Interpretation of the temperature dependence of the crystal structure of [CuL$_2$][BF$_4$]$_2$ (L = 2,6-dipyrazol-1-ylpyridine)

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The temperature dependence of the bond lengths in the high temperature phase of [Cu(L)$_2$][BF$_4$]$_2$ (L = 2,6-dipyrazol-1-ylpyridine) may be interpreted satisfactorily using a model of dynamic, Jahn–Teller (JT) vibronic coupling. The geometries of the three complexes in the asymmetric unit of the low temperature phase may be reproduced using parameters similar to those of the high temperature phase, but with significantly larger orthorhombic components of the strain interactions. The axial components of the strain for all the complexes in both phases are negative in sign and large in magnitude, and this is thought to reflect both the stronger σ-bonding power of pyridine compared with pyrazole and physical constraints of the amine ligand. A previous interpretation of the thermal behaviour of the high temperature phase in terms of a conformational equilibrium is re-evaluated.

Introduction

Six-coordinate copper(II) complexes invariably adopt geometries distorted from a regular octahedron, this normally being ascribed to Jahn–Teller (JT) vibronic coupling. The actual geometry and crystal packing is decided by a delicate balance between the JT coupling parameters, ligand characteristics and lattice interactions.[1] Sometimes, energy levels representing two geometries are so close in energy that they are in thermal equilibrium,[2] or the lattice interactions may change with temperature causing a phase change to occur on cooling.[3] The crystal structure will then depend on temperature, and analysis of such a system can provide detailed information on the JT potential surface and how this is perturbed by the surrounding crystal lattice.[4]

As part of a general study of Cu(II) complexes with tridentate amine ligands[5] we recently prepared a novel example of a compound of the above kind, [Cu(L)$_2$][BF$_4$]$_2$, L = 2,6-dipyrazol-1-ylpyridine, containing the complex:
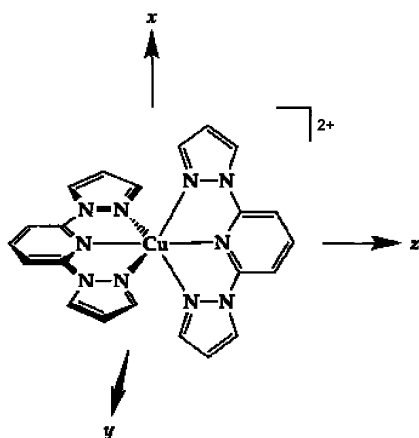
At 31 K this exists in a monoclinic unit cell with three independent complexes in the asymmetric unit [phase (I)], but above 41 K the compound adopts a new unit cell [phase (II)] with just one molecule in the asymmetric unit.[6] Moreover, upon raising the temperature progressively from 50 to 350 K the longest and intermediate Cu–N bond lengths gradually converge.[7] The temperature dependence of the bond lengths could be interpreted satisfactorily using a model involving a thermal equilibrium of conformers previously used to analyse the crystal structures of bipyridyl Cu(II) complexes of oxygen anions.[8] However, this implied an unusually small JT distortion for the basic [Cu(L)$_2$]$^{2+}$ ion involved in the equilibrium in phase (II).[7] The thermal parameters of the the nitrogen atoms also imply that a dynamic equilibrium is present in phase (II).[5] An alternative way of investigating the behaviour of 'dynamic' Cu(II) complexes is provided by a model which calculates the electronic states and vibronic wavefunctions of a six-coordinate Cu(II) complex under the influence of both JT coupling and lattice strain interactions.[2] Originally applied to the interpretation of EPR spectra, this approach was subsequently extended to the analysis of crystal structure data[9] and has been found to provide detailed information on the way in which ligand field and lattice forces influence the JT potential surface of a range of Cu(II) complexes.[1] The present paper reports the interpretation of the structural data of [Cu(L)$_2$][BF$_4$]$_2$ using this vibronic coupling model and re-evaluates the previous interpretation based upon a conformational equilibrium.

