Magnetic Properties of Chromium(III) Complexes with Some Amino Acids

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The variation of molar magnetic susceptibility with temperature of a series of Cr(III) complexes with some amino acids has been determined. The results have been used to calculate the Weiss constant and the values of effective magnetic moments. The EPR spectra for obtained polycrystalline compounds have been recorded.

In the case of the near octahedral complexes it has been shown that g factors, antiferromagnetic properties as well as effective magnetic moments can be simply related to the change on the Cr^{3+} ion in the e_g bonding orbitals. The experimental magnetic data are indicative of the exchange interaction among paramagnetic centres through the coordinated sphere.

In this paper an attempt has been made to explain the magnetic properties and nature of the prepared complexes.

Transition metal complexes with some amino acids are the model of metal—protein interaction in human body, tissue of plants or animals. Several authors have studied Cr(III) complexes with many amino acids to find out all about their structures, magnetic properties, solution behaviour, and biological activities [1—6]. Chromium is one of bioelements which participate in the biological (biochemical) processes. Its role is being known. Certainly chromium(III) compounds play a very important role in the metabolism of carbohydrates and lipids [7—10].

In the recent paper [11] we reported on the method of a preparation and the spectral studies concerning Cr(III) complexes with some amino acids of different structure: anthranilic and glutamic acids, tryptophan, histidine, cysteine, methionine, serine, and valine.

The magnetic properties and EPR data of the previously obtained [11] complexes are presented in this paper.

EXPERIMENTAL

Methods of the synthesis of the complexes have been described in [11]. Magnetic susceptibility measurements were carried out by a Faraday method over the temperature range 80—300 K using $Hg[Co(NCS)_4]$ as the susceptibility standard at five different field intensities. The obtained magnetic susceptibility data enabled us to calculate the effective magnetic moments of the compounds at various temperatures.

EPR spectra for polycrystalline samples were recorded on the spectrometer made by the Technical University in Wrocław at 9.5 GHz frequency at room temperature. The powder measurements enabled us to determine the values of g factors. DPPH ($g = 2.0036$) was used as the reference.

RESULTS AND DISCUSSION

All the prepared complexes except $Cr_2(met)_4Cl_2$ $2H_2O \cdot KCl$ exhibit a linear dependence of the inverse magnetic susceptibility $1/\chi_{mol}$ as a function of the temperature. The molar susceptibilities of prepared compounds increase together with the temperature.

Plots of these data for all the obtained compounds are shown in Figs. 1—4.

The Weiss constants have been determined from the plots $1/\chi_{mol} = f(T)$ by approximation. The studied complexes are paramagnetic with partly ferro- (for valine and histidine complexes) and antiferromagnetic properties (for other compounds).

