8–9. Five milliliters of absolute alcohol was added, the solution was placed in a freezer for 90 min, and 0.96 g (3.3 mmol) of pure $Rb_2B_9H_9$ was collected upon filtering.

The ^{11}B nmr spectra were obtained on Varian spectrometers operating at frequencies of 19.2 and 32.1 MHz. Chemical shift data are given relative to trimethoxyborane as an external standard.

Debye–Scherrer–Hull X-ray powder diffraction patterns were taken by Mr. C. Scherone of Westinghouse Electric Corp. using a 114.6-mm camera.

Acknowledgment.—We wish to thank Dr. E. L. Muetterties for providing an authentic sample of $Cs_2B_9H_9$ and for his valuable comments which allowed us to characterize these materials correctly. We gratefully acknowledge support of this research by the National Science Foundation (Grant GP-8321) and by the Pennsylvania Science and Engineering Foundation (Contract 60).

Correspondence

On the Electron Spin Resonance Spectra of Oxovanadium(IV) Dithiocarbamate Complexes[1]

Sir:

Recently we have reported on the synthesis, structure, and infrared and optical spectra of N,N-dialkyldithiocarbamate (R = CH_3, C_2H_5, i-C_3H_7, and $CH_2(CH_2)_2CH_2$) complexes of oxovanadium(IV).[2] The only prior work on these complexes was by Garif'yanov and Kozyrev,[3] who reported the results of an esr study on the ethyl-substituted compound which was prepared and studied in solution without isolation and characterization as a solid. Subsequent to our publication was a report[4] by Selbin and Vigee on five VO^{2+}–dtc complexes, only one of which (the ethyl compound) overlapped our series. Three of the compounds prepared by Selbin and Vigee were formulated with a water molecule, whereas our compounds were anhydrous; aside from this difference the complexes reported in the two studies appear to be much the same.

Of particular interest is the behavior of the complexes in solution, since large red shifts are observed for certain of the optical bands in coordinating solvents. We interpreted the red shifts in terms of the addition of a solvent molecule to the coordination position *trans* to the oxygen atom, and very recently we have reported on our success in preparing as stable solids adducts of the methyl and pyrrolidine complexes with pyridine and 4-methylpyridine.[5] Thus the conclusion that dithiocarbamate complexes of oxovanadium(IV) are completely destroyed by pyridine and DMSO, as reached by Selbin and Vigee from their esr study in DMSO, was of considerable consequence and has stimulated us to investigate the esr spectral properties of the compounds that we reported previously, as well as to reinvestigate the cyclohexyl compound reported by Selbin and Vigee.

Compounds were prepared as reported previously,[2] and esr spectra were recorded at room temperature with a Varian Model E-3 spectrometer. The reference material used was DPPH in benzene. The isotropic hyperfine splittings were measured[6] as the separation between lines 4 and 5, and the accuracy of our techniques was estimated by measuring the spectral properties of $VO(acac)_2$ and $VOSO_4$. A comparison of our results to those previously reported indicates an agreement of ±1 G for the hyperfine splittings, as shown in Table I.

Table I

Isotropic Hyperfine Splitting Constants

Compound[a]	Solvent	$\Delta H_{4,5}$[b]	Ref[c]
$VO((c\text{-}C_6H_{11})_2dtc)_2$	CH_2Cl_2	86	
	Pyridine	88	
	DMSO	85	
	DMSO	114	*d*
$VO((CH_3)_2dtc)_2$	CH_2Cl_2	89	
	Pyridine	89	
	DMSO	93	
$VO((C_2H_5)_2dtc)_2$	CH_2Cl_2	89	
	Pyridine	89	
	DMSO	91	
	Benzene	92	*e*
$VO((i\text{-}C_3H_7)_2dtc)_2$	CH_2Cl_2	88	
	Pyridine	88	
	DMSO	87	
$VO((py)_2dtc)_2$	CH_2Cl_2	88	
	Pyridine	88	
	DMSO	93	
$VO(CH_3\text{-}c\text{-}C_6H_{11}dtc)_2$	DMSO	118	*d*
$VO(acac)_2$	Pyridine	105	
	Pyridine	104	*f*
$VO(acac)_2$	Benzene	109	
	Benzene	108	*g*
$VOSO_4$	H_2O	115	
	H_2O	116	*h*
$VOSO_4$	DMSO	112	
	DMSO	113	*i*

[a] dtc = dithiocarbamate; py = pyrrolidyl; acac = acetylacetonate. [b] Values in gauss. [c] Where a reference is not given, values were obtained in this work. [d] Reference 4. [e] Reference 3. [f] F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966). [g] I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963). [h] H. A. Kuska and M. T. Rogers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 13. [i] Reference 6.

