Contribution from the Institute of Chemistry, Academy of Sciences Tajik SSR, Dushanbe, India,
and the Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India 400 005

ESR of Mixed-Ligand Complexes of Oxovanadium(IV) with Dimethyldithioarsinate as One of the Ligands

Z. R. BARATOVA, E. V. SEMENOV, P. M. SOLOZHENKIN, and B. S. PRABHANANDA*[1]

Ligand-exchange reactions have been used to prepare the mixed-ligand vanadyl complexes with dimethyldithioarsinate as one of the ligands and dibutyl dithiophosphate or diethyldithiocarbamate as the second ligand. Comparison of computer-simulated spectra with experimentally observed ESR spectra have been used to infer the presence of these complexes in reaction mixtures. The ESR parameters associated with these complexes are consistent with expectations. That the electron delocalization to the stronger bonding ligand increases at the expense of the weaker bonding ligand in the mixed-ligand complex was confirmed by the observations of ^{75}As and ^{31}P hyperfine splittings in these vanadyl complexes. When the second ligand used was diethyldithiocarbamate, the spectral features suggested the existence of two species with slightly differing ligand hyperfine structures from those of ^{75}As. The computer-simulated spectrum showed better agreement with the observed spectrum when a dynamic equilibrium between the two species with rate constants of the order of 3×10^7 s^{-1} at 20 °C was assumed.

Introduction

Ligand hyperfine structures observed in ESR spectra and contact shifts observed in NMR spectra of transition-metal complexes can be directly related to unpaired spin transfer from metal to ligand. These have been discussed on the basis of different mechanisms of spin transfer.[2-4] Recent studies have shown that ligand hyperfine splittings in the ESR of mixed-ligand complexes are useful in the discussion of dominant paths of spin transfer.[5-7] The suggestion that electron transfer to the stronger bonding ligand increases at the expense of the weaker bonding ligand[4] had found support in the observations on next-neighbor hyperfine splittings of copper(II) complexes.[5,6] We are not aware of similar ESR observations in vanadyl complexes where the spin densities on the atoms of both the ligands could be inferred. In the present work, we have prepared the mixed-ligand complex VO(dtp)(dtas) (dtp$^-$ = dibutyl dithiophosphate, $(C_4H_9O)_2PS_2^-$, and dtas$^-$ = dimethyldithioarsinate, $(CH_3)_2AsPS_2^-$). This complex can be identified by looking for the ligand hyperfine splittings associated with the next neighbors ^{75}As and ^{31}P, which have spins $^3/_2$ and $^1/_2$, respectively. However, the detection of the spectrum due to this complex, in the complex ESR spectra coming from the presence of more than one type of paramagnetic complex in the reaction mixtures, and the measurement of ESR parameters requires the use of computer simulation. For purposes of comparison, we have prepared the complex with dtc$^-$ (diethyldithiocarbamate, $(C_2H_5)_2NCS_2^-$) instead of dtp$^-$ as the second ligand. For the complex VO(dtc)(dtas), the next-neighbor hyperfine splitting from only one ^{75}As is expected.

Materials and Methods

The potassium salt $(CH_3)_2AsSSK$ (Kdtas) was prepared from $(CH_3)_2AsOOH$ by using the procedure described elsewhere.[9] $(C_2H_5)_2NCS_2Na$ (Na(dtc)) and $(C_4H_9O)_2PS_2H$ (dtpH) were prepared

Table I. ESR Parameters[a] of Vanadyl Complexes in Toluene Solutions at 20 °C

complex	g_0	$|A^V|$, G	$|A^{As}|$, G	$|A^P|$, G	α, G	β, G	γ, G
VO(dtp)$_2$	1.982	93.4		50.3	10.5	0.67	0.51
VO(dtas)$_2$	1.972	92.8	44.0		7.6	0.74	0.13
VO(dtp)(dtas)	1.977	93.4	47.8	45.6	9.2	0.72	0.44
"A" species, $\tau_A = 5 \times 10^{-8}$ s	1.973	93.5	52.1		7.6	0.74	0.26
"B" species, $\tau_B = 2.8 \times 10^{-8}$ s	1.973	93.5	40.0		7.6	0.74	0.26
unidentified species VO(X$_1$)(X$_2$)	1.983	93.6			7.6	0.74	0.26