The effective magnetic moments have been calculated using the equation

$$\mu_{eff} = 2.84 \, (\chi_{mol} \cdot T)^{1/2} \qquad (1)$$

where χ_{mol} is the molar susceptibility and T is the temperature in K. Selected representative molar magnetic susceptibility, Weiss constants, and the effective magnetic moments are listed in Table 1.
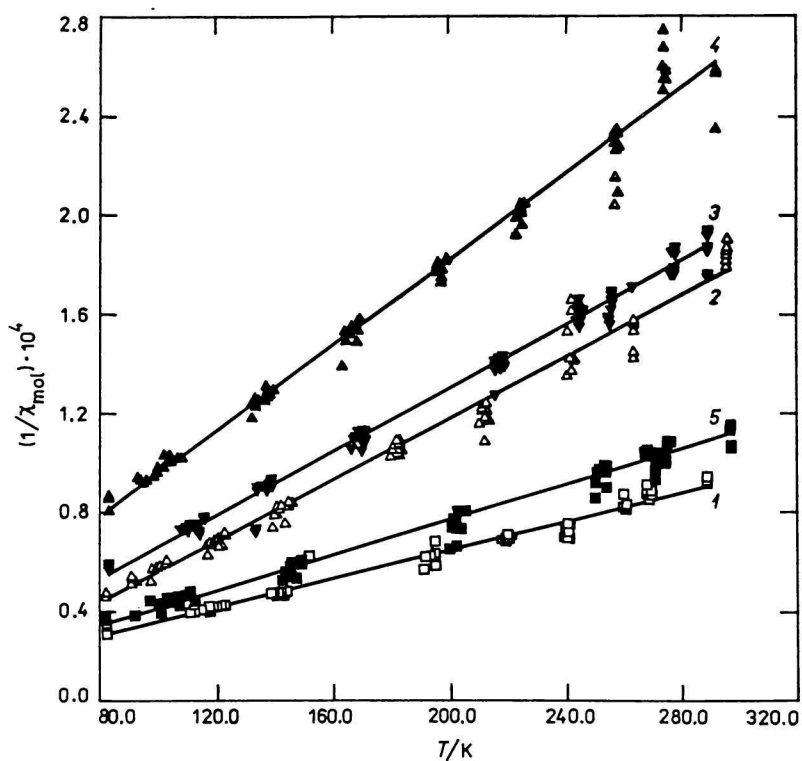
Fig. 1. Inverse magnetic susceptibility *vs.* temperature for: *1.* $Cr_2(glu)_3(OH)_2 \cdot 2H_2O \cdot KCl$, *2.* $Cr(his)_3Cl_3 \cdot 3H_2O$, *3.* $Cr(ser)_3$ $H_2O \cdot 3KCl$, *4.* $K[Cr(cys)_2] \cdot 4H_2O$, *5.* $Cr_2(tryp)_4Cl_2 \cdot 2H_2O$.
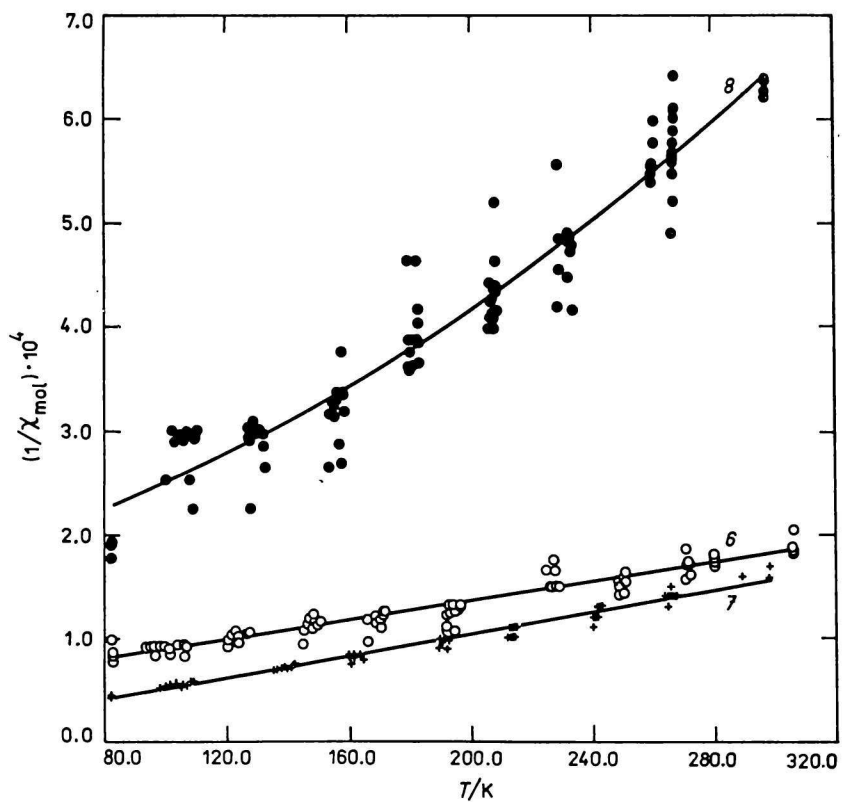
