

Magnetochemical behaviour of mixed-ligand chlorotitanium(III) complexes containing acetonitrile and tetrahydrofuran

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The magnetic properties of mixed-ligand chlorotitanium(III) complexes of the composition $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ (*I*), $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$ (*II*), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ (*III*), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ (*IV*) were investigated. On the basis of the temperature dependence of their magnetic moments the complexes (*I*), (*II*), and (*III*) could be taken for hexacoordinated monomers with distorted octahedral geometry. The found magnetic properties of (*IV*) are typical for polymeric species involving the antiferromagnetic interaction between Ti(III) atoms. These conclusions were supported also by e.s.r. spectra.

Были исследованы магнитные свойства хлорокомплексов Ti(III) с ацетонитрилом и тетрагидрофураном в качестве лигандов, имеющих состав $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ (*I*), $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$ (*II*), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ (*III*), $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ (*IV*). На основании найденной зависимости их эффективных магнитных моментов от температуры можно считать, что комплексы (*I*), (*II*), (*III*) представляют собой гексакоординированные мономеры с искаженной октаэдрической конфигурацией. Найденные магнитные свойства соединения (*IV*) типичны для полимерных соединений с антиферромагнитным взаимодействием между атомами Ti(III). Эти выводы были подтверждены спектрами ЭПР указанных соединений.

The synthesis and some properties of mixed-ligand chlorotitanium(III) complexes containing tetrahydrofuran and acetonitrile were reported in paper [1]. The prepared complexes of composition $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ (*I*), $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$ (*II*), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ (*III*) (supposed to be monomeric) were studied thermogravimetrically in the temperature range 20—350°C. According to the authors' observations the course of thermal decomposition of (*III*) seemed to be rather different from that of the other substances and the compound $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ (*IV*), probably of polymeric structure, was formed at 130°C. The preliminary conclusions on structure of the above compounds and mechanism of their thermal decompositions were drawn on the basis of values of

effective magnetic moment determined at room temperature and on the basis of diffuse reflectance spectral data. In order to confirm these assumptions the magnetic properties of these compounds were studied in more detail.

Experimental

The complexes of composition $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ (*I*), $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$ (*II*), and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ (*III*) were prepared by a direct method, described in [1], $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ (*IV*) was prepared by thermal decomposition of (*III*) at 130°C.

The magnetic susceptibility measurements were carried out under a controlled nitrogen atmosphere in the temperature range 77–293 K on an apparatus of our own construction, based on the Gouy principle.

The e.s.r. spectra were recorded at 295 and 77 K on a Varian E-4 model, band X ($\nu \sim 9.1$ GHz), modulation of magnetic field 100 kHz. For evaluation of g factors the DPPH was used as a standard.

The experimentally found values of molecular susceptibility and the values of effective magnetic moment of the investigated chlorotitanium(III) complexes are listed in Table 1.

Table 1

Magnetic susceptibilities and effective magnetic moments of the studied mixed-ligand chlorotitanium(III) complexes

$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$					
T/K	77	128	144	149	193.5
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	5421	3515	3165	3085	2440
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.64	1.70	1.71	1.71	1.74
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.64	1.69	1.70	1.71	1.74
$\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$					
T/K	201	213	225	273	293
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	2365	2252	2118	1826	1692
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.75	1.75	1.75	1.76	1.76
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.75	1.75	1.76	1.77	1.78
$\text{TiCl}_3(\text{CH}_3\text{CN})_2$					
T/K	77	144	149	165	201
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	5421	3156	3022	2773	2365
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.63	1.70	1.70	1.71	1.74
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.64	1.70	1.71	1.71	1.73

Table 1 (Continued)

<i>T/K</i>	209	231	273	276	293	
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	2275	2084	1826	1796	1692	
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.74	1.75	1.77	1.78	1.78	
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.74	1.75	1.77	1.78	1.79	
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$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$						
<i>T/K</i>	77	142	165	183	201	222
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	4155	2568	2353	2188	2062	1906
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.43	1.53	1.58	1.60	1.63	1.65
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.43	1.54	1.58	1.60	1.62	1.64
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<i>T/K</i>	245	251	263	273	293	
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	1757	1757	1691	1650	1589	
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.66	1.68	1.68	1.70	1.72	
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.66	1.67	1.68	1.69	1.70	
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$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$						
<i>T/K</i>	77	127	163	202	235	
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	1575	1534	1312	1238	1145	
$\mu_{\text{eff}}/\text{B.M. (found)}$	0.88	1.12	1.17	1.26	1.31	
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	0.85	1.11	1.22	1.32	1.36	
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<i>T/K</i>	249	280	293			
$\chi'_M \cdot 10^{11}/\text{m}^3 \text{ mol}^{-1}$	1182	1108	1069			
$\mu_{\text{eff}}/\text{B.M. (found)}$	1.37	1.41	1.42			
$\mu_{\text{eff}}/\text{B.M. (calc.)}$	1.37	1.40	1.42			
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Results and discussion

The discussed mixed-ligand chlorotitanium(III) complexes were investigated with the aim to verify the assumed coordinative unsaturation of some Ti(III) compounds (e.g. $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})$, $\text{TiCl}_3(\text{CH}_3\text{CN})$, $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$), these being allowed to react with rather different ligands, which resulted in completing the coordination number to six, the most frequent coordination number of Ti^{3+} . Our preliminary magnetic measurements at room temperature [1] suggest formation of monomeric complexes of the composition $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ and $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$ from primary polymeric compounds $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})$, $\text{TiCl}_3(\text{CH}_3\text{CN})$ [2–4]; according to their diffuse reflectance spectra these complexes possess a distorted octahedral geometry. When as a parent compound the

pentacoordinated monomeric complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ [2] was used the complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ with a distorted octahedral arrangement was formed.

