4066 *Inorg. Chem.* **1998,** *37,* 4066−4069

Further Study of Very Close Nonbonded $Cu^{I}-Cu^{I}$ Contacts. Molecular Structure of a New Compound and Density Functional Theory Calculations

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Received February 5, 1998

A new compound containing a $Cu^{I}-Cu^{I}$ unit with a short internuclear distance, 2.453(1) Å, is reported. The question of whether such a short distance justifies the postulation of a metal−metal bond is addressed using density functional theory (DFT). The new compound is $Cu_2(hpp)_2$, where hpp^- ($C_7N_3H_{12}$) is the anion derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine. $Cu_2(hpp)_2$ crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$ and cell dimensions $a = 7.320(2)$ Å, $b = 12.418(4)$ Å, $c = 8.689(2)$ Å, and $\beta = 93.76(2)°$. The density functional calculations show that the close approach of the copper atoms is predictable without involving any significant amount of covalent bonding. A DFT calculation on the $Cu_3[(p\text{-tol})N_5(p\text{-tol})]_3$ molecule also foretells the observed short Cu−Cu separation (2.35 Å observed vs 2.38 Å calculated) but, again, does not imply the formation of Cu−Cu bonds. Very short Cu^{I} to Cu^{I} distances can be attributed to a combination of strong Cu−N bonding and very short (ca. 2.2 Å) bite distances for the ligands.

Introduction

Interactions between transition metal atoms can be formulated, qualitatively, in terms of overlaps of the metal d orbitals, giving rise to σ, π, and δ bonding and antibonding molecular orbitals.[1] As long as there are fewer electrons occupying the antibonding orbitals than there are in the bonding orbitals, metal−metal bonds will be formed and ambiguity seldom arises as to the bond order. In fact, the M−M bonds of order 1−4 are well established in numerous metal compounds.[1] Similarly, a bond order of zero may also be assigned if all the bonding and antibonding orbitals are fully occupied. Examples are the d^8-d^8 $M_2(RNCHNR)_4$ compounds (M = Ni, Pd)[2] and the $d^{10}-d^{10}$ $M_2(RNCHNR)_2$ compounds (M = Cu, Ag).[3] Molecular orbital calculations[2,3] previously showed that the formal M−M bond order is indeed zero in all these compounds.

In this paper we report a new addition to the family of dinuclear compounds with a $d^{10}-d^{10}$ electronic configuration, namely, $Cu_2(hpp)_2$, where hpp^- = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate. A notable feature in the structure of this molecule is that the distance between the Cu(I) centers is only 2.4527(10) Å, which is very similar to those in $Cu_2(RNCHNR)_2$[3] (2.497 Å) and $Cu_2(RNNNR)_4$[4] (2.451 Å). The structural and electronic similarities among these Cu(I) compounds suggest that one should again not expect the formation of a Cu−Cu bond in $Cu_2(hpp)_2$.

We have already applied density functional theory (DFT) to molecules that have pairs of metal atoms bonded each other with bond orders of 1−4. It was found that DFT reliably generates the correct structures of such molecules.[5] DFT has not previously been applied to the case where, despite the presence of bridging ligands and a close approach of the metal atoms, metal−metal bonding is not believed to occur. We take this occasion to report such a study.

In addition to calculations on the new compound, $Cu_2(hpp)_2$, the DFT method has also been applied to the trinuclear, tris-bridged compound,[6] $Cu_3(ArN_5Ar)_3$, which has previously been studied by other theoretical methods.[7,8]

Procedures

Preparative and crystallographic methods have previously been described.[9]

Preparation of $Cu_2(hpp)_2$. A reaction flask was charged with 0.15 g (1.5 mmol) of CuCl and 0.22 g (1.5 mmol) of Li(hpp) and cooled to −78 °C. THF (10 mL) was added and the reaction mixture stirred while cold. After 90 min, a white solid, namely $Cu_2(hpp)_2$, was separated from the lightly purple solution via filtration. $Cu_2(hpp)_2$ was washed with 5 mL of hexane and dried under vacuum, giving a yield of 63%. Colorless crystals of $Cu_2(hpp)_2$ grew from a THF solution carefully layered with hexanes. ^{1}H NMR (C_6D_6, ppm): $\delta = 1.51$ (quin, CH_2), 2.61 (t, CH_2), 3.32 (t, CH_2). UV/vis (toluene): λ_{max} (nm) = 352 (sh), 288. IR (KBr, cm^{-1}): 2937.9, 2919.6, 2877.1, 2846.6, 1600.1, 1518.3, 1504.1, 1461.7, 1442.2, 1383.1, 1361.0, 1336.1, 1318.1, 1305.8, 1280.9, 1254.1, 1225.9, 1208.8, 1149.1, 1116.0, 1099.7, 1069.7, 1026.4, 902.7, 802.1, 764.9, 733.4, 719.7, 561.8.

