square planar, or an intermediate distorted arrangement. At present, this structure must be regarded as tentative, although the negative results with the ^{13}C acetate make it more likely than a structure involving bridging carboxylate groups, as has been determined by X-ray crystallography for $Cu_2(CH_3COO)_4 \cdot 2H_2O$.[16]

These results indicate the unusual absorption spectra observed with some of the copper enzymes could be due to Cu(I)–Cu(II) interaction, as well as be caused by Cu(II) in a highly distorted ligand field. In cytochrome *c* oxidase, *e.g.*, a broad band, centered at 830 mμ, is attributed to the copper chromophore.[17] The broad band with center at 900 mμ of the mixed-valence model complex could well correspond to this feature of cytochrome *c* oxidase.

No seven-line esr spectra of copper enzymes have been published. This does not exclude enzymatic copper–copper interaction, however, since if the exchange rate in the enzyme is considerably lower than in this model, a four-line spectrum would be observed.

Experimental Section

The spectrometric measurements were carried out with a Cary 14 E spectrophotometer. In order to exclude oxygen, a 1-cm cuvette with two side arms and a stopcock that could be flushed with N_2 and sealed off was used. The absolute methanol with suitable amounts of acetic acid and sodium acetate was deaerated in the cuvette with prepurified N_2 for 15 min and the solid copper(I) and copper(II) compounds were then introduced into the side arms. The solution and the cuvette were again deaerated for 15 min and then shaken for 5 min to mix the contents. The absorption was reproducible within ±2% absorbance. The color is stable under complete exclusion of O_2 but quickly changes to the blue of Cu(II) in the presence of traces of O_2.

Room-temperature esr measurements were made with a Varian V-4500-10, X-band spectrometer equipped with a variable-temperature accessory, using 100-kc modulation, in a flat quartz cell that was sealed after filling under an atmosphere of N_2. The *g* value was determined by comparison with the signal of 2,2-diphenyl-1-picrylhydrazyl in benzene. The low-temperature spectra were obtained by rapidly freezing the solution of the complex in liquid nitrogen. In order to obtain the complex under these conditions, it was found necessary to bubble He through the solution for at least 20 hr before freezing; otherwise, the complex immediately dissociated into green Cu(II) upon freezing. This is most likely due to the presence of a small amount of CH_3CN in the solution, which favors the formation of a Cu(I) complex over the mixed-valence complex at low temperatures (see results above). CH_3CN is probably removed by long bubbling with He, preventing the preferential formation of this complex upon freezing.

Materials. $Cu(ClO_4)_2 \cdot 6H_2O$, purchased from Fluka or G. Frederich Smith Co., was used without further purification; $Cu(CH_3CN)_4ClO_4$ was prepared as described previously;[18] absolute methanol, distilled from $Mg(OCH_3)_2$, and acetic acid (Fluka p.A.), distilled over chromic acid, were used. Sodium acetate (p.A.), free of water, was obtained from Siegfried Co. The ^{13}C sodium acetate (60% enrichment) was purchased from Nuclear Research Chemicals and used without purification.

Acknowledgment.—Thanks are expressed to the "Stiftung Volkswagenwerk" for a stipend to C. S., to the U. S. Public Health Service (Grant GM-08347, National Institute of General Medical Sciences) for financial support, and to Dr. James Sinclair for helpful discussions.

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[18] P. Hemmerich and C. Sigwart, *Experientia*, **19**, 488 (1963).

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Single-Crystal Electron Paramagnetic Resonance Studies of Copper Diethyldithiocarbamate

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Received July 1, 1968

Single-crystal electron paramagnetic resonance studies have been carried out on copper(II) diethyldithiocarbamate doped into both the zinc and nickel diethyldithiocarbamate complexes. The crystal structures of all three complexes are known, and the orientation of the principal axes of the *g* and hyperfine tensors can be related to the molecular axes. The lowering of symmetry on going from the nickel to the zinc diethyldithiocarbamate host leads to significant changes in the isotropic as opposed to the anisotropic hyperfine interaction. These changes have been attributed to increased orbital mixing upon a lowering of symmetry about the metal ion. The epr results were used to obtain molecular orbital coefficients from standard expressions employing orbitals based on the metal ion and sulfur atoms. The coefficient values were tested for their sensitivity to the various parameters in the expressions, in particular, ligand spin–orbit coupling. Molecular orbital coefficients obtained were compared with those from a Wolfsberg–Helmholtz calculation.

