Available online at www.sciencedirect.com
SCIENCE DIRECT®
Mendeleev Commun., 2007, **17**, 71–73

Mendeleev Communications

Influence of weak coordination on the electronic characteristics of the copper(II) atom: charge density analysis in the crystal of azurite

Yulia V. Nelyubina,[a,†] **Mikhail Yu. Antipin,**[a] **Elena L. Belokoneva**[b] **and Konstantin A. Lyssenko***[a,‡]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*
[b] *Department of Geology, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. E-mail: elbel@geol.msu.ru*

DOI: 10.1016/j.mencom.2007.03.005

The chemical bonding peculiarities of two nonequivalent copper atoms with coordination numbers 4 and 5 in the crystal of azurite are estimated and compared within a topological analysis of the electron density function.

The main characteristics of a metal atom in a complex are the coordination number and the type of a polyhedron. Indeed, when their difference is significant, it affects all electronic parameters of the metal including its charge, *d*-orbital populations and atomic radii. Furthermore, in structural investigations, even a weak additional coordination causes a considerable variation of metal configuration. It should be noted that an analysis of the experimental electron density distribution $\rho(r)$ function in the crystal makes possible to estimate charges, *d*-orbital occupancies,[1] *etc.*, especially within Bader's 'Atoms in Molecule' (AIM) theory[2] and thus interconnect geometrical and electronic characteristics using the same method of analysis. In order to analyse such a type of relationships, we have undertaken the high-resolution X-ray diffraction (XRD)[§] study of azurite $Cu_3(CO_3)_2(OH)_2$ **1**. The choice of the crystal of **1** was due to the presence of two independent copper atoms, which are characterised by different coordination numbers 4 and 5. In addition, the previously reported charge density investigation of **1** at 298 K focused on the qualitative description of the electron distribution (analysis of difference maps, estimation of 3*d*-orbital populations and its correlation with the antiferromagnetic properties) has shown that two copper atoms despite of the variation of coordination number are rather similar.[3]

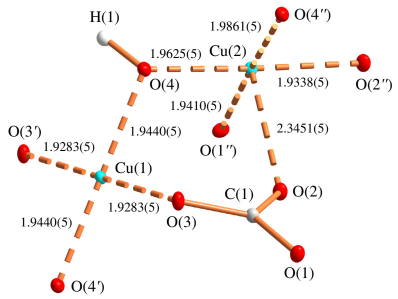

Figure 1 The general view of **1** in the representation of atoms by thermal ellipsoids at $p = 50\%$. The Cu···O distances (Å) are given. The bond lengths (Å) and angles (°) for CO_3 group are: C(1)–O(1) 1.2760(7), C(1)–O(2) 1.2881(8), C(1)–O(3) 1.2897(8), O(1)–C(1)–O(2) 121.19(6), O(1)–C(1)–O(3) 119.55(6), O(2)–C(1)–O(3) 119.26(5). The atoms O(3′) and O(4′) are obtained from the basic ones by the symmetry operation $1 - x, -y, -z$; O(1″) by $x, -y - 1/2, z + 1/2$; O(2″) by $-x + 1, -y - 1, -z$; O(4″) by $-x, -y - 1, -z$.

The XRD study has revealed that the crystal structure of azurite is built by CO_3 triangles and Cu–4O distorted squares. The Cu···O separation in these squares is in the ranges 1.9283(5)–1.9440(5) and 1.9338(5)–1.9861(5) Å for Cu(1) and Cu(2) atoms, respectively (Figure 1). It should be noted that the atoms Cu(1) (located in the special position $\bar{1}$) and Cu(2) are significantly different in a crystal. As mentioned earlier,[3] the next-nearest neighbours of Cu(2) are two oxygens at the distances of 2.3451(5) and 2.7572(5) Å. The analogous Cu(1)···O interatomic separation exceeds the corresponding one for the Cu(2) atom and is equal to 2.9748(5) Å. Thus, the coordination polyhedra of Cu(1) and Cu(2) atoms are different and can be described as square and distorted tetragonal pyramid with a square-planar Cu–4O base [the mean deviation from the plane is 0.0169(5) Å], respectively (Figure 1). The angles between oxygens of the Cu(2)–4O base and the O(2) apical atom vary in the range 88.05(2)–92.79(2)°.