[a] A^V, A^{As}, and A^P refer to the hyperfine splitting parameters of eq 1 for the nuclei ^{51}V, ^{75}As, and ^{31}P, respectively. The errors in the estimation of ligand hyperfine structures are ~±0.5 G. The sign of A^V is negative.

by following the procedure used earlier.[5] $(C_4H_9O)_2PS_2K$ (Kdtp) was obtained from dtpH by reacting it with K_2CO_3. The complexes VO(dtp)$_2$ and VO(dtas)$_2$ could be obtained by the reaction of VOSO$_4$ with the corresponding potassium salt.[10,11] The reaction of VO(dtp)$_2$ in toluene with solid Kdtas and of VO(dtas)$_2$ in toluene with solid Na(dtc) for 5–10 min at room temperature (20 °C) gave sufficient and convenient concentration of mixed-ligand complexes in solutions. The ESR spectra were recorded at room temperature with an X-band ESR spectrometer.

The observed ESR spectra were compared with spectra simulated by using a DEC-10 computer at TIFR. The ESR parameters used in the simulations were varied to obtain good agreement between the experimental and calculated spectra. In such simulations Lorentzian line shapes were used and the line positions were determined by using eq 1.[12]

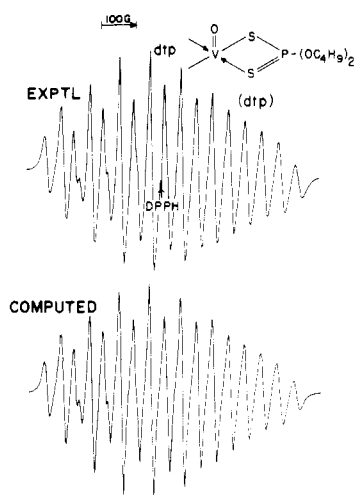$$H_j = H_0 - \sum_i \{ A^i m^i_j + (A^i)^2 [I^i(I^i + 1) - (m^i_j)^2]/2H_0 \} \quad (1)$$

The superscripts i refer to the magnetic nuclei with which the isotropic part of the hyperfine constant A^i and total nuclear spin I^i are associated. The subscripts j refer to the particular transition for which the quantum number associated with the z component of nuclear spin is m^i_j. In the case of equivalent nuclei for the degenerate case, we have to sum the spectra[12] coming from all possible values of I^i that give the same m^i_j. Experimentally observed line widths of hyperfine transitions were dependent on the ^{51}V nuclear magnetic quantum number associated with them. These were included in computer simulations using the following expression for peak to peak derivative width:[13,14]

$$W_j = \alpha + \beta m^v_j + \gamma(m^v_j)^2 \quad (2)$$

* To whom correspondence should be addressed at the Tata Institute of Fundamental Research.

(1) This work was undertaken during the visit of B. S. Prabhananda to the Institute of Chemistry in Dushanbe.
(2) (a) Kivelson, D.; Neiman, R. *J. Chem. Phys.* **1961**, *35*, 149. (b) Kivelson, D.; Lee, S. K. *Ibid.* **1964**, *41*, 1896.
(3) Fortman, J. J.; Hayes, R. G. *J. Chem. Phys.* **1965**, *43*, 15.
(4) Eaton, D. R.; Phillips, W. D. *J. Chem. Phys.* **1965**, *43*, 392.
(5) Prabhananda, B. S.; Shah, S. J.; Venkataraman, B. *Indian J. Pure Appl. Phys.* **1972**, *10*, 365.
(6) Krishnamoorthy, G.; Prabhananda, B. S. *J. Magn. Reson.* **1978**, *30*, 273.
(7) Krishnamoorthy, G.; Prabhananda, B. S.; Solozhenkin, P. M. *Proc. Indian Acad. Sci., Sect. A* **1978**, *87A*, 395.
(8) Krishnamoorthy, G.; Prabhananda, B. S. *J. Phys. Chem.* **1980**, *84*, 637.
(9) Baratova, Z. R.; Solozhenkin, P. M.; Semenov, E. V. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 1137.
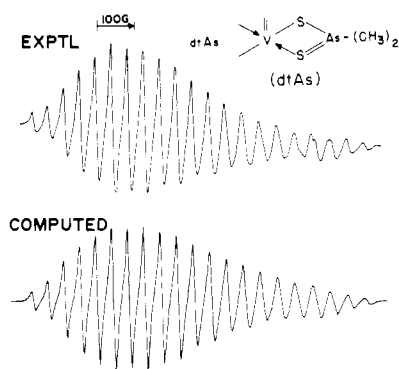
(10) Larin, G. M.; Zelentsov, V. V.; Rakitin, U. V.; Dyatkina, M. E. *Zh. Neorg. Khim.* **1972**, *17*, 2136.
(11) Day, E. D.; McClung, R. E. D. *Inorg. Chem.* **1976**, *15*, 571.
(12) Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 139.

