intermediates were estimated in a slightly different manner for the nickel, calcium, cadmium, and strontium reactions. The approach employed here causes only small changes in these values but gives a much better fit between experimental and predicted rate constants for the lead and copper reactions than would the previous estimation method.[9]

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Registry No. Cu(EDTA)$^{2-}$, 14951-91-8; EDTA, 150-43-6.

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Polarized Optical Absorption Studies on Copper and Silver Diethyldithiocarbamates

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Polarized optical absorption measurements are reported for bis(*N,N*-diethyldithiocarbamato)copper(II) and -silver(II) diluted in the corresponding zinc complex. The measurements have been made at room, liquid nitrogen, and helium temperatures. The results for the copper complex are at variance with those reported earlier by Reddy and Srinivasan. The electronic transition energies are used in conjunction with the previously reported spin-Hamiltonian parameters to derive the molecular orbital coefficients for the two complexes.

I. Introduction

N,N-Diethyldithiocarbamate (detc), $[(C_2H_5)_2NCS_2]^-$, is a rare case of a nonreducing sulfur-containing ligand which is able to coordinate with copper and silver in their formal oxidation state of 2+. In fact Ag(detc)$_2$ is one of the few known silver(II) complexes. Earlier reports on the optical absorption studies on Cu(detc)$_2$[2-4] seem to have completely missed the low-energy bands in the visible region, which is well resolved even in solution. In the case of Ag(detc)$_2$ only a broad band has been reported[3,4] in the visible region. Recently van Rens[5] has reported the EPR results on Ag(detc)$_2$. No attempt has been made so far to study in detail the optical absorption of the silver complex in a single crystal. It was thought worthwhile to undertake such a study for both the copper and the silver complexes, because the complete assignment of the electronic transitions will lead to a better understanding of the electronic structure of the complexes in the light of the spin-Hamiltonian parameters obtained earlier by the EPR studies.

II. Experimental Section

The diethyldithiocarbamates of Cu(II), Ag(II), and Zn(II) were prepared by the methods reported in the literature.[3,6] Single crystals were grown by slow evaporation of a solution of Zn(detc)$_2$ in benzene containing about 1–2% of the corresponding Cu(II) or Ag(II) complex. Large (4 mm × 2 mm) crystals in the form of parallelepipeds or hexagonal plates were obtained. The *a* axis of the crystal was identified as one of the crystal edges based on the morphology reported earlier.[2]

Optical absorption measurements were made using a Carl-Zeiss DMR-21 recording spectrophotometer, modified to accommodate polarizer prisms and a liquid nitrogen cryostat, and a Cary Model 17 spectrophotometer. For measurements below liquid nitrogen temperature the crystal was cooled by controlled boil-off from a liquid helium storage Dewar located underneath the Cary sample compartment. The polarization is referred to the *a* axis of the crystal with light incident on the (011) face.

III. Crystal Structure and Polarization of Absorption Bands

The crystal structures of Cu(detc)$_2$ and Zn(detc)$_2$ belong to the space group $P2_1/c$ with two pairs of centrosymmetrically related molecules per unit cell.[7] The copper and zinc compounds are isomorphous, though not exactly isostructural.[8] EPR results for Cu(detc)$_2$–Zn(detc)$_2$[9] and Ag(detc)$_2$–Zn(detc)$_2$[5] suggest that in mixed crystals, the copper and silver complex molecules assume a configuration more similar to that of pure Cu(detc)$_2$ rather than that of Zn(detc)$_2$. However, their principal axes remain identical with those of Zn(detc)$_2$. The complex molecules belong to a local symmetry of C_{2v} with the metal ion slightly raised above the plane of the sulfur atoms. The *x* axis is chosen as the one bisecting the projection of the shorter S–Zn–S angle as shown in Figure 1.

The relative orientations of the two molecular units have been discussed earlier.[2] The tetragonal axis of one of the molecules is in the (011) plane while that of the other is 50° out of this plane. The *a* axis bisects the projection angle which is also 50°. The usual analysis of polarization amplitudes leads to the following expressions for the intensity of absorption of the light polarized parallel and perpendicular with respect to the tetragonal axis of the complex molecule

$$I_{\parallel} = \frac{1.16 I_{\parallel}^{a} - 0.25 I_{\perp}^{a}}{1.28} \qquad (1)$$

$$I_{\perp} = \frac{1.16 I_{\perp}^{a} - 0.25 I_{\parallel}^{a}}{1.28} \qquad (2)$$

Here the superscript "*a*" refers to the polarization with respect

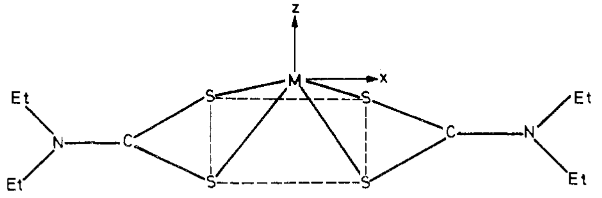

Figure 1. Molecular geometry of $Zn(detc)_2$.

to the crystallographic *a* axis which is the experimentally measured quantity.

