# Metals in biology:
# Electronic structure, properties and charge transfer for copper complexes of glyoxal and dithiene*

*Ab initio* SCF calculations

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**Summary.** In an attempt to study the role of metals in biology *ab initio* SCF calculations have been performed on a model complex simulating the binding between metals and biological materials. There is a certain distinction between the copper complexes compared to the other transition metals and in many cases the copper complexes are more similar to the Li and Be complexes than to other transition metal complexes. One special feature of the copper complexes is their strong ability for an easy transfer between the Cu (I) and Cu (II) states, allowing for a very flexible charge transfer with small energies required for the redox processes. These processes have been described in terms of orbital energies and Mulliken populations.

**Key words:** Copper complexes – Charge transfer – Charge fluctuations – Redox reactions – Orbital energies – Mulliken population analysis

## 1 Introduction

In an attempt at classification of the role of metals in biological systems we have in the group of Professor Inga Fischer–Hjalmars for several years made quantum chemical calculations on a series of simple planar model complexes, shown in Fig. 1, chosen to simulate the binding between metal and the biological system; for a summary the reader is referred to [1, 2]. Until now, the metals Li, Be, Mg, Cr, Fe, Ni, Cu and Zn have been considered. As the metals commonly bind to oxygen, nitrogen and sulfur in biological systems, the ligating atoms X in Fig. 1 are chosen to be O, N or S. The model complex is believed to simulate the binding between the metals and amino acids, peptides, catecholic structures, ascorbic acid as well as larger structures.

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* Dedicated to Professor Inga Fischer–Hjalmars on the occasion of her 75th birthday
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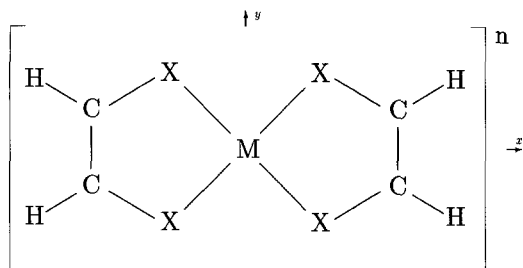
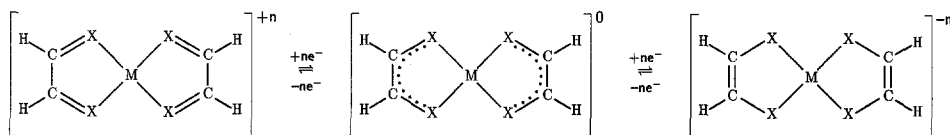Fig. 1. The model complex studied. $M = Cu$, $X = O$ or $S$ $n = +2$, $+1$, $0$, $-1$, $-2$, $-3$



Fig. 2. Possible resonance structures for the model complex

The total charge, $n$, of the system has been varied from $+2$ to $-2$ according to the canonical structures shown in Fig. 2. Thus a whole set of molecules have been studied, making a comparison between the effects obtained by interchanging one variable (metal, ligand or total charge) at a time, possible.

A further advantage of this choice of model system is that these complexes have been studied rather extensively experimentally. This is the case especially for the sulfur compounds [3]. There are also some quantum chemical calculations on the Extended Huckel level [3b], on the INDO-CI level [4] as well as on the *ab initio* level [5]. The complex has also been used as model complex for iron–sulfur proteins, especially ferredoxin and rubredoxin, molybdenum–sulfur proteins, as xanthine oxidase and nitrogenase as well as for copper proteins [3, 6].

Our calculations show that there are properties that are connected to the special metals as well as properties that are connected to the ligand dimer. An example of the latter case is the presence of the very small energy gap between the highest occupied and lowest unoccupied orbitals (which both are $\pi$ orbitals) in the $n = +1, 0, -1$ complexes. Here the role of the metal seems only to be to form a bridge between the ligand dimers [7]. Concerning the metal part, the different electronic configurations of the different metals may give rise to properties that are special to that metal. Such properties are, for example, the orbital energies of the (more or less delocalized) metal orbitals as well as the charge distributions and oxidation states of the metal. This has been discussed rather extensively in Ref. [1].

Copper can exist in several oxidation states: most common are the stable Cu (II) and the rather unstable Cu(I), but the existence of the higher oxidation states Cu(III) and Cu(IV) has also been discussed [8]. The role of copper can thus be expected to be of different type than what is expected for other transition metals, which mainly occur in the oxidation state $+ II$ and higher. Thus a more detailed investigation of the copper complexes seems appropriate.

Copper-containing compounds occur in a large amount of important industrial as well as biological processes. Copper compounds have for a long time been widely used as catalysts, as for example in the Glaser reaction for the oxidative

coupling of the acetylenes [9]. Copper also occurs in several enzymes taking part in redox reactions as well as in the binding and activation of $O_2$. The literature in this field is huge [8]. Examples of copper-containing enzymes are the blue copper proteins (azurin, stellacyanin and umecyanin which take part in electron transfer processes in the photosynthesis of algae, green leaves and other plants, laccase, ceruloplasmin and ascorbate oxidase, which reduce $O_2$ to $H_2O$ in humans, animals and plants), the non-blue oxidases (amine oxidase and galactose oxidase which reduce $O_2$ to $H_2O_2$ in animals and plants) hemocyanin (the oxygen carrier), tyrosinase, dopamine betahydroxylase as well as superoxide dismutase, which is believed to take part in the detoxification of $O_2^-$, and cytochrome c oxidase in the mitochondria functioning as terminal oxidase. Many of these reactions are known to proceed very rapidly.

Copper compounds have also been used in medicine, as for example the antitumor antibiotic bleomycin as well as the copper phenanthroline system. Copper can also have toxic effects: well known is the problem with copper pipes used for the supply of drinking water as well as the use of copper-containing cooking utensiles.

The role of copper has also raised interest in the context of the development of new types of superconductors. It should be pointed out that compounds of the type shown in Fig. 1, with X = S, have been shown to be among the most promising types for organic superconductors [10]. Also, for the ceramic superconductors, the importance of the planar $CuO_4$ structures has been stressed by several authors [11]. Also in this context a detailed understanding of the electronic structure of the model complex in Fig. 1 seems reasonable.

## 2 Method and details of the calculations

*Ab initio* RHF SCF calculations have been performed with the program system MOLECULE–ALCHEMY [12] using Gaussian basis functions. Open shell systems have been treated within the Roothaan formalism [13].

This level of sophistication has been used in order for us to compare with our previous RHF-calculations on the same series of complexes [1, 2]. Inclusion of more sophisticated methods, as MC-SCF or CI, will certainly change the quantitative and maybe even the qualitative results. However, as we are mainly interested in the comparison between different molecules in a series of similar compounds, the shifts in trends are more important than the absolute values. Thus, an even less sophisticated method could be used for our purpose. The lack of a complete series of metal parameters for the metals in question, however, restricted us from using some semiempirical method.

The basis sets are the same as in our previous calculations [1], i.e. for hydrogen the $4s$ basis of Huzinaga [14] scaled by 1.25, for carbon, oxygen and sulfur the Roos–Siegbahn basis [15] and for Cu the Roos–Veillard $12s, 6p, 4d$ basis [16] with some minor changes. Thus the innermost $s$-function was deleted, since it was not supposed to take part in the binding and also the three outermost $s$-functions because they can be described by the totally symmetric combination of the $d$-functions. (The latter was done to reduce the size of the calculations, but it turned out not to be a good choice, since the distinction between the $s$- and $d$-populations on copper could not be made any longer in the further analysis). For a better description of the binding between copper and the ligands, two additional diffuse $p$-functions with the coefficients 0.3997 and 0.1456 respectively, and one diffuse

**Table 1.** Geometry chosen for the complex

| Bond | Distance (in Ångstrom) | |
|------|-------|-------|
|      | X = O | X = S |
| CX   | 1.26  | 1.73  |
| CC   | 1.50  | 1.37  |
| CH   | 1.09  | 1.09  |
| XX   | 2.76  | 3.10  |
| XX'  | 2.95  | 2.92  |
| MX   | 2.02  | 2.13  |

The bond angles C–C–H are in all cases 120°

$d$-function with the coefficient 0.2214 were included. Contractions were mainly to double zeta basis, except for metal $1s$, $2s$ and $2p$ and sulfur $1s$ orbitals, for which a minimal basis set was chosen. On sulfur, no $d$-orbitals were included, since they have been found to be of little importance in the present model system [17] what concerns the lowest energy states. This was found to be true also in the INDO-calculations [4a].

