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A Theoretical Investigation of the Electronic Structure of the Normal and Excited States of Copper Dimethylglyoxime and its Adducts with Water and Amines

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A semi-empirical open shell SCF—MO method with zero differential overlap has been applied in an investigation of the electronic structure and excited states of copper dimethylglyoxime. The calculations confirm the existence of a strong metal ligand π-bond. An explanation of the dimerization of the complex in the crystal state is suggested. This might be due to the formation of a bond between an axially directed *ds* hybrid on copper and the lowest excited π orbital. The calculated electronic spectrum is in good agreement with experiment and assignments could be made for all absorption bands. The usual classification of excited states into ligand field and charge transfer states is found not to be valid. A considerable mixing will in some cases occur, on account of the configuration interaction invoked into the calculation of the excited states. The electron paramagnetic resonance constants have been calculated using second order perturbation theory. The good agreement with experiment is a test on the reliability of the obtained results.

A study of the spectral shifts occurring if axial ligands are added to the complex led to the conclusion that in the presence of an amine a five-coordinated adduct with copper dimethylglyoxime is formed, while the complex forms a six-coordinated adduct with water.

1. INTRODUCTION AND SUMMARY

In a previous paper [1] (hereafter referred to as I) the present author carried through a study of the π-electron systems of dimethylglyoxime (H_2D) and the anions HD^- and D^{2-}. This investigation was based on the Pariser-Parr,[2,3] Pople [4] method with zero differential overlap and semi-empirical choice of the parameters. The energies of the excited states were calculated with configuration interaction, taking into account all singly excited states. The strong absorption band in the UV spectrum of H_2D, and the two corresponding bands in HD^- and D^{2-} could be assigned to $\pi \rightarrow \pi^*$ transitions. It was proposed that the two strong absorption bands found in most metal chelates of dimethylglyoxime $Me(HD)_2$ could be attributed to the same transi-

tions as those in HD^-. The interpretation of the visible and near infrared part of the spectra of $Me(HD)_2$ is, however, difficult to accomplish. No attempts seem to have been made to explain this part of the absorption spectrum of $Cu(HD)_2$. The corresponding nickel complex $Ni(HD)_2$ has, however, been studied by several authors. Maki[5] and Császár and Fügedi [6] have interpreted this spectrum using the crystal field theory. However, as has been pointed out by Ballhausen,[7] and is confirmed by the present investigation, the simple crystal field picture breaks down, due to strong π-bonding effects. Recently Ingraham [8] performed a molecular orbital treatment of $Ni(HD)_2$ using an extended Wolfsberg-Helmholtz method. Even if it was possible to make assignments of some of the excited states by this method the results were rather uncertain. The transitions could not be corrected for electron repulsion, and configuration interaction was not included. The importance of configuration interaction in the discussion of the excited states has been discussed in a previous paper.[9] This is further enhanced in the present investigation where, due to the strong π-bonding, a considerable mixing of the ligand field and charge transfer states is obtained.

In a recent paper [9] (hereafter referred to as II) an extension of the Pariser, Parr and Pople method to transition metal complexes was discussed. It was concluded that the use of the zero differential overlap approximation could be justified also for these systems. The calculation of the SCF molecular orbitals was based upon a method for the treatment of open shell systems given by Roothaan.[10] A scheme for the determination of the semi-empirical parameters was discussed. The parameter scheme was used in an investigation of the ligand field spectra of the complex ions $Cu(NH_3)_6^{2+}$ and $Cu(H_2O)_6^{2+}$.

The present investigation deals with an attempt to use the same method in a study of the electronic structure of the normal and excited states of $Cu(HD)_2$, and the adducts formed between this complex and amines or water. In section 2 some details of the calculations are given. The general method was thoroughly discussed in II, and only additional information is given here. The $4p$ orbitals were not used in the study of the complex copper ions. The parameters necessary for the evaluation of the matrix elements for these orbitals are reported in section 2.

Section 3 deals with the ground state properties of the complex. The molecular orbitals are presented and the suggested formation of a metal to ligand donor π-bond is confirmed. In contrast with the usual picture of the bonding, as given by the simple ligand field theory, some of the metal electrons are found in bonding orbitals. The explanation of this seems to be the uneven charge distribution in the complex, due to the formation of the hydrogen bonds between the chelate molecules. The π orbitals of the chelate ring are destabilized through the interaction with the negative charges on the oxygen atoms.

In Section 4 the excited states are discussed. The absorption spectrum of $Cu(HD)_2$ in chloroform has been used for the comparison between the calculated transition frequencies and the experimental absorption bands. Good agreement has been obtained and assignments can be made for all bands. The use of configuration interaction, in the calculation of the excited states, resulted in a considerable mixing of ligand field states and charge transfer states, in some cases. This result casts some doubt on the simple molecular

orbital interpretation of the spectral and magnetic properties of the planar metal chelates.

In Section 5 the ESR data of $Cu(HD)_2$ are discussed. The g-values and hyperfine structure constants have been calculated using second order perturbation theory taking into account all appropriate excited states. The calculated constants are in good agreement with experiments, which gives some reliability to the calculated molecular orbitals and excited states.

Section 6 discusses the formation of adducts between $Cu(HD)_2$ and amines or water. Calculations of the excited states of $Cu(HD)_2 B_x$ and $Cu(HD)_2(H_2O)_x$, where B is an amine and x is one or two, have been performed. A comparison of the spectral shifts with experiments indicates that the adduct formed with B is five-coordinated with $x = 1$. This is also confirmed by solubility measurements. The adduct with water is, however, probably six-coordinated with $x = 2$.

