

Copper-substituted ethanes as a model for copper–acetylene interactions on the metal surface

Quantum mechanical study of the structure and bonding of copper–acetylene and copper–ethylene compounds $\text{Cu}_n(\text{C}_2\text{H}_2)$ ($n = 1, 2, 4$), $\text{Cu}(\text{C}_2\text{H}_2)^+$, $\text{Cu}_n(\text{C}_2\text{H}_4)$ ($n = 1, 2$) and $\text{Cu}(\text{C}_2\text{H}_4)^{+1,2}$

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Abstract

Quantum mechanical ab initio calculations are reported for the Cu and Cu⁺ complexes with acetylene and ethylene and for the dicopper-substituted ethylenes C₂H₂Cu₂ and di- and tetracopper-substituted ethanes C₂H₄Cu₂ and C₂H₂Cu₄. The geometries were optimized at the MP2 level of theory while the bond energies are predicted at CCSD(T) using relativistic effective core potentials with valence basis sets of TZ + P quality for copper. The calculated copper–acetylene and copper–ethylene complexes have C_{2v} symmetry, which is in agreement with experimental evidence. The metal–ligand bond energies of the charged species Cu⁺(C₂H₂) ($D_e = 40.6 \text{ kcal mol}^{-1}$) and Cu⁺(C₂H₄) ($D_e = 43.9 \text{ kcal mol}^{-1}$) are significantly higher than predicted in most previous studies. The neutral complexes Cu(C₂H₂) and Cu(C₂H₄) are much more weakly bonded. There are four energy minima with C_{2v} symmetry on the C₂H₂Cu₂ potential energy surface which have rather strong Cu–C bonds. The geminal isomer of dicopper-substituted ethylene is 2.8 kcal mol⁻¹ lower in energy than the trans form and 6.4 kcal mol⁻¹ more stable than the cis form. The global energy minimum structure is an end-on bonded Cu₂ complex with acetylene, which is 5.9 kcal mol⁻¹ lower in energy than 1,1-dicopperethylene. Strong Cu–C bonds are also predicted for the dicopper- and tetracopper-substituted ethanes. Two energy minima are found on the C₂H₄Cu₂ potential energy surface. The anti form of C₂H₄Cu₂ is 4.5 kcal mol⁻¹ lower in energy than the gauche form. There are also two energy minima on the C₂H₂Cu₄ potential energy surface. The gauche form of tetracopperethane is calculated as only 0.3 kcal mol⁻¹ more stable than the anti form. It is suggested that the deformed structure **5d** of C₂H₂Cu₄ with two copper atoms bridging the carbon atoms may be used as a model for the interactions between acetylene adsorbed on a copper(111) surface. The nature of the Cu–C bonding was analysed using the NBO partitioning scheme and the topological analysis of the electronic charge distribution. The charged complexes Cu⁺(C₂H₂) and Cu⁺(C₂H₄) have a T-shaped rather than a cyclic electronic structure. They are held together mainly by Coulombic interactions. The neutral complexes Cu(C₂H₂) and Cu(C₂H₄) show cyclic electronic structures. The weak Cu–C bonds of the neutral complexes Cu(C₂H₂) and Cu(C₂H₄) are caused by dispersion forces. The rather strong Cu–C bonds of the copper-substituted ethylenes and ethanes are strongly polarized towards the carbon end. Relativistic effects yield clearly shorter Cu–C and Cu–Cu bonds.

Keywords: Copper; Acetylene; Quantum mechanical study

1. Introduction

The activation of hydrocarbons by transition metals is an active field of theoretical and experimental re-

search [1–3]. Although the binding of bare transition metals to closed-shell compounds leads in most cases to complexes which are unstable in condensed phases, the study of these molecules is important, because they are potential intermediates in catalytic processes which are relevant for industrial purposes. Another interesting feature of the complexes is the unusual structure exhibited by some species. Owing to the unstable nature of the compounds, the experimental study of the geometries and thermodynamic properties of the complexes is diffi-

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cult. In spite of the impressive progress on the experimental side [4–6], there is still a lack of information about the structure and bonding of such species.

The missing information might be gained by a combination of experimental and theoretical studies. There has been an equally stunning progress in the development of quantum mechanical methods for the calculation of heavy-atom molecules including transition metal compounds in the last decade. This was made possible by utilizing effective core potentials (ECPs) [7] and modern versions of density functional theory (DFT) [8]. We could show in systematic studies that the theoretically predicted geometries and bond energies of low-spin (diamagnetic) transition metal compounds using ECPs with standard valence basis sets are in very good agreement with experimental values [9,10]. In this paper we report about the structures and bond strengths of the copper–acetylene and copper–ethylene compounds $\text{Cu}_n(\text{C}_2\text{H}_2)$ ($n = 1, 2, 4$), $\text{Cu}(\text{C}_2\text{H}_2)^+$, $\text{Cu}_n(\text{C}_2\text{H}_4)$ ($n = 1, 2$) and $\text{Cu}(\text{C}_2\text{H}_4)^+$.

The neutral and positively charged copper–acetylene and copper–ethylene complexes with one copper atom have been calculated before [11–14]. The theoretical work about the neutral compounds was done in order to give information about the structure and bond energies of the weakly bonded $\text{Cu}(\text{C}_2\text{H}_2)$ and $\text{Cu}(\text{C}_2\text{H}_4)$ species, which have been studied experimentally in low-temperature matrices [11a,13a,15,16]. The cations $\text{Cu}(\text{C}_2\text{H}_2)^+$ and $\text{Cu}(\text{C}_2\text{H}_4)^+$ may be studied in the gas phase [4–6], but it is difficult to obtain experimental information about the structure and bond energies. Lower limits for the Cu^+ –acetylene and Cu^+ –ethylene bond energies have been reported by Fisher and Armentrout, but the authors say that the experimental values are probably not very accurate [17].

Most of the theoretical studies of the cluster compounds $\text{Cu}_n(\text{C}_2\text{H}_2)$ and $\text{Cu}_n(\text{C}_2\text{H}_4)$ with $n > 1$ have been carried out in order to investigate the interactions of C_2H_2 and C_2H_4 with metal surfaces and clusters [11b,18]. The absorption of gases like acetylene and ethylene on metal surfaces is an important topic of catalytic research [19]. Naturally, this involves many more metal atoms than one. Theoretical work in this area tries to include as many atoms of the first and possibly second layer of metal atoms as possible. The usually weak overall adsorbate–substrate binding between the metal surface and the adsorbed molecules, which is difficult to determine experimentally, is then generally discussed in terms of donor–acceptor interactions [18] using the Dewar–Chatt–Duncanson model [20] of synergistic σ donation and π back-donation between the ligand and the metal.

The present work uses a different approach for the metal–adsorbate interactions, using the copper–acetylene and copper–ethylene systems as examples. The model considers the bonding between the copper

atoms and the C_2H_2 and C_2H_4 molecules as polar covalent bonds. Taken to the extreme, the adsorbed molecules would be considered as copper ethane molecules $\text{C}_2\text{H}_2\text{Cu}_4$ and $\text{C}_2\text{H}_4\text{Cu}_2$ where the copper atoms are surrounded in one hemisphere by other copper atoms. Clearly, this is an oversimplified model for the actual situation. However, there are experimental results which rationalize such an approach.

This work was initiated by the experimental observation of Bao et al. [21] using photoelectron diffraction (PED) data that the adsorption of C_2H_2 on Cu(111) leads to major structural changes in the adsorbate. The C–C bond length of the adsorbed C_2H_2 moiety increases by 0.28 ± 0.10 Å. A recent ab initio cluster study by Hermann and Witko [18c] of $\text{Cu}_7(\text{C}_2\text{H}_2)$ showed that the HCC bond angle changes from 180° to 120° . To a chemist, an HCCH moiety with a C–C bond length of 1.48 ± 0.10 Å, an HCC bond angle of 120° and a cis-arrangement of the hydrogen atoms looks more like a cis-bonded ethylene fragment than an acetylene molecule. It follows that *cis*- $\text{C}_2\text{H}_2\text{Cu}_2$ might be a good model compound to mimic the copper–acetylene interactions. However, the experimental work [21] and the cluster calculations [18c] suggest that the carbon atoms point towards adjacent three-fold hollow sites. This means that the C_2H_2 moiety is bonded to four copper atoms. The corresponding molecule would be tetracopperethane $\text{C}_2\text{H}_2\text{Cu}_4$.