The geometries of the complexes were chosen to be the same as in our previous calculations on the other metal complexes and are listed in Table 1. No geometry optimization was performed. Although there certainly are geometry changes when the central metal is changed as well as when the overall charge, $n$, of the complex is changed, we have found it convenient to use the same geometry in all the calculations, partly because it makes the calculations easier (the same integrals can be used for different total charge $n$) but mainly because a comparison between the complexes will be more straightforward. A further geometry optimization will await a second step in the calculations.

The overall charge on the complexes was varied from $n = +2$ to $n = -3$. The complex can be considered as built up from the different resonance structures according to Fig. 2, i.e. the $n = +2$ complex could be considered to consist of a complex between the doubly charged $Cu^{+2}$ ion and two neutral ligands, as shown on the left hand side in the figure. The $n = +1$ complex is, similarly, considered as built up from a singly charged $Cu^{+1}$ ion and two neutral ligands. The negatively charged structures, on the other hand, can be considered as built up from two doubly negatively charged ligands and a $Cu^{+2}$ ion (for $n = -2$) or a $Cu^{+1}$ ion (for $n = -3$), respectively, as shown on the right-hand side of Fig. 2.

The electronic configurations chosen in the calculations were for Cu(I) $d^{10}$ and for Cu(II) $d^9$. Thus the electronic configuration on copper was chosen to be $d^9$ for $n =$ even and $d^{10}$ for $n =$ odd. The open shell in the $d^9$ configuration was chosen to be within the $b_{1g}$ ($d_{xy}$) symmetry. This follows from "chemical intuition" according to the scheme in Fig. 2 as well as from ligand field theory and also more sophisticated calculations [3b, 4]. As the ALCHEMY program system makes use of the symmetry of the molecule in blocking the matrices, this symmetry will prevail during the calculations.

As pointed out in the calculations for the corresponding Fe-complexes [2], there could be several electronic configurations with about the same, or even lower

energy than the expected ground state. The unpaired electron could be in an orbital localized over the whole molecule or mainly on either the metal or the ligands. Most probably these complexes will have somewhat different geometries, as was the case for the corresponding Fe-complexes. The presence of a type of compounds that show "bond stretch isomerism" has experimentally been demonstrated by Hoffmann et al. [18]. A detailed study of different possible electronic structures of the copper complexes will await a further study, also including geometry optimization.

## 3 Results and discussion

### 3.1 Total energies

Total energies for the complexes are listed in Table 2. It is seen that for the oxygen complexes the $n = 0$ state has the lowest energy, whereas for the sulfur complexes the $n = -2$ state has the lowest energy. This is in accordance with our previous calculations for other metals [1].

As also seen from Table 2, the energy differences between the different states are very small. For the oxygen complexes the $n = -1$ state is only 1.1 eV (8600 cm$^{-1}$) higher than the $n = 0$ state and the $n = -2$ state is only 1.7 eV (12600 cm$^{-1}$) higher than the $n = -1$ state. These energy differences are just slightly larger than ordinary vibrational energies. Also, the energy differences between the $n = 0$ and $n = +1$ and between the $n = +1$ and $n = +2$ states are rather small, 5.3 eV and 9.4 eV, respectively. The $n = -3$ state is rather high in energy, and as seen below, supposed to be rather unstable.

**Table 2.** Total energies for the copper complexes[a] as well as the energy differences as a function of the overall charge $n$ of the complex

| $n$ | $E(n)$ (a.u.) | $E(n) - E(n-1)$ (eV) | (kcal/mol) | Comments |
|---|---|---|---|---|
| | | Oxygen ligands | | |
| + 2 | − 2082.68049 | 9.4 | 217 | Cu$^{2+}$ |
| + 1 | − 2083.02620 | 5.3 | 121 | Cu$^{+}$ |
| 0 | − 2083.21909 | − 1.7 | − 36 | Cu$^{2+}$ |
| − 1 | − 2083.16178 | − 1.1 | − 25 | Cu$^{+}$ |
| − 2 | − 2083.12256 | − 12.6 | − 290 | Cu$^{2+}$ |
| − 3 | − 2082.66057 | | | |
| | | Sulfur ligands | | |
| + 2 | − 3371.48939 | 9.2 | 212 | Cu$^{2+}$ |
| + 1 | − 3371.82764 | 9.9 | 229 | Cu$^{+}$ |
| 0 | − 3372.19293 | − 0.5 | − 12 | Cu$^{2+}$ |
| − 1 | − 3372.17375 | 1.3 | 30 | Cu$^{+}$ |
| − 2 | − 3372.22161 | − 10.7 | − 248 | Cu$^{2+}$ |
| − 3 | − 3371.82685 | | | Cu$^{+}$ |

[a] The corresponding energies for the free ligands are: For the oxygen ligand − 226.22535 a.u. and for the sulfur ligand − 870.68911 a.u. For Cu$^{2+}$ the corresponding value is − 1629.68147 and for Cu$^{+}$ − 1630.3301, respectively

For the sulfur complexes the energy differences are still smaller than for the oxygen complexes, i.e. the $n = -1$ state is only 1.3 eV (10 500 cm$^{-1}$) higher than the $n = -2$ state, whereas the $n = 0$ state is 0.5 eV lower than the $n = -1$ state and consequently only 0.8 eV (6300 cm$^{-1}$) higher than the $n = -2$ state.

As no geometry optimization has been done, these results may change by more accurate calculations as well as by using more sophisticated methods or better basis sets. Anyhow, the present calculations indicate that there are states with different total charge $n$ with about the same energy. This means that, unless there is a high energy barrier between the initial and final states, transitions between the different $n$ values easily can occur, i.e. the molecules can easily undergo oxidation–reduction reactions, which also is found experimentally to be the case [3, 6].


## 3.2 Binding energies

Calculated binding energies defined as the energy difference between the neutral dimers and the $Cu^{+2}$ or $Cu^{+1}$ ions, respectively, are listed in Table 3. For comparison, also the binding energies of the corresponding Li and Be complexes are included. All complexes, except the $n = -3$ oxygen complex, have positive binding energies, i.e. all complexes except the oxygen $n = -3$ complex should be stable.

The binding energies for the $n$ = odd complexes are very close to the binding energies of the corresponding Li-complexes, [1, 19] whereas the binding energies for the $n$ = even complexes are very close to the corresponding Be-complexes and much higher than for the other second row transition metals [1] in accordance with the experimentally obtained and well-known Irving–Williams diagram [20]. Thus, what concerns the binding energies copper is more like the first row atoms Be and Li than the other second row transition metals.