2. DETAILS OF THE CALCULATION

An X-ray diffraction measurement of the crystal structure of copper dimethylglyoxime has been reported by Frasson, Bardi and Bezzi.[11] According to their measurements the $Cu(HD)_2$ molecules form dimers $Cu_2(HD)_4$ in the crystal, by means of a coordination bond between a copper atom from one of the molecules and an oxygen atom from the other. Probably due to this five-coordination of the copper atom the $Cu(HD)_2$ molecule is not planar, but the two organic rings form an angle of 22° with each other. The two dimethylglyoxime molecules are bound together through two strong hydrogen bonds. Due to the dimerization these bonds are not equivalent, but have different bond lengths.

Since this investigation primarily is concerned with isolated $Cu(HD)_2$ molecules, a planar structure has been assumed, where average values have been used for the inter-nuclear distances. Studies of the infrared spectra of solid metal dioximes have shown that the hydrogen bonds are very strong.[12,13]

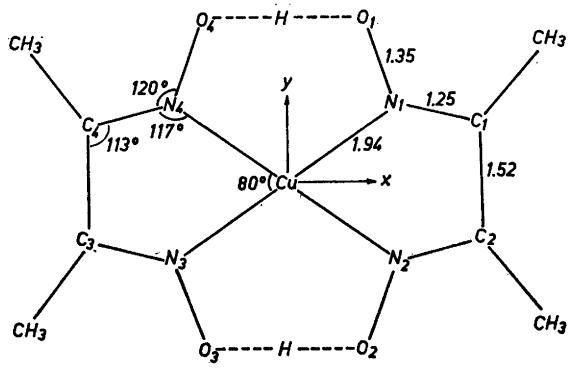

Fig. 1. Molecular structure of $Cu(HD)_2$ after Frasson, Bardi and Bezzi.[11] Bond lengths in Å.

Therefore it seems natural to assume that the four oxygen atoms all are equivalent. With these simplifications of the structure the symmetry of the complex is D_{2h}. The bond lengths and angles together with the number labels of the atoms and the symmetry axes are given in Fig. 1.

The atomic orbitals that constitute the basis for the calculations are 25; the $3d$, $4s$, and $4p$ orbitals of the copper atom, one sp^2-hybridized lone pair orbital from each nitrogen, and one π orbital from each of the nitrogen, oxygen, and carbon atoms in the ring. The number of electrons taken into account is 33; 9 from the copper ion and 12 from each ring.

Using the ordinary AO notations for metal orbitals, σ for a lone pair orbital on nitrogen and n, c, and o for the π orbitals on nitrogen, carbon, and oxygen, respectively, the following symmetry basis set can be constructed.

$$
\begin{array}{lllll}
a_g: & 4s;\ 3d(z^2);\ 3d(x^2-y^2);\ \sigma(a_g) = \frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4); & & & \\
a_u: & n(a_u) = \frac{1}{2}(n_1-n_2+n_3-n_4);\ c(a_u);\ o(a_u); & & & \\
b_{1g}: & 3d(xy);\ \sigma(b_{1g}) = \frac{1}{2}(\sigma_1-\sigma_2+\sigma_3-\sigma_4); & & & \\
b_{1u}: & 4p(z);\ n(b_{1u}) = \frac{1}{2}(n_1+n_2+n_3+n_4); & c(b_{1u}); & o(b_{1u}); & \\
b_{2g}: & 3d(xz);\ n(b_{2g}) = \frac{1}{2}(n_1+n_2-n_3-n_4); & c(b_{2g}); & o(b_{2g}); & \\
b_{2u}: & 4p(y);\ \sigma(b_{2u}) = \frac{1}{2}(\sigma_1-\sigma_2-\sigma_3+\sigma_4); & & & \\
b_{3g}: & 3d(yz);\ n(b_{3g}) = \frac{1}{2}(n_1-n_2-n_3+n_4); & c(b_{3g}); & o(b_{3g}); & \\
b_{3u}: & 4p(x);\ \sigma(b_{3u}) = \frac{1}{2}(\sigma_1+\sigma_2-\sigma_3-\sigma_4): & & &
\end{array}
$$

The calculation of the one- and two-electron integrals over the atomic basis set has been performed as in I and II. The one center integrals for the copper $3d$ and $4s$ orbitals were given in II (*cf.* Table 1). The $4p$ orbitals were not included in these calculations. The one center two-electron integrals for these orbitals have been evaluated from the atomic spectra of Cu and Cu^+, using the spectral data from Moore's tables.[14] They are collected in Table 1. The ionization potential for the $4p$ orbital in the valence state $d^{10}p$ is 3.79 eV. This value has been used in the calculation of the $4p$ diagonal element of the core operator (*cf.* eqn. (14) in II). The penetration term occurring in this expression has been evaluated according to the method used in the study of the complex copper ions. Thus the nitrogen ligands have been treated as point dipoles with a dipole moment of 2.25 D, corresponding to the dipole moment of pyridine.[15] For the evaluation of the matrix elements of the core

Table 1. Two-electron integrals for Cu orbitals including $4p$. All values in eV.

Coulomb integrals			Exchange integrals		
$J(4s, 4p)$	=	8.04	$K(4s, 4p)$	=	2.46
$J(x, xy)$	=	8.85	$K(x, xy)$	=	0.83
$J(x, z^2)$	=	8.47	$K(x, z^2)$	=	0.35
$J(x, yz)$	=	8.28	$K(x, yz)$	=	0.11
$J(z, z^2)$	=	9.04	$K(z, z^2)$	=	1.07
$J(x, x)$	=	8.90	$K(x, y)$	=	0.64
$J(x, y)$	=	7.62			

operator over ligand π orbitals, according to eqn. (15) in II, the parameters discussed in I have been used.

The total core charge of the four oxygen atoms is plus 6. This charge has been averaged out over the four oxygens leaving an effective charge of plus 1.5 at each position. The core matrix elements for the oxygen π orbitals have been chosen as the mean values of the core integrals corresponding to OH and O^-, respectively (*cf.* the study of HD^- in I).