Figure 1. ESR spectra of $VO(dtp)_2$ experimentally observed in toluene at 20 °C and computer simulated by using parameters given in Table I.
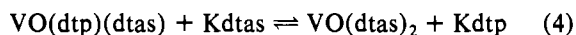

Figure 2. ESR spectra of $VO(dtas)_2$ experimentally observed in toluene at 20 °C and computer simulated by using parameters given in Table I.
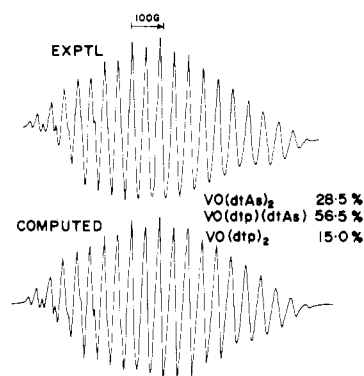
where the superscript v refers to the ^{51}V nucleus. Equilibria between two paramagnetic species expected to give similar spectra, but having different sets of ESR parameters and undergoing equilibration at rates sufficiently slow compared to the tumbling time in solutions but fast compared to nuclear relaxation times, were included in the simulations by adapting the equations of Gutowsky and Holm[15] for derivative spectra. This takes care of the exchange between two line positions (corresponding to the two species) determined by the same set of quantum numbers.

Results

The ESR spectra of $VO(dtp)_2$ and $VO(dtas)_2$ in toluene at 20 °C obtained in our experiments are similar to those observed by other workers.[10,11] The experimentally observed spectra and the spectra simulated by using the parameters given in Table I for these complexes are shown in Figures 1 and 2. The ESR spectrum obtained from toluene solutions of $VO(dtp)_2$ after allowing it to react with solid Kdtas is given in Figure 3. On the basis of experience with similar reactions[7,16] we can expect the formation of $VO(dtp)(dtas)$ and $VO(dtas)_2$ by ligand-exchange reactions 3 and 4. With use

$$VO(dtp)_2 + Kdtas \rightleftharpoons VO(dtp)(dtas) + Kdtp \quad (3)$$

$$VO(dtp)(dtas) + Kdtas \rightleftharpoons VO(dtas)_2 + Kdtp \quad (4)$$

of the positions of the lines in Figures 1 and 2 with respect

---

(13) McConnell, H. M. *J. Chem. Phys.* **1956**, *25*, 709.
(14) Wilson, R.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 154.
(15) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1957**, *25*, 1228.
(16) Prabhananda, B. S.; Shah, S. J.; Venkataraman, B. *Proc. Indian Acad. Sci., Sect. A* **1972**, *76A*, 231.