**Table 3.** Binding energies (in eV) for the complexes with reference to the free ligand and metal ion. For comparison, also the calculated binding energies for the corresponding Li- and Be complexes are included [19]

| Overall charge | | Metal | |
| --- | --- | --- | --- |
| $n$ | Cu | Li | Be |
| | Oxygen complexes | | |
| + 2 | 14.9 | | 14.0 |
| + 1 | 6.7 | 4.4 | |
| 0 | 29.6 | | 29.1 |
| − 1 | 10.3 | 7.9 | |
| − 2 | 27.1 | | 25.9 |
| − 3 | − 3.3 | | |
| | Sulfur complexes | | |
| + 2 | 11.7 | | 11.5 |
| + 1 | 3.2 | 0.9 | |
| 0 | 30.8 | | 30.9 |
| − 1 | 12.7 | 10.0 | |
| − 2 | 31.6 | | 30.8 |
| − 3 | 3.2 | | |

## 3.3 Orbital energies

The calculated orbital energies for the valence electrons as well as for some of the lowest empty orbitals are listed in Table 4 for the oxygen complexes (Table 4a for *n* even and Table 4b for *n* odd) and in Table 5 for the sulfur complexes (Table 5a for *n* even and Table 5b for *n* odd). For comparison, the corresponding orbital energies for the Li complexes are included in Tables 4b and 5b and for the Be complexes in Tables 4a and 5a [21].

Even if there is a clear mixing between the ligand orbitals and the metal orbitals, predominantly ligand orbitals can clearly be distinguished from

**Table 4a.** Calculated orbital energies (in eV) for the oxygen complexes for $n = +2, 0$ and $-2$. For comparison, the corresponding values for the Be-complexes are also given [21]

| Symmetry | Orbital type[a] | $n = +2$ | | $n = 0$ | | $n = -2$ | |
|---|---|---|---|---|---|---|---|
| | | Cu | Be | Cu | Be | Cu | Be |
| $a_g$ | C, O | − 50.6 | − 51.1 | − 39.2 | − 39.3 | − 27.7 | − 27.5 |
| $b_{3u}$ | C, O | − 50.5 | − 49.9 | − 39.0 | − 39.1 | − 27.6 | − 27.3 |
| $b_{2u}$ | C, O | − 49.5 | − 49.9 | − 38.1 | − 38.1 | − 26.6 | − 26.3 |
| $b_{1g}$ | C, O | − 49.4 | − 49.7 | − 38.1 | − 37.9 | − 26.6 | − 26.1 |
| $a_g$ | O, C | − 37.5 | − 37.8 | − 26.3 | − 26.3 | − 15.4 | − 15.2 |
| $b_{3u}$ | O, C | − 37.3 | − 37.5 | − 26.1 | − 26.0 | − 15.3 | − 14.9 |
| $b_{2u}$ | C, O | − 32.5 | − 33.1 | − 21.6 | − 21.9 | − 11.0 | − 10.9 |
| $b_{1g}$ | C, O | − 32.3 | − 32.1 | − 21.5 | − 21.1 | − 10.8 | − 10.3 |
| $a_g$ | Cu,C,O | − 31.8 | − 31.6 | − 20.7 | − 20.1 | − 9.7 | − 8.9 |
| $b_{1g}$(open) | Cu | − 31.0 | | − 19.8 | | − 8.7 | |
| $a_g$ | Cu | − 30.9 | | − 19.8 | | − 8.7 | |
| $b_{2g}$ | Cu | − 30.1 | | − 19.0 | | − 8.2 | |
| $b_{3g}$ | Cu | − 29.9 | | − 18.8 | | − 8.0 | |
| $a_g$ | Cu | − 29.5 | − 30.0 | − 18.4 | − 18.6 | − 7.5 | − 7.1 |
| $a_g$ | Cu | − 28.6 | | − 17.5 | | − 6.4 | |
| $b_{3u}$ | C, O | − 30.9 | − 31.3 | − 19.8 | − 19.9 | − 8.9 | − 8.8 |
| $b_{3u}$ | C, O | − 28.6 | − 28.5 | − 17.4 | − 16.9 | − 6.0 | − 5.2 |
| $b_{2u}$ | C, O | − 27.8 | − 28.2 | − 16.9 | − 17.0 | − 5.9 | − 5.8 |
| $b_{1g}$ | C, O | − 27.5 | − 27.4 | − 16.5 | − 16.1 | − 5.5 | − 4.6 |
| $b_{1u}$ | C, O | − 26.4 | − 26.9 | − 16.0 | − 16.2 | − 5.6 | − 5.4 |
| $b_{2g}$ | C, O | − 26.0 | − 25.6 | − 15.5 | − 15.7 | − 5.1 | − 5.1 |
| $b_{1g}$ | O | − 25.4 | − 24.5 | − 14.0 | − 13.0 | − 3.1 | − 2.5 |
| $b_{2u}$ | O | − 24.9 | − 25.5 | − 13.9 | − 14.1 | − 2.6 | − 3.1 |
| $a_u$ | O | − 24.5 | − 24.7 | − 13.8 | − 13.6 | − 3.5 | − 3.1 |
| $b_{3g}$ | O | − 24.4 | − 25.0 | − 13.9 | − 14.1 | − 3.5 | − 3.4 |
| $a_g$ | O | − 23.2 | − 23.7 | − 12.2 | − 12.4 | − 1.2 | + 1.1 |
| $b_{3u}$ | O | − 22.9 | − 23.3 | − 11.9 | − 11.9 | − 0.8 | + 1.6 |
| $b_{1u}$ | C, O | − | − | − 4.8 | − 5.0 | + 3.4 | + 3.6 |
| $b_{2g}$ | C, O | − | − | − | − | + 3.7 | + 4.1 |
| Virtual: | | | | | | | |
| $b_{1u}$ | | − 9.9 | − | − | − | − | − |
| $b_{2g}$ | | − 9.5 | − | − 1.2 | − | − | − |

[a] The orbital type describes the two most important contributions

**Table 4b.** Calculated orbital energies (in eV) for the oxygen complexes for $n = +1$, $-1$ and $-3$. For comparison, the corresponding values for the Li-complexes are also given [21]

| Symmetry | Orbital type[a] | $n = +1$ | | $n = -1$ | | $n = -3$ |
|---|---|---|---|---|---|---|
| | | Cu | Li | Cu | Li | Cu |
| $a_g$ | C, O | − 44.6 | − 44.5 | − 33.3 | − 33.1 | − 21.9 |
| $b_{3u}$ | C, O | − 44.6 | − 44.5 | − 33.2 | − 33.1 | − 21.8 |
| $b_{2u}$ | C, O | − 43.6 | − 43.5 | − 32.3 | − 32.2 | − 20.9 |
| $b_{1g}$ | C, O | − 43.6 | − 43.5 | − 32.3 | − 32.1 | − 20.9 |
| $a_g$ | O, C | − 31.9 | − 31.9 | − 21.0 | − 20.9 | − 10.4 |
| $b_{3u}$ | O, C | − 31.9 | − 31.8 | − 20.9 | − 20.8 | − 10.3 |
| $b_{2u}$ | C, O | − 26.9 | − 26.9 | − 16.3 | − 16.2 | − 5.9 |
| $b_{1g}$ | C, O | − 26.9 | − 26.6 | − 16.2 | − 16.0 | − 5.9 |
| $a_g$ | C, O | − 25.5 | − 25.3 | − 14.6 | − 14.4 | − 3.8 |
| $b_{3u}$ | C, O | − 25.3 | − 25.3 | − 14.4 | − 14.4 | − 3.7 |
| $a_g$ | C, O | − 23.7 | − 23.3 | − 12.5 | − 11.4 | − 1.3 |
| $b_{3u}$ | C, O | − 22.8 | − 22.7 | − 11.6 | − 12.1 | − 0.3 |
| $b_{2u}$ | C, O | − 22.3 | − 22.2 | − 11.4 | − 11.3 | − 0.4 |
| $b_{1g}$ | C, O | − 22.0 | − 21.9 | − 11.4 | − 10.9 | 0.0 |
| $b_{2g}$ | C, O | − 20.8 | − 20.5 | − 10.4 | − 10.1 | − 0.2 |
| $b_{1u}$ | C, O | − 20.7 | − 20.6 | − 10.4 | − 10.3 | − 0.2 |
| $b_{1g}$ | O, Cu | − 20.4 | − 18.8 | − 9.5 | − 7.6 | + 1.8 |
| $b_{2u}$ | C, O | − 19.3 | − 19.2 | − 8.2 | − 8.0 | + 3.2 |
| $b_{3g}$ | C, O | − 19.0 | − 18.6 | − 8.6 | − 8.2 | + 1.7 |
| $a_u$ | C, O | − 18.6 | − 18.5 | − 8.0 | − 7.9 | + 2.1 |
| $a_g$ | C, O | − 18.0 | − 17.2 | − 7.1 | − 6.3 | + 4.0 |
| $b_{3u}$ | C, O | − 17.2 | − 17.2 | − 6.2 | − 6.2 | + 4.8 |
| $b_{2g}$ | Cu | − 16.1 | | − 5.3 | | + 5.1 |
| $b_{3g}$ | Cu | − 16.0 | | − 5.5 | | + 5.5 |
| $a_g$ | Cu | − 16.9 | | − 5.4 | | + 5.7 |
| $a_g$ | Cu | − 15.8 | | − 5.2 | | + 6.0 |
| $b_g$ | Cu | − 14.5 | | − 3.7 | | + 7.6 |
| $b_{1u}$ | C, O | − | − | + 0.6 | + 0.7 | + 8.7 |
| $b_{2g}$ | C, O | − | − | − | − | + 9.1 |
| Virtual: | | | | | | |
| $b_{1u}$ | | − 4.3 | − | − | − | − |
| $b_{2g}$ | | − 3.9 | − | + 4.4 | − | − |