IV. Results and Discussion

1. Assignment of the Electronic Transitions. Of the four possible spin-allowed transitions only $^2A_2 \rightarrow {}^2B_1$ and $^2A_2 \rightarrow {}^2B_2$ ($xz \rightarrow xy$ and $yz \rightarrow xy$ in one-electron terminology) are allowed in C_{2v} symmetry and they are *y* and *x* polarized respectively. Figures 2 and 3 show the spectra respectively of $Cu(detc)_2$ and $Ag(detc)_2$ measured at various temperatures, with the electric vector parallel and perpendicular to the crystallographic *a* axis. The room-temperature spectra are similar to those at lower temperatures but are less resolved. Absence of any remarkable temperature dependence of band intensities shows that all of the observed bands correspond to orbitally allowed transitions. Figures 4 and 5 clearly show the polarization characteristics of the absorption bands at 7 K respectively in $Cu(detc)_2$ and $Ag(detc)_2$ relative to the tetragonal axis of the molecules.

Table I. Band Maxima (Perpendicular Polarization) for $Cu(detc)_2$ at 7 K and $Ag(detc)_2$ at 8 K

Band position, cm^{-1}	Assignment	Band position, cm^{-1}	Assignment
		(i) $Cu(detc)_2$	
14 480	$^2A_2 \rightarrow {}^2B_1$	21 800	$p\pi \rightarrow d\pi$
18 600	$^2A_2 \rightarrow {}^2B_2$	25 640	$p\pi \rightarrow d\pi$
		(ii) $Ag(detc)_2$	
16 000	$^2A_2 \rightarrow {}^2B_1$	22 100	$^2A_2 \rightarrow {}^2B_2$

The band maxima and their polarizations for $Cu(detc)_2$ are presented in Table I. It is not possible to assign all four (*x*, *y*) polarized bands as arising from d–d transitions. A lowering of symmetry from C_{2v} to C_2 will allow the otherwise forbidden transitions only in (*z*) polarization. The crystals were checked by EPR for the absence of dimer formation. Even concentrated crystals, where dimers were observed by EPR, did not show relative enhancement of any of the four bands, indicating that none of the observed bands have contributions from the dimers. Moreover, the axial perturbation caused by the remotely situated fifth sulfur atom should be expected to be too weak to have any observable effect on the electronic spectrum. The lowest energy band at 14 480 cm^{-1} and the shoulder at 18 560 cm^{-1} can be unambiguously assigned to $^2A_2 \rightarrow {}^2B_1$ and $^2A_2 \rightarrow {}^2B_2$, respectively. These two bands are probably remaining unresolved in the broad band with a maximum at 21 980 cm^{-1} reported earlier by Reddy and Srinivasan.[2] The above assignment corresponds to an *xz*, *yz* separation of 4080 cm^{-1}. Such a large separaton must be due to the large difference in π bonding involving d_{xz} and d_{yz} orbitals, brought about by the unsymmetrical dispositions of the sulfur atoms. Since the two bands at 22 990 and 26 810 cm^{-1} cannot be due to d–d transitions (vide infra), they must be charge-transfer bands. These two bands appear in benzene solution as a broad asymmetric band with a peak at 23 000