The proportionality constant in the Wolfsberg-Helmholtz formula for the resonance integrals [16] has been given two values. The value 2.88 was used in II for the 3*d* and 4*s* orbitals. This value has been retained for the 3*d* orbital. For resonance integrals including a 4*s* or 4*p* orbital the value 1.05 has been used. Transitions to the orbital $3b_{1u}$ in $Cu(HD)_2$ are very sensitive to the choice of this parameter. Thus it could be determined by means of an adaption of the calculated excited states to the absorption spectrum of $Cu(HD)_2$ (*vide infra*).

The self-consistent field molecular orbitals have been calculated using the general method given by Roothaan,[10] which has been programmed in collaboration with Dr. T. Alm, and which was thoroughly discussed in II.

Table 2. Molecular orbitals φ_i and eigenvalues ε_i for $Cu(HD)_2$.

φ_i	ε_i (a.u.)	Orbital coefficients
$1a_g$	−0.7380	0.3652 (4*s*) − 0.4329 (z^2) + 0.1854 (x^2-y^2) + 0.8030 $\sigma(a_g)$
$1b_{1g}$	−0.6715	0.5350 (*xy*) + 0.8445 $\sigma(b_{1g})$
$1b_{3u}$	−0.6100	0.3348 (*x*) + 0.9429 $\sigma(b_{3u})$
$2a_g$	−0.5950	0.0672 (4*s*) − 0.1818 (z^2) − 0.9762 (x^2-y^2) + 0.0968 $\sigma(a_g)$
$1b_{2u}$	−0.5879	0.2953 (*y*) + 0.9554 $\sigma(b_{2u})$
$1b_{2g}$	−0.5814	0.8528 (*xz*) + 0.4145 $n(b_{2g})$ + 0.2740 $c(b_{2g})$ + 0.1610 $o(b_{2g})$
$1b_{3g}$	−0.5705	0.9250 (*yz*) + 0.3261 $n(b_{3g})$ + 0.1381 $c(b_{3g})$ + 0.1379 $o(b_{3g})$
$1b_{1u}$	−0.5144	0.1106 (*z*) + 0.6895 $n(b_{1u})$ + 0.6231 $c(b_{1u})$ + 0.3522 $o(b_{1u})$
$3a_g$	−0.4900	0.3472 (4*s*) + 0.8696 (z^2) − 0.1048 (x^2-y^2) + 0.3351 $\sigma(a_g)$
$2b_{2g}$	−0.4787	0.5110 (*xz*) − 0.5370 $n(b_{2g})$ − 0.5903 $c(b_{2g})$ − 0.3194 $o(b_{2g})$
$1a_u$	−0.4677	0.7486 $n(a_u)$ + 0.4204 $c(a_u)$ + 0.5126 $o(a_u)$
$2b_{3g}$	−0.4528	0.3708 (*yz*) − 0.6703 $n(b_{3g})$ − 0.3935 $c(b_{3g})$ − 0.5083 $o(b_{3g})$
$2b_{1u}$	−0.3310	0.0125 (*z*) + 0.0519 $n(b_{1u})$ − 0.5359 $c(b_{1u})$ + 0.8426 $o(b_{1u})$
$3b_{2g}$	−0.3298	0.0183 (*xz*) − 0.0556 $n(b_{2g})$ + 0.5256 $c(b_{2g})$ − 0.8487 $o(b_{2g})$
$3b_{3g}$	−0.2807	0.0545 (*yz*) − 0.2735 $n(b_{3g})$ − 0.5232 $c(b_{3g})$ + 0.8054 $o(b_{3g})$
$2a_u$	−0.2805	0.2678 $n(a_u)$ + 0.5155 $c(a_u)$ − 0.8139 $o(a_u)$
$2b_{1g}$	−0.2030	0.8449 (*xy*) − 0.5350 $\sigma(b_{1g})$
$3b_{1u}$	0.0404	0.3892 (*z*) + 0.6306 $n(b_{1u})$ − 0.5455 $c(b_{1u})$ − 0.3915 $o(b_{1u})$
$4b_{2g}$	0.0731	0.1065 (*xz*) − 0.7326 $n(b_{2g})$ + 0.5478 $c(b_{2g})$ + 0.3896 $o(b_{2g})$
$4a_g$	0.1209	0.8611 (4*s*) − 0.1528 (z^2) + 0.0398 (x^2-y^2) − 0.4833 $\sigma(a_g)$
$3a_u$	0.1380	0.6065 $n(a_u)$ − 0.7467 $c(a_u)$ − 0.2733 $o(a_u)$
$4b_{3g}$	0.1395	0.0673 (*yz*) − 0.6079 $n(b_{3g})$ + 0.7432 $c(b_{3g})$ + 0.2721 $o(b_{3g})$
$2b_{2u}$	0.2045	0.9554 (*y*) − 0.2953 $\sigma(b_{2u})$
$4b_{1u}$	0.2051	0.9144 (*z*) − 0.3525 $n(b_{1u})$ + 0.1641 $c(b_{1u})$ + 0.1125 $o(b_{1u})$
$2b_{3u}$	0.2214	0.9423 (*x*) − 0.3348 $\sigma(b_{3u})$

3. MOLECULAR ORBITALS

The SCF molecular orbitals of $Cu(HD)_2$ have been collected in Table 2. In the ZDO approximation, the charge densities in the different atomic orbitals, are to the second order in the overlap integral, given by the diagonal elements of the density matrix.[17] Oleari *et al.*[18] used another way of treating the charges, in which the molecular orbitals were expanded by means of a complete set of orthogonal atomic orbital on one atom. Thereby they arrive at an expression in which the charge density is given by the diagonal elements of the density matrix plus an overlap population. However, in this expression the overlap population seems to have been taken into account twice. According to Fischer-Hjalmars it is already present in the diagonal elements of the density matrix, due to the fact that the basis set is formally orthogonal in the ZDO approximation.