Figure 3. ESR spectra experimentally observed from a toluene solution of $VO(dtp)_2$ after reacting it with Kdtas at 20 °C and computer simulated by using the parameters given in Table I and relative concentrations of different species as given in the figure.
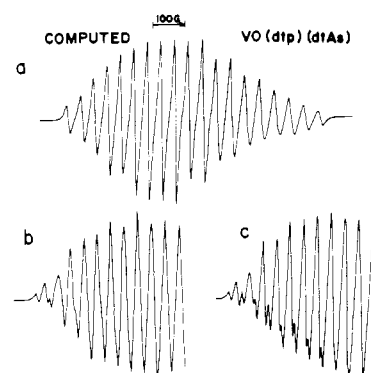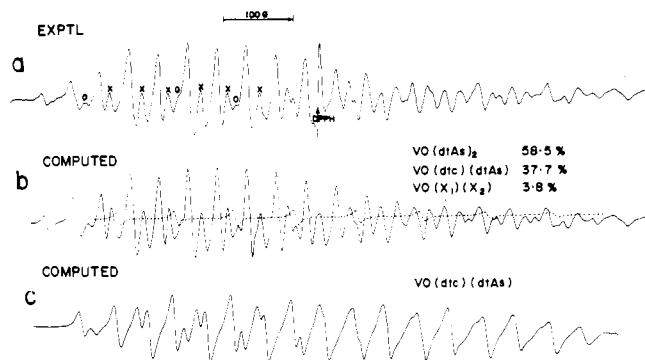

Figure 4. Computer-simulated spectra (a) for $VO(dtp)(dtas)$ with use of parameters given in Table I, (b) computer simulated for the low-field half, for the reaction mixture with $A^V = 93.4$, $A^{As} = 44.0$, and $A^P = 50.2$ G for $VO(dtp)(dtas)$ and other parameters as in Figure 3, and (c) for the reaction mixture with $A^V = 94.4$ G and other parameters as for spectrum b.

to DPPH line position, the lines belonging to $VO(dtp)_2$ and $VO(dtas)_2$ could be identified. By use of selected lines of these complexes that do not overlap much with other lines, the relative concentrations of $VO(dtp)_2$ and $VO(dtas)_2$ in the solution giving the spectrum of Figure 3 could be determined. The spectrum obtained by subtracting the spectra of these species from the spectrum of Figure 3 could be assigned to $VO(dtp)(dtas)$. This shows hyperfine interactions of unpaired spin with ^{51}V (spin $^7/_2$), ^{31}P (spin $^1/_2$), and ^{75}As (spin $^3/_2$). The relative concentration of $VO(dtp)(dtas)$ estimated from Figure 3 was substantial. Figure 3 also gives the computer-simulated spectra, which employed the estimated relative concentrations of the three paramagnetic species and the ESR parameters given in Table I. The computer-simulated spectrum for $VO(dtp)(dtas)$ component is given in Figure 4a. The ESR parameters were determined by looking for close matching between the experimental and simulated spectra, especially in the low-field end. In this spectral region, the signal to noise ratio of experimental spectrum was good and the simulated spectrum was sensitive to the choice of ESR parameters. This is demonstrated in Figure 4b,c. Comparing the ESR parameters given in Table I, we note that ^{75}As hyperfine splitting in the mixed-ligand complex is more than in $VO(dtas)_2$. However, ^{31}P hyperfine splitting in $VO(dtp)(dtas)$ was less than in $VO(dtp)_2$. Spectra simulated with use of the same values of ^{31}P and ^{75}As hyperfine splittings for the three species or hyperfine splittings showing a trend opposite to that mentioned above did not match well with the observed spectrum.
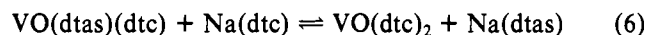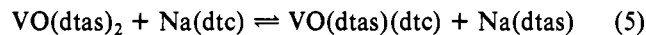
A typical ESR spectrum obtained from toluene solutions of $VO(dtas)_2$ after allowing it to react with solid $Na(dtc)$ is

Figure 5. ESR spectra (a) experimentally observed from toluene solutions of VO(dtas)$_2$ after reacting it with Na(dtc) at 20 °C, (b) computer simulated by using concentrations given in the figure and parameters given in Table I (dotted line for the unidentified species component), and (c) computer simulated for the component coming from "A" and "B" species in dynamic equilibrium.