Fig. 2. Inverse magnetic susceptibility *vs.* temperature for: *6.* $Cr(ant)_3$ H_2O, *7.* $Cr(val)_3 \cdot 2H_2O \cdot KCl$, *8.* $Cr_2(met)_4Cl_2 \cdot 2H_2O \cdot KCl$.
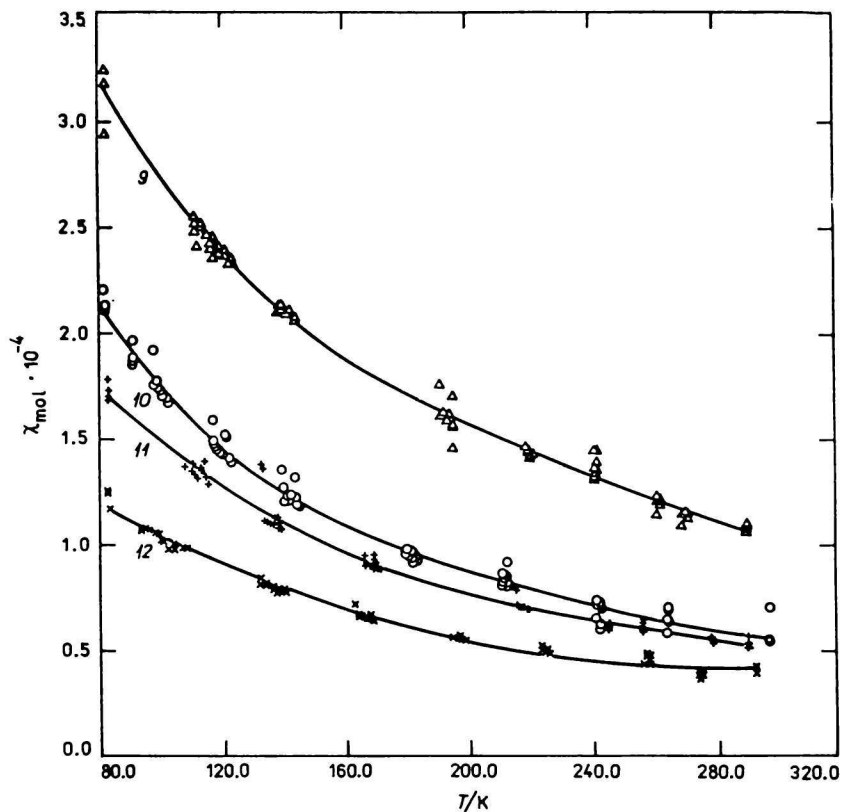
Fig. 3. Molar magnetic susceptibility *vs.* temperature for: *9.* $Cr_2(glu)_3(OH)_2 \cdot 2H_2O \cdot KCl$, *10.* $Cr(his)_3Cl_3 \cdot 3H_2O$, *11.* $Cr(ser)_3$ $H_2O \cdot 3KCl$, *12.* $K[Cr(cys)_2] \cdot 4H_2O$.
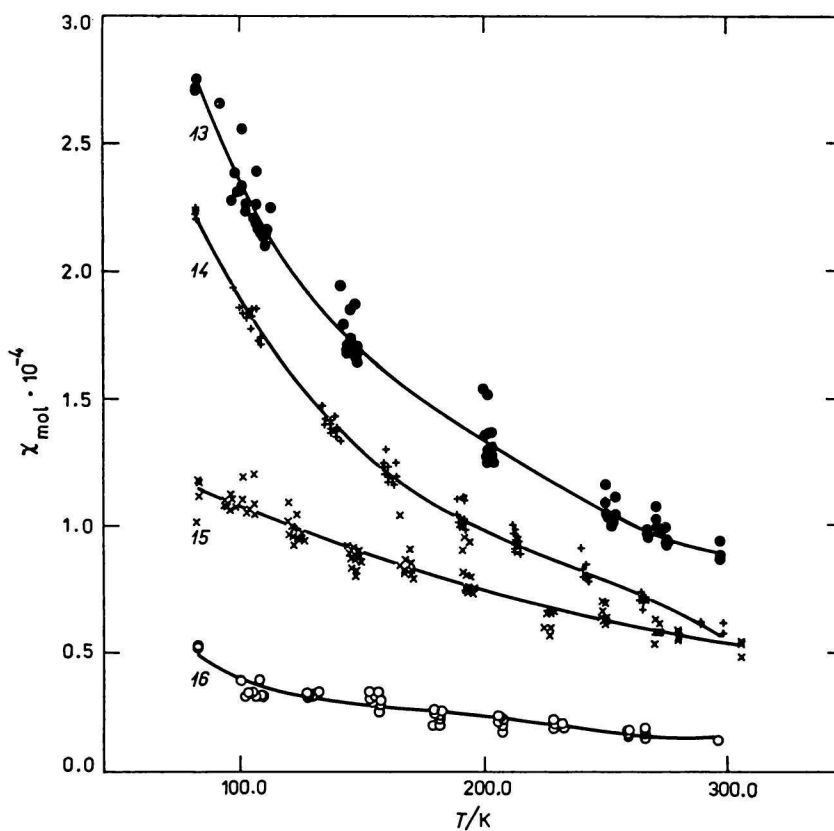
Fig. 4. Molar magnetic susceptibility *vs.* temperature for: *13.* $Cr_2(tryp)_4Cl_2$ $2H_2O$, *14.* $Cr(ant)_3 \cdot H_2O$, *15.* $Cr(val)_3$ $2H_2O \cdot KCl$, *16.* $Cr_2(met)_4Cl_2$ $2H_2O \cdot KCl$.