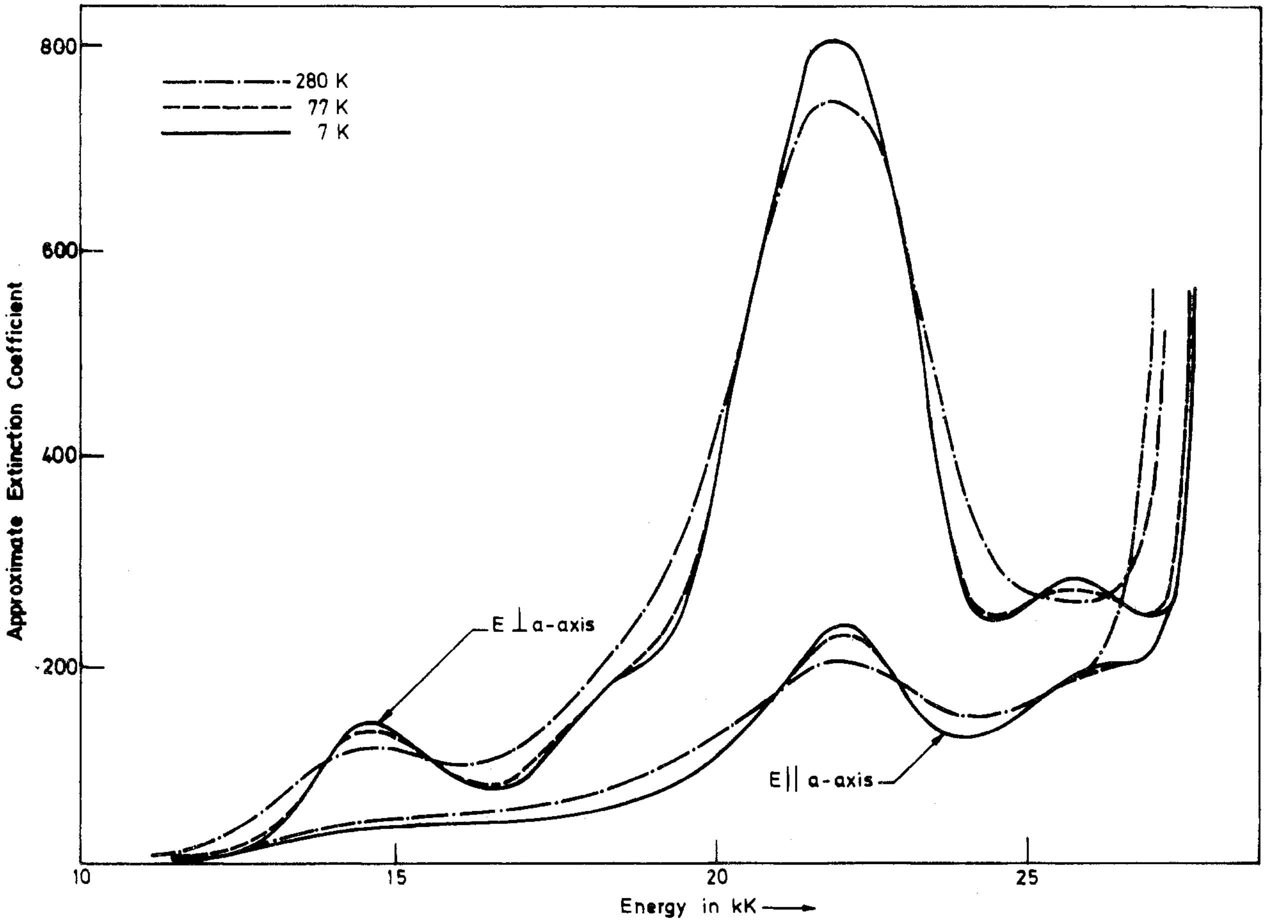

Figure 2. Polarized optical spectra of $Cu(detc)_2$ in $Zn(detc)_2$ at various temperatures. Polarizations are indicated with respect to the crystallographic *a* axis with the light incident on the (011) plane.

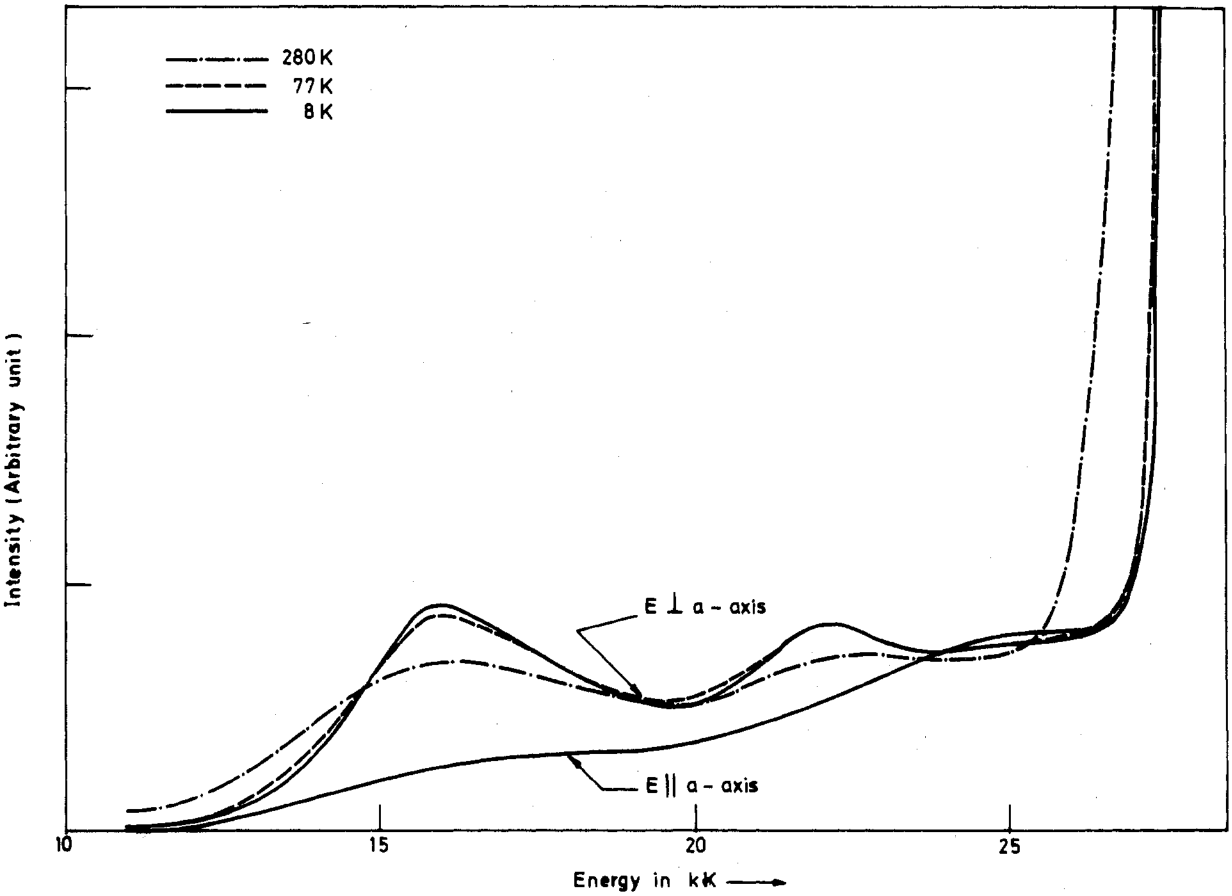

Figure 3. Polarized optical spectra of Ag(detc)$_2$ in Zn(detc)$_2$ at various temperatures. Polarizations are indicated with respect to the crystallographic *a* axis with the light incident on the (011) plane.

