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# REACTION OF CHROMOCENE WITH ALIPHATIC AMINES

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## Summary

Crystalline chromocene reacts with vapours of primary aliphatic linear ($n = 2$ to 4) amines at a temperature of 25°C to form solid aminates of the type $Cr(C_5H_5)_2(RNH_2)_x$. The reaction is reversible. The aminates are paramagnetic magnetically diluted powders. The magnetic moments approximately correspond to the spin contribution of four unpaired electrons ($d^4$) of chromium(II) atoms and show that the original low-spin configuration of metallocene has disappeared. Secondary and tertiary amines and primary amines with branched aliphatic chains do not react in this manner, but their incorporation into the crystalline structure of the aminate is promoted by the presence of the vapour of an amine which does react.

## Introduction

Several papers devoted to chromocene deal with its use in catalytic polymerisation of olefins. It has been reported that a brief prior exposure of the chromocene catalyst to ammonia gas leads to polyethylene of different mechanical properties, with viz. improved toughness [1]. It has also been shown that at low temperatures liquid ammonia reacts with crystalline chromocene to form ammoniates of the type $Cr(C_5H_5)_2 \cdot 4\ NH_3$ and $Cr(C_5H_5)_2 \cdot 9\ NH_3$, but because of their low stability these are extremely difficult to study in detail [2]. It thus seemed of interest to examine reactions of chromocene with amines and we describe below the formation, composition, and magnetic properties of chromocene alkylaminates.

## Experimental

*Measurements.* The magnetic susceptibilities of chromocene alkylaminates were measured with a ±1.5% uncertainty in the temperature range of 90—

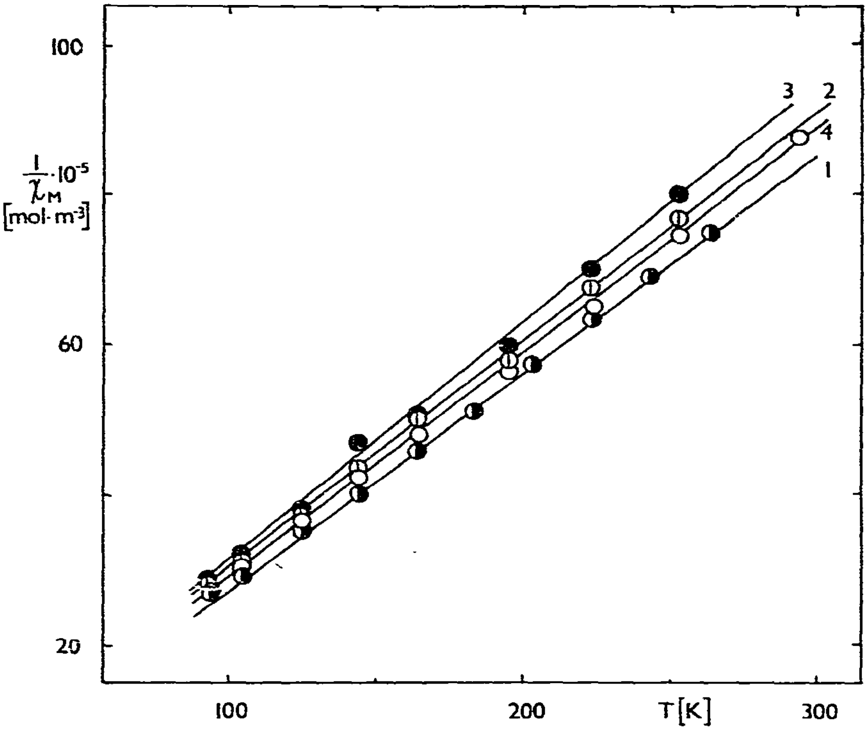

Fig. 1. The temperature dependence of reciprocal values of corrected molar magnetic susceptibilities of alkylaminates prepared. 1, ethylaminate; 2, 1-propylaminate; 3, propenyl-3-aminate; 4, 1-butylaminate of chromocene.

