for $CrCl_2^+$. Since the observed k_{Cl} may consist of both *cis* and *trans* contributions, the ratios cannot be evaluated uniquely from these data alone. The individual contributions of each of the isomeric forms can be resolved from the kinetic results in combination with Salzman and King's equilibrium quotient[4] for *cis-trans* isomerization; at 35° and 0.2 *M* ionic strength, $[cis]/[trans]$ is 1.2_7. This value undoubtedly is relatively insensitive to both temperature and ionic strength. Assuming this value at 0° and 1.0 *M* ionic strength and that the scheme in eq 6 holds for each isomer, the following values are derived: $k_{Cl}(trans) = 0.28\ M^{-2}\ sec^{-1}$, $k_{Cl}(cis) = 0.22\ M^{-2}\ sec^{-1}$, $k_{Cl}(trans)/k_t = Q_{2t} = 1.6 \times 10^{-3}\ M^{-1}$, and $k_{Cl}(cis)/k_c = Q_{2c} = 2.0 \times 10^{-3}\ M^{-1}$.

Equilibrium studies on the individual forms of Cr-Cl_2^+ have not been carried out. Gates and King[3] determined the gross stability quotient for the equilibrium mixture of dichloro species. These experiments measured the *unweighted* sum $Q_{2c} + Q_{2t}$; at 4.4 *m* univalent anion concentration and 0° (extrapolated) the value is $0.015\ M^{-1}$. Our calculation gave $0.003_6\ M^{-1}$ at $I = 1.0\ M$ and 0°. The substantial difference in ionic media being considered does not allow these two values to constitute the independent check they would otherwise provide, but the discrepancy appears not at all unreasonable.[23]

(23) The effect of this medium change on a related reaction can be seen in a comparison of values of the first stability quotient of monochlorochromium(III) which was evaluated independently in each of these two media. At 30° the values are 0.27 M^{-1} at 4.4 *m* univalent anion concentration[3] and 0.086 M^{-1} at $I = 0.96\ M$: R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

Extended Hückel Calculations of the Molecular Orbitals in Bis(β-ketoenolate) Complexes of Copper(II) and Nickel(II)

BY F. A. COTTON, C. B. HARRIS, AND J. J. WISE

Extended Hückel-type MO calculations have been carried out on bis(β-ketoenolate) complexes of Cu(II) and Ni(II), taking these as planar molecules of D_{2h} symmetry, with the ring substituents as hydrogen atoms (to limit the size of the basis set of atomic orbitals). The Wolfsberg–Helmholz approximation was used to estimate off-diagonal matrix elements. The diagonal matrix elements for the metal orbitals were estimated by Ros' procedure in which VSIP's are corrected (substantially) for the influence of the ligand atoms. The coefficient of the d_{xy} orbital in one of the MO's was constrained to have a value similar to that indicated by esr data by adjustment of the H_{ii} terms of the oxygen atoms. The results of the calculation are in good agreement with esr data and the visible spectra and are useful in interpreting ultraviolet spectra, as shown in subsequent papers.

Introduction

The interpretation of the spectra and magnetic properties and, in general, understanding of the electronic structures and chemical bonding in transition metal complexes with β-ketoenolate anions are matters of some importance in coordination chemistry and have already received considerable attention.[1-13] Nonetheless, there still remain a number of unresolved questions concerning the assignment of spectral transitions and the validity of extended Hückel molecular orbital calculations in such molecules.

(1) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).
(2) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).
(3) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).
(4) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
(5) D. W. Barnum, *ibid.*, **22**, 183 (1961).
(6) J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).
(7) H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).
(8) J. Ferguson, R. L. Belford, and T. S. Piper, *ibid.*, **37**, 1569 (1962).
(9) J. Ferguson, R. L. Belford, and T. S. Piper, *Theoret. Chim. Acta*, **3**, 287 (1965).
(10) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).
(11) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).
(12) C. Dijkgraaf, *Theoret. Chim. Acta*, **3**, 38 (1965).
(13) R. L. Belford and G. G. Belford, *ibid.*, **3**, 467 (1965).

This is the second of several papers describing new studies of the compounds $Ni(DPM)_2$ and $Cu(DPM)_2$, where DPM is an abbreviation for the anion derived from dipivaloylmethane (I). The first paper[14] in the

I
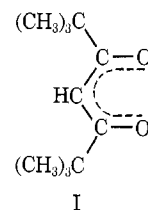
present series described the crystal structure of Ni-$(DPM)_2$. It was found that the two compounds, Cu-$(DPM)_2$ and $Ni(DPM)_2$, are crystallographically isomorphous and that the orientation of the planar molecules in the unit cells is very favorable for study of the polarization of absorption bands. The present paper describes molecular orbital calculations for these molecules. The calculations were influenced by and correlated with the results of the esr studies of $Cu(DPM)_2$

(14) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

which are described in a subsequent paper.[15] The orbital scheme thus determined then served as a guide to the interpretation of the d–d spectra and ultraviolet spectra[16] of the two compounds.

Method of Calculation

The calculations are of the extended Hückel type; that is, all overlaps are included, and the Wolfsberg–Helmholz approximation for off-diagonal elements of the energy matrix was used. In its specific details, the method closely resembles the procedure recently described by Ros.[17,18] The main steps and approximations in the calculations will now be explained.