The configuration of the copper atom is found to be $(3d)^{9.206}$ $(4s)^{0.517}$ $(4p)^{0.424}$ resulting in the oxidation number + 0.853. The charge densities on the ligand atoms have been collected in Table 3, where they are compared with

Table 3. Charge densities on the ligand atoms in H_2D and $Cu(HD)_2$.

Atom	H_2D	$Cu(HD)_2$
N(σ)	2.000	1.712
N(π)	0.932	1.102
C(π)	1.141	1.132
O(π)	1.927	1.767

the corresponding densities for *cis*-dimethylglyoxime, which were calculated in I. As expected there is a strong polarization of the π-electrons due to the presence of the copper atom.

The existence of a strong metal to ligand donor π-bond in the metal chelates of dimethylglyoxime has been suggested on the basis of UV spectrophotometric measurements,[19,20] stability constants,[21] and IR spectrophotometry.[12] Such a bond is also found, represented by the molecular orbitals of symmetry b_{2g} and b_{3g} (*cf.* Table 2). The transfer of electrons to the ligands is, however, small (0.031 electrons). An electron transfer in the opposite direction of almost the same size takes place to the $4p(z)$ orbital of copper in the molecular orbitals of symmetry b_{1u}. Thus the number of π-electrons in the chelate rings is unchanged, eight per ring. The total bond order between the metal orbitals $3d(xz)$, and $3d(yz)$ and the ligand orbitals $n(b_{2g})$ and $n(b_{3g})$ is 0.23, in spite of the fact that both the bonding and anti-bonding orbitals are doubly occupied. Thus a fairly strong bond is formed. According to the infrared data given by Burger *et al.* this bond should be increasing in strength in the order Cu < Ni < Co < Fe. However, this conclusion is drawn from a comparison of the third ionization potential of the metal to the vibration frequency of the C=N bond. The use of the third ionization potential for a discussion of

the energy of the $3d$ orbitals is somewhat doubtful since the actual effective charge of the metal atom is around one. Further, the vibration frequency of the C=N bond must also be sensitive to the strength of the ligand to metal donor σ-bond, responsible for a large part of the bonding energy.

The electrons in the bonding π orbitals $1b_{2g}$ and $1b_{3g}$ are mainly situated on the copper atom in contrast to the general assumption of the ligand field theory, where the d-electrons of the metal are supposed to be in anti-bonding molecular orbitals. That the reverse situation is found here is due to the destabilization of the ligand π-electrons in the presence of the negative charge in the hydrogen bonds.

The lowest excited orbital is $3b_{1u}$. This orbital has a considerable contribution both from the $4p(z)$ orbital of Cu and the oxygen π orbitals. This offers a possibility to explain the dimerization of $Cu(HD)_2$ in the crystal state. A covalent bond can be formed between the filled orbital, $3a_g$, being mainly a ds hybridized metal orbital, from one of the molecules, and the empty orbital $3b_{1u}$ of the other. The dimer is further stabilized through the electrostatic interaction between the negatively charged oxygen atom and the positively charged copper atom.

A good test on the reliability of the calculated molecular orbitals can be obtained from a study of the electron paramagnetic resonance parameters. However, for the calculation of these parameters, detailed information of the excited states of the complex is necessary. This information will therefore be given before the discussion of the EPR spectrum of $Cu(HD)_2$.

4. EXCITED STATES

The absorption spectrum of $Cu(HD)_2$ in different solutions has been measured by several investigators.[6,12,22] The solution spectra of $Cu(HD)_2$ have a very complicated structure and consist of a number of strongly overlapping bands. For a closer examination it has to be resolved into individual bands. Such a resolution has been undertaken on the spectra measured by Dyrssen and Petković,[22] whose original material was kindly put at my disposal. The spectra were resolved into individual bands of gaussian shape by means of a method described in an earlier paper.[23] The individual band characteristics of $Cu(HD)_2$ dissolved in chloroform and water have been collected in Table 4. The values in parenthesis are only tentative since these absorption peaks were outside the high energy limit of the spectra. These peak values were found by extrapolation. For $Cu(HD)_2$ in chloroform Császár and Fügedi [6] have reported four absorption bands with frequencies 19 600, 27 000, 36 500, and 43 900 cm^{-1}. The band at 30 700 cm^{-1} is missing. This is quite natural, since this band is completely hidden behind the strong absorption at 35 000 cm^{-1}.

A single crystal spectrum of $Cu(HD)_2$ has been reported by Yamada and Tsuchida.[24] For polarized light with the electric vectors parallel to the molecular plane, the maximum of the lowest absorption band was found at 18 000 cm^{-1}, while the corresponding value was 19 200 cm^{-1} for perpendicularly polarized light. Dichroism was observed with the parallel absorption twice as

Table 4. Resolution of experimental absorption bands of $Cu(HD)_2$ in different solvents, based on the spectra published by Dyrssen and Petković.[22]

Solvent	ν cm^{-1}	$\varepsilon_{max} \times 10^{-3}$	f
$CHCl_3$	(42 190)	(10.9)	(0.33)
	35 440	10.5	0.26
	30 710	2.3	0.038
	27 510	2.1	0.076
	~21 000	0.3	0.009
$CHCl_3$ with dodecylamine	(43 370)	(14.2)	(0.65)
	35 410	9.5	0.25
	30 550	2.5	0.043
	25 800	1.6	0.038
	19 810	0.5	0.016
$CHCl_3$ with dibutylamine	(40 060)	(35.9)	(0.51)
	35 680	13.9	0.38
	30 360	3.4	0.055
	25 810	1.7	0.044
	19 360	0.5	0.014
H_2O	44 550	16.4	0.47
	37 520	10.6	0.33
	32 710	1.2	0.018
	29 630	2.4	0.069
	21 050	0.3	0.007

large as the perpendicular. This might indicate the existence of an in plane polarized transition in this region.

