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Studies in copper(II) complexes: correlations between quantitative symmetry and physical properties

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The Continuous Symmetry Measure (CSM) methodology has been used to search for the existence of possible correlations between the degree of quantitative symmetry of the first coordination sphere of copper(II) complexes and various properties of these compounds. Several novel correlations were indeed found, employing both four- and six-coordinated copper complexes, including Blue Copper Proteins (BCPs). These include the relation between symmetry and the location of the d–d electronic transition maximum, the probability of electronic transitions, the ESR $g_{\|}$ values and structural responses to temperature changes. The trend of the identified correlations agrees with classical predictions which are based on specific geometric parameter changes, but are now expressed more generally in terms of quantitative symmetry, which, unlike the specific geometric parameters, is a global structural descriptor. Thus, the d–d electronic transition is blue shifted in tetrahedral complexes as the tetrahedricity measure increases (relating to more distorted tetrahedra), and likewise the $g_{\|}$ values decrease in response to this symmetry change; and the electronic transition becomes more allowed in octahedral complexes as the degree of octahedral distortion increases. Differences between the symmetry behaviour of $CuCl_4^{2-}$ and Cu within BCPs were identified and are analysed. It was found that temperature can affect symmetry in opposite ways, either increase or decrease it, and this phenomenon is analysed and interpreted using two different copper complexes.

1 Introduction

Most copper(II) complexes deviate from their highest possible symmetry point groups, namely the perfect tetrahedron (T_d), octahedron (O_h) or planar square (D_{4h}).[1] This structural characteristic is the result of the combined effects of the d^9 electronic configuration for which the Jahn–Teller (JT) effect operates,[2,3] with the comparatively small size of the copper ion which causes steric crowding around it. As a consequence, copper complexes provide a useful family for the search for quantitative correlations between structural parameters and physical properties.[4] Although phrases like "electronic absorption spectrum should be sensitive to the amount of distortion from ideal symmetry" are abundant in the literature[5] their translation into quantitative symmetry correlations has not been easy to carry out. In recent years we have proposed to address the main obstacle, namely the difficulty in measuring symmetry on a quantitative scale, through the introduction of the Continuous Symmetry Measure (CSM).[6,7] This measure is a global structural descriptor, which evaluates quantitatively the distance of a structure from any desired ideal symmetry point group. It has been demonstrated to be useful, both by us[8] and by others,[9,10] in many domains of chemistry that are affected by symmetry (or chirality) variations. In earlier reports the use of the CSM approach for analysing the symmetry properties of copper complexes has been described.[10,11] Here we search for quantitative correlations between the symmetry of copper complexes, and a variety of their properties. These include the locations of the maximum of the d–d electronic transition, the ESR g values, the molar absorption coefficients and the sensitivity of the structure to temperature variations. We recall in this context Alvarez's recent report[10] on the relation between the exchange coupling constants of Cu_2L_n complexes, and their CSM degree of trigonal bipyramidality.

The dependency of the properties of copper complexes on their symmetry has been known for quite some time and several attempts have been made to measure this symmetry using *local* geometry measures. For instance, two geometry parameters which have been used are the tetragonal distortion, T, of octahedral complexes[12] and θ, the flattening angle for tetrahedral complexes.[13] The tetragonal distortion, T, measures the ratio $R_S : R_L$ (R_S = short bond distance between copper and ligands, R_L = long bond distance) and refers only to the transition from O_h to D_{4h} symmetry with (usually) two short and four long bonds. The flattening (also called *trans*) angle, θ, is usually taken as a measure of the distortion from T_d symmetry, spanning from 109.5° (exact tetrahedron) to 180° (square planar). Willett and co-workers[5] have used θ in several cases to correlate geometry and electronic structure. Both these measures are local measures; they assume a certain direction of the distortion from ideal symmetry. When octahedral complexes are distorted towards a trigonal prism T has no meaning and when tetrahedral complexes are distorted towards C_3 symmetry the θ parameter is not applicable. On the other hand, the CSM is a global descriptor which takes into account, simultaneously, *all* changes in angles and bond lengths, regardless of their direction and magnitude. In this sense it is quite different from the use of structural deviation analyses that select a specific geometrical feature; and changes in specific geometric descriptors must show up in the CSM analysis, as was nicely demonstrated by Alvarez and Llunell.[10]

This report investigates the two most abundant coordination numbers of copper, four and six, by measuring, respectively, the quantitative degree of tetrahedricity and octahedricity by the CSM method. In a previous report[11] we measured tetrahedricity, $S(T_d)$, and the distance to square planarity, $S(D_{4h})$, of many four-coordinated species, and in particular of CuX_4^{2-} anions. That analysis showed that the tetrahedral to square-planar transition follows the Spread planarization path,[11] and an important observation was made: for $CuCl_4^{2-}$, the path of

