

Studies on Outer-sphere Association of Tris(1-amidino-*O*-alkylurea)- and Glycinato-bis(1-amidino-*O*-methylurea)-cobalt(III) Complexes

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Among the various available methods the measurement of electrical conductivity of dilute solution provides a valuable method of studying outer-sphere ion-association of inert complexes. The ion-association of some cobalt(III) complex ions with various anions have been reported by various workers¹. Recently, Yokoyama *et al.*² have studied conductometrically the ion-pair formation of tris(ethylenediamine)cobalt(III) ions with monovalent anions in the temperature range 0–50°. Literature shows that very little work has been done on the outer-sphere association of cobalt(III) complexes containing 1-amidino-*O*-alkylurea as primary ligands. The present study deals with the conductance behaviour and the outer-sphere ion-association of the tris(1-amidino-*O*-alkylurea)- and glycinatobis(1-amidino-*O*-methylurea)cobalt(III) complexes. The thermodynamic parameters, viz. ΔG , ΔH and ΔS , from the ion-pairs, have been calculated from the values of association constants at different temperatures. The sizes of ion-pairs have also been evaluated from limiting conductance data using Stoke's law and from the association constant using Bjerrum relationship.

Results and Discussion

Association constant : From the conductivities of the chloride, the limiting conductivities of the cations were obtained, using Onsager's method of extrapolations³ and hence Λ° , the limiting conductivities of the $[\text{Co}(\text{AAUH})_3]^{3+}$ (AAUH = 1-amidino-*O*-alkylurea) was obtained (Table 1). For the sulphate salts, Λ° (Onsager) was obtained adding 80.00 for the sulphate ion to the limiting conductivity of the cation derived from the chloride salt. This method of obtaining Λ° is preferable to obtain it by extrapolation of the sulphate conductivities, since this is a rather uncertain method with higher-valent electrolyte¹. For glycinatobis(1-amidino-*O*-methylurea)cobalt(III) com-

plexes, the limiting conductivities of the cations were taken as the mean of those of chloride and iodide complexes. The experimental conductivity plots (Fig. 1) lie below the theoretical Onsager plots in dilute solution which is considered to be due to the outer-sphere

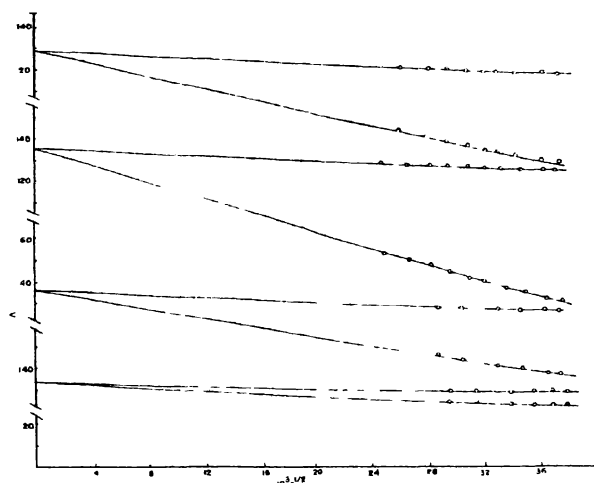
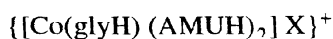
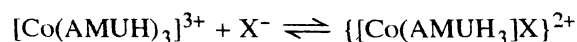


Fig. 1. Conductivities of (a) $[\text{Co}(\text{AMUH})_3]\text{Cl}_3$, (b) $[\text{Co}(\text{AEUH})_3]\text{Cl}_3$, (c) $[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{Cl}_2$ and (d) $[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{I}_2$; upper line shows calculated Λ ($= \Lambda^{\circ}_{\text{ons}} - bC^{1/2}$) vs $C^{1/2}$, and lower line shows $\Lambda^{\circ}_{\text{app}}$ vs $C^{1/2}$

