

Molecular Orbital Calculations on Transition-metal Complexes. Part IV.¹ Square Planar Copper(II) Complexes

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CNDO MO Calculations are reported for the square planar Cu^{II} complexes CuL₂ (L = dimethylglyoximate, acetylacetonate, and salicylideneiminato), Cu(porphin), Cu(H₂O)₆²⁺, Cu(C₂O₄)₂²⁻, Cu(CN)₄²⁻, and for the distorted octahedral complexes of bis(acetylacetonato)- and bis(dimethylglyoximate)-copper produced by axial co-ordination of water and also ammonia. The covalency in the resulting *d* eigenfunctions correlates extremely well with the values derived from electron paramagnetic resonance measurements. The calculations yield transferred spin densities to the ligands which are generally a factor of ca. 2 smaller than those obtained from superhyperfine couplings in the e.s.r. spectrum.

THE divalent copper ion is most commonly encountered in an environment of four ligands situated in a planar arrangement about itself, and frequently with either one or two additional ligands in the axial positions. Would-be octahedral complexes of Cu^{II} should possess an orbitally degenerate ground-state with the result that these systems are susceptible to distortions of the Jahn-Teller type leading to geometrical configurations described above, which belong to the point groups D_{4h} or D_{2h} .

In previous parts in this series¹⁻³ MO calculations using the complete neglect of differential overlap approximation have been applied to six-co-ordinate complexes of the first-transition series and the resulting eigenfunctions have proved to be very useful for describing the observed covalency, including the spin delocalisation in complex ions. We report here the calculations for a number of square planar co-ordinated Cu^{II} systems by use of the same method and parameter scheme as previously, together with those for the distorted octahedral complexes produced by the co-ordination of ligand groups along axial positions.

E.s.r. studies of paramagnetic transition-metal complexes yield information about the distribution of the unpaired electrons and hence about the nature of the bonding between the metal ion and its ligands. There have been many reports^{1,4-11} concerning the application of e.s.r. to square planar or distorted octahedral complexes of Cu^{II} and of the interpretations of the e.s.r. parameters in terms of the covalency of the metal-ligand bonding. Despite these numerous experimentally derived values for the covalency factors, *i.e.* *d* orbital mixing coefficients, there have been only a few MO calculations for either four- or six-co-ordinate (D_{4h}) copper(II) systems.

The complex unit CuF₆ which appears in complexes of the type KCuF₃, K₂CuF₄, and CuF₂ as a flattened or elongated octahedron, D_{4h} , has been subjected to several MO calculations as CuF₆⁴⁻,^{2,12,13} mostly to attempt to confirm the existence of the Jahn-Teller forms as stable entities over the regular octahedral form. Extended Huckel-type MO calculations have been applied to dipivaloylmethanato-copper(II),¹⁴ however, in this approach the input parameters were varied until the covalency of the metal orbitals agreed satisfactorily with those derived from the e.s.r. measurements. Since the initiation of the present work, a systematic study into the effect of axial ligands on the eigenfunctions and the resultant e.s.r. parameters of bis(dimethylglyoximate)-copper(II) has appeared.¹⁵ This method uses the ZDO approximations of Roos,¹⁶ which was previously applied to the hexa-aquo- and hexa-ammine-copper(II) ions.¹⁷ We have included bis(dimethylglyoximate)copper(II) in our study, by use of the CNDO approximation and where comparison is possible agreement is fairly good between our results and those of ref. 15.

METHOD

Previously we have used the CNDO MO method to examine the effects of fluoride ion and the water molecule as ligands co-ordinated to first-row transition-metal ions; the same method is used in these calculations for the extended ligand systems chelated to the divalent copper ion. The Hamiltonian elements for open-shell configurations using unrestricted Hartree-Fock wavefunctions were given in Part I. Basis sets for carbon, nitrogen, and oxygen, consist of 2s, 2p_x, 2p_y, and 2p_z with exponents 1.625, 1.950, and 2.275; for hydrogen the exponent for the 1s orbital is given the value 1.2. For copper the basis set is 3d (3.08) and 4s/4p (1.482), with the β⁰ parameters used in the estimation of the off-diagonal $F_{\mu\nu}$ terms having the values

¹ Part III, G. C. Allen, D. W. Clack, and M. S. Farrimond, *J. Chem. Soc. (A)*, 1971, 2728.