Table 1. Magnetic Data for Prepared Complexes

	Cr(ant)$_3$ · H$_2$O			$\Theta = -92.67°$		
T/K	296	265	230	195	170	140
χ^*	5509.46	5986.9	6636.39	7443.83	8152.32	9203.48
μ_{eff}/μ_B	3.61	3.56	3.49	3.41	3.33	3.21
T/K	125	100	82			
χ^*	9837.71	11114.24	12259.59			
μ_{eff}/μ_B	3.14	2.98	2.84			
	Cr(val)$_3$	2H$_2$O · KCl		$\Theta = 4.03°$		
T/K	296	265	230	195	170	140
χ^*	6294.15	7019.42	8069.20	9488.21	10851.24	13111.47
μ_{eff}/μ_B	3.88	3.87	3.87	3.86	3.85	
T/K	125	100	82			
χ^*	14635.73	18152.98	21951.2			
μ_{eff}/μ_B	3.84	3.83	3.81			
	Cr$_2$(tryp)$_4$Cl · 2H$_2$O			$\Theta = -16.70°$		
T/K	296	265	230	195	170	140
χ^*	8954.76	9940.21	11350.47	13227.04	14998.23	17869.66
μ_{eff}/μ_B	2.31	2.31	2.29	2.28	2.27	2.25
T/K	125	100	82			
χ^*	19761.33	23994.79	28370.85			
μ_{eff}/μ_B	2.23	2.20	2.17			
	Cr$_2$(glu)$_3$(OH)$_2$ · 2H$_2$O · KCl			$\Theta = -24.53°$		
T/K	296	265	230	195	170	140
χ^*	11100.86	12330.16	14092.06	16441.44	18664.0	22277.87
μ_{eff}/μ_B	2.57	2.57	2.56	2.54	2.53	2.51
T/K	125	100	82			
χ^*	24665.85	30030.93	35607.3			
μ_{eff}/μ_B	2.49	2.46	2.43			
	K[Cr(cys)$_2$] · 4H$_2$O			$\Theta = -10.43°$		
T/K	296	265	230	195	170	140
χ^*	3763.15	4186.70	4796.16	5613.30	6391.07	7665.61
μ_{eff}/μ_B	3.00	2.99	2.98	2.97	2.96	2.94
T/K	125	100	82			
χ^*	8514.64	10442.22	12475.73			
μ_{eff}/μ_B	2.93	2.90	2.87			
	Cr(ser)$_3$Cl$_3$ · 3H$_2$O			$\Theta = -3.00°$		
T/K	296	265	230	195	170	140
χ^*	5190.75	5791.17	6661.09	7838.55	8971.29	10853.38
μ_{eff}/μ_B	3.52	3.52	3.52	3.51	3.51	3.50
T/K	125	100	82			
χ^*	12125.25	15068.27	18259.19			
μ_{eff}/μ_B	3.50	3.49	3.48			
	Cr(his)$_3$Cl$_3$ · 3H$_2$O			$\Theta = 9.20°$		
T/K	296	265	230	195	170	140
χ^*	5303.03	5602.57	6766.23	7925.97	9031.71	10847.74
μ_{eff}/μ_B	3.56	3.55	3.54	3.53	3.52	3.50
T/K	125	100	82			
χ^*	12060.23	14821.26	17746.51			
μ_{eff}/μ_B	3.49	3.46	3.43			
	Cr$_2$(met)$_4$Cl$_2$ · 2H$_2$O · KCl					
T/K	296	265	230	195	170	140
χ^*	1634.28	1809.73	2059.34	2388.83	2697.06	3191.16
μ_{eff}/μ_B	1.98	1.97	1.95	1.94	1.92	1.90
T/K	125	100	82			
χ^*	3512.95	4222.61	4941.33			
μ_{eff}/μ_B	1.88	1.85	1.81			

Θ — Weiss constant, χ^* — [χ_{mol}/(cm^3 mol^{-1})].

The magnetic moments calculated from eqn (1) slightly decrease with temperature as predicted for a paramagnetic substance. Replacement of carboxylate and amine groups as ligators by only carboxylate group in anthranilic acid complex markedly enhances the depression of the magnetic moment in the range of measured temperatures.

