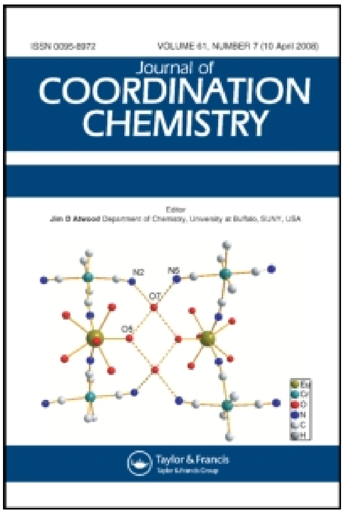

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SYNTHESIS, STRUCTURE AND SPECTRA OF AMMONIUM (SALICYLALDEHYDES *S*-METHYLTIOSEMIC ARBAZONATO) DIOXOVANADATE(V) MONOHYDRATE

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SYNTHESIS, STRUCTURE AND SPECTRA OF AMMONIUM (SALICYLALDEHYDE *S*-METHYLTHIOSEMICARBAZONATO) DIOXOVANADATE(V) MONOHYDRATE

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Crystals of ammonium (salicylaldehyde *S*-methylthiosemicarbazonato)dioxovanadate(V)monohydrate, $NH_4[VO_2L]\cdot H_2O$ were synthesized from ammonia–ethanol solution of VCl_3 and salicylaldehyde *S*-methylthiosemicarbazone (H_2L). They belong to the monocyclic system, space group $P2_{1/c}$, a, = 5.864(2), b = 16.382(7), c = 13.931(5)Å, β = 97.60(3)°, D_m = 1.62, D_c = 1.63.

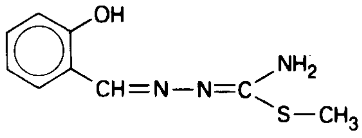
The position of the vanadium atom was determined on the basis of the distribution of Patterson function, coordinates of the other atoms on the basis of Fourier synthesis. Vanadium occurs in the complex within the VO_2^+ group, lacking d-electrons. The coordination polyhedron has the form of a deformed square pyramid.

The bands in infrared spectrum indicate the existence of valence oscillations of O=V=O group.

Absorption spectra of the complex and ligand were calculated from the measured reflectance spectra by the application of Kubelka-Munk theory. Two out of the seven absorption maxima in the spectrum, result from intraligand transitions and the others are most likely related to the transitions involving charge transfer from the ligand π and n orbitals to vacant d orbitals of vanadium.

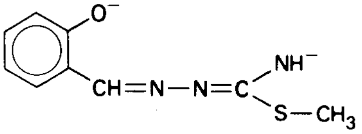
INTRODUCTION

Salicylaldehyde *S*-methylthiosemicarbazone in



(H_2L)

alcoholic solution reacts with the salts of a number of 3*d*-elements (V, Cr, Fe, Co, Ni, and Cu) producing complexes of different types.[1–5] Chemical and physical analyses showed that this tridentate NNO-ligand behaves as a neutral molecule, one-base or two-base acid, depending on the deprotonation of OH- and NH_2-groups. The reaction of different vanadium salts[1,5] served as an example to show that the above ligand stabilizes different oxidation states of vanadium: V(III), V(IV), and V(V), the last two being stabilized in the form of oxo- and dioxo-groups, respectively. Continuing our studies of the complexes of 3*d*-elements with this ligand, we present in this paper the results of the synthesis, X-ray structural and spectroscopic analyses of the complex V(V): $NH_4[VO_2L]\cdot H_2O$, where L— is the radical of salicylaldehyde *S*-methylthiosemicarbazone.



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EXPERIMENTAL

Synthesis and General Physical and Chemical Characteristics

The mixture of 1.6 g (10 mM) VCl_3 and 2.1 g (10 mM) H_2L was diluted while heating in 30 cm^3 of ethanol and left in an open vessel for 24 hrs, at room temperature. After that, 20 cm^3 of concentrated ammonium solution were added, the reaction mixture was filtered and again left at room temperature for additional 50 hrs. The resulting mixture of dark brown crystals (in larger amount) and red crystals was filtered and recrystalized from 50 cm^3 of hot concentrated ammonium solution. The resultant orange-colored crystalline substance was rinsed with the mixture of ethanol and ammonium water solution (1 : 1), then ethanol, and finally ether. The yield was 1.4 g.