² G. C. Allen and D. W. Clack, *J. Chem. Soc. (A)*, 1970, 2668.

³ D. W. Clack and M. S. Farrimond, *J. Chem. Soc. (A)*, 1971, 299.

⁴ H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, 1962, **36**, 3221.

⁵ D. Kivelson and R. Neiman, *J. Chem. Phys.*, 1961, **35**, 149.

⁶ A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31.

⁷ A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 35.

⁸ V. C. Swett and E. P. Dudek, *J. Phys. Chem.*, 1968, **72**, 1244.

⁹ H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, 1967, **71**, 109.

¹⁰ A. Longo and T. Buch, *Inorg. Chem.*, 1967, **6**, 556.

¹¹ E. M. Roberts and W. S. Koski, *J. Amer. Chem. Soc.*, 1960, **82**, 3006.

¹² C. J. Ballhausen and H. Johansen, *Mol. Phys.*, 1965, **10**, 175, 183.

¹³ L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1963, **2**, 911.

¹⁴ F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, 1967, **6**, 909.

¹⁵ K. E. Falk, E. Ivanova, B. Roos, and T. Vanngard, *Inorg. Chem.*, 1970, **9**, 556.

¹⁶ B. Roos, *Acta Chem. Scand.*, 1967, **21**, 1855.

¹⁷ B. Roos, *Acta Chem. Scand.*, 1966, **20**, 1672.

—30.0 eV (β^0_{3d}) and —35.0 eV (β^0_{4s}). The β^0 parameters for the first-row atoms are the same as used previously. All valence electrons are considered and assigned to molecular orbitals arising from a linear combination of these valence orbitals. A spin-doublet ground-state is assumed for all the complexes considered.

Geometry.—It is apparent from the crystal structures of the complexes of divalent copper with acetylacetonone (acacH),¹⁸ oxalate (ox),¹⁹ salicylideneimine (salH),²⁰ dimethylglyoxime (dmgH),²¹ porphin (porH₂),²² and water²³ as ligands that the copper atom is coplanar, or nearly so, with the entire ligand systems, and in general the copper atom is at the centre of a square made up from the four co-ordinating atoms of the ligands. Small deviations from square planarity are sometimes evident in the crystal, however we have assumed for the purposes of the calculations that these distortions will not be apparent in the free complexes. The bond lengths have been taken from refs. 18—23. The methyl groups in dimethylglyoxime and acetylacetonone have been treated as hydrogens.

RESULTS AND DISCUSSION

A survey of the e.s.r. results for square-co-ordinated copper complexes shows a tremendous variation in the reported e.s.r. parameters. In particular the values for Cu(acac)₂ in different chloroform–toluene mixtures lie between 145.5 and 194×10^{-4} cm⁻¹ for A_{\parallel} , and between 2.253—2.288 for g_{\parallel} . It is clear that these parameters are extremely sensitive to changes not only in the solvent but also to changes in the proportions of a given solvent system. We have therefore measured the e.s.r. parameters for Cu(acac)₂ in chloroform–toluene 1 : 1 v/v and examined the effect of co-ordinating groups on these parameters in the same solvent system. This solvent system was chosen as being one of the least likely to co-ordinate to the copper atom in the axial positions. The e.s.r. measurements were carried out by use of a Varian E3 spectrometer, and were recorded at room temperature to obtain the isotropic coupling, and at —140 °C to resolve the anisotropic spectrum. The concentration of the copper complex was ca. 0.01M. A sufficient quantity of water (oxygen co-ordination) and pyridine (nitrogen

