C(25)–H(25A)···O(4) (E_{int} = 2.1 and 2.3 kcal mol^{-1}, respectively) are observed in the equatorial plane of the Cd atom. Although these interactions are stronger in the gas phase (E_{int} ~ 3.3 kcal mol^{-1}), they are, nevertheless, weak as compared with the O–H···O and Cd–O bonds. All other intramolecular C–H···O interactions are even weaker with the values of E_{int} of about 1.5 kcal mol^{-1}.

Among the intermolecular interactions, we should mention several weak C–H···O hydrogen bonds with the energy of 0.7–1.2 kcal mol^{-1}, which is quite common for organic molecules, as well as weak H···H (0.2–0.6 kcal mol^{-1})[12(*b*)] and stacking interactions (1.6 kcal mol^{-1}) between the pyridine and phenyl rings (Figure S4†). One can assume that the presence of this stacking interaction leads to the variation of the pyridine orientation and thus affects the strength and number of C–H···O interactions in **1** and **1a** (Figures 1 and S1).

Thus, multiple factors compete for governing the structure of tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) and relative compounds influencing the molecular conformation and bond lengths distribution. The estimation of competing interaction energies allowed us to evaluate the degree of their influence on the coordinate binding and to grade the perturbation level of each of them. The total energy of the Cd–ligand bonds is 104.0 kcal mol^{-1} according to XRD or 113.0 kcal mol^{-1} according to DFT data. The energy of all the C–H···O interactions is 9.3 (XRD) or 15.0 kcal mol^{-1} (DFT), *i.e.*, 8 or 13% of the Cd–ligand bond energy, respectively. Together with the energy of the intramolecular H-bonds (38.5 and 33.6 kcal mol^{-1}), they contribute 46 and 43% of the energy of the coordinate bonds. The above values illustrate that, in the complexes of heavy metal atoms with high coordination numbers, so-called secondary interactions (H-bonds) occupy nearly the same place in the energetic scale as the thought-to-be conventional coordinate bonds; thus, the question emerges of which of them are true secondary interactions. This is the reason why such systems do not display a clear trend of bond length variations, meaning that the fine structure of metal complexes is hardly predictable.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.04.017.

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