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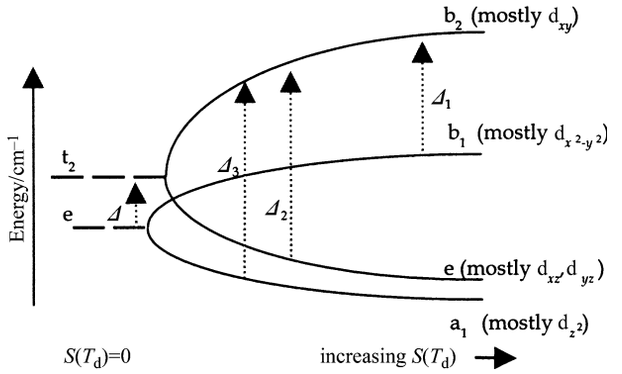

Fig. 1 The energy level system of $3d^9$ Cu^{2+} in four-coordinated complexes.[3] The degree of tetrahedral symmetry is used as a coordinate.

minimal energy corresponds to minimal symmetry pair values ($S(T_d)/S(D_{4h})$).

2 Computational details

Structural data were obtained from X-ray databases (the CSD[14] and PDB[15]). Tables 1–4 quote for each structure its CSD/PDB name and provide its symmetry values and some physical properties. The symmetry measure was computed as described repeatedly in previous publications.[6,7] Very briefly, the CSM identifies the *minimal* distance of a given (distorted) structure, composed of the ligands (first shell only) and the central atom, to a searched structure having the desired symmetry. This search can be carried out with several algorithms, and we used here two: for tetrahedricity, $S(T_d)$, and octahedricity, $S(O_h)$, measures, the algorithm described in ref. 7 which employs for the minimization procedure an input structure which has the desired symmetry but which is not of minimal distance (size and orientation) to the distorted one. For the evaluation of the degree of C_3 rotational symmetry, $S(C_3)$, we used the "folding/unfolding" algorithm, described in refs. 6 and 16. If a structure has the desired G symmetry, then the measure $S(G)$ is equal to zero; it increases with departure from G symmetry, reaching a maximal value (of up to 100). All $S(G)$ values, regardless of G, are on the same scale and therefore comparable.

3 Results and interpretations

3.1 Four-coordinated copper: symmetry effects on spectral properties

A most sensitive way to probe symmetry effects is through spectral changes, such as electronic absorption and electron spin resonance (ESR) spectra. This is particularly so for copper(II), because it is found in many geometries, from tetrahedral to square planar.[11] In an ideal tetrahedral ligand field a splitting of the five d orbitals into two degenerate e and three degenerate t_2 levels occurs (left hand side of Fig. 1); but when the ligand field is not tetrahedral, due to the JT effect or to other ligand-field distortions, further splitting occurs as shown on the right hand side of Fig. 1.[17a] This splitting increases the one allowed transition (Δ) to three:[17b] $\Delta_3(a_1 \longrightarrow b_2)$ the most energetic band, Δ_2-$(e \longrightarrow b_2)$, which also appears as $g_\perp$ in the ESR spectrum, and $\Delta_1(b_1 \longrightarrow b_2)$, which also appears as $g_\parallel$ in the ESR spectrum. The x axis in Fig. 1 is any geometric parameter that can represent the increase in deviation of the complex from tetrahedricity. For example, Halvorson *et al.* took the *trans* angle.[5] As emphasized in the previous section, taking one specific geometric parameter neglects other structural changes imposed in the molecule by that specific parameter. In this work the x axis represents schematically quantitative symmetry (the CSM) indicating the fact that all d–d transition energies increase with deviation from tetrahedricity (higher $S(T_d)$ values). Having Fig. 1 in mind, we are now ready to explore how it translates to experimental spectral observations.

Table 1 The degrees of tetrahedricity and C_3 rotation of $CuCl_4^{2-}$ copper complexes, along with the location of their d–d electronic absorption bands