TABLE 1—CONDUCTANCE DATA OF THE COMPLEXES IN AQUEOUS SOLUTION AT 25°

Compd.	$\Lambda^{\circ}_{\text{appr}}$	$\Lambda^{\circ}_{\text{ons}}$	Λ°	Λ°_1 (cation) (mean)
$[\text{Co}(\text{AMUH})_3]\text{Cl}_3$	137.24	135.78	58.44	55.35
$[\text{Co}(\text{AEUH})_3]\text{Cl}_3$	129.74	128.65	52.31	
$[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{Cl}_2$	133.13	132.91	56.57	
$[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{I}_2$	135.24	135.17	58.37	57.47

association of complex cations with the anions,



The association constants for the above equilibria have been calculated following the method of Jenkins and Monk¹. The outer-sphere association constant are given in Table 2 and follow the order : (i) $\text{SO}_4^{2-} > \text{Cl}^- > \text{I}^-$, (ii) $\{[\text{Co}(\text{AMUH})_3\text{X}]^{2+} > [\text{Co}(\text{AEUH})_3\text{X}]^{2+} > \{[\text{Co}(\text{glyH})(\text{AMUH})_2\text{X}]^+$ complex, exhibiting the influence of decreasing size of the coordination sphere and increasing charge of the anion/cation forming the ion-pair. Detailed explanations are given in the earlier works¹; with the sulphate anion the association constant of ion-pair has fairly large value. In addition to the large charge, hydrogen bond between the amine groups and the oxyanion (i.e. SO_4^{2-} ion) contributes to the stability of the complex.

Thermodynamic parameters : The change in thermodynamic properties, viz. ΔG , ΔH and ΔS for the ion-pairs of the tris(1-aminido-*O*-alkylurea)cobalt(III) complexes have been calculated from the values of the association constant at different temperature (Table 3) using the methods published earlier⁴. As seen from Table 3, there is an increase in value both in association constant and entropy of complexes with rise in temperature. A positive entropy change have been explained⁵ on the assumption that the 'iceberg' structure around the cation is broken when ion-association takes place leading to an increase in the degrees of disorderness. De and Dutta¹ suggested that with increase in temperature, such effects are responsible for

TABLE 2—OUTER-SPHERE ASSOCIATION CONSTANTS (K_A) OF THE COMPLEXES AT DIFFERENT TEMPERATURES ($\pm 0.1^\circ$)

Ion-pair	18°	25°	35°
$\{[\text{Co}(\text{AMUH})_3\text{Cl}]^{2+}$	31.83	42.00	48.08
$\{[\text{Co}(\text{AMUH})_3\text{SO}_4]^+$	-	$22.36 \cdot 10^2$	-
$\{[\text{Co}(\text{AEUH})_3\text{Cl}]^{2+}$	24.46	31.50	40.02
$\{[\text{Co}(\text{AEUH})_3\text{SO}_4]^+$	-	$17.70 \cdot 10^2$	-
$\{[\text{Co}(\text{glyH})(\text{AMUH})_2\text{Cl}]^+$	-	10.69	-
$\{[\text{Co}(\text{glyH})(\text{AMUH})_2\text{I}]^+$	-	7.46	-

TABLE 3—THERMODYNAMIC PARAMETERS OF THE COMPLEXES

Compd.	T(K)	K_A	$-\Delta G$ kJ mol ⁻¹	ΔH kJ mol ⁻¹	ΔS JK ⁻¹ mol ⁻¹
[Co(AMUH) ₃]Cl ₃	291	31.83	8.37	-	43.33
	298	42.00	9.20	4.24	45.10
	308	48.08	9.92	-	45.97
[Co(AEUH) ₃]Cl ₃	291	24.46	7.73	-	44.60
	298	31.50	8.55	5.25	46.31
	308	40.25	9.48	-	47.82

increase in association constant values and consequently in entropy changes in the tris(biguanidium)-cobalt(III) salts. However, Mishra and Singh⁴ found a reverse observation in the case of tris(2-guanidiniumbenzimidazole)chromium(III) salts. They suggested that the breaking of the covalent structure around the complexes cation is not the predominant in their system and treated them to have obeyed the simple law of increasing dissociation at higher temperatures.