Results and discussion

Potential surfaces of the complexes

The form of the potential surface of a Cu(II) complex under the influence of JT coupling, and the way in which the parameters used to characterise the surface are defined and determined, have been discussed in detail elsewhere.[1,2,9] To first order, the magnitude of the JT distortion is decided by the balance between the electronic JT coupling constant A_1 and the energy of the JT active vibration, $h\nu$. The former may be deduced from the energy of the electronic transition between the split components of the ^2E_g state of the parent octahedral complex.[10] This was determined by measuring the electronic spectrum of a single crystal of [Cu(L)$_2$][BF$_4$]$_2$. At *ca.* 17 K the spectrum of phase (I) consists of two peaks: a weak band centred at 7000 cm^{-1}, which may be assigned to the transition **E** between the components of the ^2E_g state; and a more intense peak centred at 14 000 cm^{-1} due to the transition originating from the $^2T_{2g}$ state

of the parent octahedral complex. Except for a broadening of the peaks, the spectrum changed very little on warming the crystal to 295 K. This strongly suggests that the local geometry of the 'dynamic' Cu(II) complex in the high temperature phase (II) is not very different from those of the complexes in the low temperature phase (I). Using the equation $A_1 = \sqrt{[(\mathbf{E}/2 + S_\theta) \cdot h\nu]}$,[2,10] the energy 7000 cm^{-1} implies the value $A_1 \approx 1021$ cm^{-1}, which is similar to those reported for other copper(II) complexes.[11,12]

Because the JT vibration is doubly degenerate the potential surface of the complex is conventionally described by a three-dimensional 'Mexican hat' potential surface.[1,2,13] The ligand positions reflect the proportions of the components of the vibration, as given by the position of the energy minimum in the circular trough of the potential surface warped by higher-order effects. The higher-order effects are parameterised by a coupling constant A_2, though conventionally this is usually converted into the parameter β, the energy by which the minimum is stabilised compared with the unwarped surface.[2] For six identical ligands, higher-order effects almost always favour the tetragonally elongated geometry, corresponding to the Q_θ vibrational component.[13] However, when the ligands are not equivalent, either inherently or due to lattice interactions, this often produces an orthorhombic geometry. The ligand inequivalence is conventionally represented by axial and orthorhombic strain parameters S_θ, S_ε. The strategy for determining the parameters for the present compound follows that used successfully for a range of other complexes showing similar behaviour.[2,9,10] In this procedure, the ratio of $S_\theta{:}\beta$ was varied to reproduce the orthorhombic component of the distortion observed at low temperature and the orthorhombic component of the strain, S_ε, which decides the energy separation between the two lowest minima in the potential surface, was determined by mimicking the thermal behaviour of the bond lengths in phase (II). The optimum values of the parameters (in cm^{-1} except for M which is in a.m.u.) are:

$A_1 = 1021$, $h\nu = 380$, $M = 14$, $\beta = 170$
$(A_2 = 23)$, $S_\theta = -750$, $S_\varepsilon = 100$

and produce good agreement with the bond lengths observed for phase (II) of $[Cu(L)_2][BF_4]_2$ over the temperature range 50–350 K, as may be seen from the plot in Fig. 1. Here, the experimental values represent the average of the bond lengths along each axis, since the JT vibration is centrosymmetric. The estimate of the JT vibrational energy is similar to the value $h\nu = 350$ cm^{-1} obtained by carrying out a normal coordinate analysis on the analogous zinc(II) complex.[14] However, because of the

bulky nature of the ligand, the parameters used to define the JT active vibration must be considered 'effective' rather than realistic. The above estimate of the warping parameter β lies in the middle of the range (50–500 cm^{-1}) deduced for a variety of Cu(II) complexes.[1]

In order to reproduce the geometries observed for the three $[Cu(L)_2]^{2+}$ complexes present in phase (I) of $[Cu(L)_2][BF_4]_2$ at 31 K, it was assumed that the parameters defining the underlying JT coupling were similar to those for the high temperature phase. The difference in coordination geometry between the two phases is thus ascribed to lattice effects. As may be seen from Fig. 1, satisfactory agreement with experiment may be obtained in this way, and the values of the strain parameters are discussed in the following section. The actual bond lengths of each complex in the two phases are compared with those calculated for the three lowest wavefunctions of each potential surface in Table 1. In every case those of the lowest energy level agree with the experimental values quite well. As in similar treatments of other complexes with multidentate ligands,[9] it must be stressed that the potential surfaces and wavefunctions should not be taken as quantitatively accurate. However, they should reproduce the important features of the complexes.