shown in Figure 5. For this case, we expect ligand-exchange reactions 5 and 6. In Figure 5 the lines associated with

$$VO(dtas)_2 + Na(dtc) \rightleftharpoons VO(dtas)(dtc) + Na(dtas) \quad (5)$$

$$VO(dtas)(dtc) + Na(dtc) \rightleftharpoons VO(dtc)_2 + Na(dtas) \quad (6)$$

VO(dtas)$_2$ can be easily identified by comparison with Figure 2. Among the remaining lines one can identify doublets, with doublet separation of 47.8 G. This value is close to the ^{75}As hyperfine splitting in VO(dtas)$_2$. The separation between the doublets of 93.5 G is close to the ^{51}V hyperfine splitting. In fact, we can identify eight such pairs, as would be expected from hyperfine interaction with ^{51}V. The doublets that are clearly distinguishable on the low-field end of the spectrum are marked by crosses in Figure 5. Assignment of the doublets to a fictitious vanadyl complex in which the unpaired electron interacts with one proton on the ligand is chemically unreasonable. However, we can expect VO(dtc)(dtas) in the reaction mixture. This should show eight transitions (associated with ^{51}V hyperfine interaction) each of which should be further split into quadruplets (associated with quantum numbers $\pm^3/_2$ and $\pm^1/_2$). The quadruplet separation can be expected to be close to the ^{75}As hyperfine splitting in VO(dtas)$_2$ on the basis of observations of a similar mixed-ligand complex, VO-(dtp)(dtas). Thus, it is reasonable to assign the above-mentioned doublets to the transitions associated with ^{75}As nuclear magnetic quantum numbers $\pm^1/_2$. However, the other two transitions of the quadruplet (corresponding to ^{75}As quantum numbers $\pm^3/_2$) expected on the basis of this assignment are not seen in calculated positions. A clue to the understanding of the spectrum comes from the lines marked by circles. The separation between these lines and the doublets (marked by crosses) has a value significantly different from that of the doublet separation. Nevertheless, we can assign these to some of the transitions of VO(dtc)(dtas) with ^{75}As quantum numbers $\pm^3/_2$. With such an assignment, the observed positions of the lines marked by crosses and circles are explained on the basis of an equilibrium between two species, "A" and "B", of VO(dtc)(dtas) with slightly differing ^{75}As hyperfine constants. For this situation the change in line positions of $\pm^1/_2$ transitions is 3 times less than for $\pm^3/_2$ transitions, when the complex changes from one form to another. We can use the equations of Gutowsky and Holm[15] to simulate the line shape for different values of the lifetimes τ_A and τ_B of the two species A and B. For $\tau_A \sim 5 \times 10^{-8}$ s and $\tau_B \sim 2.8 \times 10^{-8}$ s there is reasonable averaging of the line positions of $\pm^1/_2$ transitions of the two species such that single lines are observed at the average positions. However, the lines of the two species can still be distinguished for the $\pm^3/_2$ transitions for these values of τ_A and τ_B. This would lead to the spectral behavior observed

and discussed above. The spectra simulated for such a situation, with use of the parameters given in Table I, are also given in Figure 5. The spectrum of an unidentified vanadyl complex (shown by dotted lines) not showing ligand hyperfine structures had to be added to the spectra of VO(dtas)$_2$ and VO(dtc)(dtas) for better matching of the calculated and observed spectra. The relative concentration of this complex was quite small. The line positions of this complex did not correspond to that of VO(dtc)$_2$. However, when the experimental spectrum was obtained by reacting VO(dtas)$_2$ solutions with Na(dtc) for a longer time, one had to include the spectrum of VO(dtc)$_2$ in addition to the changes in the relative concentrations of other complexes in the matching simulations. Formation of VO(dtc)$_2$ is expected on the basis of reaction 6.

Spectra simulated by assuming two species of the type mentioned above but not undergoing a dynamic equilibrium showed some features of the observed spectrum. However, the assumption of a dynamic equilibrium between the two species gave better agreement between the calculated and observed spectra. Although confirmation of such an equilibrium can be made by a temperature-dependent study, it was not carried out due to the broadening of the lines, reduction in the signal to noise ratio, changes in equilibrium constants, and changes in the parameters used in the simulations of spectra, which made the analysis of the complex overlapped spectra difficult and ambiguous in the broad temperature range needed for a meaningful study.