			Wavenumber/cm^{-1}	
CSD name[a]	$S(T_d)$	$S(C_3)$	max. d–d transition	$a_1 \longrightarrow b_2$
bulvuz	0.13	0.13		9520
vapbet	2.04	2.02	7900	
tphtcc	2.87	2.84	9110	
mpeacu11	3.46	3.42	9100	
mbamcc10	3.87	3.87	8850	9200
przcua(I)	3.96	3.92		9390
pnclcu(I)	4.41	4.38		9710
bopwuy(I)	4.46	4.45		9620
przcua(II)	4.47	4.45		
sezleo	4.72	4.72		9730
teamcu10	4.84	4.83	9390	9400
mpipss10	4.91	4.90	9800	10300
przcub(III)	5.02	5.01	10200	
mpalcu(II)	5.78	5.77	10200	10800
przcub(I)	6.10	6.08	10200	
vacgub(I)	6.47	6.46		10200
mpalcu(I)	6.61	6.60	10200	10800
fisjew	6.90	6.89		9900
vacgub(II)	7.44	7.39		10200
phpipz	7.89	7.88	10750	10750
cinccu10(II)	7.90	7.90	11100	11100
aebztz	8.61	8.60	10810	
tphclc	8.99	8.92	11250	
tpasc10	9.71	9.64	11500	
bopwuy(II)	9.99	9.98		11500
gigpan	10.04	10.03	11200	12700
gigpan01	10.11	10.10	11200	12700
cinccu10(I)	11.04	11.03	11100	11100
przcub(VI)	12.84	12.78	12500	
przcub(II)	13.43	13.32	12500	
gemmiu	33.33	33.33	13500	15500
PtNH4[b]	33.34	33.33	14300	
methcc10	33.34	33.33	13200	16600
mpeacu10	33.34	33.33	13600	16900
crincc	33.34	33.33	13500	16500
bopwuy(I)	33.34	33.33		16400

[a] I, II and III refer to different copper centres in a unit cell. [b] PtNH4 is from the inorganic database (ICSD).

A The d–d absorption maxima values of $CuCl_4^{2-}$. We begin with one of the most studied anions of copper, $CuCl_4^{2-}$, for which plenty of spectral data exist. Taking the collection of spectroscopic data from Halvorson *et al.*,[5] two types of spectral information can be found (Table 1): either the location of the maximum of the observed absorption spectrum, which is usually a combination of the Δ_3 and Δ_2 bands (Fig. 1); and/or the locations of (some or all three of) the specific d–d band transitions, of which Table 1 shows only Δ_3. For each anion, the tetrahedricity content, $S(T_d)$, was calculated from the crystal structure, and it is seen (Table 1) that a wide range of distortions exists for these anions which differ from each other in their counter cations. In fact, as mentioned above, the highest $S(T_d)$ values refer to square planarity (D_{4h}), *i.e.* to situations of $S(D_{4h})$ close to zero. Since the counter cation affects mainly the crystal packing and thus the distortion of the anion (and less the electronic structure directly, since there is no chemical bonding between the two ions), this family provides a good case for electronic transition variations which are quite purely dictated by symmetry changes. It was therefore quite encouraging to detect a direct quantitative correlation between these two parameters, as shown in Fig. 2: Fig. 2(a) shows the location of the maximum of the d–d transition as a function of tetrahedricity; and Fig. 2(b) shows the correlation for one

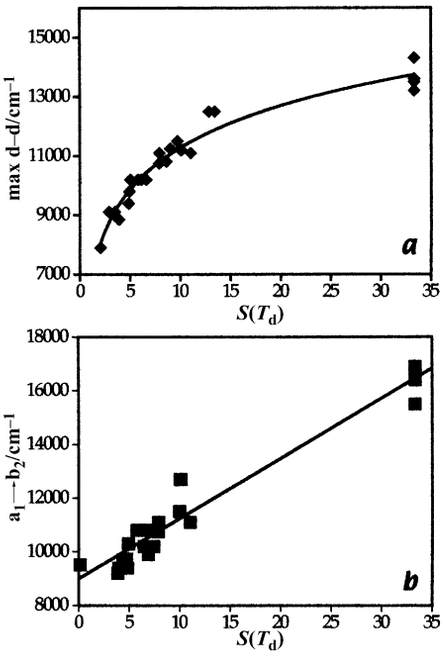

Fig. 2 The maximum value of the d–d electronic absorption spectrum as a function of the degree of tetrahedral distortion, $S(T_d)$, of $CuCl_4^{2-}$ complexes. (a) The position of the maximum absorption of the overall d–d absorption. The line shows a fit of the data by: max. d–d = 6580 + 2400 ln($S(T_d)$), $R^2 = 0.959$. (b) The position of Δ_3 (see Fig. 1; fitted by $\Delta_3 = 9000 + 224.S(T_d)$, $R^2 = 0.947$).

of the specific d–d transitions, namely $a_1 \longrightarrow b_2$. (The other transitions[5] follow a similar trend (not shown)).

We emphasize the fact that Fig. 2 shows, we believe for the first time on a quantitative level, how symmetry directly affects the energy of transition in a transition-metal complex. Two kinds of fits are shown in Fig. 2, one logarithmic and the other linear. While we are not ready yet to provide a theoretical explanation of these fits, they can be used to predict, by extrapolation, the $\Delta(e \longrightarrow t_2)$ gap of the ideally tetrahedral $CuCl_4^{2-}$. For instance, the extrapolation in Fig. 2(b) predicts 9000 cm^{-1}, in good agreement with values calculated by several authors (9938 cm^{-1} in ref. 18 and 11,101 cm^{-1} in ref. 5; the values depend on the Angular Overlap Model (AOM) parameter choice). This agreement is an important result, because it shows that the symmetry measure as defined in this study reflects the physics of systems in a proper way. Finally, since $S(T_d)$ and $S(D_{4h})$ are related to each other (not only for $CuCl_4^{2-}$ but also for many other four-coordinated species),[11] we could have used here the square-planarity measure and on doing so the same results are obtained, only with opposite trends.