TABLE I

E.s.r. parameters for Cu(acac)₂ in toluene–chloroform (1 : 1 v/v)

| | g_{\parallel} | g_{\perp} | $-A_{\parallel}/10^4$ cm ⁻¹ | $-A_0/10^4$ cm ⁻¹ |
|--|-----------------|-------------|---|---------------------------------|
| Cu(acac) ₂ | 2.2473 | 2.0289 | 173 | 75 |
| Cu(acac) ₂ (H ₂ O) | 2.2541 | 2.0264 | 170 | 74 |
| Cu(acac) ₂ (py) | 2.2611 | 2.0352 | 163 | 69 |

co-ordination) were added to the solution of the copper complex to effect complete co-ordination in the axial positions. The results are given in Table I. Co-ordination of the nitrogen donor leads to a decrease in A_{\parallel} and an increase in g_{\parallel} compared with that of the uncomplexed

Cu(acac)₂; the same situation is realised with water in the axial positions, however the shifts are considerably smaller than for the nitrogen donor. These shifts are in the same direction and are of similar magnitude to those found by other workers for axial nitrogen co-ordination. The change in covalency parameters derived from these values will be discussed later.

Molecular Orbitals.—Eigenfunctions and eigenvalues. Since it is not possible to use the present method to obtain excited states we are unable to make any estimate for the contribution of these configurations to the e.s.r. parameters. We have therefore used the e.s.r. data to obtain bonding parameters^{4,5} and to make a comparison of these with the CNDO eigenfunctions obtained for complexes both with and without the presence of axially co-ordinated groups. Smith²⁴ has recently reported a more detailed calculation for relating the g -values of square planar Cu^{II} complexes to the MO coefficients and it appears that although the expressions previously derived are only approximate, a certain degree of cancellation of second-order terms occurs with the result that reasonably good g values are obtained with neglect of a number of terms. We shall therefore use the simpler formulae and content ourselves with comparisons between a number of complexes containing various co-ordinating groups rather than obtain an accurate evaluation of the parameters for an individual complex species. The CNDO eigenfunctions yield the spin distribution as the difference between α and β spin densities and, where possible, these will be compared with values derived from superhyperfine interactions. The axial nitrogen co-ordinator was treated as NH₃ for the calculations owing to core size and time limitations.

The majority of the complexes considered belong to the point group D_{2h} . Cu(CN₄)²⁻ and Cu(por) are D_{4h} and Cu(sal)₂ is C_{2v} in type. The D_{2h} symmetry group allows $d_{x^2}, d_{x^2-y^2}$, and the s orbitals on the central copper to mix; d_{xz} and d_{yz} belong to b_{2g} and b_{3g} representation respectively; d_{xy} transforms as b_{1g} . In the higher symmetry D_{4h} group, d_{xz} and d_{yz} are degenerate, transforming as e_g type. Since it will not materially affect the results if a lower symmetry classification is considered for describing the molecular orbitals, all results will be given for D_{2h} symmetry type. The 'mainly d ' molecular orbitals applicable to this point group are:

$$\psi b_{1g} = \alpha 3d_{xy} + \alpha^1 \sigma [\text{ligand } (b_{1g})]$$

$$\psi b_{2g} = \beta 3d_{xz} + \beta^1 \pi [\text{ligand } (b_{2g})]$$

$$\psi b_{3g} = \beta_1 3d_{yz} + \beta_1^1 \pi [\text{ligand } (b_{3g})]$$

$$\psi a_g = \gamma 4s + \gamma' 3d_{z^2} + \gamma'' 3d_{x^2-y^2} + \delta \sigma [\text{ligand } (a_g)]$$

ψb_{1g} essentially represents the distribution of unpaired spin in the complexes considered. The results show that

²¹ E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, 1959, **12**, 201.

²² E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 1964, **86**, 2342.

²³ M. W. Webb, H. F. Kay, and N. W. Grimes, *Acta Cryst.*, 1965, **18**, 740.

²⁴ D. W. Smith, *J. Chem. Soc. (A)*, 1970, 3108.

¹⁸ L. F. Dahl, unpublished results, from T. S. Piper and R. L. Belford, *Mol. Phys.*, 1962, **5**, 169.

¹⁹ J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1951, **4**, 35 (for the chromium complex).