The present work is also interesting for structural chemistry. Little is known about metal-substituted organic substrates. The most systematic work done was about lithium-substituted compounds [22]. This work is the first theoretical study about copper-substituted ethane and ethylene systems. The only previous paper is a recent DFT study of the bonding of copper atom, dimer, and trimer to acetylene [11b].

In order to investigate the bonding in the copper compounds we analysed the wave function using the natural bond orbital (NBO) partitioning scheme developed by Weinhold and coworkers [23]. We also carried out a topological analysis of the electron density distribution and its associated Laplacian developed by Bader [24].

2. Methods

The geometries of the molecules have been optimized at the MP2 level (Møller–Plesset perturbation theory terminated at second order) [25] using two different basis sets as shown in Table 1. The basis set I for Cu has a nonrelativistic small-core ECP, which replaces the ten inner core electrons, in conjunction with a DZ + p quality (441/2111/41) valence basis set [26]. A 6-31G(d) basis set is used for C and H [27]. It has been shown that relativistic effects are important for the

Table 1
Basis sets used in this study

	Metal	Ligand
I	ECP (441/2111/41)	6-31G(d)
II	ECP (311111/22111/411)	6-31G(d)
III	ECP (311111/22111/411/1)	6-31 + G(d)

bond length and bond energies of Cu compounds [28]. Therefore, we optimized the geometries also using a relativistic small-core ECP [29] in conjunction with a (311111/22111/411) basis set for Cu and a 6-31G(d) basis set for C and H. This basis set is denoted as basis set II (Table 1). The harmonic vibrational frequencies were determined at the MP2/II level using numerical second derivatives.

The copper–acetylene and copper–ethylene bond energies have been calculated using coupled-cluster theory [30] with single and double excitations and a noniterative approximation of the triples CCSD(T) [31]. It has been shown that the CCSD(T) method in combination with basis sets of DZ + P quality gives very reliable bond energies for transition metal compounds [9,10]. The CCSD(T) calculations have been carried out with basis set II augmented by an f-type polarization function at Cu (exponent 3.525) [32] and a diffuse function for C [33]. This is denoted as basis set III. Unless otherwise noted, geometries are discussed at MP2/II and energies at CCSD(T)/III using MP2/II optimized geometries. The calculations have been carried using the program packages GAUSSIAN 92 [34] and ACES II [35]. For the calculation of the electron density distribution $\rho(\mathbf{r})$, the

gradient vector field $\nabla\rho(\mathbf{r})$, and its associated Laplacian $\nabla^2\rho(\mathbf{r})$, the programs PROAIM, SADDLE, GRID, and GRDVEC were used [36].

3. Structures and bond energies

Fig. 1 shows the optimized geometries of the molecules at the MP2/II level using the relativistic ECPs as described in the Methods section. The nonrelativistic geometries predicted at MP2/I are given in parentheses. Table 2 shows the calculated energies.

We begin the discussion with a comparison of the monocopper compounds $\text{Cu}(\text{C}_2\text{H}_2)$ (1), $\text{Cu}(\text{C}_2\text{H}_2)^+$ (1^+), $\text{Cu}(\text{C}_2\text{H}_4)$ (2), and $\text{Cu}(\text{C}_2\text{H}_4)^+$ (2^+). The molecules $1-2^+$ are calculated with a C_{2v} equilibrium geometry. The copper–acetylene complex 1 is predicted with a Cu–C bond distance of 2.034 Å. The C–C distance of 1 is slightly longer (1.246 Å) than in free acetylene (1.218 Å). The acetylene ligand is weakly bent (C–C–H angle 166.4°). The calculations of 1 at MP2/I did not converge. The cation 1^+ has a slightly longer Cu–C bond (2.054 Å) and a shorter C–C bond (1.242 Å) than the neutral complex 1. The bending of the acetylene moiety of 1^+ (C–C–H angle 168.7°) is also less than in 1. It follows that the optimized geometries of 1 and 1^+ suggest less interactions between the metal and the ligand in the cation than in the neutral compound. However, the copper–acetylene bond strength of 1^+ is much higher ($D_e = 40.6 \text{ kcal mol}^{-1}$) than that of 1 ($D_e = 2.3 \text{ kcal mol}^{-1}$, Table 2). It will be

Table 2
Total energies E_{tot} , relative energies E_{rel} , imaginary frequencies i , zero point energies (ZPE), bond energies D_e (ZPE-corrected energies D_0) of the complexes 1–5d

	MP2/II				CCSD(T)/III			
	E_{tot} (au)	E_{rel} (kcal mol ⁻¹)	i	ZPE ^b (kcal mol ⁻¹)	D_e (D_0) (au)	E_{tot} (kcal mol ⁻¹)	E_{rel} (kcal mol ⁻¹)	D_e (D_0)
1	-273.62814	-	0	18.0	7.5 (4.4)	-273.78005	-	2.3 (-0.8)
1^+	-273.41965	-	0	16.0	45.5 (44.1)	-273.57003	-	40.6 (39.2)
2	-274.84723	-	0	40.0	7.9 (0.0)	-275.01113	-	4.2 (-3.7)
2^+	-274.64336	-	0	31.4	48.8 (46.8)	-274.80332	-	43.9 (41.9)
3a	-470.24523	13.2	0	17.8	51.0 (47.8)	-470.52569	12.3	46.8 (43.5)
3b	-470.25250	8.7	0	18.0	55.6 (52.2)	-470.53134	8.7	50.3 (46.9)
3c	-470.25803	5.2	0	18.2	59.1 (55.5)	-470.53582	5.9	53.2 (49.6)
3d	-470.26629	0.0	0	16.6	64.2 (62.2)	-470.54521	0.0	59.1 (57.1)
4a	-471.44962	0.0	0	31.8	42.2 (39.8)	-471.73246	0.0	33.4 (31.0)
4b	-471.44242	4.5	0	31.5	37.7 (35.6)	-	-	-
4c	-471.43890	6.7	1	31.3	35.5 (33.6)	-471.72213	6.5	26.9 (25.0)
5a	-863.44598	0.0	0 ^a	18.0 ^a	117.1 (113.7)	-	-	-
5b	-863.44549	0.3	0 ^a	18.2 ^a	116.9 (113.3)	-	-	-
5c	-863.43715	5.5	1 ^a	18.0 ^a	111.6 (108.2)	-	-	-
5d	-863.43017	9.9	-	-	107.3	-	-	-

^a At MP2/I. ^b Scaled by 0.92.

shown below that the metal–ligand bonding of 1^+ and 2^+ is electrostatic, while the Cu–C bonds of 1 and 2 are caused by dispersion forces. Owing to the positive

charge the Cu^+ ion is a much harder species than neutral Cu. Cu^+ has a quasi-noble-gas electron configuration $3d^{10}4s^0$ which is difficult to penetrate.

