Synthesis & Ligating Properties of Dihydrobis(succinimidyl)borate Anion

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The reaction of potassium borohydride and succinimide in 1:2 molar ratio in the molten state affords a novel ligand potassium dihydrobis(succinimidyl)borate (PDSB). Coordination compounds of PDSB with Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II) have been synthesized. IR studies indicate that PDSB behaves as a uninegative, bidentate ligand coordinating through the oxygen atoms of the succinimide ring system. On the basis of the magnetic moment and electronic spectral data, octahedral geometry is proposed for all the complexes except the Cu(II) complex. A square-planar structure involving chlorine bridges has been proposed for the copper complex.

In recent years, syntheses1 -4 of a novel class of ligands, derived from tetrahydroborate anions by substituting nitrogen-containing heterocyclic moieties for hydrogen atoms, have been successfully achieved. It has been shown that such poly-substituted borate anions, \[H_nB(L)_{4-n}\] \(^{-}\), where \(n = 0, 1, 2\) and \(L = \text{pyrazole, indazole, imidazole and their substituted analogues}\), act as potential chelating agents. Succinimide, which is reported5 to coordinate through the nitrogen atom, has been chosen in the present study for substitution in the BH\(_4\) anion with a view to examining the effect of the formation of B – N bond on the coordinating ability of the succinimide moiety.

This paper describes the synthesis and characterization of the new ligand potassium dihydrobis(succinimidyl)borate and of its complexes with Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II).

Materials and Methods
Succinimide (Sisco, m.p. 125°C), potassium borohydride (BDH, England) and Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) chlorides (all BDH reagents), were used as such.

Estimations of halogen and boron were done gravimetrically6, 7 while the metals were estimated by titrating with standard EDTA solution8.

The IR spectra (4000-600 cm\(^{-1}\)) were recorded in nujol mull on a SP3-100 Pye Unicam spectrophotometer. Magnetic susceptibility measurements were done by the VSM technique at 23°C. Diffuse reflectance spectra were recorded on a Carl Zeiss VSU-2F spectrophotometer using MgO as the calibrant. The NMR spectra were run on A-600 analytical NMR spectrometer.

Results and Discussion
The preparation of the ligand can be summarised by Eq. 1,

\[
2(CH_2CO)_2NH + KBH_4 \rightarrow K^+ [C_8H_{10}N_2BO_4]^- + 2H_2 \quad \text{(I)}
\]

The stoichiometry of the ligand was confirmed from the results of the elemental analyses (Table I). It was also ascertained by the volume of hydrogen gas evolved during its synthesis.

Potassium dihydrobis(succinimidyl)borate
Potassium borohydride (0.54 g, 0.01 mol) and succinimide (2.0 g, 0.02 mol) were carefully heated in a flask in a paraffin bath at a temperature not exceeding 170°C (~8 hr) till the calculated two moles of hydrogen gas were evolved. The resulting black compound was heated with 500 ml ethyl alcohol on a water bath (1 hr) to remove any unreacted material. Then it was filtered, washed with warm ethanol and was finally dried in vacuo.

Preparation of the complexes
Potassium dihydrobis(succinimidyl)borate (PDSB), (1.0 g, 0.004 mol) and Cr(III) and Fe(III) chlorides (~0.40 g, 0.0013 mol) or Co(II), Mn(II), Ni(II) and Cu(II) chlorides (0.5 g, 0.002 mol) were separately dissolved in 100 ml of distilled water. After heating the solutions for ~30 min, the ligand solution was poured into the metal ion solution with continuous stirring. A shining black crystalline material appeared in each case which was further heated on a water bath for 3 hr. The resulting product was filtered, thoroughly washed, first with warm distilled water and finally with ethanol and dried in vacuo.
<table>
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<th>Compounds</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Found (Calc.), %</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>M</th>
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<td>[CsH₁₀N₂BO₄]K⁺</td>
<td>Black</td>
<td>65</td>
<td>360</td>
<td></td>
<td>38.53</td>
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<td>11.01</td>
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<td>44</td>
<td>360</td>
<td></td>
<td>38.83</td>
<td>3.48</td>
<td>10.95</td>
<td>7.29</td>
<td>9.89</td>
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<td>360</td>
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<td>3.71</td>
<td>9.24</td>
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<td>360</td>
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<td>2.72</td>
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<td>32.54</td>
<td>3.40</td>
<td>9.03</td>
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<td>360</td>
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<td>3.44</td>
<td>9.15</td>
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<td>31.40</td>
<td>3.54</td>
<td>8.80</td>
<td>11.51</td>
<td>20.43</td>
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</table>

