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Binary and Ternary Complexes of Cobalt(II) with Some Polydentate Ligands

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Potentiometric investigations on binary and ternary complexes of Co^{2+} ion with multidentate ligands; 1,3-dihydroxy-4-(2′-pyridylazo) benzene (PAR, H_2L); 1-(2′-arsonophenylazo)-2-hydroxynaphthalene-3,6-disulphonic acid (APANS, H_5L); pyrogallol sulphonaphthalene (PGR, H_4L) and the pair of ligands; PAR-ethylenediamine (en, A), PAR-1: 10-phenanthrolene (pn, A), APANS-en, APANS-pn, PGR-en, PGR-pn have been made in aqueous solution at 20°C and at an ionic strength of 0.1 M KNO_3. The analysed experimental data indicate existence of $CoHL^+$, CoHL(OH), $CoL(OH)^-$, $Co(HL)_2$, $COHL_2$, CoL^{2-}, $CoHLA^+$ (with PAR, en and pn); CoLA $(OH)^-$ (with PAR and en)′ CoH_2L^-, $CoHL^{2-}$, CoL^{3-}, CoH_2LA^-, $CoHLA^{2-}$ (with APANS, en and pn), $CoLA^{3-}$ (with APANS and en); CoL^{2-}, $CoLA^{2-}$ (with PGR, en and pn) species in steps. Equilibrium constants of these probable complex species have been evaluated and the structures have been discussed.

Key Words: Cobalt(II), Binary, Ternary complexes.

INTRODUCTION

Previous studies on Ni^{2+} and Cu^{2+} complexes involving the ligands: 1,3-dihydroxy-4-(2′-pyridylazo)benzene (PAR, H_2L); 1-(2′-arsonophenylazo)-2-hydroxynaphthalene 3,6-disulphonic acid (APANS, H_5L)′, pyrogallol sulphonaphthalene (PGR, H_4L); ethylenediamine (en, A) and 1 : 10-phenanthrolene (pn, A) have already yielded new informations[1–3]. Formation of an interesting species $C_4H_2L(OH)^-$ in addition to CuH_2L and CuH_2LA with PGR, at low pH, involving the ketonic oxygen and the adjacent phenolic oxygen has been noted. Further, coordination positions are changed to three oxygens (two —OH and —O—) in the species $CuHL(OH)^{2-}$, $CuL(OH)^{3-}$, $CuHLA(OH)^{2-}$ and $CuLA(OH)^{3-}$. Similar alterations in coordinating groups (from azo and phenolic —OH to azo, phenolic —OH and —OH attached to As) have been observed in Ni^{2+}, Cu^{2+} and tripositive rare earth-APANS complexes[1, 3–8]. In Th^{4+}-APANS the ligand behaves only as a tridentate ligand[9] involving azo, phenolic —OH, —OH bonded with As, groups in coordination.

EXPERIMENTAL

0.1923 N NaOH (carbon dioxide free), 1.0 M KNO_3 and 1.0×10^{-2} M $Co(NO_3)_2 \cdot 6H_2O$ solution were prepared using AR grade chemicals. Co^{2+} contents were determined by EDTA titrations[7]. Aqueous solutions (5.0×10^{-3} M) of each ligand PAR, APANS (disodium salt), PGR, pn (all GR, Loba) and en (BDH, AnalaR) were prepared by direct weighing (5.0 cm^3 of 0.1923 N NaOH was added in 250 cm^3 measuring flask to dissolve PGR).

A number of mixtures (i) 2.284×10^{-3} N NH_3; (ii) 5.0×10^{-4} M ligand + (i); (iii) 5.0×10^{-4} M $Co(NO_3)_2$ + (ii); (iv) 2.5×10^{-4} M $Co(NO_3)_2$ + (ii); (v) 1.0×10^{-3} M $Co(NO_3)_2$ + (ii) (only in PGR system); (vi) 5.0×10^{-4} M $Co(NO_3)_2$ + 5.0×10^{-4} M PAR/APANS/PGR + 5.0×10^{-4} M en/pn; (vii) 1.0×10^{-3} M $Co(NO_3)_2$ + 5.0×10^{-4} M PGR + 1.0×10^{-3} en/pn were prepared (keeping the total volume 50 cm^3) and titrated against NaOH (0.1923 N) pH-metrically at 20°C and $\mu = 0.1$ M KNO_3 using Systronics digital pH-meter-335 and pH *vs.* 'a' (moles of alkali used per mole of ligand) curves were obtained[1–6, 9–14].