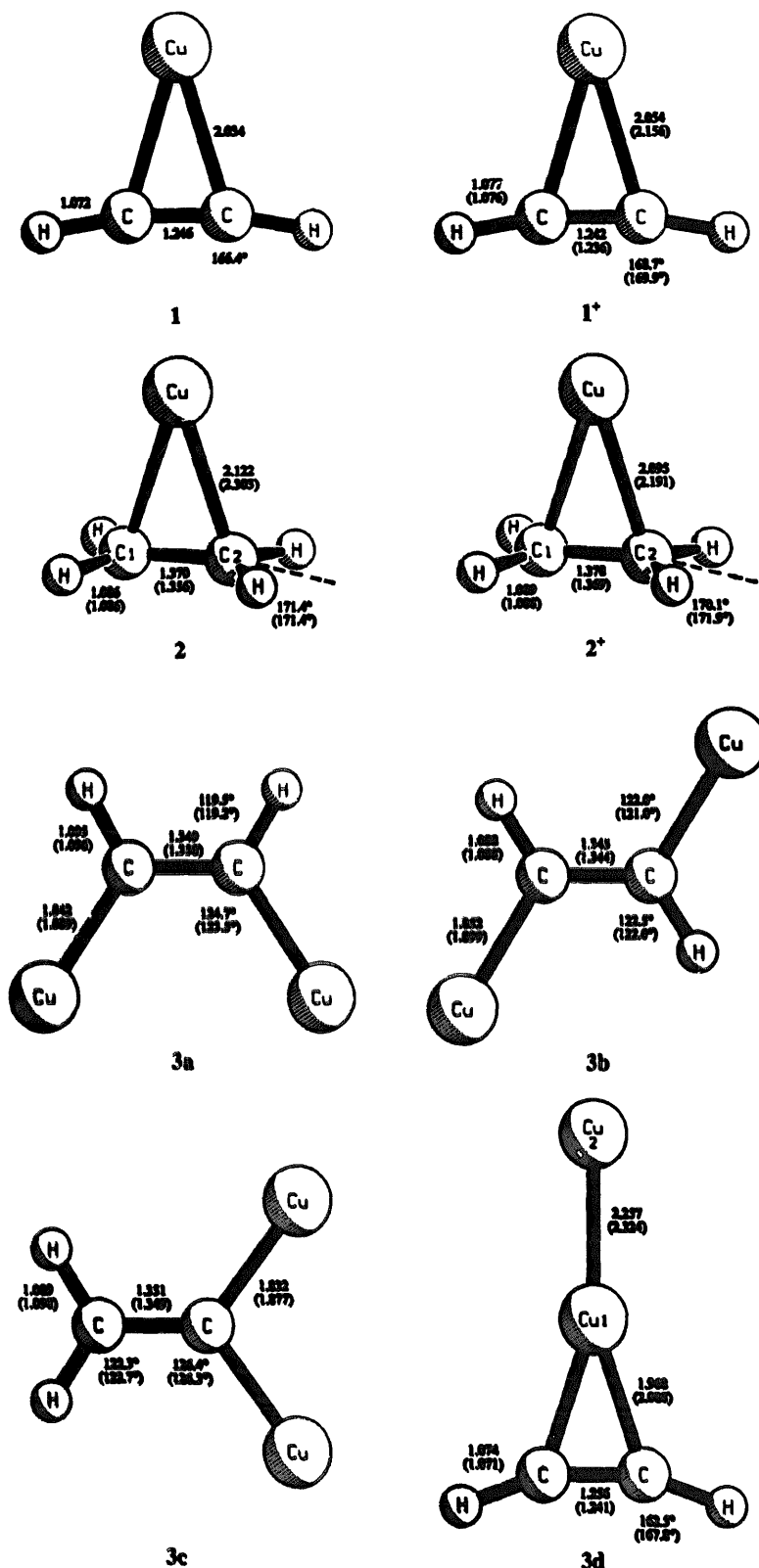


Fig. 1. Optimized geometries of the molecules at MP2/II. The nonrelativistic values calculated at MP2/I are given in parentheses. Bond distances in angstroms, angles in degrees.

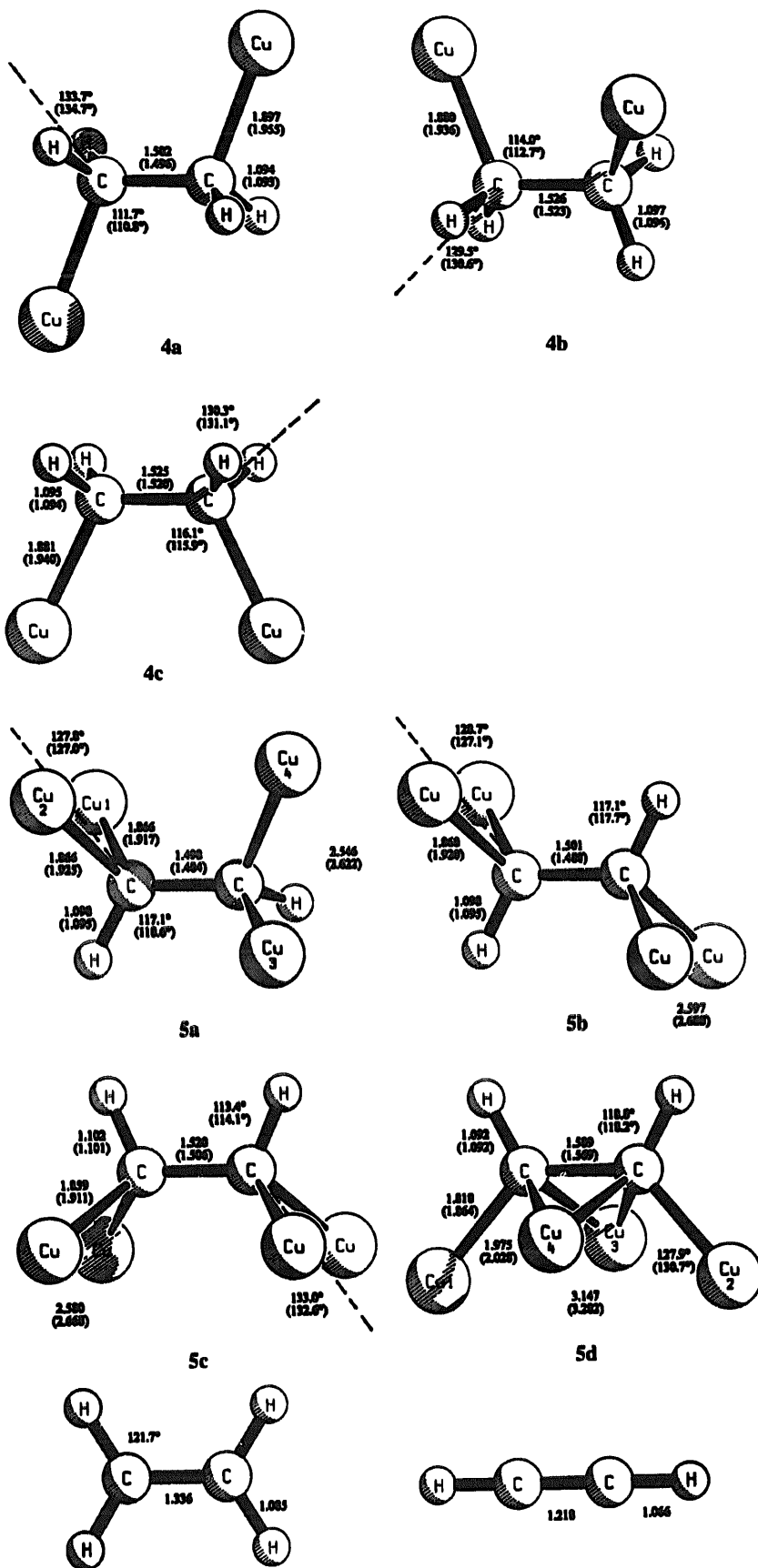


Fig. 1 (continued).