Evaluation of the H_{ii} Terms.—The H_{ii} terms are of the form

$$H_{ii} = \langle \varphi_i | \mathcal{H} | \varphi_i \rangle = \left\langle \varphi_i(1) \left| \frac{-\nabla_1^2}{2} - \frac{Z_\alpha}{r_{\alpha 1}} \right| \varphi_i(1) \right\rangle +$$
$$\sum_{j \neq i} \left\langle \varphi_i(1) \left| \frac{\varphi_j(2)\,\varphi_j(2)}{r_{12}} \right| \varphi_i(1) \right\rangle -$$
$$\sum_{j \neq i} \delta_{s_i, s_j} \left\langle \varphi_i(1) \left| \frac{\varphi_j(2)\,\varphi_j(1)}{r_{12}} \right| \varphi_j(2) \right\rangle -$$
$$\sum_{\beta} \left\langle \varphi_i(1) \left| \frac{Z_\beta}{r_{\beta 1}} \right| \varphi_i(1) \right\rangle + \sum_{k \neq i} \left\langle \varphi_i(1) \left| \frac{\varphi_k(2)\,\varphi_k(2)}{r_{12}} \right| \varphi_i(1) \right\rangle -$$
$$\sum_{k \neq i} \delta_{s_i, s_k} \left\langle \varphi_i(1) \left| \frac{\varphi_k(2)\,\varphi_k(1)}{r_{12}} \right| \varphi_i(2) \right\rangle$$

where α is the atom to which φ_i belongs. The summation j is over all occupied orbitals of the atom α. Z is the charge of the nucleus. The summation β extends over all other atoms in the molecule. The summation k extends over all occupied orbitals of the β atoms. The terms in the above equation fall into two classes. The first three terms represent the interaction of an electron on the ith atom with other electrons and the nucleus of the ith atom. The last three terms result from the interaction of this electron with other atoms in the molecule. In effect, the first three terms represent the "free-ion" portion of the energy and the last three terms represent the changes in the free-ion energy due to interaction with the other atoms in the molecule. The free-ion part can be evaluated analytically as a function of nuclear charge and valence orbital occupation. This has been done for copper by Ros.[18]

The part which represents the interaction of an electron on the ith atom with other atoms in the molecule would be difficult to evaluate analytically because of the multicenter integrals required to evaluate the Coulomb and exchange energies. However, the major contribution to this part would be expected from the first of the three terms involved. To neglect the last two terms is to assume, in effect, that the other atoms act on the electron as point charges. This point charge approximation was suggested by Pople[19] for simplified

Hückel LCAO calculations on unsaturated hydrocarbons. In many simplified molecular orbital calculations the H_{ii} have been assumed to be equal to the free-ion valence state ionization potential and no account is taken of the part representing the interaction with the other atoms. It can be seen from Ros' work on $CuCl_4{}^{2-}$ that where substantial differences in charge between atoms exist, this term is sizable. In some cases it is as much as half the magnitude of the free-ion term. It would appear that in cases of this type ignoring this term could lead to serious error. We shall discuss this point further below.

In these calculations the H_{ii} were calculated as

$$H_{ii} = \text{free-ion energy} + \sum_{\beta} \left(\frac{Z'_\beta}{r_{i\beta}} \right)$$

β is the summation over all other nuclei in the molecule, Z'_β is the effective nuclear charge, and $r_{i\beta}$ is the distance from the ith atom to the other nuclei.

In order to evaluate the H_{ii} terms it is necessary to determine the effective nuclear charge, Z'_β. If it were to be assumed that an electron in an orbital on the ith atom is screened completely from the β nuclei by the electrons on the β atom, then the Z'_β would equal the formal charge. This approximation fails to the extent to which the orbital from the ith atom penetrates the electron shell of the β atom. For orbitals of small n and l and for larger $r_{i\beta}$ the penetration effect is small. For orbitals such as the copper 4s and 4p, which are very extensive, substantial change in Z'_β would be expected, because of the penetration. Approximations have been suggested to calculate the correction due to penetration. Pohl, Rein, and Appel[20] determined the penetration correction for the hydrogen halides, where it was found to be quite large. For hydrogen fluoride, for example, for an internuclear distance of 1 A the interpenetration term would amount to almost nothing. At 0.75 A, however, the interpenetration term becomes about 3 ev and increases rapidly with shorter internuclear distances.

To evaluate the H_{ii} terms for copper the free-ion orbital energies (valence state ionization potentials, VSIP's) were calculated as functions of over-all charge and orbital occupation using Ros' relationships.[18] For carbon,[21] oxygen,[21] and hydrogen[22] atoms, the valence state ionization potentials derived from spectroscopic data were used. It was assumed that the VSIP's varied with effective charge on the atom by 10 ev/unit charge for carbon and 13 ev/unit charge for oxygen and hydrogen. VSIP's for fractional charges were interpolated linearly. The portion of H_{ii} due to interaction of the electron in question with other atoms in the molecule was calculated, following Ros' procedure, without allowance for penetration in the earlier cycles in order to save machine time. In the later cycles, shielding constants, estimated by comparison with Ros'

(15) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 915 (1967).

(16) F. A. Cotton and J. J. Wise, *ibid.*, **6**, 917 (1967).

(17) P. Ros and G. C. A. Schuit, *Theoret. Chim. Acta*, **4**, 1 (1966).