The calculation of the excited states has been performed using the method of configuration interaction. In this procedure all doublet configurations, which could be constructed from the normal state by means of an one-electron excitation, were taken into account. There are three types of excitations which have to be considered. If k labels a doubly occupied orbital, m the singly occupied $2b_{1g}$ and v a virtual orbital, the three types are: $(k \rightarrow m)$, $(m \rightarrow v)$, and $(k \rightarrow v)$. The third type gives rise to two doublet configurations $(k \rightarrow v)^+$ and $(k \rightarrow v)^-$, where the plus sign refers to the configuration with the highest energy. The plus and minus configurations have been so constructed that they do not interact, that is, the hamiltonian is diagonal in this subspace. The excited states of this type can, accordingly, be labelled plus or minus.

The calculated transitions in the frequency region below 45 000 cm^{-1} are presented in Table 5. Some forbidden or weakly allowed transitions in the region 38 000—40 000 cm^{-1} have been omitted, since they are completely hidden behind the strong absorption bands at 35 000 cm^{-1} and 42 000 cm^{-1}. The following characteristics of the excited states are given; symmetry type, transition frequency ν, oscillator strength f (calculated in the ZDO approximation), the wave function, and finally the change in the charge on the copper

Table 5. Excited states of $Cu(HD_2)$.

Symmetry	ν cm^{-1}	f	pol.	Wave function	δQ
$^{I}A_g^-$	9 290	forb.	—	$0.68(2a_u \rightarrow 3b_{1u})^- + 0.28(2b_{1u} \rightarrow 3a_u)^- + 0.28(3b_{2g} \rightarrow 4b_{3g})^- - 0.59(3b_{3g} \rightarrow 4b_{2g})^-$	−0.03
$^{I}B_{3u}^-$	9 290	0.0006	y	$0.69(3b_{3g} \rightarrow 3b_{1u})^- + 0.28(2b_{1u} \rightarrow 4b_{3g})^- + 0.28(3b_{2g} \rightarrow 3a_u)^- - 0.59(2a_u \rightarrow 4b_{2g})^-$	−0.03
$^{I}B_{2u}^-$	15 350	0.0007	x	$0.45(2a_u \rightarrow 4b_{3g})^- - 0.50(2b_{1u} \rightarrow 4b_{2g})^- + 0.57(3b_{2g} \rightarrow 3b_{1u})^- + 0.45(3b_{3g} \rightarrow 3a_u)^-$	−0.01
$^{I}B_{1g}^-$	15 480	forb.	—	$0.45(2a_u \rightarrow 3a_u)^- - 0.50(3b_{2g} \rightarrow 4b_{2g})^- + 0.57(2b_{1u} \rightarrow 3b_{1u})^- + 0.45(3b_{3g} \rightarrow 4b_{3g})^-$	−0.01
$^{II}A_g$	22 220	»	—	$0.97(3a_g \rightarrow 2b_{1g}) - 0.18(1a_g \rightarrow 2b_{1g}) + 0.16(2a_g \rightarrow 2b_{1g})$	+0.07
$^{I}B_{3g}$	22 900	»	—	$0.56(1b_{3g} \rightarrow 2b_{1g}) + 0.46(2b_{3g} \rightarrow 2b_{1g}) - 0.69(3b_{3g} \rightarrow 2b_{1g})$	−0.64
$^{I}B_{2g}$	26 840	»	—	$0.73(1b_{2g} \rightarrow 2b_{1g}) - 0.68(2b_{2g} \rightarrow 2b_{1g})$	−0.64
$^{I}A_u$	26 880	0.003	z	$0.99(2a_u \rightarrow 2b_{1g}) - 0.10(1a_u \rightarrow 2b_{1g})$	−0.71
$^{III}A_g$	27 020	forb.	—	$0.98(2a_g \rightarrow 2b_{1g}) - 0.18(3a_g \rightarrow 2b_{1g})$	+0.25
$^{I}A_g^+$	27 870	»	—	$0.79(2a_u \rightarrow 3b_{1u})^+ + 0.20(3b_{2g} \rightarrow 4b_{3g})^+ - 0.53(3b_{3g} \rightarrow 4b_{2g})^+$	−0.08
$^{II}B_{3g}$	30 530	»	—	$0.60(1b_{3g} \rightarrow 2b_{1g}) + 0.35(2b_{3g} \rightarrow 2b_{1g}) + 0.71(3b_{3g} \rightarrow 2b_{1g})$	−0.48
$^{I}B_{3u}^+$	35 360	0.70	y	$0.90(3b_{3g} \rightarrow 3b_{1u})^+ - 0.36(2a_u \rightarrow 4b_{2g})^+ + 0.15(2b_{1u} \rightarrow 4b_{3g})^+$	−0.03
$^{I}B_{2u}^+$	42 460	0.32	x	$0.82(3b_{2g} \rightarrow 3b_{1u})^+ - 0.47(2b_{1u} \rightarrow 4b_{2g})^+ - 0.21(2a_u \rightarrow 4b_{3g})^+$	−0.08

atom δQ compared to the normal state. Only those configurations, which contribute to the wave function with coefficients larger than 0.1 are given in the table.

By means of the calculated transition frequencies and oscillator strengths, spectral assignments can be made for the five absorption bands of $Cu(HD)_2$ in chloroform solution. The two strong bands found at 42 200 cm^{-1} and 35 400 cm^{-1} are clearly due to the transitions $^1B_{2u}{}^+$ and $^1B_{3u}{}^+$ at 42 460 cm^{-1} and 35 360 cm^{-1}, respectively. These two transitions are of the type $\pi \rightarrow \pi^*$ on the ligands, and are also present in the anion HD^-. The weak absorption found at 30 710 cm^{-1} might be assigned to the symmetry forbidden transition $^{II}B_{3g}$ occurring at 30 530 cm^{-1}. This excited state is a mixture of the ligand field transition $d(yz) \rightarrow d(xy)$ and the charge transfer transition $\pi \rightarrow d(xy)$. The same holds true for the other transition of the same symmetry, $^1B_{3g}$ at 22 900 cm^{-1}. The usual division of the excited states into ligand field states and charge transfer state is thus, due to the configuration interaction, not valid in this case. As is seen in the last column of Table 5, there is a considerable charge transfer in both these transitions, and also in the transition $^1B_{2g}$ at 26 840 cm^{-1}. This seems to indicate that the application of the simple ligand field theory in the discussion of the spectral and magnetic behaviour of strongly π-bonding metal chelates might lead to wrong conclusions about the bonding in these complexes.

