

## MAGNETIC PROPERTIES OF REACTION PRODUCTS OF CHROMOCENE AND ALIPHATIC ALCOHOLS

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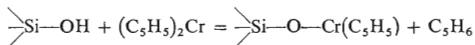
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Chromocene reacts with aliphatic alcohols ( $n = 1$  to 4) at 20°C to give cyclopentadiene and very reactive chromium(II) alcoholates. All the prepared alcoholates are antiferromagnetic compounds with the Weiss constant  $-280$  to  $-170$  K. The magnetic moment corresponds to contribution of four unpaired electrons and to  $d^4$  configuration of Cr(II) atom. An interpretation of the antiferromagnetism of the alcoholates is suggested.

Chromocene is characterized by easy oxidability with air oxygen and low stability to acids and bases. It undergoes easily to reactions connected with decomposition of its metallocene skeleton<sup>1-3</sup>. However, weak oxidizing agents can transform (without decomposition) chromocene into not very stable chromocenium cation<sup>4</sup>. Some Lewis bases give loose solvates of chromocene<sup>3,5,6</sup>. Chromocene reacts with many organic compounds<sup>2</sup>, but the reaction products were not identified in most cases. So far no reaction of chromocene with alcohol has been described, and chromium(II) alcoholates (which are formed in this reaction, as it will be documented below) are not known either.

Chromocene found an important application in catalytic polymerization of ethylene. The paper<sup>7</sup> by Karol and Wu Chisung deals with the problem of catalytic action of the chromocene bound to a carrier in polymerization of olefins. Besides others in this paper the authors verify their previous presumption that chromocene interacts with OH groups of the carrier when brought on it at temperatures up to 90°C. In this process one cyclopentadienyl ring is set free as cyclopentadiene and a formation with mono( $h^5$ -C<sub>5</sub>H<sub>5</sub>) structure remains anchored to the surface of solid phase.



Study of reactions of chromocene with alcohols can contribute to solve the problem as to whether chromocene is able to react in this way at all.

## EXPERIMENTAL

*Measurements:* Temperature dependence of magnetic susceptibility of the chromium(II) alcoholates was carried out in the range 90 to 370 K using a Variable Temperature Gouy Balance (Newport Instruments, England). The apparatus works with the accuracy of  $\pm 1.5$  per cent after calibration. The found magnetic molar susceptibilities were corrected with respect to diamagnetism with the use of the Pascal constants. The magnetic moments were computed from the Curie-Weiss equation, the effective magnetic moments were obtained from the Curie equation. Temperature dependences of reciprocal values of molar magnetic susceptibilities of the alcoholates are given in Fig. 1. The determined values of the Weiss constants and the magnetic moments at 20°C are given in Table I.

*Analyses:* For separation and identification of gaseous and liquid components of the reaction mixture we used a gas chromatograph Fraktovap GV 200 (Carlo Erba) with a flame ionisation detector. Glass chromatographic column 4 m  $\times$  4 mm packed with Chromasorb Wa.w. wetted with 20 per cent silicone oil DC 200. Temperatures: inlet chambre 190°C, column 55°C. Flow rate 50 ml N<sub>2</sub> per min. The absence of hydrogen in the reaction products was proved with a Chrom IV apparatus (Laboratorní přístroje, Prague) with a heat conductivity detecting elements. Chromium content in the alcoholates was determined by a gravimetric procedure (BaCrO<sub>4</sub>). The sample was decomposed after careful contact with air by melting with a mixture of K<sub>2</sub>CO<sub>3</sub> and KNO<sub>3</sub>. For C and H determination the ampoules with pyrophoric alcoholates were opened with a special device first inside the combustion tube. Results of the Cr, C and H determinations are given in Table I.

TABLE I

Composition and Magnetic Properties of Chromium(II) Alkoxides

Compound	Formula (m.w.)	Calculated/Found			Colour	Magnetic moment at 20°C B.M.	Weiss constant K
		% C	% H	% Cr			
Methoxide	C <sub>2</sub> H <sub>6</sub> CrO <sub>2</sub> (114.1)	21.06	5.30	45.58	blue	5.01	-280
		21.23	5.41	45.40			
Ethoxide	C <sub>4</sub> H <sub>10</sub> CrO <sub>2</sub> (142.1)	33.81	7.09	36.59	light	4.80	-260
		33.96	7.21	36.63	blue		
Propoxide	C <sub>6</sub> H <sub>14</sub> CrO <sub>2</sub> (170.2)	42.35	8.29	30.56	light	5.09	-260
		41.61	8.12	31.18	blue		
Isopropoxide	C <sub>6</sub> H <sub>24</sub> CrO <sub>2</sub> (170.2)	42.35	8.29	30.56	grey	4.85	-170
		41.82	8.18	30.48	blue		
Butoxide	C <sub>8</sub> H <sub>18</sub> CrO <sub>2</sub> (198.2)	48.47	9.15	26.23	light	5.07	-270
		48.51	9.44	25.52	pink		
Isobutoxide	C <sub>8</sub> H <sub>18</sub> CrO <sub>2</sub> (198.2)	48.47	9.15	26.23	pink	4.96	-230
		48.60	9.28	25.69			



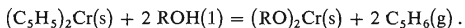
*Protective gas:* In all the operations argon was used as the protective gas. Its final purification consisted in removal of oxygen with a hydrogenation palladium catalyst Cherox (Závody ČSSP, Litvínov) and capture of moisture with KOH granules and molecular sieve Nalsit 4 (Výzkumný ústav pro ropu a uhlovodlkové plyny, Bratislava). This purification procedures warranted a decrease of oxygen and moisture content below 2 to 5 ppm.