Table II. Ultraviolet Absorption Bands of Diethyldithiocarbamates in Chloroform Solution

Band position, cm^{-1}	Assignment	Band position, cm^{-1}	Assignment
	Na(detc)		
34 700	$p_\pi \rightarrow p_{\pi*}$	38 800	$p_\pi \rightarrow p_{\pi*}$
	Cu(detc)$_2$		
23 000	Composite band (see text)	34 500	$p_\pi \rightarrow p_{\pi*}$
32 000 sh	$d_\pi \rightarrow p_{\pi*}$	37 000	$p_\pi \rightarrow p_{\pi*}$
	Zn(detc)$_2$		
32 500 sh	$d_\pi \rightarrow p_{\pi*}$	38 500	$p_\pi \rightarrow p_{\pi*}$
35 970	$p_\pi \rightarrow p_{\pi*}$		

cm^{-1} (ϵ_{max} 750), which probably includes also the band at 18 560 cm^{-1} (see Figure 6). We can safely rule out the possibility of these being intraligand transitions, since in such a case they would have been too strong to be identified in the single crystal. In order to clarify the nature of the charge transfer we measured the ultraviolet spectrum of chloroform solutions of Cu(detc)$_2$, Zn(detc)$_2$, and Na(detc).[10] The band positions are given in Table II. By comparison with the bands in the free-ligand anion, the two highest energy bands in copper and zinc complexes can be assigned to pure ligand π–π^* transitions. It is worth mentioning here that the band at about 34 000 cm^{-1} was previously assigned to a metal d–d transition.[3] The shoulder at about 32 000 cm^{-1} is present in both copper and zinc complexes and hence should correspond to a metal–ligand charge transfer. Since there is no absorption in the zinc complex below 32 000 cm^{-1}, the two bands at 21 800 and 25 640 cm^{-1} can be confidently assigned to ligand to metal charge-transfer transitions.

The spectrum of Ag(detc)$_2$ is much simpler to understand. There are only two bands, at 16 000 and 22 100 cm^{-1}. Both are (x, y) polarized and are assigned to $^2A_2 \rightarrow {}^2B_1$ and $^2A_2 \rightarrow {}^2B_2$ transitions, respectively, which gives an xz, yz separation of about 6100 cm^{-1}. As expected, the transitions are shifted to higher energy compared to Cu(detc)$_2$. The ligand–metal charge-transfer bands must have been shifted to higher energy and are probably masked by the intense intraligand transitions. It is interesting to note that the xz, yz separations reported here are in good agreement with the WHMO calculations reported by Weeks and Fackler[9] for Cu(detc)$_2$ (5000 cm^{-1}) and van Rens[5] for Ag(detc)$_2$ (5600 cm^{-1}).

2. Calculation of Molecular Orbital Coefficients. The spin-Hamiltonian parameters for Cu(detc)$_2$[2] and Ag(detc)$_2$[5] determined by EPR can be utilized to derive the molecular orbital coefficients defined by the expressions for antibonding molecular orbital functions

$$\begin{aligned} \psi_1 &= \beta_1 d_{xy} - \beta_1'\phi_{1L} \\ \psi_2 &= \beta_2 d_{x^2-y^2} - \beta_2'\phi_{2L} \\ \psi_3 &= \alpha d_{z^2} - \alpha'\phi_{3L} \\ \psi_4 &= \epsilon_1 d_{xz} - \epsilon_1'\phi_{4L} \\ \psi_5 &= \epsilon_2 d_{yz} - \epsilon_2'\phi_{5L} \end{aligned} \tag{3}$$

where ϕ_{nL}'s are normalized symmetry-adapted linear combinations of ligand orbitals. Detailed expressions for g values and hyperfine coupling constants in terms of molecular orbital coefficients, transition energies, spin–orbit coupling constants, and overlap integrals may be found elsewhere.[11]

Since the $^2A_2 \rightarrow {}^2A_1$ transition energy for Cu(detc)$_2$ could not be obtained from the optical spectrum, we used the energy of the first ligand to metal charge-transfer band as an upper