[a] The orbital type describes the two most important contributions

predominantly metal orbitals. The mixing is somewhat more pronounced for the sulfur complexes than for the oxygen complexes.

The ligand orbitals are very constant in energy (generally less than 0.5 eV) when comparing different metal complexes with given total charge, $n$. This is the case both for the transition metal complexes [1] as well as the Li and Be complexes indicating that the interaction between metal and ligand is similar for all metals studied.

For different total charges, $n$, the ligand orbital energies will go up (be more positive) by about 5.5–6 eV in the oxygen complexes and by about 4.5–5.1 eV in the sulfur complexes for each electron that is added to the system.

**Table 5a.** Calculated orbital energies (in eV) for the sulfur complexes for $n = +2$, 0 and $-2$. r comparison, the corresponding values for the Be-complexes are also given [21]

| Symmetry | Orbital type[a] | $n = +2$ Cu | Be | $n = 0$ Cu | Be | $n = -2$ Cu | Be |
|---|---|---|---|---|---|---|---|
| $a_g$ | C, S | − 41.8 | − 41.0 | − 31.6 | − 31.6 | − 21.7 | − 21.6 |
| $b_{3u}$ | C, S | − 41.7 | − 39.9 | − 31.4 | − 31.5 | − 21.6 | − 21.5 |
| $b_{2u}$ | S, C | − 37.4 | − 37.6 | − 27.5 | − 27.6 | − 17.6 | − 17.6 |
| $b_{1g}$ | S, C | − 37.2 | − 37.2 | − 27.3 | − 27.2 | − 17.4 | − 17.2 |
| $a_g$ | S, C | − 35.1 | − 37.8 | − 25.2 | − 25.1 | − 15.5 | − 15.3 |
| $b_{3u}$ | S, C | − 34.2 | − 34.3 | − 24.2 | − 24.2 | − 14.6 | − 14.5 |
| $b_{2u}$ | C, S | − 30.2 | − 30.5 | − 20.6 | − 20.7 | − 11.2 | − 11.3 |
| $a_g$ | Cu | − 30.0 | | − 20.1 | | − 10.1 | - |
| $b_{1g}$ | C, S | − 29.6 | − 29.2 | − 20.0 | − 18.8 | − 10.7 | − 10.3 |
| $b_{3g}$ | Cu | − 28.7 | | − 18.8 | | − 8.8 | |
| $a_g$ | C, Cu | − 28.6 | − 28.7 | − 18.8 | − 18.8 | − 9.2 | − 9.4 |
| $b_{2g}$ | Cu | − 28.6 | | − 18.6 | | − 9.4 | |
| $b_{3u}$ | C | − 28.5 | | − 18.7 | | − 9.3 | |
| $a_g$ | C, Cu | − 28.2 | − 27.2 | − 18.3 | − 17.5 | − 8.4 | − 7.1 |
| $a_g$ | C,S,Cu | − 26.2 | | − 16.3 | | − 6.4 | |
| $b_{1g}$(open) | Cu | − 25.4 | | − 16.0 | | − 6.2 | |
| $b_{2u}$ | C, S | − 24.4 | − 24.6 | − 14.6 | − 14.8 | − 5.0 | − 5.1 |
| $b_{3u}$ | S, C | − 24.2 | − 24.4 | − 14.3 | − 14.2 | − 4.4 | − 4.2 |
| $b_{1g}$ | C, S | − 23.5 | − 22.4 | − 13.6 | − 12.7 | − 3.8 | − 2.9 |
| $b_{1u}$ | C, S | − 22.9 | − 23.1 | − 13.9 | − 14.0 | − 4.8 | − 4.7 |
| $b_{2g}$ | C, S | − 22.4 | − 22.7 | − 13.3 | − 13.5 | − 8.8 | − 4.4 |
| $a_g$ | S, Cu | − 22.0 | − 22.4 | − 12.4 | − 12.8 | − 2.7 | − 3.0 |
| $b_{1g}$ | S, Cu | − 21.7 | − 18.8 | − 12.1 | − 9.2 | − 2.3 | + 1.0 |
| $b_{3u}$ | S, Cu | − 21.1 | − 21.5 | − 11.6 | − 11.8 | − 1.8 | − 2.0 |
| $b_{2u}$ | S, Cu | − 20.4 | − 20.9 | − 11.0 | − 11.3 | − 1.2 | − 1.5 |
| $b_{3g}$ | S | − 19.8 | − 20.1 | − 10.6 | − 10.9 | − 1.3 | − 1.6 |
| $a_u$ | S | − 19.4 | − 19.4 | − 9.9 | − 9.8 | − 1.0 | − 0.9 |
| $b_{1u}$ | C, S | – | – | − 7.4 | − 7.4 | + 0.5 | + 0.5 |
| $b_{2g}$ | C, S | – | – | – | – | + 1.8 | + 1.8 |
| Virtual: | | | | | | | |
| $b_{1u}$ | | − 11.8 | – | – | – | – | – |
| $b_{2g}$ | | − 10.6 | – | − 2.6 | – | – | – |

[a] The orbital type describes the two most important contributions

What concerns the metal $d$-orbital energies, the situation is now different and a distinction has to be made between the $n = $ odd ($d^{10}$) and $n = $ even ($d^9$) cases. In all cases the metal orbital energies are higher (less negative) for $n = $ odd than for the corresponding $n = $ even ($n + 1$, $n - 1$) cases, showing an alternating behavior, which can be explained by the smaller attraction of the $Cu^{+1}$ ion than by the $Cu^{+2}$ ion. A similar behavior, although not so pronounced, can be seen for the corresponding Fe(II) and Fe(III) complexes [2, 22] and has been used for the assignment of the oxidation state of the metal in the complexes.

