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A combined ligand field and density functional theory study of the structural and spectroscopic properties of $[Cu(dien)_2]^{2+}$

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Issues regarding assignment of the ‘d–d’ spectrum of $[Cu(dien)_2]Br_2{\cdot}H_2O$ have been resolved using density functional theory (DFT) calculations. The fully optimised structure of $[Cu(dien)_2]^{2+}$ is in good agreement with experiment with Cu–N distances within ≈0.02–0.06 Å. However, one axial contact is 0.22 Å longer than reported and the ground state Cu–N covalency is overestimated. This leads to computed EPR *g* values which are too low and to ‘d–d’ transition energies which are too high. However, the electronic structure can be tuned to the experimental *g* values by modifying the copper nuclear charge. The ‘d–d’ transition energies were computed from the optimised electronic state using Slater’s transition state approach. DFT agrees with cellular ligand field (CLF) calculations and demonstrates that amines are not π-bonding ligands and that electrostatic interactions are not required for the CLF model. Instead, the observed spectroscopic and structural data are successfully reinterpreted as arising from the superposition of two, slightly different complexes in a ratio of approximately 5.5 : 1 and aligned at about 90° to one another. This significantly improves the agreement between the calculated and ‘observed’ structures. The implications for the interpretation of the ‘d–d’ spectra of other copper(II) amine complexes are discussed.

Introduction

Density functional theory (DFT) has over the last decade become a popular choice for quantum chemical (QC) calculations on transition metal (TM) complexes.[1–3] It combines relatively fast execution times with remarkably accurate structures and energies and applications of DFT in all spheres of TM chemistry are flourishing. DFT gives a good description of the ground electronic state and, even though the density functional theorem formally refers only to this ground state, DFT is being applied to excited states with considerable success.[4–12] Recent innovations both in functional design and in the range of properties which can be computed from first principles, particularly electron paramagnetic resonance (EPR)[13] and nuclear magnetic resonance parameters,[14] polarisabilities and excited states,[15] provide a powerful computational tool for TM species.

Three decades ago the theoretical treatment of TM compounds was necessarily based on less sophisticated models. At that time there was intense interest in the magnetic and spectroscopic properties of coordination compounds but, given the theoretical complexities of the multiplet states which arise from d^n configurations, actual calculations were virtually the exclusive province of ligand field theory (LFT). LFT enjoyed a great deal of success and much of our present understanding of the nature of the coordinate metal–ligand bond derives from LFT.[16] Today, it is an important part of undergraduate teaching programmes in theoretical inorganic chemistry and remains a useful research tool particularly in its most ‘chemical’ forms, the locally parameterised angular overlap model (AOM) and its close partner the cellular ligand field (CLF) model.[17]

The CLF model and the AOM replace the global symmetry approach characteristic of the electrostatic crystal field theory (CFT) with a model based on parameters which independently describe the local σ and π bonds. Thus, they capture the qualitatively successful molecular orbital (MO) picture of the interplay between σ and π M–L bonds which explained the ligand order in the spectrochemical series while also retaining the symmetry properties of CFT which are useful for many-electron multiplet calculations of ‘d–d’ spectra and magnetic properties. However, although the overall symmetry divides the d orbitals into the same distinct sets for both the CLF model and CFT, the two models sometimes make qualitatively different predictions about the magnitudes of the d-orbital splitting.[18]

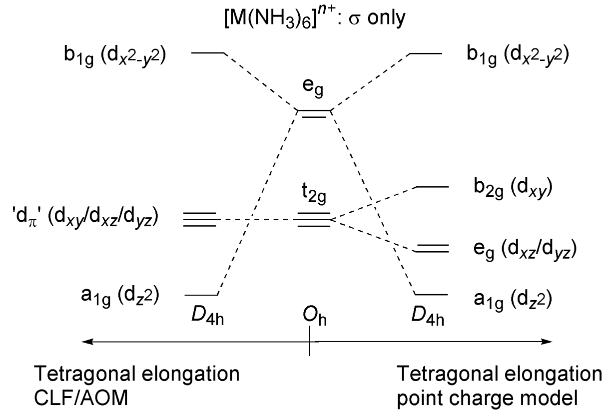

Fig. 1 Qualitative d-orbital energy levels as a function of a tetragonal elongation predicted by the CLF (or AOM) model (left) or the point charge model (right).

