Contribution from the Departments of Chemistry, West Virginia University, Morgantown, West Virginia 26506, and The University of Kentucky, Lexington, Kentucky 40506

Oxovanadium(IV) Complexes of Dimethyldithioarsinate. Evidence for Arsenic-75 Superhyperfine Interaction[1]

B. Jack McCormick,*[2a] J. L. Featherstone,[2a]
H. J. Stoklosa,[2b] and J. R. Wasson[2b]

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Complexes of oxovanadium(IV) with sulfur-containing ligands are becoming increasingly well known. Of special interest are several dithiophosphate and dithiophosphinate complexes in which very large ^{31}P superhyperfine interactions are manifested in the esr spectra.[3-6] The mechanism of this interaction is thought to involve direct vanadium 3d-phosphorus 3s, 3p orbital overlap.[4] Recent reports[7-9] on metal complexes of dimethyldithioarsinate (or dithiocacodylate, abbreviated dtcac) were of considerable interest because of the nuclear spin of ^{75}As ($I = ^3/_2$), which is 100% abundant. We have synthesized and characterized VO(dtcac)$_2$ in order to determine whether there is V-As superhyperfine interaction analogous to that found in the phosphorus-containing complexes.

Experimental Section

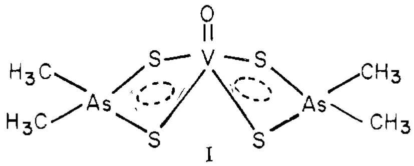
Materials and Procedures. Sodium dimethyldithioarsinate dihydrate was prepared according to published procedures.[7] Optical and infrared spectra were measured with Cary Model 14 and Beckman IR-12 recording spectrophotometers, respectively. Electron spin resonance spectra were measured with Varian E-3 and Magnion Model MVR-12 X-band spectrometers. The Magnion esr spectrometer operates at about 9.4 GHz using 6-kc field modulation and a 12-in. electromagnet. The frequency was monitored with a calibrated absorption wavemeter incorporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical. Esr spectra of saturated solutions were obtained using stoppered flattened quartz sample tubes. The solutions were flushed with purified nitrogen to exclude oxygen and measurements were made immediately after the solutions were prepared. Frozen solution spectra were obtained with a finger dewar filled with liquid nitrogen which fit into the instrument sample cavity. Mass spectra were obtained with a Nuclide Model 12-90G spectrometer. Analyses were done by Chemalytics, Tempe, Ariz.

Synthesis of VO(dtcac)$_2$. To 0.63 g (0.0034 mol) of V_2O_5 was added 4 ml of 12 M hydrochloric acid and 6 ml of 95% ethanol. Upon heating the mixture the V_2O_5 dissolved. The volume of the solution was reduced to *ca.* 1 ml by boiling, and the resultant syrupy $VOCl_2$ was diluted with 2 ml of methanol. The resulting solution was slowly added to a warm (50°) solution of 1.30 g (0.0068 mol) of sodium dimethyldithioarsinate dihydrate in 75 ml of methanol. A blue crystalline precipitate formed immediately. After filtration the precipitate was washed with three 10-ml portions of methanol and dried *in vacuo* over P_4O_{10} for 15 hr. *Anal.* Calcd for $C_4H_{12}As_2OS_4V$: C, 11.9; H, 2.98; S, 31.7. Found: C, 12.2; H, 3.21; S, 31.5.

Properties of VO(dtcac)$_2$. The complex is stable for a period of several weeks when stored dry and under an atmosphere of nitrogen. The solubility in water and noncoordinating solvents is very low and decomposition slowly takes place, even in deaereated solutions. In coordinating solvents such as pyridine the solubility is high, but the resulting green solutions are very unstable. The instability and low solubility of the compound has precluded molecular weight determinations by classical methods. The mass spectrum of the compound, as obtained by insertion of the solid into the spectrometer, shows a parent ion at m/e 405. This result suggests that the compound is monomeric, as the calculated molecular weight is 405.