**Table 5b.** Calculated orbital energies (in eV) for the sulfur complexes for $n = +1$, $-1$ and $-3$. For comparison, the corresponding values for the Li-complexes are also given [21]

| Symmetry | Orbital type[a] | $n = +1$ Cu | $n = +1$ Li | $n = -1$ Cu | $n = -1$ Li | $n = -3$ Cu |
|---|---|---|---|---|---|---|
| $a_g$ | C, S | − 36.6 | − 36.6 | − 26.5 | − 26.5 | − 16.9 |
| $b_{3u}$ | C, S | − 36.5 | − 36.6 | − 26.4 | − 26.5 | − 16.9 |
| $b_{2u}$ | C, S | − 32.2 | − 32.2 | − 22.4 | − 22.3 | − 12.6 |
| $b_{1g}$ | C, S | − 32.0 | − 31.9 | − 22.2 | − 22.0 | − 12.5 |
| $a_g$ | C, S | − 29.7 | − 29.5 | − 20.0 | − 19.7 | − 10.4 |
| $b_{3u}$ | C, S | − 29.0 | − 29.1 | − 19.2 | − 19.2 | − 9.7 |
| $b_{2u}$ | C, S | − 25.2 | − 25.2 | − 15.7 | − 15.7 | − 6.5 |
| $b_{1g}$ | C, S | − 24.8 | − 24.4 | − 15.3 | − 14.9 | − 6.1 |
| $a_g$ | C | − 23.8 | − 23.8 | − 14.1 | − 14.1 | − 4.9 |
| $b_{3u}$ | C | − 23.7 | − 23.8 | − 14.0 | − 14.1 | − 4.8 |
| $a_g$ | C, S | − 22.0 | − 21.0 | − 12.1 | − 11.1 | − 2.2 |
| $b_{1g}$ | Cu | − 20.3 | | − 10.9 | | − 0.4 |
| $b_{2u}$ | C, S | − 19.3 | − 19.3 | − 9.7 | − 9.6 | − 0.1 |
| $b_{3u}$ | C, S | − 19.0 | − 18.9 | − 9.2 | − 9.0 | + 0.5 |
| $b_{2g}$ | Cu | − 18.9 | | − 9.4 | | − 0.2 |
| $a_g$ | Cu | − 18.9 | | − 9.6 | | + 1.2 |
| $b_{2g}$ | Cu | − 18.8 | | − 9.6 | | + 1.1 |
| $b_{1u}$ | C, S | − 18.1 | − 18.1 | − 9.1 | − 9.1 | − 0.1 |
| $a_g$ | Cu | − 17.6 | − 17.5 | − 8.2 | − 7.9 | + 2.6 |
| $b_{1g}$ | C, S | − 17.3 | | − 7.8 | | + 1.9 |
| $b_{2g}$ | C, Cu | − 16.8 | − 17.8 | − 7.2 | − 8.8 | + 1.9 |
| $a_g$ | S, Cu | − 16.1 | − 16.3 | − 6.8 | − 6.7 | + 3.5 |
| $b_{3u}$ | S, Cu | − 15.9 | − 15.9 | − 6.4 | − 6.2 | + 3.5 |
| $b_{2u}$ | S | − 15.3 | − 15.3 | − 5.9 | − 5.7 | + 3.9 |
| $b_{3g}$ | S | − 14.4 | − 14.8 | − 5.3 | − 5.8 | + 4.2 |
| $a_u$ | S | − 14.3 | − 14.3 | − 5.0 | − 5.3 | + 3.9 |
| $b_{1g}$ | S, Cu | − 11.7 | − 13.9 | − 2.3 | − 4.2 | + 7.9 |
| $b_{1u}$ | | − | − | − 2.6 | − 2.4 | + 5.5 |
| $b_{2g}$ | | − | − | − | − | + 6.9 |
| Virtual: | | | | | | |
| $b_{1u}$ | | − 6.8 | − | − | − | − |
| $b_{2g}$ | | − 5.4 | − | + 2.6 | − | − |

[a] The orbital type describes the two most important contributions

Whereas, for the $n =$ even complexes, the orbital energies for the $d$-orbitals are rather low compared to the ligand orbitals, now, for the $n =$ odd complexes, the orbital energies are among the highest ligand orbital energies.

Within each of the series, $n =$ even or $n =$ odd, the trends are the same as for the corresponding ligand orbitals, i.e. the orbital energies are shifted upwards (more positive), now by about 10.5–11.2 eV for the oxygen complexes and 9.2–10.7 eV for the sulfur complexes when two electrons at a time are added to the system.

Although it should be remembered that Koopmans' theorem [23] is not valid for the transition metals [24], the orbital energy picture is in good agreement with the very comprehensive study [25] of the experimentally obtained photoelectron spectra on large series of similar molecules, including among others acetylacetonates, amides and related complexes, sulfur-containing metal complexes etc. In the study it is stated that "Ionizations are evident before ligand ionizations with early transition metals Ti(III), V(III) or Cr(III), not evident at all or masked under ligand ionization bands with late transition metals such as Cu(II) or Zn(II), and highly intermixed with the first ligand ionizations for intermediate transition metal configurations such as $d^6$ of Co(III) or $d^8$ of Ni(II). This type of behavior is probably of general occurrence and is in fact found also in other classes of coordination compounds, especially with sulfur ligands."

Generally, Koopmans theorem for transition metals give larger values than the true values by several eV [22, 25]. For the ligand orbitals, the Koopmans' theorem should still be valid. In fact, our calculated ligand orbital energies are in good agreement with the experimentally observed ionization potentials for similar compounds [25].

In an earlier paper [7] it was pointed out that when the ligand $b_{1u}$ orbital was singly or doubly occupied the orbital energy gap between the HOMO and the LUMO ($b_{2g}$) becomes very small. This small band gap suggests that electron transfer should easily occur in these types of complexes. This is a property of interest not only in biological context, but also of great relevance in electrical conductivity [26, 27]. This small band gap was found to be a function of the ligand dimer only and the role of the metal was only to bind the ligands together. The effect was called the "metal bridge effect".

In the copper complexes, for $n$ odd, the copper orbitals are high in energy. Having in mind the good conducting properties of only the copper compounds one may ask if just the small band gap between the highest occupied copper orbital and the lowest unoccupied ligand orbital is of relevance for the conducting properties. Perhaps these orbitals will even make the band gap smaller or allow charge transfer to proceed all over the molecule, the copper orbital being localized mainly on the copper atom whereas the ligand orbitals are mainly localized on the ligands.

## 3.4 Charge distributions

The electronic charge distribution is often described by the aid of Mulliken population analysis [28]. Although this scheme has its weaknesses, and many other schemes have been proposed [29], it has been extensively used and gives a useful description of the charge distribution and trends in shifts of electronic density in series of similar molecules.

In the terminology of Mulliken we define the gross charge as the sum of the positive nuclear charge and the negative gross atomic population. The net charge, again, is defined as the sum of the positive nuclear charge and the negative net atomic population.

As discussed in a previous paper [22], the use of diffuse functions will give some problems in interpreting the charge distributions. The diffuse functions may have their radial maxima nearer to the ligand atoms than to the metal atom, which was shown to be the case for the Fe orbitals in the Fe complexes. This allows for a rather large charge distribution to be localized in these orbitals. This will also be the case for the present study. After removal of these diffuse parts both the charge

and the $3d$ population were found to obtain values in line with those of the oxidation states of free metal ions.

As in this context trends in shifts in a series of similar compounds are of greater interest than the absolute values, we will in the following show that a further elaboration in terms of changes in gross and net populations will give some useful information.

## Gross charges on the metal

The gross charges on the metals show some peculiarities as already pointed out before [1]. Table 6 lists the gross charges on the Cu-atom compared with the corresponding values for Fe, Li and Be. The charges are generally unexpectedly low, and tend even to be negative in the sulfur complexes. These low charges which were not found in the INDO-CI calculations [4a] is an effect of the use of diffuse orbitals in connection with the use of Mulliken population analysis, as discussed previously [22]. Whether this effect is just an artefact or has a physical meaning may be taken under consideration.

Considering first the oxygen complexes, good agreement with the corresponding Be and Li complexes is again obvious, indicating a clear distinction between the Cu(I) and Cu(II) states, whereas the corresponding values for the Fe complexes are not so clear.