Contour energy plots of the potential surfaces are shown in Fig. 2, as are plots of the change in energy of the potential surface at a JT radius of $A_1/h\nu$ as a function of the displacement along the two components of the JT vibration.[2] The former show that the surfaces depart significantly from circular symmetry. This is because the axial strain is large. As discussed elsewhere,[2] the circular plots on the right side of Fig. 2 therefore do not describe the path of lowest energy around the Mexican hat surface accurately. However, they give an approximate guide to the way in which the energy levels relate to the potential surfaces and the lowest six levels are shown in each case. It is noteworthy that the second minimum is quite poorly defined, particularly for the complexes in phase (I). This arises because the strain is large compared with the warping parameter β. Because the upper minimum is poorly defined, the long and middle bond lengths associated with the 2nd and 3rd wavefunctions of the complex in phase (II) are significantly delocalised. For the complexes in phase (I) the two upper levels remain largely localised in the lowest minimum (Table 1). At 50 K the

Fig. 2 Left side: energy contour plots of the potential surfaces of the complexes in phases (I) and (II) plotted as a function of the displacements in the Q_θ(STA) and Q_ε(STB) normal coordinates. Right side: variation of the energy minimum of potential surfaces of the complexes at the JT radius of $A_1/h\nu$. See text for the parameters used to define the surfaces.
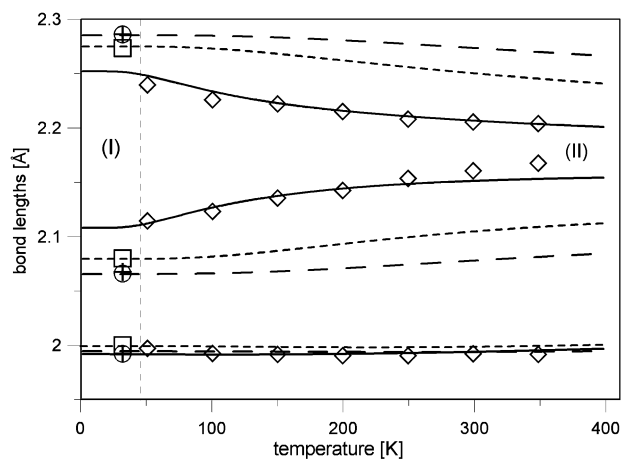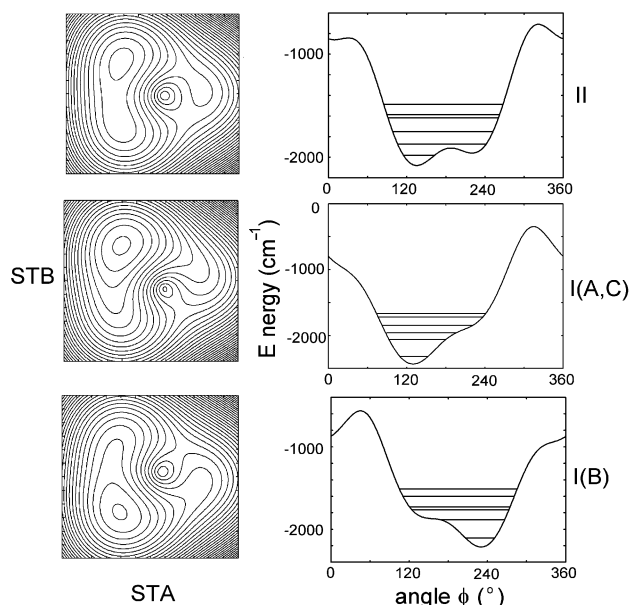

Fig. 1 Temperature dependence of the calculated and average experimental bond lengths for the complexes in phase (I) (---, + and ○ for molecules **A** and **C**; --- and □ for molecule **B**) and phase (II) (—— and ◇). See text for the method of calculation.

Table 1 Bond lengths observed for $[Cu(L)_2][BF_4]_2$ at 31 K [phase (I)] and 50 K [phase (II)]; see ref. 7 for atomic numbering and labelling of the molecules in phase (I). The values calculated for the lowest three vibronic wavefunctions are shown for comparison; see text for the method of calculation

Bonds[a]	Phase (II)				Phase (I)									
	Obs. 50 K	Calculated			Mol. A Obs. 31 K	Calculated			Mol. C Obs. 31 K	Mol. B Obs. 31 K	Calculated		
		$E=0^b$	$E=109^b$	$E=235^b$		$E=0^b$	$E=258^b$	$E=357^b$			$E=0^b$	$E=225^b$	$E=343^b$
Cu–N1	2.2527	2.249	2.157	2.193	2.290	2.285	2.268	2.284	2.306	2.088	2.079	2.122	2.126
Cu–N5	2.2259				2.282				2.266	2.072			
Cu–N6	2.108	2.114	2.208	2.168	2.056	2.066	2.087	2.063	2.058	2.261	2.275	2.239	2.229
Cu–N10	2.1210				2.076				2.077	2.286			
Cu–N8	1.9763	1.998	1.986	1.991	1.967	1.994	1.990	1.999	1.958	2.037	1.999	1.992	1.999
Cu–N3	2.0175				2.028				2.026	1.963			

