

REACTION OF CHROMOCENE WITH 1,2-ETHANEDIAMINE AND 2,2'-IMINOBISETHANAMINE

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Reaction of chromocene with excess liquid 1,2-ethanediamine (en) or its vapours in vacuum at room temperature produces the compound $[\text{Cr}(\text{en})_3](\text{C}_5\text{H}_5)_2$. Analogous reaction with 2,2'-iminobisethanamine (det) at 90°C produces the compound $[\text{Cr}(\text{det})_2](\text{C}_5\text{H}_5)_2$. The most likely bonding arrangement of the two new compounds has been suggested on the basis of results of measurements of their magnetic properties and IR spectra.

Crystalline chromocene reacts reversibly with vapours of primary aliphatic amines with linear chains at room temperature to give solid aminates of the type $\text{Cr}(\text{C}_5\text{H}_5)_2 \cdot (\text{RNH}_2)_x$, where x depends on the reaction conditions¹. Secondary and tertiary amines and primary amines with branched chains do not react with chromocene, but their incorporation into the crystal structure of the aminate is promoted by the presence of the amine vapours which do react with the chromocene. The reactions of 1,2-ethanediamine and 2,2'-iminobisethanamine represent a continuation in the study of reactions of chromocene with compounds containing an amino group.

EXPERIMENTAL

Chromocene was prepared and purified in the way described earlier². The amines were pre-dried and refluxed in a stream of argon in vacuum, and their purity was checked by chromatography. The reactions were carried out in sealed ampoules with attached extensions enabling samples to be taken for analysis³. The chromocene to amine molar ratios in the preparations varied within the limits from 1 : 10 to 1 : 20. The magnetic susceptibility was measured with a Variable Temperature Gouy Balance apparatus (Newport Instruments, England)^{1,2} in the interval $90 - 300$ K, and the values of magnetic molar susceptibilities were corrected with respect to diamagnetism with application of the Pascal constants. The magnetic moment was calculated from the Curie equation. The IR spectra were measured in Nujol suspension in the region of $4000 - 400$ cm^{-1} using a Specord IR 75 apparatus (Carl Zeiss, Jena, GDR). The volatile components were identified by means of gas chromatography^{1,2}.

Reaction of Chromocene with 1,2-Ethanediamine

Crystalline chromocene on contact with 1,2-ethanediamine vapours gave a grey-blue powdery product within 24 h at room temperature. Its formation was not accompanied by formation

of any further products in both gaseous and solid phase of the reaction mixture. The same product (which is completely unstable in air) was also formed in the reaction of crystalline chromocene with the liquid amine. The product is insoluble in benzene, hexane and diethyl ether, whereas in water and in ethanol it dissolves with simultaneous reaction. For $\text{CrC}_{16}\text{H}_{34}\text{N}_6$ calculated: 14.34% Cr, 53.02% C, 9.45% H, 23.18% N; found: 14.51% Cr, 53.35% C, 9.70% H, 22.98% N. Molar ratio of the two components reacted was determined in a sealed double ampoule enabling a contact of a known amount of chromocene with vapours of a known amount of liquid ethanediamine. The diamine decrease indicated a ratio of 1 : 3 of the reacted chromocene and diamine. The IR spectrum of the compound $\text{CrC}_{16}\text{H}_{34}\text{N}_6$ (ν , cm^{-1}): 3 357 w, 3 225 m, 3 267 s, 3 210 s, 3 125 s, 3 105 w, 3 046 m, 1 582 m, 1 328 m, 1 281 w, 1 073 w, 1 030 m, 1 005 s, 967 w, 940 m, 891 w, 867 w, 840 vw, 714 vs, 707 vs, 685 sh, 565 sh, 622 vw, 553 vw, 510 m, 486 w.