Consider perhaps the simplest coordinate bond, that between a metal and a saturated amine. Amines are generally considered to be σ bonding only. Thus, for an octahedral MN_6 complex, the π-type d orbitals remain rigorously non-bonding within the CLF and AOM approaches. Moreover, for a tetragonal distortion to D_{4h} symmetry the d_π orbitals *remain* non-bonding. In contrast, the point charge model upon which CFT is based predicts that for, say, a tetragonal elongation, any d orbital with a *z* component will be stabilised and hence predicts that the original t_{2g} orbitals will split (Fig. 1).[19] The CLF model and

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CFT give qualitatively different predictions as was recognised from the beginning.[18] Yet, many subsequent applications of the CLF and AOM schemes to metal amines assumed zero π interactions despite numerous reports[20] of 'd–d' spectra, particularly for six-coordinate copper(II) complexes, with significant 't_{2g}' splittings which in turn suggest that amines are capable of strong π interactions. Smith[18] attempted to explain this anomaly by introducing electrostatics into the AOM and this idea has emerged periodically since then. A particularly marked case of where this augmented approach might be needed is to explain the 'd–d' spectrum of $[Cu(dien)_2]^{2+}$.

Detailed, single crystal 'd–d' and EPR spectroscopic measurements have been reported[21] both for pure complexes and for $[Cu(dien)_2]^{2+}$ doped into crystals of analogous zinc complexes.[22] Band maxima for the pure complex are reported at 8800, 9900, 15400 and 15900 cm^{-1} and assigned to a d orbital sequence $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$ which implies a 't_{2g}' splitting of more than 5000 cm^{-1}. The original assignment was justified on the basis of the point charge model (PCM). In this paper we will see how a combination of LFT and DFT can be used to re-examine the spectra, demonstrate that the original assignment is incorrect and then provide a new, consistent interpretation of the experimental data.

Computational details

The CLF calculations were carried out using CAMMAG.[23] The DFT calculations were made using the Amsterdam Density Functional (ADF) program suite version 2000.01.[24–27] Geometries were optimised at the local density approximation level which has been shown to deliver good accuracy for Werner-type complexes.[28,29] EPR g values were computed with ZORA relativistic corrections including spin–orbit coupling.[30–34] The frozen-core approximation[35] was applied with orbitals 1s–2p frozen on Cu and the 1s orbital frozen for N and C. Basis set 1 (BS1) comprised triple-ζ + polarisation STO expansions on Cu (basis IV), double ζ + polarisation on N (basis III) and double ζ on C and H. BS1 was used for all geometry optimisations. A second basis, BS2, which comprised triple-ζ + polarisation STO expansions on all atoms, was employed in conjunction with the local density approximation (LDA) and the gradient corrected functionals available in ADF for various single point calculations of g values.

Results and discussion

Using the observed polarisation behaviour and vibronic selection rules based on approximate D_2 symmetry, the tentative d orbital sequence proposed by Hathaway *et al.*[21] was $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$. The splitting between d_{xy} and d_{xz}/d_{yz} is thus about 5000 cm^{-1} which was justified *qualitatively* within the PCM scheme since this model predicts that all d orbitals with a z component should be relatively stabilised. In contrast, the only available mechanism for splitting the 't_{2g}' orbitals within the (non-electrostatic) AOM (or CLF model) is through deviations of the ligand bite angles away from 90°.

CLF analysis of $[Cu(dien)_2]Br_2 \cdot H_2O$

The CLF model partitions the space around the metal into discrete cells with each cell (normally) containing a single metal–ligand bond.[16] The local M–L interaction is separated into its individual σ and π components with specific e_σ and e_π parameters to describe each bonding mode. Since saturated amines do not have any available π orbitals, e_π is normally set to zero. For a rigorously D_{4h} tetragonal $MN_4N'_2$ amine system the d-orbital energies (ignoring spin–orbit coupling) are: $E(d_{x^2-y^2}) = 3e_\sigma(N)$, $E(d_{z^2}) = e_\sigma(N) + 2e_\sigma(N')$ and $E(d_{xy}) = E(d_{xz}) = E(d_{yz}) = 0$. These energies will change if the bond angles differ from 90 or 180°. The structure of $[Cu(dien)_2]Br_2 \cdot H_2O$ reported from single crystal X-ray diffraction[36] shows a low symmetry, reasonably distorted $CuN_4N'_2$ chromophore and the coordinates as reported were employed for the subsequent CLF analyses. A schematic representation of the structure and the Cu–N distances and selected N–Cu–N angles is shown in Fig. 2.

