V. V. ZELENTSOV, I. A. SAVICH, and Academician Vikt. I. SPITSYN

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Abstract

Full Text

V. V. ZELENTSOV, I. A. SAVICH, and Academician Vikt. I. SPITSYN

ON THE STEREOCHEMISTRY OF VANADYL INNER-COMPLEX COMPOUNDS

In the present communication we shall discuss certain questions of the stereochemistry of vanadyl inner-complex compounds with azomethine derivatives of aromatic *o*-oxyaldehydes.

Inner-complex compounds of vanadyl with azomethine derivatives were first synthesized by Pfeiffer and his co-workers ([1]). Later Mukherjee and Ray ([2]) obtained and studied the magnetic susceptibility of three complex compounds of VO^{2+} with salicylaldimine acids: salicylalalanine (M_{eff} = 1.78 m_B), salicylalglycine (μ_{eff} = 1.80m_B), and salicylalanthranilic acid (μ_{eff} = 1.81 m_B). Assuming that oxygen occupies two coordination positions, they proposed that vanadium in these compounds has coordination number six, and that the bond configuration corresponds to d^2sp^3.

It was established experimentally that the magnetic moment of vanadyl complex compounds does not depend on the coordination number of the central atom. For example, as shown by Bayer, Bilig, and Hausser ([3],[4]), in vanadyl disalicylalethylenediiminate (μ_{eff} = 1.70—1.72 m_B) the coordination number is five, while in vanadyl *o*-oxyquinolinate (M_{eff} = 1.75 m_B) it is equal to six owing to coordinatively attached pyridine. This is in good agreement with theoretical considerations that, irrespective of the coordination number of the central atom, the effective magnetic moment of vanadyl complexes is equal to 1.73 m_B. Nevertheless, by comparing the magnitude of the magnetic moment with analytical data, certain conclusions can be drawn regarding the stereochemistry of vanadyl inner-complex compounds.

The inner-complex compounds, except for vanadyl 5-bromo-2-oxybenzalanilinate, were synthesized by heating stoichiometric amounts of vanadyl chloride and the aldehyde in an alcoholic medium, followed by addition of a slight excess of aqueous solutions of ethylenediamine or ammonia. Vanadyl 5-bromo-2-oxybenzalanilinate was obtained by heating for a period of time alcoholic solutions of 5-bromo-2-oxybenzalaniline and vanadyl chloride, taken in the molar ratio 2 : 1.

Table 1

Compound	Found, % V	Found, % N	Found, % C	Found, % H	Calculated, % V	Calculated, % N	Calculated, % C	Calculated, % H
Vanadyl 5-bromo-2-oxybenzalanilinate $(C_{13}H_9ONBr)_2VO$	8.42	4.45; 4.62	51.09; 49.98	3.06; 2.73	8.25	4.54	50.57	2.94
Vanadyl di(5-bromo-2-oxybenzal)-ethylenediiminate $(C_8H_6ONBr)_2VO$	10.50; 10.49	5.70; 6.03	39.24; 38.84	2.57; 2.50	10.37	5.72	39.13	2.46
Vanadyl 5-bromo-2-oxybenzaliminate $(C_7H_5ONBr)_2VO$	10.81	6.15	–	–	10.94	6.03	–	–

The resulting crystalline substances, of different shades of green, were dried to constant weight and analyzed.

The magnetic susceptibility was determined by the Gouy method at room temperature. The standard used was a repeatedly recrystallized salt

Mohr. The diamagnetic susceptibility of V^{4+} was taken as $9.2 \cdot 10^{-6}$ (8). The correction for the diamagnetism of the organic part of the inner-complex compounds was calculated from Pascal' s constants. As is seen from Table 2, the magnetic moments of the complex compounds obtained lie within the range 1.76—1.80 MB. Chemical analysis (see Table 1) convinces us that the complex compounds obtained do not contain solvent, in particular water, which could be coordinatively bound to the vanadium atom.

Table 2

Compound	$\chi_g \cdot 10^6$	χ (g-ion V^{4+}) $\cdot 10^6$	Temperature, °K	μ_{eff}, MB
Vanadyl 5-bromo-2-oxybenzalanilinate	1.76	1370	294	1.80

Compound	$\chi_g \cdot 10^6$	χ (g-ion V^{4+}) $\cdot 10^6$	Temperature, °K	μ_{eff}, MB
Vanadyl di(5-bromo-2-oxybenzal)ethylenediiminate	2.22	1290	294	1.76
Vanadyl 5-bromo-2-oxybenzaliminate	2.44	1335	295	1.78

Since the oxygen atom, as a rule, occupies one coordination position, vanadium in these compounds has coordination number five, and not six, as Mukherjee and Ray (2) assumed.

Recently George and Irving (5) expressed the supposition that vanadyl complexes with porphyrin and phthalocyanine should possess a square-pyramidal configuration. According to Kimball (6), the square pyramid corresponds to the hybridizations d^2sp^2 or dsp^3, which may be applicable in the present case.

But according to Lesnik' s concepts (7), d^2sp^2-hybridization corresponds to a tetragonal pyramid with the central atom lying in the plane of the base and with one bond normal to this plane, whereas dsp^3 hybridization presupposes that the central atom must be located inside the pyramid along its height. The supposition that the vanadium ion lies in the plane of the base of the tetragonal pyramid is apparently preferable. This may be confirmed by the fact that in vanadyl *o*-oxyquinolinate (4) a pyridine molecule is coordinatively bound to the central ion. The unshared electron pair of the nitrogen atom of the pyridine molecule occupies the free $4p$-orbital, and the square pyramid is readily built up to an octahedron.

On the basis of the foregoing we may suppose that the investigated inner-complex compounds of vanadyl with azomethine derivatives of *o*-oxybenzaldehydes have the structure of a square pyramid. The σ-bonds in this case are formed as a result of d^2sp^2-hybridization. In addition, one $3d$-orbital of vanadium participates in the formation of a strong π-bond with the oxygen atom.

The structure of these compounds may be represented by formulas A and B.

A

where:
I $R = \text{Br}{-}\text{C}_6\text{H}_3$; $R' = \text{C}_6\text{H}_5$
III $R = \text{Br}{-}\text{C}_6\text{H}_3$; $R' = \text{H}$

B

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Note: Figure translations are in progress. See original paper for figures.