Synthesis and spectral studies of some transition metal complexes of potassium bis(bismuthiol-I-yl)borate

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Potassium bis(bismuthiol-I-yl)borate and some of its complexes of the type M Ln [where n = 2 for M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), and n = 3 for M = Cr(III) and Fe(III)] have been synthesized. They have been characterized by elemental analysis, magnetic susceptibility measurements, and electronic- and infrared spectral studies. On the basis of the magnetic moment and electronic spectral data an octahedral geometry is proposed for Cr(III) and Fe(III) complexes. A square-planar structure has been proposed for Mn(II), Co(II), Ni(II) and Cu(II) complexes. The ligand field parameters Dq, B and \(\beta\) calculated for Cr(III) and Fe(III) indicate that the ligand may be placed between EDTA and H_2O in nephelauxetic series.

In the last few years a variety of ligands containing boron-nitrogen bond have been reported in literature. In continuation of our earlier studies in this area, we are reporting here the synthesis and characterization of the complexes of potassium bis(bismuthiol-I-yl)borate with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) metal ions.

Experimental

2,5-Dimercapto-1,3,4-thiadiazole (Bismuthiol-I), (Koch Light) was used without further purification. Potassium borohydride and metal chlorides (BDH) were used as received. Dimethylformamide (E Merck) was made anhydrous before distillation by keeping over anhydrous sodium carbonate for about two days.

Preparation of the potassium bis(bismuthiol-I-yl) borate

In the synthesis of bis(bismuthiol-I-yl)borate a 1:2 mixture of KBH_4 (0.20 g, 3.70 mmol) and bismuthiol-I (1.12 g, 7.40 mmol) in dimethylformamide (\(\sim 50\) ml) was refluxed for about 15 hours. The reaction mixture after cooling to room temperature yielded a colourless solid which was filtered, washed and dried in vacuo.

Preparation of the complexes

Hot ligand solution in aqueous DMF was added to the hot metal chloride in the same solvent (\(\sim 40\) ml) in 1:2 (metal:ligand) ratio (1.40:2.80 mmol) for divalent and 1:3 (metal:ligand) ratio (1.40:4.20 mmol) for trivalent metal ions and refluxed for about 7-8 hours. Same compound was obtained even when the components were taken in varying ratios. The resulting solid was filtered, washed with distilled water and dry ether and dried in vacuo.

The complexes were analysed for metal contents by standard procedure. Microanalyses of carbon and nitrogen were carried out with a Thomas and Coleman analyser, Carlo Erba 1106. The determination of sulphur was done gravimetrically. The infrared spectra (4000-200 cm\(^{-1}\)) were recorded on a Perkin-Elmer 621 spectrophotometer. Magnetic susceptibility was measured on a vibrating sample magnetometer model 155. The diffuse reflectance spectra were recorded on a Carl-Zeiss VSU-2P spectrophotometer using MgO as calibrant.

Results and discussion

The analytical data, colour and decomposition temperature of the complexes are summarized in Table 1. The results of analyses agree fairly well with the proposed stoichiometries. None of the complexes is soluble in usual organic solvent hence their molecular weight and molar conductance values could not be measured.

Of the two tautomeric form (I,II) bismuthiol-I exists predominantly in the thiono form (II).

The IR spectrum of bis(bismuthiol-I-yl) borate does not show any band in the 3300-2900 cm\(^{-1}\) region indicating the absence of N-H bond. There is no
significant change in the C-S and C=S stretching frequencies at 715 cm$^{-1}$ and 1120-1055 cm$^{-1}$, respectively of the ligand indicating that the ligand is in the thiono form even after complexation$^8$. However, the C-N absorption band$^9$ in the ligand at 1290 cm$^{-1}$ is shifted in the complexes presumably due to an association of the ligand molecules in the solid phase which on complexation are dissociated causing it to appear at a lower frequency. A strong band at about 1380 cm$^{-1}$, absent in bismuthiol-I, is due to the vB$^\prime$NIO.