Throughout the preparations and spectral measurements, great care was taken to protect the dithiocarbamate samples from oxygen. Since it does appear[5] that the complexes *slowly* decompose in DMSO, the

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(1) This work was supported by the National Science Foundation through Grant No. GP-10668.

(2) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).

(3) N. S. Garif'yanov and B. M. Kozyrev, *Teor. i. Eksperim. Khim. Akad. Nauk Ukr. SSR*, **1**, 525 (1965); *Theoret. Exptl. Chem.* (USSR), **1**, 345 (1965).

(4) J. Selbin and G. Vigee, *J. Inorg. Nucl. Chem.*, **31**, 3187 (1969).

(5) B. J. McCormick, *Can. J. Chem.*, **47**, 4283 (1969).

(6) H. A. Kuska, Ph.D. Thesis, Michigan State University, 1965.

spectra in all solvents were obtained as quickly as possible after dissolution (5–10 min). A typical spectrum is shown in Figure 1; in *all* cases eight-line spectra similar to the one shown were observed. The isotropic *g* values (corrected for second-order effects) of *ca.* 1.982 are in reasonable agreement with the previously reported values.[3,4] Isotropic hyperfine splittings, $\Delta H_{4,5}$, are given in Table I. Spectra were measured in the noncoordinating solvent methylene chloride and in the coordinating solvents pyridine and DMSO. The $\Delta H_{4,5}$ values are found in the range 89 ± 4 G. The small variation in $\Delta H_{4,5}$ probably reflects several factors such as the donor strength of the solvents, the electron-withdrawing and steric properties of the ligands,[1] and dielectric effects.[7]

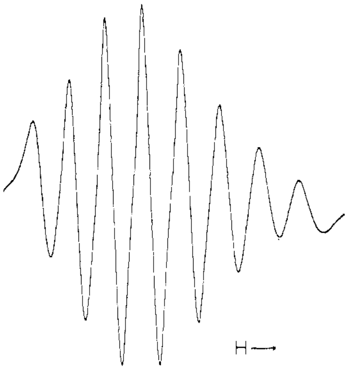

Figure 1.—Esr spectrum of bis(N,N-diethyldithiocarbamato)-oxovanadium(IV) in DMSO at room temperature.

Our results, in general, are not in good agreement with those obtained by Selbin and Vigee. The spectrum of the ethyl complex in DMSO was reported[4] to consist of two sets of eight lines, and this observation was interpreted to mean that there were two different VO^{2+} species in solution. We find for the ethyl complex in DMSO (Figure 1), as well as for all of the complexes in all of the solvents studied, typical eight-line spectra with no evidence for extra lines or splittings that might suggest two or more species in solution. In this regard our results are similar to the results obtained by Garif'yanov and Kozyrev in benzene and toluene.[3] A second point of difference relates to the magnitude of the $\Delta H_{4,5}$ values that were reported. Our value for the cyclohexyl compound in DMSO differs from that of Selbin and Vigee by 29 G but agrees with the Garif'yanov–Kozyrev results for the ethyl compound in noncoordinating solvents to within 3 G.

The reason for the discrepancies between our work and that of Selbin and Vigee is not clear. However, we have observed spectra with more than eight lines for solutions of samples that have not been adequately protected from oxygen. It may be possible that the 16-line spectra observed by Selbin and Vigee do indicate two different VO^{2+} species in solution but that the different species result from oxidation rather than dissociation to pyridine or DMSO complexes. Our esr data are quite consistent with the notion that pyridine and DMSO form adducts, as described previously,[1,5] in the absence of oxygen.

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[7] F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).