Discussion

The next-neighbor hyperfine splittings observed in vanadyl complexes were nearly 5 times that in the corresponding copper(II) complexes.[6,11] These have been explained by attributing the next-neighbor hyperfine splittings to the covalent overlap of the d$_{xy}$ orbital on the metal with the orbitals on next neighbors.[6,11] The observation that ^{75}As hyperfine splittings in the vanadyl complex with dtas and pyridine as ligands are less than those in VO(dtas)$_2$ was attributed to a change in bonding by Day and McClung.[11] In our previous studies, we had explained the change in next-neighbor hyperfine splittings on the basis of a mechanism similar to that suggested by Eaton and Phillips:[4] the electron delocalization to the stronger bonding ligand increases at the expense of the weaker bonding ligand. Table I shows that ^{75}As hyperfine splitting increases at the expense of that of ^{31}P on forming the mixed-ligand complex VO(dtp)(dtas), consistent with such an explanation. Combining this with the observations on VO(dtc)(dtp),[5,6] we can place the ligands in increasing strengths of in-plane bonding of metal d$_{xy}$ with the ligand orbitals: dtas$^-$ > dtp$^-$ > dtc$^-$. Such an ordering predicts ^{75}As splitting in VO-(dtc)(dtas) to be higher than that in VO(dtp)(dtas). The "A" species mentioned above show such a behavior. However, ^{75}As splitting associated with "B" species is less than that in VO-(dtas)$_2$. Nevertheless, the average ^{75}As hyperfine splitting calculated from the weighted average of A and B species is greater than that in VO(dtas)$_2$. It may be noted that A and B species are in dynamic equilibrium and their ESR spectral features are similar. Thus it is reasonable to speculate that the differences in the extent of departure from C_{4v} symmetry or a sixth-ligand coordination could be responsible for the differences in the ligand hyperfine splittings of A and B species. It may be noted that a dynamic equilibrium of the above type was invoked to explain the additional broadening of the ligand hyperfine split lines[17] in the case of Cu[(i-C$_3$H$_7$O)$_2$PSe$_2$]$_2$.

In the present case, the nearest neighbors of VO^{2+} are sulfurs even after a ligand-displacement reaction forms the mixed-ligand complex. (This is in contrast with the vanadyl

(17) Prabhananda, B. S. *Mol. Phys.* **1979**, *38*, 209.

complex observed by Day and McClung[11] where pyridine and dtas⁻ were involved in formation of the mixed-ligand complex.) For this case, one can expect the metal hyperfine constants and *g* of the mixed-ligand complexes to have values comparable to those of VO(dtc)₂, VO(dtp)₂, and VO(dtas)₂.[6–8] The observed values for the complexes identified as mixed-ligand complexes are consistent with this expectation. The next-neighbor hyperfine splitting observed provides additional confirmation of the identification.

Contribution from the Departments of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, and the Polytechnic of North London, London N7 8DB, England

Crystal and Molecular Structure of Dipolar Spin-Coupled Dimers of an Irregularly Pentacoordinate Copper(II) Complex, [Cu(5-MeIin)(DBM)]

ANTHONY W. ADDISON,*[1a] PHILIP J. BURKE,[1a] and KIM HENRICK*[1b]

Ternary complexes of copper(II) with the anions of dibenzoylmethane (II) and 1,3-bis(2-pyridylimino)isoindolines were synthesized. Mononuclear pentacoordinate structures are assigned to the compound III with the 5-methylpyridyl ligand (I) as well as the 4-methylpyridyl and nonmethylated complexes V and IV. The X-ray crystal structure of the 5-methylated complex III attributes it to the space group *P*2₁/*n*, with a final *R* factor of 0.047. The coordination geometry is neither square pyramidal nor trigonal bipyramidal but an intermediate structure, in which the more distant of the dibenzoylmethanate oxygen atoms could be considered to approximate the axial donor of a square pyramid. The 5-methylated complex, III, packs uniquely in the crystal lattice as symmetry-related pairs of molecules, in which the isoindolinate ligands are cofacial, with a Cu–Cu separation of 4.453 Å. Within this noncovalent dimer, a spin-exchange process operates, so that the solid state of III exhibits the electron spin resonance spectrum of a spin-coupled triplet system, though the susceptibility obeys a Curie–Weiss law above 77 K. All of III–V are irregularly pentacoordinate in nondonor solvents.