B Symmetry effects on the ESR *g* values in $CuCl_4^{2-}$. The degree of allowedness of the ESR transition depends on the polarization of the two orbitals between which the transition occurs. The *g* value, which characterizes the transition, is proportional (amongst several parameters) to the inverse of the d–d orbital gap, Δ^{-1}.[17] Therefore, following the previous section, the more distorted the $CuCl_4^{2-}$ centres are, the lower should be the *g* values. This link was indeed noticed before in terms of the *trans* angle, θ, mentioned above.[19] To search for a possible quantitative link between *g* values and symmetry, several $CuCl_4^{2-}$ complexes were taken for which the crystal structures and $g_\parallel$ values (involving the b_1, b_2 states, Fig. 1) are known (Table 2[20–24]). The searched for correlation was indeed found, and is shown in Fig. 3: the clear trend is that the less tetrahedrally distorted the $CuCl_4^{2-}$ centre is, the higher is the $g_\parallel$ value.

C Blue copper proteins: the d–d absorption maxima and ESR *g* values. Numerous metalloproteins, including Blue Copper Proteins (BCPs),[25] contain one or more copper atoms in the active site. These proteins are involved in a wide variety of biochemical functions which depend on the variation in the chemical nature and geometrical disposition of the ligands in the active site, which, in turn, determine the physical properties of the copper cation. In many cases the crystal structure of these proteins is known and this has enabled investigating the delicate interplay between geometry and electronic structure of the copper.[26] Inorganic copper complexes such as those analysed in the previous sections (which are much easier to crystallize) helped in understanding the properties of biological copper[27] but today the separation between inorganic and bioinorganic analyses is less distinct.[28] Searching for possible correlations between the degree of symmetry of a copper complex within the active site of BCPs and the electronic properties, the d–d absorption and the ESR *g* values, is therefore of great interest in itself and in comparison with the behaviour of the $CuCl_4^{2-}$ family.

Only proteins for which both the crystal structures of the copper and its ligands (all the structures are from the PDB[15]) as well as the ESR or d–d electronic spectra are known were taken (Table 3[26,27,29–33]). Fig. 4 shows the correlation between the location of the d–d maximum (mostly due to the Δ_3 transition ($a_1 \longrightarrow b_2$)), and the degree of tetrahedricity of the copper complex within the protein. It is remarkable that, despite the restrictive and imposing environment of the active site,[34] a clear trend linking this spectral feature and degree of symmetry is again observed; and that, as for crystalline $CuCl_4^{2-}$ (superimposed on Fig. 4), higher energy bands correspond to the more distorted copper centres. Comparing the two copper complex families, it is seen (Fig. 4) that, first, for a given distortion, the d–d transition in the BCPs is more energetic (blue-shifted) compared to that of $CuCl_4^{2-}$; and secondly, that the

Table 2 $S(T_d)$ and ESR $g_\parallel$ values of several $CuCl_4^{2-}$ copper complexes

Cation	CSD name	$S(T_d)$	$g_\parallel$	Ref.
Cs		2.94	2.384	20
2-Aminopyridinium	yopnas	4.28	2.371	21
4-Aminopyridinium hydrate	sezleo	4.72	2.315	20
Triamterinium	hedseo	6.54	2.38	22
2-Amino-5-methyl-pyridinium	fisjew	6.90	2.329	20
Cinchonium	cinccu10	7.90	2.292	20
1-Methylpiperazinium	vurlav	9.44	2.25	20
Cinchonium	cinccu10	11.04	2.292	20
Tris[bis(ethylenedithio)-tetrathiafulvalenium]	vufrap01	12.03	2.29	23
2-Aminobenzo-thiazolium	gemmiu	33.33	2.21	20
N-Methylphenethyl-ammonium	mpeacu11	33.34	2.221	20

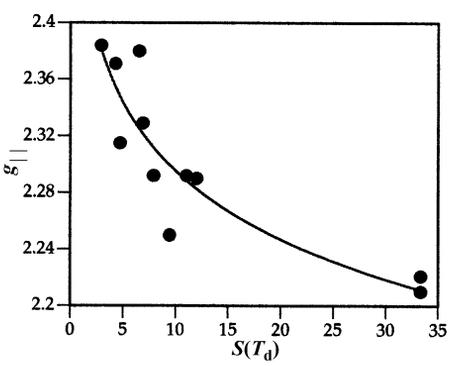

Fig. 3 $g_\parallel$ values from ESR measurements *vs.* tetrahedricity, $S(T_d)$, of $CuCl_4^{2-}$ complexes (fitted by $g_\parallel = 2.456 - 0.0698 \ln(S(T_d))$, $R^2 = 0.7964$).