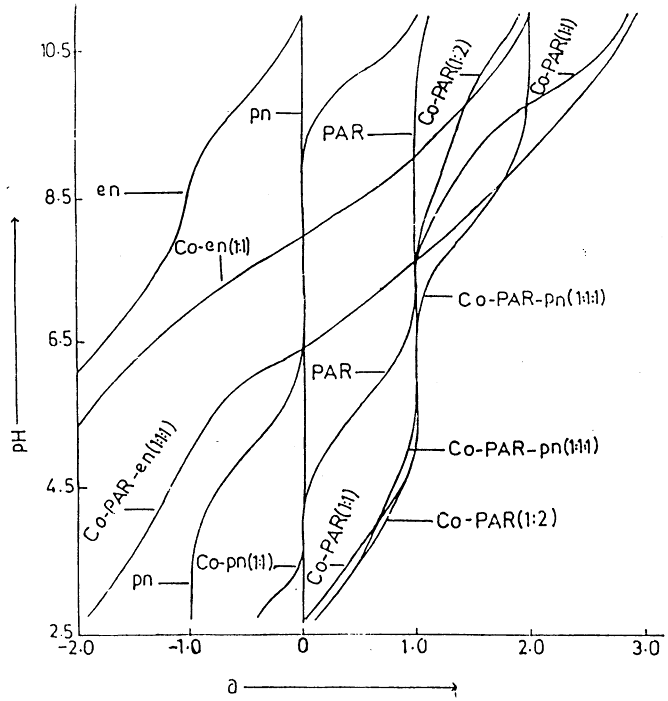
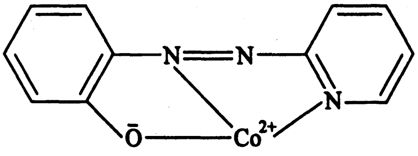


Fig. 1

RESULTS AND DISCUSSION

Binary system: The colour of 1 : 1, Co^{2+}-PAR mixture remains red throughout the experimental pH range, but pH *vs.* 'a' curve (Fig. 1) with a sharp inflection at a = 1 shows existence of $CoHL^+$ species, between a = 0 and 1 involving the same coordination positions (azo group, one phenolic oxygen and basic nitrogen, structure I) as reported earlier for other metal systems[1-3]. A further increase in 'a' value (Fig. 1) indicates deprotonation/hydrolysis of the 1 : 1 metal-ligand species.



Structure I

However, assuming the existence of the equilibria: $CoHL^+ \rightleftharpoons CoL + H^+$, $Co^{2+} + L^{2-} \rightleftharpoons CoL$, $CoL + OH^- \rightleftharpoons CoL(OH)^-$, $Co^{2+} + L^{2-} + OH^- \rightleftharpoons CoL(OH)^-$, the corresponding free ligand, free metal and complex concentrations were evaluated (beyond a = 1), and pH *vs.* pL curves were plotted (Fig. 2) as

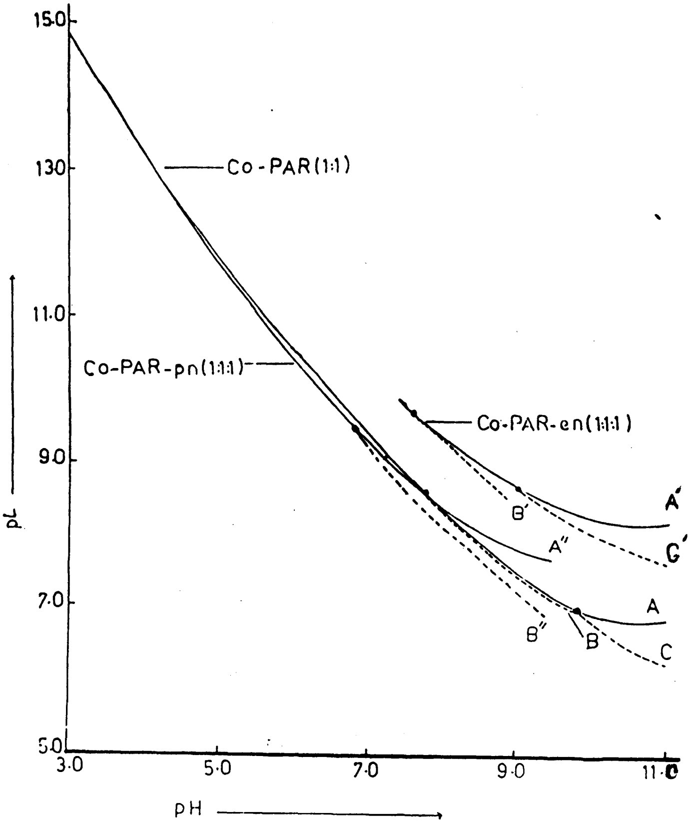
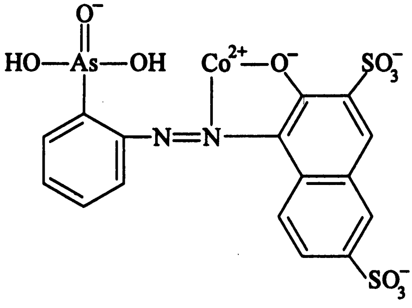


