

## Symmetry-restricted Covalence in Ligand Field Theory. Part I. The Relative Energies of the ${}^2B_{2g}$ and ${}^2E_g$ States in Tetra-amminecopper(II) Compounds

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The effects of symmetry-restricted covalence on the  $d-d$  spectra of tetra-amminecopper(II) compounds are discussed, with particular reference to the relative energies of the  ${}^2B_{2g}$  and  ${}^2E_g$  states. The  $d-d$  transition energies are expressed as the sum of a change in one-electron energy and a change in two-electron energy. The latter terms are calculated in the INDO approximation; the necessary MO mixing coefficients are obtained by appeal to experimental data and a simple approximation based on perturbation theory. For square coplanar  $\text{Cu}(\text{NH}_3)_4^{2+}$ , it is shown that the  ${}^2B_{2g}$  state should lie higher in energy than the  ${}^2E_g$  state if, as expected in a  $\sigma$ -bonded system, the  $b_{2g}$  and  $e_g$  orbitals are accidentally degenerate. This is contrary to the predictions of simple ligand field models. If axial ligands having  $\pi$ -donor orbitals are allowed to approach the metal, completing the usual tetragonal octahedral co-ordination geometry, the model predicts that, notwithstanding the destabilization of the  $e_g$  orbitals as a consequence of axial  $\pi$ -interaction, the  ${}^2E_g$  state becomes higher in energy than the  ${}^2B_{2g}$  state. These results are consistent with experimental data.

THE electronic structures of copper(II)-ammine compounds have attracted much interest and many experimental e.s.r. and optical data have been accumulated.<sup>1-3</sup> Tetragonal chromophores of the type  $\text{CuN}_4\text{X}_2$  are of particular interest since much crystallographic work has been done on them, and the relatively high micro-symmetry ( $D_{4h}$ , or sometimes  $C_{4v}$ ) should facilitate detailed theoretical analysis. Electronic and e.s.r. spectra indicate that the relative energies of the  $d-d$  states in tetra-amminecopper(II) compounds are  ${}^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$ , although the position of the  ${}^2B_{2g}$  state is not always certain. Theoretical treatments of these results have usually invoked the assumption that in the 'one-positron'  $d^9$  configuration, optical transition energies can be equated to differences between one-electron orbital energies; thus if, as is commonly found experimentally, the  ${}^2B_{2g}$  state lies *ca.* 2 kK lower in energy than the  ${}^2E_g$  state, the  $b_{2g}$  orbital ( $d_{xy}$  in crystal field terminology) is deemed to lie some 2 kK higher in energy than the  $e_g$  orbitals ( $d_{xz, yz}$ ). This result is rather surprising; the angular overlap model<sup>4</sup> predicts that in the absence of appreciable  $\pi$ -bonding in the equatorial plane (as seems appropriate for saturated nitrogen donors such as ammonia and ethylenediamine) the  $b_{2g}$  and  $e_g$  orbitals should be non-bonding and accidentally degenerate. Kibler has discussed this accidental degeneracy on a more formal basis.<sup>5,6</sup> Any significant  $\pi$ -donation from the axial ligands would be expected to destabilize the  $e_g$  orbitals, placing the  ${}^2B_{2g}$  state higher in energy than  ${}^2E_g$ .

We suggested<sup>7</sup> that the splitting of the  $b_{2g}$  and  $e_g$  orbitals could be explained if a crystal field perturbation were added in the angular overlap treatment. Thus if the ligands are represented by point charges, the  $b_{2g}$

orbital will be destabilized relative to the  $e_g$  orbitals in a tetragonally elongated system, and the magnitude of the splitting should increase with the extent of the tetragonal distortion. This model appeared to be quite successful, but subsequent work has cast some doubt on the validity of the electrostatic interpretation of the splitting of the  $b_{2g}$  and  $e_g$  orbitals. Hathaway and Stephens<sup>8</sup> redetermined the crystal structures of  $\text{Na}_4\text{Cu}(\text{NH}_3)_4[\text{Cu}(\text{S}_2\text{O}_3)_2]_2\cdot\text{L}$  ( $\text{L} = \text{H}_2\text{O}$  or  $\text{NH}_3$ ) and measured their optical and e.s.r. spectra. The compound with  $\text{L} = \text{H}_2\text{O}$  appears to represent the closest approach yet found to square coplanarity in a tetra-amminecopper(II) system; the oxygen atom of the water molecule lies on the  $z$ -axis at a distance of 2.88 Å from the metal, a much longer axial Cu-O bond than is usual. We might therefore have expected that the splitting of the  $b_{2g}$  and  $e_g$  orbitals (as measured by the relative energies of the  ${}^2B_{2g}$  and  ${}^2E_g$  states, which can be inferred from spectroscopic data) would be particularly large in this system. However, no evidence of such splitting was obtained from the optical spectrum, and the e.s.r.  $g$ -values suggested that the  ${}^2B_{2g}$  and  ${}^2E_g$  states were practically degenerate. Indeed, if the  $g$ -values are re-interpreted by use of the equations with second-order corrections given by Garner *et al.*,<sup>9</sup> isotropy of the orbital reduction factor being assumed and exchange coupling neglected, the  ${}^2B_{2g}$  state appears to lie *ca.* 1 kK higher in energy than  ${}^2E_g$ . The electrostatic interpretation of the relative energies of these states must therefore be reconsidered.