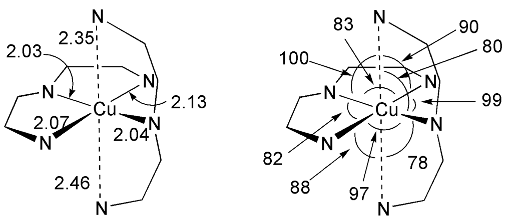

Fig. 2 Schematic representation of the crystal structure of $[Cu(dien)_2]^{2+}$.

The first model assumed four equivalent equatorial donors and two equivalent axial ligands yielding a simple two-parameter description of the ligand field potential. Each CLF parameter was varied over wide ranges: 2000 to 10000 cm^{-1} for e_σ(eq) and −3000 to 4000 cm^{-1} for e_σ(ax). In every case where transitions are computed around 15000 cm^{-1} the computed d-orbital energy pattern is always 1 : 1 : ≈3. That is, the CLF analysis only ever predicts a single low-energy transition rather than two. A typical fit to bands 1, 3 and 4 yields $e_\sigma(eq) = 5600$ cm^{-1} and $e_\sigma(ax) = 1000$ cm^{-1} and calculated transitions of 8815, 15465, 15929 and 16147 cm^{-1}. Only e_σ(ax) needs to be changed (to 400 cm^{-1}) to generate the alternative fit to bands 2, 3 and 4. The computed transition energies are now 9878, 15467, 16061 and 16149 cm^{-1}.

The second CLF model attempted to recognise the detailed differences between individual Cu–N distances and assigned a separate e_σ parameter for each donor. However, it turns out that the four equatorial parameters are virtually perfectly correlated with each other as are the two axial parameters. Since d orbitals have inversion symmetry, independent perturbations from centrosymmetrically related ligands cannot be distinguished. The d orbital responds only to the combined effect. Apparently, the bite angles in $[Cu(dien)_2]^{2+}$ are still close enough to 90 and 180° for the system to behave more-or-less as a normal, tetragonal $CuN_4N'_2$ system. Thus, assuming a σ bonding only model with no electrostatic interactions, the CLF calculations cannot reproduce the energies of all four reported 'd–d' transition energies. If this assumption is valid, the CLF results suggest that the structure is not sufficiently distorted to generate a 5000 cm^{-1} splitting of the 't_{2g}'-type d orbitals. Thus, either the CLF analysis is wrong or the interpretation of the experimental data is wrong. The CLF and AOM approaches have been applied, apparently successfully, to a large number of complexes containing amine donors assuming zero $e_\pi(N)$.[37–39] It seems unlikely that the dien ligands in $[Cu(dien)_2]^{2+}$ should suddenly be capable of large π interactions although Hitchman and Bremner have suggested non-zero π parameter values for planar copper(II) and nickel(II) complexes.[40] Moreover, the possibility of crystal field like electrostatic contributions should not be ruled out even though the notion seems largely to have fallen from favour. Consequently, we turn to DFT to explain the experimental data since any electrostatic interactions will implicitly be accounted for.

DFT calculations

The copper coordination geometry in $[Cu(dien)_2]Br_2 \cdot H_2O$ is far from ideal tetragonal octahedral. Since the CLF analysis is based on the reported molecular structure it is important to try to verify that this structure is correct whilst simultaneously testing the accuracy of DFT. Copper(II) complexes are notoriously 'plastic' and the degree of tetragonal distortion

Table 1 Comparison of observed and calculated Cu–N bond lengths (Å) and selected N–Cu–N angles (°) for $[Cu(dien)_2]^{2+}$. Numbering of N atoms as shown in Fig. 3