*B: Found, 3.9%; Calc., 24.2%.

The ligand has been further characterized by analysing its NMR and IR spectra. The ¹H NMR spectrum in DMSO reveals a singlet at δ 7.5 ppm assignable to the C–H of the succinimide nucleus. The B–H proton peak is observed as a doublet at δ 6.9 ppm. The relative areas of the peaks are 1:4 for BH₂ and CH₂ respectively.

Major bands in the IR spectrum of the ligand are listed in Table 2. The spectrum does not show any band in the region 3500-3300 cm⁻¹ indicating the absence of N–H bonds. However, the appearance of a broad band in the range 2350-2250 cm⁻¹ indicates the presence of the B–H linkage. The spectrum also shows a strong band around 1380 cm⁻¹ which is absent in succinimide and may be attributed to the νB–N vibration. The other characteristic vibrations, e.g., C–H stretching and bending and C–N stretching vibrations of succinimide moiety appear at their usual positions. The positions of νC=O bands (Table 2) are considerably lowered from that reported for succinimide. The reason for this negative shift could not be ascertained.

On the basis of the present data, structure(I) may be assigned to PDSB.

The complexes synthesized from PDSB have 1:1 and 1:2 (metal:ligand) stoichiometries for the divalent and trivalent transition metal ions, respectively. The complexation reaction may be represented by Eqs (2) and (3),

\[
\text{MCI}_2 + 2K^+[\text{C}_6\text{H}_{10}\text{N}_2\text{BO}_4^-] \rightarrow [\text{M(C}_6\text{H}_{10}\text{N}_2\text{BO}_4)_2\text{Cl}] + 2\text{KCl} \quad \text{(2)}
\]

(where M = Cr(III) and Fe(III))

\[
\text{MCI}_2 + K^+[\text{C}_6\text{H}_{10}\text{N}_2\text{BO}_4^-] \rightarrow [\text{M(C}_6\text{H}_{10}\text{N}_2\text{BO}_4\text{Cl}] + \text{KCl} \quad \text{(3)}
\]

(where M = Mn(II), Co(II), Ni(II) and Cu(II)).

It has been reported that due to steric limitations, all the three donor sites of the free succinimide molecule cannot be simultaneously involved in coordination with the same metal atom. In a number of divalent transition metal compounds with succiniminate anions, it has been shown that coordination occurs through the nitrogen atom of the imide (keto form). Nevertheless, it is possible that the coordination may occur through the carbonyl oxygen atom (i.e. enol form) in which case the relative donor capacities of the nitrogen and carbonyl oxygen atoms are reversed as has been indicated for substituted alkyl amine complexes of Cu(II) and Ni(II) imides.

Coordination through the carbonyl oxygen atom would reduce the double bond character of C=O bond, consequently decreasing the carbonyl stretching frequency. It is evident from Table 2 that in all the complexes the νC=O frequency is negatively shifted supporting the involvement of carbonyl oxygens in coordination. There is no change in the B–H, B–N and C–N stretching frequencies suggesting that the imide nitrogens do not take part in coordination in these complexes.
Dihydrobis(succinimidyl)borate and Its Complexes (values could not be measured. Heating up to even 360°C did not affect the physical nature of these complexes, which may possibly be due to polymerization. Further verification of the structure has been obtained by the magnetic moment and electronic spectral studies.