We now report the results of calculations based on a model which takes account of the different radial extensions of the orbitals of the partly-filled shell. Lohr<sup>10</sup> has succeeded in interpreting some features of the spectra of octahedral  $\text{Mn}^{II}$  systems by such a model.

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<sup>1</sup> B. J. Hathaway and A. A. G. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1.

<sup>2</sup> B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

<sup>3</sup> D. W. Smith, *Structure and Bonding*, 1972, **12**, 49.

<sup>4</sup> C. K. Jorgensen, 'Modern Aspects of Ligand Field Theory,' North-Holland, Amsterdam, 1971.

<sup>5</sup> M. R. Kibler, *Chem. Phys. Letters*, 1970, **7**, 83.

<sup>6</sup> M. R. Kibler, *Chem. Phys. Letters*, 1971, **8**, 142.

<sup>7</sup> D. W. Smith, *J. Chem. Soc. (A)*, 1969, 1708.

<sup>8</sup> B. J. Hathaway and F. S. Stephens, *J. Chem. Soc. (A)*, 1970, 884.

<sup>9</sup> C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, 320.

<sup>10</sup> L. L. Lohr, *J. Chem. Phys.*, 1971, **55**, 27.

Our aim was to develop a largely empirical method which would give us some idea of the importance of orbital expansion effects in the spectra of tetra-ammine-copper(II) systems, and perhaps afford insight into the origins of the success of simpler models which neglect such effects. We report the results for square coplanar  $\text{Cu}(\text{NH}_3)_4^{2+}$ , square coplanar  $\text{CuCl}_4^{2-}$ , and tetragonal octahedral  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ . A preliminary report has appeared.<sup>11</sup>

### THEORY

The interpretation of  $d-d$  spectra in copper(II) systems has usually involved the calculation of the one-electron energies of the relevant orbitals in terms of parameters whose absolute values are determined by appeal to experimental data;<sup>3</sup> these might be the crystal-field parameters  $a_2$  and  $a_4$  (or  $Cp$  and  $Dq$ ) or the angular overlap parameters  $e_\sigma$  and  $e_\pi$ . There is seldom much doubt as to which of these orbitals lies highest in energy, and the  $d-d$  transitions are simply regarded as excitations of electrons from each of the doubly-occupied orbitals to the singly-occupied one. The transition energies are deemed to be given by the differences between the appropriate one-electron energies. This model is valid only if all the orbitals concerned have the same radial wave function, so that all two-electron quantities concerned in the transition energies will vanish. This is, of course, true for free ions, and it should hold for complexes, within the crystal field model. If we acknowledge that covalent bonding is important, the nephelauxetic effect must be considered. Its manifestations have been separated into two components:<sup>12</sup> central-field covalence and symmetry-restricted covalence. The former may be considered to lead to a uniform expansion of the radial wave functions of the  $d$ -orbitals, as a consequence of the invasion of the metal ion by ligand electrons. If only the metal  $(n+1)s$  and  $(n+1)p$  orbitals were involved in covalent bonding, we would still be able to ignore two-electron terms in the  $d-d$  transition energies; but if the metal  $nd$  orbitals can overlap to a significant extent with the ligands, symmetry-restricted covalence must be taken into account. In terms of the ligand-field theory (in the sense that we still regard the orbitals of the partly-filled shell as essentially metal  $d$ -orbitals), symmetry-restricted covalence may be regarded as further expanding those  $d$ -orbitals which are directly involved in covalent bonding, but the radial wave function will now depend on the extent of such covalent interaction and will not be the same for all  $d$ -orbitals. Thus any appreciable amount of symmetry-restricted covalence will invalidate the approximation that optical transition energies can be simply equated to changes in one-electron energy. In terms of molecular orbital theory, we have to write down the orbitals of the partly-filled shell and evaluate the two-electron terms explicitly over the LCAO-MO's.

If the five highest occupied orbitals (*i.e.*, the crystal field  $d$ -orbitals) in a  $d^9$  system are denoted  $\phi_1, \phi_2, \dots, \phi_5$ , with  $\phi_i$  lying highest in energy, a transition corresponding to excitation of an electron from  $\phi_j$  to  $\phi_i$  will have an energy given by (1), where  $\epsilon_i$  and  $\epsilon_j$  are the one-electron

$$E_{ij} = \epsilon_i - \epsilon_j + q_{ij} \quad (1)$$

energies of the orbitals concerned and  $q_{ij}$  is a two-electron term, the change in interelectron repulsion energy accompanying the excitation  $\phi_j \rightarrow \phi_i$ , given by (2), where the  $J_{ij}$  and  $K_{ij}$  are respectively the Coulomb and exchange integrals between the valence orbitals.

$$q_{ij} = J_{ii} - J_{jj} + \sum_{k \neq i, j} (2J_{ik} - K_{ik}) - \sum_{k \neq i, j} (2J_{jk} - K_{jk}) \quad (2)$$

