# Molecular Modelling for Copper(II) Centres

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d-Electron stabilisation energies provide a general framework for extending conventional Molecular Mechanics to open-shell complexes; a single set of Force Field parameters successfully models both planar $CuN_4$ and Jahn–Teller distorted, tetragonally elongated $CuN_6$ amine complexes.

Copper(II) is present in diverse biochemical systems.[1] Its complexes display a variety of coordination numbers and geometries but few are regular. This high flexibility or 'plasticity'[2] arises from the stereochemical activity of the $d^9$ configuration[3] where the orientation of the singly occupied d-orbital exerts a profound geometrical effect. For example, the pronounced Jahn–Teller elongations of six-coordinate complexes are associated with a singly occupied $d_{x^2-y^2}$ function.[4] The accurate treatment of copper(II) species is a significant challenge for molecular modelling.

Given its important biological function, many groups have tried to develop conventional Molecular Mechanics (MM) methods for $Cu^{II}$ centres although applications are restricted mainly to four[5]- and a few five-coordinate[6] systems. The main problem with the former is imposing a planar geometry while the high flexibility of five-coordinate $Cu^{II}$ complexes presents even greater problems. Attempts to use MM for six-coordinate complexes are rare[4,7] and require additional external constraints to force the system towards the observed elongated structures.† We have therefore developed the first general Molecular Mechanics method for open d-shell complexes which handles *any* $Cu^{II}$ coordination number and molecular geometry without external constraints.[8]

This is achieved by adding to the conventional MM total energy expression a new term to model the d-electron stabilisation energy.‡ This Extended Molecular Mechanics approach has been applied to a series of $d^9$ Cu complexes with saturated amine ligands (Fig. 1 and Table 1).

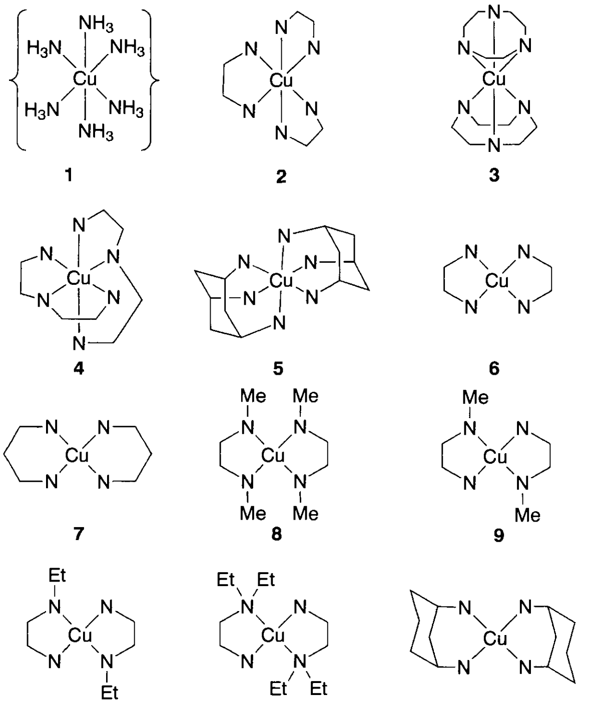

**Fig. 1** Schematic representations of the $Cu^{II}$-amine complexes modelled. All the ligands except ammonia contain saturated nitrogen donors connected by saturated hydrocarbon chains or rings. Hydrogens omitted for clarity. {Note that the existence of hexammine cations in $[Cu(NH_3)_6]X_2$ salts is debatable. The compounds may contain the pentammine species}.

The d-electron stabilisation energy is based on the Cellular Ligand Field (CLF) model.[9] The CLF scheme is independent of any assumptions of coordination number, molecular symmetry or ligand type. However, this generality precludes a simple analytical expression for the stabilisation energy. Derivatives are therefore computed using finite difference techniques.

The molecular geometry is implicit in the CLF Stabilisation Energy (CLFSE). Using a single set of Force Field parameters,§ the CLFSE favours a planar $CuN_4$ geometry and automatically generates a tetragonally elongated structure from an octahedral $CuN_6$ starting point due to the energy gain accompanying a tetragonal distortion (Fig. 2). The CLFSE term is augmented with an explicit ligand–ligand non-bonding (van der Waals) term.[7] This makes the method general enough to handle all complexes, including those where the CLFSE is zero (*e.g.* high spin $d^5$), and avoids the 'unique labelling problem'[10] associated with explicit L–M–L angle bend functions.

**Table 1** Comparison of selected average Cu–N bond lengths (Å) and N–Cu–N bond angles (°) for the saturated amine complexes shown in Fig. 1. The angle data represent the averaged equatorial ligand bite angles

| | $Cu–N_{eq}$ | | $Cu–N_{ax}$ | | N–Cu–N | | |
|---|---|---|---|---|---|---|---|
| Complex | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Ref. |
| **1** | 2.04 | ($2.15^a$) | 2.48 | ($2.45^a$) | 90.0 | ($90.0^a$) | 12 |
| **2** | 2.09<br>2.03 | 2.10<br>1.99 | 2.44 | 2.41 | 86.4 | 85.1 | 13 |
| **3** | 2.06 | 2.06 | 2.36 | 2.32 | 83.3 | 83.3 | 14 |
| **4** | 2.11<br>2.01 | 2.10<br>2.04 | 2.44 | 2.41 | 84.6 | 82.1 | 15 |
| **5** | 2.01 | 2.07 | 2.29 | 2.35 | 83.4 | 85.4 | 16 |
| **6** | 2.02 | 2.02 | | | 85.4 | 84.1 | 17 |
| **7** | 2.00 | 2.04 | | | 84.8 | 86.7 | 18 |
| **8** | 2.04 | 2.06 | | | 86.7 | 85.3 | 19 |
| **9** | 2.01<br>2.04 | 2.01<br>2.06 | | | 86.3 | 85.9 | 20 |
| **10** | 2.03 | 2.02 | | | 86.2 | 85.0 | 21 |
| **11** | 2.02<br>2.10 | 2.01<br>2.08 | | | 85.2 | 84.9 | 22 |
| **12** | 2.00 | 2.02 | | | 85.5 | 87.6 | 23 |

[a] The existence of $[Cu(NH_3)_6]^{2+}$ has been questioned. The X-ray data may refer to salts containing the pentammine cation.

