Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **2(1),** 45-49, Jan. **(2012)** *Res.J.Chem.Sci.*

Mixed Ligand Cobalt (III) Complexes with 1-Amidino-O-Methylurea and Amino Acids

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Available online at: www.isca.in
(Received 24th October 2011, revised 24th November 2011, accepted 9th December 2011)

Abstract

Reactions of 1-amidino-O-methylurea with cobaltous chloride in presence of water and liquor ammonia resulted in the formation of diammine bis(1-amidino-O-methylurea) cobalt(III) chloride. The present work describes the result of our investigations on the synthesis and characterization of mixed ligand complexes of 1-amidino-O-methylurea with some amino acids. Reactions of $[Co(NH_3)_2(AMU)_2]Cl.2.5H_2O$ with amino acids viz. L-valine, DL-alanine and glycyl-glycine in equimolar ratio, in water, resulted in the formation of $[Co(val)(AMUH)_2]Cl_2.2H_2O$, $[Co(ala)(AMUH)_2]Cl_2.2.5H_2O$ and $[Co(gly-gly)(AMUH)_2]Cl_2.H_2O$ respectively. These complexes have been characterized by elemental analysis and molar conductance values. Octahedral structure has been proposed on the basis of IR , magnetic moment and electronic spectra of the complexes.

Keywords: Mixed ligand complexes,1-amidino-O-methylurea, L-valine, DL-alanine, glycyl-glycine.

Introduction

Besides the obvious interest in the synthesis, mixed ligand complexes are expected to provide valuable information on magnetic properties, electronic spectra, flexidentate behavior of polydentate ligands, spectrochemical equilibrium etc[1].

The ligand 1-amidino-O-methylurea serve as a bidentate ligand satisfying both the primary and secondary valencies with the formation of inner metallic complexes. Amino acids, on the other hand, are well known chelating agents with multifunctional groups and are biologically active, creating considerable interest in their metal complexes[2,3,4]. Because cobalt(III) is consistently hexacoordinate in its complexes, the synthesis and elucidation of the structure through elemental analysis, conductance measurements, spectral analysis and magnetic moment measurements etc. have been undertaken.

Material and Methods

The ligand 1-amidino-O-methylurea (AMUH) and the intermediate compound diammine bis(1-amidino-O-methylurea) cobalt(III)monochloride were prepared by published procedure[5,6]. All chemicals used were of analytical grade. Elemental analyses were carried out on Elementar Vario El III Carlo Erba 1108 at Regional Sophisticated Instrumentation Centre, CDRI, Lucknow and the conductance was measured with EUTECH CON510 at 25^0C in water. The infrared spectra were run on potassium bromide phase from 400-4000 cm^{-1} range, with a Shimadzu FTIR 8400 S at Chemistry Department, Manipur University. Solution spectra for the compound were recorded with a Shimadzu uv-visible spectrophotometer UV-2450 at Chemistry Department, Manipur University.

Preparation of Bis(1-amidino-O-methylurea) L-valinato cobalt(III) chloride: Diammine bis (1-amidino-O-methylurea) cobalt(III) chloride (1g) and L-valine (0.2918g) were dissolved in 15 ml of distilled water. The mixture was heated on a water bath until evolution of ammonia ceases. After completion of the evolution of ammonia, the dark red solution was concentrated and neutralized with HCl (2N). Cooling followed by addition of acetone to this solution produced an oily layer, from which rose red crystals of bis(1-amidino-O-methylurea)L- valinato cobalt(III)chloride crystallized out. The crystals were removed by adding acetone, followed by scratching. This complex was recrystallized from a minimum volume of hot double distilled water and again treated with acetone and scratched to obtain the pure product which was filtered and dried in a desiccator.

Similarly, the complexes bis(1-amidino-O-methylurea)DL-alaninato cobalt(III) chloride and bis(1-amidino-O-methylurea) glycyl-glycinato cobalt(III) chloride were prepared by following the above procedure by taking DL-alanine or glycyl-glycine in place of L-valine.