Crystallographic Studies. A crystal was mounted on the tip of a quartz fiber and cooled to −60 °C under a nitrogen stream on the diffractometer. Data were collected on a Nonius FAST area-detector system. Unit cell dimensions were obtained by indexing 131 strong reflections in the 2θ range 13.5−41.6°. Axial lengths and Laue symmetry were confirmed from axial images. Details of the use of the FAST in our laboratory have been described elsewhere.[9a] These highly redundant data sets were corrected for Lorentz and polarization

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Table 1. Crystal Data for $Cu_2(hpp)_2$

formula	$C_{14}H_{24}Cu_2N_6$	Z	2
fw	403.47	ρ_{calc}, g/cm	1.700
space group	$P2_1/c$	μ, mm^{-1}	2.703
a, Å	7.320(2)	radiation (λ, Å)	Mo Ka (0.710 73)
b, Å	12.418(4)	temp, °C	−60
c, Å	8.689(2)	R1,[a] wR2[b] [$I > 2s(I)$]	0.031, 0.074
β, deg	93.76(2)	R1,[a] wR2[b] (all data)	0.034, 0.080
V, Å^3	788.1(4)		

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w$able $= 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[9b]

The structure was solved by direct methods and refined using the SHELXTL programs.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined constrained to their parent atoms. Crystallographic parameters are summarized in Table 1.

Computational Procedures. Geometry optimizations were performed for both $Cu_2(hpp)_2$ and $Cu_3(HNNNNNH)_3$ assuming C_{2h} and C_2 symmetries, respectively. To study the applicability of DFT calculations to the molecular structure of the metal−metal nonbonded species, various forms of DFT were tested in the calculations of $Cu_2(hpp)_2$: (1) SVWN, namely, local spin density calculations utilizing Slater exchange[11a] and Vosko−Wilk−Nusair correlation functionals;[11b] (2) SLYP, Slater exchange and Lee−Yang−Parr correlation functionals;[11c] (3) BLYP, Becke's gradient-corrected exchange[11d] and LYP correlation functionals and its hybrid form B3LYP;[11e] and (4) BPW91, Becke's exchange and Perdew−Wang gradient-corrected correlation functionals[11f] and the hybrid form B3PW91. Calculations using the conventional ab initio restricted Hartree−Fock (RHF) method were also carried out. Calculations on $Cu_3(HNNNNNH)_3$, on the other hand, were performed with the BPW91 and B3PW91 functional forms.

The basis set used for Cu was that developed by Wachters.[12a] The s and p primitives were contracted using contraction scheme 3, while the d functions were contracted according to Hay[12b] with 6 primitives. The 6-31G basis sets were used for all other atoms.

All calculations were carried out by using the Gaussian 94 program[13] and on SGI Power Challenge computers. The calculated molecular structure drawings were generated with optimized atomic coordinates by using the SHELXL-93 program.[10]

Results and Discussion

Experimental Results. The preparation of $Cu_2(hpp)_2$ from Li(hpp) and CuCl was straightforward, and crystals suitable for X-ray crystallography were easily obtained. The results of the crystallographic work are shown in Figure 1 and listed in Table 2. The molecular structure is as expected from a previous study of $Cu_2[(p\text{-tol})NC(H)N(p\text{-tol})]_2$.[3] The Cu−N distances are essentially the same, but the Cu−Cu distance is somewhat shorter, namely, 2.4527(10) Å compared to 2.497(2) Å, previously.

Density Functional Theory Calculations. In our previous DFT calculations of molecular structures of dinuclear species,[5] simplified model ligands were often used to make the computations more feasible. In the case of $Cu_2(hpp)_2$, we were able to calculate the structure by complete geometry optimization for the entire molecule. The results of geometry optimization on $Cu_2(hpp)_2$ by using various DFT functional forms are shown in Table 3, where pertinent structural parameters are listed and compared with those from the X-ray crystal structure.

