ATRANES

IX. Structure And Some Physicochemical Properties Of 1-Oxovanadatranes*

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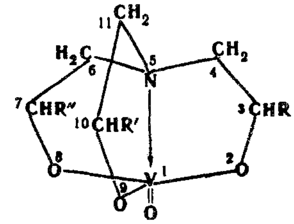
Magnetic susceptibilities and dipole moments of 1-oxovanadatranes are measured, and their IR spectra investigated. The results obtained show these compounds to contain a transannular dative V←N bond.

A previous communication described a method of synthesizing the previously unknown 2,2',2"-aminotriethylorthovanadates $\underbrace{O = V(OCH_2CH_2)_3N}$ (1-oxovanadatranes). Here the structures and some physicochemical properties of these compounds will be considered.

Previously the silatranes molecule $\underbrace{XSi(OCH_2CH_2)_3N}$ was conclusively shown to have a transannular coordinate link between the silicon and nitrogen atoms [2–6]. The similarly constituted 1-oxovanadatranes might be expected to possess an analogous structure (I), characterized by the presence of a transannular dative bond V ← N, since the vanadium atom has an unfilled 3rd level, able to take the unshared electron pair of the nitrogen.



I

Ia R = R′ = R″ = H
Ib R′ = R″ = H; R = CH₂Cl
Ic R = R′ = R″ = CH₃

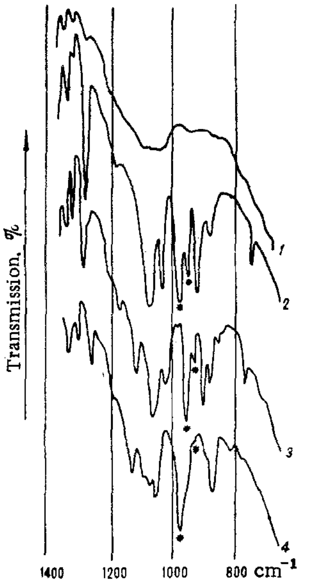
We have investigated the magnetic susceptibilities, IR spectra, and dipole moments of 1-oxovanadatrane (Ia), 1-oxo-3-(chloromethyl)-vanadatrane (Ib), and 1-oxo-3,7,10-(trimethyl) vanadatrane (Ic).

Table 1
Specific Magnetic Susceptibility of Compounds I

Compound	χ_{sp}, 10^{-6}		$\Delta\chi_{sp}$, 10^{-6}
	Found	Calculated	
Ia	−0.170	−0.485	+0.315
Ib	−0.330	−0.501	+0.171
Ic	0	−0.548	+0.548

Gouy's method [7] was used to measure the specific magnetic susceptibilities (χ_{sp}) in the solid state, and Table 1 shows the results.

As expected [7], all the I compounds proved to be diamagnetic, thus confirming that their vanadium atom was 6-covalent, and providing indirect evidence that these compounds are monomeric in the solid state. Comparision of experimental magnetic susceptibilities with those calculated by Pascal's new method, indicates considerable polarization paramagnetism (Table 1). Actually the value of $\Delta\chi_{sp}$ is affected by the presence of the V ← N bond, not taken into account in the calculation, and also by the presence of some asymmetry of the I molecule.



IR spectra of 1-oxovanadatranes: 1) vaseline, 2) Ia, 3) Ib, 4) Ic.

More detailed data regarding the structure of I were obtained by investigating the IR spectra (Fig. 1). The spectra were measured with a single beam IKS-12 spectrometer, in the 800–1700 cm^{-1} region (NaCl prism), and for the condensed phase. Mulls of the compounds in vaseline were prepared as usual [8].

Basically the I absorption bands lie in the 800–1300 cm^{-1} region, where there are no peaks due to the air and vaseline. Here basically interpretation of the IR spectra led to assigning of an absorption band corresponding to V—O group valence vibrations. In the case of $O = VCl_3$[9] such vibrations provide a peak of average intensity at 1035 cm^{-1}. It is known that the vanadyl group frequency can be exhibited over a wide range of 900–1100 cm^{-1}, depending on the kinds of substituents linked directly to the vanadium atom [10–12].

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*For Part VIII see [19].

Table 2

Dipole Moments of 1-Oxovanadatranes, and Associated Data for Determining Them*

Compound	N	ε^{25}	d_4^{25}	n_D^{25}	P_{or}			μ, D
					Solvent	Solution	Compound	
Ia	0.00157	5.0537	1.4783	1.4443	32.0984	35.7094	2332.102	10.67
Ia	0.00216	5.1525	1.4786	1.4444	32.0984	36.8112	2213.935	10.40
Ib	0.00090	4.8482	1.4796	1.4439	32.0334	33.4209	1573.666	8.77
Ib	0.00089	4.8478	1.4792	1.4439	32.0334	33.4241	1587.583	8.80
Ic	0.00098	4.8757	1.4787	1.4439	32.0334	33.7327	1764.220	9.28
Ic	0.00085	4.8537	1.4785	1.4440	32.0334	33.4918	1755.900	9.26

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*N, ε^{25}, d_4^{25}, n_D^{25}, P_{or}, μ are respectively the mole fraction, dielectric constant, density, refractive index, orientation polarization, and dipole moment.

