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The Structure and Spectra of Dithiocarbamate Complexes of Oxovanadium(IV)

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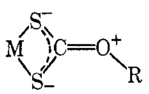
Four bis(N,N-disubstituted dithiocarbamato)oxovanadium(IV) complexes with the N substituents CH_3–, C_2H_5–, *i*-C_3H_7–, and –$CH_2CH_2CH_2CH_2$– have been prepared and characterized. The complexes are slightly soluble in numerous organic solvents, and molecular weight studies in tetramethylene sulfone show that the compounds are monomeric. The compounds have a tetragonal-pyramidal structure, but the open coordination position *trans* to the oxygen atom can accept a sixth ligand, such as pyridine or dimethyl sulfoxide, to give a pseudo-octahedral structure. Infrared spectral studies indicate that ligand to metal π interactions are of some significance in these compounds and the electronic spectral bands have been assigned using a molecular orbital scheme which involves equatorial π bonding.

Introduction

Among the more frequently considered sulfur-containing ligands that have been studied in the past few years are O-alkyl xanthates, N,N-disubstituted dithiocarbamates, and, to a lesser extent, other similar ligands which form four-membered chelate rings with sulfur as the sole donor atom. The primary objective of part of the past work has been to establish the relative importance of canonical structures I and II in xanthates[1] and dithiocarbamates,[2] respectively. Recent work by Coucouvanis and Fackler[3] has confirmed the fact that structure I is less important in nickel(II) xanthates than is structure II in nickel(II) dithiocarbamates.



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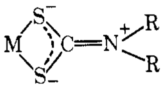

II

In addition, a qualitative order for the resonance shift of π-electron density for a group of related ligands was established.

In connection with our interest in sulfur-containing ligands, we have begun an investigation of complexes of early transition metal ions, especially oxovanadium(IV), with such ligands. The VO^{2+} ion would seem to be well suited to such studies since it has been extensively characterized[4] and continues to be subjected to thorough examination,[5,6] although it is evident that almost all of the research reported heretofore has involved either oxygen or nitrogen donors. It appears that there have been only four reports on oxovanadium(IV)–sulfur chelates. An interesting maleonitrile dithiolate (MNT) complex having the formula $[(C_6H_5)_3PCH_3]_2[VO(MNT)_2]$ has been prepared,[7] and the results of two esr studies on dithiocarbamate chelates have been published.[8,9] A preliminary account of the present work has appeared.[10]

We report here the details of the preparation and characterization of bis(N,N-dimethyldithiocarbamato)oxovanadium(IV), bis(N,N-diethyldithiocarbamato)oxovanadium(IV), bis(N,N-diisopropyldithiocarbamato)oxovanadium(IV), and bis(pyrrolidine-N-carbodithioato)oxovanadium(IV) as well as spectral assignments and some qualitative conclusions concerning the bonding in these complexes.

Experimental Section

Materials.—Vanadyl sulfate dihydrate (Fisher Scientific Co., purified grade) was used as received. Sodium N,N-diethyldithiocarbamate and dimethylammonium N,N-dimethyldithiocarbamate were obtained from Eastman and were used without further purification. Ammonium pyrrolidine-N-carbodithioate was prepared from carbon disulfide, pyrrolidine, and ammonium hydroxide in absolute ethanol and was purified by reprecipitation from methanol with diethyl ether–ethanol mixtures. Sodium N,N diisopropyldithiocarbamate was prepared from carbon disulfide, diisopropylamine, and sodium hydroxide in diethyl ether and was recrystallized from warm water. Solvents were obtained as follows. Pyridine (analytical reagent grade) and dimethyl sulfoxide (DMSO) were distilled under dry N_2 from potassium hydroxide and calcium hydride, respectively; sulfolane (tetramethylene sulfone, Phillips Petroleum Co.) was vacuum distilled from potassium hydroxide; and 1,2-dibromoethane was distilled from calcium hydride. Immediately before use the solvents were deaerated with dry nitrogen.

Preparation of Complexes.—All preparations were carried out under an atmosphere of dry nitrogen.