The relevant molecular orbitals  $\phi_i$  of a tetragonal ( $D_{4h}$ ) copper(II) compound can be written as (3)–(7),

$$\phi_1(b_{1g}) = a_1 d_{x^2-y^2} - a_2 \cdot \frac{1}{2} (-p_x^1 + p_y^2 + p_x^3 - p_y^4) \quad (3)$$

$$\phi_2(a_{1g}) = b_1 d_{z^2} - b_2 \cdot \frac{1}{2} (p_x^1 + p_y^2 - p_x^3 - p_y^4) \quad (4)$$

$$\phi_3(b_{2g}) = c_1 d_{xy} - c_2 \cdot \frac{1}{2} (p_y^1 + p_x^2 - p_y^3 - p_x^4) \quad (5)$$

$$\phi_4(e_g1) = d_1 d_{xz} - d_2 \cdot 2^{-\frac{1}{2}} (p_x^5 - p_x^6) - d_3 \cdot 2^{-\frac{1}{2}} (p_z^1 - p_z^3) \quad (6)$$

$$\phi_5(e_g2) = d_1 d_{yz} - d_2 \cdot 2^{-\frac{1}{2}} (p_y^5 - p_y^6) - d_3 \cdot 2^{-\frac{1}{2}} (p_z^2 - p_z^4) \quad (7)$$

where the labelling of the orbitals follows the conventions we have used previously.<sup>13</sup> The ligands are assumed to use only  $p$ -orbitals for bonding to the metal. Ligand-ligand overlap has been neglected for simplicity; some of the calculations reported here were repeated with full allowance for ligand-ligand overlap and although the results were affected in detail, the essential conclusions were unchanged.

It is generally agreed that  $\phi_1(b_{1g})$  should lie highest in energy, so that the  $d-d$  transitions can be regarded as excitations  $\phi_j \rightarrow \phi_1$  and the transition energies are given by (8). The relative values of  $\epsilon_1$  and  $\epsilon_j$  can be

$$E_{1j} = \epsilon_1 - \epsilon_j + q_{1j} \quad (8)$$

estimated by appeal to the angular overlap model. We suggest, following Lohr,<sup>10</sup> that the  $q_{1j}$  may be calculated in the INDO approximation.<sup>14</sup> The integrals  $J_{ij}$  and  $K_{ij}$  are evaluated over the MO's (3)–(7); after expanding these, we retain all one-centre integrals and two-centre Coulomb integrals, while all other integrals are neglected. We are then left with (i) one-centre Coulomb and exchange integrals between metal  $d$ -orbitals, which can be expressed in terms of the Racah parameters  $A$ ,  $B$ , and  $C$ , (ii) one-centre Coulomb and exchange integrals between ligand orbitals, which are expressed in terms of the parameters  $F_0$  and  $F_2$ , and (iii) two-centre Coulomb integrals between metal and ligand orbitals, and between ligand orbitals centred on different atoms, which we

<sup>11</sup> D. W. Smith, *Chem. Phys. Letters*, 1972, **16**, 426.

<sup>12</sup> C. K. Jorgensen, *Prog. Inorg. Chem.*, 1962, **4**, 73.

<sup>13</sup> D. W. Smith, *J. Chem. Soc. (A)*, 1970, 3108.

<sup>14</sup> J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

approximate as the repulsion of point charges separated by the internuclear distance. Thus we arrive at expressions (9)–(26). In these equations,  $F_0$  and  $F_2$

$$J_{11} = a_1^4 A + 4a_1^4 B + 3a_1^4 C + a_2^4 F_0/4 + a_2^4 F_2 + 2a_1^2 a_2^2/R_e + 2^{1/2} a_2^4/4R_e + a_2^4/8R_e \quad (9)$$

$$J_{22} = b_1^4 A + 4b_1^4 B + 3b_1^4 C + b_2^4 F_0/4 + b_2^4 F_2 + 2b_1^2 b_2^2/R_e + 2^{1/2} b_2^4/4R_e + b_2^4/8R_e + \frac{1}{2} b_3^4 F_0' + 2b_3^4 F_2' + 2b_1^2 b_3^2/R_a + b_3^4/4R_a + b_2^2 b_3^2/(R_e^2 + R_a^2)^{1/2} \quad (10)$$

$$J_{33} = c_1^4 A + 4c_1^4 B + 3c_1^4 C + c_2^4 F_0/4 + c_2^4 F_2 + 2c_1^2 c_2^2/R_e + 2^{1/2} c_2^4/4R_e + c_2^4/8R_e \quad (11)$$

$$J_{44} = J_{55} = d_1^4 A + 4d_1^4 B + 3d_1^4 C + \frac{1}{2} d_3^4 F_0 + 2d_3^4 F_2 + 2d_1^2 d_3^2/R_e + d_3^4/4R_e + \frac{1}{2} d_2^4 F_0' + 2d_2^4 F_2' + 2d_1^2 d_2^2/R_a + d_2^4/4R_a \quad (12)$$

