

into account. As before, k_{23} is 500 sec^{-1} ; however, K_{ip} for a neutral uncharged species is about $0.1 M^{-1}$. From the HT⁻ result, taking $k_{34}/(k_{32} + k_{34}) \approx 0.1$, an upper limit for k_1 of $5 M^{-1} \text{ sec}^{-1}$ can be obtained. Whether this rate constant is in fact equal to zero cannot be definitely concluded from the experiments. This experimentally determined low value for k_1 is the reason the reaction of ambident bitartrate to produce an anionic complex was neglected in the relaxation expression.

The same model may be applied to the complexation of a second ligand molecule. Relative to the first complexation, competing factors are operative. The water-exchange rate of the remaining equatorial waters is considerably enhanced.³² This effect has been interpreted in the case of VO^{2+} solely on electrostatic grounds wherein the negatively charged coordinating group of the ligand neutralizes in part the high positive charge, leading to labilization of the remaining waters. In the case of vanadyl, two orders of magnitude may be involved. However, the ion-pairing constant is also affected. The complex VOT is neutral, leading to a much lower K_{ip} from electrostatic considerations. There are also fewer binding sites and unfavorable steric requirements, which lower K_{ip} .

(32) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968).

From the considerations above, we see that an *a priori* calculation of the relative rates of the first and second complexations is not possible. In the latter case, the value of k_2' experimentally determined from relaxation methods is $277 M^{-1} \text{ sec}^{-1}$, reflecting a compromise of the competing trends. The value of k_1' was confirmed by the initial rate stopped-flow experiments, the interpretation of which does not depend on the stability constant. The value of k_2' (although its standard error is smaller) is directly dependent on the equilibrium quotients.

Since all of the experiments were performed at $\text{pH} \leq 1.85$, the hydroxovanadyl species, VOOH^+ , was not postulated in the overall mechanism. The coordinated hydroxyl would lead to an increase in the rate *via* a labilization of the remaining waters as described above. This path was not included on the basis of the work of Rossotti and Rossotti¹⁷ and that of Jones and Ray.⁷ In the vanadyl complexation studies by, for example, Wendt and Schlund,³³ this pathway was included. The work in this case was done in the pH range 3–5. Extrapolation of their data to lower pH indicates that pathways incorporating hydroxy species are unimportant at the acidities of this study.

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Vanadyl(IV)-Monothio- β -diketone Complexes. I. Square-Pyramidal Compounds

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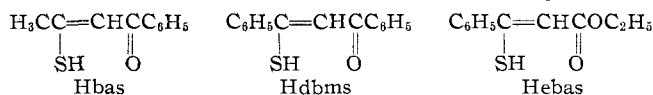
Three vanadyl(IV) complexes of monothio- β -diketones, $\text{RC}(\text{SH})=\text{CHCOR}'$ ($\text{R} = \text{C}_6\text{H}_5$, $\text{R}' = \text{C}_6\text{H}_5$, $\text{C}_2\text{H}_5\text{O}$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$), have been prepared and characterized by infrared, electron spin resonance, and optical spectral studies as well as by the usual analytical methods. The complexes are monomeric and appear to be square pyramidal. The behavior of the complexes in a variety of solvents indicates that solvent effects are comparable to those previously observed for vanadyl(IV) β -diketones. Some qualitative conclusions about the nature of the bonding in these complexes have been reached and some spectral assignments are discussed.

Introduction

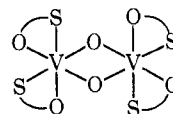
Although vanadyl(IV) complexes have been the objects of many studies,^{1,2} there still is not a large body of information pertaining to any but compounds with V–O or V–N bonds. Accordingly, we have undertaken an investigation of vanadyl(IV) compounds involving second-period donor atoms, with emphasis on sulfur.^{3,4}

In view of recent developments in the coordination chemistry of monothio- β -diketones,⁵ it seemed partic-

ularly worthwhile to investigate vanadyl(IV) complexes of such ligands in detail. The ligands used in this work and our abbreviations for these ligands are



Livingstone⁶ has reported a dimeric complex formed from a fluorinated monothio- β -diketone and VO^{2+} , for which the following structure was proposed



(6) R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *ibid.*, **19**, 1179 (1966).