300 K using a Variable Temperature Gouy Balance (Newport Instruments, England). The magnetic molar susceptibilities found were corrected for diamagnetism using Pascal constants. The temperature dependences of reciprocal values of corrected molar magnetic susceptibilities of all alkylaminates prepared are given in Fig. 1. Magnetic moments calculated from the Curie equation by means of experimentally found susceptibilities are given in Table 1. X-ray dif-

TABLE 1

MOLAR RATIOS OF CHROMOCENE AND AMINE IN AMINATES PREPARED

| | Methods[a] | | | | $\mu$(BM), 293 K |
|---|---|---|---|---|---|
| | A | B | C | D | |
| Ethylamine | 1/4.98 | — | 1/5.30 | — | 4.68 |
| 1-Propylamine | 1/4.78 | 1/4.90 | 1/5.02 | 1/5.05 | 4.58 |
| Propenyl-3-amine | 1/4.48 | — | 1/4.58 | — | 4.47 |
| 1-Butylamine | 1/4.49 | 1/4.58 | 1/4.36 | 1/4.46 | 4.51 |

[a] A, by gravimetric determination of Cr content; B, by acido titration of amine released by thermal decomposition of aminate; C, by weighing of chromocene and amine after the decomposition of aminate; D, by measuring of liquid amine volume absorbed in a given amount of chromocene.

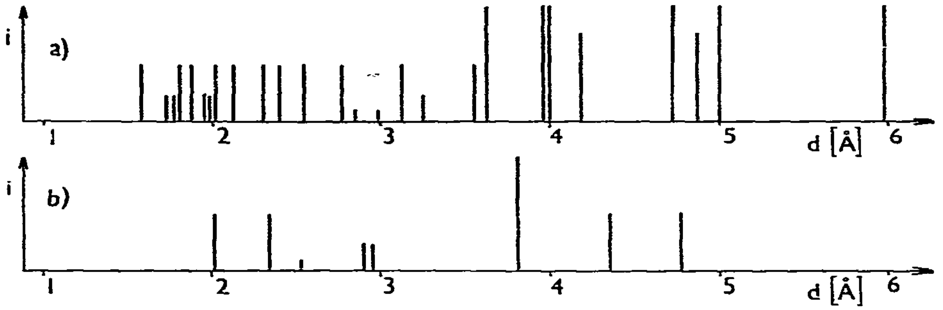

Fig. 2. X-ray diffractograms of powder samples. (a) of chromocene; (b) of 1-butylaminate of chromocene.

fractograms of 1-butylaminate of chromocene,chromocene obtained by decomposition of aminates and resublimated chromocene were measured by means of Debye—Scherrer powder method using Micrometa (Chirana, Czechoslovakia) with Cr-$K_\alpha$ radiation with a vanad filter. Interplanar spacings are presented in Fig. 2.

*Analyses.* Experimentally found molar ratios of chromocene and amine in solid reaction products are given in Table 1. The ratios were found by means of four independent ways, i.e. by gravimetric determination of the Cr content in aminates such as $BaCrO_4$ (Table 1, column A), by acidic titration of amine released by thermal decomposition of aminate (column B), by weighting chromocene and amine after decomposition of aminate in evacuated apparatus (column C) and by measuring the volume of liquid amine absorbed by a measured quantity of chromocene (column D). Ratios given in Table 1 are averages of at least three determinations. For identification of gaseous components of the reaction mixtures and quantitative determination of individual amines in mixed aminates a Fractovap GV 200 (Carlo Erba, Italy) gas chromatograph with a flame ionisation detector was used. (Cromasorb W.AW, 15% Apiezon L, 3% KOH or Celite 545, 8% Carbowax 20 M, 13% KOH. Temperatures: inlet chamber 190° C, column 60° C; flow rate 40—50 ml $N_2$ per min.)

*Protective gas.* In all operations argon containing <5 ppm of oxygen [3] was used as a protective gas.

*Preparations.* Chromocene was prepared and purified as previously described [3,4]. Aliphatic amines (Fluka AG, Switzerland) were dried and then refluxed under argon. The reactions of chromocene with vapours of primary amines were carried out in sealed evacuated glass ampoules with a sealed-on liquid-amine container. Extensions permitting magnetic measurements of the aminates, recording of X-ray diffractograms, or isolation of samples for analyses, were sealed to the ampoules. Reactions were carried out at 25° C.

## Results

Crystalline chromocene react at room temperature with vapours of primary linear aliphatic amines. The ruby chromocene crystals became violet, and finally disintegrate to a violet powder. The reaction time depends on both the size of chromocene crystals and the type of amine, and varies from about one hour with ethylamine to three days with 1-butylamine. The volume of the products invariably exceeds that of the original chromocene several fold. They are unstable, and in contact with air undergo fast oxidation with liberation of the amine. Lowering the vapour pressure of amine above the adduct causes reversal of the aminates to amine and a very fine chromocene, which very readily ignites in the air. The identity of the regenerated chromocene was confirmed by analysis (Cr, found 28.67; calcd. 28.54%), sublimation, and examination of the X-ray powder diffractogram. Amine was identified using gas chromatography.