Reaction of Chromocene with 2,2'-Iminobisethanamine

This reaction takes place only on direct contact of crystalline chromocene with the liquid amine at 90°C, and it produces a single product, grey in colour, insoluble in non-polar solvents, soluble in water and ethanol with simultaneous reaction, unstable in air. For $\text{CrC}_{18}\text{H}_{36}\text{N}_6$ calculated: 13.38% Cr, 55.64% C, 9.34% H, 21.63% N; found: 13.78% Cr, 55.70% C, 9.67% H, 21.28% N. IR spectrum (ν , cm^{-1}): 3 310 m, 3 190 b, 3 127 s, 3 044 m, 1 590 m, 1 343 w, 1 320 w, 1 292 w, 1 233 vw, 1 179 w, 1 145 m, 1 105 vw, 1 053 m, 1 020 w, 1 006 s, 948 s, 891 vw, 878 vw, 860 vw, 781 m, 717 vs, 710 vs, 667 m, 524 m, 490 vw. At 160 °C the reaction gives a pink-brown product which is extremely sensitive to the presence of oxygen. It is insoluble in non-polar solvents, and it immediately reacts with water and ethanol. For $\text{CrC}_8\text{H}_{24}\text{N}_6$ calculated: 20.28% Cr, 37.49% C, 9.44% H; found: 20.65% Cr, 38.00% C, 9.58% H. The nitrogen content had to be determined by calculation, as neither the Kjeldahl nor the hydrogenation analysis methods gave reproducible results. IR spectrum (ν , cm^{-1}): 3 210 m, 3 130 s, 3 093 s, 3 043 m, 1 570 m, 1 342 vw, 1 315 vw, 1 281 w, 1 103 sh, 1 088 m, 1 037 s, 1 005 s, 883 vw, 873 w, 775 w, 724 sh, 715 vs, 710 sh, 575 w, 545 m, 479 w.

RESULTS AND DISCUSSION

The reaction of chromocene with 1,2-ethanediamine (en) produces the compound $\text{CrC}_{16}\text{H}_{34}\text{N}_6$ even at room temperature. No other products are formed in this reaction. The reacted amounts of chromocene and 1,2-ethanediamine are in molar ratio 1 : 3. The temperature dependence of reciprocal corrected molar magnetic susceptibility indicates that the compound is paramagnetic without antiferromagnetic interactions. The value of magnetic moment $\mu = 4.80$ B.M. calculated from the Curie equation fully corresponds to a pure spin contribution of four unpaired electrons at the Cr(II) atom. This means that the oxidation state of chromium did not change during the reaction, but the character of the metal-ring interaction was substantially changed. The original low-spin arrangement of valence electrons of chromium in the chromocene molecule $(e_{2g})^3(a_{1g})^1$ with two unpaired electrons was changed into a high-spin arrangement. The compound prepared is stable in vacuum up to 150° C. This fact is remarkable when compared with the reversible reaction of chromocene with aliphatic amines¹. The adducts of chromocene with primary amines are decomposed as low as at room temperature by merely decreasing

the partial pressure of the amine. Comparison of IR spectra of the reaction product with that of chromocene⁴ confirmed the presumed change in the character of bonds between chromium and cyclopentadienyl rings. The intensive band assigned to antisymmetrical breathing vibration of the ring $\nu(\text{C}-\text{C})$ at $1\,095\text{ cm}^{-1}$ practically disappeared from the spectrum of the product. As this vibration is IR-inactive in the case of the ring ionically bound, it can be presumed that the particle present is C_5H_5^- . This presumption is also confirmed by the shift of the very intensive band due to the out-of-plane deformation vibration of $\text{C}-\text{H}$ by 50 cm^{-1} from the value 765 cm^{-1} to lower wavenumbers (a very intensive band in the product at 714 cm^{-1}). The band of antisymmetric valence vibration ring-metal-ring, which is found at 408 cm^{-1} in chromocene, and which should appear with the crystalline sample and with the ionically bound ring, too, is probably shifted below 400 cm^{-1} , i.e. into the region which was not measured. The presumption of the ionically bound ring, moreover, admits the idea of three 1,2-ethanediamine molecules forming an octahedral complex of chelate type $[\text{Cr}(\text{en})_3]^{2+}$. The results of X-ray structural analysis of the 1,2-ethanediamine complexes indicate that always the *gauche* form⁵ of the diamine is present as the chelate ligand, whereas the *trans* form is characteristic for the diamine in the role of the bridge ligand⁶. Our results, however, allow no unequivocal statement about 1,2-ethanediamine being present in its *gauche* form in the compound $[\text{Cr}(\text{en})_3](\text{C}_5\text{H}_5)_2$. The compound discussed is decomposed above 150° C in vacuum. The gaseous decomposition products contain cyclopentadiene and 1,2-ethanediamine besides smaller amounts of methane, ethane and traces of hydrogen. The solid powdery brown residue is pyrophoric. Chemical analyses gave irreproducible results, especially those of determination of nitrogen. The magnetic moment $\mu = 2.80\text{ B.M.}$, the Weiss constant $\Theta = 168\text{ K}$.