Fig. 2

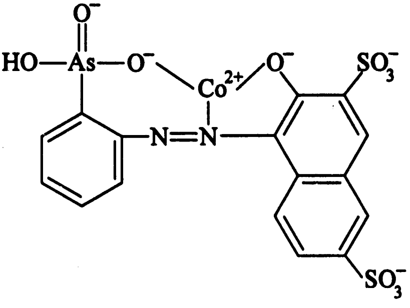
described earlier[1–3, 5, 6] to achieve informations on most probable mode of reaction (deprotonation or hydrolysis). As expected, unlike Ni^{2+} and Cu^{2+} systems, here in Fig. 2 curve B (obtained considering $CoHL^+$) coincides with curve A (obtained considering $CoHL^+ + CoL + CoL(OH)^-$ and curve C (obtained considering $CoHL^+ + CoL$) deviates from it indicating the formation of CoHL(OH) and $CoL(OH)^-$ species between a = 1 and 2 and 2, and 3, respectively. The calculated log K values are given in Table-1.

The pH *vs.* 'a' curve of 1 : 2, Co^{2+}-PAR mixture shows a sharp inflection at a = 1 (pH *ca.* 5.69, Fig. 1) indicating the formation of $Co(HL)_2$ species between a = 0 and 1. Under the experimental condition, the maximum value of 'a' is 2.0. Like Ni system formation of $CoHL_2$, CoL_2 complex species (between a = 1 and 1.5, 1.5 and 2, respectively) were confirmed by the pH *vs.* pL curves (curves omitted). The corresponding equilibrium constants are given in Table-1.

Gradual colour change from light orange to dark orange (between pH *ca.* 2.6 and 5.2) and a weak inflection in pH *vs.* 'a' curve at a = 1 in the system of 1 : 1, Co^{2+}-APANS mixture (figure omitted) indicate the existence of equilibrium $Co^{2+} + H_2L^{3-} \rightleftharpoons CoH_2L^-$ between a = 0 and 1 involving azo and phenolic —OH in coordination (structure II) as observed in earlier studied complexes[1–3, 7]. The evaluated log K values have been reported in Table-1. Further, beyond a = 1 the equilibria $Co^{2+} + HL^{4-} \rightleftharpoons CoHL^{2-}$, $CoH_2L^- \rightleftharpoons CoL + L^{2-} + H^+$ (between a = 1 and 2) and $Co^{2+} + HL^{4-} \rightleftharpoons CoL^{3-} + H^+$, $CoHL^{2-} \rightleftharpoons CoL^{3-} + H^+$ (between a = 2 and 3) have been confirmed by the previously described methods[1–3]. These reactions are similar to those studied with Ni^{2+}, Cu^{2+} and tripositive rare earth ions[1–3, 7] where azo, phenolic —OH and one —OH bound to As are expected to be associated with Co^{2+} through coordinate bonds (structure III).



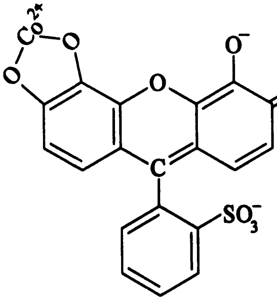
Structure II



Structure III

Composite pH *vs.* 'a' curve (omitted) of the ligand with 1 : 1, Co^{2+}-APANS system coincides with pH *vs.* a curves of 1 : 2, Co^{2+}-APANS mixture indicating absence of 1 : 2 complex species.