Table-1
Characterization table of the complexes: found/(calculated)%

Complex	State/Colour	Co	C	H	N	Anion	H_2O
$[Co(L\text{-}val)(AMUH)_2]Cl_2.2H_2O$	Crystal/Rose red	11.30 (11.40)	25.40 (25.60)	5.60 (5.20)	24.36 (24.46)	13.06 (13.7)	6.40 (6.90)
$[Co(DL\text{-}ala)(AMUH)_2]Cl_2.2.5H_2O$	Crystal/Rose red	11.70 (11.9)	21.84 (21.80)	5.00 (4.60)	25.80 (25.40)	13.80 (14.30)	8.80 (9.00)
$[Co(gly\text{-}gly)(AMUH)_2]Cl_2.H_2O$	Crystal/ Rose red	11.30 (11.50)	23.00 (23.40)	5.20 (4.60)	27.10 (27.34)	13.30 (13.80)	3.60 (3.50)

Table-2
Molar Conductance data and Electronic Spectra of Cobalt (III) complexes

Complex	Λ_m,ohm^{-1}cm^{2}mol^{-1} 0.001M at 25^{0}C	λ_{max}(nm)	Assignments
$[Co(L\text{-}val)(AMUH)_2]Cl_2.2H_2O$	251	501,362,294	$^1A_{1g}\rightarrow{}^1T_{1g}$, $^1A_{1g}\rightarrow{}^1T_{2g}$, LMCT
$[Co(DL\text{-}ala)(AMUH)_2]Cl_2.2.5H_2O$	248	499,360,284	$^1A_{1g}\rightarrow{}^1T_{1g}$, $^1A_{1g}\rightarrow{}^1T_{2g}$, LMCT
$[Co(gly\text{-}gly)(AMUH)_2]Cl_2.H_2O$	242	501,355,284	$^1A_{1g}\rightarrow{}^1T_{1g}$, $^1A_{1g}\rightarrow{}^1T_{2g}$, LMCT

Table-3
IR frequencies (cm^{-1}) of Cobalt (III) complexes

Compounds	N–H	C=N	C–O–C	ν_{as} COO$^-$	ν_sCOO$^-$	Co–N	Co–O	H_2O
$[Co(NH_3)_2(AMU)_2]Cl.2.5H_2O$	3290	1624	1236	-	-	482	-	3348
$[Co(L\text{-}val)(AMUH)_2]Cl_2.2H_2O$	3250	1637	1232	1606	1359	497	619	3661
$[Co(DL\text{-}ala)(AMUH)_2]Cl_2.2.5H_2O$	3240	1629	1230	1604	1361	480	621	3450
$[Co(gly\text{-}gly)(AMUH)_2]Cl_2.H_2O$	3275	1614	1222	1606	1379	486	615	3460

Where, L-val=L-Valine, DL-ala=DL-Alanine and gly-gly=Glycyl glycine and AMUH=1-Amidino-O-methylurea.

Results and Discussion

All the complexes were coloured, highly soluble in water, stable and non-hygroscopic. Based on the analytical and conductivity data the formulae of the complexes are listed in the table 1.

Conductivity and magnetic moment: The molar conductance values of the newly synthesized mixed ligand complexes registered 230-270 ohm^{-1} cm^2 mole^{-1} at 0.001M in water at 25^{0}C, indicating that the complexes are uni-bivalent electrolytes [6,7] (table 2). The newly synthesized mixed ligand complexes were diamagnetic indicating a low spin octahedral geometry.

