PHYSICAL CHEMISTRY

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1964

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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MAGNETIC SUSCEPTIBILITY OF VANADYL COMPOUNDS WITH CARBOXYLIC ACIDS

(Presented by Academician V. I. Spitsyn, 14 XI 1963)

It was first shown by one of us that the magnetic properties of inner-complex compounds (ICC) of vanadyl depend substantially on the nature of the ligands. It was noted ([1]) that vanadyl ICC formed by tridentate ligands of the salicylal-*o*-oxyaniline type have an anomalous magnetic susceptibility. A detailed investigation of χ for three vanadyl ICC over a wide temperature interval convincingly showed that their paramagnetism is due to the triplet state ($S = 1$). However, the splitting between the ground (singlet) and first excited states is a function of temperature ([2]). Such unusual properties of these compounds led us to the idea that the anomaly of the magnetic susceptibility of vanadyl compounds is not confined only to the case of tridentate ligands. For this purpose, several vanadyl compounds with carboxylic acids were synthesized* and their magnetic susceptibility was studied. The study of the magnetic properties of vanadyl alkanoates as a function of temperature is also of interest because compounds of divalent copper with carboxylic acids are representatives of a very distinctive class of substances with intramolecular antiferromagnetism.

Fig. 1. Dependence of $\chi_M(T)$. The designations here and in the following figures: **1** —vanadyl formate; **2** —vanadyl benzoate; **3** —vanadyl *o*-I-benzoate.

This article presents the results of measurements of the magnetic susceptibility of vanadyl formate, benzoate, and *o*-I-benzoate in the temperature interval 300–140° K. The results are given in Figs. 1–3 and in Table 1. The magnetic susceptibility of the V(IV) ion was calculated by the formula $\chi_{V^{4+}} = \chi_g \cdot M - (-\chi_{dia}) - \chi_{n.p.}$, where χ_g is the specific magnetic susceptibility, M is the molecular weight, χ_{dia} is the diamagnetic correction, and $\chi_{n.p.}$ is the temperature-independent paramagnetism.

The correction for diamagnetism included the susceptibility of the acid ([3],[4]), with subtraction of the susceptibility of the hydrogen atom, and the diamagnetic susceptibility of vanadyl ([5]); $\chi_{n.p.}$ was taken equal to $100 \cdot 10^{-6}$ CGSM ([6]) for all compounds, which, however, is not entirely justified, since Van Vleck paramagnetism depends on the structure of the molecule.

The magnetic susceptibility of all three compounds is lower than only the spin

value for one unpaired electron. Such a considerable decrease in susceptibility undoubtedly reflects the very complex character

* The method of obtaining them will be published elsewhere.

Table 1

Magnetic susceptibility of vanadyl formate, benzoate, and *o*-iodobenzoate

Compound	T, K	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$(\chi_{V^{4+}} + \chi_{dia}) \cdot 10^6$	$\chi_{V^{4+}} \cdot 10^6$	$1/\chi_{V^{4+}}$	μ_{eff}, μ_B	J, cm^{-1}
$VO(HCOO)_2 \cdot 0.5H_2O$	293	5.65	940	1006	906	1105	1.46	177
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	269	5.98	992	1058	958	1032	1.44	176
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	254	6.26	1040	1106	1006	944	1.44	168
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	238	6.91	1147	1213	1113	897	1.46	144
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	219	7.80	1295	1361	1261	792	1.49	117
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	203	8.22	1365	1431	1331	750	1.48	116
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								

Compound	T, K	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$(\chi_{V^{4+}} + \chi_{dia}) \cdot 10^6$	$\chi_{V^{4+}} \cdot 10^6$	$1/\chi_{V^{4+}}$	μ_{eff}, μ_B	J, cm^{-1}
$VO(HCOO)_2 \cdot 0.5H_2O$	182	9.15	1520	1586	1486	674	1.48	104
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(HCOO)_2 \cdot 0.5H_2O$	142	13.01	2160	2226	2126	470	1.56	100
$\chi_{dia} = -66 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	298	2.37	734	897	797	1255	1.38	235
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	272	2.38	735	898	798	1253	1.32	243
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	255	2.41	748	911	811	1233	1.29	243
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	235	2.46	768	923	823	1215	1.25	243
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	203	2.66	822	985	885	1130	1.24	227
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	186	2.71	837	1000	900	1111	1.17	223
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	167	2.90	896	1059	959	1043	1.14	208
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								
$VO(C_6H_5COO)_2$	141	3.62	1118	1281	1181	847	1.15	168
$\chi_{dia} = -160 \cdot 10^{-6}$								
$g = 1.966$								