Introduction

Our interest in five-coordinate copper(II) complexes as possible models for the active sites of some copper-containing proteins[2] has led us to synthesize a number of compounds with stereochemistries based upon trigonal symmetries.[3] We have prepared complexes by combination, on the copper(II) ion, of a tridentate chelating agent with a bidentate one, distortions away from C_{4v} symmetry being assisted where possible by the use of sterically constraining substituents.

During the course of this work it was found that the complex formed with the anions of the ligands 1,3-bis((5-methyl-2-pyridyl)imino)isoindoline (5-MeIinH, I) and dibenzoylmethane
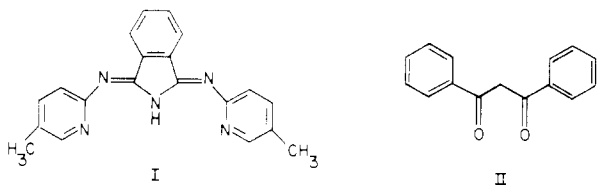
(HDBM, II) exhibited a solid-state, powder ESR spectrum suggestive of magnetically coupled copper(II) centers. Microanalytical data for the complex were consistent with the formulation Cu(5-MeIin)(DBM), and an examination of molecular models indicated that regular trigonal-bipyramidal geometry would not be unfavorable. No mode for coordinative dimerization (ligand bridging) was apparent. In order to examine possible pathways for magnetic coupling, we have determined the crystal and molecular structure of the complex. The results of the study are reported here together with some of the results of solution and solid-state ESR measurements.

Table I. Crystal Data for Cu(5-MeIin)(DBM)

dimens	0.32 × 0.31 × 0.12 mm	no. of reflctns used to determine cell constants and their 2σ limits, deg	25, 20 < 2θ < 30
mol wt	613.17		
cell constants			
a, Å	20.520 (4)	*Z*	4
b, Å	11.187 (2)	ρcalcd, g cm⁻³	1.411
c, Å	12.658 (3)	μ, cm⁻¹	7.59
β, deg	96.83 (5)		
V, Å³	2885.12		

Experimental Section

The preparation of the ligands is described elsewhere.[4,5] Commercial dibenzoylmethane (Aldrich) was used without further purification.

The compound (dibenzoylmethanato)(1,3-bis((5-methyl-2-pyridyl)imino)isoindolinato)copper(II) (III) was prepared by refluxing copper(II) acetate hydrate (0.60 g, 3 mmol), 5-MeIinH (0.98 g, 3 mmol), HDBM (0.67 g 3 mmol), and Et₃N (0.60 g, 6 mmol) in MeOH solution (80 mL) for 30 min. The green precipitate was collected by filtration and crystallized from DMF (*N,N*-dimethylformamide). The yield was essentially quantitative. Anal. Calcd for C₃₅H₂₇CuN₅O₂: C, 68.6; H, 4.44; N, 11.4. Found: C, 68.4; H, 4.44; N, 11.6. A crystal suitable for structure determination was obtained by slowly cooling a DMF solution of the complex.

[Cu(Iin)(DBM)] (IV) and [Cu(4-MeIin)(DBM)] (V) were prepared in an analogous fashion. In the latter case, crystallization was effected at 255 K, and the yield was considerably lower. Anal. Calcd for C₃₃H₂₃CuN₅O₂ (IV): C, 67.7; H, 3.96; N, 12.0. Found: C, 67.8; H, 3.95; N, 11.9. Calcd for C₃₅H₂₇CuN₅O₂ (V): C, 68.6; H, 4.44. Found: C, 68.9; H, 4.39.

Electron spin resonance spectra were obtained at 77 K and ambient temperature with a Varian Associates E-12 X-band spectrometer. Microanalyses were performed by Canadian Microanalytical Service Ltd. Variable-temperature magnetic susceptometry was performed

(1) (a) Drexel University. (b) The Polytechnic of North London.
(2) A. W. Addison, M. Carpenter, L. K.-M. Lau, and M. Wicholas, *Inorg. Chem.*, **17**, 1545 (1978).
(3) A. W. Addison and P. J. Burke, to be submitted for publication.
(4) A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, **18**, 803 (1981).
(5) W. O. Siegel, *J. Org. Chem.*, **42**, 1672 (1977).