- (1) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
- (2) J. Selbin, *Angew. Chem., Intern. Ed. Engl.*, **5**, 712 (1966).
- (3) B. J. McCormick, *Inorg. Chem.*, **7**, 1065 (1968).
- (4) B. J. McCormick, *Can. J. Chem.*, **22**, 4283 (1969).
- (5) S. E. Livingstone, *Quart. Rev. (London)*, **19**, 386 (1965); R. C. Mehrotra, V. P. Gupta, and D. Sukhani, *Inorg. Chim. Acta Rev.*, **2**, 111 (1968); S. E. Livingstone and E. A. Sullivan, *Australian J. Chem.*, **22**, 1363 (1969), and previous papers.

Two complexes of dbms, $\text{VO}(\text{dbms})_2^7$ and $\text{VO}(\text{dbms})_2 \cdot (\text{H}_2\text{O})_8$, have been briefly described. Aside from these three reports, there appear to be no other vanadyl(IV) monothio- β -diketones.

Experimental Section

Materials.—Vanadyl(IV) sulfate dihydrate (Fisher Scientific Co., purified grade) was used as received. Dibenzoylmethane, benzoylacetone, and ethyl benzoylacetate were obtained from Eastman Organic Chemicals and were used as received. Pyridine (py), dimethyl sulfoxide (DMSO), and other solvents were distilled and deaerated with dry nitrogen before use.

Measurements.—Electronic spectra were measured in solution at room temperature with a Cary Model 14 spectrophotometer and 10-mm matched quartz cells fitted with Teflon stoppers. Diffuse reflectance spectra were determined with the same instrument equipped with a Model 1411 reflectance attachment. Infrared spectra were obtained with a Beckman IR-12 spectrometer. The compounds were dispersed in either Nujol or halocarbon oil; spectra of the addition products were determined by mulling the parent complex with Nujol containing an excess of the addendum. ESR spectra were obtained with a Varian E-3 spectrometer and a standard quartz solution cell at room temperature. The instrument was calibrated with a solution of DPPH in benzene.

Magnetic susceptibility measurements were made at room temperature with a Gouy balance of standard design by using $[\text{Ni}(\text{en})_2]\text{S}_2\text{O}_3^9$ as the calibrant. The reported magnetic moments were corrected for diamagnetic contributions by using Pascal's constants.¹⁰

Molecular weights were determined with a Hitachi Perkin-Elmer Model 115 vapor pressure osmometer by using benzene or methylene chloride as solvent. The measurements were made within 5 min of preparing the solutions. Elemental analyses were done by Galbraith Microanalytical Laboratories.

Syntheses.—The ligand Hbas was prepared by previously reported procedures.^{11,12} The remaining two ligands, Hdbms and Hbas, were prepared by modifications of Livingstone's¹³ method, as described below.

Hdbms.—A solution of 4.0 g of dibenzoylmethane in 22 ml of absolute ethanol was cooled to -70° . Hydrogen sulfide was bubbled into the solution for 38 min followed by dry hydrogen chloride for 31 min. A CaCl_2 -filled drying tube was attached to the reaction flask and the solution was warmed to room temperature. After 4 hr it was again cooled to -70° , hydrogen sulfide was introduced for 5 min, and the mixture was treated with dry hydrogen chloride for 30 min. The drying tube then was replaced and the solution was warmed to room temperature where it was permitted to stand for 22 hr. The resulting deep red solution was then poured into 600 ml of ice water and the mixture was kept (with occasional stirring) in an ice bath for 40 min. After the red crystalline product was filtered off, washed with water, and recrystallized from ether under nitrogen, it was dried over P_4O_{10} for 8 hr.

