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A comparative study of a mixed-ligand copper(II) complex by the theory of atoms in molecules and the Voronoi tessellation

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The chemical bonding in a crystal of a new mixed-ligand copper(II) complex was characterized using the Bader theory of atoms in molecules and the Voronoi tessellation.

The topological analysis of the electron density distribution function $\rho(r)$ in a crystal of $Sn_2(OCH_2CH_2NMe_2)_2(OPh)_2$[1] in terms of the Bader theory of atoms in molecules (AIM)[2] revealed the agreement between the atomic and molecular descriptors obtained by AIM and Voronoi tessellation[3] approaches. Similar analysis performed for the complex $(C_4H_{11}N_2)_2(C_4H_{12}N_2)[Mo(CN)_8]$[4] has outlined some limits of a Voronoi tessellation in localizing weak van der Waals interactions in a crystal. We focused our attention on the energetic characteristics of coordination bonds that can be obtained within these two approaches.

It was found[5] that the energy of a closed-shell or an intermediate type of interactions (E_{int}) can be estimated using the Espinosa correlation[6]

$$E_{int} \approx -1/2v^e(r). \quad (1)$$

At the same time, within the Voronoi tessellation approach, the solid angle (Ω, in percentage of 4π steradian) of a common face for the Voronoi polyhedra (VPs) of atoms A and X is expected to be in proportion with the A–X interaction strength.[7] Thus, the shortening of an interatomic distance is typically accompanied by the strengthening of an interaction and enlargement of a solid angle. A comparison of these parameters obtained by two approaches will allow us to determine the limits of a Voronoi tessellation in analyzing coordination bonds and simplifying calculations of atomic and molecular descriptors.

The mixed-ligand copper complex [Cu(ppc)(MeOH)]·MeOH (**1**, ppc = *P*,*P*′-diphenylmethylenediphosphinate) was chosen for this purpose; high-resolution X-ray studies (Figure 1)† and multipole refinement were used to obtain the electron density distribution in the crystal of **1**.‡ In complex **1**, the Cu(1) atom adopts a distorted CuO_5 square pyramid geometry with a copper atom situated 0.2147(2) Å above the pyramid base. The base and vertex of the pyramid are formed by the oxygen atoms of two ppc ligands and methanol. The axial Cu–O bond is significantly longer than the equatorial ones (Figure 1); thus, one can expect the energies of Cu–O(ppc) bonds to be roughly comparable and to exceed that of the Cu–O(1S) bond. Note that crystal packing

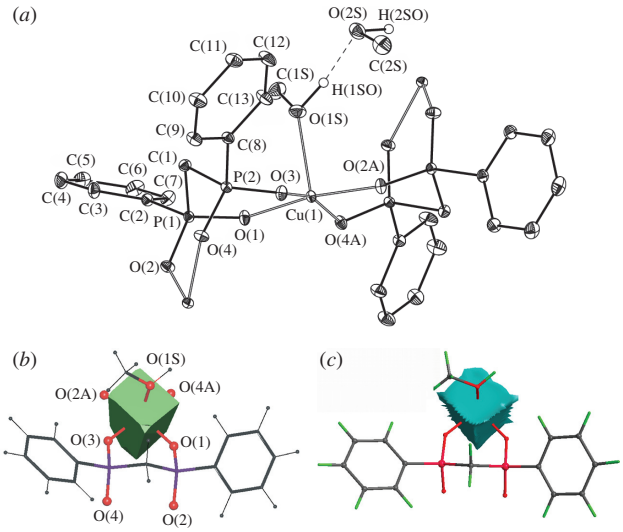

Figure 1 (*a*) General view of **1** in the representation of atoms by thermal ellipsoids (given with p = 70%) and atomic basins of the Cu(1) atom bounded with (*b*) VP faces and (*c*) a zero-flux surface. The O(2A) and O(4A) atoms are obtained from the basic one by the symmetry operation $-x+2, y+0.5, -z+0.5$. Selected bond distances (Å): Cu(1)–O(1) 1.9501(4), Cu(1)–O(2A) 1.9571(4), Cu(1)–O(3) 1.9590(4), Cu(1)–O(4A) 1.9878(4), Cu(1)–O(1S) 2.2339(4), C(1S)–O(1S) 1.4297(8), C(2S)–O(2S) 1.4292(10), P(1)–O(1) 1.5126(4), P(1)–O(2) 1.5169(4), P(1)–C(1) 1.8143(5), P(2)–O(3) 1.5108(4), P(2)–O(4) 1.5227(4), P(2)–C(1) 1.8138(5).