$$J_{12} = a_1^2 b_1^2 A - 4a_1^2 b_1^2 B + a_1^2 b_1^2 C + a_2^2 b_2^2 F_0/4 + a_2^2 b_2^2 F_2 + a_2^2 b_1^2/R_e + a_1^2 b_2^2/R_e + 2^{1/2} a_2^2 b_2^2/4R_e + a_2^2 b_2^2/8R_e + a_1^2 b_3^2/R_a + a_2^2 b_3^2/(R_e^2 + R_a^2)^{1/2} \quad (13)$$

$$J_{13} = a_1^2 c_1^2 A + 4a_1^2 c_1^2 B + a_1^2 c_1^2 C + a_2^2 c_2^2/R_e + a_1^2 c_2^2/R_e + 2^{1/2} a_2^2 c_2^2/4R_e + a_2^2 c_2^2/8R_e + a_2^2 c_2^2 F_0/4 - \frac{1}{2} a_2^2 c_2^2 F_2 \quad (14)$$

$$J_{14} = J_{15} = a_1^2 d_1^2 A - 2a_1^2 d_1^2 B + a_1^2 d_1^2 C + a_2^2 d_2^2/R_e + a_1^2 d_3^2/R_e + 2^{1/2} a_2^2 d_3^2/4R_e + a_2^2 d_3^2/8R_e + a_2^2 d_3^2 F_0/4 - \frac{1}{2} a_2^2 d_3^2 F_2 + a_1^2 d_2^2/R_a + a_2^2 d_2^2/(R_e^2 + R_a^2)^{1/2} \quad (15)$$

$$J_{23} = b_1^2 c_1^2 A - 4b_1^2 c_1^2 B + b_1^2 c_1^2 C + b_2^2 c_2^2 F_0/4 - \frac{1}{2} b_2^2 c_2^2 F_2 + b_1^2 c_2^2/R_e + b_2^2 c_1^2/R_e + 2^{1/2} b_2^2 c_2^2/4R_e + b_2^2 c_2^2/8R_e + b_3^2 c_1^2/R_a + b_3^2 c_2^2/(R_e^2 + R_a^2)^{1/2} \quad (16)$$

$$J_{24} = b_1^2 d_1^2 A + 2b_1^2 d_1^2 B + b_1^2 d_1^2 C + b_2^2 d_3^2 F_0/4 - \frac{1}{2} b_2^2 d_3^2 F_2 + b_1^2 d_3^2/R_e + b_2^2 d_1^2/R_e + 2^{1/2} b_2^2 d_3^2/4R_e + b_2^2 d_3^2/8R_e + \frac{1}{2} b_3^2 d_2^2 F_0' - b_3^2 d_2^2 F_2' + b_1^2 d_2^2/R_a + b_3^2 d_1^2/R_a + b_3^2 d_2^2/4R_a + b_3^2 d_3^2/(R_e^2 + R_a^2)^{1/2} + b_2^2 d_2^2/(R_e^2 + R_a^2)^{1/2} \quad (17)$$

$$J_{34} = J_{35} = c_1^2 d_1^2 A - 2c_1^2 d_1^2 B + c_1^2 d_1^2 C + c_2^2 d_3^2 F_0/4 - \frac{1}{2} c_2^2 d_3^2 F_2 + c_1^2 d_3^2/R_e + c_2^2 d_1^2/R_e + 2^{1/2} c_2^2 d_3^2/4R_e + c_2^2 d_3^2/8R_e + c_1^2 d_2^2/R_a + c_2^2 d_2^2/(R_e^2 + R_a^2)^{1/2} \quad (18)$$

$$J_{45} = d_1^4 A - 2d_1^4 B + d_1^4 C + 2d_1^2 d_3^2/R_e + 2^{1/2} d_3^4/R_e + \frac{1}{2} d_2^4 F_0' - d_2^4 F_2' + 2d_1^2 d_2^2/R_a + d_2^4/4R_a + 2d_2^2 d_3^2/(R_e^2 + R_a^2)^{1/2} \quad (19)$$

$$K_{12} = 4a_1^2 b_1^2 B + a_1^2 b_1^2 C + a_2^2 b_2^2 F_0/4 + a_2^2 b_2^2 F_2 - a_2^2 2^{1/2} b_2^2/4R_e + a_2^2 b_2^2/8R_e \quad (20)$$

$$K_{13} = a_1^2 c_1^2 C + 3a_2^2 c_2^2 F_2/4 \quad (21)$$

$$K_{14} = K_{15} = 3a_1^2 d_1^2 B + a_1^2 d_1^2 C + 3a_2^2 d_3^2 F_2/4 \quad (22)$$

$$K_{23} = 4b_1^2 c_1^2 B + b_1^2 c_1^2 C + 3b_2^2 c_2^2 F_2/4 \quad (23)$$

$$K_{24} = K_{25} = b_1^2 d_1^2 B + b_1^2 d_1^2 C + 3b_3^2 d_2^2 F_2'/2 + 3b_2^2 d_3^2 F_2/4 \quad (24)$$

$$K_{34} = K_{35} = 3c_1^2 d_1^2 B + c_1^2 d_1^2 C + 3c_2^2 d_3^2 F_2/4 \quad (25)$$

$$K_{45} = 3d_1^4 B + d_1^4 C + 3d_2^4 F_2'/2 \quad (26)$$

<sup>15</sup> J. B. Mann, Los Alamos Scientific Laboratory Report LA 3690, 1967.

refer to the equatorial ligand atoms, while  $F_0'$  and  $F_2'$  refer to the axial ligand atoms.  $R_e$  and  $R_a$  refer to the equatorial and axial metal–ligand distances respectively.