Analysis: Calculated for $VC_9H_{13}N_4O_3S{\cdot}H_2O$
(M = 326.12):
V – 15.62; C – 33.12; H – 4.63;
N – 17.17; H_2O – 5.52.
Found: V – 15.43; C – 33.09; H – 4.61;
N – 17.24; H_2O – 5.63.

The substance was soluble in alcohols, unsoluble in ether, decomposable by water. The obtained complex was diamagnetic indicating, among other things, that vanadium is in the oxidation state 5^+ (d^0-system). Molar conductivity of 1.10^{-3} mol/dm^3 of the methanolic solution was 67 Ω^{-1} cm^2 mol^{-1}, i.e., the complex behaved in solution as binary electrolyte. At 110°C, the compound loses crystalline water changing its color from orange to dark brown.

Infrared Spectrum

The bands at 922 and 868 cm^{-1} are present on the IR spectrum of this compound (Figure 1) while they are absent in the spectra of the other complexes V(III) and VO(IV) with this ligand. The bands originate from the valence oscillations ν_{as} and ν_s, of O=V=O-group.[6,7]

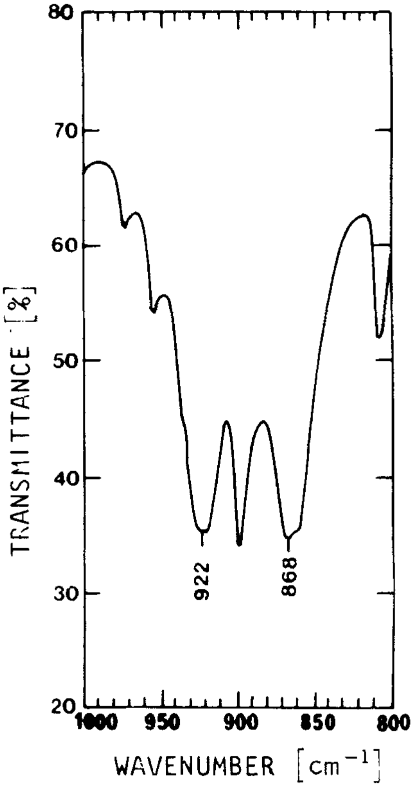

FIGURE 1 IR spectrum of $NH_4[VO_2L]{\cdot}H_2O$ in region of VO_2 vibrations (in KBr).

Crystal Data, Structure Determination and Refinement

$C_9H_{15}N_4O_4SV$, M = 326.2, monoclinic, a = 5.864(2), b = 16.382(7), c = 13.931(5), β = 97.60(3), V = 1326.5 Å^3, D_m = 1.62 (by flotation), D_c = 1.63 Mg/m^3, space group $P2_{1/c}$ (from systematic absences).

Intensities of 2739 independent reflexions were collected on a SYNTEX P1 computer-controlled four-circle diffractometer equipped with a graphite monochromator and using MoK_α radiation (λ = 0.7107 Å). Cell constants were determined during the alignment procedure by least-squares refinement of the setting angles of 15 carefully centred reflexions. Data were not corrected for absorption. The 1911 reflexions with $I \geq 2\sigma(I)$ were used in the analysis.

Coordinates of vanadium atom were determined by the Patterson method. A subsequent cycle of structure factor and Fourier electron density calculation revealed the position of all the non-hydrogen atoms (Table I). The structure was refined by block-diagonal least-square calculations to R = 0.070 for 1911 reflexions.

Measurement of Electronic Spectra

Diffusion–reflection spectra were measured on a monochromator SPM-2 (ZEIS–Jena) and a reflection cell of the type R-45/0, at room temperature and within the interval 10000 to 40000 cm^{-1}.

Samples were prepared to comply with the hypothesis of Kubelka–Munk theory.[8] The obtained values of Kubelka-Munk function for the complex $NH_4[VO_2L]{\cdot}$

TABLE I
Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$)[a] for all the non-hydrogen atoms. Estimated standard deviations are in parentheses.