*Preparations:* Chromocene was prepared by conversion of tetrahydrofuran solution of sodium cyclopentadienide with crystalline  $\text{CrCl}_2$ , see ref.<sup>8</sup>. Chromium(II) chloride was obtained by reduction of a suspension of tetrahydrofuranate of chromium(III) chloride in tetrahydrofuran by action of  $\text{LiAlH}_4$ . The raw chromocene crystallized from the concentrated solution and was sublimated in vacuum. The sublimation was repeated before its use in further reactions. The interactions of the crystalline chromocene with liquid aliphatic alcohols were carried out in an evacuated apparatus without solvent. The used all-glass apparatus without ground joints made it possible to transfer the solid reaction products to measuring tubes for the magnetic measurements and to ampoules for analyses, the sealing of the evacuated apparatus being maintained.

## RESULTS

Reactions of chromocene with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol were investigated. In all the cases reaction proceeds at room temperature. Within several tens of minutes a blue, blue-violet, grey-blue or brown suspension of the solid reaction product in excess alcohol is formed. The powder products of light colours obtained on complete evaporation of liquid phase in vacuum correspond to the respective chromium(II) alcoholates in their C, H and Cr content (Table I). The gas phase present in the reaction apparatus as well as the condensate trapped in the freezing trap during vacuum distillation of the liquid reaction products were submitted to chromatographical analysis. In all the studied cases they only contained the starting alcohol and the cyclopentadiene set free in the reaction. The gas chromatography also excluded the possibility of presence of  $\text{H}_2$  in the gas reaction phase. The reaction mixture did not contain any further products detectable chromatographically (not even in traces).

The mentioned facts indicate that the reactions of chromocene with selected aliphatic alcohol follow the equation



Under the given conditions the equilibrium is shifted to the right. Removal of cyclopentadiene and alcohol vapours makes it possible to obtain very pure chromium(II) alcoholate in all the cases. The alcoholates are insoluble in excess alcohol, in aliphatic hydrocarbons, and in cyclopentadiene. They are characteristically pyrophoric. On contact with traces of oxygen they turn green and hot.

Fig. 1 gives results of the measurements of temperature dependence of the corrected molar susceptibility  $\chi_{\text{M}}$  of the chromium(II) alcoholates. Position of straight parts of the dependences  $\chi_{\text{M}}^{-1}$  vs  $T$  indicates that all these compounds are antiferromagnetic.

The values of the Weiss constants (Table I) were obtained by extrapolation of these straight parts. The dependences of magnetic moments and effective magnetic moments on temperature calculated with the use of the Curie-Weiss and the Curie equations, respectively, are given in Fig. 2. Magnetic moments of all the alcoholates are constant within a large temperature range and approach the value  $\mu = 4.90$  B.M., which corresponds to a pure spin contribution of four unpaired electrons. This is fully in accord with the idea that Cr atom of all the alcoholates is in its II oxidation state and the system of  $d^4$  electrons has high-spin arrangement and is placed in a weak crystal field. The effective magnetic moments  $\mu_{\text{eff}}$ , on the contrary, show a temperature dependence and are lowered with respect to the  $\mu$  values due to considerable anti-ferromagnetic interaction.

Antiferromagnetism of chromium(II) alkoxides suggests the individual paramagnetic centres to be coupled. It can be presumed that these compounds in solid phase have a structure enabling such coupling. This structure could have bonds between Cr(II) atoms or more probably oxygen bridges between chromium atoms. The latter idea of polynuclear arrangement of the alcoholates would agree with their insolubility in the mentioned solvents. Out of the pairs of isomeric alcoholates lower antiferromagnetic interaction (lower absolute value of the Weiss constant) is encountered with those having more highly branched chains, which can be interpreted by lower probability of formation of a more extensive polynuclear arrangement in the cases of molecules having sterically hindered branched aliphatic chains.

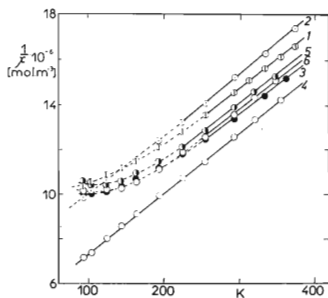


FIG. 1

Temperature Dependence of Reciprocal Corrected Molar Magnetic Susceptibilities of Chromium(II) Alcoholates

4 1 Methoxide, 2 ethoxide, 3 propoxide, isopropoxide, 5 butoxide, 6 isobutoxide.

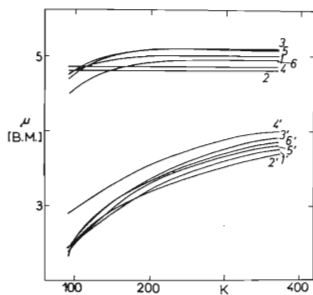


FIG. 2

Temperature Dependence of Magnetic Moment  $\mu$  (curves 1 to 6) and Effective Magnetic Moment  $\mu_{\text{eff}}$  (curves 1' to 6') of Chromium(II) Alkoxides

For numbers of the curves see Fig. 1.

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