For the sulfur complexes, the gross charges on the metals are very low, especially for the Cu and Fe complexes. Here there is no possibility to distinguish between the different oxidation states. Instead, what concerns the Cu complexes, the charge on the metal will be continuously more positive, the more negative the overall charge $n$ on the complex will be, whereas again the trends for the corresponding Fe values are less clear. A comparison with the corresponding Li and Be complexes no longer

**Table 6.** Gross charges on the metal in the complex. For comparison also the charges on the metals Li, Be [21] and Fe [2d] in the corresponding complexes are included

| Overall charge $n$ | Gross charges on the metal | | | | | |
|---|---|---|---|---|---|---|
|  | Cu(I) | Cu(II) | Fe(II) | Fe(III) | Li | Be |
| | | | Oxygen complexes | | | |
| + 2 |  | 1.12 | 1.12 |  |  | 1.14 |
| + 1 | 0.57 |  | 1.00 | 1.27 | 0.57 |  |
| 0 |  | 0.93 | 0.87 |  |  | 1.05 |
| − 1 | 0.49 |  | 0.79 | 1.11 | 0.38 |  |
| − 2 |  | 0.84 | 0.71 |  |  | 1.02 |
| − 3 | 0.33 |  |  |  |  |  |
| | | | Sulfur Complexes | | | |
| + 2 |  | 0.09 | − 0.04 |  |  | 0.73 |
| + 1 | 0.17 |  | − 0.05 | − 0.05 | 0.29 |  |
| 0 |  | 0.23 | − 0.07 |  |  | 0.74 |
| − 1 | 0.31 |  | 0.01 | 0.08 | 0.22 |  |
| − 2 |  | 0.44 | 0.09 |  |  | 0.82 |
| − 3 | 0.43 |  |  |  |  |  |

seems to be useful. A more detailed analysis of the charge distributions seems necessary.

### Gross charges: Oxygen complexes

The gross charges on the atoms are shown in the diagram in Fig. 3a. The Cu, C and H atoms are all positively charged, whereas O is negatively charged. On the ligand side, by adding more electrons to the system, there will be a nearly continuous addition of negative charge. In fact, when one electron is added to the $n = +2$ complex, resulting in the $n = +1$ complex, the copper atom gains about half of the added electron, whereas the rest of the electronic distribution will be spread over the regions around the four carbon and four hydrogen atoms. The region around the four oxygen atoms do not gain anything, instead the gross charge around the oxygen will be slightly less negative. The changes in gross populations when one electron at a time is added to the system is schematically shown in Fig. 4.

The copper atom will alternatingly gain or lose electronic population, so that addition of one electron for $n = $ even always results in a gain in electronic population and a (smaller) loss on oxygen, whereas addition of one electron to
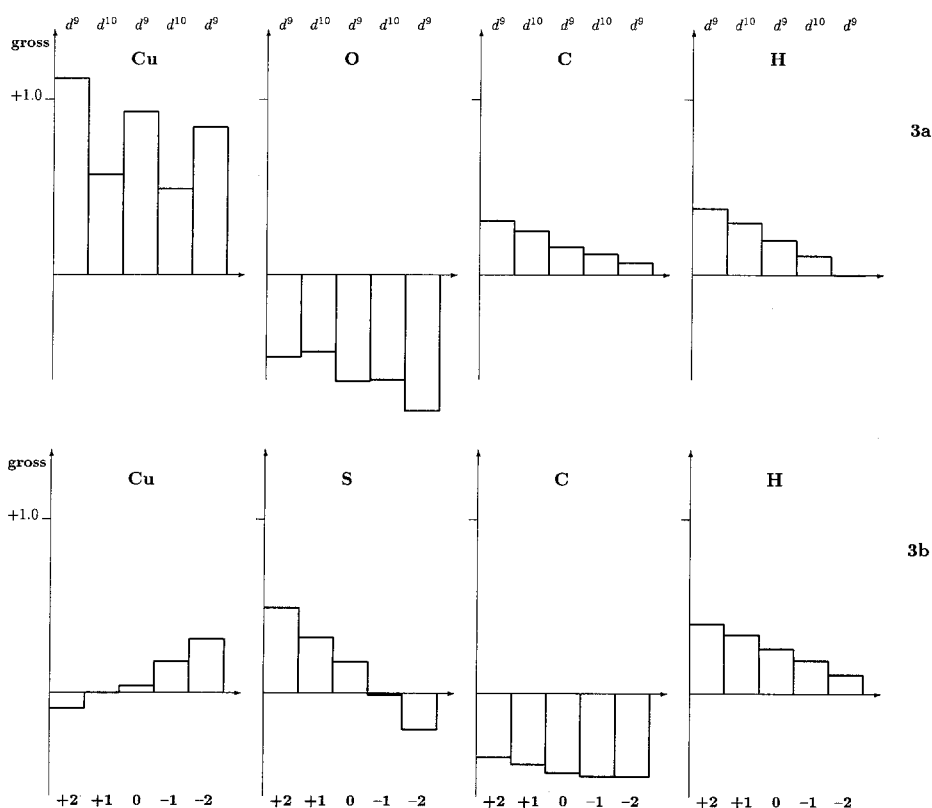
**Fig. 3a, b.** Gross charges on the atoms. **a** Oxygen complexes, **b** Sulfur complexes
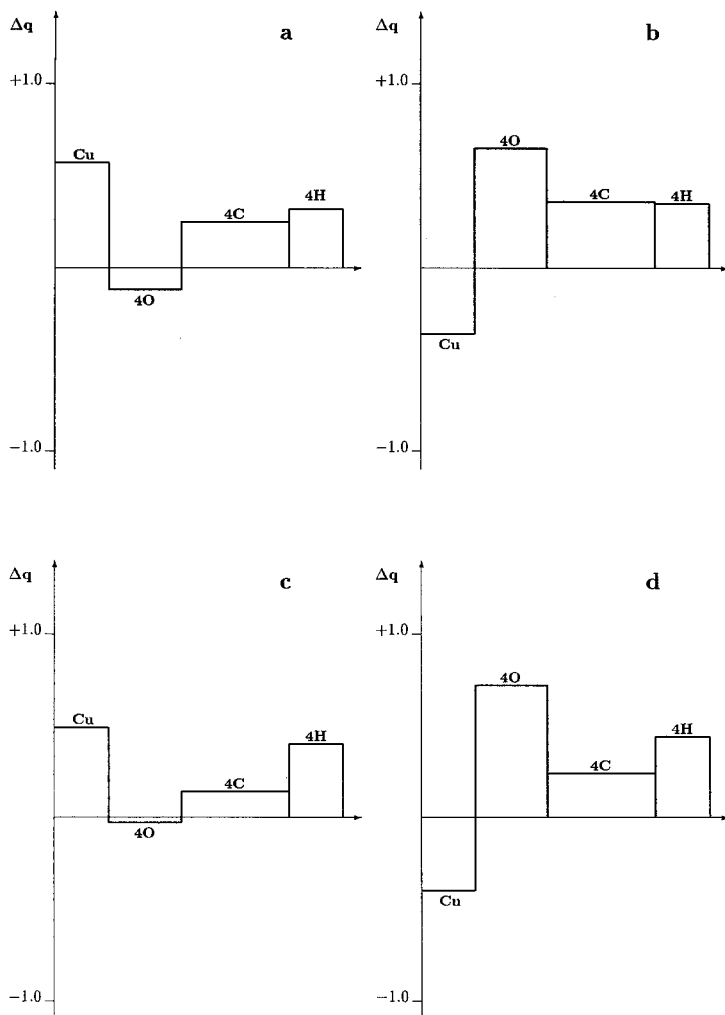
**Fig. 4a–d.** Differences in gross populations, $q$, upon addition of electrons. Oxygen complexes. **a** $n = +2$ to $n = +1$, **b** $n = +1$ to $n = 0$, **c** $n = 0$ to $n = -1$, **d** $n = -$ to $n = -2$

$n =$ odd results in a gain in the oxygen region and a (smaller) loss on copper. By pumping electrons into the system (reduction of the system), the copper atom will alternatingly be reduced or oxidized leading to large charge fluctuations all over the molecule which maybe can be related to the well known flexible reactivity of copper complexes.