(18) P. Ros, Doctoral Dissertation, Technical University of Eindhoven, 1964, gives more details than does ref 17.

(19) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(20) H. Pohl, R. Rein, and K. Appel, *J. Chem. Phys.*, **41**, 3385 (1964).

(21) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1965, p 122.

(22) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

values for $CuCl_4{}^{2-}$ (and therefore not as accurate as his), were introduced. The relation assumed was that the shielding parameter for the metal orbital in Cu-(DPM)₂, S_{oxy}, was equal to $S_{Cl}(M_{oxy}/M_{Cl})$, where S_{Cl} is the shielding parameter of Ros for $CuCl_4{}^{2-}$, and M_{oxy} and M_{Cl} are the magnitudes of the radial wave function of the metal orbital 1.92 A from the O atom or 2.22 A from the Cl atom.

Evaluation of the H_{ij} Terms.—These were evaluated from the H_{ii}, H_{jj}, and S_{ij} using the Wolfsberg–Helmholz relation

$$H_{ij} = KS_{ij}(H_{ii} + H_{jj})/2$$

with the value of K being varied. As explained below, a value of 1.80 appears optimum. This is close to the value of 1.75 recommended by Hoffmann[23] for hydrocarbons.

Choice of Geometry, Basis Set, and Atomic Wave Functions.—The molecules were taken to have D_{2h} symmetry with the molecular z axis perpendicular to the plane, the x axis as the bisector of the O–M–O angles within the chelate rings, and the y axis as the bisector of the O–M–O angles between the rings.

In order to keep the basis set to a manageable size, the aliphatic groups on the rings were treated as hydrogen atoms. Thus the calculations were actually made for complexes of the diformylmethanido ion. The distances and angles used were those reported[14] for Ni-(DPM)₂, except that for the copper compound a metal–oxygen distance of 1.92 A was used.[24]

The basis set consisted of the 4s, 4p, and 3d orbitals of the metal atoms, the 2s and 2p orbitals for carbon and oxygen, and 1s for the hydrogen atoms, making a total of 55.

The atomic wave functions used were the real, nodeless, single Slater-type orbitals (STO's). The exponent used in the STO's for the hydrogen orbital was 1.000. For carbon s and p orbitals the values used were those of Clemmenti and Raimondi[25] for neutral atoms with a slight adjustment made to allow for the change in the extension of the radial wave function with charge on the atom. Orbital exponents were adjusted by multiplying by $Z_{chg}/Z_{neutral}$, where Z is the effective nuclear charge as computed in the usual way for STO's. For the oxygen and copper orbitals the radial wave function exponents were chosen so that the area under the radial curve would match that obtained from self-consistent field (SCF) calculations. This was carried out using a program written for the purpose. In this program the overlap between the 2s orbitals centered on the two oxygen atoms in the chelate ring was calculated at the observed internuclear distance by numerically integrating the SCF radial wave functions.[26] By trial and error an exponent was found for the single STO's which gives the same overlap area. Values for the 2p

orbital exponent were found in a similar manner. Using SCF data for the oxygen 2p and the copper 3d wave function, a numerical integration was made to calculate the overlap between copper and oxygen at the observed internuclear distance. An exponent was then found for the 3d STO which with the calculated STO for oxygen matches this area. By like procedure the copper 4s and 4p exponents were evaluated. Slight adjustments were made to allow for changes with charge on the atom as described previously. This method of "calibrating" an STO to give overlap results equivalent to SCF results is believed to be justified since the orbitals are used only to calculate overlaps. The use of a linear combination of STO's which would probably give more accurate overlaps especially for the more distant ones (which are, of course, small) is not believed to give enough improvement to change the results significantly or warrant the additional computational effort required.

Calculation Tactics.—The tactical nature of the present calculation is somewhat different, both in philosophy and procedural detail, from most of the extended Hückel calculations of metal complexes recently carried out[27] and thus requires some explanation.

This calculation was not iterated to self-consistency in charge, although self-consistency is actually closely approached. Instead, the dependence of the results upon variations in several parameters was explored, subject to the constraint that the d-orbital splittings together with the coefficients of the d orbitals had to yield g values in good agreement with the measured ones[15] for the copper complex. Since all g values depend strongly on the value of the coefficient of the d_{xy} orbital in the b_{1g} MO (no. 23), while at the same time choices of orbital energies and other parameters tend to affect the mixing coefficients for all d orbitals in approximately the same way, it was sufficient to set the single requirement that the coefficient of d_{xy} be in agreement with that required by esr data for the copper complex.

For the nickel complex, essentially identical parameters were used. While the Ni–O bond is ~0.08 A shorter than the Cu–O bond, inspection of the SCF wave functions shows that the Ni 3d function has its maximum about this much closer to the nucleus. Hence, the overlaps for the Ni complex should be about equal to those for the Cu complex. The charge distribution and hence the H_{ii} values for the Ni complex were then also assumed to be the same as those for the Cu complex, except that the d orbitals of Ni were estimated to be 1.2 ev less stable, based upon differences in free-ion energies of the two atoms.[21]

Results

Table I gives the input parameters for the copper complex and Table II the calculated energies of the MO's. Using the eigenvectors, a Mulliken population analysis was carried out, with the results given in Table III. Figure 1 shows the energy distribution of some of

(23) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(24) L. F. Dahl, quoted by T. S. Piper, *Mol. Phys.*, **5**, 169 (1962), gives this distance for Cu(acac)₂.