²⁰ J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, 1959, **12**, 842 (for the nickel complex).

each complex gives rise to a ${}^2B_{1g}$ ground state with the greater part of the unpaired spin residing in the central copper $3d_{xy}$ orbitals, as expected.

TABLE 2

d Molecular orbital coefficients for tetragonal copper(II) complexes

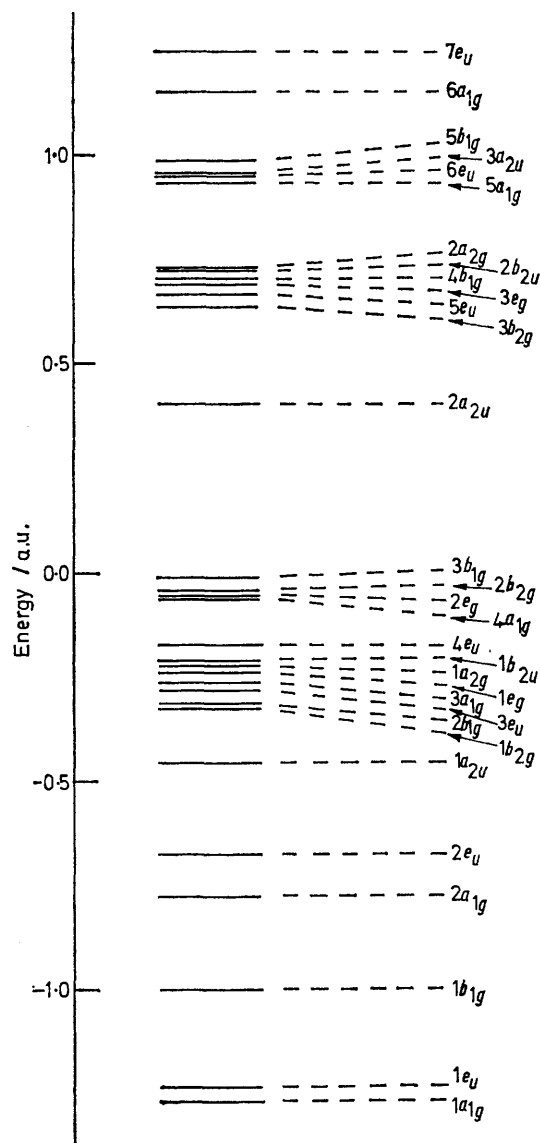
| | α | β | β_1 | γ' | γ'' | α derived |
|---|----------|---------|-----------|-------------------|-------------------|---------------------|
| Cu(dmg) ₂ | 0.79 | 0.97 | 0.97 | 0.80 | 0.33 | |
| Cu(dmg) ₂ (H ₂ O) ₂ | 0.83 | 0.97 | 0.97 | 0.93 | 0.20 | 0.86 ^a |
| Cu(dmg) ₂ (NH ₃) ₂ | 0.84 | 0.97 | 0.97 | 0.94 | 0.09 | 0.86 ^a |
| Cu(acac) ₂ | 0.89 | 0.95 | 0.96 | 0.81 | 0.51 | 0.88 ^b |
| Cu(acac) ₂ (H ₂ O) ₂ | 0.87 | 0.96 | 0.96 | 0.91 | 0.24 | 0.89 ^b |
| Cu(acac) ₂ (NH ₃) ₂ | 0.86 | 0.97 | 0.96 | 0.92 | 0.10 | 0.87 ^b |
| Cu(H ₂ O) ₆ ²⁺ | 0.95 | 0.98 | 0.98 | 0.99 ^c | 0.83 ^c | 0.91 ^d |
| Cu(por) | 0.86 | 0.82 | 0.82 | 0.81 ^e | 0.90 ^e | 0.86 ^e |
| Cu(sal) ₂ | <i>f</i> | 0.79 | 0.94 | <i>f</i> | 0.87 | 0.91 ^g |
| Cu(ox) ₂ ²⁻ | 0.96 | 0.94 | 0.92 | 0.85 | 0.45 | 0.92 ^h |
| Cu(CN) ₄ ²⁻ | 0.85 | 0.96 | 0.96 | 0.95 ^c | 0.98 ^c | 0.78 ⁱ |