Introduction

In recent years there had been interest, both in this laboratory[1] and elsewhere,[2] in the complexes formed by transition metals with chelating ligands bonding through sulfur. In this paper, we report the results that have been obtained from single-crystal epr studies of copper(II) diethyldithiocarbamate, $Cu(dtc)_2$, doped into single crystals of both the zinc and nickel diethyldithiocarbamate complexes. Pettersson and

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[1] J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2784 (1968).

[2] H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 239 (1965).

Vänngård[3] presented data for copper(II) dithiocarbamates in solution and in dilute powders and recently Reddy and Srinivasan[4] published the results of a single-crystal epr examination of Cu(dtc)$_2$ diluted in the zinc complex. Detailed crystal structures were not available, however, so that the principal magnetic axes could not be related to the geometry of the molecule in the crystal.

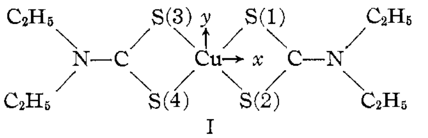
Molecular orbital coefficients may be calculated from epr and optical data following the procedure of Maki and McGarvey,[5] if the relative orientations of the molecular and magnetic axes are known. Since the detailed X-ray crystal structures of Zn(dtc)$_2$ and Ni(dtc)$_2$ have become available,[6,7] we considered it of interest to determine accurate magnetic parameters for Cu(dtc)$_2$ doped into these two host lattices which have different geometries of the sulfur atoms about the metal ion. These data have been used in conjunction with molecular orbital calculations to explore the bonding in these complexes.

Experimental Procedures and Crystal Structures

The copper, nickel, and zinc complexes were prepared by adding sodium diethyldithiocarbamate to aqueous solutions of the respective metal salts, the complexes being recrystallized from chloroform. The dilute crystals (1:500, Cu:Zn, Cu:Ni) were obtained by slow evaporation of a solution in 20:80 v/v carbon tetrachloride–chloroform.

Dilute single crystals of the dithiocarbamates were oriented on a Buerger precession camera and then transferred directly to a small crystal holder. This was in the form of three sides of a box, each outer face having a small stub, with the axes of the stubs oriented accurately at right angles. Epr spectra were readily obtained about each of the three mutually perpendicular axes by rotation on the stubs which were inserted in turn in a central post in the spectrometer cavity.

Measurements were made at 15 or 20° intervals in each plane using a Varian V-4500 spectrometer (X-band). The field sweep was calibrated using a deuterium nmr probe, and polycrystalline DPPH was used as a g marker. The klystron frequency was measured directly with a wavemeter.



I

copper diethyldithiocarbamate

Rotation data were fitted by least squares to expressions of the type given by the Schonland,[8] diagonalization then giving the eigenvalues and vectors for the g and hyperfine tensors. Second-order corrections to line positions were made.

The crystal structures of the copper,[9] nickel,[7] and zinc[6] diethyldithiocarbamates have been given by Bonamico and coworkers. In Zn(dtc)$_2$, the geometry of the sulfur atoms about the metal ion may be considered either as distorted trigonal bipyramidal or distorted square pyramidal, by way of a dimeric structure. Cu(dtc)$_2$ has a similar structure, though a small change in the metal ion position leads to a configuration which is somewhat closer to planar four-coordination. The Ni(dtc)$_2$, however, shows a rigorously planar four-coordinate structure, with no apparent bonding to sulfur atoms of neighboring molecules. The local symmetry about the metal ion is nearly D_{2h}.

Molecular weight measurements were made on copper diethyldithiocarbamate in chloroform solution using a Mechrolab vapor phase osmometer. The solution species is monomeric.

Results

In Table I are given the calculated direction angles, relative to certain crystallographic axes, for the mean molecular axes, z and x, or the mean vector direction for S(4)–M–S(1) (see I) in the case of the (Zn,Cu)(dtc)$_2$ system. Also given are the principal values for the g and hyperfine tensors, together with the direction angles for the principal axes relative to the crystallographic axes. The absolute signs of the principal hyperfine values are discussed below. They are concluded to be negative in the present case.