(25) E. Clemmenti and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(26) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963.

(27) *Cf.* H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966), for an outline of one of the common procedures (of the "self-consistent in charge distribution" type) and an extensive list of references.

Table I
Input Parameters for Molecular Orbital Calculation on Cu(DPM)₂

Orbital no.	Atom Kind	Atom No.	Orbital type	Coordinates,[a] X	Y	Orbital exp	H_{ii}
1	Cu	1	4s	0.0	0.0	1.420	−3.10
2	Cu	1	4p$_z$	0.0	0.0	1.420	−0.30
3	Cu	1	4p$_x$	0.0	0.0	1.420	−0.30
4	Cu	1	4p$_y$	0.0	0.0	1.420	−0.30
5	Cu	1	d$_{z^2}$	0.0	0.0	3.140	−11.50
6	Cu	1	d$_{xz}$	0.0	0.0	3.140	−11.50
7	Cu	1	d$_{x^2-y^2}$	0.0	0.0	3.140	−11.50
8	Cu	1	d$_{yz}$	0.0	0.0	3.140	−11.50
9	Cu	1	d$_{xy}$	0.0	0.0	3.140	−11.50
10	O	2	2s	1.320	1.402	1.892	−33.80
11	O	2	2p$_z$	1.320	1.402	1.640	−17.40
12	O	2	2p$_x$	1.320	1.402	1.640	−17.40
13	O	2	3p$_y$	1.320	1.402	1.640	−17.40
14	O	3	2s	−1.320	1.402	1.892	−33.80
15	O	3	2p$_z$	−1.320	1.402	1.640	−17.40
16	O	3	2p$_x$	−1.320	1.402	1.640	−17.40
17	O	3	2p$_y$	−1.320	1.402	1.640	−17.40
18	O	4	2s	1.320	−1.402	1.892	−33.80
19	O	4	2p$_z$	1.320	−1.402	1.640	−17.40
20	O	4	2p$_x$	1.320	−1.402	1.640	−17.40
21	O	4	2p$_y$	1.320	−1.402	1.640	−17.40
22	O	5	2s	−1.320	−1.402	1.892	−33.80
23	O	5	2p$_z$	−1.320	−1.402	1.640	−17.40
24	O	5	2p$_x$	−1.320	−1.402	1.640	−17.40
25	O	5	2p$_y$	−1.320	−1.402	1.640	−17.40
26	C(1)	6	2s	2.560	1.150	1.638	−21.40
27	C(1)	6	2p$_z$	2.560	1.150	1.598	−12.70
28	C(1)	6	2p$_x$	2.560	1.150	1.598	−12.70
29	C(1)	6	2p$_y$	2.560	1.150	1.598	−12.70
30	C(1)	7	2s	−2.560	1.150	1.638	−21.40
31	C(1)	7	2p$_z$	−2.560	1.150	1.598	−12.70
32	C(1)	7	2p$_x$	−2.560	1.150	1.598	−12.70
33	C(1)	7	2p$_y$	−2.560	1.150	1.598	−12.70
34	C(1)	8	2s	2.560	−1.150	1.638	−21.40
35	C(1)	8	2p$_z$	2.560	−1.150	1.598	−12.70
36	C(1)	8	2p$_x$	2.560	−1.150	1.598	−12.70
37	C(1)	8	2p$_y$	2.560	−1.150	1.598	−12.70
38	C(1)	9	2s	−2.560	−1.150	1.638	−21.40
39	C(1)	9	2p$_z$	−2.560	−1.150	1.598	−12.70
40	C(1)	9	2p$_x$	−2.560	−1.150	1.598	−12.70
41	C(1)	9	2p$_y$	−2.560	−1.150	1.598	−12.70
42	C(2)	10	2s	3.370	0.0	1.608	−19.50
43	C(2)	10	2p$_z$	3.370	0.0	1.568	−10.60
44	C(2)	10	2p$_x$	3.370	0.0	1.568	−10.60
45	C(2)	10	2p$_y$	3.370	0.0	1.568	−10.60
46	C(2)	11	2s	−3.370	0.0	1.608	−19.50
47	C(2)	11	2p$_z$	−3.370	0.0	1.568	−10.60
48	C(2)	11	2p$_x$	−3.370	0.0	1.568	−10.60
49	C(2)	11	2p$_y$	−3.370	0.0	1.568	−10.60
50	H(1)	12	1s	3.140	2.050	1.000	−14.50
51	H(1)	13	1s	3.140	−2.050	1.000	−14.50
52	H(1)	14	1s	−3.140	2.050	1.000	−14.50
53	H(1)	15	1s	−3.140	−2.050	1.000	−14.50
54	H(2)	16	1s	4.440	0.0	1.000	−14.50
55	H(2)	17	1s	−4.440	0.0	1.000	−14.50

[a] Z coordinate is zero for all atoms in D$_{2h}$ symmetry.