The optimized geometry of **1** is in agreement with experimental observations. Matrix isolation ESR studies [16] and the analysis of the vibrational spectrum [11a] have shown that the copper–acetylene complex **1** has C_{2v} geometry. This is not a trivial result, because the analogous silver and gold complexes have a vinyl structure [16]. There are no experimental binding energies of **1** and 1^+ available. The only previous theoretical study of the structure and bond energy of **1** using density functional theory gave a vinyl form with a short Cu–C bond (1.847 Å) as energy minimum structure and a bond energy $D_e = 13.3 \text{ kcal mol}^{-1}$ [11b]. Since the experimental work [11a,16] established unambiguously that **1** has a C_{2v} structure as equilibrium geometry, we think that the calculated bond energy is questionable. Previous theoretical studies of 1^+ give a C_{2v} structure as energy minimum form as calculated here [12]. However, the Cu–C bond lengths which were calculated in those studies are much longer and the metal–ligand bond energies are significantly lower than predicted here. The calculated Cu–C distances of the former work were 2.232 Å at the CI level with a fixed geometry of the acetylene ligand [12a] and 2.33 Å at the HF level using a nonrelativistic pseudopotential [12b].

Fig. 1 shows that the inclusion of relativistic effects at the MP2/II level yields a shortening of the Cu–C bond of 1^+ by nearly 0.1 Å. It has been recognized that copper shows the strongest relativistic effects among the elements of the first transition metal row [9j,28]. We believe that the Cu–C bond length reported here for 1^+ (2.054 Å) should be more reliable than previous values [12], because relativistic effects and the relaxation of the acetylene ligand are included in the calculations. For the same reason we think that the metal–ligand bond energy for 1^+ shown in Table 2 ($D_e = 40.6 \text{ kcal mol}^{-1}$) is more accurate than the lower values ($D_e = 26.8 \text{ kcal mol}^{-1}$ [12a]; $D_e = 32.8 \text{ kcal mol}^{-1}$ [12b]) reported before. An experimental study of the metal–ligand bond energy of 1^+ gave a lower limit of only $D_0 > 5.1 \pm 2.3 \text{ kcal mol}^{-1}$ [17]. The authors say that this is not a very accurate value. The correct value should be much higher.

The Cu–C bond length of the copper–ethylene complex **2** is predicted to be slightly longer (2.122 Å) than in the cation 2^+ (2.095 Å). The C–C distance of the ethylene ligand increases from 1.336 Å in free ethylene to 1.370 Å in **2** and 1.378 Å in 2^+ . The Cu–C bond lengths of the copper–ethylene compounds **2** and 2^+ are clearly longer than in the copper–acetylene molecules **1** and 1^+ (Fig. 1). Nevertheless, the calculated metal–ligand bond energy of the charged ethylene complex 2^+ ($D_e = 43.9 \text{ kcal mol}^{-1}$) is higher than that of the acetylene complex 1^+ (Table 2). The neutral complex **2** has a bond energy of only $D_e = 4.2 \text{ kcal mol}^{-1}$. The inclusion of ZPE correction yields no bonding between copper and ethylene (Table 2). The work term pV and the corrections for translational and rota-

tional degrees of freedom yield for **2** a weakly Cu– C_2H_4 bonding enthalpy.

There are no experimental values for the bond lengths of **2** and 2^+ known to us. The predicted C_{2v} form for **2** is in agreement with matrix isolation ESR [16b] and UV [13a] studies of copper–ethylene complexes, which show clearly that $Cu(C_2H_4)$ in the electronic ground state has C_{2v} symmetry. A previous theoretical study of **2** using a modified MP2 term gave a significantly longer Cu–C bond (2.65 Å) and a lower Cu–ethylene bond energy ($D_e = 3 \text{ kcal mol}^{-1}$) than reported here [13c]. However, the geometry of the complex was not completely optimized in the calculation. The ethylene ligand was kept fixed with planar (D_{2h}) symmetry and a C–C bond length of 1.338 Å. We believe that the present results which are obtained with complete geometry optimization are probably more accurate.

The copper–ethylene cation 2^+ has been the subject of previous theoretical studies [14]. Bauschlicher and coworkers [14c] reported a Cu–C bond length of 2.35 Å calculated at the SCF level. The metal–ligand bond energy at the MCPF level was $D_e = 36.0 \text{ kcal mol}^{-1}$. A systematic comparison of theoretical and experimental metal–ligand bond energies led to the conclusion that the calculated binding energy for 2^+ is 7–9 kcal mol⁻¹ too small [14c]. The estimated value would then be $D_e = 43–45 \text{ kcal mol}^{-1}$, which is in excellent agreement with our value $D_e = 43.9 \text{ kcal mol}^{-1}$. Earlier studies of 2^+ at the SCF level gave a bond energy of 27.9 kcal mol⁻¹ and a Cu–C bond length of 2.390 Å [14b]. The metal–ligand bonding of 2^+ has also been studied by Ziegler and Rauk [14a] using the Hartree–Fock–Slater (HFS) method. The calculated Cu–C bond length (1.95 Å) is clearly too short and the Cu^+ –ethylene bond energy ($D_e = 79.7 \text{ kcal mol}^{-1}$) is too high. There is an experimental value for the lower limit of the Cu^+ –ethylene interactions ($D_0 \geq 26.1 \pm 2.5 \text{ kcal mol}^{-1}$) [17]. Again, the authors say that this value is probably not accurate. A clearly larger bond energy $D_0 = 42.8 \pm 1.7 \text{ kcal mol}^{-1}$ was measured for the Co^+ – C_2H_4 bond [17].

Now we discuss the compounds $Cu_n(C_2H_2)$ and $Cu_n(C_2H_4)$ with $n > 1$, i.e. structures **3–5**. Four isomers **3a–3d** were found as energy minima on the $C_2H_2Cu_2$ potential energy surface (Fig. 1). The isomeric forms **3a–3c** may be considered either as dicopper–acetylene complexes or dicopper–substituted ethylenes. The short Cu–C bond length (1.832–1.852 Å, Fig. 1) and the long C–C bond distances (1.345–1.351 Å) indicate that these structures should rather be considered as dicopperethylenes, while **3d** looks like a dicopper–acetylene complex. The latter structure is predicted to be the global energy minimum structure on the $Cu_2C_2H_2$ potential energy surface. The *cis*-dicopperethylene **3a** is least stable, it is 12.3 kcal mol⁻¹ higher in energy than **3d** (Table 2). The *trans* form **3b** is

3.6 kcal mol⁻¹ more stable than **3a**. The geminal isomer **3c** is the most stable form of the dicopperethylenes **3a–3c**. The Cu–C bond energies of dicopperethylenes **3a–3c** are significantly higher than the Cu–C bond energy of the weakly bonded complex **1**. The dissociation energies of the isomeric forms of **3** into ethylene and two Cu (²S) atoms are between $D_e = 46.8$ kcal mol⁻¹ (**3a**) and $D_e = 53.2$ kcal mol⁻¹ (**3c**). This gives a mean Cu–C bond energy of $D_e = 23.4$ – 26.6 kcal mol⁻¹ for the isomeric forms of dicopperethylene. The Cu₂–C₂H₂ bond energy of **3d** is $D_e = 59.1$ kcal mol⁻¹. The recent theoretical study of Fournier [11b] using DFT methods gave shorter Cu–C bond lengths for **3a** (1.809 Å), **3b** (1.814 Å) and **3d** (1.926 and 1.958 Å for a slightly disturbed C_{2v} form) and higher bond energies ($D_e = 68.3$ kcal mol⁻¹ for **3a**, $D_e = 71.9$ kcal mol⁻¹ for **3b**, $D_e = 71.1$ kcal mol⁻¹ for **3d**). The geminal isomer **3c** was not calculated in this work. The geometries were optimized with gradient corrections at the local DFT level only [11b]. We think that the present values are more accurate, because the DFT study gave a wrong equilibrium geometry for the Cu(C₂H₂) complex [11b].