TABLE I

PRINCIPAL VALUES AND AXES FOR THE g AND HYPERFINE TENSORS

(Cu,Ni)(dtc)$_2$					(Cu,Zn)(dtc)$_2$				
		Direction angles,[a] deg					Direction angles,[a] deg		
Parameter	Value	b	c	$\perp c$	Parameter	Value	b	c	$\perp c$
$\mathbf{z}^c$		61.7	35.2	71.3	$\mathbf{z}$		59.6	101.0	33.4
x^c		43.5	125.0	67.6	S(4)–M–S(1)^c		33.2	85.5	120.4
$g_1{}^a$	2.020	45.3	127.0	67.6	$g_1{}^a$	2.025	33.3	84.3	123.0
g_2	2.025	123.0	96.4	33.8	g_2	2.033	88.6	12.4	77.7
g_3	2.084	62.8	37.7	66.0	g_3	2.107	56.4	101.0	35.8
$A_1{}^{a,b}$	36	46.8	128.0	67.0	$A_1{}^{a,b}$	7	32.7	81.1	121.0
A_2	42	123.7	95.3	34.5	A_2	27	88.1	14.0	76.2
A_3	159	62.0	38.5	66.0	A_3	143	57.3	100.5	34.8

[a] Estimated errors for eigenvectors g_1, g_2, A_1, and A_2, ±3.5°; g_3 and A_3, ±1.0°; eigenvalues g_1 and g_2, ±0.001; g_3, ±0.0005; A_1 and A_2, ±2.5; A_3, ±1.0. [b] Copper-63; for discussion of sign see text; A_i in cm^{-1} × 10^4. [c] See structure I.

The spin Hamiltonian used in the analysis of the data may be written

$$\mathcal{H} = g_{xx}S_xH_x + g_{yy}S_yH_y + g_{zz}S_zH_z + A_{xx}I_xS_x + A_{yy}S_yI_y + A_{zz}I_zS_z$$

where S and I are the electron and nuclear spins, respectively. This assumes that $\mathbf{g}$, the g tensor, and $\mathbf{A}$, the hyperfine tensor, have the same axis system. The agreement, within experimental error, between the values found for the direction angles for the g and hyperfine tensors suggests (Table I) that this assumption is valid. If it were not true, cross terms would have to be included in the above expression.

For the doped Zn(dtc)$_2$, agreement is found to be fair between the direction angles determined for g_3 and those calculated for the z direction, *i.e.*, the normal to the least-squares plane through the four sulfur atoms of the formula unit. The dot product between the axis g_3 and $\mathbf{z}$ shows that there is an angle of 2.5° between the two vectors. Of the two principal axes that must lie in the mean plane of the sulfur atoms, g_1 lies along the S(4)–M–S(1) direction. This direction contains the pair of bonds that are considerably elongated in the zinc complex.[6] These results imply that the copper ion occupies a site in the doped Zn(dtc)$_2$ similar to that which it occupies in Cu(dtc)$_2$. Hence the copper ion appears to be

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[6] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19**, 898 (1965).

[7] M. Bonamico, G. Dessy, C. Mariani, A Vaciago, and L. Zambonelli, *ibid.*, **19**, 619 (1965).

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[9] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19**, 886 (1965).

closer to the plane of the sulfur atoms than is the zinc ion, while it experiences the marked disparity in bond lengths of the zinc complex. For $Cu(dtc)_2$ doped in $Ni(dtc)_2$, the axis g_3 is again close to the calculated normal to the plane of the sulfurs. The dot product shows an angle of 5° between these latter two vectors, considerably outside experimental error and larger than that found for the doped zinc complex where the deviations from the plane are significant. This result may indicate that the substitution of nickel by copper has not taken place entirely without lattice distortion. However, the in-plane principal g axes bisect the S–M–S bond angles consistent with a local D_{2h} symmetry.

The magnetic parameters in solution are given in Table II together with the averaged g and hyperfine values obtained from the doped crystals. To check the results from the single-crystal studies the powder epr spectra were taken of $Cu(dtc)_2$ doped into the zinc and nickel complexes. The values obtained for $g_{||}$, $g_{\perp}$, and $A_{||}$, $A_{\perp}$ (where the symbols $||$ and $\perp$ refer to the values parallel with or perpendicular to the average plane of sulfur atoms) agreed very closely with the values found from the single-crystal studies. The in-plane anisotropy could not be effectively resolved and g was compared with the mean of g_1 and g_2. The hyperfine data were treated similarly.