Chromocene reacts with 2,2'-iminobisethanamine (det) at 90° C to give the compound $\text{CrC}_{18}\text{H}_{36}\text{N}_6$ which can (with regard to the reactants present) be formulated as the adduct of chromocene with two molecules of 2,2'-iminobisethanamine. The gas-chromatographical analysis showed that the reaction produced no gaseous and liquid products. The temperature dependence of reciprocal value of corrected molar magnetic susceptibility was used for calculation of the magnetic moment $\mu = 4.69\text{ B.M.}$, which again corresponds quite well to a contribution of four unpaired electrons of $\text{Cr}(\text{II})$. In the IR spectrum of this product, the cyclopentadienide ring was assigned the bands at $1\,006\text{ cm}^{-1}$ (a medium band of in-plane deformation vibration of $\text{C}-\text{H}$), the very strong band at 717 cm^{-1} (the out-of-plane deformation vibration of $\text{C}-\text{H}$; in chromocene it is found at 765 cm^{-1}) and at $3\,044\text{ cm}^{-1}$ ($\text{C}-\text{H}$ valence vibration). The $\text{C}-\text{C}$ valence vibration is in the region of Nujol absorption. Hence, in analogy to the reaction product of chromocene with 1,2-ethanediamine, it is possible to observe a change in character of the bond of the cyclopentadienide rings and formation of a high-spin arrangement of electrons at the $\text{Cr}(\text{II})$ atom. The coordination of two molecules of 2,2'-iminobisethanamine

around Cr(II) cannot be explained as unequivocally as in the case of the above reaction product. However, both the NH_2 groups of the molecule of 2,2'-iminobisethanamine are bound to the central atom, because the IR spectrum of this product contains bands at 3 310, 3 290, and 3 127 cm^{-1} , whereas the corresponding bands of 2,2'-iminobisethanamine itself are found at 3 353, 3 273, and 3 193 cm^{-1} . Also the other bands due to the ligand show shifts towards lower wavenumbers as compared with the spectrum of the free ligand. At 160°C chromocene reacts with 2,2'-iminobisethanamine to give the product $\text{CrC}_8\text{H}_{24}\text{N}_6$, which is extremely sensitive to oxygen. The compound of the same composition was also obtained by heating the product obtained at 90°C to the temperature of 160°C in vacuum. This decomposition only sets free cyclopentadiene. The hydrogen needed for formation of cyclopentadiene from the cyclopentadienide ring probably comes from the amino group. The IR spectrum of the compound isolated at 160°C, however, proves the presence of the remaining rings which are bound to the central atom probably by means of ionic bond. A substantial change is observed in the way of bonding of the amine. The band of NH_2 group was completely absent from the spectrum (in the spectra of 2,2'-iminobisethanamine and the reaction product obtained at 90°C it is found at 3 353 and 3 310 cm^{-1} , respectively). Positive charge of the central atom is compensated by the remaining cyclopentadienide rings and probably also by the amides formally derived from the reacting amine. The magnetic moment of this compound $\mu = 2.53$ B.M. is slightly lower than the value belonging to two unpaired electrons of Cr(II), presuming that two of its electrons are paired. The Weiss constant $\Theta = 20$ K indicates a certain form of coupling of the paramagnetic centres.

The above results show that the diamines (en and det) react with chromocene in similar way as aliphatic monoamines. Their reactions, however, are irreversible, and the compounds formed, in which the diamine molecules are bound to the Cr(II) atoms by both amino groups, exhibit a higher thermostability. The first phase of thermal decomposition of these compounds, however, consists in releasing of the ionically bound rings with formation of cyclopentadiene, whereas the products of the reaction of chromocene with primary aliphatic monoamines are decomposed to the starting compounds.

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