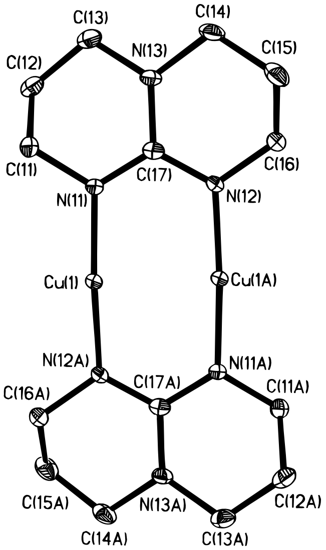

Figure 1. The X-ray crystallographic structure of $Cu_2(hpp)_2$. Atoms are represented by their thermal displacement ellipsoids at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cu_2(hpp)_2$

Cu1−Cu1A	2.4527(10)	Cu1−N11	1.862(3)
Cu1−N12A	1.863(3)	N11−C17	1.339(5)
N12A−Cu1−N11	175.98(13)	N11−C17−N12	119.8(3)

As can be seen in Table 3, the values for a given bond angle calculated by different forms of DFT are all very close and display excellent agreement with the experimental values. The same is true for the calculated bond distances between the atoms in the ligands. Significant differences exist in the values given by different DFT calculations for the nonbonded Cu−Cu distance and the Cu−N1 distances. The DFT calculations involving some form of local density approximation, namely, SLYP and SVWN, produced Cu−Cu and Cu−N1 distances that are shorter than those either from nonlocal calculations or from the experiments. The results given by the BLYP and B3LYP calculations, on the other hand, are very similar, and both are in overall good agreement with the crystal structure.

The most accurate calculated structures are those obtained by using the BPW91 and B3PW91 functionals. The nonbonded Cu−Cu distances and all other bond parameters in these calculations differ from the corresponding experimental values by only 1% or even less. As a matter of fact, as shown in Figure 2, the structure of $Cu_2(hpp)_2$ as the result of the B3PW91 geometry optimization appears to be almost exactly the same as that in Figure 1 determined from X-ray crystallography. Thus the DFT calculations, particularly those using BPW91 type of functionals, can be used to predict accurate molecular structures for the type of dinuclear compounds with a $d^{10}-d^{10}$ electron configuration.

Also listed in Table 3 are the optimized structure parameters for a "free" hpp^- ligand (see also Figure 2a). It is interesting to note that the structure of the free ligand did not change to any significant degree after reacting with the metal atoms to

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Table 3. Calculated and Experimental Structural Parameters for $Cu_2(hpp)_2$

	$Cu_2(hpp)_2$								hpp$^-$ ligand
	SLYP	SVWN	BLYP	B3LYP	BPW91	B3PW91	RHF	expt	B3PW91
					Distances (Å)				
Cu−Cu	2.402	2.410	2.507	2.499	2.471	2.472	2.557	2.4527(10)	
Cu−N1	1.820	1.834	1.905	1.899	1.888	1.886	1.954	1.863(3)	
N1−C1	1.349	1.349	1.369	1.355	1.364	1.351	1.336	1.342(5)	1.340
N2−C1	1.382	1.384	1.411	1.398	1.403	1.391	1.384	1.371(5)	1.459
N1−C2	1.453	1.454	1.488	1.473	1.478	1.467	1.461	1.460(5)	1.451
N2−C4	1.448	1.451	1.486	1.472	1.476	1.465	1.462	1.456(5)	1.451
C2−C3	1.515	1.516	1.544	1.532	1.537	1.527	1.522	1.504(5)	1.537
C3−C4	1.508	1.509	1.539	1.527	1.532	1.522	1.519	1.507(6)	1.527
					Angles (deg)				
Cu−Cu−N1	89.06	88.92	88.04	87.79	88.40	88.08	86.52	88.01(10)	
Cu−N1−C1	120.68	120.86	121.76	121.96	121.46	121.72	123.25	121.0(2)	
Cu−N1−C2	121.46	120.97	120.20	119.74	120.48	120.01	117.90	118.65(2)	
N1−C1−N1	120.52	120.45	120.40	120.49	120.28	120.40	120.46	119.8(3)	121.37
N1−C1−N2	119.74	119.77	119.80	119.76	119.86	119.80	119.77	120.1(3)	119.32
C1−N2−C4	123.35	123.32	123.39	123.45	123.36	123.44	123.60	123.2(3)	123.22
C4−N2−C4	113.29	113.36	113.21	113.10	113.29	113.12	112.80	113.6(3)	113.56

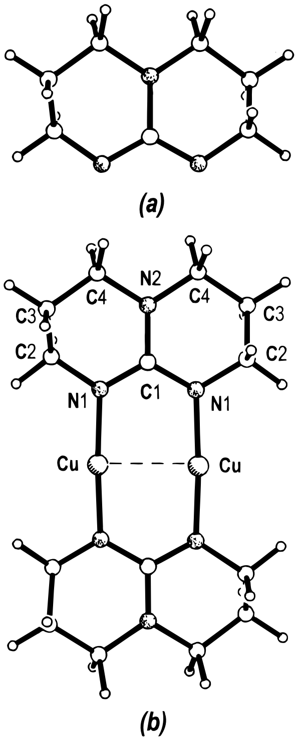

Figure 2. Optimized molecular structures from DFT B3PW91 calculations for (a) the free hpp$^-$ ligand and (b) the $Cu_2(hpp)_2$ molecule.

form the complex. In particular, the geometries around the ligand bite sites, for example, the N1−C1 distance and the N1−C1−N1 angle, are practically identical before and after binding to the metal centers.