Table II

Averaged Magnetic Parameters in the Solid State and in Solution

	$\langle g\rangle^a$	$A_{iso}{}^{a,b}$	$A_{anis}{}^b$
$(Cu,Zn)(dtc)_2$	2.055	59	42
$(Cu,Ni)(dtc)_2$	2.043	79	40
$Cu(dtc)_2$ $CHCl_3$ soln	2.045	80	

[a] For solid-state $\langle g\rangle$, A_{iso} is the mean of the principal values. [b] See eq 5 in text. A_i in $cm^{-1} \times 10^4$.

An absolute sign for the principal values of the hyperfine tensor can be ascertained when forbidden transitions ($\Delta m = \pm 1$) are observed in the crystal spectra,[10] though such transitions were not seen in the present study. For copper(II), both the isotropic and anisotropic hyperfine splittings (eq 5) have been predicted to be negative.[11,12] In those studies in which the sign could be determined, A_z has indeed been found to be negative,[13] and this is taken to be the case here. From the magnitude of the averaged hyperfine splitting in solution (Table II), it can be seen that all three principal values of the hyperfine tensor must have the same sign.

Discussion

For $Cu(dtc)_2$ doped in $Zn(dtc)_2$ the results show that the effective environment about the copper ion, as noted above, is approximately planar, while the in-plane distortion is demonstrated in the orientation of the magnetic eigenvectors. For the purposes of evaluating molecular orbital (MO) coefficients it would seem a poor approximation to use D_{2h} or D_{4h} symmetry in setting up the necessary equations, if the magnetic parameters from the doped zinc complex were to be used. Thus, in discussing the MO coefficients we will use the results from the doped nickel complex where the symmetry is more clearly defined.

The two previous studies of the present system[3,4] and also the study of Gersman and Swalen[14] utilized a slight extension[15] of the treatment given by Maki and McGarvey[5] to obtain MO coefficients, assuming D_{4h} symmetry. The necessary molecular orbitals are of the type given in eq 1–3, where S is the group overlap integral.

$$\mathrm{b_{1g}} = \alpha \mathrm{d}_{x^2-y^2} - \alpha'(-\sigma_x{}^{(1)} + \sigma_y{}^{(2)} + \sigma_x{}^{(3)} - \sigma_y{}^{(4)})/2 \qquad (1)$$

$$\mathrm{b_{2g}} = \beta \mathrm{d}_{xy} - \beta'(\mathrm{p}_y{}^{(1)} + \mathrm{p}_x{}^{(2)} - \mathrm{p}_y{}^{(3)} - \mathrm{p}_x{}^{(4)})/2 \qquad (2)$$

$$\mathrm{e_g} = \begin{matrix} \gamma \mathrm{d}_{xz} - \gamma'(\mathrm{p}_z{}^{(1)} - \mathrm{p}_z{}^{(3)})/\sqrt{2} \\ \gamma \mathrm{d}_{yz} - \gamma'(\mathrm{p}_x{}^{(2)} - \mathrm{p}_x{}^{(4)})/\sqrt{2} \end{matrix} \qquad (3)$$

$$\sigma^{(i)} = n\mathrm{p}^{(i)} \pm (1 - n^2)^{1/2}\mathrm{s}^{(i)}$$

$$\alpha^2 - 2\alpha\alpha' S + \alpha'^2 = 1$$

There is general agreement that the *in-plane σ bonding is rather covalent* ($\alpha^2 = 0.5$–0.6).[4,14] However, the results for the π bonding have been somewhat diversified, due, not so much to variations in magnetic results, but to uncertainties in the energies and assignments of electronic transitions. This uncertainty remains, unfortunately, and the discussion will in general be formulated in terms of D_{4h} symmetry. A reduction to D_{2h} symmetry would give equations for g_1 and g_2 that differ only in the MO coefficient labels and the values of the excitation energies, though the full expression would require differences in the overlap for the x and y out-of-plane π bonding.