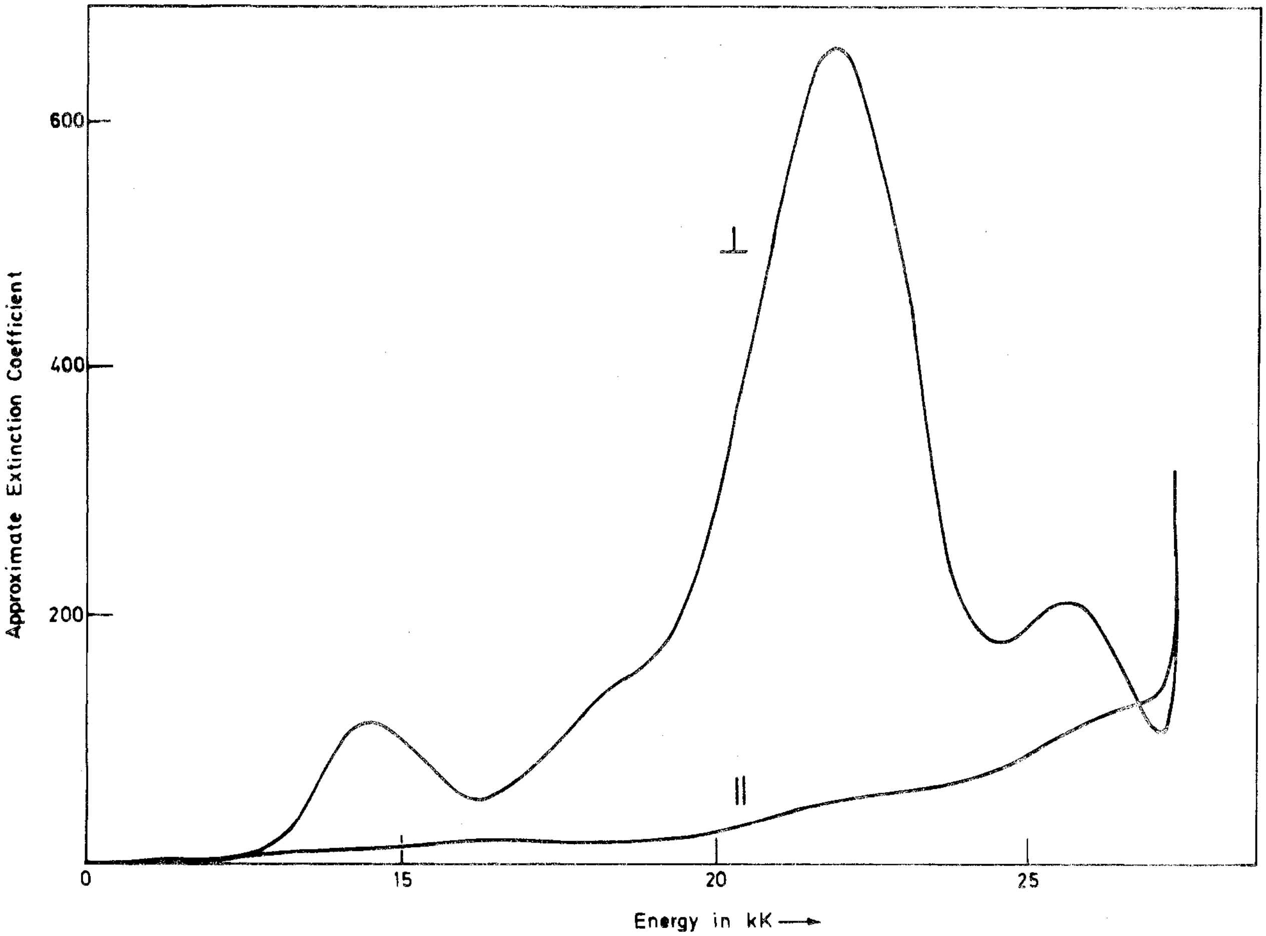

Figure 4. Calculated spectra of $Cu(detc)_2$ in $Zn(detc)_2$ with respect to the molecular tetragonal axis at 7 K.

limit for this transition. In the case of the silver complex we estimated a value of 25 640 cm^{-1} for this transition on the basis of the shift experienced by the $^2A_2 \rightarrow {}^2B_2$ transition on going from the Cu(II) to the Ag(II) complex and assuming that d_{yz} and $d_{x^2-y^2}$ are largely nonbonding. The uncertainty in the energy of the $^2A_2 \rightarrow {}^2A_1$ transition will affect the reliability of the value obtained for β_1. The overlap integrals were calculated using Clementi functions[12] for ligand s and p orbitals and double-ζ functions developed by Richardson et al.[13] for d orbitals. The calculated values are, for $Cu(detc)_2$, $S_{xy} = 0.0109$, $S_{xz} = 0.004\,11$, $S_{yz} = 0.0033$; and for $Ag(detc)_2$, $S_{xy} = 0.146$, $S_{xz} = 0.0604$, $S_{yz} = 0.0482$. The value of $S_{x^2-y^2}$ is taken to be zero in both cases. A value of 0.44 was used for the integral $T(n)$ as calculated by Gersmann and Swalen[14] which corresponds to a situation somewhere between pure $p\sigma$ orbital and sp^2-hybridized orbitals on sulfur. The spin–orbit coupling constant for copper and silver are −828 and −1843 cm^{-1}, respectively. With the above set of values the equations for **g** and **A** tensor components were iteratively solved for the molecular orbital coefficients. The values are tabulated in Table III.