Atom	X/A	Y/B	Z/C	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
V	596(2)	1798(1)	918(1)	248(3)	5(2)	1(2)	17(1)	6(1)	25(1)
S	6609(3)	4163(1)	1244(1)	327(7)	51(4)	68(5)	24(1)	22(1)	64(1)
O_1	2175(10)	2058(3)	92(3)	451(21)	−7(11)	69(12)	26(1)	4(3)	41(2)
O_2	2504(8)	1115(2)	1798(3)	261(15)	−14(8)	−5(10)	18(1)	1(3)	35(2)
O_3	4586(11)	4248(4)	4415(5)	285(20)	−1(14)	−4(16)	57(3)	−15(6)	84(4)
O_4	8864(9)	1056(3)	457(3)	286(16)	−9(9)	−33(11)	23(2)	−17(3)	50(2)
N_1	8055(10)	2619(3)	835(4)	250(18)	2(11)	−15(13)	22(2)	−5(4)	37(3)
N_2	1579(10)	2714(3)	2010(4)	256(17)	−1(10)	−8(12)	18(2)	−9(4)	30(2)
N_3	9799(12)	4541(3)	3599(4)	372(22)	13(13)	−1(14)	21(2)	−10(4)	36(3)
N_4	210(11)	3420(3)	1989(4)	308(20)	34(11)	16(13)	21(2)	−12(4)	35(3)
C_1	3436(14)	2722(5)	2615(5)	200(21)	−7(15)	11(15)	23(3)	−1(5)	36(3)
C_2	4976(14)	2050(4)	2764(5)	211(22)	−17(13)	40(15)	28(2)	6(5)	30(3)
C_3	7126(15)	2159(5)	3373(5)	275(26)	−47(17)	5(17)	39(3)	11(6)	33(3)
C_4	8669(14)	1539(6)	3553(6)	196(22)	18(17)	5(17)	40(4)	13(7)	39(4)
C_5	8152(30)	780(9)	3180(11)	297(47)	−14(31)	57(34)	45(6)	−5(11)	43(7)
C_6	6106(24)	641(8)	2558(9)	224(38)	38(24)	60(28)	28(4)	2(9)	42(6)
C_7	4476(20)	1272(6)	2363(7)	195(31)	8(20)	26(22)	22(4)	7(7)	27(5)
C_8	8417(25)	3299(8)	1328(9)	148(41)	−6(26)	−6(30)	28(5)	2(10)	28(8)
C_9	4307(25)	3905(7)	305(10)	236(42)	11(26)	24(30)	30(5)	−8(10)	50(8)

[a] The temperature factor expression used was $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$.