Bis(pyrrolidine-N-carbodithioato)oxovanadium(IV).—A solution of VO^{2+} was prepared by dissolving 3.98 g (0.02 mol) of $VOSO_4 \cdot 2H_2O$ in 25 ml of warm H_2O, to which was added 25 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 then was added slowly to an efficiently stirred solution of 6.56 g (0.04 mol) of ammonium pyrrolidine-N-carbodithioate in 50 ml of 50% ethanol, whereupon a pale, greenish gray precipitate formed. After filtration the precipitate was washed with 300 ml of H_2O and 15 ml each of ethanol and diethyl ether and dried *in vacuo* over P_4O_{10} for 24 hr. The yield was nearly quantitative. *Anal.* Calcd for $C_{10}H_{16}N_2OS_4V$: C, 33.4; H, 4.49; N, 7.79; S, 35.7; mol wt, 360. Found: C, 33.5; H, 4.65; N, 7.70; S, 35.9; mol wt, 369.

Bis(N,N-dimethyldithiocarbamato)oxovanadium(IV).—This

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[1] G. W. Watt and B. J. McCormick, *Spectrochim. Acta.*, **21**, 753 (1965).

[2] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

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[6] J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

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[8] N. S. Garif'yanov and B. M. Kozyrev, *Teor. i Eksperim. Khim. Akad. Nauk Ukr. SSR*, **1**, 525 (1965).

[9] I. V. Miroshnichenko, E. G. Rukhadze, and S. F. Zapuskalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1658 (1966); *Chem. Abstr.*, **66**, 60585*s* (1967).

[10] B. J. McCormick, *Inorg. Nucl. Chem. Letters*, **3**, 293 (1967).

gray compound was prepared from dimethylammonium N,N-dimethyldithiocarbamate by procedures similar to those described above. *Anal.* Calcd for $C_6H_{12}N_2OS_4V$: C, 23.5; H, 3.94; N, 9.12; S, 41.8; mol wt, 307. Found: C, 23.8; H, 4.13; N, 8.91; S, 41.9; mol wt, 287.

Bis(N,N-diethyldithiocarbamato)oxovanadium(IV).—Procedures analogous to the preceding ones were used to prepare this gray complex from sodium N,N-diethyldithiocarbamate. *Anal.* Calcd for $C_{10}H_{20}N_2OS_4V$: C, 33.1; H, 6.06; N, 7.71; S, 35.3; mol wt, 363. Found: C, 32.8; H, 5.44; N, 7.38; S, 34.8; mol wt, 337.

Bis(N,N-diisopropyldithiocarbamato)oxovanadium(IV).—Techniques comparable to those described previously were used in the preparation of this tan complex from sodium N,N-diisopropyldithiocarbamate. *Anal.* Calcd for $C_{14}H_{28}N_2OS_4V$: C, 40.0; H, 6.72; N, 6.72; S, 30.60; mol wt, 420. Found: C, 39.5; H, 6.64; N, 6.47; S, 30.10; mol wt, 417.

Properties of Complexes.—The four complexes prepared in this work are oxidized by air (rapidly in solution); however, in the solid state the pyrrolidyl derivative is oxidized only slowly. When stored under dry nitrogen, either as solids or in solution, the complexes are stable for an indefinite period of time. The oxidation products were not investigated in detail. The complexes are slightly soluble in numerous organic solvents but are insoluble in water.

When treated with pyridine or DMSO the complexes form green addition products. Several attempts were made to isolate in pure form the pyridine addition product of the pyrrolidyl derivative. However, the pyridine was very loosely coordinated and, hence, was quickly removed by washing with noncoordinating solvents or by pumping at mechanical pump pressures. The gray product resulting from the removal of pyridine was identical with the starting pyrrolidyl derivative. Similar results were obtained with the methyl and ethyl derivatives. The isopropyl complex, on the other hand, formed a pyridine addition product which was isolated as a dark green solid by dissolving bis(N,N-diisopropyldithiocarbamato)oxovanadium(IV) in pyridine in the absence of air and then removing unreacted pyridine by pumping for 24 hr. *Anal.* Calcd for $C_{19}H_{33}N_3OS_4V$: C, 45.7; H, 6.67. Found: C, 45.2; H, 6.54.

Spectra.—Reflectance spectra were measured at room temperature with a Beckman Model DU spectrophotometer equipped with a standard reflectance attachment which was modified so that a continuous purge of dry nitrogen could be passed through the sample chamber during the measurements. As an added precaution against oxidation, the reflectance attachment was enclosed by a plastic bag which was purged with dry nitrogen during the measurements. Samples were prepared in the bag and were not exposed to air at any time. The reflectance standard was $MgCO_3$.

Solution studies were made with a Cary Model 14 spectrophotometer in conjunction with 10-mm matched quartz cells fitted with ground-glass stoppers. All solutions for the spectral measurements were prepared under anaerobic conditions. The data obtained from the measurements are given in Table I.