Note that the distance of 2.3451(5) Å observed for Cu(2) in **1** is rather common for the intermolecular Cu···O contact for Cu^{II} atom with the 4 + 1 type of coordination. We found at least 134 ordered complexes in the Cambridge Structural Database (CSD) with a Cu···O separation in the range of 2.25–2.4 Å.

[†] A student of the Higher Chemical College (HCC) of the RAS.

[‡] A former student of the HCC RAS (1991–1995), now a lecturer at the HCC RAS.

[§] The crystal of azurite was provided by the V. I. Vernadsky State Geological Museum of the Russian Academy of Sciences, Moscow.

Crystallographic data: crystals of **1** ($C_2H_2Cu_3O_8$, $M = 344.66$) are monoclinic, space group $P2_1/c$, at 100 K: $a = 4.9970(2)$ Å, $b = 5.8315(5)$, $c = 10.3326(9)$ Å, $\beta = 92.279(4)°$, $V = 300.85(4)$ Å^3, $Z = 2$ $(Z' = 1/2)$, $d_{calc} = 3.805$ g cm^{-3}, (MoKα) = 105.52 cm^{-1}, $F(000) = 330$. Intensities of 33891 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 105°$] and 3484 independent reflections ($R_{int} = 0.0352$) were used in 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. Hydrogen atom was located from the Fourier synthesis of the electron density and refined in the isotropic approximation. For **1**, the refinement converged to $wR_2 = 0.0378$ and GOF = 1.005 for all independent reflections [$R_1 = 0.0190$ was calculated against F for 2795 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0. CSD 417591 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshsafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de; http://www.fizkarlsruhe.de/ecid/Internet/en/DB/icsd/depot_anforderung.html).

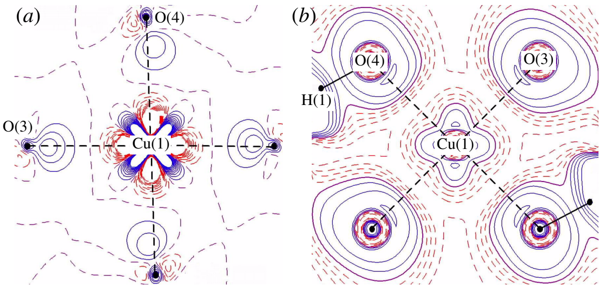

Figure 2 (*a*) DED and (*b*) ELF in the section of Cu(1)–4O square in the crystal of **1**. The contours are drawn with 0.1 eÅ^{-3} steps; (*a*) the negative contours and (*b*) contours with ELF < 0.5 are dashed.

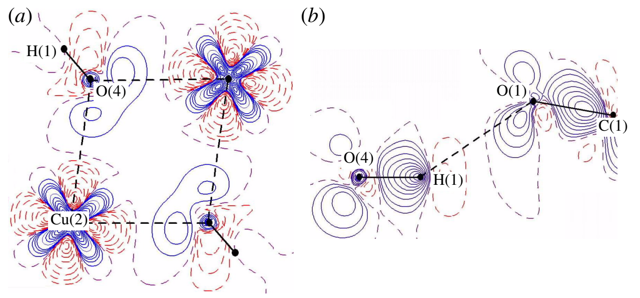

Figure 3 The DED in the sections of (*a*) Cu(2)–Cu(2) dimer and (*b*) H-bond in the crystal of **1**. The contours are drawn with (*a*) 0.4 and (*b*) 0.1 eÅ^{-3} steps; the negative contours are dashed.