In order to evaluate these integrals, and hence obtain the  $q_{ij}$  terms, we have to find the MO mixing coefficients. This could be done by performing a full MO calculation, but we prefer to adopt a simple, empirical approach. In the angular overlap model, the destabilization suffered by a metal  $d$ -orbital is proportional to the square of the group overlap integral between the  $d$ -orbital and the appropriate symmetry-adapted combination of ligand orbitals, in accordance with second-order perturbation theory. It seems reasonable to suppose that the extent of ligand–metal mixing should be proportional to the group overlap integral. Consider a chromophore of the type  $\text{CuX}_n$  (all ligands identical). The molecular orbitals which constitute the partly filled shell can be written as (27), where  $\psi_i(\text{M})$  is a metal  $d$ -orbital and the

$$\phi_i = \alpha_i \psi_i(\text{M}) - \sum_j \beta_{ij} \psi_j(\text{X}) \quad (27)$$

$\psi_j(\text{X})$  are ligand group orbitals. We suggest that the ratio  $\beta_{ij}/\alpha_i$  (which may be regarded as a measure of the extent of metal–ligand mixing) is proportional to the group overlap integral  $G_{ij}$  between  $\psi_i(\text{M})$  and  $\psi_j(\text{X})$ , as represented by (28). Thus if any one mixing coefficient

$$\beta_{ij}/\alpha_i = k_{\text{MX}} G_{ij} \quad (28)$$

can be found from experimental data or otherwise estimated, the proportionality constant  $k_{\text{MX}}$  can be found, and all other coefficients are obtainable from the normalisation conditions. In the case of a chromophore where all the ligands are not identical, *e.g.*,  $\text{CuX}_n\text{Y}_m$ , the proportionality constant  $k_{\text{MX}}$  in (28) will obviously depend on which ligand is involved in the group orbital. It will then be necessary to determine the proportionality constants  $k_{\text{MX}}$  and  $k_{\text{MY}}$  separately by appeal to experimental data for binary chromophores of the types  $\text{CuX}_n$  and  $\text{CuY}_n$ .

The interelectron repulsion parameters which appear in equations (9)–(26) present some problems, since they include the Racah parameter  $A$  and the Condon–Shortley parameter  $F_0$ . These are likely to be very large quantities and are inaccessible from experimental data. They can be calculated from Hartree–Fock wave functions, but there is good reason to believe that such calculated values will be too high since electron correlation is neglected in the Hartree–Fock scheme. In order to determine suitable values of these awkward parameters, we have taken Hartree–Fock values<sup>15</sup> of  $A$ ,  $B$ ,  $C$ ,  $F_0$ , and  $F_2$  and scaled these down uniformly in order to obtain values of  $B$ ,  $C$ , and  $F_2$  in reasonable agreement with spectroscopic data for the free atoms or ions.<sup>16,17</sup> In the case of  $\text{Cu}^{2+}$ , the Racah parameters were further reduced by 10% to take account of central-field covalence.

<sup>16</sup> C. E. Moore, 'Atomic Energy Levels,' National Bureau of Standards, Washington, 1947–56.

<sup>17</sup> J. S. Griffith, 'Theory of Transition Metal Ions,' Cambridge Univ. Press, 1961.

*Square Coplanar*  $\text{Cu}(\text{NH}_3)_4^{2+}$ .—Ammonia is regarded as a ligand capable of only  $\sigma$ -bonding to metals. Thus the coefficients  $c_1$  and  $d_1$  in equations (3)—(7) are set equal to unity, while  $b_3$ ,  $c_2$ ,  $d_2$ , and  $d_3$  should be zero. A copper–nitrogen distance of 2.00 Å was assumed, on the basis of the available crystallographic data for tetraamminecopper(II) compounds with large tetragonal distortions.<sup>1,2,8</sup> The interelectron repulsion parameters were found (as described above) to be  $A = 170.0$  kK,  $B = 1.1$  kK,  $C = 4.1$  kK,  $F_0 = 113.0$  kK, and  $F_2 = 2.0$  kK. The MO coefficient  $a_1$  was chosen to be 0.85; this was considered to be the most reasonable value, consistent with e.s.r. data<sup>8,13</sup> and semiempirical MO calculations.<sup>18,19</sup> The remaining coefficients  $a_2$ ,  $b_1$ , and  $b_2$  were then found as described above, account being taken of metal–ligand (but not ligand–ligand) overlap integrals in the normalisation conditions; the wave functions of Richardson *et al.*<sup>20</sup> for  $\text{Cu}^+$  and of Clementi<sup>21</sup> for N were used in the computation of overlap integrals. The two-electron terms  $q_{ij}$  in equation (1) could then be evaluated. These (as might be expected) turned out to be large and negative, illustrating the considerable covalency (and hence delocalisation) of the  $b_{1g}$  MO:  $q_{12} = -96.4$  kK,  $q_{13} = -152.2$  kK, and  $q_{14} (= q_{15}) = -155.0$  kK. The difference between  $q_{13}$  and  $q_{14}$  is of paramount importance for our purposes and is rather small (again, as might be expected). It might be thought that, regard being had to the gross approximations and assumptions inherent in our primitive model, this difference is insignificant. However, a closer examination of (2), with use of equations (9)—(26), leads to a very simple analytic form for the difference  $q_{13} - q_{14}$ , given by (29). Whatever the nature of the approximations made in order to evaluate  $a_1$  and  $b_1$ , it seems