Table 3 Blue Copper Proteins: symmetry values and electronic data

Name	Source	PDB name	$S(T_d)$	$S(C_3)$	max. d–d band/cm^{-1}	Ref.	$g_{\|}$	Ref.
Cucumber basic protein	Cucumber	2CBP	4.11	3.06	14100	26	2.207	27
Rusticyanin	Cyanoacterium	1RCY	2.89	1.75	13333	29	2.229	27
Amicyanin	*Paracoccus dentrificans*	1AAC	3.23	1.89			2.239	27
PseudoAzurin	*Achr. cycloclastes*	1ZIA	3.11	2.19	13280	30	2.21	30
PseudoAzurin	*Achr. cycloclastes*	1BQK	3.18	2.24	13280	30	2.21	30
PseudoAzurin	*Alcaligenes faecalis*	8PAZ	2.77	2.00	13300	31		
PseudoAzurin	*Alcaligenes faecalis*	1PAZ	3.00	2.38	13300	31		
Stellacyanin	Cucumber	1JER	2.04	1.03	12800	26	2.287	27
Plastocyanin	Spinich Asp8Gly	1AG6	2.62	1.37	13950	33	2.226	27
Nitrite reductase	*Alc. xylosoxidans*	1BQ5	3.08	2.26	12800	32	2.208	27
Nitrite reductase	*Achr. cycloclastes*	1NIC	5.13	4.44	14900	33	2.195	32
Ascorbate oxidase	Zucchini	1AOZ	2.00	0.81	12000	34	2.227	27

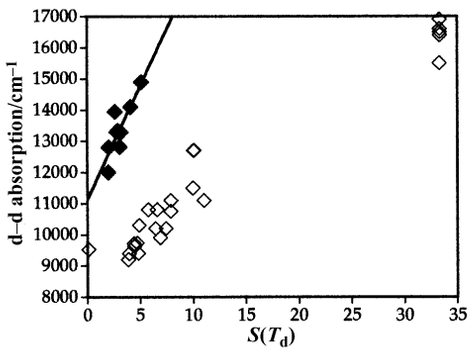

Fig. 4 The maximum of the d–d electronic absorption of Blue Copper Proteins as a function of the degree of tetrahedricity of the copper centres (filled diamonds, fitted by max. $\Delta = 11140 + 728S(T_d)$, $R^2 = 0.722$), superimposed on Fig. 2(b), $CuCl_4^{2-}$, open diamonds).

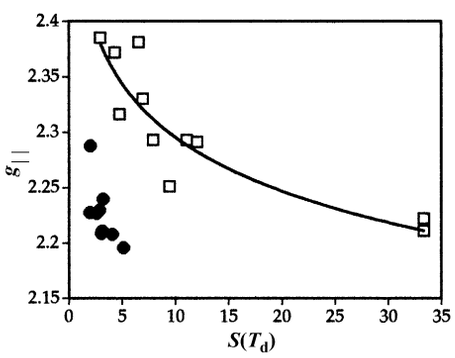

Fig. 5 ESR $g_{\|}$ values as a function of the tetrahedricity of copper centres in BCPs (filled circles), superimposed on Fig. 3 (the $CuCl_4^{2-}$ data, open squares).

sensitivity of the location of the d–d maximum to changes in symmetry (the slope in Fig. 4) is also higher in the protein.

In the next section we comment on the possible origin of the difference between the two families, which, in fact, is also evident in the ESR spectra: unlike $CuCl_4^{2-}$, where all $g_{\|}$ are molecular values (these are ESR values measured in the crystal with the Z axis of the molecule as the g_z axis), for BCPs the $g_{\|}$ values are crystal values and depend therefore on the copper orientation inside the crystal, thus making the observation less accurate. Yet in Fig. 5 one can see for the BCPs a similar trend to that found for the $CuCl_4^{2-}$ complexes, only shifted to lower $g_{\|}$ values and again with a steeper correlation. Recalling that $g_{\|}$ is related to the inverse of the d–d gap, the lower values found for the ESR spectra are consistent with the higher values found for the absorption maxima (Fig. 4).