The Cu(1) and Cu(2) atoms play different roles in the formation of the crystal packing of azurite. Thus, Cu(2) atoms are assembled into centrosymmetric dimers by the Cu(2)···O(4)–H(1) bonds with the Cu···Cu separation equal to 2.9800(8) Å. In addition to cation···anion interactions, we can fetch out anion···anion ones, namely, the O(4)–H(1)···O(1) and O(4)···O(3) [2.9973(5) Å] contacts. The former according to the O···O distance [2.9817(8) Å] and the OHO angle [150.5(3) Å] corresponds to a weak hydrogen bond.

In order to estimate whether or not the above Cu···O interatomic 'contacts' observed in the crystal of **1** (Figure 1) correspond to attractive interactions and estimate their influence on the electronic configuration of copper atoms, we performed the topological analysis of the $\rho(r)$ in **1**.¶

The static deformation electron density (DED) distribution function in the section of the carbonate group in the crystal of **1** is characterised by expected features. The DED accumulation is observed in the area of C–O bonds. The DED peaks attributed to electron lone pairs (LPs) are located in the vicinity of all O atoms.

The DED and electron localization function (ELF)[11] in sections containing copper atoms are characterised by a significant anisotropy in the vicinity of Cu(1) and Cu(2) that is common for transition metal complexes.[12] Analysis of ELF and DED in **1** clearly shows the 'cross' type of the charge density accumulation in the vicinity of copper atoms, which can be attributed to 3*d* orbitals. It is important that all of the Cu···O interactions in Cu–4O squares correspond to the 'peak to hole' type (Figure 2).[13] The same pattern was observed for the DED function in the plane of the Cu(2)–Cu(2′) dimer [Figure 3(*a*)], where maxima corresponding to LPs of the O(4) atom are located along the Cu···O lines. Finally, despite of a significant deviation of the O–H···O angle from 180°, the inspection of DED distribution for the O(4)–H(1)···O(1) contact [Figure 3(*b*)] has revealed the principal characteristics of charge distribution (in particular, the polarization of LP involved into the interaction) that are common for H-bonds.

In spite of the presence of additional Cu(2)···O(2) interaction, the analysis of DED and ELF has not shown any meaningful charge redistribution. As it can be seen (Figure 4), the accumulation of charge in the vicinity of Cu atoms above and below the Cu–4O base for both functions is almost the same. Note that the apical Cu(2)···O contact, in contrast to the above Cu···O ones, corresponds to the 'peak to peak' type.

Thus, we can conclude that, despite of the variation of coordination polyhedron, the qualitative picture of charge distribution for the copper atoms Cu(1) and Cu(2) is almost the same.

The analogous tendency is observed for the 3*d* orbital occupancies of copper atoms. The corresponding parameters were estimated by means of the orbital population analysis for transition metals proposed by Holladay *et al.*[8] Before the calculation, the copper atoms were restrained by symmetry. On the basis of their coordination polyhedra, the coordination systems of Cu(1) and Cu(2) atoms were chosen as for 4/*mmm* and *mm*2 point groups, respectively. The *x* and *y* axes were directed to the corners of the Cu–4O squares and the *z* axis to its normal, which in the case of Cu(2) coincides with the line of the Cu(2)···O(2) additional contact. According to this analysis, the non-bonding d_{xy} [2.24/2.22 for Cu(1)/Cu(2)] and d_{z^2} (2.08/2.22) orbitals of copper ions are most populated with the occupancy of both d_{xz} and d_{yz} equal to 2.06/1.96. In accordance with the published data,[3] the $d_{x^2-y^2}$ orbital was found to be depopulated (1.37/1.49). Although the orbital occupancies vary slightly, the value of total *d*-population is the same (9.81). This fact also demonstrates the similarity of copper atoms in the crystal of azurite.