We studied several isomeric forms of C₂H₄Cu₂. The calculated C–C distances of **4a–4c** (1.502–1.526 Å, Fig. 1) show clearly that the molecules should be considered as dicopper-substituted ethanes. The Cu–C bonds of dicopperethanes **4a–4c** are slightly longer (1.880–1.897 Å) than the Cu–C bonds of the dicopperethylenes **3a–3c** (1.832 Å–1.852 Å, Fig. 1). This can be explained by the hybridization of the Cu–C bonds at the carbon ends, which has a clearly higher percentage s character in the copperethylenes than in the copperethanes (see the discussion below). The anti conformation **4a** is predicted as the energetically lowest lying form. The gauche form **4b** is 4.5 kcal mol⁻¹ (MP2/II, Table 2) higher in energy than **4a**. CCSD(T) calculations of **4b** were not possible for technical reasons (2 GB single file limit). Table 2 shows that the relative energies of the isomeric forms of **3** at MP2/II and CCSD(T)/III are very similar. Therefore, we think that the energy difference between **4a** and **4b** at MP2/II should be reliable. The eclipsed conformation **4c** is not a minimum on the potential energy surface, it is rather a transition state for rotation about the C–C bond. The barrier is not very high, it is only 2.2 kcal mol⁻¹ (2.0 kcal mol⁻¹ with ZPE correction) using **4b** as reference conformation. The Cu–C bond energy of dicopperethane is clearly lower compared with dicopperethylene. The dissociation energy of **4a** yielding two copper atoms and ethylene is $D_e = 33.4$ kcal mol⁻¹ (Table 2). This gives a mean Cu–C bond energy of 16.7 kcal mol⁻¹. The Cu–C bond energy of **4b** can be estimated from the difference of the MP2/II values for **4a** and **4b** (4.5 kcal mol⁻¹) and the CCSD(T) value for **4a** [37]. This gives for **4b** a total metal–ligand bond energy of

$D_e = 28.9$ kcal mol⁻¹ and a mean Cu–C bond energy of $D_e = 14.5$ kcal mol⁻¹.

We now come to the molecules with the formula C₂H₂Cu₄ (**5**). Fig. 1 shows the optimized geometries of the stationary points **5a–5d** on the potential energy surface. The gauche form **5a** and the trans form **5b** are energy minima ($i = 0$). The energy difference is very low, only 0.3 kcal mol⁻¹ at MP2/II (Table 2). Structures **5a** and **5b** are nearly degenerate when the ZPE corrections are considered. The calculated C–C distances (1.498 and 1.501 Å) suggest that **5a** and **5b** should be considered as tetracopper-substituted ethanes. It is interesting to see that the Cu–C bonds of the tetracopperethanes **5a** and **5b** are shorter (1.866 and 1.868 Å) than those of the dicopperethanes **4a** and **4b** (1.897 Å and 1.880 Å, Fig. 1). This can be explained by the hybridization and the charge of the carbon atoms (see the discussion below). The Cu–C bond energies of **5a** and **5b** are also higher compared with **4a** and **4b**. The MP2/II calculations give dissociation energies $D_e = 117.1$ kcal mol⁻¹ (**5a**) and $D_e = 116.9$ kcal mol⁻¹ (**5b**). Calculations of C₂H₂Cu₄ at the CCSD(T)/III level were not possible for technical reasons (less than 2 GB single file limit). The calculated bond energies of 1–4 at MP2/II and CCSD(T)/III indicate that MP2/II overestimates the Cu–C bond energy by ca. 5 kcal mol⁻¹. Since there are four Cu–C bonds in **5** we estimate that the true dissociation energy of **5a** and **5b** should be around $D_e = 95$ – 100 kcal mol⁻¹. This gives a mean bond energy of about 25 kcal mol⁻¹ for the Cu–C bonds of **5a** and **5b**. The eclipsed conformation **5c** is a transition state for rotation about the C–C bond ($i = 1$). The calculated rotational barrier at MP2/II is 5.5 kcal mol⁻¹ relative to the gauche form **5a**.

It should be noted that the Cu–C bonds of **3–5** and the Cu–Cu bond of **3d** are predicted to be clearly shorter at the relativistic level (MP2/II) than at the nonrelativistic level (MP2/I). Reliable calculations of copper compounds must be carried out with inclusion of relativistic effects!

The eclipsed conformation **5c** shall be used as a starting point for a comparison with the experimental [21] and theoretical [18c] results on the structure of the adsorbate and the bonding of acetylene on a Cu(111) surface. The PED studies showed that the adsorption leads to major structural changes of the adsorbate. In particular, the C–C bond length of the adsorbed acetylene becomes 1.48 ± 0.10 Å [21]. This value is in excellent agreement with the C–C bond length of **5c**, which could therefore be taken as a model for an adsorbed acetylene molecule on a copper surface. However, the analysis of the PED data suggest that the carbon atoms of the acetylene molecule occupy the two symmetrically distinct three-fold coordinated hollow sites on the surface [21]. A theoretical study of a cluster model Cu₇(C₂H₂) confirmed the experimental finding [18c].

The calculations show that the C_2H_2 molecule is strongly stabilized when the two carbon atoms point towards adjacent three-fold hollow sites, as suggested by the PED data. The calculations also predicted that the CCH angle of the adsorbed acetylene unit becomes 120° [18c]. In order to mimic the bonding of acetylene to the four closest copper atoms on the Cu(111) surface as suggested by these studies, we calculated the structure **5d** shown in Fig. 1. The two copper atoms Cu1 and Cu2 are bonded to one carbon atom each, while the copper atoms Cu3 and Cu4 are in a bridging position. The Cu–C bonds of the bridging copper atoms are longer (1.975 Å) than the terminal Cu–C bonds (1.818 Å). The C_{2v} structure of **5d** matches exactly the local $C_2H_2Cu_4$ moiety on the Cu(111) surface [38]. The difference is that the copper atoms on the surface are bonded to other copper atoms. A comparison of the calculated structure and binding property of **5d** with the experimental [21] and theoretical [18c] studies of the bulk property should give information about the specific copper–acetylene interactions on the surface.

We note first that the C–C bond length of **5d** (1.589 Å) is at the upper limit of the experimental value for the adsorbed acetylene molecule (1.48 ± 0.10 Å) [21]. The PED data also showed that the C–C axis is almost parallel to the copper surface, and that the carbon atoms are 1.38 ± 0.03 Å above the copper layer of the f.c.c. hollow site. The distance between carbon and the copper layer of the h.c.p. site is slightly longer (1.44 ± 0.03 Å). The calculated distances between the carbon atoms and the two layers represented by the copper atoms of **5d** are 1.435 Å (Cu1 and Cu2) and 0.890 Å (Cu3 and Cu4). The first value is in excellent agreement with the experimental data [21]. It should be noted that the measurements refer to copper atoms of a metal surface,

which are still held together by metal–metal interactions. The calculated C–C–H angle of **5d** (118.8°) is also in good agreement with the theoretical value of the $Cu_4C_2H_2$ cluster optimization (C–C–H 120°) [18c]. In summary, the optimized geometry of **5d** suggests that the structure of the doubly-bridged tetracopperethane might be a good model for the local bonding site of adsorbed acetylene on a Cu(111) surface.