There are four possible assignments for the absorption band at 27 510 cm^{-1}. The symmetry forbidden $\pi \rightarrow \pi^*$ transition $^1A_g{}^+$ at 27 870 cm^{-1} is probably of little intensity and may be neglected. The intensity of this band is then probably taken from the three transitions $^{III}A_g$, ^1A_u, and $^1B_{2g}$. The state $^{III}A_g$ is a pure ligand field state of the type $d(x^2-y^2) \rightarrow d(xy)$. As mentioned above the state $^1B_{2g}$ is a mixture of the ligand field transition $d(xz) \rightarrow d(xy)$ and a charge transfer transition. The state ^1A_u, finally, is a weakly allowed charge transfer transition from the π-system to the orbital $2b_{1g}$.

The absorption band at around 21 000 cm^{-1} may be assigned to the transitions $^1B_{3g}$ and $^{II}A_g$, where $^{II}A_g$ is a ligand field transition of the type $d(z^2) \rightarrow d(xy)$. This absorption band will be further discussed in Section 6, in connection with spectral shifts due to further coordination.

To the $\pi \rightarrow \pi^*$ transitions of plus type, found in the high energy part of the spectrum, correspond similar transitions of minus type. The separation of the plus and minus states is surprisingly large for these transitions, and the minus states are therefore found in the low energy region. These transitions are symmetry forbidden or only weakly allowed, with f around 10^{-4}. They are not found in any solution spectrum of $Cu(HD)_2$. The allowed transitions $^1B_{3u}{}^-$ and $^1B_{2u}{}^-$ might, however, be responsible for some of the in plane polarized absorption found in the single crystal spectrum by Yamada and Tsuchida.[24] These transitions should in the crystal move to shorter wavelengths due to the anti-bonding character of the orbital $3b_{1u}$ in the dimer $Cu_2(HD)_4$.

5. ELECTRON PARAMAGNETIC RESONANCE

The results discussed in the previous sections exhibit some unusual features. Most of the electron density in the metal orbitals $d(xz)$ and $d(yz)$ comes from bonding orbitals instead of anti-bonding, as is usually assumed to be the case. Further, the classification of the excited states into ligand field and charge transfer states is not valid. Electron paramagnetic resonance is a powerful tool for the investigation of the bonding properties. The g-values and the hyperfine structure constants are very sensitive to the electron distribution in the normal and excited states. A calculation of these parameters should thus be a good test on the reliability of the calculated electron structure.

The theory of paramagnetic resonance has been given by Abragam and Pryce.[25] The crystal field case has been treated by Bleaney and Stevens.[26] Molecular orbitals were introduced into the calculations by Maki and McGarvey,[27] whose method was further developed by Kivelson and Neiman.[28] The expression for the g-values and the hyperfine structure constants has to be somewhat modified in the present treatment since configuration interaction is invoked for the excited states. Using the general formalism given by Abragam and Pryce the following expressions are obtained

$$g_{zz} = 2.0023 - 8\lambda_0\alpha^2 \sum_n^{(A_g)} \frac{(R_{2n})^2}{E_n - E_0}$$

$$g_{xx} = 2.0023 - 2\lambda_0\alpha \sum_n^{(B_{2g})} \frac{\alpha P_{1n}^2 + tP_{1n}P_{2n} \sin\theta \sqrt{1-\alpha^2}}{E_n - E_0}$$

$$g_{yy} = 2.0023 - 2\lambda_0\alpha \sum_n^{(B_{3g})} \frac{\alpha Q_{1n}^2 + tQ_{1n}Q_{2n} \cos\theta \sqrt{1-\alpha^2}}{E_n - E_0}$$

$$A_{zz} = P\left\{-\alpha^2(\tfrac{4}{7} + \varkappa_0) + g_{zz} - 2.0023 - \tfrac{3}{7}\alpha^2\lambda_0\left[\sum_n^{(B_{2g})} \frac{P_{1n}^2}{E_n - E_0} + \sum_n^{(B_{3g})} \frac{Q_{1n}^2}{E_n - E_0}\right]\right\}$$

$$A_{xx} = P\left\{\alpha^2(\tfrac{2}{7} - \varkappa_0) - \lambda_0\alpha^2\left[2\sum_n^{(B_{2g})} \frac{P_{1n}^2}{E_n - E_0} - \tfrac{3}{7}\sum_n^{(B_{3g})} \frac{Q_{1n}^2}{E_n - E_0} - \frac{8\sqrt{3}}{7}\sum_n^{(A_g)} \frac{R_{1n}R_{2n}}{E_n - E_0}\right]\right\}$$

$$A_{yy} = P\left\{\alpha^2(\tfrac{2}{7} - \varkappa_0) - \lambda_0\alpha^2\left[2\sum_n^{(B_{3g})} \frac{Q_{1n}^2}{E_n - E_0} - \tfrac{3}{7}\sum_n^{(B_{2g})} \frac{P_{1n}^2}{E_n - E_0} + \frac{8\sqrt{3}}{7}\sum_n^{(A_g)} \frac{R_{1n}R_{2n}}{E_n - E_n}\right]\right\}$$

The sums occurring are to be taken over the excited states of the indicated symmetry. α is the coefficient of $d(xy)$ in the orbital $2b_{1g}$, λ_0 the spin-orbit coupling constant of the free copper atom, which has been given the value -828 cm^{-1}.[27] The coefficients R_{in}, P_{in}, and Q_{in} are defined as follows.