^a From ref. 15. ^b This work. ^c These entries refer to the coefficients for the d_{xy} and d_{z^2} , b_{2g} and a_{1g} in D_{4h} . ^d W. B. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, 1966, **45**, 4003. ^e From ref. 11. ^f No molecular orbital with main contribution from these orbitals was observed owing to mixing under C_{2h} symmetry. ^g From ref. 7. ^h B. G. Malmstrom and T. Vanngard, *J. Mol. Biol.*, 1960, **2**, 118. ⁱ From ref. 10.

Table 2 shows the *d*-orbital coefficients α , β , β_1 , γ' , and γ'' obtained from the calculations together with the values derived from the e.s.r. measurements. For the systems studied the trends in the calculated α values (b_{1g}) parallel the experimental values with Cu(por) and the Cu(CN)₄²⁻ ion exhibiting more covalency in the σ -orbital than any other complex, and the Cu(H₂O)₆²⁺ complexes showing the most ionic bonding in this orbital. Addition of axial ligands to Cu(dmg)₂ leads to an increase in the calculated b_{1g} orbital coefficient, *i.e.* a decrease in covalency in harmony with the results of Roos *et al.*;¹⁵ however these authors calculated only an extremely small change in the values for α^2 on axial co-ordination of oxygen and nitrogen donors whereas the present calculations indicate greater changes in this parameter. The differences might well arise from the choice of basis sets for the ligands where we have considered all valence orbitals explicitly, whereas Roos, apart from the σ orbitals on the nitrogens only takes account of π type orbitals. In fact our results imply that even the hydrogen-bonded protons make a fairly substantial contribution (11%) into the mainly 'd' a_g molecular orbitals. The effect of co-ordinating axial groups on the in-plane σ bonding appear to be in the opposite sense for Cu(acac)₂ where the value of α^2 decreases on co-ordination. The overall magnitude of this parameter in general correlates extremely well with the derived values from e.s.r. measurements.

The relative contributions to the a_g molecular orbitals change considerably on co-ordination, with the axial groups co-ordinating mainly through the d_{z^2} metal orbital, while the other a_g component reverts primarily to $d_{x^2-y^2}$ character. The out-of-plane π bonding orbitals b_{2g} and b_{3g} exhibit in the main only a small degree of covalency, which changes surprisingly little on co-ordination and tends to increase slightly with the

extended ligand systems. The eigenfunctions for Cu(por) however indicate considerable covalent bonding in the e_g orbitals which are delocalised over the entire π system of the ligand; on the other hand Gouterman's extended Huckel calculations for metal porphyrins²⁵ suggested certainly no greater degree of covalency in this orbital than in any other of the metal orbitals in line with the known spectroscopic properties of metal porphyrins. For

Molecular orbital levels for Cu(CN)₄²⁻

the Cu(por) an increase in the copper-nitrogen distance of 0.04 Å realised a large change in the covalency of this orbital, the value of β changing from 0.82 to 0.96.

The Figure shows the molecular orbital levels for the simplest square planar system examined, Cu(CN)₄²⁻; the associated eigenfunctions are given in Table 3. The 49 valence electrons are accommodated in the lowest 25

²⁵ M. Gouterman and M. Zerner, *Theor. Chim. Acta*, 1966, **4**, 44.

molecular orbitals, with the b_{1g} orbital unoccupied in the β set of eigenfunctions. The highest-filled molecular orbitals are found to have main contributions from the copper $3d$ atomic orbitals, which is also the case for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The first virtual orbital in $\text{Cu}(\text{CN})_4^{2-}$ is of π -type symmetry a_{2u} , with a main contribution from the copper $4p_z$ orbital. The other complexes studied have extended ligand systems and in all these complexes the computed results indicate that the molecular orbitals which are predominantly copper $3d$ in character lie deeply buried in the bonding molecular orbitals and are not the highest

reversal of this sequence takes place. The same scheme is also found for the axially co-ordinated species where the splitting of the d orbitals is slightly increased over square complexes, with this group of metal orbitals, excluding the open-shell b_{1g} orbital, usually being spread over about 1 eV. Recent *ab initio* results for the square planar CuCl_4^{2-} ion²⁶ yield a similar picture with the d molecular orbitals lying some 8 eV within the bonding orbitals.