In agreement with earlier reports[2,4,5,9] the in-plane σ bonding is more or less purely covalent in both $Cu(detc)_2$ and $Ag(detc)_2$ as can be seen from the value of β_1^2. In the case of silver complex the unpaired electron is in a largely ligand dominated molecular orbital. Increased covalency is to be expected in going from copper to silver and it is reflected in the magnitudes of the other coefficients as well. In the case of β_2, ϵ_1, and ϵ_2 the previous reports are in disagreement among themselves and with our results. This is mainly due to uncertainty in the assignment of the optical transitions rather than due to any significant differences in the EPR parameters. In contrast to earlier reports, our results indicate considerable in-plane and out-of-plane π bonding. The importance of π-type interaction is probably the reason for considerable differences[3] in the ease of formation of dithiocarbamate complexes having different alkyl substituents.

Table III. Square of MO Coefficients for $Cu(detc)_2$ and $Ag(detc)_2$

Coeff	$Cu(detc)_2$	$Ag(detc)_2$	Coeff	$Cu(detc)_2$	$Ag(detc)_2$
β_1^2	0.55	0.31	ϵ_1^2	0.43	0.34
$\beta_1'^2$	0.46	0.83	$\epsilon_1'^2$	0.57	0.72
β_2^2	0.73	0.56	ϵ_2^2	0.53	0.59
$\beta_2'^2$	0.27	0.44	$\epsilon_2'^2$	0.48	0.46

The Fermi contact term κ was calculated to be 0.44 in the case of $Cu(detc)_2$ while the values reported earlier are 0.23[2] and 0.27.[4] Our value is in better agreement with those reported for other copper complexes.[11,15] κ for $Ag(detc)_2$ was found to be 1.34 which is comparable with the results of van Rens,[5] who reported 1.084 for $Ag(detc)_2$–$Zn(detc)_2$ and 1.72 for $Ag(detc)_2$–$Ni(detc)_2$.

It must be pointed out that two factors have been neglected in the above calculations: (1) contribution from ligand spin–orbit coupling and (2) terms involving charge-transfer transitions, which should be of some importance in view of the fact that charge-transfer energies are fairly low for these complexes. It has been shown[9] that the contributions from the above two terms to the MO coefficients are opposite in sign. Hence they can be expected to cancel to some extent so that the qualitative arguments regarding bonding are unaffected.

In conclusion it can be said that the correct assignment of electronic transitions helps in extracting reliable information

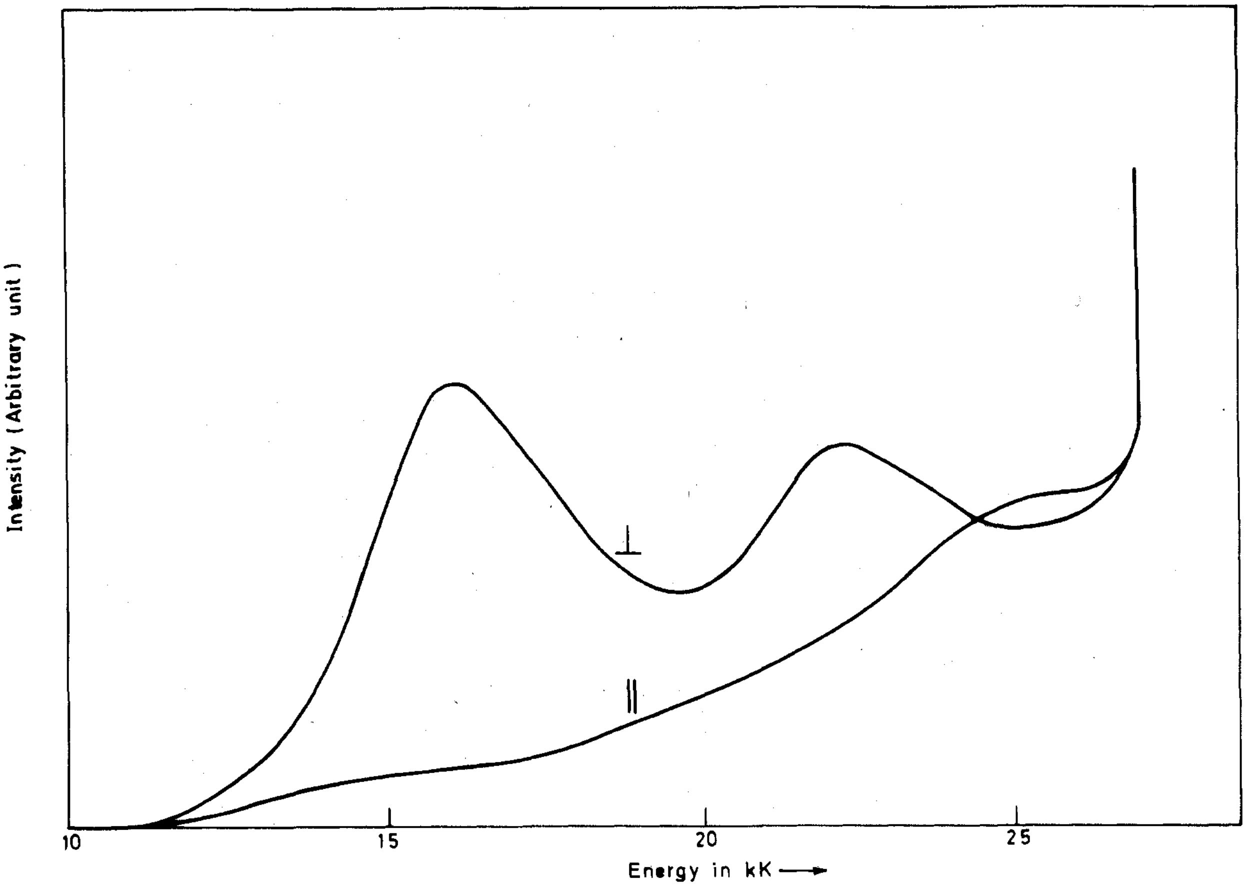

Figure 5. Calculated spectra of $Ag(detc)_2$ in $Zn(detc)_2$ with respect to the molecular tetragonal axis at 8 K.