	Cu–N/Å			N–Cu–N/°	
	Obs.	Calc.		Obs.	Calc.
Cu–N1	2.06	2.06	N1–Cu–N2	82	83
Cu–N2	2.03	2.03	N2–Cu–N3	83	83
Cu–N3	2.13	2.07	N1–Cu–N3	163	159
Cu–N4	2.46	2.68	N4–Cu–N5	78	75
Cu–N5	2.04	2.03	N5–Cu–N6	80	80
Cu–N6	2.35	2.33	N4–Cu–N6	157	155

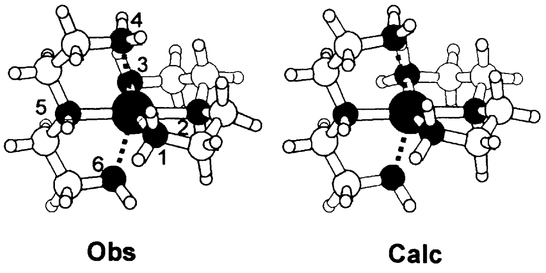

Fig. 3 Comparison of observed (left) and DFT optimised (right) structures of $[Cu(dien)_2]^{2+}$.

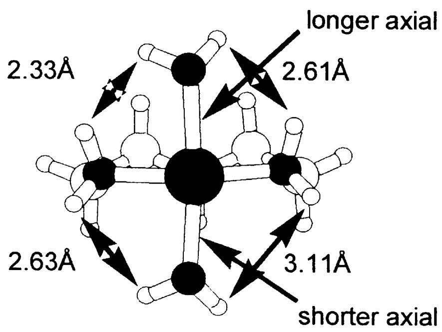

Fig. 4 Disposition of equatorial primary amine H atoms with respect to axial groups showing nearest H · · · H contacts. Most of the second dien ligand has been removed for clarity.

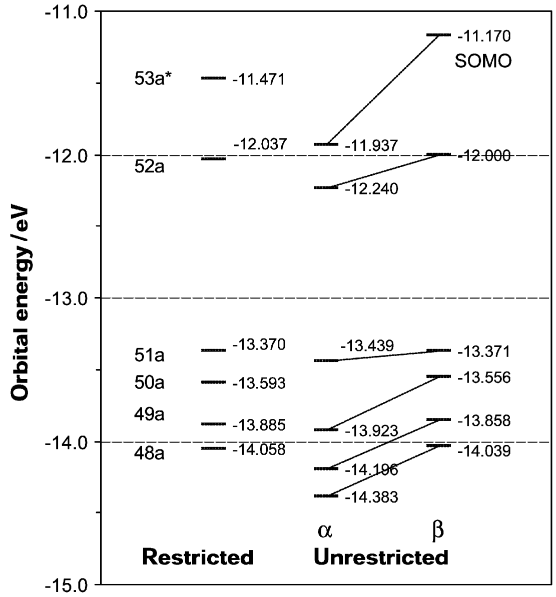

Fig. 5 Valence orbital energies for $[Cu(dien)_2]^{2+}$. The asterisk on the label for MO 53a denotes the (partially empty) HOMO.

for a given system can fluctuate wildly depending on the crystalline environment. However, Kundu *et al.* have shown[29] that DFT gives an excellent description of the structures and energies of both elongated and compressed octahedral forms of $[Cu(en)_3]^{2+}$ and a similarly reasonable description of the gas-phase geometry of $[Cu(dien)_2]^{2+}$ can be expected. A comparison of observed and computed (LDA/BS1) structures is presented in Fig. 3 and Table 1.

The comparison between theory and experiment is qualitatively good. DFT predicts a tetragonal elongation and four out of the six Cu–N distances are within 0.02 Å of experiment. However, Cu–N3 is computed 0.06 Å too short while Cu–N4 is apparently calculated 0.22 Å too long. Although the latter is a large discrepancy, the axial interactions are relatively weak so that the energy difference involved is small. Moreover, as discussed below, there are good reasons to suppose that the 'experimental' Cu–N3 and Cu–N4 distances do not correspond to the true metal–ligand distances.