The pH *vs.* 'a' curve of PGR and 1 : 1 Co^{2+}-PGR system coincides below a = 2 (figure omitted). There is separation in the curves beyond a = 2 (pH *ca.* 8.6) which may be expected due to the formation of the CoL^{2-} complex species (between a = 2 and 4) involving two adjacent phenolic oxygens in coordination (unlike Ni^{2+} and Cu^{2+} complexes) as shown in structure IV. Calculated equilibrium constant is reported in Table-1. Co^{2+}-PGR, 1 : 2 and 2 : 1 complexes are not formed as shown by the comparison, pH *vs.* 'a' curves of ligands, 1 : 1, 1 : 2 and 2 : 1 Co^{2+}-PGR mixtures.



Structure IV

Ternary system: Formation of Co^{2+}-PAR-en (1 : 1 : 1) species is evident from the comparison of the pH *vs.* 'a' curves of ligands and their binary (1 : 1, 1 : 2, metal-ligand), ternary (1 : 1 : 1, metal-PAR-en) mixtures. Ethylenediamine acting as a secondary ligand gets attached with $CoHL^+$ species from pH *ca.* 5.65. The log K value for the reaction $CoHL^+ + A \rightleftharpoons CoHLA^+$ is given in Table-1. The pH *vs.* pL curves (Fig. 2) plotted for obtaining the information on the real route of complexations beyond a = 1 show the existence of the equilibria $CoHLA + OH^- \rightleftharpoons CoHLA(OH)$ (between a = 1 and 2) and $CoHLA(OH) \rightleftharpoons CoLA(OH)^- + H^+$ (between a = 2 and 3) respectively. The equilibrium constants are given in Table-1. The colour of the 1 : 1 : 1, Co^{2+}-PAR-pn mixture is similar to that of 1 : 1, Co^{2+}-PAR mixture from low to high pH. But, pH *vs.* 'a' curves of pn, PAR, and their binary and ternary complex systems (figure omitted) indicate that metal-pn association takes place up to pH 3.0 (a = 0) and PAR acts as a secondary ligand between pH *ca.* 3.0 and 5.65. Independent existence of equilibrium $CoA^{2+} + HL^- \rightleftharpoons CoAHL^+$ is indicated by a steep inflection of pH *vs.* 'a' curves at *a* = 1. Beyond a = 1, existence of the equilibria $CoA^{2+} + HL^- \rightleftharpoons CoAL + H^+$ or $CoAHL^+ \rightleftharpoons CoAL + H^+$ is confirmed by the pH *vs.* pL curves discussed above.

Formation of 1 : 1 : 1, Co^{2+}-APANS-en complex is evident by gradual colour change from light orange (pH *ca.* 2.60) to red (pH *ca.* 7.10) and comparison of the pH *vs.* a curves of APANS-en and their binary and ternary complex systems (figure omitted). It is indicated that ethylenediamine, acting as a secondary ligand, gets attached with CoH_2L^- species between pH 5.15 and 7.10. The log K values of the existing equilibrium $CoH_2L^- + A \rightleftharpoons CoH_2LA^-$ is given in Table-1. Beyond a = 1, deprotonation of the species CoH_2LA^-, $CoHLA^{2-}$ (between a = 1 and 2, 2 and 3, respectively) is indicated by the pH *vs.* pL curves. In species $CoHLA^{2-}$ and $CoLA^{3-}$ the same coordinating groups of APANS are expected as described for $CoHL^{2-}$ or CoL^{3-} species. 1 : 1 : 1, Metal-pn-APANS species is formed below a = 1 in steps (pn: primary ligand, APANS: secondary ligand) which is evident by the colour change of 1 : 1 : 1, metal-pn-APANS mixture from light orange to red and also by the comparison of the titration curves as described in aforesaid systems.

Further, 'a' values does not exceed 2.0. As expected, existence of equilibrium $CoAH_2L \rightleftharpoons CoAHL^{2-} + H$ or $CoA^{2+} + HL^{4-} \rightleftharpoons CoAHL^{2-}$ has been confirmed by the pH *vs.* pL curves. The corresponding log K values are given in Table-1.

