TABLE VI
EFFECT OF VARIATION OF K ON MO COEFFICIENT AND d–d SPLITTING

K^a	Cu $3d_{xy}$ MO coefficient	d–d splitting max, cm^{-1}
2.00	0.797	30,600
1.80	0.849	21,200
1.60	0.915	13,200

[a] All other parameters same as in Table I.

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]

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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 P_2O_5) in the molar ratio 10^{-5}. 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

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[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).

mounted on quartz rods which were mounted in an aluminum holder fitting the neck of the cavity. A circular dial, 1 in. in diameter, with 100 divisions was used to measure relative angular rotations. Measurements were made about the *a*, *b*, and $\perp ab$ crystal axes.

Results

The results were plotted as curves showing the variation of resonant field as a function of rotation angle about each crystal axis. Using a least-squares procedure the parameters (g, the gyromagnetic ratio, and α, β, γ constants to be determined) in the equation

$$g^2 = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta$$

were evaluated. In this equation, θ is the angle of rotation of the crystal from the magnetic field direction. Using Schonland's procedure[5] the elements of the g tensor were determined. The tensor was then diagonalized to give the principal components $g_x = g_y = 2.0505$ and $g_z = 2.2438$.

The vector representing the orientation of the unique magnetic axis (g_z) in the cell was found to make an angle of 65.5° with the *b* axis of the cell. The vector representing the *z* molecular axis (*i.e.*, the perpendicular to the O–Ni–O plane as found from the crystallographic study)[4] makes an angle of 67.2° with the *b* axis of the cell. The slight discrepancy may be due in part to error or to packing deformation. In regard to the latter, the Cu–O bond should be about 0.08 A longer than the Ni–O bond. To accommodate the $Cu(DPM)_2$ molecule in the $Ni(DPM)_2$ host, it is not unreasonable that a slight twist might be required to minimize packing interactions. The in-plane magnetic vectors were found to be between rather than coincident with the metal–oxygen bonds, as is of course required by the D_{2h} molecular symmetry.

Discussion

Similarity to $Cu(acac)_2$.—It may first be noted that the magnitudes of the g_i's for $Cu(DPM)_2$ are nearly identical with those[6,7] for $Cu(acac)_2$, as shown in Table I. This confirms the assumption that the electronic structures of the two complexes are essentially the same and that results obtained on $Cu(DPM)_2$ may be assumed valid, except as to precise numerical values, for $Cu(acac)_2$.

Table I

Components of the Diagonalized g Tensor for $Cu(acac)_2$ and $Cu(DPM)_2$

Complex	State	Ref	g_x	g_y	g_z
$Cu(DPM)_2$	Crystal	This work	2.051	2.051	2.244
$Cu(acac)_2$	Crystal	6	2.053	2.053	2.266
$Cu(acac)_2$	Glass	7	2.036	2.036	2.264

Amount of d-Orbital Mixing.—The second purpose of obtaining experimental g values for $Cu(DPM)_2$ was to obtain a fairly accurate estimate of the coefficients of the Cu d orbitals, especially the d_{xy} orbital, in the molecular orbitals of the complex, so that this information could serve as a guide in adjusting some parameters in the MO calculation.[2]

In order to do this, use was made of the relations

$$g_z = 2.0023 - 8\lambda\alpha^2\beta^2/|E(d_{xy}) - E(d_{x^2-y^2})|$$

$$g_x = 2.0023 - 2\lambda\alpha^2\delta^2/|E(d_{xy}) - E(d_{xz})|$$

$$g_y = 2.0023 - 2\lambda\alpha^2\omega^2/|E(d_{xy}) - E(d_{yz})|$$

where α, β, δ, and ω are the coefficients of the d_{xy}, $d_{x^2-y^2}$, d_{xz}, and d_{yz}, orbitals, respectively, in the molecular orbitals to which they contribute, and λ is the spin–orbit coupling constant (-828 cm^{-1}).

Assuming[3] ΔE_i in the range 15,000–20,000 cm^{-1} and that β, γ, and δ would be in the range 0.93–0.98, various combinations of coefficients were tested. It was found that the best all around agreement (calculated values: $g_z = 2.26$, $g_x = 2.07$, $g_y = 2.06$) was obtained with $\alpha \approx 0.85$, $\beta \approx \delta \approx \omega \approx 0.96$. The final values from the MO calculation,[2] in which α was fixed at 0.849, were $\beta = 0.978$, $\delta = 0.939$, and $\omega = 0.977$. These values together with the observed ΔE's lead to calculated g values of $g_z = 2.253$, $g_x = 2.065$, and $g_y = 2.060$, in reasonable agreement with the experimental values of $g_z = 2.244$, $g_x = g_y = 2.051$.

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