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# The Influence of Off-axial Ligands on the Crystal-field Energies of the Copper(II) Ion

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The assignment of the electronic spectra of various complexes of the copper(II) ion has been put on a sounder basis recently by the polarised single-crystal measurements of several workers.[1–10] This has resulted in the reassessment[11–13] of the various theoretical methods used to calculate the *d*-electron energy levels in the copper(II) ion. Both crystal-field[12,13] and orbital overlap[11] methods have been used and found to be in general agreement.[14] The crystal-field approach being the simpler approach, while perhaps not giving as good a physical picture as the orbital overlap method, has been adopted here, as virtually similar results are obtained by both procedures.

One of the problems highlighted by this reinvestigation was the role played by the off-axial ligands in determining the energy of the one-electron *d*-orbitals, especially in the case of the complex $CaCu(CH_3CO_2)_4 \cdot 6H_2O$, which has $D_{2d}$ symmetry, where several reports have been published.[15,16] Off-axial coordination is also found in basically axial copper(II) systems, *e.g.* $Cu(NH_3)_2(CH_3CO_2)_2$ (Ref. 17). This note reports the effect on the *d*-electron orbitals of the inclusion of off-axial coordination and discusses the importance of their contribution in determining the energy-level sequences.

*Crystal-field Calculations.* These calculations were based on a point charge model described by Krishnamurthy and Schaap[18] and Garner and Mabbs.[13] The same approximations as in Refs. 12 and 13 are made, that is, *Dq* and *Cp* of the long bonded ligand have been taken to be:

$$(Dq)' = Dq \times a^5$$

$$\text{and } (Cp)' = Cp \times a^3$$

where $a = R_E/R_A$ (where $R_E$ and $R_A$ are the lengths of the equatorially and axially bonded ligands respectively) and $\theta$ is the angle between the axial ligand and the *z*-axis. The eigenvalues and eigenfunctions resulting from the perturbation by the crystal fields have been evaluated for various values of *a* and $\theta$.

## Results and Discussion

The values chosen for the parameters *Dq*, *Cp*, $\theta$, and *a* were in line with those of other workers,[13,20] and correspond to known physical situations in order that the sensitivity of the energy-levels to the variation of the parameters may be meaningful. The results are presented graphically and are conveniently split into two types, the first representing the variation of the energies of the *d*-orbitals with *a* (at several values of $\theta$) and the second the variation with $\theta$ (at different values of *a*).

*(a) The Effect of Varying a.* The effect of the variation of *a* on the *d*-orbital energy-levels, while maintaining a fixed value of *Dq* (=1000 cm$^{-1}$) and *Cp* (=4000 cm$^{-1}$) is shown in Fig. 1 which represents several values of $\theta$.

Figure 1 represents the changes in energy of the one electron orbitals, when *a* is varied, and the angle between the *z*-axis and the long bonded ligands is 5, 15, and 25° respectively. From these figures it can be

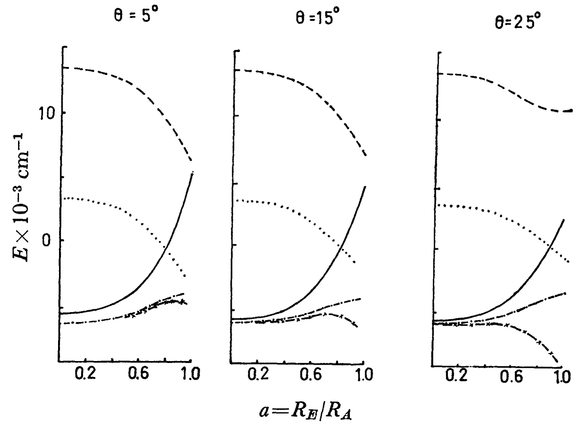

Fig. 1. The variation of the *d* orbital energies with *a*, when $\theta$=5, 15, and 25°.
——: $d_{z^2}$, – – – –: $d_{x^2-y^2}$, ⋯⋯: $d_{xy}$, –·–·: $d_{xz}$ ×–×–: $d_{yz}$