Table II
Molecular Orbital Energy Levels for Copper Complex

MO (ψ)	Energy, ev	No. of electrons	Symmetry	MO (ψ)	Energy, ev	No. of electrons	Symmetry
1	77.424	0	b$_{3u}$	28	−11.537	2	b$_{2u}$
2	72.527	0	a$_g$	29	−12.036	2	b$_{1g}$
3	71.583	0	b$_{1g}$	30	−12.479	2	b$_{2g}$
4	68.309	0	b$_{1u}$	31	−12.591	2	b$_{1u}$
5	55.000	0	b$_{3u}$	32	−14.122	2	b$_{3u}$
6	52.582	0	a$_g$	33	−14.612	2	a$_g$
7	43.518	0	b$_{2u}$	34	−14.670	2	b$_{3u}$
8	31.628	0	b$_{1g}$	35	−15.523	2	a$_g$
9	29.268	0	b$_{3u}$	36	−15.787	2	b$_{2g}$
10	25.829	0	b$_{2u}$	37	−16.924	2	b$_{2u}$
11	24.226	0	a$_g$	38	−17.670	2	b$_{2g}$
12	21.808	0	b$_{3u}$	39	−18.157	2	a$_u$
13	21.697	0	a$_g$	40	−18.179	2	b$_{2u}$
14	12.585	0	a$_g$	41	−18.538	2	b$_{3g}$
15	12.408	0	b$_{3u}$	42	−18.619	2	b$_{3u}$
16	12.008	0	b$_{1g}$	43	−18.656	2	b$_{1g}$
17	11.715	0	b$_{2u}$	44	−19.111	2	a$_u$
18	3.032	0	b$_{1u}$	45	−19.710	2	a$_g$
19	−4.511	0	b$_{2g}$	46	−20.046	2	b$_{3u}$
20	−4.989	0	b$_{1u}$	47	−20.780	2	a$_g$
21	−8.403	0	a$_u$	48	−21.470	2	b$_{1g}$
22	−8.576	0	b$_{3g}$	49	−22.772	2	b$_{2u}$
23	−8.872	1	b$_{1g}$	50	−25.626	2	b$_{3u}$
24	−11.250	2	a$_g$	51	−25.987	2	a$_g$
25	−11.288	2	b$_{2g}$	52	−35.371	2	b$_{1g}$
26	−11.336	2	a$_g$	53	−37.299	2	b$_{2u}$
27	−11.512	2	b$_{3g}$	54	−37.965	2	a$_g$
				55	−38.113	2	b$_{3u}$

Table III
Orbital and Atomic Charges for Copper Complex

Atom	Orbital	Orbital charge	Atomic charge[a]
Copper			+1.73
	4s	−0.14	
	4p$_z$	−0.02	
	4p$_x$	−0.29	
	4p$_y$	−0.23	
	3d$_{z^2}$	1.98	
	3d$_{xz}$	1.99	
	3d$_{x^2-y^2}$	1.99	
	3d$_{yz}$	1.92	
	3d$_{xy}$	1.37	
Oxygen			−0.82
	2s	1.78	
	2p$_z$	1.70	
	2p$_x$	1.56	
	2p$_y$	1.94	
Carbon(1)			+0.28
	2s	1.04	
	2p$_z$	0.77	
	2p$_x$	0.87	
	2p$_y$	1.02	
Carbon(2)			+0.06
	2s	1.03	
	2p$_z$	1.10	
	2p$_x$	0.90	
	2p$_y$	0.90	
Hydrogen(1)			+0.07
	1s	0.92	
Hydrogen(2)			0.00
	1s	1.00	

[a] Charge on copper atom adjusted to exclude negative contribution from 4s and 4p orbitals. The oxygen atoms are correspondingly adjusted to remove overlap contribution.
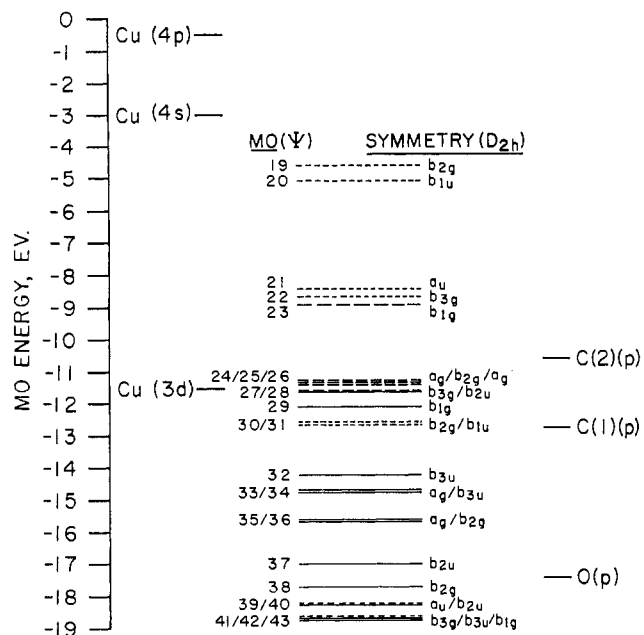
the molecular orbitals. All of these results were obtained using the "optimum" parameters as explained in the Discussion section. Tables of other numerical results have been filed with the American Documentation Institute.[28]

Tables IV and V give the main results of the calculation for Ni(DPM)₂.

Discussion

Before discussing the results reported above, the criteria for selection of the parameters require comment.

(28) Tables of overlaps, eigenvectors, and population analyses for both Cu(DPM)₂ and Ni(DPM)₂ have been deposited as Document No. 9307 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for 35-mm microfilm, payable to: Chief, Photoduplication Service, Library of Congress.