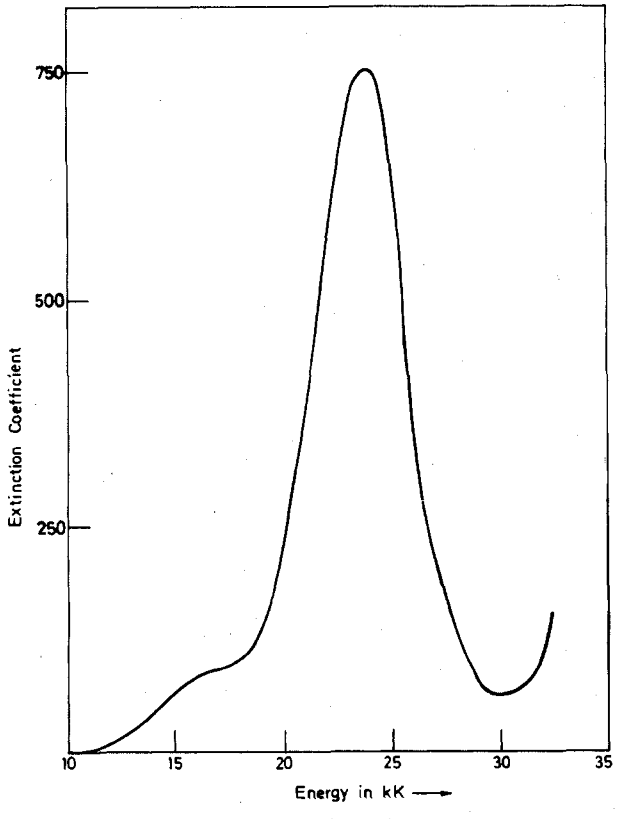

Figure 6. Optical spectrum of $Cu(detc)_2$ in benzene solution at 300 K.

from spin-Hamiltonian parameters. It should also be noted that near-axial symmetry of the spin Hamiltonian does not necessarily mean in-plane degeneracy in the molecular energy levels as is usually supposed.

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Oxidation–Reduction Properties of Peroxo- and Superoxo-Bridged Cobalt Complexes[1,2]

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Kinetics of reduction of a series of μ-peroxo-bridged cobalt complexes $[Co(en)_2(\mu\text{-}(O_2,OH))Co(en)_2]^{3+}$, $[Co(dien)(\mu\text{-}(O_2,OH))Co(dien)]^{3+}$, $[Co(trien)(\mu\text{-}(O_2,OH))Co(trien)]^{3+}$, and $[Co(tep)(\mu\text{-}O_2)Co(tep)]^{4+}$ by Fe^{2+} were studied, where en is ethylenediamine, dien is diethylenetriamine, trien is triethylenetetramine, and tep is tetraethylenepentamine. The rate is first order in both oxidant and reductant, with second-order rate constants $k_{2(en)} = 400 \pm 20$ M^{-1} s^{-1}, $k_{2(dien)} = 140 \pm 10$ M^{-1} s^{-1}, $k_{2(trien)} = 25 \pm 3$ M^{-1} s^{-1}, $k_{2(tep)} = 3.0 \pm 0.5$ M^{-1} s^{-1}. The data are explained in terms of an inner-sphere mechanism and compared with results previously obtained for μ-amino-μ-peroxo systems. For the corresponding μ-superoxo complexes $[Co(en)_2O_2Co(en)_2]^{5+}$, $[Co(trien)O_2Co(trien)]^{5+}$, and $[Co(tep)O_2Co(tep)]^{5+}$, $k_2'_{(en)} > 8000$ M^{-1} s^{-1}, $k_2'_{(trien)} = 430 \pm 10$ M^{-1} s^{-1}, and $k_2'_{(tep)} = 380$ M^{-1} s^{-1}.

Introduction

The nature of the bonding and reactivity of metal–dioxygen complexes has recently been the subject of intensive investigation.[4,5] Although factors influencing the thermodynamics[6] and kinetics[4d,7] of oxygen complexation are becoming better understood, the reactivities of such complexes, particularly the dioxygen moiety, remain to be elucidated. Recently Sykes[8] has reported a detailed study of the reduction of $[Co(en)_2(\mu\text{-}O_2,NH_2)Co(en)_2]^{3+}$ by Cr^{2+} and V^{2+} where en is ethylenediamine. This work is a progression from earlier studies of Taube[9] and Sykes and co-workers[10–12] on reduction of superoxo and peroxo oxygen complexes. However, no consistent series of complexes has been examined for the superoxo- nor peroxo-bridged complexes.