In spite of the above resemblance of the Cu(1) and Cu(2) atomic parameters, the characteristic set of bond critical points (CPs) (3, –1) for them is different in principle. Thus, around the Cu(1) atom, we have found only four CPs (3, –1) corresponding to Cu–O bonds, while in the case of the Cu(2) atom in addition to critical points (3, –1) for Cu–4O base the bond CP for apical Cu(2)···O(2) contact was located. Moreover, the CPs (3, –1) were also found for the O–H···O H-bond and rather unusual

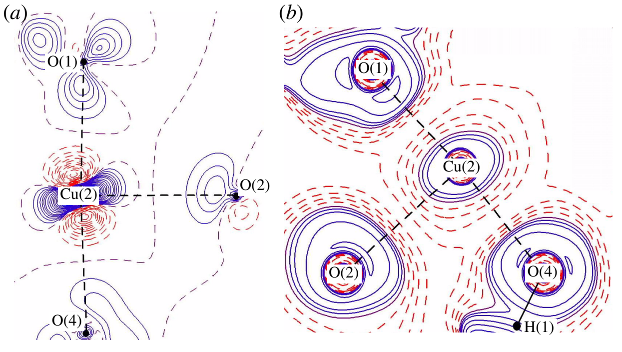

Figure 4 (*a*) DED and (*b*) ELF in the section of the additional Cu(2)···O(2) contact in the crystal of **1**. The contours are drawn with (*a*) 0.2 and (*b*) 0.1 eÅ^{-3} steps; (*a*) the negative contours and (*b*) contours with ELF < 0.5 are dashed.

¶ The multipole refinement was carried out within the Hansen–Coppens formalism[4] using the XD program package[5] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[6] Before the refinement, C–H bond distances were normalised to the values of 0.97 Å obtained from the neutron data.[7] The level of multipole expansion was hexadecapole for copper and octupole for carbon and oxygen atoms. The dipole D_{10} and the hexadecapole H_{40} were refined for hydrogen atom for more accurate description of hydrogen bonds. The multipole occupancies of the Cu(1) and Cu(2) atoms were refined with the 4/*mmm* and *mm*2 symmetry restrains, respectively.[8] The refinement was carried out against *F* and converged to $R = 0.0135$, $wR = 0.0165$ and GOF = 0.90 for 1555 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[9] (difference of the mean square displacement amplitudes along the bonds was not larger than 3×10^{-4} Å^2). The residual electron density was no more than 0.23 eÅ^{-3}. Analysis of topology of the $\rho(r)$ function was carried out using the WINXPRO program package.[10]

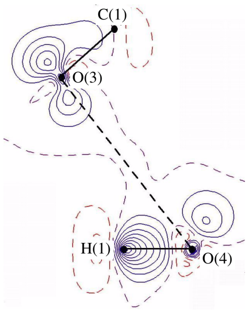

Figure 5 The DED section in the plane of O(4), H(1) and O(3) atoms. Contours are drawn with a 0.1 eÅ^{-3} step; the negative contours are dashed.

anion···anion O(3)···O(4) interaction.[14] As it can be seen from the DED in the plane of O(3)···O(4)–H(1), the latter corresponds to charge transfer from the LP of carbonate oxygen to the O(4) atom (Figure 5). Although this interaction formally can be considered as a weak H-bond (O···H equal to 2.52 Å), the closer examination of the $\rho(r)$ topology has revealed that the bond path[2] is actually observed between O(3) and O(4) atoms.

The $\rho(r)$ values in CPs (3, –1) for Cu···O interactions vary slightly (0.54–0.60 eÅ^{-3}) with the only exception of apical one for which the corresponding parameter is only 0.23 eÅ^{-3}. The above decrease of $\rho(r)$ in CPs (3, –1) is also reflected in the type of interatomic interactions. Thus, all of the Cu–O bonds in the Cu–4O squares correspond to the intermediate type of interactions with positive values of $\nabla^2\rho(r)$ (9.24–11.15 eÅ^{-5}) and negative electron energy densities [$h_e(r)$] varying in the range –0.01284 to –0.01039 a.u.[2] In contrast, the apical Cu···O contact is closer to O–H···O and O···O ones and is of the closed-shell type [$\nabla^2\rho(r) = 3.64$ eÅ^{-5} and $h_e(r) = 0.0023$ a.u.]. The values of the $\rho(r)$ function for H-bond and anion···anion interaction are equal to 0.07 and 0.08 eÅ^{-3}, respectively.