MO(Ψ)   SYMMETRY(D2h)

Cu (4p)

Cu (4s)

19 -------------- b2g
20 -------------- b1u

21 ------------ au
22 ------------ b3g
23 ------------ b1g

Cu (3d) 24/25/26 ======== ag/b2g/ag   — C(2)(p)
         27/28 ======== b3g/b2u
         29 ------------ b1g
         30/31 ============ b2g/b1u   — C(1)(p)

32 ------------ b3u
33/34 ========== ag/b3u
35/36 ========== ag/b2g

37 ------------ b2u
38 ------------ b2g   — O(p)
39/40 ---------- au/b2u
41/42/43 ======== b3g/b3u/b1g

Figure 1.—A diagram showing some of the MO energies and atomic orbital energies for Cu(DPM)₂. Solid lines represent those MO's which are in-plane, mainly ligand orbitals. Short-dashed lines represent out-of-plane, mainly ligand orbitals. Long-dashed lines represent MO's which are mainly Cu d orbitals.

TABLE IV

MOLECULAR ORBITAL ENERGY LEVELS FOR NICKEL COMPLEX

MO (ψ)	Energy, ev	No. of electrons	Symmetry	MO (ψ)	Energy, ev	No. of electrons	Symmetry
1	77.424	0	b_{3u}	28	−11.537	2	b_{2u}
2	72.525	0	a_g	29	−11.793	2	b_{1g}
3	71.582	0	b_{1g}	30	−12.399	2	b_{2g}
4	68.309	0	b_{2u}	31	−12.591	2	b_{1u}
5	55.000	0	b_{3u}	32	−14.122	2	b_{3u}
6	52.582	0	a_g	33	−14.580	2	a_g
7	43.518	0	b_{2u}	34	−14.670	2	b_{3u}
8	31.628	0	b_{1g}	35	−15.512	2	a_g
9	29.268	0	b_{3u}	36	−15.640	2	b_{1g}
10	25.829	0	b_{2u}	37	−16.924	2	b_{2u}
11	24.222	0	a_g	38	−17.652	2	b_{1g}
12	21.808	0	b_{3u}	39	−18.157	2	a_u
13	21.697	0	a_g	40	−18.179	2	b_{2u}
14	12.584	0	a_g	41	−18.530	2	b_{3g}
15	12.408	0	b_{3u}	42	−18.619	2	b_{3u}
16	12.008	0	b_{1g}	43	−18.649	2	b_{2g}
17	11.715	0	b_{2u}	44	−19.111	2	b_{1u}
18	3.032	0	b_{1u}	45	−19.703	2	a_g
19	−4.508	0	b_{2g}	46	−20.046	2	b_{3u}
20	−4.989	0	b_{1u}	47	−20.773	2	a_g
21	−8.144	0	b_{1g}	48	−21.452	2	b_{1g}
22	−8.403	0	a_u	49	−22.772	2	b_{2u}
23	−8.511	0	b_{3g}	50	−25.626	2	b_{3u}
24	−10.105	2	a_g	51	−25.985	2	a_g
25	−10.162	2	a_g	52	−35.368	2	b_{1g}
26	−10.180	2	b_{2g}	53	−37.299	2	b_{2u}
27	−10.390	2	b_{3g}	54	−37.965	2	a_g
				55	−38.113	2	b_{3u}

The manner in which the calculation was guided in its final stages so that the half-filled orbital consisted primarily of a metal 3d orbital with a reasonable coefficient was primarily by control of the H_{ii} of the oxygen atoms. Since it is not self-evident that the arbitrary

TABLE V

ORBITAL AND ATOMIC CHARGES FOR NICKEL COMPLEX

Atom	Orbital	Orbital charge	Atomic charge[a]
Nickel			+1.71
	4s	−0.14	
	$4p_z$	−0.03	
	$4p_x$	−0.29	
	$4p_y$	−0.23	
	$3d_{z^2}$	1.98	
	$3d_{xz}$	1.99	
	$3d_{x^2-y^2}$	2.00	
	$3d_{yz}$	1.81	
	$3d_{xy}$	0.51	
Oxygen			−0.79
	2s	1.79	
	$2p_z$	1.71	
	$2p_x$	1.55	
	$2p_y$	1.93	
Carbon(1)			+0.26
	2s	1.04	
	$2p_z$	0.80	
	$2p_x$	0.88	
	$2p_y$	1.02	
Carbon(2)			+0.06
	2s	1.03	
	$2p_z$	1.10	
	$2p_x$	0.91	
	$2p_y$	0.89	
Hydrogen(1)			+0.08
	1s	0.92	
Hydrogen(2)			0.00
	1s	1.00	

[a] Charge on nickel atom adjusted to exclude negative contribution from 4s and 4p orbitals. The oxygen atoms are correspondingly adjusted to remove overlap contribution.

adjustment of the oxygen H_{ii} is the only reasonable adjustment which would accomplish the desired end, in the following paragraphs the effects of variation of the various free parameters will be discussed. An attempt will be made to show that the adjustment of the oxygen H_{ii} was in fact the only reasonable way to proceed.