Unpaired Spin Distribution.—4s Contribution. Paramagnetic transition-metal complexes with unpaired d

TABLE 3
Eigenfunctions for $\text{Cu}(\text{CN})_4^{2-}$

| | Cu (%) | | | C (%) | | | N (%) | | |
|-----------|--------|-------|-------|-------|-------------|----------|-------|-------------|----------|
| | $3d$ | $4s$ | $4p$ | $2s$ | $2p_\sigma$ | $2p_\pi$ | $2s$ | $2p_\sigma$ | $2p_\pi$ |
| $1a_{1g}$ | 0.15 | 23.19 | | 48.44 | 0.06 | | 22.60 | 5.55 | |
| $1e_u$ | | | 19.00 | 39.79 | 0.90 | 2.21 | 29.38 | 8.34 | 0.35 |
| $1b_{1g}$ | 0.00 | | | 22.66 | 14.40 | | 57.82 | 5.09 | |
| $2a_{1g}$ | 0.91 | 12.90 | | 2.85 | 40.85 | | 42.46 | 0.00 | |
| $2e_u$ | | | 15.48 | 5.05 | 30.38 | 7.19 | 38.26 | 0.73 | 2.90 |
| $1a_{2g}$ | | | 22.25 | | | 49.70 | | | 28.09 |
| $1b_{2g}$ | 6.46 | | | | | 43.27 | | | 50.27 |
| $2b_{1g}$ | 0.65 | | | 17.25 | 0.04 | | 24.50 | 57.56 | |
| $3e_u$ | | | 0.33 | 3.49 | 4.06 | 14.65 | 12.42 | 43.04 | 22.00 |
| $3a_{1g}$ | 1.63 | 1.11 | | 1.07 | 13.75 | | 17.25 | 65.15 | |
| $1e_g$ | 7.61 | | | | | 43.99 | | | 48.38 |
| $1a_{2g}$ | | | | | | 32.65 | | | 67.35 |
| $1b_{2u}$ | | | | | | 43.48 | | | 56.52 |
| $4e_u$ | | | 3.22 | 2.08 | 18.00 | 13.50 | 2.20 | 22.48 | 38.53 |
| $4a_{1g}$ | 96.69 | | 1.62 | | 0.47 | | | 1.23 | |
| $2e_g$ | 91.58 | | | | | 1.50 | | | 6.92 |
| $2b_{2g}$ | 91.41 | | | | | 0.37 | | | 8.21 |
| $3b_{1g}$ | 21.43 | | | 30.58 | 38.61 | | 0.28 | 9.10 | |
| $2a_{2u}$ | | | 33.45 | | | 4.25 | | | 62.32 |
| $3b_{2g}$ | 2.11 | | | | | 56.37 | | | 41.53 |
| $5e_u$ | | | 1.19 | 6.37 | 1.81 | 54.80 | 0.05 | 0.35 | 35.41 |
| $3e_g$ | 0.79 | | | | | 54.52 | | | 44.68 |
| $4b_{1g}$ | 73.22 | | | 18.01 | 2.75 | | 1.41 | 4.60 | |
| $2b_{2u}$ | | | | | | 56.52 | | | 43.48 |
| $2a_{2g}$ | | | | | | 67.35 | | | 32.65 |
| $5a_{1g}$ | | 6.23 | | 37.80 | 16.89 | | 14.49 | 24.60 | |
| $6e_u$ | | | 2.47 | 28.43 | 26.38 | 1.47 | 15.68 | 25.34 | 0.28 |
| $3a_{2u}$ | | | 44.30 | | | 46.05 | | | 9.63 |
| $5b_{1g}$ | 4.70 | | | 11.48 | 44.19 | | 16.00 | 23.66 | |
| $5a_{1g}$ | 0.63 | 54.94 | | 9.81 | 27.96 | | 3.21 | 3.44 | |
| $7e_u$ | | | 58.25 | 12.92 | 18.48 | 6.16 | 1.90 | 1.89 | 0.39 |