D Comparison of the symmetry effects on $CuCl_4^{2-}$ and on blue copper proteins. The two families of copper complexes behave

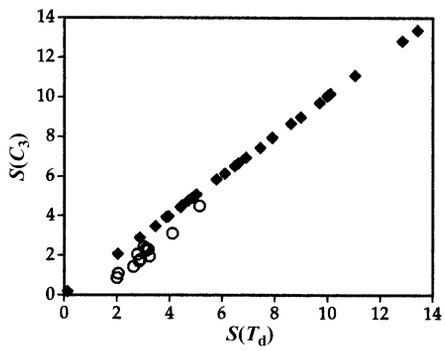

Fig. 6 $S(C_3)$ *vs.* $S(T_d)$ for the $CuCl_4^{2-}$ complexes (filled diamonds) and for the copper centres in BCPs (open circles).

similarly: the higher the tetrahedricity value (*i.e.* the higher the distortion), the larger becomes the d–d separation, and with it the absorption maxima are shifted to higher frequencies and the ESR signals to lower g values. Figs. 2 and 4 thus express in *quantitative* terms a correlation that has been predicted either qualitatively, or in conjunction with specific geometric parameters.[5] Yet we also noticed an interesting delicate change in the symmetry-trend behaviour between the two families, which has been detailed in the previous section. What could be the origin of this difference?

First, it reflects the different ligand fields: the copper in BCP is complexed by two nitrogens from histidine and by two sulfur atoms, one from cysteine and the other from methionine. N and S create a stronger ligand field separation on the ion,[3] compared with the weak Cl^- ligand field, thus increasing the d–d separation. Secondly, it may reflect the difference in the modes of distortion. Thus, whereas the distortion of $CuCl_4^{2-}$ anions follows the Spread mode which links tetrahedricity to D_{4h} square planarity,[11] the copper in BCPs behaves differently: the distortive mode is not towards D_{4h} but towards a C_3 elongated pyramid, with the sulfur from the methionine on the Z (long) axis.[25] Indeed, this is nicely seen in Fig. 6 in which the tetrahedricity content *vs.* the degree of C_3 symmetry is plotted for both the $CuCl_4^{2-}$ anions and the copper centres of BCPs. It is seen that for $CuCl_4^{2-}$ the $S(C_3)$ values are very close to the $S(T_d)$ values, meaning that the closest C_3 symmetric object for this family is very close to an ideal tetrahedron. However, in general, one expects to have $S(C_3) \leq S(T_d)$, since C_3 is a subgroup of the T_d point group and therefore it is less demanding to reach the nearest ideal C_3 structure than the nearest perfect T_d. This situation is indeed fulfilled for copper in the BCPs, namely there is a nearest C_3 structure, which is not an ideal tetrahedron, but of lesser symmetry, the elongated pyramid. We note that both kinds of distortion (towards an elongated pyramid and towards square planarity) can be assessed and analysed by the CSM, regardless of the specific origin of the distortion. The two

Table 4 The temperature dependence of the degree of octahedricity of two copper centres

Copper centre	CSD name	T/K	$S(O_h)$
$CuCl_6^{4-}$ [a]	virrix01	295	0.39
	virrix03	248	0.37
	virrix05	214	0.36
	virrix07	156	0.35
CuN_6 [b]	zubkow, site A	295	0.39
	zubkow01, site A	123	0.63
	zubkow02, site A	93	0.64
	zubkow, site B	295	0.05
	zubkow01, site B	123	0.10
	zubkow02, site B	93	0.12

[a] From $[3\text{-}ClC_6H_4NH_3]_8CuCl_{10}$. [b] From hexakis(1-methyltetrazole)-copper(II).

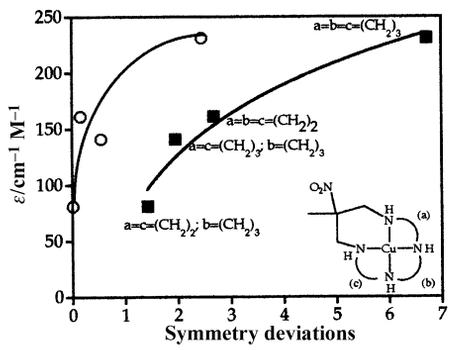

Fig. 7 Spectral absorption coefficients, ε, of CuN_4O_2 chromophores as a function of the degree of octahedral distortion, $S(O_h)$ (filled squares), fitted by $\varepsilon = 64.759 + 206.9 \log(S(O_h))$, $R^2 = 0.949$. Also shown is the centrosymmetry, S(i), behaviour (open circles, with a line to lead the eye).