† *Crystallographic data*. Crystals of **1** ($C_{15}H_{20}CuO_6P_2$, M = 421.79) are monoclinic, space group $P2_1/c$, at 100 K: a = 10.9357(2), b = 9.2133(2) and c = 18.0899(3) Å, β = 104.605(1)°, V = 1763.73(6) Å^3, Z = 4, d_{calc} = = 1.588 g cm^{-3}, μ = 1.447 cm^{-1}, $F(000)$ = 868. Intensities of 158 415 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 120°$] and 25 891 independent reflections (R_{int} = 0.0461) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to wR_2 = 0.0803 and COF = 0.985 for all independent reflections and to R_1 = 0.0300 for 18 899 observed reflections with $I > 2\sigma(I)$. All calculations were performed using SHELXTL PLUS 5.0.[11]

CCDC 975047 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

‡ The multipole refinement was carried out within the Hansen–Coppens formalism[12] using the XD program package[13] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[14] The level of multipole expansion was hexadecapole for the copper atom and octapole for other nonhydrogen atoms. The refinement was carried out against F and converged to R = 0.0250, wR = 0.0265 and GOF = 0.8560 for 18 466 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld criteria. The residual electron density was no greater than 0.39 eÅ^{-3}. Analysis of the topology of $\rho(r)$ function was carried out using the WinXPRO program package.[15]

Table 1 Topological parameters of $\rho(r)$ in the BCPs for the Cu–O bonds.[a]

Bond	$\rho(r)$/eÅ^{-3}	$\nabla^2\rho(r)$/eÅ^{-5}	$v^e(r)$/a.u.	$h^e(r)$/a.u.	E_{int}/kcal mol^{-1}	Ω (%)
Cu(1)–O(1S)	0.33	4.9	–0.055	–0.002	17.3	16.5
Cu(1)–O(1)	0.60	9.9	–0.136	–0.017	42.8	20.5
Cu(1)–O(2)	0.59	9.5	–0.131	–0.016	41.1	20.9
Cu(1)–O(3)	0.59	9.6	–0.131	–0.016	41.1	21.1
Cu(1)–O(4)	0.55	8.7	–0.118	–0.014	37.1	21.0

[a] For all bonds, d_1 and d_2 are the distances from Cu and O atoms to the BCPs, $d_1/d_2 = 0.99$; $\rho(r_{BCP})$ is the electron density at the BCP; $\nabla^2\rho(r_{BCP})$ is the corresponding Laplacian; $v^e(r)$ stands for the potential energy density; $h^e(r)$ is the electron energy density; E_{int} is the energy of interaction calculated as $-1/2v^e(r)$; and Ω is the solid angle of the VP face corresponding to the bond.

effects (see bellow) cause the equatorial Cu–O bond distances to vary from 1.9501(4) to 1.9876(4) Å. This gives an opportunity to compare not only the equatorial and axial Cu–O bonds but also the two models (AIM and a Voronoi tessellation) in describing the small features of E_{int}(Cu–O) perturbations.

The ppc ligand has a pseudo-perpendicular ($\varphi = 101°$) arrangement of phenyl groups, and it is ligated in a bridge tetradentate bischelate mode. As a result, the infinite zig-zag chains of [Cu(ppc)(MeOH)] are formed in parallel with the crystallographic *b* axis. Three hydrogen bonds [O(2S)–H(2SO)···O(4), O(1S)–H(1SO)···O(2S) and O(2S)–H(2SO)···O(1)] also occur in **1**; the O···O separations are 2.797(1), 2.776(1) and 3.059(1) Å and OHO angles are 171(1), 172(1) and 119(1)°, respectively. The O(2S)–H(2SO)···O(4) H-bond may be the reason why the Cu(1)–O(4) bond is elongated in comparison with the remaining Cu–O(ppc) bonds.