[a] All bond lengths in Å. [b] Energies of lowest three wavefunctions for the two phases in cm⁻¹.

thermal population of upper levels of the complex in phase (II) is small (Fig. 1), and the geometry calculated for the lowest level agrees quite well with that observed in the crystal structure at this temperature. Our results suggest that the speculation[6] of disorder to be the cause of the lower JT distortion found in phase (II) compared with phase (I) is incorrect.

Interpretation of the strain parameters

An important characteristic of the $[Cu(L)_2]^{2+}$ ion is the large value of the axial strain. This acts along the direction of the Cu–pyridine bonds and the negative sign indicates that the perturbation raises the d-orbitals in energy. This parameter represents two main effects: the difference in σ-bonding of the central pyridine compared with the terminal pyrazole groups, and the physical constraints of the ligand ring system. Analysis of the electronic spectra of the octahedral complexes formed by the tripodal ligand bis(pyrazol-1-yl)(pyridin-2-yl)methane with Co(II) and Ni(II) suggests that pyridine is indeed a stronger σ-donor than pyrazole,[15] the difference (*ca.* 500 cm⁻¹) being somewhat less than that deduced for the present complex. It seems likely that in $[Cu(L)_2]^{2+}$ the physical constraints of the ligand also contribute to S_θ, with the rigid nature of the planar ring system pushing the central amine close to the Cu(II) ion. Effects due to the surrounding lattice are likely to be less significant. It is these which cause the smaller orthorhombic perturbations. The value of S_ε in phase (II) of $[Cu(L)_2][BF_4]_2$ is quite similar to those deduced for other 'dynamic' Cu(II) complexes in monoclinic unit cells. For the hexa-aqua ion in the Cu^{2+} doped Tutton salts $M_2[Zn(H_2O)_6][SO_4]_2$, for instance, this parameter varies from 55 to 200 cm⁻¹ depending upon the nature of the cation M.[2]

The low temperature phase (I) of $[Cu(L)_2][BF_4]_2$ differs from phase (II) in that, while the space group remains the same, the asymmetric unit increases from one to three complexes. These stack in the antiferrodistortive manner often seen in Cu(II) compounds.[6,7] The short bonds to the pyridyl groups of all three complexes are parallel, while the long and intermediate bonds of the central complex (**B**) are interchanged in direction compared with the outer two complexes (**A** and **C**).[6] The present model ascribes the switch in direction to a change in sign of the orthorhombic component of the strain. The strain parameters in cm⁻¹ giving optimum agreement with experiment for phase (I) are:

Molecules **A** and **C**: $S_\theta = -800$, $S_\varepsilon = 500$;
molecule **B**: $S_\theta = -700$, $S_\varepsilon = -300$.

The geometries of the outer molecules (**A** and **C**) are quite similar (Table 1), so that these are reproduced satisfactorily by the same set of parameters. Moreover, the directions of the long and intermediate bonds of these molecules coincide with those of phase (II). The overall JT distortions of the molecules in phase (I) are slightly larger than that in phase (II), and the orthorhombic distortions are smaller (Fig. 1 and Table 1). The present model ascribes both trends to the larger orthorhombic strain interactions in the low temperature phase. This acts to counteract the large axial compression, hence increasing the overall JT distortion and shifting the lowest minimum towards a tetragonally elongated geometry.[1,16] Why the more complicated packing arrangement in phase (I) should produce larger orthorhombic lattice strain interactions than that in phase (II) is unclear. However, for other compounds where the strain parameters alter with temperature this invariably appears to involve a decrease in the orthorhombic strain on warming.[12,17,18] Perhaps this reflects a general loosening of crystal packing forces as the temperature rises.