$$q_{13} - q_{14} = 15B(b_1^2 - a_1^2) \quad (29)$$

perfectly clear that  $q_{13} - q_{14}$  must be positive for square coplanar  $\text{Cu}(\text{NH}_3)_4^{2+}$  within the INDO model; the  $b_{1g}$  orbital is clearly more covalent than  $a_{1g}$ . In the framework of the present calculation, this difference is *ca.* 3 kK. Thus if (as indicated by the angular overlap model) the  $b_{2g}$  and  $e_g$  orbitals are accidentally degenerate and non-bonding in  $\text{Cu}(\text{NH}_3)_4^{2+}$ , the  ${}^2B_{2g}$  state should lie *ca.* 3 kK higher in energy than the  ${}^2E_g$  state. Such a statement is in complete conflict with the simple ligand field models; however, it is consistent with the available experimental evidence for tetraamminecopper(II) compounds which approach the limit of square coplanarity.

If we apply the angular overlap model to obtain the relative values of the one-electron energies  $\epsilon_i$  and set the angular overlap parameter  $e_\sigma$  equal to 57.5 kK (*i.e.*,  $\sigma^* = 11.5$  kK in the alternative nomenclature), and use (8) to calculate the  $d$ – $d$  transition energies for  $\text{Cu}(\text{NH}_3)_4^{2+}$ , the  ${}^2A_{1g}$ ,  ${}^2E_g$ , and  ${}^2B_{2g}$  states are predicted to lie at 18.6 kK, 17.5 kK, and 20.3 kK respectively above the

ground state. Experimentally,<sup>8</sup> for  $\text{Na}_4\text{Cu}(\text{NH}_3)_4$ – $[\text{Cu}(\text{S}_2\text{O}_3)_2]_2 \cdot \text{H}_2\text{O}$  (which is almost, but not quite, an example of a square coplanar tetraamminecopper(II) system), the  ${}^2E_g$  state has been definitely assigned at 19.2 kK, with the  ${}^2A_{1g}$  state at 18.4 kK. The position of the  ${}^2B_{2g}$  state is uncertain but, as discussed above, we think that it probably lies at *ca.* 20–21 kK on the basis of the e.s.r. results. Thus our model seems to give results in admirable accord with experiment; the predicted position of the  ${}^2A_{1g}$  state is particularly gratifying.

In practice, of course, all tetraamminecopper(II) compounds seem to have one or two axial ligands, forming relatively long bonds to the metal. We must therefore consider the effects of such an axial field on the relative energies of the  ${}^2B_{2g}$  and  ${}^2E_g$  states. In most tetraamminecopper(II) systems studied so far, the axial ligands have usually been polyatomic ions or molecules (*e.g.*, nitrite groups) co-ordinated (or semi-co-ordinated<sup>2</sup>) to the metal *via* one atom. The donor atom concerned usually has orbitals available for  $\pi$ -bonding to the metal, though we have argued that such interaction will be very weak<sup>22</sup> since  $\pi$ -overlap integrals involving 3d-orbitals fall off rapidly with increasing internuclear distance. For simplicity, we have chosen to consider  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$  in detail, although the electronic properties of this particular compound have not been studied in detail. Chlorine may be regarded as typical of a  $\pi$ -donor ligand.

Before we can set about calculating the relevant  $q_{ij}$  for this system, we must look at a binary copper(II)–chlorine system in order to establish a suitable value of the constant  $k_{MX}$  in equation (28) for MO's involving chlorine group orbitals. Moreover, we will have to find the angular overlap parameter  $e_\pi$  over a convenient range of Cu–Cl distances in order to determine the extent of destabilization of the  $e_g$  orbitals as a consequence of axial  $\pi$ -bonding; this will be equal to  $2e_\pi$ .