Static deformation electron density (DED) distribution in the region of the Cu–O bonds in **1** shows them to be of both peak-to peak and peak-to-hole types. The former interactions involve the Cu(1)–O(1S) bond with the DED maximum located in the vicinity of the O(1S) atom and directed toward the DED maximum attributed to *d*-orbitals of Cu(1) [Figure 2(*a*)]. Four Cu(1)–O(ppc) bonds belong to the peak-to-hole type with the lone pairs of oxygen atoms directed toward the region of the DED depletion near Cu(1) [Figure 2(*b*)]. Despite differences in chemical bonding patterns for the Cu–O bonds, the topological parameters of $\rho(r)$ at corresponding bond critical points (BCPs) [positive $\nabla^2\rho(r)$ and negative electron energy density $h^e(r)$ values in BCP, Table 1] clearly indicate that all of them are of the intermediate type of interactions. In comparison with a long apical Cu–O interaction in $Na_2Cu(CO_3)_2$,[5(a)] the Cu(1)–O(1S) bond is not weak enough to change its type to the closed-shell one.

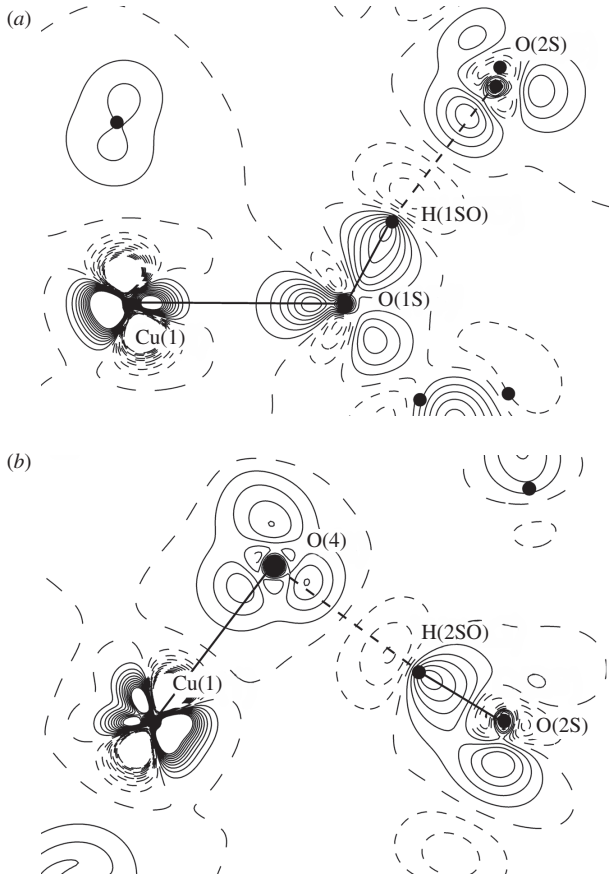

Figure 2 Sections of the static deformation density in the (*a*) Cu(1)O(1S)O(2S) and (*b*) Cu(1)O(4)O(2S) planes. Contours are drawn with a 0.1 eÅ^{-3} interval, the nonpositive contours are dashed.

For the Cu–O bonds, the BCPs almost equally divide the corresponding bond paths (Table 1). This fact, together with the VP shape of the copper atom (Figure 1), indicates that VP(Cu) is a good approximation of the copper atom in **1**: the number of its major faces coincides with CN(Cu) = 5 and its volume [V_{VP}(Cu) = 9.9 Å^3] represents well the volume of the copper atomic basin [V_{AIM}(Cu) = 12.1 Å^3]. The BCPs of C–H and O–H bonds are significantly shifted from their centers, so that the atomic V_{VP} and V_{AIM} values significantly deviate from each other. Nevertheless, the molecular VP volume approximates well the volume of a molecular domain for MeOH molecules. The found mean volumes of methanol molecules are 58.3 and 50.0 Å^3 for the two models. The AIM volumes and the atomic charges were obtained by the integration of $\rho(r)$ over the atomic basins. We obtained +0.94e for Cu(1) and –0.79e for the ppc anion, and the coordinated and uncoordinated methanol species have the AIM charges of –0.19e and –0.02e, respectively. The difference between the latter values can be caused by electron density transfer from the copper atom to the ligated methanol molecule. An almost neutral charge of the uncoordinated methanol is rather common for solvate molecules.[5(c)]

As mentioned above,[5(h)] the energies of closed-shell interactions and those of the intermediate type (E_{int}) can be estimated using correlation (1).[6] The values of E_{int} for hydrogen bonds obtained in this way are 1.7–5.5 kcal mol^{-1} with the largest one for the H-bond O(2S)–H(2SO)···O(4). Note that although all H-bonds involve the O(2S) atom of a solvate molecule, the latter is characterized by rather high mobility and the crystal decomposes in air in a matter of seconds.