The equilibrium composition of chromocene aminates reached after a long contact between amine vapours and chromocene at 25°C (Tab. 1) varies from 1/4.4 to 1/5.3 for the molar ratio of chromocene to amine. The highest amine content at a given temperature is given by ethylamine (which is the most volatile) and the lowest by 1-butylaminate. Gas chromatographic analyses of gaseous phases of all reaction systems investigated shows unambiguously that no volatile components, such as hydrogen, cyclopentadiene, or other hydrocarbons, are liberated during the reactions. It is clear that chromocene reacts with gaseous amines (ethylamine, 1-propylamine, propenyl-3-amine, 1-butylamine) in the same way as with liquid ammonia [2]. An ammoniate with the composition $Cr(C_5H_5)_2 \cdot 9\ NH_3$ was formed at —50°C, but with increasing temperature the composition progressively changed to $Cr(C_5H_5)_2 \cdot 4\ NH_3$, while above —15°C a spontaneous decomposition to chromocene and ammonia was observed. The aminates would be expected to have the composition $Cr(C_5H_5)_2$-$(RNH_2)_4$, and higher amine contents must be attributed either to formation of some higher aminates and/or to capillary condensation of amine vapours into the very finely powdered 1/4 aminate.

Valuable information about the aminates is given by their magnetic properties. From the nature of the dependence of the reciprocal values of the corrected molar magnetic susceptibility on temperature (Fig. 1) it follows that all the four aminates prepared are paramagnetic substances, without antiferromagnetic interaction. The magnetic moments found (Tab. 1) are only slightly lower than would correspond to a purely spin contribution of four unpaired electrons in $d^4$ configuration of the chromium(II) atom, and thus suggests that in the aminates, as in chromocene, the Cr atom is present in the oxidation state II. But the original bonding arrangement in the chromocene, marked by $(e_{2g})^3$-$(a_{1g})^1$ electronic configuration and paramagnetism associated with two unpaired electrons [5], must, after attachment of the amine groups, change to bonding arrangement involving a $d^4$ high spin configuration. The absence of any antiferromagnetic interaction in aminates is a fairly convincing indication of their mononuclear structure. A sharp increase in the magnetic moment upon aminate formation indicates destruction of the original sandwich structure. The interaction of chromocene and amines seems to be accompanied either with displacement of both the rings away from the central atom, or, more likely, by their bending out to pass from the $h^5$-structure to $h^3$-, or $h^1$-coordination with respect to the central atom. In any case both the rings remain in the proximity of the central atom, and after elimination of amine molecules will resume the original sandwich arrangement. The fundamental nature of the structural change occuring in the formation of the 1-butylaminate of chromocene are also evident from the X-ray diffractograms of chromocene and its aminate (Fig. 2).

Chromocene reacts in the way described only with linear primary amines. Secondary amines (diethylamine and bis(2-methylpropyl)amine), tertiary amines (triethylamine), and primary amines containing a branched carbon chain (2-propylamine, 2-methylpropylamine and 2-butylamine) do not react. After several days of contact they distill isothermally on to the chromocene and dissolve it to give a red brown solution.

If chromocene is brought into contact with a mixture of vapours of two amines one reactive and the other normally non-reactive, reaction does take place but very slowly. Large, leafy light violet crystals of amine are formed, and these contain both amines. An aminate prepared by reaction of chromocene with mixed vapours of 1-propylamine and 2-propylamine at partial pressure determined by their vapour pressure at 25°C contains 36% of 2-propylamine. Under the same conditions 2-methylpropylamine forms about 19% in the aminate produced in the presence of 1-butylamine. It seems likely that steric hindrance normally prevents reaction of chromocene with branched amines, but when the metallocene structure is damaged by the penetration of molecules of non-branched amines, the more voluminous molecules of branched amines can enter the coordination sphere.

## References

1 F.J. Karol and N.J. Somerset, U.S. Pat. 3, 813, 381; May 28, 1974.

2 G.W. Watt and L.J. Baye, J. Inorg. Nucl. Chem., 20 (1964) 2099.

3 K. Handlíř, J. Holeček, J. Klikorka and V. Mráz, Čs. A. O. 178 309; April 12, 1977.

4 J. Votinský, J. Kalousová, M. Nádvorník, J. Klikorka and K. Komárek, Collection Czechoslov. Chem. Commun., 44 (1979) 80.

5 R. Krieger and J. Voitländer, Z. Naturforsch. A, 27 (1972) 1082.