The full expressions for the g and hyperfine values, in terms of the parameters used in Table III, are not given here as they are listed in the literature.[13,15]

Table III

Molecular Orbital Coefficients Obtained from the Epr Data[a]

	$V_L = 0.00^b$				$V_L = 0.45^b$			
Input[c]	α	α'	β	γ	α	α'	β	γ
	0.74	0.77	0.72	0.82	0.74	0.78	0.84	0.91
$S = 0.05$	0.72	0.70	0.70	0.79	0.72	0.70	0.80	0.88
$S = 0.20$	0.76	0.82	0.75	0.84	0.76	0.82	0.89	0.95
$T(n) = 0.05$	0.71	0.80	0.69	0.77	0.71	0.80	0.80	0.87
$\Delta_2 = 16,000$	0.74	0.77	0.72	0.76	0.74	0.77	0.85	0.88
$\Delta_2 = 24,000$	0.74	0.77	0.72	0.87	0.74	0.78	0.86	0.96
d	0.76	0.75	0.77	0.87	0.76	0.75	0.88	0.95

[a] Values of input parameters, unless otherwise specified in the table: $A_{||} = 0.016$ cm^{-1}; $A_{\perp} = 0.004$ cm^{-1}; $g_{||} = 2.084$; $g_{\perp} = 2.023$; $\lambda = 828$ cm^{-1}; $\Delta_1 = 16{,}000$ cm^{-1}; $\Delta_2 = 20{,}000$ cm^{-1}; $S = 0.125$; $T(n) = 0.35$; $P = 0.036$ cm^{-1}. See text for significance of symbols; metal–ligand overlap is only included for the b_{1g} MO. See eq 1. [b] $V_L = \xi_{lig}/\xi_d$, where ξ_{lig} and ξ_d are the one-electron SOC constants on ligand atom and metal ion, respectively. [c] Parameter value not as listed above. [d] $A_{||} = 0.0143$; $A_{\perp} = 0.002$; $g_{||} = 2.107$; $g_{\perp} = 2.029$. Data for $(Cu,Zn)(dtc)_2$.

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[11] H. A. Kuska and M. T. Rogers, to be submitted for publication.

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[15] D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).

Following ref 15, we have

$$\alpha^2 = (-A_{\parallel}/P) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04$$

where $P = 2\gamma_N\beta_N\beta_0\langle r^{-3}\rangle$, γ_N is the gyromagnetic ratio of the nucleus in question, β_N is the nuclear magneton, β_0, the Bohr magneton, and $\langle r^{-3}\rangle$ is the mean inverse cube vacancy–metal nucleus distance. This is based on the assumption that $\kappa = \alpha\kappa_0$, where κ and κ_0 are the Fermi contact terms (in units of P) in the complex and free metal ion, respectively. The results of Kuska and Rogers[16] have shown, however, that this is not a good approximation, and the expression may be rewritten in terms of the isotropic hyperfine constants A_s and isotropic g factor g_s[11]

$$\alpha^2 = \frac{7}{4}\left[(A_s/P) - (A_{\parallel}/P) + (g_{\parallel} - g_s) + \frac{3}{7}(g_{\perp} - 2.0023) + \text{small terms}\right] \quad (4)$$

Thus an initial value of α may be obtained without any knowledge of the excitation energies, those of interest here being $\Delta_1(d_{x^2-y^2} \rightarrow d_{xy})$ and $\Delta_2(d_{x^2-y^2} \rightarrow d_{xz})$. The treatment of ref 11 neglects ligand spin–orbit coupling (SOC). As discussed by McGarvey,[13] this may not be a good approximation for sulfur-bonded ligands. We have evaluated sets of MO coefficients both excluding and including SOC to estimate the importance of this term. The coefficients were also checked for their sensitivity to the parameters about which there is some uncertainty in the numerical value. The free ion value was used for λ (SOC constant), and any reduction due to shielding leads to a small effect on the MO coefficients. The electronic spectrum of $Cu(dtc)_2$ in solution shows a shoulder at ~16,000 cm^{-1} (ϵ_0 ~700), which may be assigned to a d–d transition, probably Δ_1, a value similar to that seen for $Cu(i\text{-mnt})_2$.[17] In two earlier studies,[3,4] the positions of what are probably two charge-transfer bands, occurring at higher energy, were used for Δ_1 and Δ_2, leading to rather high values for the MO coefficients for the d orbitals in the antibonding MO's. These charge-transfer bands obscure the region above ~6000 Å and thus no value can be given for Δ_2, though it is presumably $\geq$ 16,000 cm^{-1}. Gersman and Swalen[14] have given a value of 0.005[4,14] for the group overlap integral $\langle d_{x^2-y^2}| -\sigma_x^1 + \sigma_y^2 + \sigma_x^3 - \sigma_y^4\rangle/2$, which seems rather low. We have used values up to 0.2.