Compound	T, K	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$(\chi_{V^{4+}} + \chi_{dia}) \cdot 10^6$	$\chi_{V^{4+}} \cdot 10^6$	$1/\chi_{V^{4+}}$	μ_{eff}, μ_B	J, cm^{-1}
VO(o-I–C_6H_3COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	293	0.905	508	762	662	1511	1.25	305
VO(o-I–C_6H_4COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	267	0.930	522	776	676	1479	1.21	307
VO(o-I–C_6H_4COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	249	0.960	538	792	692	1445	1.18	288
VO(o-I–C_6H_4COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	229	0.990	556	810	710	1408	1.15	280
VO(o-I–C_6H_3COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	213	1.010	567	821	721	1387	1.11	273
VO(o-I–C_6H_4COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	188	1.070	600	854	754	1326	1.07	257
VO(o-I–C_6H_4COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	167	1.140	640	894	794	1259	1.01	239
VO(o-I–C_6H_3COO)$_2\chi_{dia}$ = −254·$10^{-6}g$ = 1.957	143	1.220	685	939	839	1192	0.98	218

exchange interactions between paramagnetic ions. Attention is drawn to the fact that if one assumes in these compounds the existence of an exchange interaction of only one type, for example, direct exchange with the formation of a δ bond (the copper acetate type), then the exchange integral (J) would retain a constant value over the entire temperature interval. However, calculation shows that in reality the magnitude J is a function of temperature.

This can, on the one hand, be explained by equilibrium between the nonmagnetic ($S = 0$) and paramagnetic ($S = 1$) states and, on the other, by the presence, in

addition to direct exchange interaction, also of indirect exchanges carried out through bridging oxygen atoms and bridging carboxyl groups, as shown in the scheme:

[Structural scheme of a polynuclear vanadyl carboxylate chain with bridging O and carboxyl groups; atoms labeled V, O, C, and substituents R.]

The formation of a polynuclear structure, leading to a significant increase in molecular weight, also explains the circumstance that the compounds studied do not dissolve in any of the known solvents. It is precisely this fact that did not allow us to determine the molecular weights or to record the electronic absorption spectra.

The assumption of a polynuclear polymeric structure explains well the increase in magnetic susceptibility with decreasing temperature. It may be supposed that, unlike copper alkanoates, where exchange

an interaction of the Cu–Cu type because of the short distance permitting overlap of the $d_{x^2-y^2}$ orbitals; here direct exchange is expressed much more weakly, and indirect exchange interactions come to the fore. The circumstance that the magnetic susceptibility does not decrease with decreasing temperature still does not indicate the absence of an antiferromagnetic interaction. An antiferromagnetic transition may occur at lower temperatures, but the fact that the exchange integral decreases as the temperature is lowered argues in favor of the existence of different exchange interactions, one of which predominates. It is also possible that the two resultant exchange interactions will compensate one another; then the susceptibility will remain constant over some temperature interval. The small change in the magnetic moment for vanadyl formate, as well as the small Weiss constant and its negative sign, probably indicate that exchange between the magnetically active ions is effected mainly through the formate grouping: –OV–(O CH O)–VO–.

Fig. 2. Dependence of $1/\chi_{V^{4+}}(T)$

Fig. 3. Dependence of $J(T)$

A more detailed explanation of the nature of the anomaly in the magnetic susceptibility of vanadyl compounds with carboxylic acids and other compounds can be given after studying the magnetic properties of a larger number of compounds over a wider temperature range.

Moscow Institute of Physics and Technology
Received
31 X 1963

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