Hbas.—A solution of 4.0 g of benzoylacetone in 210 ml of absolute ethanol was cooled to -70° . Hydrogen sulfide was bubbled into the solution for 38 min followed by dry hydrogen chloride for 37 min. A CaCl_2 -filled drying tube then was attached to the reaction flask and the solution was warmed slowly to room temperature. After the solution had remained at room temperature for 2 hr, hydrogen sulfide was bubbled into the solution for 5 min, followed by hydrogen chloride for 7 min. The drying tube was replaced, and after 17 hr at room tempera-

ture, the deep orange solution was poured into 550 ml of ice water. The mixture was kept in an ice bath for 30 min, whereupon a red oil separated and then solidified. The red compound was separated by filtration, washed with ice cold water, and dried in a stream of air.

$\text{VO}(\text{dbms})_2$.—A solution of VO^{2+} was prepared by dissolving 0.40 g (0.002 mol) of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ in 1 ml of warm H_2O , to which was added 1 ml of ethanol after dissolution of the sulfate had taken place. This solution was prepared and used as quickly as possible to prevent extensive hydrolysis of the VO^{2+} . The VO^{2+} solution was then added to a solution of 0.96 g (0.004 mol) of Hdbms in a minimum of warm absolute ethanol. Then a solution of 0.60 g (0.004 mol) of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 2.5 ml of a warm 60:40 water-ethanol mixture was added slowly, whereupon a precipitate formed. After filtration, the precipitate was washed three times each with water and petroleum ether. The olive brown microcrystals were then dried *in vacuo* over P_4O_{10} for 20 hr. *Anal.* Calcd for $\text{C}_{30}\text{H}_{20}\text{O}_8\text{S}_2\text{V}$: C, 66.07; H, 4.04; S, 11.75; mol wt 545. Found: C, 66.02; H, 4.33; S, 11.39; mol wt 555 (in benzene).

$\text{VO}(\text{bas})_2$.—A VO^{2+} solution, prepared as described above, was added slowly to a stirred solution of 0.75 g (0.0042 mol) of Hbas in 5.5 ml of warm absolute ethanol, whereupon a precipitate formed. The solution was cooled in an ice bath for 5 min and then filtered. The olive green complex was washed and dried as described above. *Anal.* Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_8\text{S}_2\text{V}$: C, 57.00; H, 4.31; S, 15.22; mol wt 421. Found: C, 57.56; H, 4.48; S, 15.60; mol wt 426 (in benzene).

$\text{VO}(\text{ebas})_2$.—This compound was synthesized under nitrogen. A solution of VO^{2+} was prepared as described above except that 4 ml of ethanol was added to the dissolved sulfate. The VO^{2+} solution then was added to a solution of 1 ml (~ 0.004 mol) of Hbas in 16 ml of absolute ethanol. A sodium acetate solution, prepared as described above, was added slowly to the thoroughly stirred solution, whereupon a green precipitate formed. After this solution was cooled in an ice bath for 10 min, a green compound was separated, washed, and dried as described earlier. *Anal.* Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_8\text{S}_2\text{V}$: C, 54.88; H, 4.60; S, 13.32; mol wt 481. Found: C, 54.32; H, 4.59; S, 13.38; mol wt 420 (in methylene chloride).

Other Compounds.—The vanadyl(IV)- β -diketone complexes used for purposes of comparison were prepared by conventional procedures.¹⁴

Results

The ligands were prepared either by known procedures or modifications of them. Early in the synthetic aspects of this work it appeared that the sulfur atom of dbms exchanged with oxygen atoms from the solvent to give a β -diketone complex of VO^{2+} . However, it was subsequently found that our initial samples of Hdbms were heavily contaminated with the β -diketone analog. The modified preparation procedures given above have obviated this difficulty.

The complexes were prepared by straightforward procedures involving the treatment of vanadyl(IV) sulfate with the ligand in mixed ethanol-water solutions. Except in the case of Hbas, a weak base such as acetate is required in the preparations for the removal of the acidic proton from the ligands. It is interesting to note in this regard that Livingstone used metal acetates in much of his work.^{6,13} The analytical and infrared data indicate that none of the complexes is solvated, in contrast to one of the previous reports⁸ in which $\text{VO}(\text{dbms})_2$ was formulated with a water molecule. Molecular weight studies in-

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dicates that VO(dbms)₂, VO(bas)₂, and VO(ebas)₂ are monomeric in noncoordinating solvents. Melting points, all of which are lower than those for corresponding β -diketone complexes, are given in Table III.