IR spectra: The IR spectra (table 3) of the intermediate compound $[Co(NH_3)_2(AMU)_2]Cl.2.5H_2O$ and the newly synthesized mixed ligand complexes, Fig.1,2 and 3, exhibits significant bands at around 3240-3290 cm^{-1}, 1614-1637 cm^{-1} and 1222-1236 cm^{-1} which may be assigned to υ(N–H)[8,9,10], υ(C=N)[10-16] and υ(C–O–C)[11,17,18] stretching vibrations respectively. On comparision with the intermediate compound, the newly synthesized mixed ligand cobalt(III) complexes show appearance of new bands in the region 1604-1606 cm^{-1} which may be assigned to the asymmetric vibration of coordinated carboxylate groups [υ_{as}(COO$^-$)] and the bands in the region1359-1397 cm^{-1} may be attributed to the symmetric vibration of [υ_{as}(COO$^-$)] carboxylate group [υ_s(COO$^-$)][8,12,15,19]. The large differences between the frequencies of [υ_{as}(COO$^-$)] and [υ_s(COO$^-$)], [$\Delta\upsilon\geq$200cm^{-1}] in all the complexes are indicative of the involvement of the coordination of the carboxylate groups to the metal ion in a monodentate fashion[15,19,20]. Other low intensity bands observed in the region, 480-497 cm^{-1} are assigned to υ(Co–N)[8,21,22] stretching vibrations, indicating the coordination of the nitrogen atom of the amino acids to cobalt(III) ion. The presence of lattice water [8,19,23] molecules are indicated by the broad band at the range of 3348-3460 cm^{-1}. Thus, the overall IR spectra indicate that the ligand 1-amidino-O-methylurea (AMUH) coordinate to the metal ion as a neutral bidentate ligand and the amino acids act as monobasic bidentate ligand in all the newly synthesized complexes.

Electronic spectra: The electronic spectra of the newly synthesized mixed ligand cobalt(III) complexes $[Co(L\text{-}val)(AMUH)_2]$ $Cl_2.2H_2O$, $[Co(DL\text{-}ala)(AMUH)_2]Cl_2.2.5H_2O$ and $[Co(gly\text{-}gly)(AMUH)_2]Cl_2.H_2O$ are consistent with the octahedral structures assigned, showing three absorption bands in the range of λ_1= 499-501nm, λ_2= 355-362 nm and λ_3= 284-297nm (Table 2) which are attributed to $^1A_{1g}\rightarrow{}^1T_{2g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and LMCT transitions respectively. These transitions are comparable to six coordinated cobalt(III) complexes[13,24]. The diamagnetic nature of the complexes also suggested an inner octahedral stereochemistry[25,26,27].

Conclusion

It has been observed that the reaction of diammine bis (1-amidino- O-methylurea) cobalt(III) chloride with amino acids resulted in the formation of mixed ligand complexes of type $[Co(L)(AMUH)_2]Cl_2$ where, L = amino acids (L- valine or DL- alanine or glycyl-glycine). All the ligands are coordinated as bidentate ligands and an octahedral geometry was observed in all the complexes.

Acknowledgements

The authors would like to acknowledge the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for providing the necessary analytical data.

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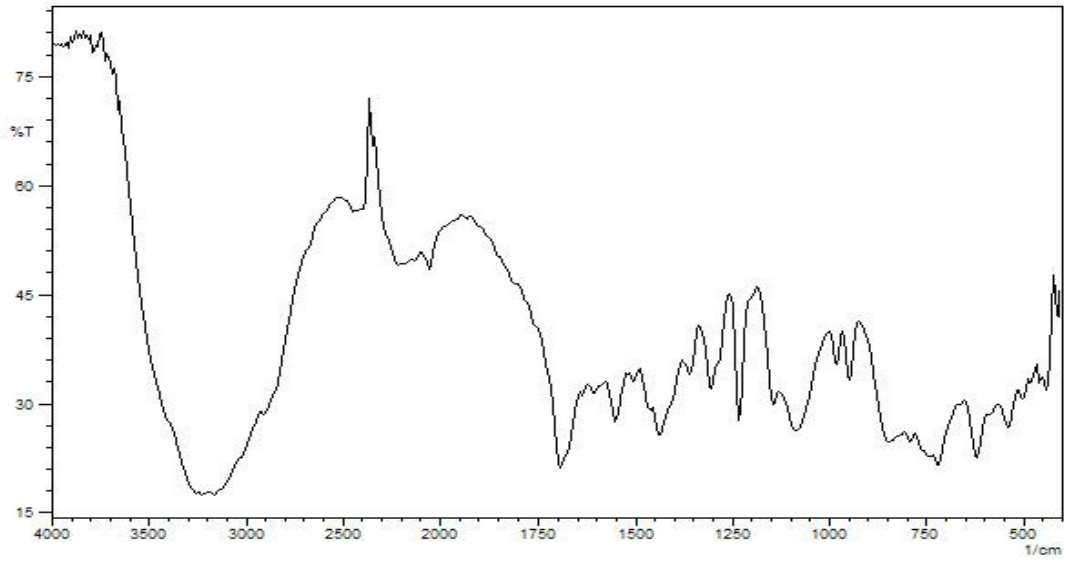