It should be noted that the formation of a three-dimensional framework results in the presence of numerous ring and cage critical points. In particular, we can mention the CP (3, +1) [$\rho(r) = 0.19$ eÅ^{-3}] at the centre of the Cu_2O_2 ring, which clearly shows the absence of direct metal···metal interactions.

The energy of the contacts (E_{cont}) was estimated on the basis of the Espinosa correlation scheme.[15] Thus, the values of the Cu–O bonds energy vary in the ranges 42.9–43.7 and 10.4–44.0 kcal mol^{-1} for Cu(1) and Cu(2), respectively, with the smallest one in the case of the apical Cu(2)···O(2) interaction. Surprisingly, the overall energies of the contacts formed by copper atoms (173.3 and 175.4 kcal mol^{-1}) are very close to each other: their difference is ~2 kcal mol^{-1}. For comparison, E_{cont} for the weak O(4)–H(1)···O(1) hydrogen bond equal to 1.7 kcal mol^{-1} is even smaller than E_{cont} for the O(3)···O(4) contact (2.0 kcal mol^{-1}).

To investigate the effective charge distribution in the crystal of **1**, we determined the atomic basins (Ω) surrounded by a zero-flux surface [the integrated value of $-1/4\nabla^2\rho(r)$ for copper was no more than 1.5×10^{-4} a.u.][2] and integrated $\rho(r)$ over Ω. The charges obtained according to this procedure lead to +0.71/+0.74 and –0.69 e for Cu(1)/Cu(2) and the CO_3 group, respectively. The atomic volumes for copper atoms are slightly different and equal to 12.95 and 10.65 Å^3.

Consequently, in spite of the different coordination polyhedra of Cu(1) and Cu(2) atoms, their topological characteristics, such as charge, *d*-orbital populations and the energy of Cu···O contacts, are practically identical. However, even such insignificant variations in the surrounding of coppers cause a considerable difference in their atomic energies. The corresponding parameter was estimated by the integration of the experimental $h_e(r)$[2] over Ω that leads to atomic contribution to total energy of the system. According to this procedure, the Cu(1) and Cu(2) atom energies (E_{at}) have been obtained and the value of $\Delta E_{at} = E_{Cu(1)} - E_{Cu(2)}$ was 138.2 kcal mol^{-1}. Although such an estimation of E_{at} as a function of polyhedron variation has not been carried out previously, the analysis of available published data (*e.g.*, see ref. 16) shows that our value is quite reliable. It is important to indicate that the difference in corresponding E_{at} for carbonate oxygen atoms is also substantial with a maximum absolute value for O(2) and ΔE_{at} for O(1) and O(3) equal to 96.6 and 30.6 kcal mol^{-1}. Furthermore, the same trend is observed for total E_{cont} calculated according to the Espinosa correlation[15] [45.7, 54.0 and 43.8 kcal mol^{-1} for O(1), O(2) and O(3) atoms, respectively].

Thus, we may conclude that, for copper atoms with the same ligands, the exchange of 4-coordination to 4 + 1 and, probably, 4 + 2 or 4 + 1 + 1 affects almost negligibly the electron accumulation domains (according to various functions), 3*d* occupancies and even metal charges. However, the careful consideration of an atomic contribution to the total energy gives us the possibility not only to reveal these differences but also to estimate them quantitatively.