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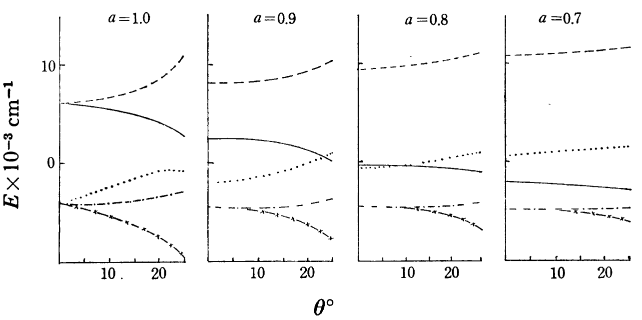

Fig. 2. The variation of the $d$ orbital energies with $\theta°$, when $a=1.0$, 0.9, 0.8, and 0.7.
——: $d_{z^2}$, ----: $d_{x^2-y^2}$, ……: $d_{xy}$, -·-·: $d_{xz}$, ×-×-: $d_{yz}$

seen that, although the ligands are not directed along the $z$-axis, they still have a profound effect upon the $d$-orbital energies. The first obvious difference in these diagrams is the easily intuitively predictable stabilization of the $d_{z^2}$ orbital as $\theta$ increases, at least at larger values of $a$. This effect is still small at $\theta=5°$, but when $\theta=15$ and $25°$ the $d_{z^2}$ orbital is stabilized by approximately 1500 and 2000 cm$^{-1}$ respectively at $a\approx1.0$. Similarly the $d_{x^2-y^2}$ and $d_{xy}$ orbitals are increased in energy by a corresponding amount. The other obvious feature is the lifting of the degeneracy of the $d_{xz}$ and $d_{yz}$ orbitals, the $d_{xz}$ orbital being destabilized due to the larger potential of the off-axial ligands as they become closer, while the $d_{yz}$ orbital is lowered in energy. The energy-level sequences show little variation with change in the angle $\theta$ and are essentially similar to the tetragonal-octahedral case; we might therefore expect similar experimental data. The experimental data available for the complex Cu(ethoxyacetate)$_2\cdot2H_2O$ (Ref. 21) ($a=0.84$; $\theta=15°$) gives the energy level sequence of the one-electron orbitals as $d_{x^2-y^2}>d_{z^2}>d_{xy}>d_{yz}>d_{xz}$, with the $d_{xy}$ orbital lying close to the $d_{z^2}$ orbital. This is in reasonable agreement with Fig. 1 ($\theta=15°$) with, in fact, the $d_{xy}$ orbital as suggested in Ref. 21, lying very close in energy to the $d_{z^2}$ orbital. However, the relative ordering of the $d_{xz}$ and $d_{yz}$ orbitals are reversed. This may be a result of $\pi$-bonding or any covalency effects which are totally ignored in the crystal-field approach.

*(b) Variation with θ.* A significant feature of all these diagrams is that at values of $a\approx0.7$, the energy-levels obtained for the one-electron orbitals vary very little with the angle $\theta$. This suggests that, although the off-axial ligands have a significant effect on the crystal-field potential as the metal-ligand distance alters (just as in the tetragonal-octahedral case), the variation of $\theta$ has little significance and, therefore, the actual position of the ligands (be it axial or off-axial) is of little importance compared with the metal-ligand distance. Thus only when $a\approx1.0$ do the $d$-orbital energy-levels vary significantly with the angle $\theta$ and this is shown most clearly in Fig. 2 which plots the energy of the $d$-orbitals as $\theta$ varies (for several values of $a$). When $a\approx0.8$, a variation of $\theta$ produces little change in the one-electron energy-levels, but at $a=1.0$, the $d$-orbital energies have been altered by approximately $\pm4000$ cm$^{-1}$, a not insignificant change.

In short then, when attempting the assignment of the electronic spectra of copper(II) complexes, which contain off-axial ligands, we may in essence treat the problem as being that of assigning a tetragonal-octahedral complex, as the most important contribution in determining the energy of the one-electron $d$-orbitals is the metal-ligand distances and the actual value of $\theta$ is, at best, only a secondary consideration. Notwithstanding this, when $a\approx1.0$, then the value of $\theta$ does become significant and may cause a change in transition energy by as much as 4000 cm$^{-1}$.

Nevertheless, it must be noted that the crystal-field approach will tend to overestimate the contribution due to the long-bonded ligands,[14] much smaller effects being predicted when using the orbital overlap procedure and a certain amount of care must be employed in the assignment of these spectra.

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