Variation of H_{ii} for Oxygen.—The esr results indicate[15] that the molecular orbital coefficient for the $3d_{xy}$ orbital of copper should be in the vicinity of 0.85. The effect of variation of the oxygen H_{ii} is shown in Figure 2. It can be seen that for an H_{ii} of −33.8 ev for oxygen 2s and −17.4 for oxygen 2p the calculated MO coefficient for the $3d_{xy}$ orbital is 0.849. Also, the calculated d–d splitting is found to agree reasonably well with the observed values.[16] As less stable H_{ii} for oxygen are used, more mixing occurs, the molecular orbital coefficient of the $3d_{xy}$ orbital becomes untenable, and the d–d splitting becomes excessive. On the other hand, as the oxygen orbital is assumed to be more stable, less mixing is obtained. Eventually, however, a ligand π^* orbital would fall below the orbital containing the $3d_{xy}$ orbital. This, of course, gives the unacceptable result of having the odd electron distributed primarily in the ligand system. In effect, the values found to satisfy our criterion are the only values to do so (within 1 ev or so) assuming no other changes in the input parameters.

The conclusion to be drawn is that the H_{ii} are not

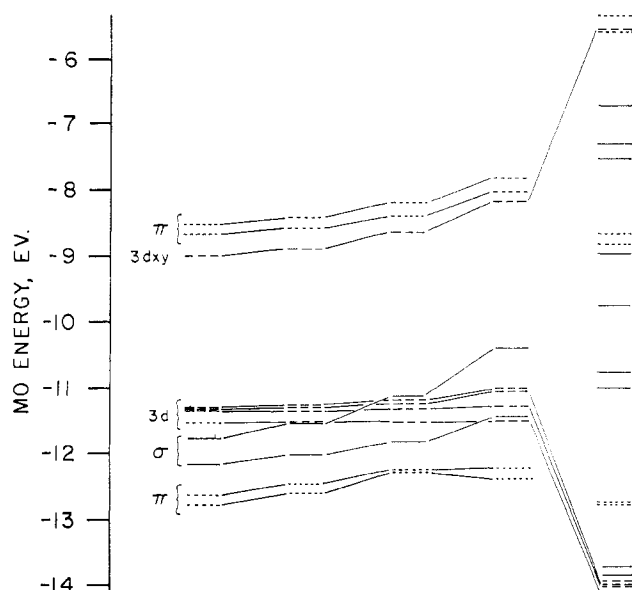| OXYGEN H_{ii}					
2s	-35.8	-33.8	-31.8	-29.4	-27.0
2p	-19.4	-17.4	-15.4	-13.4	-8.0
MO COEF. Cu 3d$_{xy}$	0.881	0.849	0.795	0.708	0.324

Figure 2.—The effect of varying the oxygen orbital energies on the energies of the MO's and on the MO coefficient of the Cu 3d$_{xy}$ orbital. All other parameters were those given in Table I, except at the extreme right where H_{ii} for the Cu 3d orbitals was taken as -14.0 ev. A Wolfsberg–Helmholz factor of 1.80 was used: $-\ -\ -\ -$, mainly π-ligand orbital; ————, mainly σ-ligand orbital; — —, mainly Cu 3d orbital.

correctly estimated by the procedure used, since an arbitrary adjustment of the H_{ii} is required. This is presumably due to insufficient allowance for the interpenetration term. Allowance for penetration always makes the H_{ii} more negative. A plot of SCF wave functions for neutral copper, oxygen, and carbon does in fact show that even neutral oxygen would penetrate the copper nucleus to some extent. Negatively charged oxygen would have more extended orbitals and would penetrate even more. Undoubtedly, if allowance was also made for penetration into the carbon atom, as well as into the copper atom, the calculated H_{ii} would approach the values found to be required.

Variation of H_{ii} for Copper.—One could consider the possibility of satisfying the esr criterion by assuming a less stable H_{ii} for the copper 3d orbital. It is obvious, however, that this approach would be neither justifiable nor successful. It could not be justified because allowance for penetration of the 3d orbital into the oxygen shell would make the orbital more stable rather than less. It would not be successful because it would result in lowering of a π^* orbital below the copper 3d$_{xy}$ level giving an improper ground state.

It is appropriate at this point to discuss the behavior of the copper 4s and 4p orbitals. The 4s orbital is very extended, having in fact its maximum beyond the oxygen atom. The 4p orbital is even more extensive. The interpenetration effect for the copper 4s and 4p orbitals will be large. It is found, even after allowing for interpenetration, that these orbitals are quite unstable. In the population analysis, however, due to the fact

that the overlap term is negative and larger than the net charge term, there is negative occupation indicated for these orbitals. Physically this is impossible. In calculating charges on the copper and oxygen atoms, the copper charge is adjusted to remove the negative terms from the 4s and 4p orbitals. Physically, the 4s and 4p orbitals should make little contribution to the bonding or to the charge on the metal. The latter quantity was therefore computed using only the 3d valence orbitals. Likewise, the charge on the oxygen atoms has been adjusted to compensate for this artifact.

In effect, the calculation suggests that the 4s and 4p orbitals of the metal could have been omitted in the beginning and quite reasonable results concerning other aspects of the electronic structure obtained straightforwardly. However, it would have been difficult to justify such an approach before the fact. It did not, however, seem worthwhile to expend time and effort on such a calculation after the fact, since it is now evident that it would be feasible. It is well to keep in mind that the major goal in this calculation was to determine the pattern of the d levels and its dependence on parameters used in the calculation, so that the observed visible spectrum could be assigned. This has been accomplished successfully. It is true, of course, that the ability of the calculation to give a reasonable account of the ultraviolet spectrum may be seriously impaired by inaccuracies in the treatment of the metal 4s and 4p orbitals.

