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Abstract

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MAGNETIC SUSCEPTIBILITY OF INNER-COMPLEX COMPOUNDS OF VANADYL WITH TRIDENTATE LIGANDS

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Magnetic data for inner-complex compounds of vanadyl are very limited ($^{1-5}$), owing to the fact that, regardless of the stereochemistry of the complex, the magnetic moment proves to be close to the value $1.73\mu_B$, since in the ground state $^2D_{3/2}$ tetravalent vanadium has one unpaired electron. Indeed, it has previously been shown that inner-complex compounds of vanadyl with bidentate Schiff bases have magnetic moments very close to the spin-only value for one unpaired electron. It is assumed that they have the structure of a square pyramid d^2sp^2, with the oxygen of the vanadyl ion at the apex (^{5}).

Some deviations from the theoretical value μ_{eff} are due to incomplete quenching of the orbital component, which ultimately depends on the nature of the ligands.

The study of inner-complex compounds of vanadyl is also of interest from the point of view of the recently advanced proposal by H. B. Jonassen (^{6}) to distinguish as a separate group complexes in which the role of addends is played by a separate oxygen or nitrogen atom. The presence of different types of bonds accounts for the fact that the number of ligands for a given central atom may be variable.

We have previously shown that inner-complex compounds of uranium, which in this sense are analogues of vanadyl complexes, since they also contain different types of bonds, form, depending on the nature of the ligands, compounds in which uranium(VI) has a variable coordination number from 6 to 8 (^{7}). It is known from the literature that vanadyl compounds also possess this same feature. Thus, it was shown that vanadyl oxiquinolinate adds a molecule of pyridine, completing the coordination number of tetravalent vanadium to 6 (^{3}).

It appeared possible to us to obtain vanadyl compounds with a coordination number less than 5 by using tridentate ligands for this purpose, for example salicylal-*o*-oxyaniline. Schiff bases of the salicylal-*o*-oxyaniline type have the feature that they contain two oxy groups arranged in such a way with respect to the azomethine group that, upon replacement of the hydrogen atoms by a divalent cation, for example vanadyl, a very stable inner-complex compound is formed, containing one five- and one six-membered ring.

[structural formula of salicylal-*o*-oxyaniline] + $VO^{2+} \longrightarrow$ [structural formula of the vanadyl complex] + 2H

Vanadium(IV), having here an anomalous coordination number, like other transition elements, in particular copper ([8,9]), should possess certain peculiarities in its properties in comparison with compounds in which ···

whose coordination number is 5 and 6. We assumed that these vanadyl inner-complex compounds should possess anomalously low paramagnetic susceptibility. Indeed, a study of the magnetic susceptibility at room temperature of the vanadyl inner-complex compounds synthesized by us showed, as can be seen from Table 1, that their effective magnetic moments are considerably lower than even the spin-only value for one electron.

The anomalous magnetic properties of vanadyl inner-complex compounds with tridentate ligands are apparently explained by the formation of a metal—metal bond.

Table 1

Compound	T, °K	$\chi_g \cdot 10^6$	$\chi_{ion} \cdot 10^6$	μ_{eff}, μ_B
Vanadyl salicylal-*o*-oxyanilinate $(C_{13}H_9NO_2)VO$	291	1.73	652	1.24
Vanadyl 5-chlorosalicylal-*o*-oxyanilinate $(C_{13}H_8NO_2Cl)VO$	291	1.92	753	1.33
Vanadyl 5-bromosalicylal-*o*-oxyanilinate $(C_{13}H_8NO_2Br)VO$	292	2.00	914	1.47

The δ-bond arising between the vanadium atoms is formed as a result of the partial overlap of the clouds of two d-electrons belonging to different vanadium atoms.

This leads to partial pairing of the electrons and, consequently, to a decrease in the effective magnetic moment. The observed slight increase in the effective magnetic moment for vanadyl 5-chlorosalicylal-*o*-oxyanilinate ($\mu_{eff} = 1.32\,\mu_B$) and vanadyl 5-bromosalicylal-*o*-oxyanilinate ($\mu_{eff} = 1.40\,\mu_B$) in comparison with vanadyl salicylal-*o*-oxyanilinate ($\mu_{eff} = 1.19\,\mu_B$) is apparently explained by the influence of the chlorine and bromine atoms. Replacement of hydrogen by chlorine and bromine increases the size of the molecule of the inner-complex compound, and this in turn leads to some lengthening of the δ-bond V—V and, consequently, to an increase in paramagnetism owing to a decrease in the exchange interaction.

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