The energy necessary to distort the equilibrium structure **5a** towards **5d** is not very high. The calculated total energy difference is only $9.9 \text{ kcal mol}^{-1}$ (Table 2). Table 2 shows that the calculated dissociation energy of **5d** yielding acetylene and four copper atoms at MP2/II is rather high ($D_e = 107.3 \text{ kcal mol}^{-1}$). We estimate that the true copper–acetylene bond energy of **5d** should be $D_e = 85\text{--}90 \text{ kcal mol}^{-1}$. This is much higher than the binding energy of acetylene on a copper surface. Experimental results show that the adsorbate–substrate interactions for acetylene adsorption at 3d metal surfaces are rather weak [39]. The C_2H_2 –Cu(111) adsorption system even has to be cooled to rather low temperatures to stabilize acetylene on the surface [39]. In contrast, the strong deformation of the acetylene moiety on the copper system suggests that the local interactions are rather strong. It should be noted that the Cu_4 – C_2H_2 bond energy of **5d** was calculated with respect to free copper atoms. The binding energy of acetylene on a Cu(111) surface is the net result of the local binding between C_2H_2 and copper atoms, and the loss of binding energy between these copper atoms and the surrounding bulk. The good agreement between the calculated structure **5d** and the analysis of the PED data for the local adsorption structure of acetylene on a Cu(111) site [21] suggests that the major copper–acetylene interactions involve four copper atoms. The

Table 3
Results of the NBO analysis calculated at HF/II using geometries at MP2/II

	Symmetry	Population(Cu)			Cu–C bond ^a						Charges ^b			
		4s	3d	4p	Pop.	%Cu	%4s (Cu)	%4p (Cu)	%3d (Cu)	%2s (C)	%2p (C)	<i>q</i> _{Cu}	<i>q</i> _C	
1⁺	C_{2v}	0.11	9.93	0.01	–	–	–	–	–	–	–	0.95	–0.30	
2⁺	C_{2v}	0.14	9.94	0.00	–	–	–	–	–	–	–	0.91	–0.49	
3a	C_{2v}	0.56	9.90	0.02	1.97	23.6	94.0	0.4	5.7	23.9	76.1	0.52	–0.70	
3b	C_{2v}	0.58	9.91	0.01	1.95	24.5	94.2	0.4	5.4	23.4	76.6	0.49	–0.69	
3c	C_{2v}	0.58	9.90	0.01	1.96	24.5	93.9	0.3	5.8	26.6	73.3	0.50	–0.45 ^c , 0.93 ^d	
3d	C_{2v}	0.78	9.83	0.02	1.99 ^c	36.9	96.4	1.6	2.1	–	–	0.35	–0.32	
		1.27	9.99	0.01	–	63.1	98.1	1.0	0.9	–	–	–0.28	–	
													Cu1	
														Cu2
4a	C_{2v}	0.69	9.91	0.00	1.94	29.7	93.7	0.3	6.0	13.6	86.3	0.39	–0.82	
4b	C_2	0.64	9.90	0.00	1.98	27.9	93.5	0.3	6.2	12.5	87.5	0.45	–0.85	
5a	C_1	0.71	9.90	0.01	1.92	30.6	93.0	0.4	6.6	15.4	84.6	0.36	–1.0	
		0.66	9.90	0.02	1.95	28.8	93.3	0.4	6.3	13.6	86.4	0.41	–1.0	
													Cu1, Cu3	
5b	C_{2v}	0.70	9.90	0.01	1.92	29.8	92.9	0.5	6.6	15.5	84.4	0.38	–0.98	
													Cu2, Cu4	

^a %Cu gives the contribution of the Cu–C bond orbital at Cu; %4s (Cu), %4p (Cu), %3d (Cu) give the hybridization of the Cu–C bond at Cu; %2s (C), %2p (C) give the hybridization of the Cu–C bond at C. ^b *q*_{Cu} and *q*_C are the partial charges at Cu and C respectively. ^c Carbon bonded at H. ^d Carbon bonded at Cu. ^e Cu1–Cu2 bond.

structure and binding of the local adsorption site may be modelled with structure **5d** embedded in surrounding copper atoms.

The present approach to understand the major structural changes of acetylene upon adsorption on a Cu(111) surface in spite of the overall weak surface–adsorbate interactions is complementary to the breakdown of the energy contributions given by Hermann and Witko [18c]. These workers discuss the deformation energy of the acetylene moiety (estimated as 1–1.5 eV), which has to be compensated by the C₂H₂–Cu(111) interactions. Here we consider the bond energy between acetylene and four copper atoms in the compound **5d**, which has an optimized geometry that is close to the experimental findings for acetylene adsorbed on a copper surface. The overall weak interactions are then a partial compensation of the bond energy of **5d** and the loss of Cu–Cu bonding on the copper surface. The calculations show that the local C₂H₂–Cu(111) interactions must be as strong as calculated for **5d**. Copper–acetylene species with a weaker interaction such as **3** clearly have a shorter C–C bond length than experimentally observed [21]. It follows that the model compound **5d** has real meaning for the analysis of the C₂H₂–Cu(111) interactions.

4. Bonding analysis

Table 3 shows the results of the NBO analysis for the closed-shell copper compounds. Table 4 gives the results of the topological analysis of the electron density distribution of **1**–**5**. The contour line diagrams of the

Laplacian distribution of some compounds are shown in Fig. 2 [40].