All of the complexes are stable for an indefinite period of time when stored under dry nitrogen. They very slowly decompose when stored in air. In solution the complexes decompose at varying rates, but in all cases the rate seems to be accelerated by oxygen. For studies involving solutions of the complexes, fresh samples were prepared under nitrogen and used for the measurements as quickly as possible (5–10 min). In general, the complexes are soluble in coordinating solvents but are only slightly soluble in other organic solvents.

Infrared spectra were recorded in the 200–4000-cm⁻¹ region and given in Table I are some selected

TABLE I
INFRARED DATA

Assignment	Str freq, cm ⁻¹		
	VO(dbms) ₂	VO(bas) ₂	VO(ebas) ₂
V=O	992	984	996
(V=O) (py ^a)	956	955	964
(V=O) (DMSO ^a)	955	954	959
C=O ^b	1512 ^c	1537	1518
C=S ^b	1265	1272	1250
C=C ^b	1512 ^c	1547	{1568} {1580}

^a V=O stretching frequency in presence of compound indicated. ^b Assignments based on work reported in ref 13, 15, and 16. ^c Bands broad and not clearly resolved.

frequencies and tentative assignments.^{13,15,16} The V=O stretching frequencies were easily recognized since there were no serious interferences from ligand bands and were 5–10 cm⁻¹ lower than those observed for corresponding β -diketone complexes. In the presence of coordinating solvents the V=O stretching frequencies are reduced 30–40 cm⁻¹.

Electronic spectra of the solid compounds were measured by diffuse-reflectance techniques from 11.5 to 25.0 kK, and most of the solution spectra were measured in the 8.5–33.0-kK region. Spectral scans were made to 7.2 kK in pyridine, and no bands were found other than those discussed below. We feel confident that all of the d–d transitions are located within the band envelopes reported. Molar extinction coefficients (M⁻¹ cm⁻¹) for the bands in the 12.5–22.7 and 22.7–33.0-kK regions varied within the ranges 40–400 and 4000–18,000, respectively. Electronic spectral data are summarized in Table II. The limited solubility of the complexes in noncoordinating solvents coupled with the “tailing-off” of charge-transfer bands into the visible region made studies in these solvents difficult. The most satisfactory noncoordinating solvent found for spectral studies was 1,2-dibromoethane.

Magnetic susceptibility measurements were made on the solid complexes, and the results are given in

TABLE II
ELECTRONIC SPECTRAL PROPERTIES OF
VANADYL(IV) MONOTHIO- β -DIKETONES^a

Medium ^b	E_{max}			
		VO(dbms) ₂	VO(bas) ₂	VO(ebas) ₂
A	14.7	...	21.3	24.4
B	13.0 ^c	15.9	22.8	...
C	12.5 ^c	16.4	23.6	...
D	11.1 ^c	<i>d</i>
		VO(bas) ₂		
A	16.3	...	22.0	28.4
B	13.2 ^c	16.7	23.3	30.4 ^c
C	12.8 ^c	17.0	25.0	31.3
D	12.1 ^c	16.7 ^c
		VO(ebas) ₂		
A	15.4	17.5 ^c	20.4 ^c	25.0
B	13.1	16.4 ^c	20.0 ^c	26.4
C	12.7	14.9	20.0	27.0
D	10.5 ^c	17.3

^a Spectral data are in kilokaisers (kK). ^b A, solid; B, pyridine; C, DMSO; D, 1,2-dibromoethane. ^c Shoulder. ^d Obscured.