## Gross charges: Sulfur complexes

The gross charges in the sulfur complexes are given in Fig. 3b. The copper atom, slightly negatively charged in the $n = +2$ case, will continuously be more positively charged as electrons are added to the system. The largest part of the
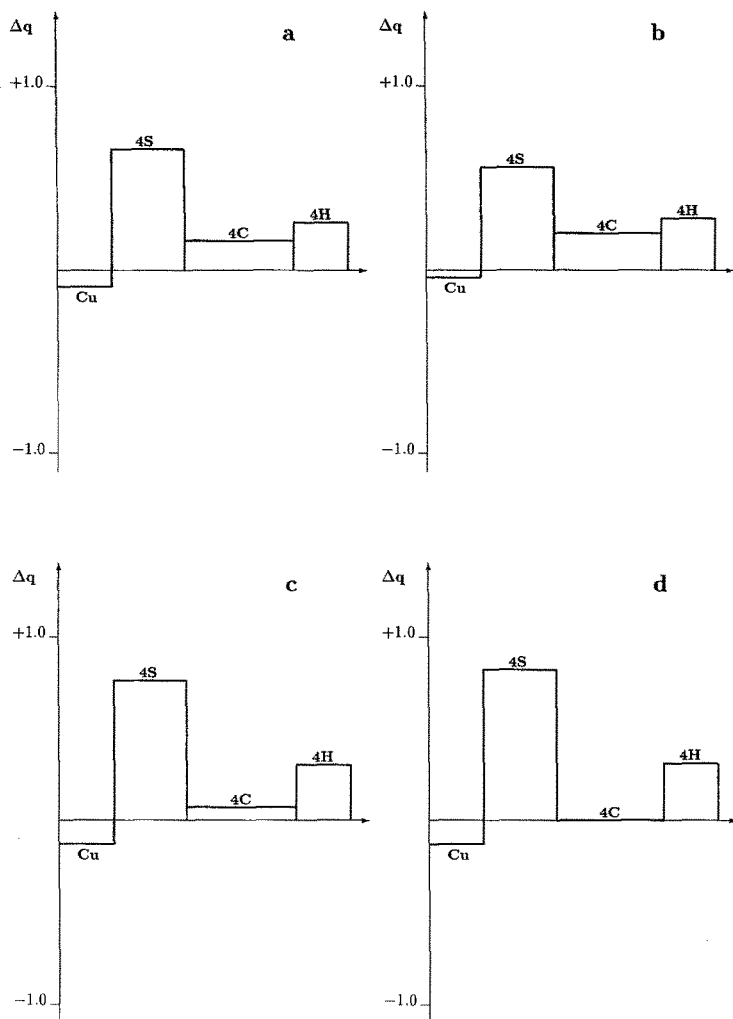
**Fig. 5a–d.** Differences in gross populations, $q$, upon addition of electrons. Sulfur complexes. **a** $n = +2$ to $n = +1$, **b** $n = +1$ to $n = 0$, **c** $n = 0$ to $n = -1$, **d** $n = -1$ to $n = -2$

added negative charge will now go to the (positively charged) sulfur region, which becomes even negatively charged (for $n = -1, -2$) and a smaller part to the (already negatively charged) carbon region as well as the (positively charged) hydrogen region. The difference in electronic population is schematically shown in Fig. 5. The pattern for change in electronic distribution is now similar for all cases, i.e. for addition of one electron at a time to the $n = +2, +1, 0$ and $-1$ state. Now, the largest part of the added electron goes to the sulfur region and a smaller part to the hydrogen region. The carbon region gains electronic distribution, but to a small extent. Only the copper region loses some electronic population, but also to a very small extent. Thus, upon reduction of the molecules studied, the copper atom does not seem to take part in the reduction process. Instead, only the ligand, and mostly the sulfur atoms, are acceptors for the added electrons.

*Net charges: Oxygen complexes*

The net charges on the oxygen complexes are given in Fig. 6a. Also the overlap populations (negative) in the bonding regions are shown. The alternating behavior for the charge on the copper atom, present for the gross charges is now still more exaggerated for the net charges. A similar trend can also be seen for the overlap population between copper and oxygen. For a high positive charge on copper (less electronic population) we find a high overlap population in the Cu–O bond. For a low positive charge on copper we find a smaller overlap population in the Cu–O bond.

Thus, there seems to be a very flexible electron transfer between the copper atom and the Cu–O bond.

For the ligand atoms, O, C and H, the pattern is similar both for the gross charges as well as the net charges.

Fig. 7 demonstrates the charge fluctuations over the molecule when one electron at a time is added to the system.
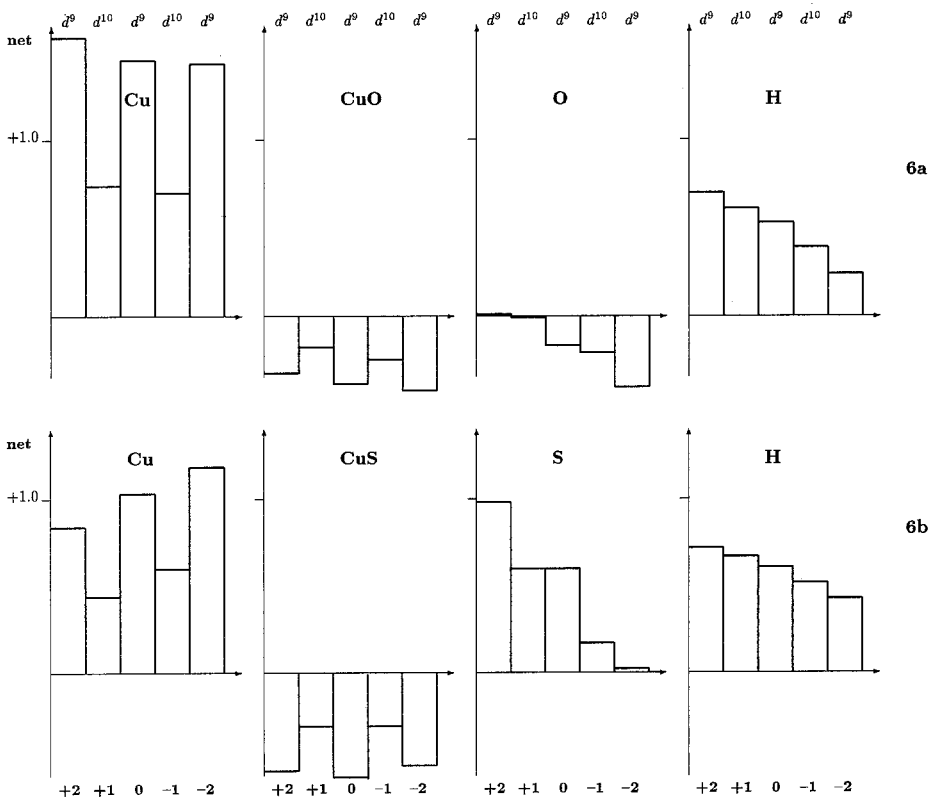