Results and Discussion

Vanadyl(IV) chloride reacts readily with sodium dimethyldithioarsinate to provide bis(dimethyldithioarsinato)oxovanadium(IV), VO(dtcac)$_2$, which is assumed to have the tetragonal-pyramidal geometry, I, in common with most other oxovanadium(IV) complexes.[10]



I

In the 250-1800-cm^{-1} region the infrared spectrum of the complex is virtually identical with that reported[7] for Ni(dtcac)$_2$ with the exception of a very strong, sharp band at 986 cm^{-1}, which is assigned to the vanadium-oxygen stretching frequency.[10] The electronic spectrum of VO(dtcac)$_2$ in the solid state (Nujol mull and diffuse reflectance) is similar to those reported for oxovanadium(IV) dithiocarbamate[11] and dithiophosphinate[3] complexes. The dominant features of the spectrum are a shoulder at 14,930 cm^{-1} on the low-energy side of the 16,810-cm^{-1} peak and another shoulder at 23,810 cm^{-1} occurring just before the onset of strong absorption in the ultraviolet region. The limited solubility and instability of the compound have precluded our making a detailed study of band intensities and band shifts in solvents of varying donor strengths; however, an air-free, saturated benzene solution (10^{-2}-10^{-3} M) shows exactly the same spectral features as the solid compound. When prepared carefully, these benzene solutions showed no spectral changes over a period of 1 day.

The isotropic esr spectrum of VO(dtcac)$_2$ in benzene is shown in Figure 1, wherein at least 27 discernible component lines are exhibited. In chloroform a similar spectrum is obtained, which shows 21 well-resolved lines and a number of shoulders and line asymmetries. All of the spectral features in both solvents are reproducible. Since interaction of an unpaired electron with a ^{51}V nucleus ($I = ^7/_2$) gives rise to only eight lines, it is clear that additional interactions must be considered in VO(dtcac)$_2$. The possibility that the 27 lines observed in benzene arise from several different species formed by decomposition or dissociation can be ruled out since the optical spectra of the solid and benzene solutions are identical. Furthermore, a mixture would be expected to produce a spectrum differing considerably in appearance from that which is observed.

Interaction of the electron with one or two equivalent ^{75}As nuclei should, in principle, give rise to 32- and 56-line spectra, respectively. Clearly there is interaction with at least one ^{75}As atom. It is not surprising that fewer than the theoretical number of lines is observed because of the large

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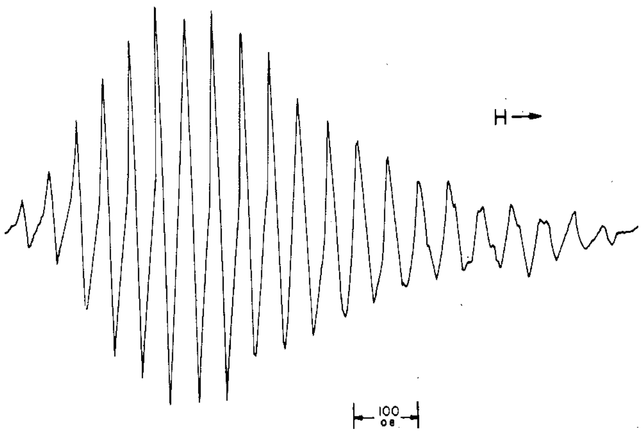

Figure 1. Esr spectrum of VO(dtcac)$_2$ in benzene. $\nu = 9.348$ GHz.

Table I. Esr Data for $VO(S_2As(CH_3)_2)_2$

Solvent	$\langle g \rangle$ (± 0.0006)	$A(^{51}V)$,^{a} G	$10^{-4}A(^{51}V)$,^{b} cm^{-1}	$10^{-4}A(^{75}As)$, cm^{-1}
Benzene	1.9731	90.63	83.02	41.74
Chloroform	1.9757	90.63	81.78	41.80

^{a} Uncorrected for second-order effects. ^{b} Correct to second order.