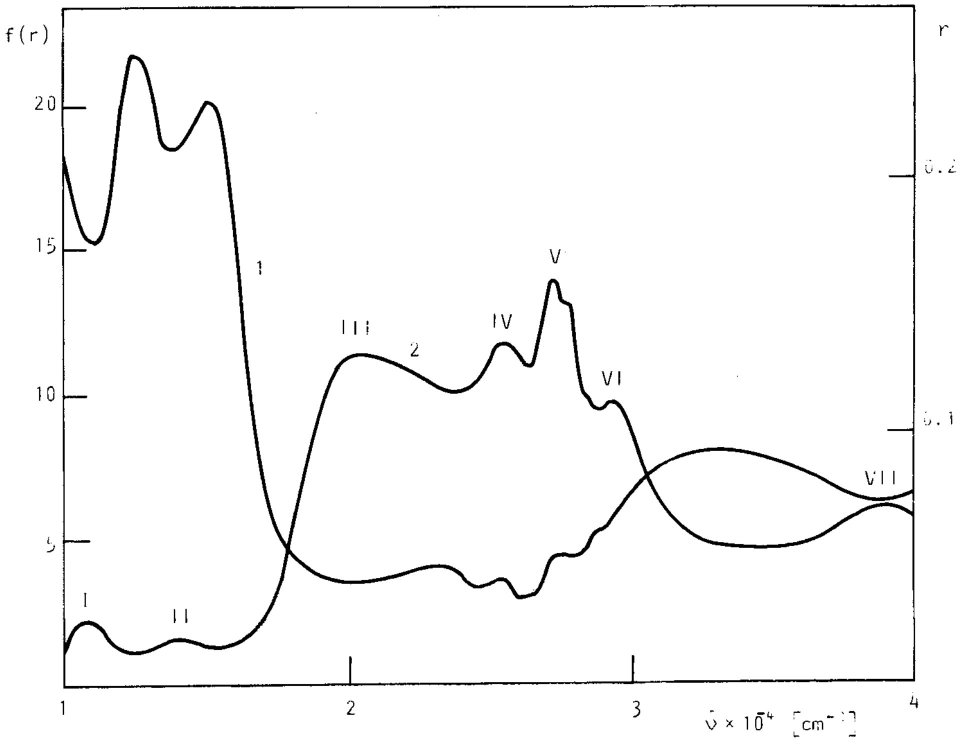

FIGURE 2 Reflection spectrum of $NH_4[VO_2L]\cdot H_2O$

Ordinates: $r = \dfrac{R_{sample}}{R_{stand}}$ (curve 1) and Kubelka-Munk function $f(r) = \dfrac{(1-r)^2}{2r}$ (curve 2)

Abscissa: Wave number (cm^{-1})

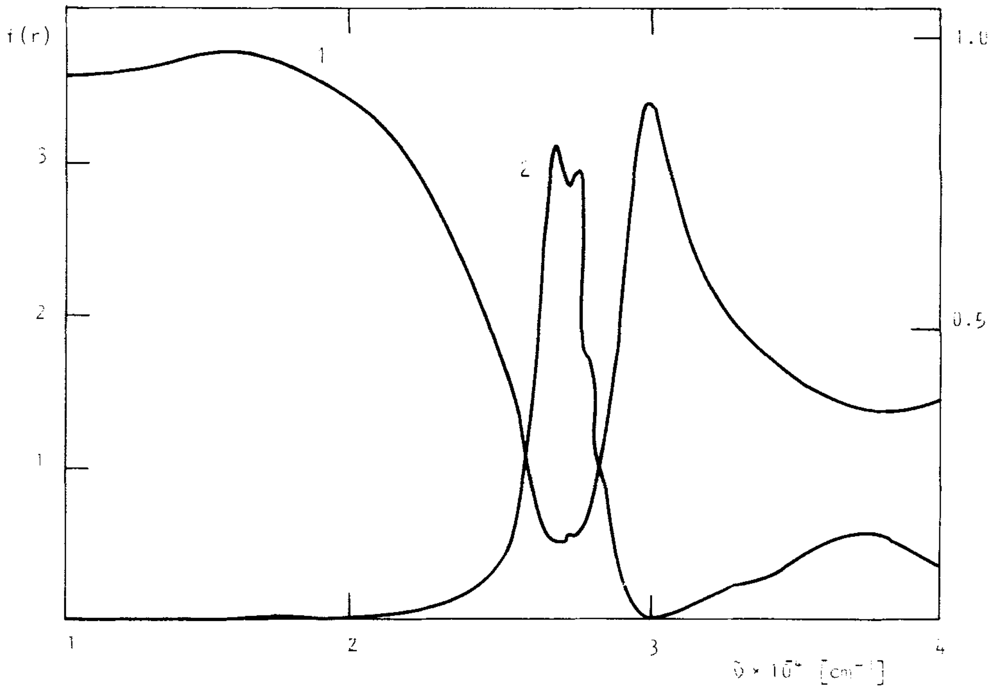

FIGURE 3 Reflection spectrum of H_2L

Ordinates: $r = \frac{R_{sample}}{R_{stand}}$ (curve 1) and Kubelka-Munk function (curve 2)
Abscissa: Wave number (cm^{-1}).

H_2O and the free ligand H_2L, together with the corresponding reflectances are shown in Figures 2 and 3.

MgO was used as white standard.