Electronic spectra and magnetic susceptibilities

The observed magnetic moments of Co(III) (3.77 B.M.) and Fe(III) (5.56 B.M.) complexes are indicative of an octahedral geometry. The magnitudes of the magnetic moments are somewhat lower than the theoretically expected values. The observed ligand field bands at 18.2 and 23.8 kK for the chromium complex may be assigned to \(4T_{2g}(F) \rightarrow 4A_{2g}(F)\) and \(4T_{2g}(F) \rightarrow 4A_{g}(F)\) transitions, respectively, characteristic of a d\(^{3}\) ion in an octahedral environment. In the case of Fe(III) complex the observed bands at 23.8 and 17.8 kK are consistent with the transitions \(4T_{2g}(G) \rightarrow 6A_{1g}\) and \(4T_{1g}(G) \rightarrow 6A_{1g}\) respectively. The observed 1:2 (metal:ligand) stoichiometry could yield an octahedral structure only through halogen bridging in a polymeric octahedral fashion. This lowering of the magnetic moment might be due to antiferromagnetic exchange occurring in the complex through halogen bridging due to the polymeric nature of the complexes.

Polymeric complexes of Fe(III) and Cr(III) involving halogen bridging are not uncommon. The electronic spectrum of the Mn(II) complex is indicative of an octahedral environment around the manganese ion. It shows two bands at 22.7 and 19.2 kK assignable to \(4T_{2g}(G) \rightarrow 6A_{1g}\) and \(4T_{1g}(G) \rightarrow 6A_{1g}\) transitions respectively. The observed magnetic moment (4.44 B.M.) is considerably lower than the expected spin-only value (5.92 B.M. for \(S = 5/2\)). It has been reported that for bivalent manganese complexes with Schiff bases the magnetic moment ranges from 4.74 to 5.70 B.M. at room temperature, which is due only to the magnetically non-dilute nature of these compounds. However, in the present complex the magnetic moment value is even lower, presumably due to an antiferromagnetic exchange. The polymerization of the complex having the stoichiometry MLX could be visualized through ligand bridging in which two carbonyl oxygen atoms from each ligand molecule are coordinated to one metal and the other two are coordinated to an adjacent metal ion. The remaining two coordination positions of the octahedron are satisfied by bridging chlorines in the axial positions.

The magnetic moment of the cobalt complex is 3.90 B.M. which is close to the expected value of 3.92 B.M. for the square-planar geometry. However, its electronic spectrum exhibits bands at 18.5 and 10.4 kK attributable to the transitions \(4T_{1g}(F) \rightarrow 4T_{1g}(F)\) and \(4T_{2g}(F) \rightarrow 4T_{1g}(F)\), respectively, characteristic of an octahedral array of ligands around the cobalt ion. Therefore, even though the square planar geometry can not be completely ruled out, it seems more likely that the complex has an octahedral polymeric structure. The lowering of the magnetic moment to such an extent may reasonably be attributed to the antiferromagnetic exchange similar to that suggested for the manganese(II) complex.

The nickel(II) complex may have an octahedral polymeric structure similar to that proposed for the manganese(II) complex. It has a magnetic moment of 2.92 B.M. Its electronic spectrum is consistent with an octahedral structure. It shows two bands at 23.3 and 13.5 kK due to the transitions \(3T_{1g}(F) \rightarrow 3A_{2g}(F)\) and \(3T_{1g}(F) \rightarrow 3A_{1g}(F)\) respectively.

The observed magnetic moment of 1.60 B.M. for the copper(II) complex may be explained on the basis of a square-planar structure for the complex. This geometry is further supported by the observed electronic spectrum of the solid complex which shows weak bands at 17.8 and 15.4 kK assignable to \(2B_{1g} \rightarrow 2B_{1g}\) and \(2A_{1g} \rightarrow 2B_{1g}\) transitions, respectively. A weak broad band observed at 12.5 kK is characteristic of square planar geometry for the d\(^{9}\) system. The observed \(\mu_{eff}\) value (1.60 B.M.) is, however, lower than the expected value (1.90 B.M.) and, therefore, suggests an antiferromagnetic interaction in the complex, obviously through the chlorine bridges. A dimeric structure is tentatively proposed for this complex.

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