The similarity between the optimised and the crystal structures suggests that the complex in $[Cu(dien)_2]Br_2{\cdot}H_2O$ is more or less at the limit of its tetragonal distortion and that the crystalline environment is not perturbing this too much. Nevertheless, the calculations reveal some differences which will be relevant to the subsequent interpretation of the d–d spectra. Note in particular that the axial Cu–N distances are not equal. The conformation of the ethylene chains forces the terminal amine hydrogens to adopt pseudo axial and pseudo equatorial positions such that the two pseudo axial H point at one axial N while the pseudo equatorial H are directed away from the other axial N (Fig. 4). The effect is for the pseudo axial H to push the nearest N away from the Cu while the other axial group moves in to compensate. This is quite a pronounced *structural* effect since the computed difference in axial bond lengths is some 0.3 Å.

The other relevant feature of the computed structure is that there are pairs of equal bond lengths for the equatorial donors. The Cu–N distance to the primary amines is 2.06 Å and to the secondary amines, 2.03 Å. The crystal structure shows a much more distorted pattern in the equatorial plane. However, these changes in bond lengths will not affect the CLF analysis since it is the angular geometry around the metal which is important and the DFT and crystal structures are very similar in this respect.

DFT excited states

The ground state Kohn–Sham valence orbital energies of $[Cu(dien)_2]^{2+}$ at the optimised geometry are shown in Fig. 5. On the left are the energies from a spin restricted calculation while on the right are the spin-unrestricted α- and β-spin orbital energies. The 53a and 52a functions have about 43 to 50% d character and correspond to the mainly σ-antibonding $d_{x^2-y^2}$ and d_{z^2} orbitals respectively. The 50a, 49a and 48a orbitals have 76 to 89% d character and are the nominal d_π-type functions. Level 51a is only about 20% d in character, *i.e.* it is a ligand-based function.

The spin-polarisation splitting is shown clearly in Fig. 5. This is more pronounced for the orbitals with higher d character than for the 51a ligand orbital. However, on the basis of the energy differences between the occupied functions and the 53a HOMO (53a* in Fig. 5 or SOMO in the spin unrestricted case), the DFT calculations suggest only one low-energy transition (52a $\longrightarrow$ 53a) at around 5000 to 8000 cm^{-1} with four higher energy transitions, three of which correspond to 'd–d' absorptions, starting at around 18000 cm^{-1}. There is a splitting of the 't_{2g}' orbitals but a rise of about 8000 cm^{-1} in one of the low energy orbitals is required before there is even qualitative agreement between theory and the reported 'd–d' transitions.

Of course, ground state orbital energy differences are not necessarily the best estimates of transition energies. This would only be the case if something like Koopmans' Theorem applied. However, Koopmans' theorem is only strictly applicable to HF theory. Slater has shown in the context of the exchange-only Xα model[41] that, while the leading energy term obtained by subtracting the total energy expressions for ground and excited states is indeed the eigenvalue difference between donor and acceptor orbitals, there are significant correction terms. The leading term can be removed and the remaining higher order terms reduced by performing the same analysis but now for a hypothetical state obtained by removing only half the electron from the donor orbital and placing it in the acceptor orbital. This so-called Slater transition state (STS) accounts for most of the orbital relaxation accompanying the excitation. Alternatively, the total energies of converged calculations on the ground and excited states can be subtracted directly, the ΔSCF procedure. STS and ΔSCF results are normally very similar.

Spin restricted STS and ΔSCF estimates of the first 'd–d' transition for $[Cu(dien)_2]^{2+}$ (at the optimised geometry) are 10792 and 10783 cm^{-1} while the corresponding spin unrestricted values are 10865 and 10867 cm^{-1}. These values are all very similar to each other but around 2000 cm^{-1} higher than the first reported 'd–d' band maximum (8800 cm^{-1}). However, there are some interesting features particularly of the STS calculations. Based on the percentage d orbital compositions, it appears that the ligand level (51a in the ground state) has now fallen below the d_π levels while these same d_π functions have compressed together and are now separated by less than 1500 cm^{-1}. The DFT electronic structure in the excited state is adopting the pattern suggested by the CLF calculations. Unfortunately, this also leads to severe SCF convergence problems. The d_π levels are now so close in energy that the STS and ΔSCF calculations become unstable due to level swapping. Moreover, the first STS calculation suggests that the transitions from the d_π levels would be higher than 20000 cm^{-1} anyway. It appears that the present calculations predict d-orbital splittings which are too large.