Sizes of ion-pairs : From the knowledge of the limiting conductivity of the ions, the ionic radii have been calculated using Stoke's law⁶ (Table 4). Expectedly, the orders of sizes of the complex cations are as

TABLE 4—IONIC RADII OF IIR COMPLEXES AND IIR ION-PAIRS

Cation/Anion/Ion-pair	ION-PAIRS	
	Radius from Stoke's law Å	Radius from Bjerrum eqn. Å
$[\text{Co}(\text{AMUH})_3]^{3+}$	4.62	-
$[\text{Co}(\text{AEUH})_3]^{3+}$	5.25	-
$[\text{Co}(\text{glyH})(\text{AMUH})_2]^{2+}$	3.19	-
Cl^-	1.20	-
I^-	1.19	-
SO_4^{2-}	2.29	-
$\{[\text{Co}(\text{AMUH})_3\text{Cl}]^{2+}$	5.82	5.24
$\{[\text{Co}(\text{AMUH})_3\text{SO}_4]^+$	6.91	4.59
$\{[\text{Co}(\text{AEUH})_3\text{Cl}]^{2+}$	6.45	6.29
$\{[\text{Co}(\text{AEUH})_3\text{SO}_4]^+$	7.54	4.76
$\{[\text{Co}(\text{glyH})(\text{AMUH})_2\text{Cl}]^+$	4.39	5.82
$\{[\text{Co}(\text{glyH})(\text{AMUH})_2\text{I}]^+$	4.38	7.04

$[\text{Co}(\text{AEUH})_3]^{3+}$ (5.25 Å) > $[\text{Co}(\text{AMUH})_3]^{3+}$ (4.62 Å) > $[\text{Co}(\text{BigH})]^{3+}$ (4.03 Å)¹ (BigH = biguanide) > $[\text{Co}(\text{en})_3]^{3+}$ (3.68 Å)¹ > $[\text{Co}(\text{glyH})(\text{AMUH})_2]^{2+}$ (3.19 Å) > $[\text{Co}(\text{NH}_3)_6]^{3+}$ (2.77 Å)¹. The association constants were also utilised to determine the radii of the ion-pairs from Bjerrum relationship⁶. The Bjerrum distances of the ion-pairs do not agree well with those of Stoke's radii. Such discrepancies have also been reported by Jenkins and Monk¹, De and Dutta¹ and Mishra and Singh⁴. However, no proper explanation has been offered so far.

Experimental

Tris(1-aminido-*O*-methylurea)cobalt(III) chloride and sulphate, tris(1-amidino-*O*-ethylurea)cobalt(III) chloride and sulphate, and glycinatobis(1-amidino-*O*-methylurea)cobalt(III) chloride and iodide complexes were prepared by following the reported procedure⁷. The compounds were purified by recrystallisations and their purity was examined by conventional chemical analysis and spectral measurements. The results were in good agreement with the theoretical values (as shown in parentheses). The percentage composition of the elements and water are : (i) $[\text{Co}(\text{AMUH})_3]\text{Cl}_3 \cdot 4.5\text{H}_2\text{O}$ {Co, 10.10 (9.92); N, 28.35 (28.26); Cl, 17.75 (17.91); H₂O, 13.78 (13.62)}, (ii) $[\text{Co}(\text{AEUH})_3]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ {Co, 9.25 (9.140); N, 26.20 (26.82); Cl, 16.63 (16.50); H₂O 13.92 (14.09)}, (iii) $[\text{Co}(\text{AMUH})_3]_2(\text{SO}_4) \cdot 8\text{H}_2\text{O}$ {Co, 9.58 (9.62); N, 27.37 (27.40); SO₄, 23.31 (23.49); H₂O, 11.50 (11.74)}, (iv) $[\text{Co}(\text{AEUH})_3]_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ {Co, 8.59 (8.64); N, 24.43, (24.60); SO₄, 21.12 (21.09), H₂O; 13.23 (13.15)}, (v) $[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ {Co, 11.06 (11.20); N, 24.92 (24.60); Cl, 13.23 (13.40); H₂O, 17.30 (17.10)}, (vi) $[\text{Co}(\text{glyH})(\text{AMUH})_2]\text{I}_2$ {Co, 9.64 (9.5); N, 20.38 (20.3) : I, 41.33 (41.0)}. The complexes were then dried at 110°.

The solutions of different concentrations were carefully prepared by dissolving requisite amount of the salt in conductivity-water of low specific conductance. Their electrical conductivities were measured at 1 kHz

by a D.D.R. conductivity meter (Systronics 304) in a thermostatic bath. The complete measurement for one solution was accomplished within 5 h after the preparation of the solution. The corrections for the conductivity change considered due to the decomposition of the complex were made¹.

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