energy occupied orbitals. This feature was also evident in Roos' ZDO MO calculations on $\text{Cu}(\text{dmg})_2$ ¹⁵ and in Gouterman's extended Huckel calculations for $\text{Cu}(\text{por})$.²⁵ For $\text{Cu}(\text{dmg})_2$ the ' d ' molecular orbitals lie together as a group some 8 eV below the highest-filled orbital, in good agreement with previous calculations although the splitting pattern is somewhat different. Our results give the order $b_{2g}(xz) < b_{3g}(yz) < a_g(x^2 - y^2) < a_g(z^2) < b_{1g}(xy)$ while Roos' results indicate the sequence $a_g(x^2 - y^2) < b_{2g}(xz) < b_{3g}(yz) < a_g(z^2) < b_{1g}(xy)$, the variations presumably arising from a larger choice of σ -type basis functions on the ligands in our calculations which in turn affect the position of the a_g orbital. This pattern is repeated for the majority of the remaining complexes although in some cases the b_{2g} , b_{3g} , and a_g orbitals lie extremely close together (0.2 eV) and a

electrons exhibit an isotropic hyperfine interaction which can only be attributed to a finite unpaired spin in s -type orbitals on the central ion. Attempts to calculate the magnitude of this unpaired spin considered the polarisation of the inner s orbitals by the unpaired d electrons and these suggested that the polarisation of the inner $2s$ and $3s$ orbitals is significant with the dominant negative contribution arising from the $2s$ orbital.^{27,28} In the present valence orbital calculations the inner orbitals are treated as a core and effects such as the one above cannot be estimated however, a certain amount of unpaired spin does appear in the $4s$ orbital as a result of the unrestricted nature of the method. The calculated values ρ_{4s} are given in Table 4 and all have a negative sign, which is also apparent in the observed coupling con-

²⁶ J. Demuynek and A. Veillard, *Chem. Phys. Letters*, 1970, **6**, 204.

²⁷ R. E. Watson and A. J. Freeman, *Phys. Rev.*, 1960, **120**, 1134; 1961, **123**, 2027.

²⁸ V. Heine, *Phys. Rev.*, 1957, **107**, 1002.

stants. In order to compare these spin densities with the coupling constants a value for $|\phi_{4s}(O)|^2$ is required. Although we have used Slater-type functions as basis

TABLE 4
Unpaired spin in the copper 4s orbital

| | f_{4s} (%) |
|--|--------------|
| Cu(dm g) ₂ | -0.27 |
| Cu(dm g) ₂ (H ₂ O) ₂ | -0.21 |
| Cu(dm g) ₂ (NH ₃) ₂ | -0.18 |
| Cu(acac) ₂ | -0.31 |
| Cu(acac) ₂ (H ₂ O) ₂ | -0.24 |
| Cu(acac) ₂ (NH ₃) ₂ | -0.20 |
| Cu(H ₂ O) ₆ ²⁺ | -0.12 |
| Cu(por) | -0.32 |
| Cu(sal) ₂ | -0.36 |
| Cu(ox) ₂ ²⁻ | -0.37 |
| Cu(CN) ₄ ²⁻ | -0.51 |

orbitals, which have all nodes collapsed at the nucleus and are therefore unsuitable for this purpose, if we use the value 50×10^{24} obtained from Watson's functions²⁹

these additional magnetic nuclei. The magnitude of these interactions can then be used to evaluate the percentage of unpaired spin in the ligand orbitals. Table 4 shows the computed % spin transfer together with the values derived from the superhyperfine interactions, using the value 33.4×10^{24} for $|\psi_{2s}^N(O)|^2$. It can be seen that the calculated values are of the correct order of magnitude but in general are a factor of two too small for the nearest-neighbour interactions. Two other points emerge from these spin transfer results. Firstly no appreciable transfer of spin takes place to the axially co-ordinated groups (<0.03%) and therefore no additional coupling to these groups is expected. Secondly, no unpaired spin resides in π -type orbitals which means that all the spin is delocalised through a σ -mechanism. For Cu(dm g)₂ fairly substantial negative spin densities are found in the bridge hydrogens and in the oxygen 2s orbital. A slight decrease in $f_{2s}(N)$ is calculated for this complex on axial co-ordination which is reflected in the