DISCUSSION

Description of the Structure

The vanadium atom is pentacoordinated in a distorted square-pyramidal arrangement (Tables II and III). This is the first dioxovanadate(V) complex with a square pyramidal arrangement around the vanadium atom to the knowledge of the authors. The basal plane of the pyramid is defined by two nitrogens (N_1, N_2) and oxygen (O_2) of the tridentate salicylaldehyde *S*-methylthiosemicarbazonato ligand and one oxygen (O_3) of the dioxo group. The apex of the pyramid is occupied by the second oxygen (O_1) of the dioxo moiety (Figure 4). The vanadium atom is displaced from the basal plane of square-pyramide by 0.50 Å toward the apical oxygen. The same atom arrangement around the vanadium is found in the structure of *N,N'*-ethylenebis-(acetylacetoneiminato)-oxovanadium(IV).[9] The VO_2 group is in the *cis* configuration with O—V—O angle of 107.2°.

TABLE II
Bond distances (Å) with their e.s.d.s[a] and bond angles (°)

V—O_1	1.625(5)	N_2—C_1	1.286(9)
V—O_2	1.910(5)	C_2—C_1	1.412(9)
V—O_3	1.659(5)	C_2—C_7	1.398(10)
V—N_1	1.999(6)	C_2—C_3	1.435(10)
V—N_2	2.160(5)	C_3—C_4	1.373(11)
S—C_9	1.729(8)	C_4—C_5	1.401(11)
S—C_8	1.761(7)	C_5—C_6	1.390(11)
C_8—N_1	1.321(9)	C_6—C_7	1.408(11)
C_8—N_3	1.309(9)	C_7—O_2	1.347(8)
N_3—N_2	1.405(8)		
O_1VO_2	105.5	C_8N_1V	118.1
O_1VO_3	107.2	$C_8N_3N_2$	107.2
O_1VN_1	105.8	VN_2N_3	117.3
O_1VN_2	101.1	$N_3N_2C_1$	115.9
O_2VO_3	95.5	VN_2C_1	126.3
O_3VN_1	93.3	$N_2C_1C_2$	123.7
N_1VN_2	72.6	$C_1C_2C_7$	123.6
N_2VO_2	82.8	$C_1C_2C_3$	118.3
C_9SC_8	105.2	$C_7C_2C_3$	118.1
SC_8N_1	125.8	$C_2C_3C_4$	121.4
SC_8N_3	110.7	$C_3C_4C_5$	119.8
$N_1C_8N_3$	123.5	$C_4C_5C_6$	120.0
$C_6C_7O_2$	118.4	$C_5C_6C_7$	120.7
$C_2C_7O_2$	121.6	$C_6C_7C_2$	120.0
C_7O_2V	130.5		

[a] The e.s.d.s are in the range of 0.2°–0.8°.

The V—O distances are 1.625 and 1.659 Å implying substantial double bonding. The O—V—O angle and V—O distances (Table IV) are the same as in the structure of ammonium-(dihydrogen ethylenediaminotetraacetato)-dioxovanadate(V)-trihydrate.[10]

TABLE III
Hydrogen bonds (Å)

N_4—O_3	2.87(1)	O_4—O_3	2.77(1)
N_4—O'_3	2.89(1)	O_4—O_1	2.80(1)
N_4—O_2	2.93(1)	O_4—N'_4	2.93(1)
N_4—N'_3	2.93(1)	O_4—O'_4	2.96(1)

The *S*-methylthiosemicarbazonato moiety is planar (max. dev. 0.02 Å), but the two V—N distances are significantly different (2.160, 1.999 Å).This difference can be correlated with the presence of multiply and single bonded oxygen atoms in the basal plane. Thus, the long V—N distance is *trans* to the multiply bonded oxygen atom, and this is considered to produce a lengthening and weakening effect in the bond *trans* to it. This lengthening (by 0.16 Å) and weakening of the