Since the superoxo complex is thought to be reduced by an outer-sphere mechanism[8,10–12] whereas an inner-sphere mechanism has been proposed for the reduction of the peroxo-bridged complex, it was felt that the study of a homologous series of compounds might shed some light on mechanistic details. Furthermore, in order to use the information gained from model compound studies in furthering our understanding of oxidase enzymes,[13] detailed knowledge of their redox chemistry is of fundamental importance. Thus we have examined the reduction by Fe^{2+} of the following μ-peroxo complexes: $[Co(en)_2(\mu\text{-}(O_2,OH))Co(en)_2]^{3+}$, $[Co(dien)(\mu\text{-}(O_2,OH))Co(dien)]^{3+}$, $[Co(trien)(\mu\text{-}(O_2,OH))Co(trien)]^{3+}$, and $[Co(tep)(\mu\text{-}O_2)Co(tep)]^{4+}$, where dien is diethylenetriamine, trien is triethylenetetramine, and tep is tetraethylenepentamine.

In addition, reactivity of these compounds toward acid decomposition (i.e., charge transfer with concomitant protonation of the amine leading to aquation) has been examined, as well as the 1 e reduction of the corresponding μ-superoxo complexes $[Co(en)_2(\mu\text{-}O_2)Co(en)_2]^{5+}$, $[Co(trien)(\mu\text{-}O_2)Co(trien)]^{5+}$, and $[Co(tep)(\mu\text{-}O_2)Co(tep)]^{5+}$.

Experimental Section

Acid salts of polyamine ligands ethylenediamine dihydrochloride, diethylenetriamine trihydrochloride, triethylenetetramine disulfate, and tetraethylenepentamine 2.5-sulfate were obtained from commercial sources and used without further purification. The tetrahydrochloride salt of triaminotriethylamine (tren) was prepared by the method of Mann and Pope.[14]

Table I. Rate of Reduction of Cobalt–Oxygen Complexes by Ferrous Ion ($\mu = 0.2$ M (KNO_3); $T = 25$ °C)

Complex	k_2, M^{-1} s^{-1}	$\log k_{O_2}$	$E^{\ddagger}$, kcal mol^{-1}
$[Co(en)_2(\mu\text{-}(O_2,OH))Co(en)_2]^{3+}$	400 ± 20	8.0 ± 0.1	4.2
$[Co(dien)(\mu\text{-}(O_2,OH))Co(dien)]^{3+}$	140 ± 10	1.1 ± 0.1	7.0
$[Co(trien)(\mu\text{-}(O_2,OH))Co(trien)]^{3+}$	25 ± 3	8.0 ± 0.1	
$[Co(tep)(\mu\text{-}O_2)Co(tep)]^{4+}$	3 ± 0.5	15.0 ± 0.1	

Solutions of the oxygen complexes containing these ligands were prepared by mixing standard aliquots of cobalt nitrate solution (standardized by EDTA titration with murexide indicator) with stoichiometric amounts of ligand (2:1 for en; 1:1 for all other ligands) adding the stoichiometric quantity of KOH required to reach the potentiometric end point, thus ensuring complete formation of the single μ-peroxo or μ-peroxo-μ-hydroxo species.[6,15] Ionic strength was adjusted to 0.2 M with KNO_3 in most cases, although $NaClO_4$ was used in some runs to check for a possible specific ion effect. Ferrous ammonium sulfate solutions were prepared immediately before use. Such solutions were always used within 30 min of preparation.

In a typical experiment, solutions of ferrous salt and of the cobalt–oxygen complex were mixed in a Durrum Jasco D-150 stopped-flow spectrophotometer and the change in absorbance at 360 nm (corresponding to λ_{max} for the oxygen complex) was monitored. The concentration of ferrous ion was made up in large excess of that of the cobalt–dioxygen complex, so that pseudo-first-order kinetics were observed, as indicated in Figure 1. Duplicate runs were performed at each concentration on two separately prepared solutions, for a total of four runs per concentration. Five different concentrations were investigated for each complex. Concentration of Fe(II) ranged from 1×10^{-3} to 5×10^{-2} M; Co(II) concentration ranged from 1×10^{-4} to 5×10^{-3} M. Temperature-dependence studies on the $[Co(en)_2(\mu\text{-}(O_2,OH))Co(en)_2]$ and $[Co(dien)(\mu\text{-}(O_2,OH))Co(dien)]$ systems were performed over the range 20–45 °C in order to test the validity of the relative rates. Activation parameters were obtained using a standard Arrhenius plot.

For experiments involving cobalt–superoxo complexes, decrease in absorbance at 710 nm, corresponding to λ_{max} for the superoxo complex, and increase in absorbance at 360 nm (λ_{max} of peroxo–cobalt product) were followed with identical results.

Spectral characterization of the intermediate in the reduction of the peroxo product was afforded by repeated kinetic runs at 5-nm intervals over the range 700–330 nm, after the method of Sykes.[8]

Results and Discussion

The second-order rate constants for ferrous ion reduction of some μ-peroxo bis(cobalt chelates) are given in Table I. It was initially suspected that the rate might depend in some simple manner on the degree of Co(III) character at the metal