Infrared measurements were made with Perkin-Elmer Model 21 and Beckman IR-8 spectrometers on both Nujol mulls and KBr disks. Significant differences between mull and disk spectra were not observed. The spectra were calibrated against the known absorption bands of polystyrene, and the V=O stretching frequencies are believed to be accurate to ±2 cm^{-1}. The infrared spectra of the addition products were measured by mulling the complexes with Nujol containing excess pyridine or DMSO. The infrared data are given in Table II.

TABLE I

ELECTRONIC SPECTRA OF DITHIOCARBAMATE COMPLEXES[a]

Derivative	Medium[b]	Assignment[c]		
		b_1^*	e_π^*	a_1^*
Methyl	A	16.0[d]	17.6	22.5
	B	16.0[d]	18.0	22.5[d]
	C	16.0[d]	18.0 (ϵ 50)	22.7[d]
	D	15.0 (ϵ 38)[d]	12.7 (ϵ 48)	
	E	16.1 (ϵ 37)[d]	13.2 (ϵ 64)	
Ethyl	A	16.0[d]	17.6	22.5
	B	16.0[d]	18.1 (ϵ 54)	21.7[d]
	C	16.0[d]	18.1 (ϵ 52)	23.3[d]
	D	15.4 (ϵ 51)	12.7 (ϵ 58)	
	E	16.1 (ϵ 41)[d]	13.1 (ϵ 68)	
Isopropyl	A	16.4[d]	18.2	22.7[d]
	B	16.0[d]	18.2 (ϵ 63)	22.2[d]
	C	16.0[d]	18.3 (ϵ 85)	22.2[d]
	D	16.5 (ϵ 57)	12.3 (ϵ 46)	
	E	16.4 (ϵ 45)	13.0 (ϵ 61)	
Pyrrolidyl	A	16.5[d]	17.8	22.8
	B	16.0[d]	17.9 (ϵ 53)	22.9 (ϵ 118)
	C	16.0	18.0 (ϵ 49)	22.9 (ϵ 80)
	D	15.3 (ϵ 40)[d]	12.7 (ϵ 51)	
	E	15.9 (ϵ 40)[d]	13.2 (ϵ 71)	

[a] Absorption maxima are in kilokaisers (kK); ϵ values are in l. mol^{-1} cm^{-1}. [b] A, reflectance; B, 1,2-dibromoethane; C, sulfolane; D, dimethyl sulfoxide; E, pyridine. [c] Excited state; all transitions are assigned with the b_2 level as the ground state. [d] Shoulder; $\tilde{\nu}_{max}$ and ϵ, where given, should be regarded as approximate.

TABLE II

V=O AND $C\overset{\cdots}{=}N$ STRETCHING FREQUENCIES OF DITHIOCARBAMATE–OXOVANADIUM(IV) COMPLEXES AND THE PYRIDINE AND DIMETHYL SULFOXIDE ADDUCTS[a]

Derivative		$\tilde{\nu}$(V=O)	$\tilde{\nu}(C\overset{\cdots}{=}N)$
Methyl	Nujol mull	982	1546, 1539[b]
	Pyridine adduct	946	1518[b]
	DMSO adduct	949	1550, 1536[b]
Ethyl	Nujol mull	984	1517[b]
	Pyridine adduct	946	1491[c]
	DMSO adduct	950	1509, 1522[b]
Isopropyl	Nujol mull	995	1492
	Pyridine adduct	956	1493[b,c]
	DMSO adduct	950	1493[b]
Pyrrolidyl	Nujol mull	992	1510
	Pyridine adduct	960	1492[c]
	DMSO adduct	945,[c] 951	1510,[c] 1492

[a] Absorption maxima are in cm^{-1}; all of the bands are strong. [b] Broad. [c] Shoulder.

TABLE III

MAGNETIC PROPERTIES OF OXOVANADIUM(IV)–DITHIOCARBAMATE COMPLEXES

Compound	$10^6\chi_g$, cgs units	μ_{eff}^{cor}, BM
$VO(S_2CN(CH_3)_2)_2$	3.39	1.69
$VO(S_2CN(C_2H_5)_2)_2$	2.90	1.73
$VO(S_2CNC_4H_8)_2$	3.01	1.74
$VO(S_2CN(C_3H_7)_2)_2$	2.55	1.77