Cu–N covalency

The large d orbital splitting is related to the high metal–ligand covalency. The d contribution to the SOMO is only 49%. However, experimental estimates of Cu–N covalency suggest a much higher d component, say around 65 to 70% based on EPR and ENDOR experiments.[42,43] A recent innovation in ADF is the capability to compute EPR parameters from first principles and since these only depend on the ground state a comparison of observed and calculated *g* values should provide an excellent test of the accuracy of DFT. The *g* values calculated at the optimised geometry using basis BS1 and the LDA are 2.107, 2.045 and 2.022 compared to the experimental ones[22] of 2.213, 2.097 and 2.045. Very similar results are obtained with any of the ADF gradient corrected functionals (*i.e.* Becke88/Perdew86, Perdew–Wang91 or Becke/Lee–Yang–Parr), even for the larger triple-ζ + polarisation basis BS2. The largest change from the LDA/BS1 results is an increase of 0.006 in the largest *g* value found with Perdew–Wang91 and BS2. This general underestimate of the *g* values is consistent with bonding which is too covalent and excited states which are too high in energy. However, the error can be corrected.

Solomon and co-workers have made detailed experimental and theoretical determinations of metal–ligand covalency, especially for chlorocuprate(II) complexes.[44,45] Using the multiple scattering Xα method, the extent of sphere overlap in the muffin-tin potential was adjusted until the calculated EPR parameters matched experiment. More recently, a similar philosophy was applied using the ADF package.[46] Again, DFT gave a too covalent Cu–Cl interaction but, by modifying the nuclear charge on the Cu, the covalency was reduced to that determined from experiment. Simultaneously, the energies of the 'd–d' and charge transfer states came into excellent agreement with experiment. The authors argue that in the 'standard' ground state the d levels are below the chloride valence orbitals which results in the antibonding functions having greater ligand character rather than the expected greater d character. By reducing the nuclear charge on the metal, thus making the metal atom effectively negative, the d levels rise above the ligand functions and the expected picture is restored.

Table 2 Orbital energy differences ΔE/cm^{-1} calculated from Slater transition state configurations in column 2 with Q(Cu) = 28.2

STS	Valence MO occupation numbers (lowest to highest)	ΔE
1	2 2 2 1.5 1.5	10445
2	2 2 1.5 2 1.5	Did not converge
3	2 1.5 2 2 1.5	Did not converge
4	1.5 2 2 2 1.5	18100
5	1.75 1.75 2 2 1.5	16301
6	1.75 2 1.75 2 1.5	Did not converge
7	2 1.75 1.75 2 1.5	16152
8	1.833 1.833 1.834 2 1.5	15557

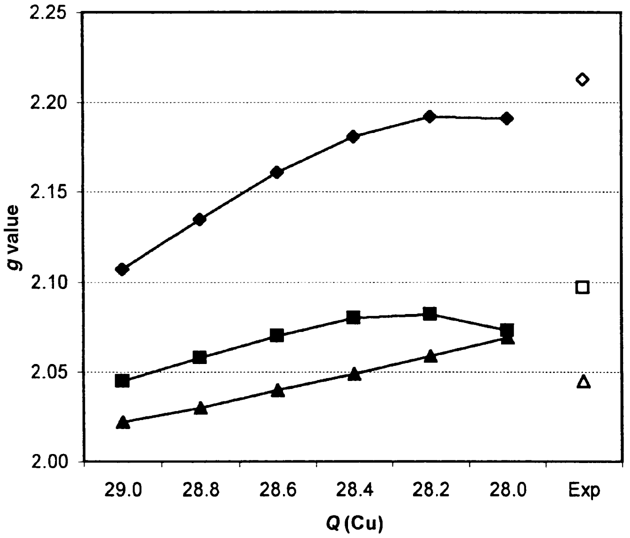

Fig. 6 Variation of computed *g* values as a function of the copper nuclear charge, Q(Cu). The experimental values are shown on the extreme right.