$$R_{in} = \sum_k C_{nk}\ \beta_{ik}$$

$$P_{in} = \sum_k C_{nk}\ \gamma_{ik}$$

$$Q_{in} = \sum_k C_{nk}\ \delta_{ik}$$

where C_{nk} is the coefficient of the configuration $(k \rightarrow 2b_{1g})$ or $(2b_{1g} \rightarrow k)$, in the excited state n. The quantities β_{1k} and β_{2k} are the orbital coefficients of

$d(z^2)$ and $d(x^2-y^2)$ in the molecular orbitals ka_g. Correspondingly the coefficients γ_{1k} and γ_{2k} are the orbital coefficients of $d(xz)$ and $n(b_{2g})$ in kb_{2g}, while δ_{1k} and δ_{2k} refer to the orbitals $d(yz)$ and $n(b_{3g})$ in kb_{3g}. The angle between the x-axis and the Cu—N_1 bond is denoted θ. The constant t is the degree of p-character in the nitrogen sigma orbital. Assuming sp^2 hybridization, t equals $(2/3)^{1/2}$. Finally P is defined as $2\ \gamma\ \mu_0\mu_N\ \langle r^{-3}\rangle$, where μ_0 is the Bohr magneton, μ_N the nuclear magneton, γ the gyromagnetic ratio of the nucleus, and $\langle r^{-3}\rangle$ the average value of $1/r^3$ for a $3d$ orbital on copper. The value of P has been chosen to be 0.036 cm^{-1}.[28] The expressions for g and A have been determined with the assumption of zero differential overlap, and also assuming the orbital exponents of the $2s$ and $2p$ orbitals of nitrogen to be equal.

The constant $\varkappa_0$ represents the isotropic Fermi contact interaction between spin densities in copper orbitals of s-type and the nucleus. This contribution to the hyperfine structure constants is hard to estimate. For free copper Abragam, Horowitz and Pryce [29] have reported the values 0.43 for Cu^0 and 0.32 for Cu^{+2}. The value of $\varkappa_0$ in the complex cannot be determined *a priori* and it has therefore been left as an empirical parameter. The normal state wave function contains, through configuration interaction with the excited configurations $(ka_g \rightarrow 4a_g)^{\pm}$, with $k = 1$, 2, and 3, a non-zero spin density in the $4s$ orbital. It might be of interest to investigate whether this will have any effect on $\varkappa_0$. The contribution to $\varkappa_0$ from this spin density has been calculated with the use of the $4s$ orbital given by Watson.[30] The contribution to $\varkappa_0$ from these terms in the wave function has been found to be 0.08, which is far from negligible. It therefore seems doubtful to assume that the free atom value 0.43 could be used in the complex, especially since the effective charge of copper is close to one.

The electron paramagnetic resonance spectrum of $Cu(HD)_2$ has been measured by Wiersema and Windle.[31] The data reported by them are given in Table 6 together with the calculated values of the parameters. The obtained value of $\varkappa_0$ is 0.29, which is close to the value for Cu^{+2} (*cf.* Ref. 29).

Table 6. Electron paramagnetic resonance parameter for $Cu(HD)_2$. Experimental values from the work of Wiersema and Windle.[31]

	Exptl.	Calc.
g_{zz}	2.15	2.179
$g_{xx} = g_{yy}$	2.05	2.044
$A_{zz} \times 10^4$ cm^{-1}	144 ± 10	152
$A_{xx} \times 10^4$ cm^{-1}	14.6 ± 0.5	14.3
$A_{yy} \times 10^4$ cm^{-1}		14.5

Wiersema and Windle calculated the value of α^2 directly from the Fermi contract interaction between the $2b_{1g}$ electron and the nitrogen nucleus, giving rise to an extra hyperfine structure. They obtained the value 0.76 in good agreement with 0.714 found in the present calculations. This is also an indication that the assumed sp^2 hybridization of the nitrogen lone pair is reasonable.

6. ADDUCTS WITH WATER AND AMINES

Solubility measurements have shown, that if $Cu(HD)_2$ is dissolved in chloroform or benzene in the presence of an amine or pyridine, a five-coordinated complex $Cu(HD)_2B$, where B is an amine or pyridine, is formed.[22,32] In water solution an adduct of the type $Cu(HD)_2(H_2O)_x$ is probably formed, where the water molecules, if x equals two, are added above and below the molecular plane.[33] Absorption spectra of these adducts have been measured by Dyrssen and Petković [22] and resolved into individual absorption bands by the present author (*cf.* Table 4). It might be of interest to investigate whether the spectral shifts can be correlated to the formation of a five-coordinated adduct with amines, and also if it is possible to determine the number of water molecules attached to the complex in water solution. A calculation of the electronic structure and spectra of the adducts $Cu(HD)_2B_x$ and $Cu(HD)_2(H_2O)_x$ ($x = 1$ and 2), has therefore been undertaken.

Only the lone pair electrons of the axial ligands have been considered. The lone pair orbital has been taken to be an sp^3 hybrid on nitrogen or oxygen. The matrix elements of these orbitals have been evaluated by means of the methods given in II. For the calculation of the core integral for the nitrogen lone pair, the ionization potential for diethylamine 8.51 eV [34] has been used (*cf.* eqn. (20) in II). The dipole moment of diethylamine used in the calculation of the penetration integrals is 1.0 D.[15] The other parameters necessary for the evaluation of the matrix elements are those reported in II.

The calculated transition frequencies are given in Table 7 for the case $R = 2.50$ Å, where R is the distance between the copper atom and the nitrogen or oxygen atom of the ligand. For $Cu(HD)_2$ in chloroform the decomposition of the absorption spectrum in the region 20 000—30 000 cm^{-1} into two absorption bands was found to be in agreement with the theoretical transition frequencies (*cf.* Table 4). As is seen in Table 7 the addition of axial ligands makes the spectrum in this region more complicated with a larger spread of the

Table 7. Calculated transition frequencies for $Cu(HD)_2B_x$ and $Cu(HD)_2(H_2O)_x$ for $R = 2.50$ Å. All values in cm^{-1}.