If the O = V ← N dative bond were absent from the I molecule, the V = O valence vibrations probably ought to appear in the 1030 cm^{-1} region or somewhat lower, the electronegativity of the oxygen atoms in I being less than that of the chlorine atoms in O—VCl_3 [13]. When the V ← N transannular bond is present, the vanadyl group absorption should be displaced towards the longer wavelength region, as has been observed for analogous complexes of vanadyl and uranyl derivatives coordinated with molecules able to give a lone pair of electrons to the metal [14,15].

Table 3

Effect of Temperature on the Dipole Moments of Ia and Ic

Temperature °C	μ, D	
	Ia	Ib
5	9.35	10.65
10	9.75	10.58
15	9.35	10.68
20	9.14	10.31
25	8.96	10.20
30	9.13	10.36
35	9.01	10.19
40	9.05	10.17

Comparions of the spectra of Ia–c with one another and with data in the literature [10–12, 14, 15], leads to a conclusion that in these compounds V—O group vibrations are manifest as the doublet 929, 961 (Ia); 932, 959 (Ib), and 957 cm^{-1} (Ic).

Thus the IR spectra of I exhibit a longwave shift of the V = O absorption band confirming that they contain the V ← N dative bond. The relevant data also favor the monomeric nature of I, since if this did not obtain [16] the IR spectra should exhibit wide absorption bands in the 800–900 cm^{-1} region.

To check these conclusions we determined the dipole moments of I in chloroform at 25°. One of us has previously described the method of measurement [17], and the method of calculation [18]. Table 2 gives the results of the measurements.

The results obtained show that all the Is exhibit high polarity in chloroform. Some part of the dipole moments is due to their interaction with the polar solvent. However in general that effect does not exceed 1-2D. Approximate calculations for dipole moments of I($\mu_{V=O} \approx 2D$) which we made by the vectorial method, in a way similar to that previously described [3], showed the calculated values (5–5.5 D) for the moments to be considerably lower than those found experimentally. This can be explained by the omission of the moment of the highly polar dative V ← N bond from the calculation.

We also investigated the dependence of the dipole moments of Ia and Ic in chloroform on temperature (Table 3). The results tabulated there show that from 5 to 40° dipole moments of I are practically constant. This indicates the relative stability of the V ← N dative bond, as its rupture would lead to a sharp drop in molecule dipole moment.

REFERENCES

1. M. G. Voronkov and S. F. Lapsin, KhGS [Chemistry of Heterocyclic Compounds], 357, 1966.
2. M. G. Voronkov and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 51, 1965.
3. M. G. Voronkov, I. B. Mazheika, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 58, 1965.
4. M. G. Voronkov and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 210, 1965.
5. A. N. Egorochkin, V. A. Pestunovich, M. G. Voronkov, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 300, 1965.
6. Yu. P. Egorov, M. G. Voronkov, T. B. Lutsenko, and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 24, 1966.
7. P. W. Selwood, Magnetochemistry [Russian translation], IL, Moscow, 1958.
8. J. S. Ard, Anal. Chem., 25, 11, 1743, 1963.
9. F. A. Miller and L. R. Consins, J. Chem. Phys., 26, 329, 1957.
10. C. G. Barraclogh, J. Lewis and R. Nyholm, J. Chem. Soc., 3552, 1959.
11. J. Selbin, L. H. Holmes and S. P. McGlynn, Chem. Ind., 746, 1961.
12. R. L. Dutta and Lahiry Subrata, J. Indian Chem. Soc., 40, 657, 1963.

13. M. E. Dyatkina, V. P. Markov, I. V. Tsapkina, and Yu. N. Mikhailov, ZhNKh, **5**, 575, 1961.

14. K. Hakamoto, V. Morimoto and A. E. Martell, J. Am. Chem. Soc., **83**, 4522, 1961.

15. J. Selbin, H. R. Manning and G. Cessac, J. Inorg. Nucl. Chem., 25, 1253, 1963.

16. Yu. Ya. Kharitonov and Yu. A. Buslaev, Izv. AN SSSR, OKhN, 393, 1962.

17. O. A. Osipov, ZhOKh, **26**, 322, 1956.

18. O. A. Osipov, ZhFKh, 31, 1542, 1957.

19. M. G. Voronkov and G. I. Zelchan, KhGS [Chemistry of Heterocyclic Compounds], 511, 1966.

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