*Square Coplanar*  $\text{CuCl}_4^{2-}$ .—We take square planar  $\text{CuCl}_4^{2-}$  as a simple example of a binary copper(II) chlorine chromophore. Although there is some doubt as to whether such a species actually exists as a discrete entity, we should be able to predict its electronic properties approximately by extrapolation from the available data for tetragonal chlorocuprates(II). The Cu–Cl bond length was taken as 2.30 Å. The MO coefficients  $b_3$  and  $d_2$  are zero, and  $a_1$  was assumed to be 0.80 on the basis of e.s.r. data for tetragonal chlorocuprates(II)<sup>13</sup> and the results of a semiempirical MO calculation<sup>23</sup> for  $\text{CuCl}_4^{2-}$ . The remaining coefficients were then found by appeal to (28) and the normalisation conditions. The interelectron repulsion parameters for Cl were taken to be  $F_0 = 86.0$  kK, and  $F_2 = 2.0$  kK. The relevant  $q_{ij}$  were found to be:  $q_{12} = -136.9$  kK,  $q_{13} = -138.4$  kK, and  $q_{14} (= q_{15}) = -188.6$  kK. The angular overlap model was then applied in order to obtain

<sup>18</sup> S. I. Shupack, *Inorg. Chim. Acta*, 1967, **1**, 435.

<sup>19</sup> B. Roos, *Acta Chem. Scand.*, 1966, **20**, 1673.

<sup>20</sup> J. W. Richardson, W. C. Nieupoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

<sup>21</sup> E. Clementi, Supplement to *IBM J. Res. Development*, 1965, **9**, 2.

<sup>22</sup> D. W. Smith, *J. Chem. Soc. (A)*, 1970, 1498.

<sup>23</sup> P. Ros and G. C. A. Schuit, *Theoret. Chim. Acta*, 1966, **4**, 1.

a suitable value for the constant  $e_\sigma/(S^{\sigma_{MX}})^2 [= e_\pi/(S^{\pi_{MX}})^2]$  so that we can gauge the effect of chlorine ligands on the one-electron energies of the MO's in any chromophore. The relative energies of the one-electron levels in  $\text{CuCl}_4^{2-}$  can be written as previously described,<sup>24</sup> but without the electrostatic terms. With  $e_\sigma = 80.0$  kK the  ${}^2A_{1g}$ ,  ${}^2B_{2g}$ , and  ${}^2E_g$  states were predicted to lie at 23.1, 23.2, and 12.4 kK respectively above the ground state. These do not look particularly close to what we might expect for square planar  $\text{CuCl}_4^{2-}$  but they are of the correct order of magnitude; values of  $e_\sigma$  close to 80 kK will be required in order to obtain transition energies which are at all reasonable. Bearing in mind the magnitude of the  $q_{ij}$  terms (which are strongly dependent on the mixing coefficients chosen), we can regard the calculated transition energies as eminently reasonable. With this value of  $e_\sigma$  we can determine both angular overlap parameters over any range of internuclear distances from their assumed proportionality to the square of the appropriate diatomic overlap integral. The assumption that  $a_1 = 0.80$  enables us to fix the constant  $k_{MX}$  in equation (28), which we assume to hold for all chromophores containing chlorine.

**Tetragonal Octahedral  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ .**—We wish to determine the relative energies of the  ${}^2B_{2g}$  and  ${}^2E_g$  states in  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$  as functions of the tetragonal distortion; accordingly we have performed the calculations for six axial metal-ligand bond lengths in the range 2.6–3.6 Å. In equations (3)–(7) the only vanishing MO coefficients are  $c_2$  and  $d_3$ . We assume the equatorial bond length to be constant at 2.00 Å; this ignores the small variation in the equatorial distance which might be expected in a series of tetra-amminecopper(II) compounds of varying tetragonality.<sup>1,2</sup> The possible consequences of this neglect will be discussed later. The MO mixing coefficients can be obtained by appeal to the results already obtained for  $\text{Cu}(\text{NH}_3)_4^{2+}$  and  $\text{CuCl}_4^{2-}$ ;  $a_1$  is assumed to be constant at 0.85, and the remaining coefficients are obtained from (28) and the normalisation conditions. With the same values of the interelectron repulsion parameters as used previously, the relevant  $q_{ij}$  two-electron terms were calculated. These are collected in the Table. Account being taken of the

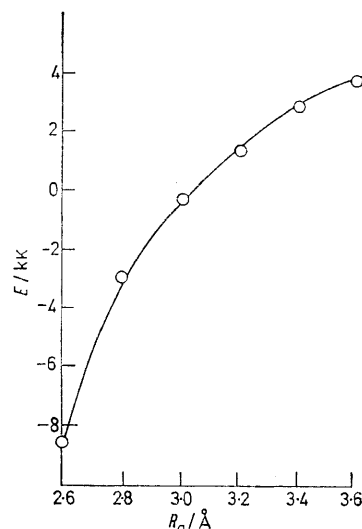
Two-electron terms  $q_{ij}$  over range of axial metal-ligand distances for  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$

