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Coordination Compounds of Chromium(III), Manganese(II), and Iron(III) with Diphenyl Thiocarbazide

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Abstract—Complexes of chromium(III), manganese(II), and iron(III) with diphenyl thiocarbazide were synthesized.

Burns *et al.* [1] have described the synthesis of a chromium(III) thiocarbazide complex by refluxing under agron and noted that this complex is extremely sensitive to traces of water and is readily solvated by various solvents. No syntheses of 3*d*-metal complexes with diphenyl thiocarbazide have not yet been reported. We earlier studied [2] the effect of aryl substituents on complex formation of a series of 3*d* metals with ligands structurally similar to thiocarbazide, specifically thiourea and thiosemicarbazide derivatives, and showed that phenyl substituents exert a substantial effect on the composition and properties of the resulting complexes. The composition of the chromium(III) thiocarbazide complex described in [1] is $[CrL_3] \cdot H_2O$ (L^- is monodeprotonated thiocarbazide). We considered it interesting to synthesize and study aryl analogs of thiocarbazide complexes of chromium(III) and its neighbors by the Periodic System. In the present work we synthesized chromium(III), manganese(II), and iron(III) complexes of diphenyl thiocarbazide (HL) and studied their structure and properties.

According to the chemical analysis (see Experimental), the synthesized chromium(III) diphenyl thiocarbazide complex has the same composition as the complex in [1], except that it contains no associated water. The same composition is also characteristic of the iron(III) diphenyl thiocarbazide complex regardless of whether it is prepared from an iron(II) or iron(III) salt. The role of oxidant in the case of iron(II) is played by air oxygen. With manganese, a 1 : 2 complex is formed.

The synthesized complexes all give a blue-shifted thioamide II band (1295 cm^{-1}) with unchanged intensity. The thioamide III band has an almost unchanged frequency (903 cm^{-1}) but is considerably weaker. The tioamide IV band (760 cm^{-1}) shifts red. The thioamide I band (1500 cm^{-1}) is almost unchanged. It is known [3] that such changes of thioamide bands correspond to bidentate coordination of the ligand, involving the sulfur and nitrogen atoms. Consequently, diphenyl thiocarbazide is coordinated to metals via the hydrazine nitrogen atom and the sulfur atom of the thioenol tautomer. Burns *et al.* [1] proposed that unsubstituted thiocarbazide is coordinated to chromium(III) in the same way.

As shown in [1], the complex with unsubstituted thiocarbazide and with Cr^{3+} in an octahedral S_3N_3 coordination environment gives in the diffuse reflection spectrum bands at 17 300 and 23 300 cm^{-1} (578 and 429 nm). For the Cr^{3+} diphenyl thiocarbazide complex obtained in the present work we observed similar bands at rather close frequencies: 418 [$^4A_{2g} \to {}^4T_{1g}(F)$] and 515 nm ($^4A_{2g} \to {}^4T_{2g}$). We thus may suggest that both the chromium(III) and the iron(III) ($^6A_1 \to {}^4E_g$ band at 413 nm) complexes synthesized have octahedral coordination polyhedra. The manganese complex is likely to have a tetrahedral structure [$^6A_{1g} \to {}^4T_2(G)$ band at 420 nm]. Evidence for the assumptions concerning the structure of the manganese(II) and iron(III) complexes and based on their diffuse reflection spectra can be obtained from the effective magnetic moments of the complexes. The chromium(III) diphenyl thiocarbazide complex has a lower μ_{eff} compared with the octahedral complex with unsubstituted thiocarbazide (μ_{eff} 4.0 at room temperature), which implies exchange interaction between atoms. This fact suggests that the chromium(III) diphenyl thiocarbazide complex is dimeric, and its ligand is bridging. Polynuclear complexes with ligands containing nitrogen and sulfur atoms bearing amine or thiocyanate groups are quite characteristic of chromium(III) [4]. The molar electrical conductivities λ_m of the chromium(III), manganese(II), and iron(III) complexes were found to be 47, 78, and 68 $\Omega^{-1}\,cm^2\,mol^{-1}$. In view of data in [5], we can conclude that that the chromium(III) diphenyl thio-

Thermogravimetric analysis of complexes **I**–**III**

Comp. no.	Exo effects		$\Sigma\Delta m$, %
	t, °C	Δm, %	
I	70–215 (200)	25.0	83.8
	270–380 (350)	11.3	
	380–500 (480)	37.5	
II	100–215 (190)	21.0	50.0
	335–380 (360)	3.0	
	380–480 (415)	11.0	
III	110–200 (180)	13.8	53.8
	360–420 (405)	5.0	
	420–500 (470)	20.0	

carbazide complex, unlike the complex with unsubstituted thiocarbazide, undergoes no solvolysis, whereas the manganese(II) and iron(III) complexes are solvated by DMF, and this process is accompanied by partial expulsion of diphenyl thiocarbazide from the inner coordination sphere.

Analysis of thermoanalytical data (see table) shows that the thermolysis onset temperature for the chromium(III) complex is much lower than for the manganese(II) and iron(III) complexes. This fact suggests that dimeric complexes are thermally less stable than monomeric, probably because bonds joining two structural units of a complex to form a dimer are much weaker than other chemical bonds in complexes. The TGA curves of the synthesized complexes all show exothermic effects exclusively; probably, they relate to thermolysis of the complexes with burnout of their organic part.

EXPERIMENTAL

The IR spectra were obtained on an IKS-29 instrument in KBr. The diffuse reflection spectra were measured on an SF-18 spectrophotometer, reference MgO, β_{MgO} 100 %.

The magnetic susceptibilities were measured by the Gouy method (at 291 K) [6]. The electrical conductivities of 10^{-3} DMF solutions of the complexes were measured using an R-5010 ac bridge at 20°C. Thermal analysis was performed on a Paulik–Paulik–Erdey derivatograph, heating rate 10 deg/min.

Analytical grade chromium(III), manganese(II), iron(II), and iron(III) chlorides and diphenyl thiocarbazide were used.

Analysis of the isolated complexes for metals was performed by complexometry [7], for sulfur, by the Schoenherr method with weighing as barium sufate [8], and for nitrogen, by the Dumas method [8].

Chromium(III), manganese(II), and iron(III) diphenyl thiocarbazide complexes (I–III). Ligand HL, 5 mmol, was dissolved with heating in 50 ml of ethanol, and corresponding metal chloride, 5 mmol, was added with stirring to the hot solution. With chromium(III), the solution got dark brown, and with manganese(II), iron(II), and iron(III), dark red. The mixture was left to stand to let the solvent to evaporate spontaneously. The precipitate that formed was washed with a little ethanol and dried in air to constant weight.

Complex **I**, μ_{eff} 2.79 BM. IR spectrum, cm^{-1}: 1500, 1320, 900, 755. Found, %: Cr 6.1; N 20.1; S 11.6. $C_{39}H_{39}CrN_{12}S_3$. Calculated, %: Cr 6.3; N 20.4; S 11.7. Complex **II**, μ_{eff} 5.90 BM. IR spectrum, cm^{-1}: 1490, 1310, 900, 750. Found, %: Mn 9.9; N 19.6; S 11.1. $C_{26}H_{26-}$ MnN_8S_2. Calculated, %: Mn 9.7; N 19.7; S 11.2. Complex **III**, μ_{eff} 5.83 BM. IR spectrum, cm^{-1}: 1490, 1305, 905, 750. Found, %: Fe 6.5; N 20.1; S 11.3. $C_{39}H_{39}FeN_{12}S_3$. Calculated, %: Fe 6.8; N 20.3; S 11.6.

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