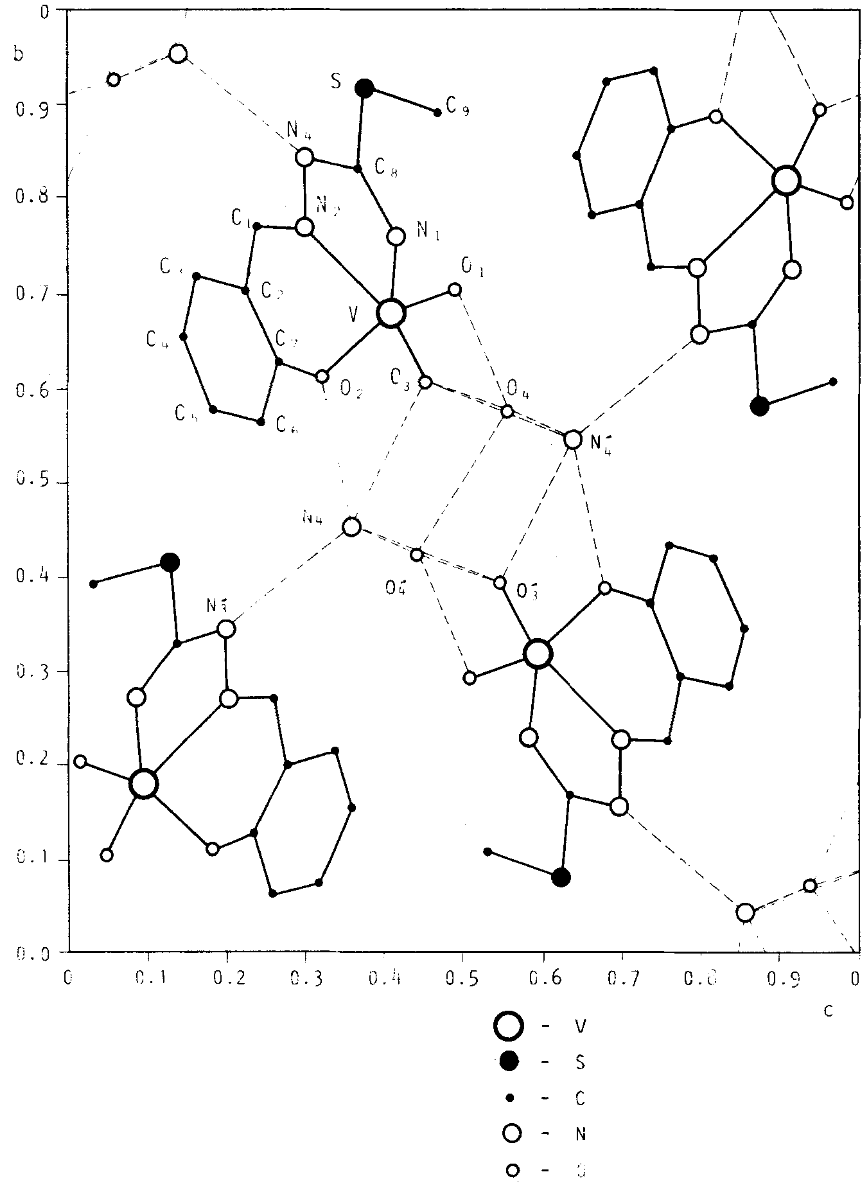

FIGURE 4 Projection of the structure along a axis.