Figure-1
Infrared Spectra of $[Co(L\text{-}val)(AMUH)_2]Cl_2.2H_2O$

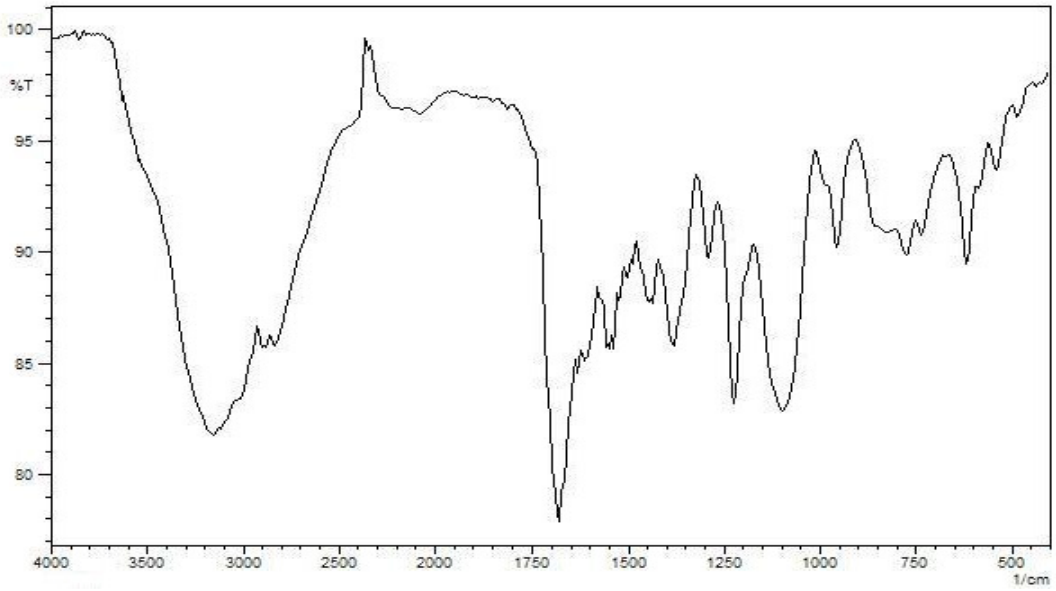

Figure-2
Infrared Spectra of $[Co(DL\text{-}ala)(AMUH)_2(AMUH)_2]Cl_2.2.5H_2O$

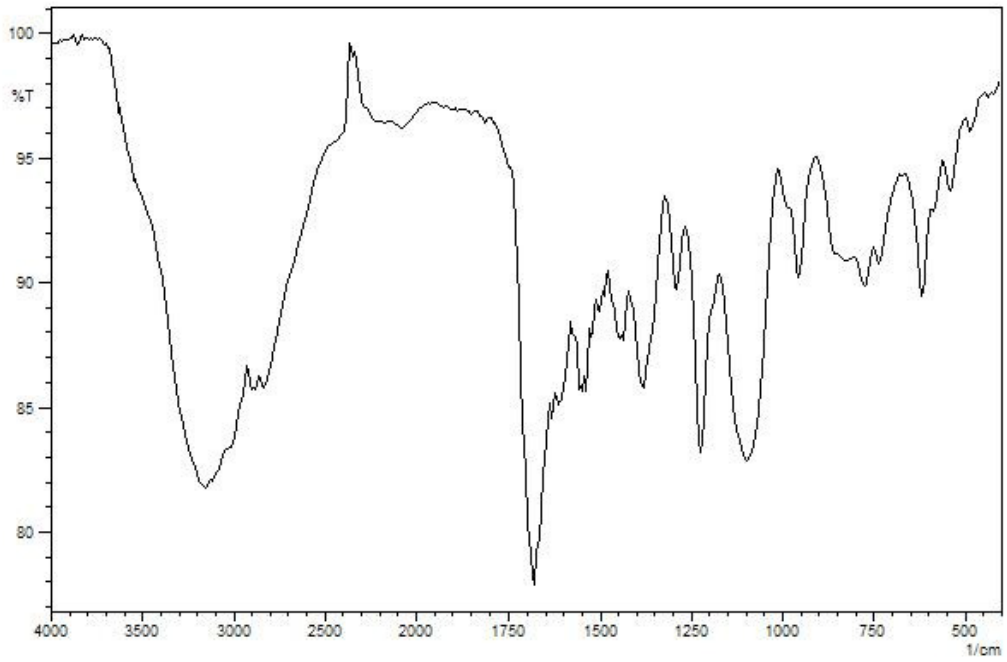

Figure-3