Magnetic Measurements.—Magnetic susceptibility measurements (Table III) were made at three field strengths at ambient room temperature (*ca.* 25°) with a Gouy balance of standard design. The calibrant was $[Ni(en)_3]S_2O_3$.[11] The sample tubes were packed under dry nitrogen; however, during the period of the measurements (*ca.* 5 min) no particular attempt was made to protect the samples from air. Significant oxidation did not take place during the measurements. Each run was repeated 15 min after attaching the sample tube to the balance, and no changes from the initial susceptibility values were observed. The susceptibilities were field independent, and the reported magnetic moments are corrected for diamagnetic contributions using Pascal's constants.[12]

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(12) B. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

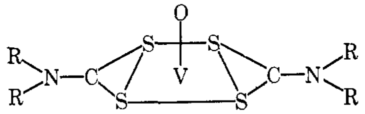
Molecular Weight Determinations.—Molecular weights were determined by the freezing point depression method using anaerobic techniques in sulfolane as solvent. In this solvent the complexes are monomeric. It was not possible to determine molecular weights in other solvents owing to low solubilities.

Analyses.—All of the elemental analyses were performed by Galbraith Microanalytical Laboratories.

Results and Discussion

The ability of dithiocarbamate ligands to form stable four-membered chelate rings with metal ions has long been known.[13] However, it has been found only recently that these ligands are somewhat unique in several respects. For example, it appears that the donor properties of the $S_2CNR_2^-$ group depend significantly on the nature of the substituents on the nitrogen atom. An interesting manifestation of this effect is found in tris(dithiocarbamato)iron(III) complexes, where it is found that the magnetic moments vary between the limits of 2.62 to 5.83 BM, depending on the particular substituents on nitrogen.[14] The N,N-diisopropyl and pyrrolidyl derivatives give the lowest and highest moments, respectively. The four ligands studied in the present work were chosen specifically in order to represent a range of donor characteristics which can be provided by dithiocarbamate ligands, as judged from the Fe(III) studies.

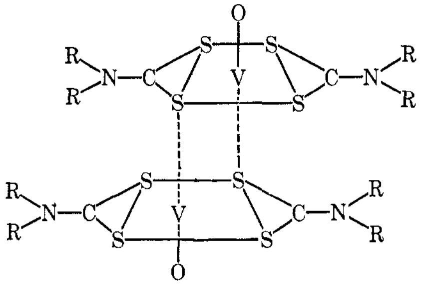
The four compounds reported here, which have the general formula $VO(S_2CNR_2)_2$, are easily prepared from oxovanadium(IV) sulfate and an appropriate dithiocarbamate salt. In conjunction with spectroscopic results, the analytical and magnetic data are consistent with the assignment of a tetragonal-pyramidal (C_{4v}) structure to the complexes



The structure undoubtedly is quite similar to that of $VO(acac)_2$.[15] The magnetic moments (Table III) correspond very closely to the spin-only value of 1.73 BM, which indicates that there are no direct intermolecular V–V interactions.

The distinct spectral changes that occur when the complexes are dissolved in coordinating solvents indicate that the coordination position *trans* to the apical oxygen atom is more or less open for coordination by a sixth ligand. This type of addition reaction has been studied extensively in the $VO(acac)_2$ case.[4,16] Qualitatively, it appears that the tendency to bond to a sixth ligand is lower in the dithiocarbamate complexes than in the acetylacetonate complex, since even in very weakly coordinating solvents the electronic spectrum of $VO(acac)_2$ changes significantly from that measured by reflectance techniques, whereas a strongly coordinating solvent is required to effect significant spectral shifts in the dithiocarbamates. The low coordinating ability of the sixth spatial position in the dithiocarbamate complexes also is reflected in the ease of removal of pyridine from certain of the bis(dithiocarbamato)oxovanadium(IV)-pyridine adducts.

Since the sixth coordination position can sustain the attachment of a ligand and since it appears that a sulfur atom of a dithiocarbamate ligand may simultaneously bond to two metal ions to form a bridge,[17,18] it would seem that there is the possibility that the complexes are dimeric with the structure



These studies do not rule out such a structure in the solid state. Nevertheless, if dimerization occurs in the solid state, the intermolecular bonding must be very weak. The complexes are monomeric in sulfolane, which appears to be a noncoordinating solvent.