The same idea works here. EPR *g* values were computed at the optimised geometry for metal nuclear charges, Q, ranging from 29 to 28 in 0.2e steps (Fig. 6). The largest calculated *g* value approaches experiment up to about $Q = 28.2$ and then levels off. The lower two *g* values also move towards the experimental values but their anisotropy decreases rapidly from $Q = 28.2$ onwards. A reasonable reproduction of the observed *g* values is obtained for $Q = 28.2$ and, at the same time, the d contribution to the SOMO rises to 69%. The improvement in the *g* values also carries over to the 'd–d' transitions. With $Q = 28.2$ the mainly d orbitals are now well separated from the ligand-based functions and SCF convergence problems are less severe. More of the STS calculations converge satisfactorily (Table 2).

In D_{4h} symmetry d_{xz} and d_{yz} are degenerate. If this remains approximately true for $[Cu(dien)_2]^{2+}$ it could explain why the STS 2 and STS 3 in Table 2 failed to converge. In an attempt to try and simulate transitions from potentially degenerate orbitals, STSs were calculated with $\frac{1}{4}$-e removed from two donor levels (STSs 5, 6 and 7). STS 7 corresponds to a combination of STS 2 and 3. STS 8 corresponds to a notional transition in which all three d_π levels are degenerate but is of questionable relevance. The best estimate of the 'd–d' transitions is given by STS 1, 7 and 4 (10445, 16152 and 18100 cm^{-1} respectively) corresponding to a d-orbital sequence $d_{x^2-y^2} \gg d_{z^2} > d_{xz} \approx d_{yz} > d_{xy}$. Note that, even with the improved electronic state, DFT still predicts a single lower energy band in agreement with the CLF calculations.

This conclusion is not particularly sensitive to geometry. Transition energies and *g* values were recalculated for a [Cu(dien)$_2$]$^{2+}$ complex where the CuN$_6$ chromophore was fixed at the X-ray crystallographic geometry while the rest of the molecule was allowed to relax. The new 'd–d' transition energies are 8195, 15333 and 17197 cm^{-1} and the *g* values are 2.171, 2.074 and 2.040 (all for $Q = 28.2$).

Jahn–Teller effects

In 'normal' tetragonally elongated CuN$_4$X$_2$ complexes three 'd–d' transitions are expected but often only two are resolved. The lower energy band is assigned to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition while the higher energy band corresponds to $d_{xz}/d_{yz} \longrightarrow d_{x^2-y^2}$ transitions. The $d_{xy} \longrightarrow d_{x^2-y^2}$ is often obscured but can be observed *via* detailed single crystal measurements.[20] For [Cu(dien)$_2$]$^{2+}$ all the theoretical evidence so far points to only a single low energy 'd–d' band rather than the two reported. However, the changes in calculated 'd–d' transition energies between the optimised structure and the constrained geometry show shifts of a magnitude which suggests that the two low energy bands could arise from two similar but distinct complexes.

To a first approximation, there are two equivalent elongation axes for [Cu(dien)$_2$]$^{2+}$, one for each ligand. This is consistent with the EPR data for [Cu(dien)$_2$]$^{2+}$ doped into analogous diamagnetic zinc host crystals.[22] Given the low-symmetry space group, it only requires a relatively minor difference in crystal packing forces for one elongation axis to dominate. The DFT structure showed that the two axial Cu–N distances are not identical but that the equatorial bond lengths are quite similar. If the observed structure is a weighted average of two elongated geometries arranged approximately perpendicular, then the superposition of the asymmetric axial elongation of the minor component onto the equatorial plane of the major component will generate a large difference in equatorial bond lengths. For example, an 85%/15% weighted average of the optimised bond lengths gives Cu–N distances in fair agreement with crystallography, *viz.* 2.10, 2.03, 2.16, 2.59, 2.04 and 2.29 Å calculated *versus* 2.06, 2.03, 2.13, 2.46, 2.04 and 2.35 Å observed. Thus, the apparent 0.22 Å error between the reported and calculated Cu–N4 distances in Table 1 is based on slightly misleading experimental data and is rather overestimated.

This interpretation of the structure is also consistent with CLF calculations. Empirical e_σ values for a series of copper(II) complexes have been fitted by a straight line in the context of the ligand field/molecular mechanics (LFMM) method.[47–49] The slope is -8650 cm^{-1}. To first order, the displacements of the axial ligands for the tetragonal mode of the Jahn–Teller-active ε_g vibration are twice the magnitude of the equatorial ligand movements. A change of only 0.021 Å in the equatorial Cu–N distance of an ideal tetragonal hexaamine complex alters the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition energy by 1100 cm^{-1} and the $d_\pi \longrightarrow d_{x^2-y^2}$ transitions by 550 cm^{-1}.