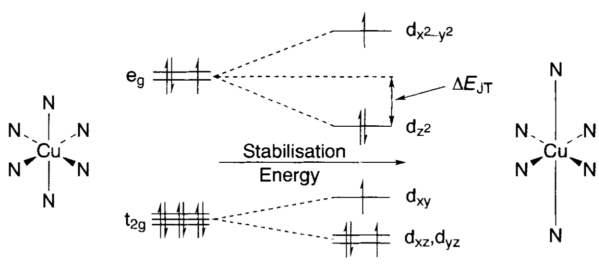

**Fig. 2** Schematic representation of the Jahn–Teller stabilisation energy, $\Delta E_{JT}$ accompanying the tetragonal distortion of an octahedral $d^9$ copper complex

Finally, a bond-stretch term defines the M–L distances. Given the wide range of Cu–N bond lengths, we use a Morse function. However, the CLFSE makes a strong contribution and the Morse function parameters are determined in the presence of the CLFSE on a trial and error basis. The 'optimal' Cu–N bond length in the Morse function (2.283 Å) is rather longer than that for a typical, reasonably strongly bound ligand (*ca.* 2.0–2.1 Å).

The remainder of the molecule is treated by conventional MM. (Note that the force constants for any torsional terms involving the metal are set to zero).

Five $CuN_6$ and seven $CuN_4$ amine complexes have been located. All bar $[Cu(NH_3)_6]^{2+}$[¶] are in the Cambridge Structural database.[11] Overall, the performance of the CLFSE/MM model is good. The root mean square deviation between observed and calculated Cu–N distances is about 0.02 Å while the N–Cu–N angles are accurate to within 3°. For the six-coordinate complexes, the calculated structures are all tetragonally elongated. Some complexes {*e.g.* $[Cu(tach)_2]^{2+}$} display multiple solid state structures due to the Jahn–Teller effect. Given that the 'intrinsic' geometry is an elongated octahedron, our computed structures are compared to the X-ray structure showing the largest tetragonal distortion. However, the computed structures are more symmetrical than apparently observed. In particular, the axial Cu–N distances for a given molecule are generally computed to be within about 0.03 Å of each other while the observed differences can be much larger, *e.g.* 0.16 Å in $[Cu(ethylenediamine)_3]^{2+}$.[13] This discrepancy could easily arise from relatively subtle crystal packing forces which are not yet included in the model.

The four-coordinate species are better treated since they have reached the limit of the Jahn–Teller elongation and are therefore less 'plastic'. Overall, the bond length variations of the equatorial ligands of all twelve molecules are well reproduced. In the planar systems both theory and experiment agree where there are two different equatorial contacts. For example, the substituted and unsubstituted Cu–N distances observed in [Cu(*N*-methylethylenediamine)$_2$]$^{2+}$ **9** and [Cu(*N*,*N*-diethylethylenediamine)$_2$]$^{2+}$ **11** differ by 0.05 and 0.07 Å respectively *versus* calculated differences of 0.03 and 0.08 Å.

To summarise, the main achievements of the CLFSE/MM scheme are (i) it generates the correct molecular symmetry (approximately $D_{4h}$ for the present complexes) (ii) it automatically treats the Jahn–Teller effect in six-coordinate species and (iii) it models very different Cu–N interactions and coordination numbers using a single set of Force Field parameters and without recourse to any external constraints. This contrasts with conventional MM which requires independent parameter sets for 'short' Cu–N bonds and 'long' Cu–N bonds even though the ligands are identical.

Finally, the CLFSE can easily be parameterised for other metal–ligand combinations to provide a completely general framework for mixed ligand coordination compounds. The CLFSE/MM method is the first such general, empirical scheme and promises to make a significant impact in the field of molecular modelling of open-shell metal systems in general and $d^9$ copper(II) complexes in particular.

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## Footnotes

[†] *E.g.* Deeth and Hitchman[4] and Comba and Zimmer[7] are able to generate tetragonally elongated geometries only by imposing a concerted motion of the ligands along the $Q_\theta$ normal mode which constrains the molecule to tetragonal geometries.

[‡] The program DOMMINO (D-Orbitals in Molecular Mechanics for INOrganics) has been developed by adding routines for the CLFSE and its derivatives to in-house Molecular Mechanics software. DOMMINO is not presently in a suitable form for distribution. However, CLFSEs could, in principle, be added to any suitable MM package.

[§] CLFSE: $e_\sigma = 21629 - 8235\, r\,(\mathrm{cm}^{-1})$; Cu–N Morse function: $D_0 = 80.0$ kcal mol$^{-1}$ (1 cal = 4.184 J); $r_0 = 2.283$ Å; $\alpha = 0.45$; Remaining parameters derived from literature.[5,6]

[¶] There is some evidence that the $[Cu(NH_3)_6]X_2$ salts may contain the pentammine cation rather than the hexammine.

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