Table III. The corrected magnetic moments lie in the range 1.70–1.78 BM and are consistent with the spin-only value for a d¹ case.¹⁰ These results suggest that there are no direct V–V interactions in the solid complexes. Electron spin resonance studies were carried out at room temperature in a variety of solvents. A typical spectrum is shown in Figure 1, and the nuclear isotropic *g* values and vanadium hyperfine splitting constants are presented in Table III. The *g*

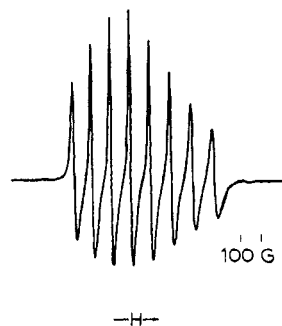


Figure 1.—Esr spectrum of VO(ebas)₂ in pyridine.

values are corrected for second-order effects.¹⁷ In all cases, eight-line spectra were observed, and there were no extra lines or splittings that might suggest the presence of two or more vanadyl(IV) species in the solutions.

The *g*₀ values are in the range expected for vanadyl(IV) complexes.¹⁸ The *A*₀ values measured in the noncoordinating solvent methylene chloride all lie at 97 ± 1 G. Significant reduction of the *A*₀ values occurs when the complexes are dissolved in coordinating solvents. In general, pyridine causes the greatest reduction.

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TABLE III
MAGNETIC PROPERTIES, ELECTRON SPIN RESONANCE
PARAMETERS, AND MELTING POINTS OF VANADYL(IV)
MONOTHIO- β -DIKETONES

Medium ^a	10 ⁵ X _g , cgsu	$\mu_{\text{eff}}^{\text{or}}$, BM	g_0	A_0	Mp, °C
VO(dbms) ₂					
Solid	2.05	1.72			89
A			1.975	98.0	
B			1.974	94.0	
C			1.976	93.0	
VO(bas) ₂					
Solid	2.50	1.72			172
A			1.976	96.0	
B			1.973	94.0	
C			1.975	93.0	
VO(ebas) ₂					
Solid	2.25	1.76			132
A			1.975	98.0	
B			1.973	96.0	
C			1.975	93.0	

^a A, methylene chloride; B, DMSO; C, pyridine.

Discussion

A wide variety of monothio- β -diketone (mtdk) complexes have now been prepared and investigated^{3, 6, 13, 16} in some detail, and in most cases structures have been proposed in which chelating mtdk ligands bond through sulfur and oxygen atoms to provide six-membered rings. In this respect mtdk ligands are similar to β -diketones. In a few instances involving "b" class¹⁹ metals or mixed-ligand complexes such as Pd-(C₄H₃SCS=CHCOCF₃)₂(P(C₆H₅)₃), it is thought that mtdk ligands bond only through sulfur atoms.^{16, 20, 21}

Infrared studies on the complexes prepared in this work are quite indicative of the bonding mode of the ligands. In no case were bands observed that could be attributed to free carbonyl groups, and the assigned C=O frequencies^{22, 23} in Table I agree closely with those reported for compounds in which the carbonyl function is coordinated. That the carbonyl groups are bound is not surprising in view of the class "a" character¹⁹ of V(IV), but it was thought initially that the sulfur atoms might not coordinate, since sulfur is a class "b" donor atom. However, C=S bands were found at frequencies very close to those that have been reported previously for mtdk complexes bonded through sulfur atoms. In view of these infrared results and the stoichiometry of the complexes, it seems certain that the ligands are bidentate. The infrared spectral studies on the green, monomeric complexes VO(dbms)₂, VO(ebas)₂, and VO(bas)₂ confirm the presence of the vanadyl(IV) group since very characteristic V=O stretching frequencies are observed at *ca.* 990 cm⁻¹.

The structures of the complexes reported here cannot be assigned in detail in the absence of X-ray results, but, in view of the great tendency of vanadyl(IV) complexes to adopt a square-pyramidal geometry,^{1, 2, 24, 25} it can reasonably be assumed that VO(dbms)₂, VO(ebas)₂, and VO(bas)₂ do not deviate grossly from this structure. This supposition is supported by the optical and esr spectral work, as discussed below. At this point, there is no direct information that can be brought to bear on the question of whether the complexes have *cis* (C_s) or *trans* (C_{2v}) configurations. A brief reference¹⁶ to X-ray work on Pd(dbms)₂ and Pt(dbms)₂ indicated that the compounds have a *trans* square-planar configuration, but this conclusion is confused by the report²⁶ that both complexes are *cis*. Obviously, more work is needed in this area.