Infrared Spectra of $[Co(gly\text{-}gly)(AMUH]_2Cl_2.H_2O$

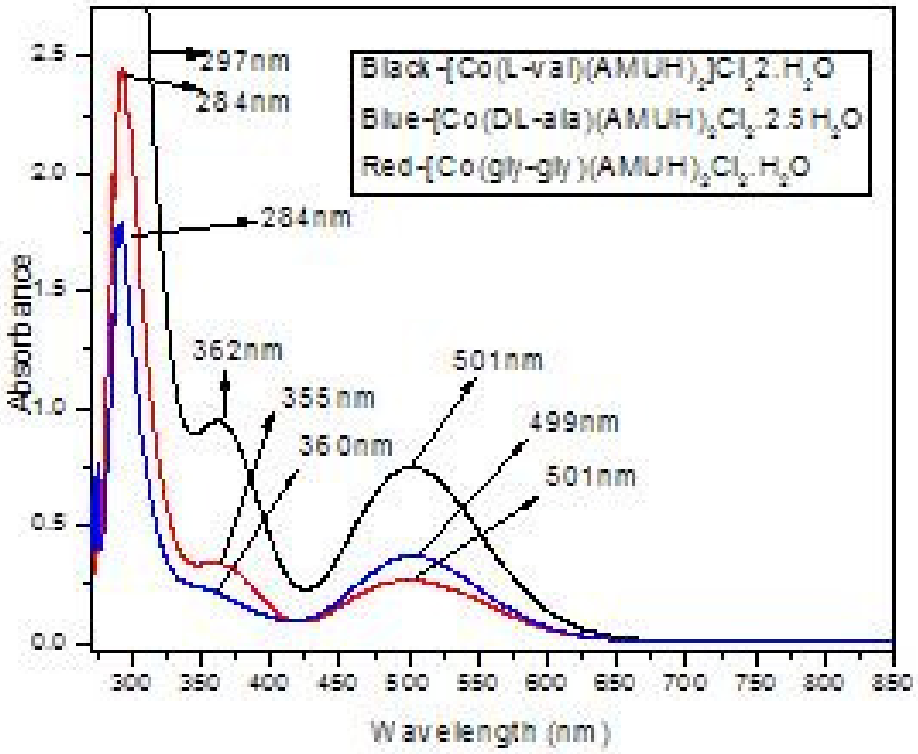

Figure-4
Overlay spectra of $[Co(L\text{-}val)(AMUH)_2]Cl_2.2H_2O$, $[Co(DL\text{-}ala)(AMUH)_2(AMUH)_2]Cl_2.2.5H_2O$ and $[Co(gly\text{-}gly)(AMUH)_2]Cl_2.H_2O$, showing three absorption bands