The term $T(n)$,[5,15] an integral of ligand radial wave functions, has been evaluated by Pettersson and Vänngård[3] using hydrogen-like wave functions. To obtain a numerical value the state of hybridization must be known; sp^2 hybridization has been assumed in some previous studies. However, if the results of Pettersson and Vänngård[3] on the isotropic hyperfine interaction for ^{33}S are correct, then the s-orbital contribution is rather small. (We have attempted to observe the superhyperfine interaction in dilute crystals and solution but have not been able to make any definite assignments.)[18] Thus $T(n)$ could range from 0.66 (p_σ only) to 0.07 for sp^2 hybridization.

In Table III is shown a selection of the results obtained from the calculation of the MO coefficients using various values for the input parameters. The inclusion of ligand SOC, $V_L = 0.45$ (Table III), is seen to lead to a significant reduction in the extent of the ligand character in the π orbitals, while the effect on the σ term is negligible. The values of α, β, and γ are primarily dependent on $A_{\parallel}$, $g_{\parallel}$, and $g_{\perp}$, respectively, as is shown by the virtually unchanged values of α and β as Δ_2 is altered. The small effect on α of inclusion of ligand SOC is expected from a consideration of the form for $A_{\parallel}$,[13] where the terms containing V_L (see Table III) are small. Thus, whether or not ligand SOC is considered, the present data lead to highly covalent σ bonding, *via* eq 4.

The expressions used in the above treatment are deficient in that they do not contain terms in the charge-transfer (CT) transitions. These CT expressions are of the same form as those for the d–d transitions with certain terms dropped. For the present complexes the CT terms could be of some importance in that it is clear from the electronic spectrum that CT transitions occur at fairly low energy (~25,000–30,000 cm^{-1}), though the symmetry is not known and they could be noninteracting. The spin–orbit coupling constant will be of the same sign for both the d–d and CT terms. The latter would then make a positive contribution to the g value, the calculated MO coefficients above accordingly being too large.

It was considered of interest to compare the results from the epr investigation with calculated molecular orbital coefficients obtained using the current Wolfsberg–Helmholtz (WH) iterative extended Hückel approach. The general procedure that was used is given in some detail in ref 19. MO's (π) on the ligand, perpendicular to the plane of the complex, were obtained from a separate Hückel calculation fitted to the optical spectrum of the sodium salt of the ligand. Metal and ligand orbitals were then combined under D_{2h} symmetry. The Coulomb integrals (charge and configuration dependent) were approximated by valence orbital ionization potentials.[20] Iteration was carried out to charge and configuration consistency using a Mulliken population analysis on each cycle. The one-electron orbital energies obtained gave a reasonable ordering and ground state ($^2B_{1g}$), Table IV. The en-

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(16) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **43**, 1744 (1965).

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(18) We are at present studying dilute single crystals of copper diethyldithiophosphate in which the ^{31}P superhyperfine interaction is clearly observed.

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(20) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 458 (1965). Overlap integrals were calculated using a program written by Peter O'D. Offenhartz (Amherst College) for atom wave functions expressed as linear combinations of Slater-type orbitals. Radial wave functions for copper were taken from Richardson, *et al.*, *J. Chem. Phys.*, **36**, 1057 (1962), and for the ligand atoms from E. Clementi, Tables of Atomic Functions, Supplement to *IBM J. Res. Develop.*, **9**, 2 (1965).

Table IV

Calculated Orbital Energies (Wolfsberg–Helmholtz)

MO	Type[a]	Energy,[b] cm^{-1} × 10^3
$5a_g$	4s	50.4
$4b_{1u}$	$4p_z$	−3.9
$3b_{3u}$, b_{2u}	$4p_x$, $4p_y$	−21.6
$4b_{2g}$	L_π	−66.0
$3b_{1u}$	L_π	−66.7
$3b_{1g}$	$3d_{xy}/S_\sigma$	−74.9
$4a_g$	$3d_{x^2-y^2}/S_\pi$	−82.2
$2b_{3g}$	$3d_{yz}/L_\pi$	−87.6
$3b_{2g}$	$3d_{xz}$	−92.6
$3a_g$	$3d_{z^2}$	−95.8
$2b_{1g}$	S_π	−100.0
$2b_{3u}$,b_{2u}	S_σ	−100.0
$1a_u$	L_π	−100.0
$1b_{3u}$, b_{2u}	S_π	−100.5
$2b_{1u}$	L_π	−105.8
$1b_{3g}$	$3d_{yz}/L_\pi$	−107.9
$2b_{2g}$	L_π	−108.6
$2a_g$	$3d_{x^2-y^2}/S_\pi$	−111.1
$1b_{1g}$	$3d_{xy}/S_\sigma$	−114.8
$1a_g$	S_σ	−120.1
$1b_{1u}$	L_π	−133.4
$1b_{2g}$	L_π	−133.5