In the far IR spectra of the complexes there is a new band of medium intensity at around 370-410 cm$^{-1}$ which is absent in the free ligand. It is assigned to M-N stretching frequency suggesting coordination of the metal through the nitrogen atom of the bismuthiol-I.

**Magnetic susceptibility and electronic spectra**

In order to obtain information about the mode of coordination of the ligand around the metal ions and the ligand field strength, the magnetic moment of the complexes was measured and their reflectance spectra recorded.

The observed magnetic moment (3.61 B.M.) of the Cr(III) complex is slightly less than the expected value for an octahedral geometry. The bands at 23,809 and 16,129 cm$^{-1}$ may reasonably be assigned to $^4T_{1g}(G)$ $\leftrightarrow$ $^4A_{2g}(F)$ and $^4T_{2g}(G)$ $\leftrightarrow$ $^4A_{2g}(F)$ transitions, respectively. These are the characteristic of an octahedral array of ligands around Cr(III) ion$^{11}$. The ligand field parameters 10 $Dq$, $B$ and $\beta$ have been evaluated as 16,129 cm$^{-1}$, 721 cm$^{-1}$ and 0.73 respectively.

The magnetic moment for square-planar Mn(II) ion in spin-free state is expected to be 5.92 B.M. while for spin-paired configuration, the magnetic moment ranges from 1.73 to 2.2 B.M. The magnetic moment value of 4.90 B.M. in the present case is lower than the spin-free and greater than the spin-paired moment. This intermediate value may, therefore, be regarded to be due to partial spin pairing as has also been observed in the manganous phthalocyanine complex. The reflectance spectrum of the Mn(II) complex in this case shows the strong charge transfer bands at 40,816 and 31,250 cm$^{-1}$. The band at 22,727 cm$^{-1}$ is characteristic of a square-planar Mn(II) ion with the ground term $^4A_{1g}$($b_{2g}$, $e_g$, $a_{1g}$).

Reflectance spectrum of Fe(III) complex shows two absorption bands at 17,241 and 22,727 cm$^{-1}$ assignable to $^4T_{1g}(G)$ $\leftrightarrow$ $^6A_{1g}$ and $^4T_{2g}(G)$ $\leftrightarrow$ $^6A_{1g}$ transitions, respectively, corresponding to an octahedral Fe(III) ion$^{12}$. The magnetic moment value (5.83 B.M.) is slightly less than that calculated (5.92 B.M.) for an octahedral, high-spin Fe(III) ion. This deviation in $\mu_{\text{eff.}}$ value is probably due to antiferromagnetic effect. The 10 $Dq$, $B$ and $\beta$ values have been computed as 13,438 cm$^{-1}$, 905 cm$^{-1}$ and 0.82 respectively.

A square-planar Co(II) complex commonly has a $\mu_{\text{eff.}}$ value between 2.1 and 2.8 B.M. The $\mu_{\text{eff.}}$ value of 2.75 B.M. and the charge-transfer band at 28,000 cm$^{-1}$ (without the presence of any other band) also suggest a square-planar Co(II) complex$^{13}$. The solid state reflectance spectrum of the Ni(II) complex exhibits one main band at 22,727 cm$^{-1}$ assigned to $^1B_{1g}$$\leftrightarrow$$^1A_{1g}$ transition. The observed
magnetic moment value of 2.27 B.M. also supports the square-planar geometry of Ni(II) ion\(^{14}\).

A square-planar structure is proposed for the Cu(II) complex on the basis of the observed magnetic moment value (1.74 B.M.). The above geometry is supported by the presence of a weak band at 12,658 cm\(^{-1}\) attributable to \(T_{2g} \rightarrow E_{g}\) transition\(^{15}\).

The Zn(II) complex is diamagnetic as expected. From the stoichiometry, this complex is tentatively suggested to possess tetrahedral geometry, since tetrahedral geometry is a more preferred structure for Zn(II) complexes\(^{16}\).

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References