The observed temperature dependences of effective magnetic moment of complexes $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$, $\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$, and $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$ were interpreted with the aid of the Figgis' method [5], which is a suitable method for estimation of magnetic properties of ions with formal cubic field orbital triplet ground state, perturbed simultaneously by the effect of an axial field distortion and spin-orbit coupling. The found numerical data are listed in Table 2.

Table 2

Values of parameters obtained by means of the Figgis' method

Compound	$-\Theta/\text{K}$	λ'/cm^{-1}	k	δ'/cm^{-1}
$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$	24	70	0.6	350
$\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$	27	130	0.9	1040
$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$	69	135	0.6	270

The theoretical values of μ_{eff} are shown in Table 1. The Weiss' constants were calculated using the least square method. The magnetic properties of the complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ prepared from $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3$ by a substitution reaction were reported also in [6]. Our experimentally obtained values of μ_{eff} in dependence on temperature are in good agreement with the data reported in [6]. Consequently the two complexes, though prepared by different procedures must have an identical arrangement of ligands. This fact can be explained on the basis of crystal structure of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3$ which has been recently published [7]. It follows that in the molecular structure of this complex the oxygen atom of one molecule of tetrahydrofuran, which is in *trans* position to chlorine atom is placed in longer distance from Ti than the other two oxygen atoms. This tetrahydrofuran molecule is the first which can be thermally split off (resulting in origin of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$), or substituted by another molecule of neutral ligand, e.g. in nonaqueous medium. Though, it can be reasonably supposed that the coordinatively unsaturated $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ reacts with acetonitrile forming the same substance as can be obtained by direct substitution of tetrahydrofuran by acetonitrile. It is obvious that the final products even prepared in different ways have the same ligand arrangement, *af*-bis(tetrahydrofuran)-*b*-acetonitrile-*cde*-trichlorotitanium(III).

The experimentally obtained temperature dependence of μ_{eff} corroborated the antiferromagnetic interaction between Ti(III) atoms in the structural arrangements of the compound $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ predicted on the basis of anomalously lowered value of effective magnetic moment at room temperature, which is in

agreement with the proposed Scheme 1-3 in [1]. The found relatively high value of Weiss' constant ($\Theta = -360$ K) and the possibility to interpret the experimental results by means of Ising model of linear antiferromagnetism [8] confirmed the polymeric structure of this compound, in contrast to monomeric complex $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ with the same mole ratio $\text{Ti:L}=1:5$ [2]. The experimentally obtained magnetic data were compared with theoretical curves computed on the basis of the equation

$$\mu_{\text{eff}} = \frac{g}{2} \left[\frac{e^{4K} + (2 + K^{-1}) e^{2K} - K^{-1} e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} \right]^{1/2} \quad (1)$$

where $K = J k^{-1} T^{-1}$.

When $g = 1.90$ (evaluated from e.s.r. spectrum), the best fit with experimental values was achieved for $J = -85 \text{ cm}^{-1}$ ($-17 \cdot 10^{-22} \text{ J}$). Using the modified Ising equation (1) in the form (2) [9]

$$\log \left(\frac{4k}{N\beta^2} \chi'_M T \right) = 2 \log g + \frac{J}{kT} \quad (2)$$

the following values are obtained for the interaction energy and the g factor $J = -70 \text{ cm}^{-1}$ ($-14 \cdot 10^{-22} \text{ J}$) and $g = 1.88$.

The conclusions drawn on the basis of the obtained values of effective magnetic moment were confirmed also by the e.s.r. spectra. The found temperature dependences of signal intensity are consistent with the results obtained from magnetic susceptibility measurements. The e.s.r. spectra of the studied chlorotitanium(III) compounds at room temperature show a single symmetric absorption peak, the numerical values of g factors and line widths (peak to peak) are presented in Table 3. The e.s.r. spectra of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$, prepared as described in the present paper, are in good agreement with those of $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$ prepared by a substitution reaction [6]. Hence it follows

Table 3

ESR spectral data obtained at room temperature

Compound	g	$\Delta H/\text{mT}$
$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})$	1.90	8.5
$\text{TiCl}_3(\text{CH}_3\text{CN})(\text{C}_4\text{H}_8\text{O})_2$	1.90	8.5
$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})_2$	1.91	17.5
$\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$	1.90	17.0

that in both cases the symmetry of coordination polyhedra is identical. The e.s.r. spectrum of polymeric compound $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{CN})$ recorded at 77 K is rhombic, $g_1 = 1.95$, $g_2 = 1.91$, and $g_3 = 1.88$. The character of spectra of all other complexes studied remains unchanged even at this temperature.

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