Infrared Spectra.—There is much evidence that canonical forms of type II (above) play an important role in the description of the structure of dithiocarbamate complexes. Such complexes almost invariably have a strong, usually broad band at *ca.* 1500 cm^{-1}, which is intermediate between C—N and C═N stretching frequencies. This 1500-cm^{-1} band (thioureide band) has been assigned to the C$\overset{...}{-}$N stretching vibration.[2,3,19] A normal-coordinate treatment by Nakamoto and co-workers[20] has confirmed this assignment. Numerous X-ray crystallographic studies also emphasize the importance of structure type II in that the C$\overset{...}{-}$N bond distance is shorter than that of C—N bonds, but longer than that of C═N bonds.[21]

The C$\overset{...}{-}$N frequency assignments for the oxovanadium(IV) complexes are given in Table II and a typical infrared spectrum is shown in Figure 1A. The frequencies decrease with increasing length of alkyl group, with the C$\overset{...}{-}$N frequency of the pyrrolidyl derivative lying very close to that of the ethyl complex. Addition of a sixth ligand results, in general, in a shift of the C$\overset{...}{-}$N band to lower frequencies, although some of the shifts are difficult to determine accurately owing to the complexity of the spectra and the broadness of the bands.

In their study of square-planar nickel(II) complexes of dithiocarbamates and related ligands, Coucouvanis

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[19] J. Chatt, L. A. Duncanson, and L. M. Vananzi, *Nature*, **177**, 1042 (1956).

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[21] Recent data can be found in: G. Peyronel and H. Pignedoli, *Acta Cryst.*, **23**, 398 (1967); G. F. Gasparri, M. Nardelli, and A. Villa, *ibid.*, **23**, 384 (1967).

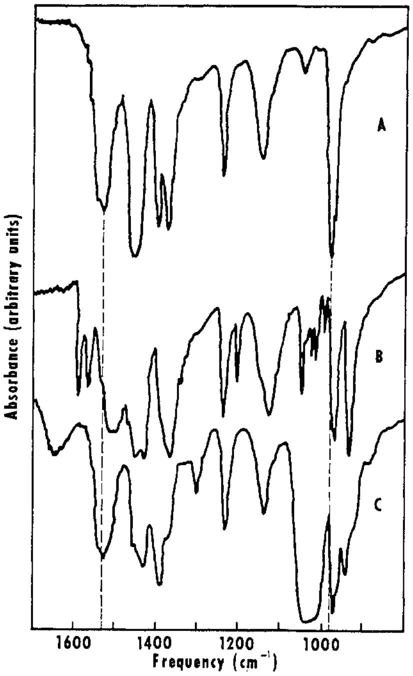

Figure 1.—Infrared spectra: A, $\mathrm{VO(S_2CN(CH_3)_2)_2}$; B, $\mathrm{VO(S_2CN(CH_3)_2)_2}$-py; C, $\mathrm{VO(S_2CN(CH_3)_2)_2}$-DMSO.

and Fackler[3] found that the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ frequencies were lowered in adducts formed with nitrogenous bases and the decrease was taken as an indication of decreased double-bond character for the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond. Such a decrease is expected if the high $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ frequencies in nickel(II) dithiocarbamates are the result of electron donation by the sulfur atoms into a nonbonding molecular orbital containing the $4p_z$ function of nickel, as suggested originally by Cotton and McCleverty.[22]

The adduct-forming ability of $\mathrm{VO^{2+}}$–dithiocarbamate complexes appears to parallel that of $\mathrm{Ni^{2+}}$–dithiocarbamate complexes, at least as far as pyridine is concerned. In the pyridine adducts of the methyl, ethyl, and pyrrolidyl derivatives, the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ frequencies are lower than those found in the pyramidal dithiocarbamate complexes. A typical spectrum is shown in Figure 1B. However, for the isopropyl derivative the addition of pyridine does not result in a shift of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ band to lower energies (Table II). Thus the spectral changes that occur upon adduct formation suggest that there is appreciable interaction between sulfur π orbitals of a_1 symmetry and the vanadium $4p_z$ (a_1 symmetry) orbital. It is interesting to note in this respect that pyridine appears to bond more firmly to the isopropyl complex than to the pyrrolidyl, methyl, or ethyl complex. This result is entirely consistent with the postulation of sulfur–vanadium π bonding since the $4p_z$ orbital is expected to be less engaged in such π bonding and, hence, more available for bonding to a sixth ligand in the isopropyl derivative than in the other derivatives, as judged from the fact that the isopropyl complex has the lowest $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ frequency of any of the four complexes.