**Fig. 6a, b.** Net charges on the atoms. **a** Oxygen complexes, **b** Sulfur complexes. The net charges on C are fairly constant (1.2 for $n = +2$ and 1.0 for $n = -2$ in the oxygen complexes and 0.3 and 0.4, respectively, in the corresponding sulfur complexes) and omitted in the figure
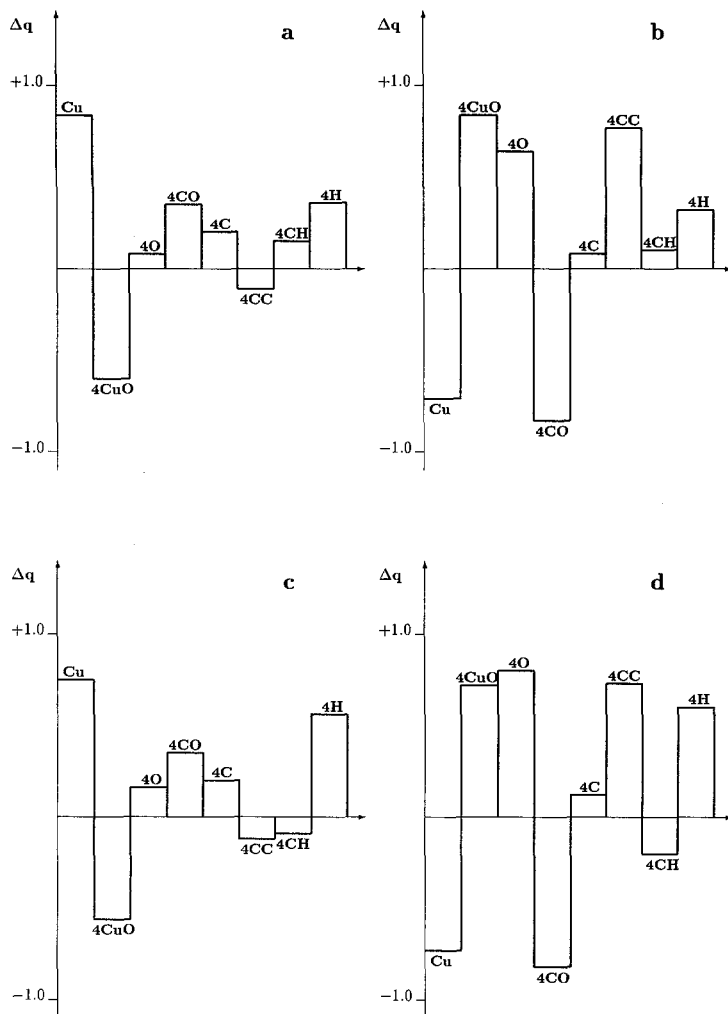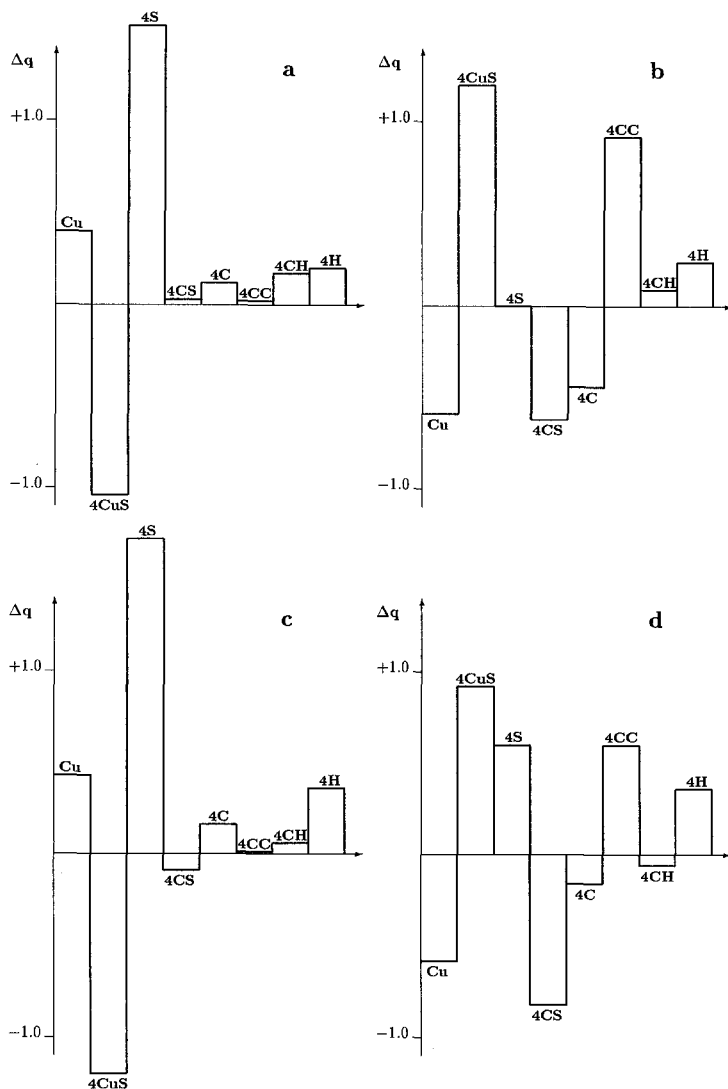
**Fig. 7a–d.** Changes in net populations, $q$, upon addition of electrons. Oxygen complexes. **a** $n = +2$ to $n = +1$, **b** $n = +1$ to $n = 0$, **c** $n = 0$ to $n = -1$, **d** $n = -1$ to $n = -2$

## Net charges: Sulfur complexes

The net charges on the atoms as well as the overlap populations in the CuS bond are shown in Fig. 6b. When comparing the net charges in the sulfur complexes with the corresponding gross charges, we now see that the net charges on copper show another behavior than the gross charges. Now the net charges on copper show a similar alternating behavior as for the corresponding oxygen complexes. Also, the Cu–S overlap population show an alternating behavior. Now the picture for the sulfur complexes is similar to the picture for the oxygen complexes. However, the net charge on copper is always smaller for the sulfur complexes than for the

**Fig. 8a–d.** Changes in net populations, $q$, upon addition of electrons. Sulfur complexes. **a** $n = +2$ to $n = +1$, **b** $n = +$ to $n = 0$, **c** $n = 0$ to $n = -1$, **d** $n = -1$ to $n = -2$

oxygen complexes, whereas the Cu–S overlap is always larger for the sulfur complexes than for the oxygen complexes.

Fig. 8 demonstrates the charge fluctuations when one electron at a time is added to the system.

### Comparison between oxygen and sulfur complexes

When comparing the oxygen complexes with the sulfur complexes the picture obtained from the gross populations is quite different from the picture obtained

from the net populations. Thus the importance of studying both gross and net populations when using the Mulliken population scheme is clearly demonstrated. The diffuse charge distribution all over the molecule resulting in a very flexible charge transfer maybe can be connected with the fast and flexible reactions that are so common for copper complexes. Such effects have been described in terms of dynamic electron transfers which have been suggested to be initiated by small vibrations [30]. The existence of charge fluctuations has also been discussed in connection with superconductivity [31, 32, 33].

## 4 Conclusion

The copper complexes show some special features compared to the other transition metals studied by us. What concerns the binding energies the copper complexes are more similar to the first row beryllium and lithium complexes than to the other transition metals. The special properties can be traced back to the ability of the copper ion to exist in two different oxidation states, Cu(II) with a $d^9$ electronic configuration and Cu(I) with the full shell $d^{10}$ electronic configuration. In the complexes studied by us oxidation and reduction between these two oxidation states are energetically very feasible requiring energies of about the size of vibrational energies. Upon oxidation and reduction large charge reorganizations take place in the whole molecule, both at the metal and the ligands, in the $\sigma$ as well as in the $\pi$ system. The charge distribution seems to be very flexible allowing for internal oxidations and reductions at the metal when electrons are pumped one at a time starting from the $n = +2$ complex (reduction of the system).

The overall pictures of the charge distributions in the complexes are quite different if gross or net populations are studied. The diffuseness of the metal orbitals allows for a spread of charge distribution over large parts of the molecule. For an understanding of the charge distributions in the complexes by aid of Mulliken population analysis, both gross and net populations should be studied.

These charge fluctuations may be connected both with the fast oxidation–reduction reactions in the copper enzymes as well as the superconducting properties of the organic copper superconductors and the ceramic superconductors. Such types of electron transfer is also aided by the small energy gap between the highest filled and lowest empty orbitals.

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