Synthesis and characterization of manganese(II), cobalt(II), nickel(II), and palladium(II) complexes of DL-aspartic acid

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DTL-Aspartic acid reacts with Mn(II), Co(II), Ni(II) and Pd(II) to give stable complexes. It forms 1:1 complexes with Co(II) and Ni(II), where both the carboxylic acid groups remain deprotonated with 2:1 complexes with Mn(II) and Pd(II), where at least one carboxylic acid group is protonated. The spectral, thermal and electrolytic properties of the complexes have been studied.

We have earlier reported the metal complexes of Cu(II), Zn(II), Cd(II), Hg(II), Mo(VI), and Pd(II) with DL-aspartic acid. Based on spectral and other studies it was suggested that in most of the compounds both the carboxylic acid remains deprotonated and participate in the bond formation, in the Pb compound prepared from Pb(NO3)2, the carboxylic acid group remain deprotonated and take part in the bond formation to the metal atom along with α-amino group whereas, in the Hg(II) compounds the ligand remains intact in its zwitterionic form with overall charge neutrality. In this note we describe the preparation and properties of some new complexes of this important amino acid with Mn(II), Co(II), Ni(II) and Pd(II) to gain more insight about the nature of metal-amino acid interactions.

Experimental

The chemicals and ligand used in all preparative and analytical works were of AR grade (E Merck, BDH and Aldrich). Micro analytical data for C, H and N were obtained from the Institute for Chemical Reaction Science, Tohoku University, Japan. The metal contents were determined by following standard methods. IR spectra of all the compounds were recorded on a Shimadzu IR spectrophotometer, Model IR 470 of Japan in the region of 4000-400 cm⁻¹ using KBr pellet technique. The electronic spectra of the complexes were recorded with nujol in a Shimadzu UV-Visible recording spectrophotometer, Model UV-160A, in the wave length range 200-1100 nm. The melting points were measured in a heating device, MEL-TEMP(II), with a FLUKE 51 KJ thermometer. The conductivity of the water soluble compounds were measured using a conductometer, Model CM-55, TOA Electronics Ltd. Japan. TG and DTA of the samples were recorded on a Rigaku Thermal Analyzer TAS 100 TG/DTA unit.

Preparation of the complexes

Bis (DL-aspartato) manganese(II) tetrahydrate

Mn(C4H6NO4)2.4H2O

Aqueous solutions of DL-aspartic acid (1.33 g in 80 ml) and MnCl2 (1.98 g in 30 ml) were prepared separately. The two solutions were mixed together after neutralizing the ligand solution with aqueous KOH. The volume of the solution was reduced to 20 ml by gently heating and left for crystallization at room temperature after filtration. Light pink crystals were obtained after two days. The compound is stable in air and light. It is slightly soluble in water but soluble in hot water and insoluble in organic solvents like MeOH, EtOH and acetone etc., m.p. 110-112 °C, yield 46% (on metal content). Anal: [Found: C 24.61; H 5.80; Mn 12.54; Reqd for Mn(C4H6NO4)2.4H2O C 24.56; H 5.11; N 7.10; Mn 14.05%].

IR bands (cm⁻¹): 3415(s,b), 3272(m), 2950(w), 1681(m), 1569(m), 1461(s), 1407(vs), 1306(s), 1059(s), 815(s), 650(m,b), 547(s).

Co (II) aspartate dihydrate, Co(C4H6NO4)2.2H2O

Aqueous solutions of DL-aspartic acid (1.33 g in 80 ml) and Co(OAc)2 (2.48 g in 30 ml) were prepared separately and mixed together after neutralizing the ligand solution with aqueous KOH. The volume of the solution was reduced to 15 ml by gentle heating and left for crystallization at room temperature after filtration. Violet powdered product was separated by filtration, washed with ethanol and dried over silica gel. The compound is soluble in water, sparingly soluble in methanol, ethanol and CHCl3 and insoluble in DMSO, CCl4 etc. and stable in air and light. M. pt=334-335 °C. Anal: [Found: C 21.24; H 3.98; N 6.19; Co 25.61, Reqd. for Co(C4H6NO4)2.2H2O C 21.25; H 3.99; N 6.20; Co 26.07%].

IR bands (cm⁻¹): 3420(vs), 3350(sh), 3125(s).
Nickel aspartate dihydrate, Ni\((C_6H_7NO_3)\cdot2H_2O\)

This compound was obtained by heating DL-aspartic acid with excess Ni\((CO_3)\) in aqueous medium on a water bath for about 1 h. The resulting blue solution was reduced to 20 ml and kept in a desiccator containing ethanol. A blue solid product was obtained after about one week. The product was separated by filtration, washed with ethanol and dried over silica desiccator containing 21.26; H 3.97; N 6.20; Ni 24.65%.

The pale blue solid product was obtained immediately after mixing the aqueous solutions of DL-aspartic (1.33 g in 60 ml) acid and PdCl\(_2\) (0.88 g in 50 ml). The pale yellow powdered product was separated by filtration, washed with hot water and dried over silica gel.