TABLE-1

EQUILIBRIUM CONSTANTS OF Co^{2+} COMPLEXES AT 20°C

(μ = 0.1 M KNO_3)

Ligands	Reaction	log K
PAR	$Co^{2+} + HL^- \rightleftharpoons CoHL^+$	5.53 ± 0.17
	$Co^{2+} + L^{2-} \rightleftharpoons CoL$	8.44 ± 0.09
	$Co^{2+} + L^{2-} + OH^- \rightleftharpoons CoL(OH)^-$	12.26 ± 0.04
	$CoHL^+ + OH^- \rightleftharpoons CoHL(OH)$	5.04 ± 0.05
	$CoHL(OH) \rightleftharpoons CoL(OH)^- + H^+$	−10.18 ± 0.02
	$Co^{2+} + 2HL^- \rightleftharpoons Co(HL)_2$	11.90 ± 0.19
	$Co^{2+} + 2HL^- \rightleftharpoons CoHL_2^- + H^+$	3.52 ± 0.17
	$Co^{2+} + 2HL^- \rightleftharpoons CoL_2^{2-} + 2H^+$	−6.56 ± 0.012
	$Co(HL)_2 \rightleftharpoons CoHL_2^- + H^+$	−8.95 ± 0.04
	$CoHL_2 \rightleftharpoons CoL_2^- + H^+$	−10.51 ± 0.03
APANS	$Co^{2+} + H_2L^{3-} \rightleftharpoons CoH_2L^-$	5.36 ± 0.05
	$Co^{2+} + HL^{4-} \rightleftharpoons CoHL^{2-}$	9.75 ± 0.14
	$Co^{2+} + HL^{4-} \rightleftharpoons CoL^{3-} + H^+$	1.26 ± 0.10
	$CoH_2L^- \rightleftharpoons CoHL^{2-} + H^+$	−6.32 ± 0.03
	$CoHL^{2-} \rightleftharpoons CoL^{3-} + H^+$	−8.51 ± 0.02
PGR	$Co^{2+} + HL^{3-} \rightleftharpoons CoL^{2-} + H^+$	−6.58 ± 0.04
PAR-en	$CoHL^+ + A \rightleftharpoons CoHLA^+$	7.55 ± 0.19
	$CoHLA^+ + OH^- \rightleftharpoons CoHLA(OH)$	5.74 ± 0.05
	$CoHLA(OH) \rightleftharpoons CoLA(OH)^- + H^+$	−9.94 ± 0.02
PAR-pn	$CoA^{2+} + HL^- \rightleftharpoons CoAHL^+$	5.51 ± 0.05
	$CoA^{2+} + HL^- \rightleftharpoons CoAL + H^+$	−2.58 ± 0.05
	$CoAHL^+ \rightleftharpoons CoAL + H^+$	−8.17 ± 0.05
APANS-en	$CoH_2L^- + A \rightleftharpoons CoH_2LA^- + H^-$	7.33 ± 0.09
	$CoH_2LA^- \rightleftharpoons CoHLA^{2-} + H^+$	−7.71 ± 0.07
	$CoHLA^{2-} \rightleftharpoons CoLA^{3-} + H^+$	−9.23 ± 0.03
APANS-pn	$CoA^{2+} + H_2L^{3-} \rightleftharpoons CoAH_2L^-$	4.40 ± 0.03
	$CoA^{2+} + HL^{4-} \rightleftharpoons CoAHL^{2-}$	7.49 ± 0.07
	$CoAH_2L^- \rightleftharpoons CoAHL^{2-} + H^+$	−7.72 ± 0.02
PGR-en	$CoA^{2+} + HL^{3-} \rightleftharpoons CoAL^{2-} + H^+$	−6.19 ± 0.37
PGR-pn	$CoA^{2+} + HL^{3-} \rightleftharpoons CoAL^{2-} + H^+$	−6.22 ± 0.33

Comparison of the titration curves of en, PGR and their binary and ternary complex systems (figure omitted) indicates the existence of the equilibrium $CoA^{2+} + HL^{4-} \rightleftharpoons CoAL^{2-} + H^{+}$ between a = 2 and 4. Colour of the 1 : 1 : 1, Co^{2+}-PGR-pn mixture is identical to the colour of PGR solution below pH 9.0. A gradual colour change to red between pH 9.6 and 11.6 is an indication of mixed ligand complex formation (the PGR solution under the similar pH environment is brown red). The ternary complex formation is again supported by the comparison of pH *vs.* 'a' curves of the ligands and their binary and ternary complex systems. An inflection is titration curve at a = 4 (figure omitted) indicates independent existence of the $CoAL^{2-}$ species. Further, titration curves do not show the formation of 2 : 1 : 1, 2 : 1 : 2, Co^{2+}-PGR-en and Co^{2+}-PGR-pn complexes.

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