A characteristic,^{3, 4, 27} but not inviolate,²⁸ property of square-pyramidal vanadyl(IV) complexes is their tendency to add a sixth ligand *trans* to the oxygen atom. We have found that treatment of the complexes with coordinating ligands such as pyridine or DMSO results in a downward shift of the V=O stretching frequency by *ca.* 30 cm⁻¹. Such a shift is expected if a sixth ligand is added with a concomitant increase in electron density on the vanadium atom.³

Extensive study of the complexes in solution is difficult owing to their tendency to decompose upon standing, even in the absence of air. For example, a benzene solution of VO(dbms)₂ decomposed in a period of 1 hr to give a black insoluble precipitate that was not characterized further. It is possible that redox processes are facilitated in solution with the formation of ligand oxidation products. Analogous behavior has been observed previously for Fe(dbms)₃.¹⁶

The solution electron spin resonance spectra are quite typical of those that have been reported previously for VO²⁺ complexes, and the isotropic g values (g_0) are in accord with the theory that places the single unpaired electron in a nonbonding d_{xy} orbital.¹ The g_0 values are somewhat higher (~ 0.005) than those observed for the corresponding β -diketone complexes. This is consistent with the notion that electron delocalization increases in going from β -diketone to monothio- β -diketone complexes.

The observed isotropic vanadium hyperfine splittings, A_0 , depend on both the ligand system and the solvent. While there has been some uncertainty as to the relation between A_0 values and the nature of metal-ligand bonds,¹⁸ it is now thought that the amount of 4s contribution to ground-state σ bonding is the primary factor in determining the variation of A_0 .²⁹ However, it is probable that covalency effects also

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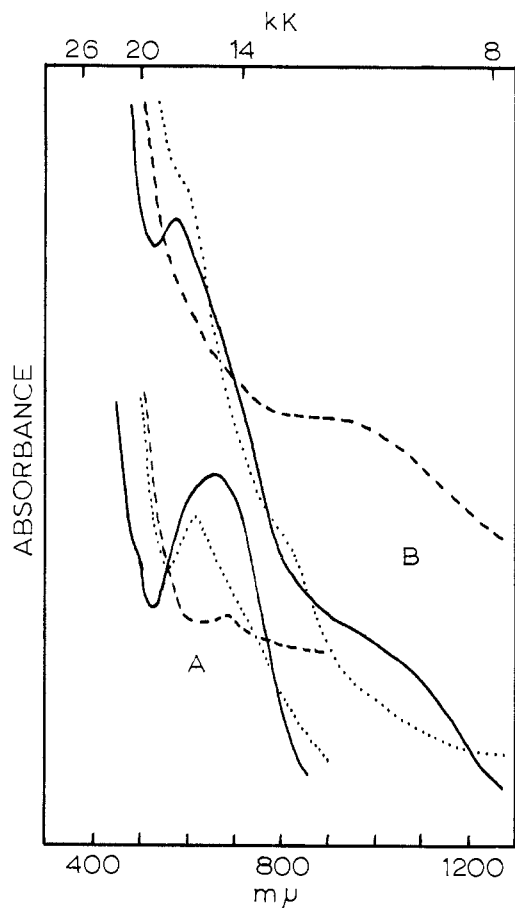


Figure 2.—Reflectance spectra (A) and spectra measured in 1,2-dibromoethane solutions (B): ---, VO(dbms)₂; ···, VO(bas)₂; —, VO(ebas)₂.