The DFT calculations also provide a straightforward description of the Cu(I)−Cu(I) interaction, especially concerning any possible formation of a Cu−Cu bond. Among the occupied DFT orbitals, one can find 10 orbitals that have predominantly the metal orbital parentage. Very similar to the situation in $Cu_2(HNCHNH)_2$,[3] these are the five Cu−Cu bonding orbitals (one σ, two π, and two δ orbitals) and their antibonding counterparts. Therefore, as expected, the results of the DFT calculations fully support the conclusion drawn from the previous qualitative Xα−SW calculations on $Cu_2(HNCHNH)_2$,[3] namely, that there is no net Cu−Cu bond formation in dinuclear Cu(I) compounds such as $Cu_2(hpp)_2$. Without formation of any metal−metal bond, the short Cu−Cu distance must, therefore, be mainly determined by the bite size of the ligands[7] to most effectively form Cu−N bonds.

It is interesting to note that all these DFT metal orbitals are of d character with only negligible s and p characters. Natural bond orbital[14] (NBO) analysis also shows a total d population of 9.8 electrons and an occupation of 0.6 electron in the 4s orbital of each metal center. The metal centers are thus positively charged according to the orbital populations, but the formal charge, +1, is reduced to +0.6 as a result of electron donation from the ligand nitrogen atoms to the metal 4s orbitals to form Cu−N bonds.

For comparison, the molecular structure of $Cu_2(hpp)_2$ was also optimized by using the conventional ab initio restricted Hartree−Fock (RHF) method which does not take into account electron correlation effects for electrons of opposite spins. As shown in Table 3, the RHF calculation predicted much longer Cu−N and Cu−Cu distances than those obtained from both the experiment and the DFT calculations. It has been shown that interactions between two closed-shell Au(d^{10}) species are repulsive at the Hartree−Fock level.[15] The attractive nature of the nonbonded Au(I)−Au(I) interactions can be recovered when the systems are treated at correlated levels through configuration interaction which is necessary to incorporate van der Waals or dispersion interactions.[15,16] If similar repulsive interactions exist between the two Cu(I) centers in $Cu_2(hpp)_2$ at the RHF level, as suggested by the larger Cu−Cu separation in this case, the shortened Cu−Cu distance in the DFT calculations may then be taken as an indication of weakly attractive Cu(I)−Cu(I) interactions at this level of theory. In the calculated vibrational frequencies for $Cu_2(hpp)_2$ by the B3PW91 functional, one can easily identify a totally symmetric vibration that is largely a Cu−Cu stretching mode at 213 cm^{-1} with a force constant of 0.98 mdyn/Å. These results may be compared to the similar vibrational mode in the Cu_2 molecule in its ground state, which was found to be 264.55 cm^{-1} (k = 1.72 mdyn/Å).[17] It is not clear to us, however, how the attractive interactions arise. Dynamical correlation effects are included in the DFT calculations but in a way different from those in conventional ab initio techniques. In addition, DFT calculations on diatomic mol-

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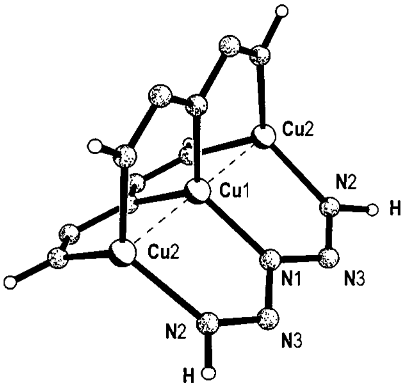

Figure 3. Optimized molecular structures from DFT B3PW91 calculations for $Cu_3(HNNNNNH)_3$. Selected bond distances (Å) and angles (deg) (experimental values for $Cu_3[(p\text{-tol})N_5(p\text{-tol})]_3$ are given in parentheses): Cu1−Cu2 2.389 (2.353(2)), Cu1−N1 1.947 (1.941(5)−1.962(6)), Cu2−N2 2.007 (2.006(5)−2.052(6)), N1−N3 1.343 (1.320(6)−1.354(7)), N2−N3 1.290 (1.267(6) −1.296(6)); N1−N3−N2 112.68 (109.7(6)−113.9(6)), N3−N1−N3 111.59 (109.7(6)−113.9(6)), N1−Cu1−N1 119.84 (116.6(2)−121.7(2)), N2−Cu2−N2 119.03 (114.0(2)−123.1(2)).