$R_a/\text{Å}$	$-q_{12}/\text{kK}$	$-q_{13}/\text{kK}$	$-q_{14}/\text{kK}$
$\infty$	96.4	152.2	155.0
3.6	90.6	152.2	154.8
3.4	84.9	152.1	153.9
3.2	74.5	152.0	152.6
3.0	57.0	150.1	147.9
2.8	31.9	147.8	140.2
2.6	2.0	144.0	126.4

destabilization of the  $e_g$  orbitals relative to the  $b_{2g}$  orbital as a result of axial  $\pi$ -interaction, the relative energies of the  ${}^2B_{2g}$  and  ${}^2E_g$  states will be given by (30). The angular overlap parameter  $e_\pi$  was obtained

$$\Delta E({}^2B_{2g} - {}^2E_g) = q_{13} - q_{14} + 2e_\pi \quad (30)$$

over the range of axial metal-ligand distances from the data obtained for  $\text{CuCl}_4^{2-}$ . Thus the energy difference  $\Delta E$  as a function of  $R_a$  could be calculated; this is shown in the Figure.  $\Delta E$  decreases sharply as the axial ligands approach the metal, notwithstanding the increasing importance of the term  $2e_\pi$  in (30) as  $R_a$  decreases. This arises from the fact that  $q_{14}$  becomes rapidly less negative as covalence begins to contaminate the  $e_g$  orbitals. At an axial bond length of ca. 3.0 Å,  $\Delta E$  becomes negative; this point corresponds to a tetragonality  $T$  (as defined by Tomlinson *et al.*<sup>21</sup>) of ca. 0.76. We have<sup>22</sup> pointed out that there is a close relationship between this concept of tetragonality and axial overlap integrals, and it seems reasonable to suppose that calculations performed for other axial ligand atoms in



Plot of  $E({}^2B_{2g} - {}^2E_g)$  against axial bond length  $R_a$  in  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$

$\text{Cu}(\text{NH}_3)_4\text{X}_2$  would lead to similar results, with  $\Delta E$  changing sign somewhere around  $T = 0.76$ . It is significant to note that in  $\text{Na}_4\text{Cu}(\text{NH}_3)_4[\text{Cu}(\text{S}_2\text{O}_3)_2]_2 \cdot \text{H}_2\text{O}$ ,  $T$  is ca. 0.70, at which point our calculations would predict  $\Delta E$  to be ca. +1.5–2.0 kK. Thus our calculations may be said to be consistent with the available experimental data for tetra-amminecopper(II) systems with low values of  $T$ . For the more usual values of  $T$  around 0.78–0.80,  $\Delta E$  is predicted to be ca. –2 kK, in accordance with experimental results.

**Conclusions.**—The model set out in this paper has successfully explained some hitherto mysterious electronic properties of tetra-amminecopper(II) systems. The introduction of two-electron terms in theoretical expressions for  $d-d$  transition energies in  $d^9$  compounds represents a dimension of complexity which does not arise in the simple ligand field models which have been applied in the past. We conclude this paper with some discussion of the relationship between the present model and the simple ligand field approaches, and of the possible reasons for the apparent success of conventional

<sup>24</sup> D. W. Smith, *J. Chem. Soc. (A)*, 1969, 2529.

ligand field theory in many problems related to non-cubic complexes.

We have neglected spin-orbit coupling in this paper; to first order, this has the effect of splitting the  ${}^2E_g$  state, while to second order these components of the  ${}^2E_g$  state may become mixed, one with the  ${}^2A_{1g}$  state and the other with the  ${}^2B_{2g}$  state. As we have shown in more detail elsewhere,<sup>3</sup> the overall effect of this is small; spin-orbit coupling will make some contribution to the splitting of the  ${}^2B_{2g}$  and  ${}^2E_g$  states but the conclusions at the end of the previous section are not appreciably affected.

The magnitude of the  $q_{ij}$  terms is noteworthy, although these depend strongly on the assumed extent of covalence, *i.e.*, on the value chosen for  $a_1$ . However, in our model the  $q_{ij}$  turn out to be an order of magnitude greater than the one-electron splitting parameters. It appears that the magnitude of  $q_{ij}$  is closely proportional to the relative one-electron energies  $\varepsilon_i$  and  $\varepsilon_j$  (as estimated by the angular overlap model), and the success of any simple model which ignores the  $q_{ij}$  terms must depend on such a proportionality.

It may be noted that  $-q_{13}$  for  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$  decreases by *ca.* 8 kK as axial chlorines are brought up from

infinity to a distance of 2.6 Å from the metal. Thus we might predict that the  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  transition should increase in energy as the axial ligands approach. However, experimental evidence<sup>1,2</sup> suggests that the reverse is true. It must be remembered that in our calculations no allowance was made for an increase in the equatorial metal-ligand distance as the axial distance is reduced. There are not enough quantitative data available to enable us to predict the effects of such an equatorial elongation, but we can say that the splitting parameter  $e_\sigma$  should decrease as  $R_a$  decreases. This might well be sufficient to offset the decrease in  $-q_{13}$ , it being borne in mind that the transition energy is given by  $3e_\sigma + q_{13}$ .

We feel that the conventional ligand field models will continue to be valuable in the interpretation of  $d-d$  spectra for copper(II) systems for some time; however, it is evident that some phenomena demand a more sophisticated model and we should be able to apply simpler models more intelligently if we have some insight into the reasons for their success, *e.g.*, fortuitous cancellations, *etc.* The model advocated in this paper seems to offer promise and we are applying it to a variety of other non-cubic  $d^9$  systems.

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