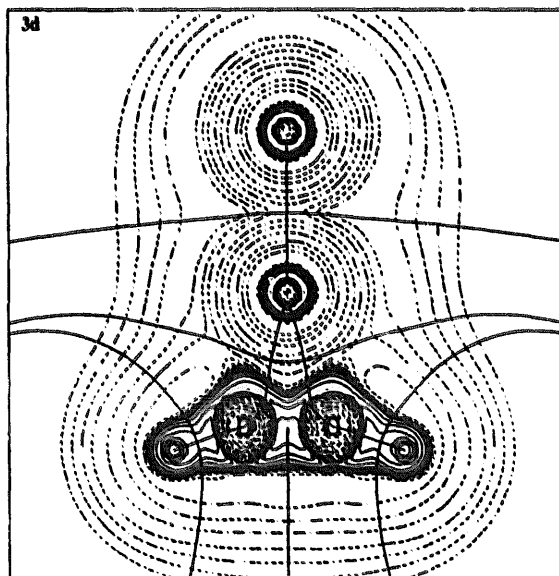
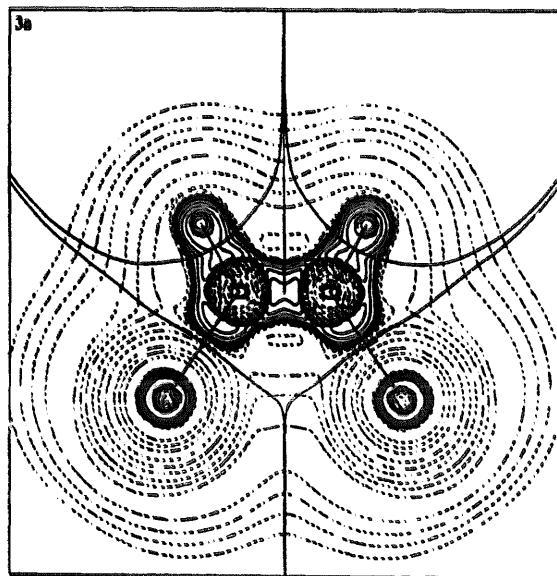
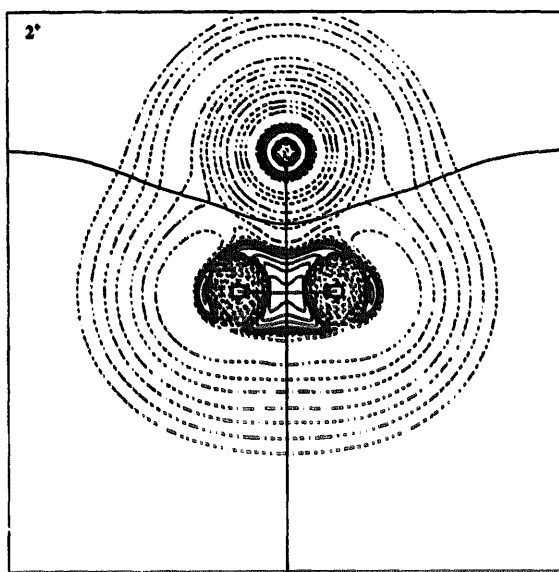
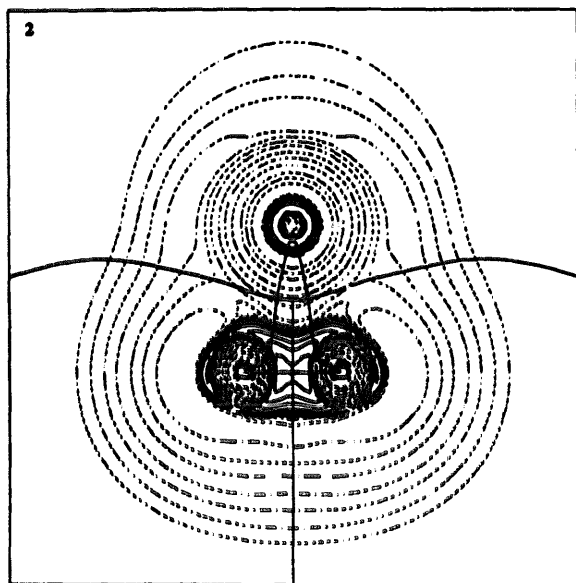
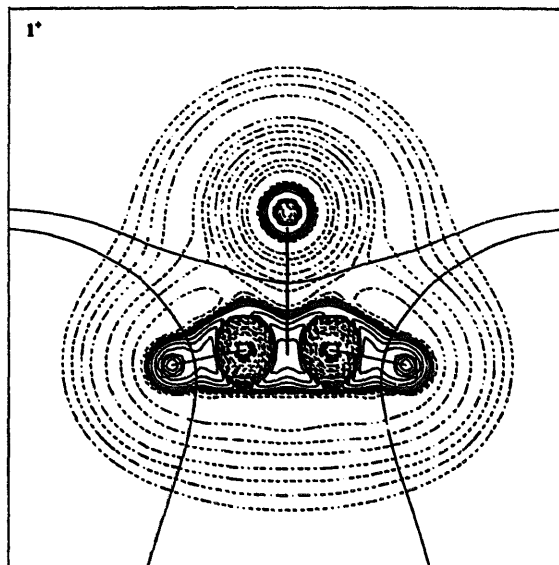
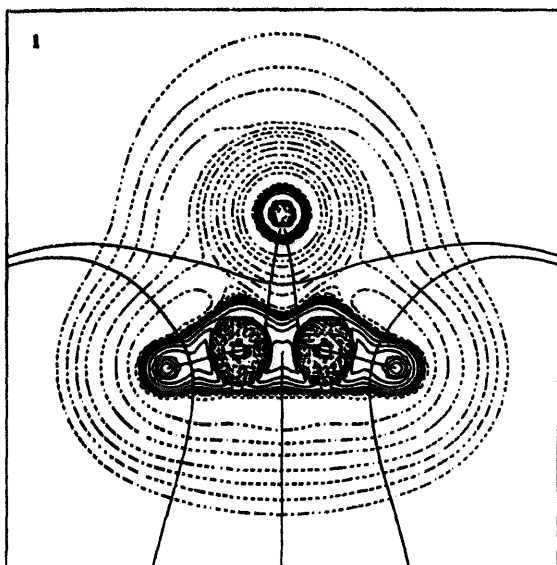
The NBO analysis of the charged compounds **1**⁺ and **2**⁺ gives no copper–ligand bond orbitals (Table 3). The positive charge is mainly located at the copper atom, the partial charges at Cu are +0.95 for **1**⁺ and +0.91 for **2**⁺. It follows that the NBO results indicate a Coulomb-type metal–ligand bonding in **1**⁺ and **2**⁺. This interpretation is supported by the results of the topological analysis. Fig. 2 shows that there is no bond path in **1**⁺ and **2**⁺ from the copper atom to the carbon atoms. There is also no ring critical point for the CuC₂ moiety of **1**⁺ and **2**⁺. There is a bond path from Cu to the midpoint of the C–C bond of the acetylene ligand in **1**⁺ and to the ethylene ligand in **2**⁺. Thus, the topological analysis of the electron density distribution suggests that **1**⁺ and **2**⁺ have a T-shaped structure, and that these molecules should not be considered as cyclic compounds. The energy density at the bond critical points H_b for the Cu–CC_{midpoint} bonds suggests that there are only negligible covalent contributions [41]. The neutral copper–ethylene complexes **1and 2** have cyclic electronic structures as revealed by the bond paths and by the critical points (Fig. 2). There are two bond paths from the copper atom to the carbon atoms. There is also a ring critical point in **1and 2**. The energy densities H_b for the Cu–C bonds of **1and 2** indicate negligible covalent contributions. The weak metal–ligand interactions in **1and 2** are caused by dispersion forces, while the strong metal–ligand bonding in the charged species **1**⁺ and **2**⁺ is caused by Coulomb interactions.

The Cu–C bonding of the compounds **3**–**5** is clearly different from the neutral and charged Cu–acetylene

Table 4
Results of the topological analysis of the electron density at MP2/II^a

	X–Y	$\rho(r_b)$	H_b	$R(\text{Cu} - r_b)$	$-\nabla^2\rho(r_b)$
1	C–Cu	0.559	–0.080	0.922	9.244
1 ⁺	C–Cu ^b	0.555	–0.076	0.999	8.754
2	C–Cu	0.475	–0.066	1.030	6.552
2 ⁺	C–Cu ^b	0.517	–0.071	1.022	7.040
3a	C–Cu	0.904	–0.377	0.943	6.432
3b	C–Cu	0.873	–0.353	0.949	6.336
3c	C–Cu	0.904	–0.378	0.941	6.742
3d	C–Cu	0.649	–0.139	0.974	9.584
	Cu–Cu	0.444	–0.150	1.116 ^c	2.586
4a	C–Cu	0.799	–0.304	0.971	5.067
4b	C–Cu	0.843	–0.335	0.960	5.267
4c	C–Cu	0.835	–0.330	0.962	5.199
5a	C–Cu1	0.847	–0.335	0.956	6.122
	C–Cu2	0.844	–0.337	0.960	5.676
5b	C–Cu	0.844	–0.335	0.958	5.847
5c	C–Cu	0.863	–0.349	0.954	5.940
5d	C–Cu1	0.915	–0.392	0.946	6.512
	C–Cu3	0.642	–0.181	0.991	7.180

^a Charge density at the bond critical point $\rho(r_b)$ (e Å⁻³); energy density at the bond critical point H_b (Hartree/Å³); location of the bond critical point r_b given by the distance from the copper atom $R(\text{Cu} - r_b)$ (Å); Laplacian at the bond critical point $\nabla^2\rho(r_b)$ (e Å⁻⁵). ^b Bond between Cu and the midpoint of the C–C bond. ^c Distance from Cu1.