[a] MO type: L_π significantly based on a ligand π orbital perpendicular to the plane of complex; S_σ/S_π significantly based on in-plane sulfur σ/π orbitals. [b] Changes of several thousand cm^{-1} in the ligand atom Coulomb integrals do not affect the relative ordering of the predominantly metal atom based MO's.

ergy level spacings of the predominantly d-orbital-based MO's were somewhat smaller than would be expected from the optical spectrum of the complex, *e.g.*, $4a_g \rightarrow 3b_{1g}$ is calculated to be 7300 cm^{-1}, while the first observed electronic transition (>4000 cm^{-1}), appears at 16,000 cm^{-1}. There are numerous variations that can be made on the calculational theme, and it is possible that a more empirical treatment of the ligand Coulomb terms would improve the energy level spacings.[21] The MO coefficients from the epr data and those for the relevant metal d orbital from the Wolfsberg–Helmholtz calculation are given in Table V, the agreement being qualitatively satisfactory. The implication in the WH calculated MO's of rather more extensive π bonding may well be a consequence of the approximations used;[22] a similar discrepancy has been noted previously.[23] In that the value of α (eq 1) from the epr data is not sensitive to the overlap, degree of hybridization, or spectral assignments, the agreement between the two sets of coefficients might be expected to be best for the in-plane σ bond.

Table V

MO Coefficients from Epr Data and WH Calculations

	$\alpha(x^2 - y^2)$[a]	α'	$\beta(xy)$	$\gamma(xz, yz)$
Epr[b]	0.759	0.821	0.892	0.945
Calcd	0.808	0.766	0.792	0.891, 0.786

[a] See eq 1–3. [b] Table III: $S = 0.20$, $V_L = 0.45$.

The results given here for Cu(dtc)$_2$ can be compared with those from Cu(mnt)$_2^{2-}$ in dilute single crystals.[24] Both complexes give magnetic and hyperfine parameters that are very similar, though the value of Δ_1 for Cu(mnt)$_2^{2-}$ appears to be only 8300 cm^{-1}.[25] The MO coefficients for the in-plane σ bonding from the epr data will thus be essentially the same for the two complexes. The amount of metal character calculated for the b_{2g} (d_{xy} in D_{4h}) orbital will, however, be considerably smaller for Cu(mnt)$_2^{2-}$. This is reflected in the calculated eigenvectors given by Shupack, *et al.*,[26] there being significantly metal-based excited states lying at higher energy. The similarity that has been noted for the *g* and hyperfine parameters for a range of sulfur-bonded chelates would appear to be due to a compensation of effects. The observed small in-plane anisotropy of the *g* tensor for Cu(dtc)$_2$ would be consistent with the calculated ordering of the out-of-plane π orbitals, in which the orbital with the largest metal character, d_{xz}, lies at lower energy than the orbital of d_{yz} symmetry.[27]

Since Cu(dtc)$_2$ is monomeric in solution, we might expect the molecule to adopt an essentially planar configuration. The observed similarity between the *g* and hyperfine parameters from solution and the averaged parameters for Cu(dtc)$_2$ doped in the nickel complex suggest that this interpretation of the solution structure is correct (Table II).

The hyperfine data from both the doped nickel and zinc complexes, using the mean of the in-plane parameters, may be fitted to eq 5 to obtain the values given in

$$\begin{aligned} A_{\parallel} &= A_{\text{iso}} + 2A_{\text{anis}} \\ A_{\perp} &= A_{\text{iso}} - A_{\text{anis}} \end{aligned} \tag{5}$$