ecules of noble elements also failed to produce van der Waals attraction in these systems.[16,18]

The molecular structure of a trinuclear, tris-bridged Cu(I) compound, $Cu_3(RNNNNNR)_3$,[6] was also examined by DFT calculations. To lessen the computational burden, geometry optimization was carried out for a model compound with the tolyl groups replaced by H atoms. Shown in Figure 3 is a drawing of the optimized structure of $Cu_3(HNNNNNH)_3$ together with comparison of pertinent structural parameters with experimental results (in parentheses) for $Cu_3(RNNNNNR)_3$. These are the results obtained from the B3PW91 calculation, and the BPW91 calculation yielded very similar results. The molecular structure in Figure 3 was calculated with a C_2 symmetry constraint. Thus, for example, for a given bond, two or three different lengths would be expected from the geometry optimization. The resultant structure, however, turned out to have almost perfect D_{3h} symmetry.

As can be seen from Figure 3, the DFT calculations rather accurately reproduced the main structural features of this trinuclear compound. In particular, we note that both the calculations and experiment agree on a longer Cu2−N2 distance and a shorter Cu1−N1 distance, and numerical agreement for each bond length is also excellent. The calculated nonbonded Cu−Cu distance (2.389 Å) also compares favorably to the measured value, namely, 2.353(2) Å, which is the shortest Cu(I)−Cu(I) contact experimentally observed.

While the DFT calculations correctly predicted the very short Cu−Cu distance, careful examination of the DFT orbitals reveals no evidence for any possible formation of a Cu−Cu bond of a meaningful order. This is also in agreement with one previous analysis of the Cu(I)−Cu(I) interaction in this compound.[8] In another,[7] it was suggested that $s + p_z + d_{z^2}$ mixing was of importance, but that is not supported by this work. The very short Cu−Cu distance must be associated with the strong Cu−N bonding and the small bite size of the RN_5R^- ligand, when compared to the situation in the dinuclear species. In fact, the distance between an N1 and an N2 atom (see Figure 3) has a fairly constant value, namely, 2.20 Å, in the compound and in both "free" ligands HN_5H^- and PhN_5Ph^- according to the calculations. Such a bite size is considerably shorter than the corresponding distance, 2.35 Å, between two N1 atoms (see Figure 2b) in $Cu_2(hpp)_2$.

Similar to the case in the dinuclear $Cu_2(hpp)_2$ compound, the RHF calculation on $Cu_3(HNNNNNH)_3$ also yielded a very long Cu−Cu distance, namely, 2.48 Å, as compared to 2.389 Å given by the DFT calculation. Thus, again, if the RHF result is an indication of Cu−Cu repulsion, attractive interactions then seem to be introduced into the nonbonded Cu(I) pair in the DFT treatment. In addition, the DFT B3PW91 vibrational frequency calculation predicted four vibration modes that involve essentially only the three metal atoms, behaving as a trinuclear linear molecule. These are one symmetric ($n = 187$ cm^{-1}) and one antisymmetric ($n = 268$ cm^{-1}) Cu−Cu−Cu stretching mode and two bending modes perpendicular to each other ($n = 141$ and 143 cm^{-1}).

The question of how to interpret correctly Cu···Cu contacts may in the future have some biochemical relevance. Recent work[19,20] on the Cu_A site of cytochrome *c* oxidase led to the proposal that there is a dinuclear unit in which the Cu to Cu distance is 2.46 Å. One group proposed that this can be attributed to a copper−copper bond,[19] but the other group proposed only that this does not rule out a direct metal−metal bond.[20] A third pair of authors expressed skepticism regarding the correctness of the experimental result itself and questioned whether it justified the postulate of a metal−metal bond even if it was correct.[21] We report here two things that have a bearing on the question of copper−copper bonding: (1) a new compound with one of the shortest Cu−Cu distances established accurately and (2) some observations on the question of whether even such a short distance necessarily connotes the existence of a Cu−Cu bond.

Acknowledgment. We thank Dr. L. M. Daniels and Prof. C. A. Murillo for their interest and advice and the Robert A. Welch Foundation for support under Grant No. A494. We are also grateful to the Supercomputing Facility and the Department of Chemistry of Texas A&M University for granting computer time.

Supporting Information Available: An X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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