Synthesis and study of binuclear vanadyl complexes with acyldihydrazones of salicylaldehyde and dicarboxylic acids

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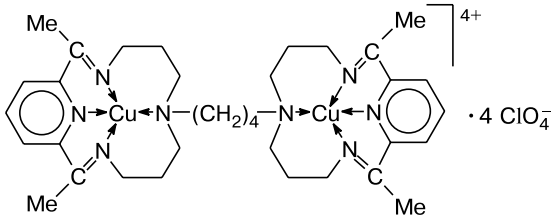
The binuclear vanadyl(II) complexes $[(VO)_2 \cdot 2Py \cdot 2EtOH] \cdot mH_2O$ with acyldihydrazones of salicylaldehyde (H_4L) and dicarboxylic acids were synthesized and studied. In these complexes, two chelate vanadyl(II) complexes with the tridentate bicyclic ligands are linked to each other by the polymethylene bridges $—(CH_2)_n—$ of different lengths varying from one to four units. The ESR spectra of solutions of these complexes, unlike those of analogous copper(II) complexes, have an isotropic signal with an eight-line hyperfine structure (g = 1.972, a_V = $93 \cdot 10^{-4}$ cm^{-1}) typical of monomeric vanadyl complexes, which indicates that no exchange interactions occur between the paramagnetic centers through the polymethylene chain.

Key words: ESR spectroscopy, hyperfine structure, spin-spin exchange interactions, binuclear vanadyl(II) complexes, acyldihydrazones of salicylaldehyde and dicarboxylic acids.

Spin-spin exchange interactions between paramagnetic cations separated by large distances (up to 10 Å), which were found about 20 years ago,[1] attracted considerable attention in recent years. In the majority of coordination compounds in which this unusual phenomenon is observed, the oxalate or terephthalate anions serve as bridging ligands. Less consideration has been given to exchange interactions in complexes in which the coordination polyhedra are separated by the polymethylene chain, which seemingly cannot serve as a channel of the magnetic exchange, although three types of such complexes have already been described.

A copper(II) coordination compound has been studied,[2] in which the exchange interaction between the paramagnetic centers occurs through the tetramethylene chain. The composition of this complex corresponds to the formula $[Cu_2B](ClO_4)_4$, where B is the octadentate organic base generated by condensation of 2,6-diacetylpyridine with *N*,*N*,*N*´,*N*´-tetra(3´-aminopropyl)-1,4-diaminobutane.



Exchange interaction between the copper(II) cations separated by the polymethylene chain has also been found[3,4] in coordination compounds of acetylacetone acyldihydrazones. The ESR spectra of solutions of this type of complexes based on acyldihydrazones of malonic, succinic, and adipic acids have a signal with a seven-line hyperfine structure from two equivalent copper nuclei. The mechanism of spin-spin exchange interactions between the Cu^{2+} ions through the chain of σ bonds of the polymethylene bridge was proposed in the studies.[2—4] More recently,[5—7] weak exchange interactions between the Cu^{2+} cations in coordination compounds of salicylaldehyde acyldihydrazones were studied by ESR spectroscopy.

All complexes with weak spin-spin magnetic exchange interactions through the polymethylene chain studied to date are copper(II) coordination compounds. In this connection, it was of interest to examine a possibility of such interactions for paramagnetic cations of other metals. For this purpose, we synthesized binuclear complexes of the vanadyl (VO^{2+}) cation with salicylidene hydrazones of aliphatic dicarboxylic acids (from malonic to adipic acid

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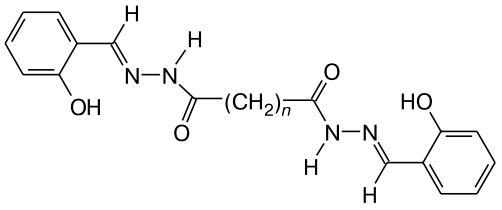
inclusive) and studied these complexes by ESR spectroscopy.



H_4L^1 (n = 1), H_4L^2 (n = 2), H_4L^3 (n = 3), H_4L^4 (n = 4)

Experimental

The coordination compounds were synthesized as follows. Vanadyl acetate (4 mmol) was added to a suspension containing the corresponding acyldihydrazone (2 mmol) and pyridine (3 mL) in EtOH (25 mL). The reaction mixture was stirred for several hours until visible particles of the acyldihydrazone disappeared, and then the mixture was kept for one day. The precipitate that formed was filtered off, washed with EtOH, and dried in air. The resulting compound was dissolved in pyridine (25 mL), kept for one day, and filtered off. The filtrate was slowly concentrated in a desiccator over H_2SO_4 at ~20 °C. The oil that formed was washed with several portions (25 mL each) of ether until a crystalline compound precipitated. The product was dried in air to a constant weight. The yields were 50—60% of the stoichiometry.