The strain values deduced from the above analysis may be used to estimate the distortions which would be produced in a Cu(II) complex in the absence of JT coupling.[9] For the lowest

wavefunction of phase (II) these are: $\delta x = 0.021$, $\delta z = -0.034$, $\delta y = 0.013$ Å, with the z-axis parallel to the Cu–pyridine bonds. The relative values compare reasonably well with those observed for the isomorphous Zn(II) complex, which is JT inactive, at 100 K:[7] $\delta x = 0.027$, $\delta z = -0.052$, $\delta y = 0.025$ Å. While there is no reason to expect an exact correspondence, because the Cu(II) lattice involves a much more distorted complex, the similarity is pleasing and lends credence to the present interpretation. In particular, the short Zn–pyridine bonds are consistent with ligand constraints pushing this section of the ligand towards the metal.

Comparison with models based on conformational equilibria

In a previous treatment,[7] the way in which the bond lengths in phase (II) change between 50 and 350 K was analysed in terms of a thermal equilibrium between two conformers of the $[Cu(L)_2]^{2+}$ ion. The procedure followed that used to analyse the temperature dependence of the crystal structure of $[Cu(bipyridyl)_2(ONO)]NO_3$.[8] In this, the distortion of the complex given by the crystal structure at temperature T, D_T, is represented by differences between the Cu–ligand bond lengths as shown in eqn. (1).

$$D_T = \sqrt{\{[(Cu\text{–}L_{S1} - Cu\text{–}L_{S2})^2 + (Cu\text{–}L_{L1} - Cu\text{–}L_{M1})^2 + (Cu\text{–}L_{L2} - Cu\text{–}L_{M2})^2]/2\}} \quad (1)$$

Here, $Cu\text{–}L_{S1}$, $Cu\text{–}L_{S2}$, $Cu\text{–}L_{M1}$, $Cu\text{–}L_{M2}$, $Cu\text{–}L_{L1}$, $Cu\text{–}L_{L2}$ are the pairs of short, medium and long Cu–ligand bond lengths. The two conformers are assumed to differ solely by having the directions of the long and intermediate Cu–ligand bond interchanged in the crystal lattice. Because the structure analysis yields the weighted average of those of the conformers, D_T decreases as the temperature rises. The equilibrium constant is given by eqn. (2),

$$K = (D + D_T)/(D - D_T) \quad (2)$$

where D is the distortion of each conformer given by eqn. (1). If the model is realistic, a plot of $\ln K$ vs. $1/T$ should give a straight line passing through the origin, and the bond lengths observed between 50 and 350 K for $[Cu(L)_2][BF_4]_2$ were found to satisfy these criteria well, with $D = 0.130$ and an energy separation between the conformers of 173 cm^{-1}.[7]

The value of D may be compared with the JT distortion ρ, as defined conventionally by eqn. (3):

$$\rho = \sqrt{\left(\sum_{i=1}^{6} \delta_i^2\right)} \quad (3)$$

Here δ_i is the difference between each Cu–ligand bond length and the average of the six bond lengths. For the complexes in phase (I), ρ varies between 0.287 and 0.311 Å, and these values are very similar to those observed for analogous Cu(II) complexes.[9,19] If D is taken to represent the JT distortion, as was the case in the previous studies,[7,8] the value of 0.130 is anomalously small, and it was speculated that this might be due to unusual lattice effects.[7] However, in the present study the JT radius estimated using the bond lengths of the lowest wavefunction of phase (II) using eqn. (3) is $\rho = 0.26$ Å, which is only slightly smaller than the values in phase (I). The estimate is not significantly affected by the fact that in the present approach the complex is modelled by a centrosymmetric molecule. Substitution of the actual bond lengths observed for the $[Cu(L)_2]^{2+}$ ion at 50 K into eqn. (3) yields a similar value for ρ, which is consistent with the present interpretation because higher vibronic levels have only a small population at this temperature. The reason for the large discrepancy between D and ρ for phase (II) of $[Cu(L)_2][BF_4]^2$ may be understood by considering these