Table II. In eq 5 A_{iso} and A_{anis} are isotropic and anisotropic dipolar hyperfine splitting, respectively. Thus, on lowering the geometry about the metal ion from D_{2h} to C_1, the most significant change is in the isotropic as opposed to the anisotropic hyperfine interaction (Table II). This result can be examined in relationship to some of the mechanisms proposed for the origin of the contact interaction. It is suggested that the isotropic contact term arises in part from an exchange polarization of core s electrons by the unpaired d electron.[28,29] Calculation has indicated that the net spin at the nucleus from this effect will be negative.[30,31] If the s and d orbitals transform similarly under the symmetry of the complex, then mixing will occur, leading to a direct contribution to the isotropic contact term of positive sign. The observed negative sign for A_{iso} is then attributed to the greater magnitude of the exchange polarization term. In D_{2h} symmetry there will be no mixing of the s orbital (a_g) with the or-

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bital containing the unpaired electron (b_{1g}). However, on lowering the symmetry about the metal ion, as when going from the nickel to the zinc host lattice, increased mixing of the s and d orbitals may occur. This increased mixing would lead to a more positive value for A_{iso}, consistent with the present results. It may be noted that displacement toward a distorted tetrahedral configuration leads to a mixing in of the 4p orbitals.[32] It is suggested[32] that this could lead to a shift in the isotropic interaction but would also give appreciable reduction in the anisotropic interaction, in contrast to the present results. Thus, mixing of the 4p orbitals is not anticipated to be a significant factor.

An entirely parallel reduction in A_{iso} is seen on base adduct formation. Thus, for $Cu(dtc)_2$ in a frozen glass of 40:60 $CHCl_3$–toluene, $A_{iso} = 78 \times 10^{-4}$ cm^{-1},[14] while in 40:60 $CHCl_3$–pyridine glass, $A_{iso} = 60 \times 10^{-4}$ cm^{-1}.[14]

Acknowledgment.—The support of the National Science Foundation, under Grant GP-7889, is acknowledged. Thanks also are extended to the Ferro Corp. which has made possible certain aspects of this study through a grant to the CWRU Center for the Study of Materials.

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Synthesis of Some Pyrochlore-Type Oxides of Platinum(IV) at High Pressure[1]

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Received July 11, 1968

The synthesis of 15 cubic pyrochlore-type double oxides, $A_2Pt_2O_7$, is described. The trivalent A atoms may be scandium, indium, yttrium, or any rare earth from praseodymium through lutetium. Cell parameters are reported and compared with other pyrochlore series. Thermal analysis shows that most platinum pyrochlores are stable to at least 1000°. Infrared spectra to 95 cm^{-1} are presented and interpreted.

We reported recently on the high-pressure synthesis of a new oxide of platinum, $Tl_2Pt_2O_7$.[2] Although pressure is frequently used to force an ion into an unusually high coordination configuration, it was employed in this instance to prevent decomposition of two reactants at the temperature required to achieve complete reaction and good product crystallinity. The crystal structure of $Tl_2Pt_2O_7$ could not be unambiguously determined from X-ray powder data, but the composition, the radii of its cations, and the properties of the double oxide all strongly suggest that the structure is that of pyrochlore, space group Fd3m.

In the general pyrochlore formula, $A_2B_2O_7$, the A atoms may be divalent with pentavalent B or trivalent with tetravalent B. The approximate radius range reported for A ions is 0.75–1.05 Å (based on Templeton and Dauben radii[3]) and for B ions is 0.6–0.8 Å. Details of the structure have been given by several workers.[4,5] Very briefly, the A and B atoms together with one of the oxygen atoms (O_I) occupy special positions in the unit cell. The remaining six oxygen (O_{II}) atom sites contain a single variable parameter, $x(O_{II})$. Each B atom is bonded to six O_{II} atoms in a trigonal antiprism, and each A atom forms two short collinear bonds to O_I atoms and six longer bonds to O_{II} atoms lying near a plane normal to the A–O_I axis.

Pyrochlore series in which trivalent rare earths constitute the A atoms and in which titanium, ruthenium, iridium, and tin constitute the B atoms have been reported.[6–12] In addition, partial series have been prepared with tetravalent technetium,[13] zirconium,[14] and hafnium.[15] Since high pressure proved to be an effective technique in the synthesis of the thallium–platinum pyrochlore, the same procedure has now been used to study the reaction of platinum dioxide with a series of metal sesquioxides.

Experimental Section

Platinum dioxide was prepared by the reaction of K_2PtCl_6 with molten KNO_3 at 400°. Reaction appeared to be complete within minutes, but heating was continued for at least 24 hr to

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