contribute,¹⁸ and in this respect it is of interest to note that A_0 values for vanadyl(IV) complexes decrease in the order β -diketone (~ 110 G) > monothio- β -diketone (~ 96 G) > N,N-dialkyldithiocarbamate (~ 90 G)³⁰ > maleonitriledithiolate (70 G).³¹ It is possible that this trend reflects, in part, increasing covalency in going from class "a" (oxygen) to class "b" (sulfur) donor atoms. It is anticipated that additional information on these points will be forthcoming from low-temperature esr studies that are currently under investigation. The observed decrease in A_0 with increasing donor strength of solvent may reflect the decrease in π donation from the axial oxygen atom to the metal, as well as the increased interaction between the mtdk ligands and the vanadium atom brought about by a movement of the metal closer to the basal plane of the square pyramid when a sixth ligand is coordinated.^{4,32}

In the present study a fundamental objective has been to compare the optical spectra of the O-S bonded mtdk complexes to those of O-O and S-S bonded β -diketone and dithiocarbamate complexes, respectively. While there has been a great deal of controversy surrounding the interpretation of the electronic

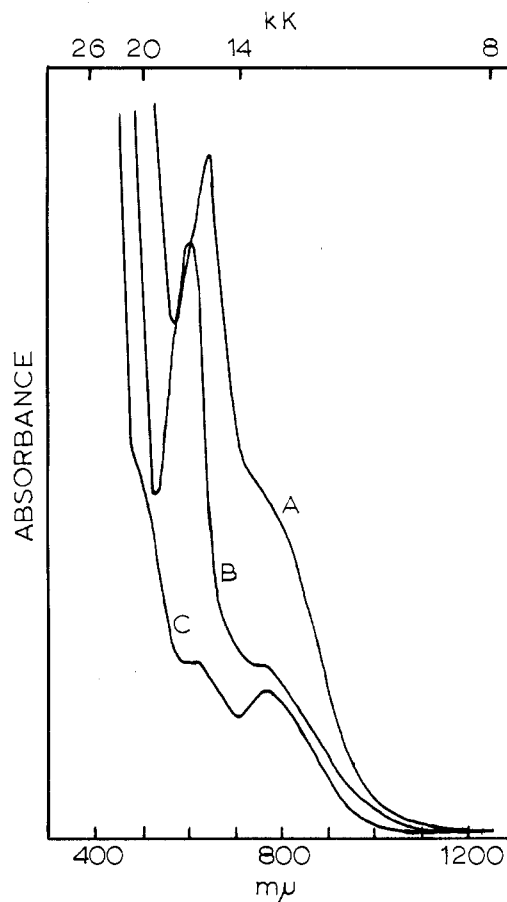


Figure 3.—Spectra measured in pyridine solutions: A, VO(dbms)₂; B, VO(bas)₂; C, VO(ebas)₂.

spectra of vanadyl(IV) complexes,^{1,2,3,30,33} it appears that recent molecular orbital calculations³⁴ can be used as a basis for successful spectral interpretations. These calculations place the single unpaired electron in a nonbonding metal d_{xy} orbital, and the expected d-d transitions for β -diketone complexes are $d_{xy} \rightarrow d_{xz}$, d_{yz} (I), $d_{xy} \rightarrow d_{x^2-y^2}$ (II), and $d_{xy} \rightarrow d_{z^2}$ (III), in order of increasing energy. In mtdk complexes the $d_{x^2-y^2}$ level is expected to lie close to the d_{xz} , d_{yz} level, since the ligand field strength of mtdk ligands is low^{35,36} and the $d_{x^2-y^2}$ level decreases in energy with decreasing donor strength.

The mtdk complexes reported here show a rich spectrum in the 9-33-kK region. Spectral data are summarized in Table II and representative spectra are shown in Figures 2 and 3. The intense bands found higher than 18 kK undoubtedly arise from transitions of the types $L_{\pi^*} \rightarrow M_d$ or $L_{\pi^*} \rightarrow L_{\pi^*}$, where L_{π^*} refers to a ligand molecular orbital. Such bands have been discussed and assigned previously by Chaston and Livingstone²¹ in their study of Ni(II)-mtdk complexes.