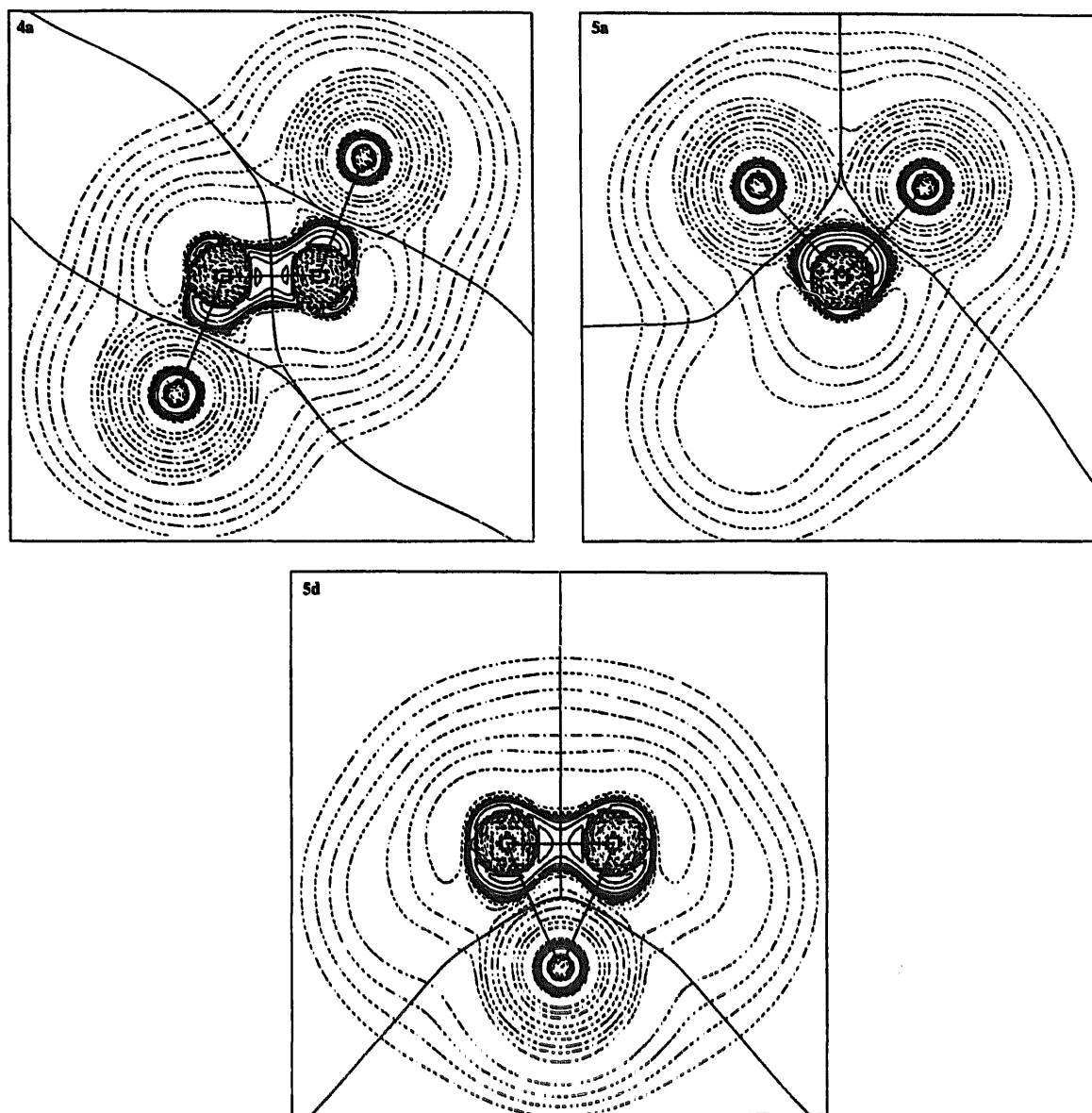


Fig. 2. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ of compounds 1–5d at MP2/II. Dashed lines indicate charge depletion ($\nabla^2\rho(r) > 0$), solid lines indicate charge concentration ($\nabla^2\rho(r) < 0$). The solid lines connecting the atomic nuclei are the bond paths, the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points r_b . See note [40] for the missing C–C bond paths of 1, 1⁺, 3a and 3d.

and Cu–ethylene complexes 1 and 2. The NBO analysis gives for the compounds 3a–3c Cu–C bond orbitals which are strongly polarized towards the carbon end (Table 3). Only about 24% of the Cu–C bond is at the copper end. The hybridization at Cu indicates that virtually only the 4s orbital is involved in the bonding. The hybridization of the Cu–C bonds shows that the carbon atoms in dicopperethylene 3a–3c are sp^3 -hybridized, while the carbon atoms of the copperethanes 4 and 5 have a much lower s-character. The s-character at the carbon atom is higher for the Cu–C bonds in the tetracopperethanes 5a and 5b than in the dicop-

perethanes 4a and 4b. This explains why 5a and 5b have shorter and stronger Cu–C bonds than 4a and 4b. The results of the topological analysis indicate some covalent contributions to the Cu–C bonds of 3a–3c (see the H_b values in Table 4). There is no Cu–C NBO in the complex 3d (Table 3). The Cu–Cu NBO of 3d is strongly polarized towards the terminal Cu atom. This shows that the metal–ligand bonding of 3d is mainly caused by induced dipole interactions.

The Cu–C bonding in the dicopperethane molecules 4a and 4b is similar to the bonding in 3a–3c. The NBO results show that the Cu–C bonds of 4a and 4b are

slightly less polarized towards the carbon end, and that the positive charge at Cu is lower than in **3a–3c** (Table 3). Similar results are obtained for **5a** and **5b**. Note the rather high negative partial charge at the carbon atoms of **5a** and **5b**. The H_p values for the Cu–C bonds of the isomers of **4** and **5** show some covalent contributions to the bonding. It follows that the NBO partitioning scheme and the topological analysis of the electron density distribution reveal strongly polar covalent Cu–C bonds for copperethylene **3** and copperethanes **4** and **5**. The contour line diagrams shown in Fig. 2 demonstrate clearly the charge concentration at the carbon end pointing towards the Cu atoms.

5. Summary and conclusion

The complexes of Cu^+ with acetylene and ethylene are strongly bonded compounds with a bond energy $D_c = 40.6 \text{ kcal mol}^{-1}$ for $\text{Cu}^+(\text{C}_2\text{H}_2)$ (1^+) and $D_c = 43.9 \text{ kcal mol}^{-1}$ for $\text{Cu}^+(\text{C}_2\text{H}_4)$ (2^+). The geometries of the charged complexes have C_{2v} symmetry, but the analysis of the electronic structure shows a T-shaped structure. The bonding is caused by the charge attraction between Cu^+ and the electronic charge of the CC π -bonds. The neutral complexes $\text{Cu}(\text{C}_2\text{H}_2)$ (**1**) and $\text{Cu}(\text{C}_2\text{H}_4)$ (**2**) have cyclic electronic structures. The neutral complexes **1** and **2** have weak metal–ligand bonds which are mainly caused by dispersion forces. The calculated geometries and bond energies of $\text{C}_2\text{H}_2\text{Cu}_2$ (**3**), $\text{C}_2\text{H}_4\text{Cu}_2$ (**4**) and $\text{C}_2\text{H}_2\text{Cu}_4$ (**5**) suggest that these molecules should be considered as copper-substituted ethylenes and ethanes, which have rather strong Cu–C bonds. The mean Cu–C bond strength for $\text{C}_2\text{H}_2\text{Cu}_2$ is $D_c \approx 25 \text{ kcal mol}^{-1}$, for $\text{C}_2\text{H}_4\text{Cu}_2$ it is $D_c \approx 16 \text{ kcal mol}^{-1}$ and for $\text{C}_2\text{H}_2\text{Cu}_4$ it is $D_c \approx 25 \text{ kcal mol}^{-1}$. There are four energy minima with C_{2v} symmetry on the $\text{C}_2\text{H}_2\text{Cu}_2$ potential energy surface. The geminal isomer of dicopper-substituted ethylene **3c** is $2.8 \text{ kcal mol}^{-1}$ lower in energy than the trans form **3b** and $6.4 \text{ kcal mol}^{-1}$ more stable than the cis form **3a**. The global energy minimum structure is an end-on bonded Cu_2 complex with acetylene **3d**, which is $5.9 \text{ kcal mol}^{-1}$ lower in energy than **3a**. Two energy minima are found on the $\text{C}_2\text{H}_4\text{Cu}_2$ potential energy surface. The anti form of $\text{C}_2\text{H}_4\text{Cu}_2$ **4a** is $4.5 \text{ kcal mol}^{-1}$ lower in energy than the gauche form **4b**. There are also two energy minima on the $\text{C}_2\text{H}_2\text{Cu}_4$ potential energy surface. The gauche form of tetracopperethane **5a** is only $0.3 \text{ kcal mol}^{-1}$ more stable than the anti form **5b**. The deformed structure of $\text{C}_2\text{H}_2\text{Cu}_4$ **5d** may be used as a model for the interactions between acetylene adsorbed on a copper(111) surface. The Cu–C bonds of copperethylene and copperethane are strongly polarized towards the carbon end. Relativistic effects yield clearly shorter Cu–C and Cu–Cu bonds.

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