According to the data from elemental analysis, the compositions of the complexes correspond to the general formula $[(VO)_2L \cdot 2Py \cdot 2C_2H_5OH] \cdot mH_2O$.

Complex $[(VO)_2L^1 \cdot 2Py \cdot 2C_2H_5OH] \cdot 6H_2O$ (1). Found (%): C, 44.15; H, 4.10; N, 11.35; V, 12.08. $C_{31}H_{46}N_6O_{14}V_2$. Calculated (%): C, 44.94; H, 5.60; N, 10.14; V, 12.08.

Complex $[(VO)_2L^2 \cdot 2Py \cdot 2C_2H_5OH] \cdot 8H_2O]$ (2). Found (%): C, 44.32; H, 4.23; N, 9.67; V, 11.34. $C_{32}H_{52}N_6O_{16}V_2$. Calculated (%): C, 43.74; H, 5.96; N, 9.56; V, 11.59.

Complex $[(VO)_2L^3 \cdot 2Py \cdot 2C_2H_5OH] \cdot 8H_2O$ (3). Found (%): C, 44.30; H, 4.40; N, 10.73; V, 11.04. $C_{33}H_{54}N_6O_{16}V_2$. Calculated (%): C, 44.40; H, 6.10; N, 9.41; V, 11.41.

Complex $[(VO)_2L^4 \cdot 2Py \cdot 2C_2H_5OH] \cdot 6H_2O$ (4). Found (%): C, 46.26; H, 4.16; N, 11.52; V, 11.36. $C_{34}H_{52}N_6O_{14}V_2$. Calculated (%): C, 45.95; H, 6.02; N, 9.65; V, 11.70.

The vanadium percentages were calculated from the thermogravimetric data after thermal decomposition of weighed samples at 800 °C (V_2O_5 as the weight form). The nitrogen percentages were determined by the Duma microchemical method. The carbon and hydrogen percentages were determined by a micromethod.[8] The thermogravimetric curves were obtained on a Paulik—Paulik—Erdey Q derivatograph in a static air atmosphere; the rate of heating was 10 °C min^{-1}; samples were placed in a ceramic crucible without a lid; calcined aluminum oxide was used as the standard. The IR spectra were measured in the range of 4000—400 cm^{-1} on a Specord IR-75 spectrophotometer in KBr pellets. The ESR spectra were recorded on an ADANI PS 100.X instrument in the X range; the concentrations of the complexes were $1—5 \cdot 10^{-3}$ mol L^{-1}; pyridine or a 1 : 1 chloroform—pyridine mixture were used as the solvent.

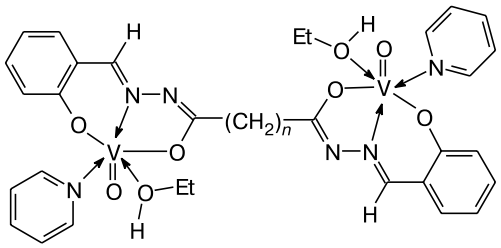
The spectra were simulated using a program package described in the monograph.[9] The ESR parameters were determined by comparing the experimental spectra with the theoretical spectra constructed by summation of the line shapes of the individual transitions centered at the resonance field (H_{res}). The line shapes were described as the sums of the Lorentz and Gaussian fitting curves. According to the relaxation theory, the one-center contributions to the line widths were specified by the equation

$$\Delta H_{res}(i) = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the projection of the nuclear spin onto the direction of the external magnetic field, and α, β, and γ are the parameters of the line width.

Results and Discussion

Salicylaldehyde acylhydrazones generally form[10] dimeric complexes in which the metal cations are linked *via* the phenoxide bridges and contain the M_2O_2 fragments. Treatment of the dimers with Lewis bases, for example, with pyridine, or the synthesis in the presence of a base leads to the cleavage of the oxo bridges giving rise to monomeric complexes. Since vanadium complexes are no exception, the reactions of vanadyl acetate with salicylidene acylhydrazones of dicarboxylic acids in the presence of pyridine afforded binuclear complexes in which the coordination polyhedra are linked *via* the polymethylene bridge.



1—4

n = 1 (**1**), 2 (**2**), 3 (**3**), 4 (**4**)

Analysis of the IR spectra of compounds **1—4** confirmed the assumption that the ligand was transformed into the tetradeprotonated imidol form because the spectra of the complexes have no amide I band, which is observed in the IR spectra of free acyldihydrazones in the region of 1665—1580 cm^{-1}, whereas two new absorption bands appear with maxima in the regions of 1615—1600 cm^{-1} (stretching vibrations of the >C=N—N=C< group) and 1530—1510 cm^{-1} (C—O stretching vibrations of the —N=C—O— fragment).