The vanadium d_{xz} and d_{yz} orbitals also have the proper symmetry (e) for equatorial π bonding to orbitals of the four sulfur atoms. However, in contrast to the $4p_z$ orbital, the d_{xz} and d_{yz} orbitals are involved in the π bonding between the vanadium and oxygen atoms. Thus the $4p_z$ orbital undoubtedly plays a more important role in the bonding of a sixth ligand than do the d_{xz} and d_{yz} orbitals. In their molecular orbital treatment of the aquated oxovanadium(IV) ion, $\mathrm{VO(H_2O)_5{}^{2+}}$, Ballhausen and Gray[23] considered the sixth ligand to be bonded to the vanadium $4p_z$ orbital only.

The infrared spectra of the DMSO adducts are complex in the 1500-cm^{-1} region and no clear interpretation analogous to that given for the pyridine adducts is possible. A typical spectrum is shown in Figure 1C.

Extensive studies of V=O stretching frequencies in various complexes have been made[4,24] with the hope that the location of the absorption band could be related to various structural parameters. The bulk of these studies indicates that, although the V=O stretching frequency does depend on the nature of the equatorial ligands, its position is affected by several variables which make its use as a structural probe rather limited. However, the V=O stretching frequency in the dithiocarbamate derivatives (Table II) falls in the "normal" range[4] and there is a regular trend with methyl < ethyl < pyrrolidyl < isopropyl. Thus the increase in V=O stretching frequency parallels the decrease in $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching frequency. This observation is quite reasonable if the d_{xz} and d_{yz} orbitals are involved in both axial and equatorial π bonding. The V=O stretching frequencies should be lowered as a consequence of the decrease in axial π bonding (oxygen to vanadium) brought about by increased sulfur to metal π bonding.

As electron density on vanadium is increased by coordination to the sixth position, the axial π bonding should decrease with consequent lowering of the V=O stretching frequency. Thus the pyridine and DMSO adducts show new bands at *ca.* 950 cm^{-1} which are assigned to the V=O stretching vibration (Table II). Some typical spectra are shown in Figure 1. In the adducts there appears to be little correlation between band frequency and the nature of the ligands.

Electronic Spectra.—Interpretation of the electronic spectra of oxovanadium(IV) complexes is a subject of continuing investigation and discussion.[6] Most complexes thus far reported show three prominent bands in the electronic spectral region, and Selbin[4] has designated these as bands I (11,500–14,500 cm^{-1}), II (15,000–18,000 cm^{-1}), and III (24,000–29,000 cm^{-1}). The Ballhausen and Gray[23] scheme (BG scheme) for the interpretation of the electronic spectrum of the aquated oxovanadium(IV) ion is summarized in Figure 2A. In this scheme band I is assigned as $b_2 \rightarrow e_\pi{}^*$, band II as $b_2 \rightarrow b_1{}^*$, and band III as $b_2 \rightarrow a_1{}^*$. In recent reviews Selbin[4,6] has questioned the general applicability of the BG scheme and has summarized the currently available

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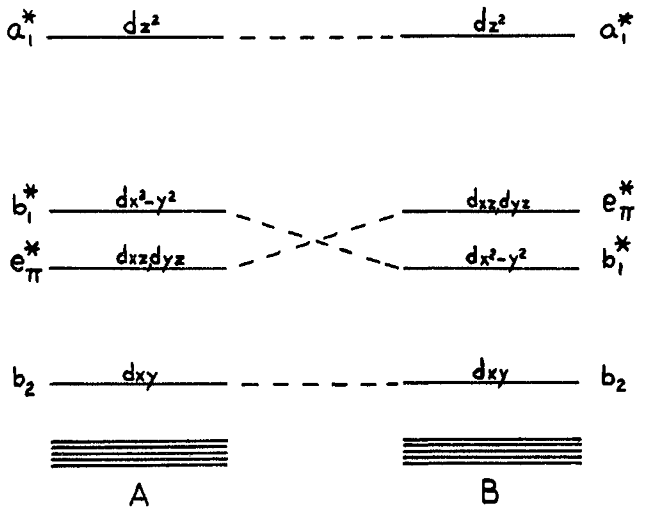

Figure 2.—Energy level schemes for oxovanadium(IV) complexes: A, Ballhausen–Gray scheme;[23] B, inverted level scheme.[6] The closely spaced lines represent filled bonding levels. The splittings are not drawn to scale.

information which applies to the problem. Of particular significance here are the firm conclusions that the ground level is the singly occupied, nonbonding b_2 orbital and that the e_π^* and b_1^* levels may be very close in energy and may cross one another from complex to complex. In addition, it should be pointed out that for $VO(acac)_2$, bands I and II are displaced toward lower and higher energies, respectively, when the complex is dissolved in solvents which add to the sixth position *trans* to the apical oxygen atom.