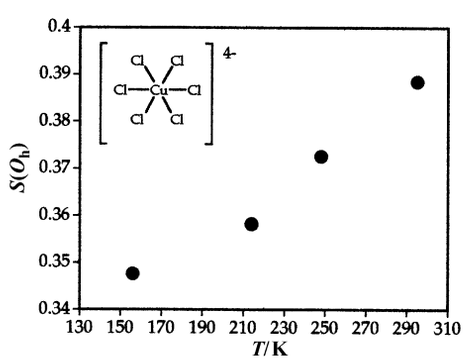

Fig. 8 The temperature dependence of the degree of octahedricity, $S(O_h)$, of $CuCl_6^{4-}$ in $[3\text{-}ClC_6H_4NH_3]_8CuCl_{10}$.

trends for the two families (BCPs and $CuCl_4^{2-}$) also demonstrate the limits of the CSM approach: the type of chemical interactions must always be considered; this, in fact, is a limitation of any geometrical descriptor in chemistry.

3.2 Six-coordinated copper

A Symmetry effects on the probability of electronic transitions: molar absorption coefficients in octahedral copper. One of the more central links between symmetry and a physical property is manifested in the role that symmetry plays in the degree of forbiddenness/allowedness of electronic transitions, expressed through the absorption coefficients. The CSM approach opens a possibility to link quantitatively the two parameters;[35] here we report the identification of such a correlation.

In the octahedral group of Cu all d–d transitions are forbidden according to Laporte's rule (which states that, in centrosymmetric environments, transitions can only occur between states of opposite parity[3]). Therefore, distortions which (permanently or temporarily) remove octahedricity (and thus affect the centrosymmetry), render the d–d transition less forbidden. It is therefore expected that the farther a six-coordinate copper complex is from octahedricity, the more intense its d–d transition will be.[3] To test this prediction within the CSM methodology, we re-analyse the data of Comba[36] who studied a family of CuN_4O_2 chromophores with tetraazamacrocyclic ligands (where the oxygens originate from solvating water molecules). The structures of the complexes were calculated in ref. 36 by using MM-AOM methods with the program packages MOMEC[37] and CAMMAG.[38] The electronic spectra were recorded in solution and the absorption coefficients, ε, measured at the maximum of each of the electronic spectra. Fig. 7 shows ε as a function of the calculated degree of octahedricity (and, for reference, the degree of centrosymmetry[39]). The clearly evident correlation indicates, as predicted, that the higher the octahedral distortion, the more allowed is the transition. It can be fitted by a logarithmic dependency, eqn. (1) with

$$\varepsilon = a + b \log(S(O_h)),\ R^2 = 0.949 \qquad (1)$$

$a = 64.795$, $b = 206.86$. As in the case of the location of the d–d transitions, this too is an empirical fit. Yet, although it is not derived from first principles it reflects them, because of the inherent way symmetry dictates the transition probability. We therefore regard it as one of our more important demonstrations of the applicability and suitability of the CSM as a general symmetry analysis tool. A theoretical explanation will hopefully emerge in a future study.

B Temperature effects on symmetry. In all previous analyses of experimental data we asked how does symmetry affect spectral properties? Our final analysis goes the opposite way: how does an external parameter, temperature in this case, affect symmetry? There are two main modes by which raising temperature may affect the apparent structure of a molecule packed in a crystal lattice: increasing the general size of the molecule; and changing the relative population of several existing structural minima. We analyse here these two different effects, applying the CSM methodology to two six-coordinated copper(II) complexes, the crystal geometries of which were reported to change with temperature.[40,41]

Our first example is the $CuCl_6^{4-}$ anion of $[3\text{-}ClC_6H_4NH_3]_8CuCl_{10}$.[40] As seen in Table 4 and Fig. 8, its degree of octahedricity, $S(O_h)$, increases with temperature, namely it becomes more distorted. Two models were suggested in ref. 40 for this observation, and for simplicity we use here one of these to interpret the trend in Fig. 8: as illustrated in Fig. 10, the spatial three-dimensional arrangement of the molecules in the lattice is such that two collinear Cl–Cu–Cl bonds are aligned on the same axis with the neighbouring Cl–Cu–Cl bonds, and quite close to each other (approx. 4 Å). In fact, they are so close that the effect of increasing temperature, which causes a general expansion in the total volume of $CuCl_6^{4-}$, cannot be expressed along the Cu–Cl···Cl–Cu axis. These two bonds actually shorten (from 2.29 Å at 156 K to 2.27 Å at 295 K), while the other four Cu–Cl bonds are not subject to this axial strain and are elongated (2.37 Å at 156 K and 2.39 Å at 295 K). It is this unequal behaviour of the Cu–Cl bonds in $CuCl_6^{4-}$ which is the cause for the behaviour seen in Fig. 8.