At room temperature, the values of effective magnetic moments are close to the "spin only" value for three unpaired electrons, e.g. 3.87 μ_B calculated from the equation

$$\mu = 2[S(S+1)]^{1/2} = 3.87 \, \mu_B \qquad (2)$$

The "spin only" value can be reduced in the calculated magnetic moment of most prepared compounds as a result of the exchange interaction among paramagnetic centres through the coordinated sphere. Lower values of the magnetic moments could be the considerable electron charge transfer from the ligator to the Cr(III) ion in e_g bonding orbitals as a result of formation of π bonds. Evidently the possibility of magnetic exchange between Cr(III) ions could lead to antiferromagnetic properties. The negative value for Θ and the decrease in the effective magnetic moment at low temperature is consistent with antiferromagnetic coupling between the two Cr(III) centres, especially in chloride bridges dimers.

It is interesting that the effective magnetic moment of Cr$_2$(met)$_4$Cl$_2$ 2H$_2$O KCl as well as the magnetic susceptibility is extremely small in comparison to other Cr(III) amino acids compounds. It can be explained by the strong interaction which occurs when bridging groups such as chloride ions are present or when a direct chromium—chromium bond is formed.

EPR spectra for each of the complexes were recorded for polycrystalline samples. The first derivative of the absorbance curve in EPR spectra is a large curve with wide peaks. The $\pm 1/2 \leftrightarrow \pm 3/2$ electron transition in metal terms due to the broadening of EPR lines. The magnitude of the linewidths is what would be expected from dipolar interactions between chromium ions in the sample. The powder measurements enabled us to determine the Zeeman splitting g factors.

Values g of prepared complexes are presented in Table 2. It has been observed that the g factor for complexes containing Cr—S bonds is much closer to 2.0023 (value for free electron) than for Cr—N or Cr—O bonds. This could be due to just a contribution from the spin—orbit coupling of the sulfur atoms.

The obtained complexes show a distorted octahedral symmetry. It can be known from their EPR spectra. Some resonance curves with g factors between 2 and 4 have been observed. The values of g are those expected for Cr(III), where g is normally about 2 since the ^4F term is split under a cubic crystal field into an orbital singlet lying lowest and two orbitals triplets sep-

Table 2. Values of g Factors from EPR Spectra

Compound	g
$Cr(ant)_3 \cdot H_2O$	1.912, 2.077, 2.279
$Cr(val)_3 \cdot 2H_2O \cdot KCl$	1.945, 2.308
$Cr_2(tryp)_4Cl_2 \ 2H_2O$	1.958, 3.141
$Cr_2(glu)_3(OH)_2 \ 2H_2O \cdot KCl$	1.981
$K[Cr(cys)_2] \cdot 4H_2O$	1.993, 2.095, 2.592, 3.073
$Cr(ser)_3 \cdot H_2O \cdot 3KCl$	1.967, 2.488
$Cr(his)_3Cl_3 \cdot 3H_2O$	2.109, 2.873
$Cr_2(met)_4Cl_2 \cdot 2H_2O \cdot KCl$	1.959, 2.782, 3.208, 3.954

er obtained compounds. As mentioned in the previous paper [11] on the basis of the electronic absorption spectra these compounds have lower symmetry than the octahedral ones, however, the splitting of the $^4T_{2g}$, $^4T_{2g}$, ^2E_g terms is very small.

These facts presented in our papers may help to understand the behaviour of chromium(III) ion in biological systems because of the presence of some amino acids in glucose tolerance factors and the role of this element in molecular biology.

arated by an energy value are greater than kT. In chromium(III) complexes of lower symmetry ($\mathbf{D}_{4h}$ or $\mathbf{C}_{4v}$), the splitting factor D of which in the magnetic field in electron Hamiltonian is greater than $h\nu$, we can see some resonance curves in the EPR spectra [12].

After cooling the samples to 80 K no differences in EPR spectra have been observed. The compound $Cr_2(glu)_3(OH)_2 \cdot 2H_2O \cdot KCl$ is one of several obtained complexes. Its g factor equal to 1.981 (Table 2) and effective magnetic moment equal to $3.74 \mu_B$ ("spin only" value for a d^3 system) indicate the regular symmetry of coordination sphere around the central ion as well as the absence of the interactions among paramagnetic centres. In most thoroughly studied complexes this is the one in which two OH groups act probably as a bridge between Cr^{3+} ions. It is apparent that these hydroxylate-bridged dimers of Cr(III) have $\mathbf{C}_{4v}$ symmetry.

From the lower magnetic moments and g factors we have been able to infer about the symmetry of oth-

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