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Co(II) Complex with N_6-Macrocyclic Ligand Hexacyclen

M. MITEWA, P. R. BONTCHEV, D. VASSILEVA

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

E. ZHECHEVA, D. MECHANDJIEV

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

and K. KABASSANOV

Institute of Solid State Physics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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The complexation ability of the macrocyclic ligand 1,4,7,10,13,16-hexaazaoctadecane (hexacyclen), the N-analogue of 18-crown-6, has not been studied very much. Only a few data are available concerning its Co(III), Ni(II,III) and Cu(II) complexes [1–4]. Recently its extracting ability was also studied [5, 6]. On the other hand, considering its rather flexible chain, it might be expected to be a good ligand for a series of metal ions. For that reason its complexation ability towards different types of metal ions was studied as well as the structure of some of the complexes formed [7]. In the present paper the data concerning the structure of the Co(II)–hexacyclen complex are reported.

Experimental

Physical Measurements

The electronic, IR and EPR spectra were recorded on a Specord UV–Vis, Perkin-Elmer 580 (KBr disks) and ERS 220 (GDR) respectively. The magnetic susceptibility measurements were taken in the range 130–350 K in an argon atmosphere according to the Faraday method.

Synthetic Procedure

The complex was obtained by mixing Co(II) solution (1×10^{-2} M) with 'free' hexacyclen solution ($\sim 5 \times 10^{-3}$ M). The latter was obtained from hexacyclen·$3H_2SO_4$ (Aldrich) after treatment with $BaCl_2$ solution for 1 h at ~90 °C (water bath) and filtering off the $BaSO_4$ [3]. The complex formed in the solution was precipitated with $B(C_6H_5)_4^-$ (TPB) as a counter ion.

Results and Discussion

The complexation between Co(II) and hexacyclen resulted in a shift of the two d–d bands (λ_{max} = 508 nm; sh ~490 nm) to 482 nm and appearance of two new intense bands at 233 nm and sh 340 nm. A significant shift of the ν(NH) band was observed too: instead of the band at 3440 cm^{-1} in the spectrum of Co(Hex)xTPB$_2$, two bands at 3260 and 3220 cm^{-1} were observed, indicating the presence of two different types of NH-groups in the complex.

In order to obtain more detailed structural information, magnetochemical and EPR measurements were performed. The temperature dependence of the magnetic susceptibility and of the effective magnetic moment μ_{eff} are shown in Fig. 1. These dependences as well as the μ_{eff} value of 2.68 BM (20 °C) are typical for the structures like these of Co(II)–phthalocyanine and porphyrin complexes [8, 9]. For Co^{II}(phthalocyanine) μ_{eff} values are found to be in the range 2.4–2.7 BM, while for high- and low-spin octahedral complexes the corresponding μ_{eff} values are expected to be ~5.2 BM ($\lambda = -170$ cm^{-1}) and 1.80–1.85 BM ($\lambda = -515$ cm^{-1}) [8]. For tetrahedral Co(II) complexes the μ_{eff} values vary in the range 4.50–4.60 BM [8].

The EPR data obtained are also consistent with the 'phthalocyanine-like' structure of the Co(II)–hexacyclen complex: an anisotropic EPR spectrum

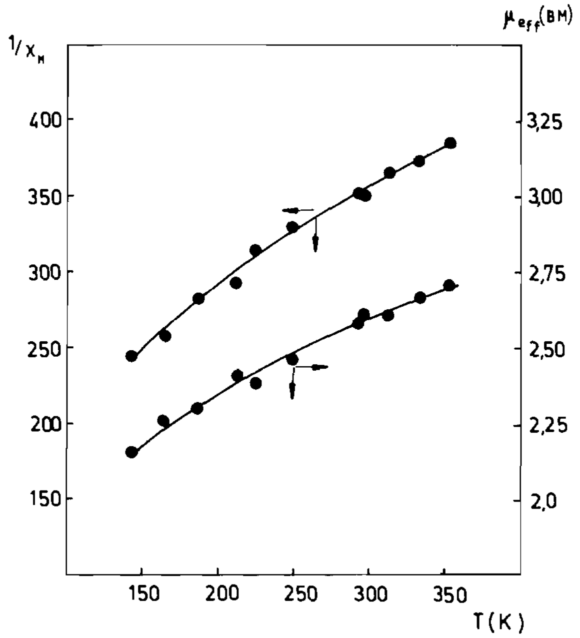

Fig. 1. Temperature dependence of magnetic susceptibility ($1/\chi_M$) and effective magnetic moment (μ_{eff}) of Co(Hex)·2TPB.

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was observed at 77 K (polycrystalline sample) with $g_\parallel = 1.985$, $g_\perp = 2.200$ and $A_\parallel = 180$ Oe. For the Co^{II}(phthalocyanine) and Co^{II}(octaethylporphyrin) complexes very similar data are reported — $g_\parallel = 2.007$; $g_\perp = 2.422$ [9] and $g_\parallel = 2.02$; $g_\perp = 2.60$ [10] respectively. On the other hand for tetrahedral Co(II) complexes the g values are expected to vary in the range 2.2–2.7 with $g_\parallel \sim 2.2$–2.4 [11, 12].

On the basis of all these data it should be concluded that the structure of Co(Hex)$_x$TPB is very similar to that of Co^{II}(phthalocyanine), *i.e.* a planar one. They are unsufficient, however, to conclude whether all 6 N atoms are coordinated to Co(II), or only 4 of them. Bearing in mind that in the ν(NH) region two bands are observed, it seems more likely that the 6 N atoms are not equivalently coordinated to Co(II).

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