The compound is stable in air and light. It is slightly soluble in water, soluble in hot water and insoluble in organic solvents like MeOH, EtOH, CCl\(_4\), acetone etc. M.pt.-decomposed at 273°C, yield=0.97 g (50% on metal content). Anal: [Found: C 25.88; H 3.45; N 7.45; Reqld. for Pd\((C_6H_7NO_3)\cdot2H_2O\) C 24.71; H 3.60; N 7.21%]

IR bands (cm\(^{-1}\)):
- 3430(vs), 3280(s), 3228(w), 2920(sh), 1699(vs), 1622(sb), 1558(sh), 1394(s), 1085(w), 585(m).

Results and discussion

The complex compounds of DL-aspartic acid with dispositive metal ions Mn(II), Co(II), Ni(II) and Pd(II) have been synthesized in aqueous medium. The complexes were characterized by comparing the elemental analysis data and different spectral analysis.

The important IR band assignments have been done empirically on the basis of standard references\(^4\) and by comparing with the spectrum of the ligand. The relatively broad signals of the compounds in the region 3395-3430 cm\(^{-1}\), Mn-asp at 3415, Co-asp at 3425, Ni-asp at 3395, and Pd-asp at 3430 cm\(^{-1}\), are due to –OH stretching of H\(_2\)O and –COOH group. The broadness indicate the presence of lattice water and probable participation in the hydrogen bond formation. Two bands in the region 3125-3280 cm\(^{-1}\) (Mn-asp at 3272 and 3171, Co-asp at 3234 and 3139, Ni-asp at 3250 and 3198, and Pd-asp at 3280 and 3228 cm\(^{-1}\)), are assigned due to asymmetric and symmetric NH stretching of the NH\(_2\) group.

In the 1800-1350 cm\(^{-1}\) region, the complexes absorb for asymmetric and symmetric stretching vibration of the –COO ion when both the carboxylic acid groups are in the deprotonated and/or metalated state (Mn-asp at 1599 and 1407, Co-asp at 1619 and 1379, Ni-asp at 1620 and 1413, and Pd-asp at 1622 and 1400 cm\(^{-1}\)). If at least one carboxylic group remains intact (in the protonated state), the compound absorbs for (C=O) stretching vibration also. Among the metal complexes presented here, Mn and Pd complexes show absorption due to (C=O) stretching at 1681 and 1699 cm\(^{-1}\) respectively, while the other two do not.

On the basis of Nakamoto’s work\(^7\), from the relative \(\Delta v\) values of the complexes, Mn-asp (192 cm\(^{-1}\)), Co-asp (240 cm\(^{-1}\)), Ni-asp (217 cm\(^{-1}\)), and Pd-asp (222 cm\(^{-1}\)), we can predict the order of covalency of metal-oxygen bonds as Co(II) > Pd(II) > Ni(II) > Mn(II). Following the procedure of Kagarise\(^9\) and Stimson\(^10\), the relationship between electronegativity of the central metal atom and asymmetric stretching frequency of –COO group in cm\(^{-1}\) unit was examined. A linear relationship (Fig. 1) was observed which is in agreement with that of Kagarise and Stimson and may be shown by the equation,

\[\nu_{\text{asym}}(\text{COO}) = 33.14 \times (\text{electronegativity}) + 1558\]
The electronic spectra of the ligand and all the compounds have been studied by nujol mull technique. The ligand absorb due to $\pi \rightarrow \pi^*$ transition for $> \text{C}=\text{O}$ of carboxylic acid group and also absorb for $n \rightarrow \pi^*$ transition of lone pair electrons of O-atom of carboxylic acid groups at 228 and 301 nm respectively. The $n \rightarrow \pi^*$ transition due to lone pair on N-atom may not be possible since it remains protonated. All the complexes also show similar absorption peaks in the UV region due to ligand part of the complexes (Mn-aspart 240 and 301, 343, Co-aspart at 253 and 300, 342, Ni-aspart at 244 and 300, 343, and Pd-aspart at 249, 299 and 319, 355 nm) but at little higher wavelengths than those of the ligand. The compounds show additional absorption peak(s) due to $d \rightarrow d$ transitions in the visible region (above 380 nm).

Cobalt and nickel compounds show relatively strong absorptions (Co-aspart at 380, 531 and Ni-aspart at 393, 643, 1058 nm), whereas the light coloured Mn and Pd compounds show very weak absorptions. Absorption bands of Pd compound near 420 nm are masked with those for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, and in case of Mn compound the absorption near 640 nm is very weak.

The equivalent conductance data (solution strength calculated on the basis of formula weight) of the ligand and the complexes show that with the decrease in concentration, the equivalent conductance increases rapidly. This implies that all the complexes and the ligand are weak electrolytes.

The thermal analysis studies of the complexes were also carried out. The thermograms (Fig. 2) are rather complicated to interpret. In all the cases there is a general trend of losing water molecule at relatively lower temperature range 80-180 °C and removal of organic parts in complicated steps at the higher temperature range 200-600 °C. The weight of the residue correspond to respective metal oxides. In the differential thermal analysis also, we observe endotherms at lower temperature indicating the expulsion of water and the removal of organic parts are indicated by several overlappings and or separate exotherms.

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References