An opposite temperature effect on symmetry was identified for the CuN_6 unit within hexakis(1-methyltetrazole)copper(II) $[Cu(mtz)_6]^{2+}$.[41] This compound was found to crystallize with two non-equivalent molecules in the unit cell, one distinctly more distorted (site A) than the other (site B).[41] Based on ESR measurement and on other arguments, it has been proposed in the original paper that the CuN_6 unit in site A is confined predominantly to one of the three potential wells of a "Mexican hat" potential surface,[42] whereas the CuN_6 unit in site B has a scattering density which has been interpreted as originating from all three wells of the "Mexican Hat". As

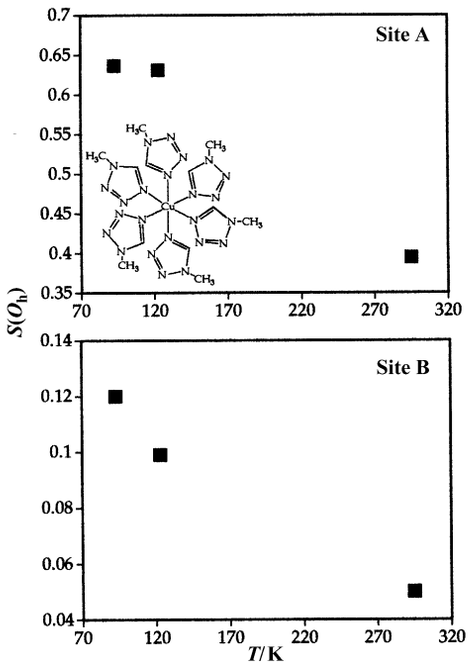

Fig. 9 The temperature dependence of the degree of octahedricity, $S(O_h)$, of CuN_6 centres from hexakis(1-methyltetrazole)copper(II), $[Cu(mtz)_6]^{2+}$. Two different sites are shown, see text.

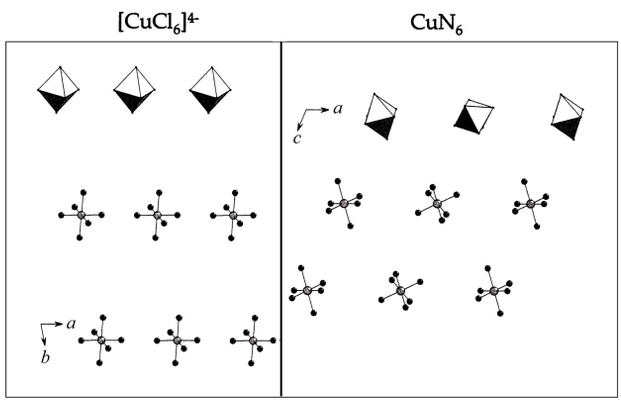

Fig. 10 The spatial arrangement, corresponding to Figs. 8 and 9.

shown in Table 4, the degree of octahedricity, $S(O_h)$, for the two sites indicates higher distortion in A, and lowering of the distortion as the temperature goes up (Fig. 9). Both observations are interpretable in terms of an increase in hopping rate between the wells as the temperature is increased: at low temperatures, the lowest energy minimum is mainly the populated one, and the observed asymmetric structure reflects mainly that well. On raising the temperature thermal population of the higher energy minima occurs (a dynamic JT[42]), thus equalizing more the various populations which, in turn, results in averaging of the different types of distortions (characteristic to each well) into a less distorted apparent structure. Note that, unlike the previous example, there is enough room for the $[Cu(mtz)_6]^{2+}$ molecule to expand upon temperature increase (Cu–N average bond length at 93 K is 2.14 Å and at 295 K is 2.15 Å (Fig. 10)). Finally, the existence of temperature effects on symmetry and the smooth correlation between these two parameters have recently been corroborated in a detailed study of temperature and pressure effects on the symmetry of the SiO_4 and $Si(OSi)_4$ building blocks of quartz, silicates and zeolites.[43]

4 Concluding remarks

The main objective of this work was to identify possible correlations between symmetry and physical properties on a quantitative level. Such a search is made possible if symmetry can be quantified as a gradually changing structural property. As detailed in the previous sections, such correlations have been identified, using the CSM methodology. These include the energetics of d–d electronic transitions, the probability of electronic transitions, the *g* factor in ESR spectra, and temperature effects, all demonstrated on copper(II) complexes. The quantitative symmetry analysis was also found sensitive enough to detect the differences between copper in $CuCl_4^{2-}$ and in Blue Copper Proteins. Such dependencies can be used in a predictive way: within a given family of complexes one can deduce spectral features from the degree of symmetry. A word of caution is in order here: the identification of a correlation between quantitative symmetry and physical parameters does not imply that the parameter depends uniquely on symmetry. This is particularly so for cases where geometry plays a secondary role, such as in charge transfer phenomena.[44]

The quantitative approach to symmetry offers a more natural way of analysing symmetry related phenomena, by replacing the binary language "an object is either symmetric or non-symmetric" with a description which represents reality in a more accurate way. In this context we draw attention again to the correlation we found between symmetry and the level of allowedness of electronic transitions (the molar absorption coefficients), linking these two intimately related parameters.

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