In the diffuse reflectance spectra (Figure 3) of the oxovanadium(IV) dithiocarbamate complexes in the visible region there are two characteristic bands. The first is a rather broad, asymmetric band (band A) located at 17.7–18.2 kK which shows some indication of structure on top of the broad-band envelope. There is a definite shoulder at 15.8–16.4 kK. A sharper, apparently more intense second band (band B) is located in the 22.2–23.2-kK region. In noncoordinating or weakly coordinating solvents such as 1,2-dibromoethane, chloroform, or sulfolane, the absorption bands, as shown in Figure 4, are essentially identical with those observed in the reflectance spectra except that a very intense, presumably charge-transfer band begins to dominate the spectra at *ca.* 25 kK. No additional bands of electronic origin were found at lower energies.

A study was made of the visible-region spectral changes that occur when the solid methyl derivative is exposed to air. After a period of several hours bands A and B started to decrease in intensity; after 5 days these bands disappeared, and the spectrum consisted of only a single strong band originating at 22.2 kK. This maximum of this single band was not located, although it appeared to be in the ultraviolet region. Since oxidation presumably converts the d^1 V^{4+} to d^0 V^{5+}, as has been mentioned previously for $VO(acac)_2$,[25] the disappearance of bands A and B implies that these result from d–d transitions in the VO^{2+} compounds.

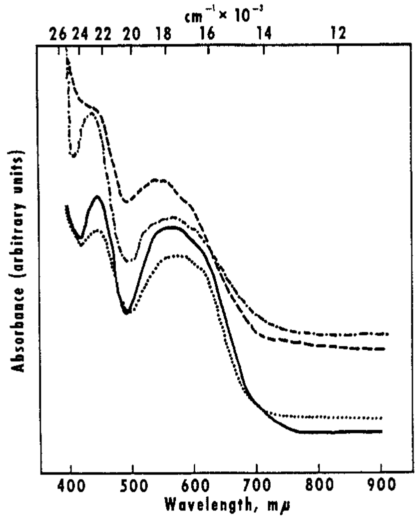

Figure 3.—Reflectance spectra: ———, $VO(S_2CN(C_2H_5)_2)_2$; – – – –, $VO(S_2CN(C_3H_7)_2)_2$; – · – ·, $VO(S_2CNC_4H_8)_2$; . . . ., $VO(S_2CN(CH_3)_2)_2$.

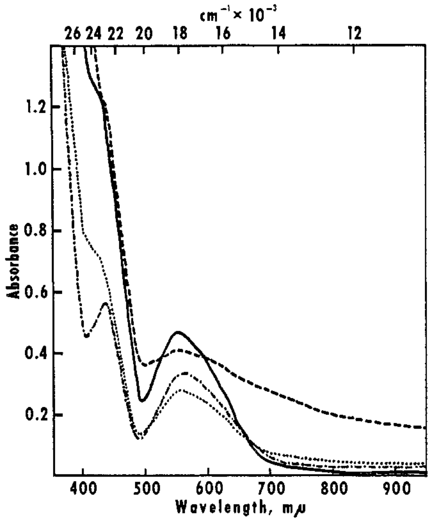

Figure 4.—Spectra measured in sulfolane solutions: ———, $VO(S_2CN(C_2H_5)_2)_2$; – – – –, $VO(S_2CN(C_3H_7)_2)_2$; – · – ·, $VO(S_2CNC_4H_8)_2$; . . . ., $VO(S_2CN(CH_3)_2)_2$.

Distinct spectral changes are observed in the visible region when the complexes are treated with a donor solvent such as pyridine or DMSO. Band A disappears and a new band appears in the region of 13.2 kK. Associated with the new band is a distinct shoulder centered at 15.9–16.4 kK. In the isopropyl derivative the shoulder has been resolved. Spectra are shown in Figures 5 and 6. Band B may be buried under the intense absorption originating at *ca.* 20 kK in these solutions.

Since there is strong evidence for π interaction between the vanadium atom and the ligands, the electronic spectra must be interpreted in terms of an energy level scheme in which equatorial π bonding is taken into consideration. As pointed out by Selbin,[6] the primary effect of equatorial π bonding may be to invert the order of the b_1^* and e_π^* levels from that of the BG scheme, as shown in Figure 2B.