The more elongated structure would generate the higher energy transitions, 9900 and 15900 cm^{-1} *versus* 8800 and 15400 cm^{-1}. A simple fit by a D_{4h} model system gives $e_\sigma(\mathrm{eq}) = 5133$ and $e_\sigma(\mathrm{ax}) = 733$ cm^{-1} for the former and $e_\sigma(\mathrm{eq}) = 5300$ and $e_\sigma(\mathrm{ax}) = 350$ cm^{-1} for the latter. These values fit very well with previously reported data. In particular, the positive values of $e_\sigma(\mathrm{ax})$ reflect the restricted axial elongation permitted by the tridentate dien ligand. The same behaviour was observed for another tridentate donor 1,3,5-triaminocyclohexane where the axial Cu–N distance is 2.36 Å and $e_\sigma(\mathrm{ax}) = 700$ cm^{-1}.[39] When there are no restrictions on the axial donor as in, for example, the [Cu(NH$_3$)$_6$]$^{2+}$ chromophore in Na$_4$[Cu(NH$_3$)$_4$][Cu(S$_2$O$_3$)$_2$]$_2$·NH$_3$, $e_\sigma(\mathrm{eq}) = 5800$ and $e_\sigma(\mathrm{ax}) = -1000$ cm^{-1}. Moreover, the sum, Σ, of all the CLF parameter values for the dien systems is about 22000 cm^{-1} which is also in excellent agreement with the Σ values for a range of tetragonal CuN$_4$X$_2$ species.

Conclusion

The d orbital sequence originally proposed for [Cu(dien)$_2$]$^{2+}$ based on single crystal spectroscopy using plane-polarised light splits the nominal d_π orbitals by at least 5000 cm^{-1}. A 'standard' ligand field analysis based on the locally parameterised cellular ligand field model and assuming amines are σ bonding only can only raise the d_π degeneracy through distortions of the N–Cu–N angles away from their ideal D_{4h} values but these are insufficient to reproduce a splitting of this magnitude. This leaves three options: (1) the standard CLF model is unsuited to this type of complex and must be extended by adding explicit electrostatic contributions to the d-orbital energies; (2) there is a significant π component to copper–amine bonding or (3) there is an alternative explanation of the experimental data.

DFT calculations are used to probe these issues. However, the 'standard' DFT ground state overestimates the Cu–N covalency. The d contribution to the SOMO is too low (≈49%) which gives rise to 'd–d' transition energies which are too high and EPR *g* values which are too low. The electronic structure of [Cu(dien)$_2$]$^{2+}$ must first be tuned to the experimental EPR *g* values by modifying the metal's nuclear charge. This procedure has successfully been used by Solomon to correct the description of the Cu–Cl bond in d^9 chlorocuprate complexes in order to obtain good agreement between theoretical and experimental measures of metal–ligand covalency.[46] The 'd–d' transition energies were then estimated *via* Slater's transition state method, using the tuned electronic state, which brings the DFT results into good agreement with the CLF analysis, *i.e.* DFT also gives only one low-energy 'd–d' transition. Hence, the first two options may be discounted. There is no evidence in the DFT for Cu–N π bonding and since electrostatic interactions are implicit in the DFT and since the DFT and CLF energy levels are basically the same one concludes that additional, explicit electrostatic terms are not required in the CLF model. The theoretical data point to a problem with the experiment.

Examination of the experimental and theoretical molecular structures gives a clue to a different interpretation of the experimental data. Instead of a single complex giving rise to four 'd–d' bands, it is suggested that the crystal contains two distinct complexes in a ratio of about 5.5 : 1 aligned approximately orthogonally and each generating only two transitions. Both DFT and the CLF model show that the Cu–N bond lengths need only differ by a few hundredths of an Ångstrom to accommodate the reported band maxima.

In the light of this study, any tetragonal copper(II) amine complex where the reported splitting of the nominal t_{2g} orbitals is more than a few thousand wavenumbers should be treated with caution and the interpretation of the 'd–d' spectra may need to be re-evaluated.

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