The C—O stretching band of the phenoxide group is observed at 1390—1380 cm^{-1}. This is indirect evidence for the absence of the oxo bridges[10] and the formation of complexes in which each V atom is coordinated by two O

atoms of the deprotonated phenoxide and imidol groups and also by the imine N atom. The coordination number of the central V atom increases to six due to an additional coordination of two pyridine molecules.

In the IR spectra of compounds **1—4**, the V=O stretching band is observed at 915—930 cm^{-1}.

According to the data from thermogravimetric analysis, the water elimination began already at 40 °C, which confirms the assumption that the water molecules are located in the outer sphere. Apparently, the H_2O molecules occupy cavities in the crystal structures, which are typical of monomeric binuclear metal complexes with bis(salicylidene) hydrazones.[6] The removal of water was accompanied by elimination of the coordinated pyridine and ethanol molecules and the hydrolytic cleavage of the azomethine bond due to which desolvation smoothly gave way to decomposition of the complex and burning-out of the organic residue. Thermolysis was completed at 700—750 °C, and the weight of the residue corresponded to the formation of vanadium(V) oxide.

The ESR spectra of solutions of the complexes under study have a well-resolved isotropic signal with an eight-line hyperfine structure from one vanadium nucleus ($I = 7/2$) (Fig. 1) characterized by the spin-Hamiltonian parameters and the ratio of the line widths ($\alpha \gg \gamma > \beta$) typical of monomeric complexes of the oxovanadium(II) cation (Table 1).

This indicates that binuclear vanadyl complexes with salicylaldehyde acyldihydrazones, unlike the analogous copper(II) complexes, have no spin-spin exchange interactions between the paramagnetic centers through the polymethylene chain. This result can be explained within the framework of the concept of orientations of the magnetic orbitals, *i.e.*, orbitals containing an unpaired electron.[1]

In copper(II) complexes, the magnetic orbital or hybrid orbitals involving the magnetic orbital are oriented along the line of the bonds between the metal atom and the donor atoms of the ligand, which facilitates the indirect exchange between the paramagnetic centers in binuclear complexes.

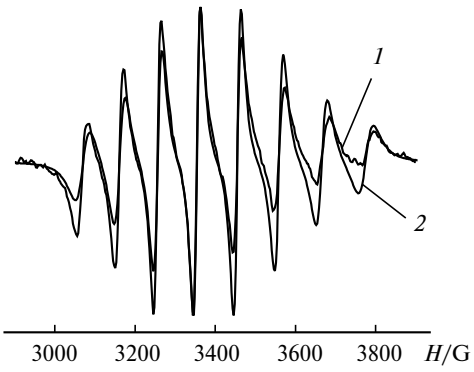
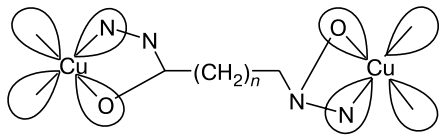


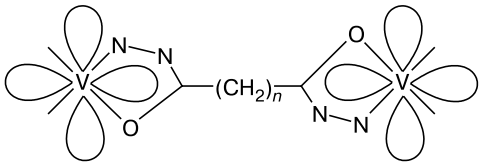
Fig. 1. Experimental (*1*) and calculated (*2*) ESR spectra of a solution of complex **1** at 293 K.

Table 1. Parameters of the ESR spectra of the vanadyl complexes with salicylaldehyde acyldihydrazones

Complex	g	$a_V \cdot 10^4$ /cm^{-1}	Parameters of the line width/G			δ (%)
			α	β	γ	
1	1.972	92.9	17.7	−0.08	1.65	6.1
2	1.973	92.7	18.2	−3.03	1.62	2.01
3	1.973	92.5	18.1	−2.95	1.73	3.4
4	1.972	92.5	17.3	−3.05	1.89	7.3



In complexes of the oxovanadium(II) cation, the d_{xy} orbitals oriented between the lines of the metal—ligand bonds serve as magnetic orbitals. In this case, the orbitals of the ground state containing unpaired electrons form a π bond of the plane, which cannot efficiently overlap with the σ bonds of the polymethylene chain thus hindering an indirect exchange.



However, in the case of short distances, two d_{xy} orbitals of the ground state can overlap with one another and the direct exchange can occur. Hence, the ESR spectra of some dimeric vanadium(IV) complexes show a 15-line hyperfine structure from two equivalent vanadium nuclei.[11,12]

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