TABLE 5

% Spin transfer to ligand 's' orbitals in Cu^{II} complexes; values in parentheses are derived from e.s.r. data

| | $f_{2s}(N)$ | $f_{2s}(O)$ | $f_{2s}(C)$ | $f_{1s}(H)$ |
|--|-------------------------|-------------------------|-------------------|--|
| Cu(dm g) ₂ | 0.79 (3.0) ^a | -0.02 | -0.40 | -0.15(br); 3.35 (C) |
| Cu(dm g) ₂ (H ₂ O) ₂ | 0.76 (2.9) ^a | -0.02 | -0.40 | -0.12(br); 4.40 (C) |
| Cu(dm g) ₂ (NH ₃) ₂ | 0.75 (3.0) ^a | -0.02 | -0.41 | -0.12(br); 3.43 (C) |
| Cu(acac) ₂ | | 0.38 | 0.06 (CO) | 0.31 (CHO) |
| Cu(acac) ₂ (H ₂ O) ₂ | | 0.38 | 0.06 (CO) | 0.31 (CHO) |
| Cu(acac) ₂ (NH ₃) ₂ | | 0.39 | 0.06 (CO) | 0.32 (CHO) |
| Cu(H ₂ O) ₆ ²⁺ | | 0.30 (1.1) ^b | | 0.05 (0.01) ^b |
| Cu(por) | 1.08 (2.8) ^c | | 0.10 (α) | All 0.03 |
| Cu(sal) ₂ | 1.36 (2.0) ^d | 0.72 | 0.10 | 0.74 (NH); 0.35 (1.09) ^d (CH) |
| Cu(ox) ₂ ²⁻ | | 0.30 | -0.01 | |
| Cu(CN) ₄ ²⁻ | 0.10 | | 4.13 | |

^a See ref. 16. ^b W. B. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, 1966, **45**, 4003. ^c See ref. 11. ^d See ref. 7.

we arrive at a contribution of between 3×10^{-4} and 5×10^{-4} cm⁻¹ to the coupling constant from this mechanism, in the complexes examined. While this value is only *ca.* 5% of the total interaction it does have a negative sign and therefore acts in the same direction. The changes in the isotropic coupling constants roughly parallel the changes in the spin occupancy of the 4s orbital and in particular there is a decrease in the net β spin on co-ordinating groups axially in line with the observed decrease in A_{iso} on co-ordination.

Ligand 2s contribution. When some of the unpaired spin is delocalised on the ligand atoms which possess a nuclear spin, the quartet of lines in the e.s.r. spectrum is further split owing to superhyperfine interactions with

observed coupling constants. The results for Cu(CN)₄²⁻ indicate a large transfer to the carbon 2s orbital with only 0.1% reaching the more distant nitrogen 2s orbital. Finally, Cu(sal)₂ exhibits an unusual coupling to the more distant hydrogen of the C-H group [H(1)] rather than to the hydrogen of the N-H group [H(2)] and the proximity of this latter hydrogen to the $b_{1g}(D_{2h})$ nodal plane was considered important in this respect.⁷ However, these protons in fact lie some 0.8 Å from this plane. The calculations yield 0.74% for H(2) and 0.35% for H(1) both of which arise through a σ delocalisation and it is difficult to find a satisfactory explanation for this transfer in view of the fact that H(1) lies more than 1 Å further from the central copper atom than does H(2).

²⁹ R. E. Watson, *Phys. Rev.*, 1960, **119**, 1934.