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(35) Monothio- β -diketone ligands have been placed between dithiocarbamates and dithiophosphates in the spectrochemical series.³⁶

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Intrusion of charge-transfer bands into the visible region renders the study of d-d transitions difficult. The most satisfactory reflectance spectrum was provided by VO(ebas)₂, and this can be attributed to the fact that the charge-transfer bands begin some 3–4 kK higher than do those in VO(bas)₂ and VO(dbms)₂. It seems clear that bands occurring at frequencies lower than 16.5 kK can be attributed to d-d transitions. Such bands are found in the reflectance spectra of VO(ebas)₂, VO(bas)₂, and VO(dbms)₂ at 15.4, 16.3, and 14.7, kK, respectively, and in solutions of 1,2-dibromoethane at 17.3 kK for VO(ebas)₂ and 16.7 kK (shoulder) for VO(bas)₂. The corresponding band for VO(dbms)₂ in 1,2-dibromoethane is totally obscured by a charge-transfer "tail." The reason that the bands are shifted to slightly higher energies in 1,2-dibromoethane is not clear, but it is not uncommon to find small differences between reflectance spectra and those measured in noncoordinating solvents.¹⁴ An additional absorption is seen as a very poorly defined shoulder in 1,2-dibromoethane at approximately 10.5, 12.1, and 11.1 kK in the ebas, bas, and dbms complexes, respectively. Thus, the spectra are qualitatively similar to those of β-diketone complexes in the 10–20-kK region, except that only two bands are observable. Provisionally, the shoulders at 10.5–12.1 kK are assigned to transition I while the bands at 14.7–17.3 kK are assigned to transition II. It is possible, of course, that these assignments should be reversed, as has been proposed for other cases,^{3,14} and it is unfortunate

that the poor resolution of the bands does not permit more detailed study. Transition III may be barely discernible as a shoulder at *ca.* 21 kK in the reflectance spectrum of VO(ebas)₂.

Spectra measured in the coordinating solvents dimethyl sulfoxide and pyridine (Figure 3) show a band at about 16 kK that corresponds well with the band assigned above to transition II. The resolution of the band was satisfactory in all solvents studied only in the case of VO(ebas)₂, and in this case a red shift was observed in the coordinating solvents. The shoulders found at 10.5–12.1 kK in 1,2-dibromoethane are shifted to the blue in coordinating solvents. The magnitude of the shift is very difficult to ascertain owing to the broadness of the shoulders, but it may be as much as 2 kK. The observed red and blue shifts are so poorly defined that conclusions about the spectral assignments are perilous; however, it should be pointed out that similar shifts have been observed by Selbin and coworkers¹⁴ for several β-diketone complexes in which the low-energy shoulder was assigned as transition II. The spectral shifts observed in coordinating solvents do support the view that the complexes can add a sixth ligand.

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Proton Nuclear Magnetic Resonance Investigation of Some Paramagnetic Transition Metal Tris Chelates with Unsymmetrically Methyl-Substituted *o*-Phenanthrolines

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The proton nmr spectra of the Cr(II), Fe(III), Co(II), and Ni(II) tris chelates with a series of unsymmetrically methyl-substituted *o*-phenanthrolines have been observed. A set of four equally intense resonance peaks for a given ligand proton indicates that the two possible geometrical isomers, *cis* and *trans*, are formed in statistical amounts for all complexes. The extent of magnetic dissymmetry for a given metal ion was found to depend on the position(s) of methyl substitution, with the greatest effect noted for methyl groups at the 4 position. Analysis of the isotropic shifts for the Cr(II) and Fe(III) chelates suggests that the π-contact interaction is more sensitive to unsymmetrical methyl substitution than either the σ-contact interaction or the dipolar interaction. For the Co(II) complexes, the magnetic dissymmetry is concluded to arise primarily from the dipolar interaction.

Introduction

A recent analysis¹ of the ligand contact shifts for tris *o*-phenanthroline (phen) and α,α'-bipyridine (bipy) chelates with Cr(II) has indicated that, although metal-ligand π bonding is present, it plays a relatively minor role in the spin-delocalization mechanism, in spite of the fact that these ligands had been previously

considered very good π acceptors. It was therefore suggested that the anomalous "spin-only" magnetic moments² for these Cr(II) chelates result from a strong trigonal distortion³ rather than from delocalization⁴ of the magnetic electrons.

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