value of the ^{75}As superhyperfine splitting constant and second-order and other effects which lead to line overlapping. Attempts to simulate the spectra[12] suggest that two equivalent arsenic nuclei giving rise to superhyperfine splitting provide the best fit to the observed data. Esr parameters are summarized in Table I. It is noted that the ^{75}As superhyperfine splitting constant for VO(dtcac)$_2$ is appreciably larger than the 26.9×10^{-4} cm^{-1} reported[13] for the ill-defined species formed from vanadium trichloride and dibutylvinylarsine. The frozen-solution spectra yielded parameters within experimental error of those reported for the analgous dithiophosphate chelates.[4] However, no ^{75}As superhyperfine splitting was observed in the frozen solutions and the spectra obtained were very similar to those obtained for other VO^{2+} complexes at low temperatures, *e.g.*, VO(acac)$_2$.[14] This rather anomalous behavior has also been reported[15] for a frozen solution of VOF_5^{3-} in 48% HF, which exhibits ^{19}F superhyperfine splitting when doped into $(NH_4)_3AlF_6$. Except for the possibility of a fortuitous cancelation of superhyperfine splitting in frozen solutions, the reason for the lack of superhyperfine splitting in the frozen solutions remains obscure.

The interpretation of the ^{75}As superhyperfine splitting is similar to that proposed[4] for ^{31}P superhyperfine splitting observed in vanadyl dithiophosphinates and dithiophosphates. In C_{2v} symmetry the unpaired electron resides in a $^2A_1$ ground state which is approximately[16] 4.5% of d_{z^2} and 94.4% of $d_{x^2-y^2}$ orbital character. The $d_{x^2-y^2}$ orbital is not strongly σ bonding with respect to sulfur but does possess the correct symmetry to interact *directly* with arsenic 4s and 4p orbitals. It is possible that the *major* source of the ^{75}As superhyperfine splitting in VO(dtcac)$_2$ is attributable to direct vanadium 3d–arsenic 4s, 4p interaction. However, delocalization of the unpaired electron onto the arsenic atoms *via* metal-sulfur interaction can also contribute to the observed ^{75}As superhyperfine structure. The relative importance of these two mechanisms cannot be assessed at present. The isotropic ^{75}As splitting is given by

$$A(^{75}\mathrm{As}) = \frac{8\pi}{3} g_e g_n \beta_e \beta_n |\psi 4s(0)|^2 C_s^2$$

where C_s is the coefficient of the As 4s orbital in the molecular orbital containing the unpaired electron and $|\psi 4s(0)|^2$ is the 4s electron density at the nucleus. The evaluation of C_s^2 is accomplished by taking the ratio of the observed isotropic ^{75}As superhyperfine splitting, A_{obsd}, to that calculated,[17] A_{calcd}, for an unpaired electron residing totally in an arsenic 4s orbital, *i.e.*

$$C_s^2 = A_{\mathrm{obsd}}/A_{\mathrm{calcd}} = \frac{A_{\mathrm{obsd}}}{3430\ \mathrm{G}}$$

For VO(dtcac)$_2$ C_s^2 is found to be 0.0132 which is very close to the 0.0135 found for vanadyl dithiophosphates. This further illustrates the great similarity in the bonding in these VOS$_4$ chelates.

Registry No. VO(dtcac)$_2$, 37448-72-9.

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[12] Spectra were simulated using the program SIMESRQL written by Professor R. E. D. McClung. A 1000-G sweep was considered and spectra were calculated using lorentzian lines with a peak to peak width of 12 G.

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Contribution from the Laboratorio per lo studio della
Stereochimica ed Energetica dei composti di
Coordinazione del CNR, Florence, Italy, and Istituto
Chimico Policattedra dell 'Universita, Cagliari, Italy

Single-Crystal Polarized Electronic Spectra of a CoN_5 Chromophore

I. Bertini, M. Ciampolini,* and D. Gatteschi

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In recent years the isotropic electronic spectra of a number of trigonal-bipyramidal high-spin complexes of cobalt(II) have been measured.[1,2] Using the crystal field approach two assignments of the observed transitions were proposed.[3,4] It was felt that polarized single-crystal spectra should be useful for a substantiated assignment.

With this aim, the complex [Co(NCS)(Me$_6$tren)] SCN·H$_2$O

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