TABLE IV
The geometry of VO_2 moiety in some vanadium complexes

Compound	V—O distances (Å)	O—V—O angle	Reference
$(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$	1.635(2) 1.648(2)	103.8(1)°	Scheidt *et al.*, 1971[13]
$NH_4[VO_2AH_2]\cdot 3H_2O$; A = ethylenediaminetetraacetate	1.623(2) 1.657(2)	107.1(1)°	Scheidt *et al.*, 1971[10]
$Na_3[VO_2A]\cdot 4H_2O$	1.639(2) 1.657(1)	106.96(8)°	Scheidt *et al.*, 1971[15]
$VO_2FC_{10}H_8N_2$	1.60(1) 1.69(1)	107.0°	Edwards *et al.*, 1973[16]
$K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$	1.628(2) 1.639(2)	104.35(10)°	Drew *et al.*, 1974[17]
$(C_5O_2)VO_2(C_{12}N_2)$	1.613(4) 1.670(5)	105.2(2)°	Isobe *et al.*, 1975[18]
$K[VO_2(C_2O_4)]\cdot 2H_2O$	1.61(1) 1.80(1) 1.62(1) 1.79(1)	104.7(5)° 101.7(5)°	Rieskamp *et al.*, 1976[19]
$(NH_4)_2VO_2F(C_2O_4)$	1.617(4) 1.614(4)	107.5(2)°	Rieskamp, Mattes, 1976[12]
$(C_{10}H_8N_2)VO_2F$	1.618(8) 1.691(7)	106.6(4)°	Edwards *et al.*, 1977[20]
$Cs[VO_2(discip.)]\cdot H_2O$ discip = pyridine-2,6-dicarboxylate	1.610(6) 1.615(6)	109.9(3)°	Nuber *et al.*, 1978[21]
$NH_4[VO_2L]\cdot H_2O$	1.625(5) 1.659(5)	107.2°	Present work

bond to the atom lying *trans* to the oxo ligand provides a striking example of the well-known structural *trans* influence.[11-14] The lengthening of the V—O_3 distance by 0.034 Å compared with V—O_1, is partly due to the reverse effect of the nitrogen atom *trans* to it, and partly to the stronger hydrogen bond of O_4 atom to it (2.77 Å).

The least-squares plane of *S*-methylthiosemicarbazonato moiety forms a dihedral angle of 7.7° and 9.9° with the least-squares basal plane of the pyramide and salicylaldehyde moiety respectively. The dihedral angle between the basal plane of the pyramide and salicylaldehyde plane is 8.0°.

The C_8—N_1 bond distance in the *S*-methylthiosemicarbazonato ligand is somewhat longer (0.03 Å), while C_8—N_3 is slightly shorter (0.03 Å) than the corresponding average values calculated for 35 compounds containing thiosemicarbazide or thiosemicarbazone ligands.[22]

Both the water molecule (O_4) and ammonium ion (N_4) form four hydrogen bonds and join to the complex salicylaldehyde *S*-methylthiosemicarbazonato dioxovanadate anions in the crystal (Table III).

Interpretation of Optical Spectra

The following seven maxima were registered in the spectrum of the examined complex $NH_4[VO_2L]\cdot H_2O$: 10,700(I); 14,400(II); 20,500(III); 25,500(IV); 27,500(V); 29,400(VI); 38,500(VII) cm^{-1}.

The first two maxima were significantly weaker than the others.

The maximum at 20,500 had not only a considerable intensity but also a large width.

It is obvious that the maxima V and VII result from the transition of interligand character because they correspond to the transitions detected also in the spectrum of the free ligand (Figure 3).

The electron configuration of vanadium (V) was identical with that of argon, having no *d* electrons. In this case, *d*–*d* transitions are absent and the remaining five spectral bands of the examined complex compound may be attributed to the charge transfer from the orbitals of the ligand to the vacant *d* orbitals of the central vanadium ion.

Although the vanadium atom has a heteroatomic coordination, it may be taken tentatively that the difference in the actions of nitrogen and oxygen is partially compensated by the differences in their distance from the central ion. In this case we could consider the coordination as comprised of equal atoms. However, the number of detected transitions indicates the possibility of point group C_{2v} replacing C_{4v}, which enables the complete interpretation of the charge transfer spectrum.

The bands at 10,700 cm^{-1} and 14,400 cm^{-1}, with the lowest intensity, can be attributed to the charge transfer from the non-bonding orbital to $1a_1$ and $2a_1$, respectively.

The wide spectral band at 20,500 cm^{-1} corresponds to the charge transfer from the ligand π-orbital to two similar vanadium orbitals, b_1 and b_2. The intensity of the band agrees with the type of transition while its large width may be interpreted by a relatively small energy distance between the levels b_1 and b_2 which, in turn, were formed by the splitting of e— level following the lowering of the symmetry from C_{4v} to C_{2v}.

The bands at 25,500 cm^{-1} and 29,400 cm^{-1} can be attributed to the charge transfer from the ligand π-orbital to the levels $1a_1$ and $2a_1$, respectively.

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