The values of E_{int} for the coordination bonds Cu–O are 17.3 and 37.1–42.7 kcal mol^{-1} in the axial and the equatorial bonds, respectively. The E_{int} of the Cu(1)–O(1S) bond (17.3 kcal mol^{-1}) exceeds the energy of methanol adsorption on copper (8.3 kcal mol^{-1})[8] and agrees with the binding energy between the Cu^+ ion and MeOH (13.4–13.9 kcal mol^{-1})[9] that should be weaker than Cu^{2+}–MeOH interaction in **1**. While there are no experimental or theoretical estimations for Cu^{2+}–(O–P) bonds, one can note an almost linear correlation between the Cu–O bond length and the value of E_{int} (Table 1).

The value of Ω for the axial Cu–O interaction is lower than those for the equatorial ones, in which the higher the value of Ω, the weaker the Cu–O(ppc) bond. To attest the assumption that Ω

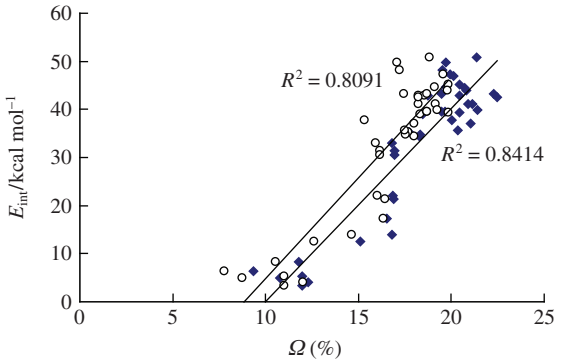

Figure 3 Plot of E_{int} *vs.* Ω for 41 Cu–O interactions. Solid rhombs and empty circles represent Ω values for the faces of the Voronoi polyhedra constructed with and without minor faces, respectively.

of a VP(Cu) face is proportional to the strength of the Cu–O interactions, we calculated E_{int} for the compounds containing Cu–O bonds that have been previously investigated by means of AIM, namely, $Cu_2(AcO)_4(H_2O)_2$,[10(a)] $[Cu_2(ap)_2(L)_2]$ (ap = 3-aminopropanolate; L = NO_2^-, NO_3^-, $HCOO^-$),[10(b)] $[Cu(glygly)(H_2O)_2]\cdot H_2O$ (glygly = glycylglycinato),[10(c)] $[Cu(iz)_2(CN_3O_2)_2]$ (iz = imidazole),[10(d)] $[Cu(cfx)(H_2O)_3]SO_4\cdot 2H_2O$ (cfx = ciprofloxacin)[10(e)] and $Na_2Cu(CO_3)_2$.[5(a)] The estimated values of E_{int}(Cu–O) were compared with the corresponding values of Ω to find a linear correlation between these parameters (Figure 3). Calculation of Ω(Cu–O) for the polyhedron with minor faces removed [so that the coordination number is equal to the number of VP(Cu) faces] allows increasing the correlation factor from 0.81 to 0.84. The resulting linear dependence

$$E_{int} = 4.02\Omega - 40.2 \text{ (kcal mol}^{-1}\text{)} \quad (2)$$

indicates that chemical bonding is characterized by $\Omega > 10\%$ {as it was obtained for Mo–N and H-bonds in $(C_4H_{11}N_2)_2(C_4H_{12}N_2)[Mo(CN)_8]$}[4] and allows one to perform the semiquantitative estimation of coordination bond strength. At the same time, note that the discussion of small E_{int} perturbations for this type of interactions is beyond the scope of correlation (2), and the values of Ω should be calculated for the polyhedron with major faces only.

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