Variation of H_{ii} for Carbon.—While the H_{ii} of the carbon atoms were not studied extensively, it is apparent that the same considerations discussed for oxygen would also be applicable for carbon. Owing to interpenetration, the H_{ii} probably should be more negative than those calculated using simply a $1/r$ correction. The correction required would be expected to be smaller than that required for oxygen since the charges on the surrounding atoms are smaller. The first two π^* levels are sensitive to changes in the carbon(1) H_{ii} since it is a large component of these levels. Using the same input parameters as in Table I, but stabilizing the carbon(1) 2p orbital (to -14.7 ev) results in lowering the first two π^* levels below the copper 3d$_{xy}$ level, giving an improper ground state. For the input parameters used, the H_{ii} of carbon(1) cannot be changed by more than about 1 ev and still satisfy our criterion.

Variation of K.—Using the input parameters of Table I, calculations were made in which the K factor in the Wolfsberg–Helmholz equation was set at 2.0, 1.8, and 1.6. The effect of changing K on the d–d splitting and the coefficient for the 3d$_{xy}$ orbital in the last occupied (half-filled) molecular orbital is shown in Table VI. The d–d splitting changes from 30,600 to 13,200 cm^{-1} when K is varied from 2.0 to 1.6. A K of 1.8 gives results consistent with observed values.

The main features of the results of the calculation for Cu(DPM)$_2$ are the following.

(1) The pattern of "d orbitals," that is, those molec-

ular orbitals which consist mainly of metal d orbitals and which are responsible for the visible spectra of the molecules, is found to consist of four closely spaced, relatively nonbonding ones, with the fifth one ("d_{xy}") lying some 18,000–21,000 cm^{-1} above them. Although the magnitudes of the separations of the d orbitals depend upon the value of K used, the order of the orbitals is relatively insensitive to this parameter.

(2) This result is obtained using a set of parameters which simultaneously leads to d-orbital coefficients in the eigenvectors from which, as shown in the following paper,[15] satisfactory g values may be computed.

(3) The pattern of "d levels" obtained is in agreement with the results of a polarization study of the visible spectrum of the copper complex.[16]

(4) The MO energies for both the copper and the nickel complexes can be used to make assignments of the ultraviolet spectra of these molecules.

(5) The calculated charge distributions in these molecules leave relatively large positive charges on the metal atoms. This is a direct consequence of correcting the VSIP's for the influence of the ligand atoms, as Ros[18] has emphasized. Had this not been done, the higher absolute values of the H_{ii} for the metal atoms together with their steep dependence on metal ion charge would have led to much more covalence in the metal–ligand bonds. This, in turn, would have given lower charges on the metal atoms and lower g values. The use of Ros' method or some similar one to obtain H_{ii} values from the VSIP's instead of using the VSIP's themselves[27] as H_{ii}'s seems clearly to be necessary.

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The Electron Spin Resonance Spectrum of Bis(dipivaloylmethanido)copper(II)[1]

BY F. A. COTTON AND JOHN J. WISE

The electron spin resonance spectrum of Cu(DPM)₂ doped into the isostructural, diamagnetic Ni(DPM)₂ has been measured. The results $g_z = 2.244$ and $g_x = g_y = 2.051$ are in good agreement with those for Cu(acac)₂ and indicate that the electronic structures of these molecules are, as expected, virtually identical. The observed g values together with approximate energies of optical transitions served to set limits on the MO coefficients of the d orbitals, especially d_{xy}. The results of an MO calculation subject to such constraints can be used to calculate g values close to the observed ones.

Introduction

As part of a broad study[2,3] of the electronic structures of the isomorphous compounds Cu(DPM)₂ and Ni(DPM)₂, where DPM represents the dipivaloylmethanido ion, the electron spin resonance spectrum of the copper complex has been measured. This paper reports the results and discusses their relationship to the molecular orbital description of the electronic structure which was presented in an earlier paper.[2] Another purpose of this study was to obtain evidence that the electronic structure of Cu(DPM)₂ does not differ in any essential way from that of the acetylacetonate.

The crystal structure of Ni(DPM)₂, which was used as a host for the Cu(DPM)₂, has recently been reported.[4]

Experimental Section

The Cu(DPM)₂ and Ni(DPM)₂ were dissolved in benzene (which had been distilled from P₂O₅) in the molar ratio 10⁻⁶. By allowing acetonitrile (spectral grade) to diffuse slowly into the benzene solution, large platelike crystals were obtained. X-Ray examination showed that the large faces were [001] planes; this is the same morphology as previously found for the pure Ni-(DPM)₂ crystals.[4]

The resonances were measured with a Varian 4500 spectrometer equipped with a 100-kc field modulation unit and a Varian Model V-4533 cylindrical cavity. The magnetic field was measured with a proton resonance magnetometer. All measurements were made at room temperature.

The crystals were aligned by X-ray and optical methods and

(1) Dipivaloylmethanido is a common semisystematic name for the enolate anion derived from 2,2,6,6-tetramethyl-3,5-dionoheptane.

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

(3) F. A. Cotton and J. J. Wise, *ibid.*, **6**, 917 (1967).

(4) F. A. Cotton and J. J. Wise, *ibid.*, **5**, 1200 (1966).