The energy level scheme in Figure 2B can be used

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(25) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964)

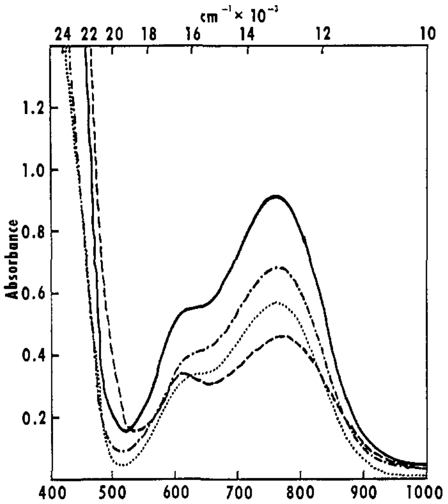

Figure 5.—Spectra measured in pyridine solutions: ———, $VO(S_2CN(C_2H_5)_2)_2$; – – – –, $VO(S_2CN(C_3H_7)_2)_2$; – · – ·, $VO(S_2CNC_4H_8)_2$; . . . ., $VO(S_2CN(CH_3)_2)_2$.

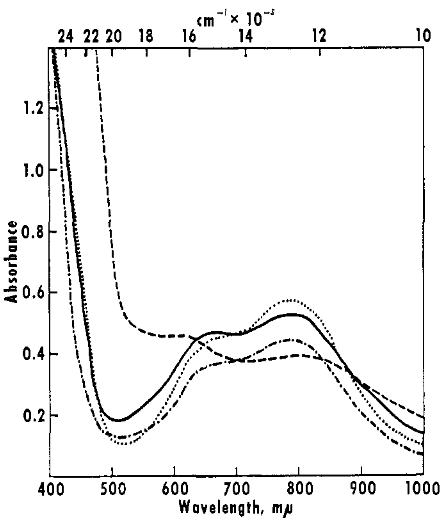

Figure 6.—Spectra measured in dimethyl sulfoxide: ———, $VO(S_2CN(C_2H_5)_2)_2$; – – – –, $VO(S_2CN(C_3H_7)_2)_2$; – · – ·, $VO(S_2CNC_4H_8)_2$; . . . ., $VO(S_2CN(CH_3)_2)_2$.

successfully as a basis for the assignment of the d–d bands in the dithiocarbamate complexes. Thus, considering the ethyl derivative, the absorption bands at 16.0, 17.6, and 22.5 kK can be assigned as the $b_2 \rightarrow b_1^*$, $b_2 \rightarrow e_\pi^*$, and $b_2 \rightarrow a_1^*$ transitions, respectively. The absorption bands of the other complexes can be assigned similarly.

These assignments are compatible with the spectral changes that occur when the complexes are dissolved in a donor solvent such as pyridine. The energy of the b_1^* antibonding level is expected to be little affected by the addition of a ligand to the sixth coordination position; hence, the frequency of the $b_2 \rightarrow b_1^*$ transition should be relatively unchanged in a donor solvent from that in the solid state (or solutions in noncoordinating solvents). On the other hand, the energy of the e_π^* level is expected to be reduced by coordination of a sixth ligand owing to concomitant reduction of the influence of the VO^{2+} oxygen atom in the orbital functions which contain a z component. Thus the $b_2 \rightarrow e_\pi^*$ transition should be shifted to lower energies in donor solvents. Shifts in the absorption band associated with the remaining transition, $b_2 \rightarrow a_1^*$, are less predictable than those for the two lower energy bands.

As can be seen in Table I, the band assigned as the $b_2 \rightarrow b_1^*$ transition remains relatively unchanged in position in going from solid spectra through solutions of weakly coordinating solvents to strongly coordinating solvents such as pyridine and DMSO. The band associated with the $b_2 \rightarrow e_\pi^*$ transitions is shifted by about 5 kK to lower energies. Thus, the assignments are in accord with the expected shifts due to solvent effects. It should also be pointed out that in the reflectance spectra the band assigned as the $b_2 \rightarrow e_\pi^*$ transition shows some sign of structure on top of the broad-band envelope that may indicate a partial lifting of the degeneracy of the e_π^* level. It would be interesting to investigate the low-temperature spectra of the complexes in an effort to resolve the fine structure of band A. In any case, it can be concluded from this work that the e_π^* and the b_1^* levels are very close in energy and that solvent perturbations may cause the levels to cross.

The remaining transition, $b_2 \rightarrow a_1^*$, is assigned as shown in Table I. The fate of this band when the complexes are dissolved in strongly coordinating solvents is not known. The intense band originating at about 20 kK in both pyridine and DMSO solutions obviates any firm conclusions.

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