parameters in terms of the two components of the JT vibration, as illustrated below:
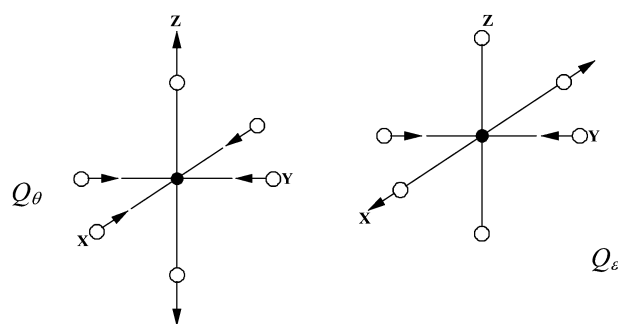
To first order, for the Q_θ normal coordinate each axial ligand moves twice as far as each in-plane ligand. Taking the displacement of one in-plane ligand as δ and substituting all ligand displacements into eqns. (1) and (3) yields the values $D = 3\delta$ and $\rho = \sqrt{12}\delta$ so that $D = \sqrt{3}\rho/2 \approx 0.87\rho$. Thus, for a distortion along this normal coordinate, D approximates quite well to the JT radius. For the Q_ε normal coordinate the four ligands which move do so by equal amounts. If the displacement of one is Δ, substituting all the ligand motions in eqns. (1) and (3) yields the values $D = \Delta$ and $\rho = 2\Delta$ so that in this case $D = \rho/2$. This means that for a distortion along the orthorhombic component of the JT vibration eqn. (1) produces a significant underestimate of the JT radius as conventionally defined. The reason that D is much less than ρ for $[Cu(L)_2]^{2+}$ in phase (II) is now apparent. The bond lengths of the complex in this phase are highly orthorhombic (Fig. 1, Table 1), so that the distortion is predominantly along the Q_ε normal coordinate. The orthorhombic component of the distortion is considerably smaller for the complexes in phase (I), and here the values of D are much closer to the JT radii ($D = 0.22$, $\rho = 0.29$ Å for complexes **A** and **C**).

In fact, eqn. (1) represents a more comprehensive distortion than that due solely to conventional JT coupling because it incorporates any difference between the short bonds. Such an effect is absent for a distortion along the centrosymmetric JT active vibration, which is represented solely by the two last terms in eqn. (1). The complex $[Cu(L)_2]^{2+}$ provides a good example of a distortion which includes a non-centrosymmetric component, the bond to one pyridine being slightly shorter than that to the other (Table 1). However, the difference (ca. 0.06 Å) is not large enough to contribute significantly to the distortion parameter D. The Cu–N(pyrazole) bonds of intermediate length are to the ligand with the closer pyridine, while the long pair of Cu–N bonds are to the ligand with the more distant pyridine. The rigid nature of the ligand may influence this disposition. It may also explain why the longer Cu–N(pyridine) bond actually appears to *decrease* in length by ca. 0.02 Å as the temperature rises from 50 to 350 K.[7] The bonds to the pyrazole groups on this ligand become shorter as higher levels are thermally populated (Table 1) and this will pull the pyridine ligand closer to the metal.

The parameter D may be a useful way of representing the distortions of Cu(II) complexes, particularly for a mixed-ligand complex such as $[Cu(bipyridyl)_2(ONO)]NO_3$ where it is difficult to estimate an average Cu–ligand bond length to evaluate ρ using eqn. (3). It might be thought that it is better to discuss the distortions in such mixed-ligand complexes in terms of pseudo-JT coupling. However, this is only likely to be fruitful if the distortion represents a displacement along an actual normal coordinate, and eqn. (1) does not satisfy this condition. In our view, it is therefore better to consider that D simply represents an empirical distortion, and it is important to bear in mind that it does not quantitatively describe a JT distortion in the conventional sense.

In principle, the thermal behaviour of $[Cu(L)_2]^{2+}$ in phase (II) could be due to a conformational equilibrium of the above kind, but with the distortions represented by ρ and ρ_T rather than D and D_T. Such a model was originally developed by Silver and Getz to interpret the temperature dependence of the g-values of Cu^{2+}-doped $K_2[Zn(H_2O)_6](SO_4)_2$,[20] but has subsequently been used to analyse the bond lengths observed for several pure Cu(II) compounds.[21] However, the model is only realistic if the wavefunction of the higher level involved in the equilibrium approximates a geometry in which the middle and long bonds are interchanged in direction compared with the ground level. Analysis by the dynamic JT model suggests that this is often, but not always the case.[2,9] Inspection of the wavefunctions for $[Cu(L)_2]^{2+}$ in phase (II) (Table 1) suggests that this condition is not satisfied well for the present complex. Although the longest and intermediate bonds in the two excited levels are reversed in direction compared with the ground level, the lengths are significantly closer to one another in the upper levels. Such a convergence implies that the upper levels are not localised in the second minimum, and the plots of the potential surface confirm that this minimum is indeed not well defined (Fig. 2). It therefore seems unlikely that the Silver/Getz approach is realistic for the present compound.

Acknowledgements

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