	$Cu(HD)_2B$	$Cu(HD)_2B_2$	$Cu(HD)_2(H_2O)$	$Cu(HD)_2(H_2O)_2$
$^1A_g^-$	10 160	11 000	10 210	11 080
$^1B_{3u}^-$	10 170	11 000	10 220	11 080
$^1B_{2u}^-$	16 160	16 940	16 200	17 020
$^1B_{1g}^-$	16 300	17 080	16 330	17 130
$^{II}A_g$	19 650	17 260	20 360	18 670
$^1B_{3g}$	23 570	23 960	23 570	23 620
$^1B_{2g}$	26 700	26 540	26 250	25 680
^1A_u	29 170	31 250	30 420	33 770
$^{III}A_g$	26 790	26 592	26 260	25 550
$^1A_g^+$	28 540	29 190	28 660	29 360
$^{II}B_{3g}$	31 910	33 550	32 710	35 520
$^1B_{3u}^+$	35 920	36 582	36 140	36 900
$^1B_{2u}^+$	43 070	43 680	43 190	43 840

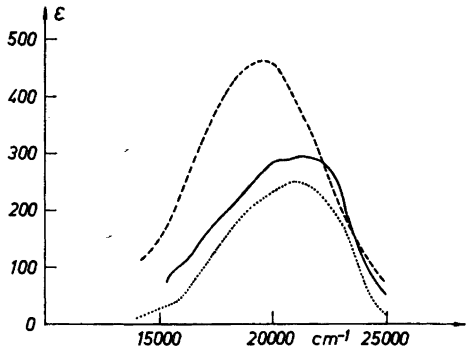

Fig. 2. The 20 000 cm^{-1} band of $Cu(HD)_2$, in chloroform solution (solid line), in chloroform with dibutylamine (dashed line) and in water solution (dotted line).

transition frequencies. The discussion of the spectrum will therefore be limited to the two absorption bands at around 20 000 cm^{-1} and 35 000—37 000 cm^{-1}. The band at 20 000 cm^{-1} for $Cu(HD)_2$ in chloroform, $Cu(HD)_2$ in chloroform with dibutylamine, and $Cu(HD)_2$ in water are given in Fig. 2, where the bands of higher energy have been withdrawn. The absorption band measured at 21 000 cm^{-1} in chloroform solution is highly asymmetric and might be decomposed into two bands with peak values at 22 000 cm^{-1} and 20 000 cm^{-1}. The corresponding bands in chloroform with dibutylamine are located at 20 000 cm^{-1} and 18 500 cm^{-1}, while in water solution the frequencies are 21 000 cm^{-1} and 18 000 cm^{-1}. Since the transition $^1B_{3g}$ is shifted to higher energies when axial ligands are added this state must be associated with the absorption band at 20 000 cm^{-1} in chloroform, and $^{II}A_g$ with the band at 22 000 cm^{-1}. This order of the transitions is shifted by the addition of axial ligands. Following these assignments the shifts of the calculated and experimental transition frequencies have been collected in Table 8. A comparison between the experimental and calculated values shows that the adduct formed between $Cu(HD)_2$ and amines is probably five-coordinated, as was also found in the solubility measurements, while in water solution two ligand molecules are added and thus the adduct $Cu(HD)_2(H_2O)_2$ is formed.

Table 8. Energy shifts of the transitions $^{II}A_g$ and $^1B_{3g}$ due to the addition of further ligands. Calculated values obtained with a ligand metal distance of 2.50 Å. All values in cm^{-1}.

	$^{II}A_g$		$^1B_{3g}$	
	Calc.	Obs.	Calc.	Obs.
$Cu(HD)_2B$	2570	3500	670	~ 0
$Cu(HD)_2B_2$	4960		1060	
$Cu(HD)_2(H_2O)$	1860	4000	670	1000
$Cu(HD)_2(H_2O)_2$	3550		720	

This result is confirmed also by the shift of the $\pi \rightarrow \pi^*$ transition $^1B_{3u}{}^+$. For $Cu(HD)_2B$ only a small shift is expected. Experimentally no shift is found (*cf.* Tables 4 and 7). For $Cu(HD)_2$ in water, on the other hand, the experimental shift is 2000 cm^{-1}, which supports the formation of a six-coordinated compound in that case.

7. CONCLUSIONS

The application of semi-empirical methods with zero differential overlap seems to lead to results which are compatible with experiments. The same conclusion can be drawn from the study of chromate and permanganate ions, using similar methods, made by Oleari *et al.*[18] Some of the results obtained here are not in agreement with the simple molecular theory, especially the description of some of the metal electrons as bonding rather than anti-bonding. The classification of excited states as ligand field or charge transfer has been outruled by the introduction of configuration interaction. Such configurational mixing will occur if two conditions are fulfilled. The metal ligand π-bond should be comparatively strong. This strength will determine the magnitude of the matrix element between the ligand field and charge transfer configuration. Secondly, the two transitions should be of the same symmetry and the same order of energy. The general agreement between theory and experiment gives some reliability to these qualitative results. Especially the EPR constants are a good test on the validity of the calculated electronic structure of the ground and excited states.

The methods for the choice of the semi-empirical parameters should be further investigated. The use of the Wolfsberg-Helmholtz formula for the resonance integrals is, as was also pointed out in II, theoretically unsatisfactory. The crude point dipole approximation used for the determination of the penetration integrals should also be refined. A further development of the methods for the parameter choice necessitates calculations on a number of complexes. It is probably also necessary to introduce new experimental quantities for the determination of the parameters. The results obtained in the calculation of the EPR constants might indicate a possibility of using these constants in the discussion of the parameters, together with the spectral data, which is the only information used hitherto.

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