This study was supported by the Russian Foundation for Basic Research (project no. 06-03-32557), the Foundation of the President of the Russian Federation (Federal Programme for the Support of Leading Scientific Schools, grant no. NSh 1060.2003.30, and Young Doctors, grant no. MK-1054.2005.3), and the Russian Science Support Foundation.

References

1 (*a*) V. G. Tsirelson and R. P. Ozerov, *Electron Density and Bonding in Crystals: Principles, Theory and X-Ray Diffraction Experiments in Solid State Physics and Chemistry*, IOP Publishing Ltd., Bristol and Philadelphia, 1996; (*b*) T. S. Koritsanszky and P. Coppens, *Chem. Rev.*, 2001, **101**, 1583; (*c*) C. Gatti, *Z. Kristallogr.*, 2005, **220**, 399.

2 R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.

3 E. L. Belokoneva, Yu. K. Gubina and J. B. Forsyth, *Phys. Chem. Minerals*, 2001, **28**, 498.

4 N. K. Hansen and P. Coppens, *Acta Crystallogr.*, 1978, **A34**, 909.

5 T. S. Koritsansky, S. T. Howard, T. Richter, P. Macchi, A. Volkov, C. Gatti, P. R. Mallinson, L. J. Farrugia, Z. Su and N. K. Hansen, *XD – A Computer Program Package for Multipole Refinement and Topological Analysis of Charge Densities from Diffraction Data*, 2003.

6 Z. Su and N. K. Hansen, *Acta Crystallogr.*, 1998, **A54**, 646.

7 F. Zigan and H. D. Schuster, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, 1972, **135**, 416.

8 A. Holladay, P. C. Leung and P. Coppens, *Acta Crystallogr.*, 1983, **A39**, 377.

9 F. L. Hirshfeld, *Acta Crystallogr.*, 1976, **A32**, 239.

10 (*a*) A. Stash and V. Tsirelson, *WinXpro, A Program for Calculation of the Crystal and Molecular Properties Using the Model Electron Density*, 2001, a further information available at http://xray.nifhi.ru/wxp/; (*b*) A. Stash and V. J. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371.

11 V. Tsirelson and A. Stash, *Chem. Phys. Lett.*, 1998, **285**, 170.

12 (*a*) P. Macchi and A. Sironi, *Coord. Chem. Rev.*, 2003, **238–239**, 383; (*b*) F. Cortes-Guzman and R. F. W. Bader, *Coord. Chem. Rev.*, 2005, **249**, 633; (*c*) K. A. Lyssenko, A. A. Korlyukov, D. G. Golovanov, S. Yu. Ketkov and M. Yu. Antipin, *J. Phys. Chem.*, 2006, **A110**, 6545.

13 (*a*) V. Tsirelson and A. Stash, *Chem. Phys. Lett.*, 1998, **285**, 170; (*b*) V. G. Tsirelson, P. F. Zou, T. H. Tang and R. F. W. Bader, *Acta Crystallogr.*, 1995, **A51**, 143.

14 (*a*) A. M. Pendas, A. Costales and V. Luana, *J. Phys. Chem.*, 1998, **102**, 6937; (*b*) V. Tsirelson, A. S. Avilov, G. G. Lepeshov, A. K. Kulygin, J. Stahn, U. Pietsch and J. C. H. Spence, *J. Phys. Chem.*, 2001, **105**, 5068; (*c*) Yu. V. Nelyubina, M. Yu. Antipin and K. A. Lyssenko, *J. Phys. Chem.*, 2007, **111**, 1091.

15 (*a*) E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170; (*b*) E. Espinosa, I. Alkorta, I. Rozas, J. Elguero and E. Molins, *Chem. Phys. Lett.*, 2001, **336**, 457.

16 (*a*) R. F. W. Bader and D.-C. Fang, *J. Chem. Theory Comput.*, 2005, **1**, 403; (*b*) I. Alkorta and J. Elguero, *Chem. Phys. Lett.*, 2006, **417**, 367.

Received: 24th October 2006; Com. 06/2802