



Synthesis and Resolution of (α -picolinato) bis (biguanidinium) Cobalt (III) salts into their dl ($\pm$) enantiomers

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Abstract: $[(\alpha\text{-Picolinato})\text{bis}(\text{biguanidinium})\text{cobalt(III)}]$ salts, $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{X}_n\text{H}_2\text{O}$, ($\text{X} = \frac{1}{2}\text{SO}_4^{2-}$, Cl^- , Br^- , NO_3^- and $\frac{1}{2}\text{C}_2\text{O}_4^{2-}$, $n = 1, 2, 4$ or 6) were prepared by oxidative insertion of α -picolinic acid ($\alpha\text{-pic H}$) into $[\text{bis}(\text{biguanidinium})\text{cobalt(II)}](\text{OH})_2$ by aerial oxidation in aqueous medium and neutralising the base with appropriate acids or metathetic reactions. The d(+) and l(-) enantiomers of complex were separated by treating the complex sulphate $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{SO}_4 \cdot \text{H}_2\text{O}$ with calculated amount of barium salt of camphore-d-sulphonic acid, into their diastereoisomers. The less soluble d(+) isomers separated first and highly soluble l(-) isomer were obtained after evaporation and fractionation of its mother liquor. The complexes were characterised by electronic absorption, I.R. Spectra, electrical conductivity, magnetic susceptibility and measuring molar optical rotation by polarimeter. The dextro and laevo enantiomers of pure complex salts could not be isolated in pure form due to assymetric transformation of second order.

Keywords: Synthesis, Cobalt(III), Biguanide(BgH^+), picoline picolinic acid (PicH), Distereoisomers, Resolution.

I. Introduction

The complexes of biguanide (BgH^+) and substituted biguanides with transition and post transition metal ions have extensively been studied.¹⁻³ The disubstituted bis (biguanidinium)cobalt(III) complex salts $[\text{Co}(\text{BgH}^+)_2(\text{B.B.})]^{n+}$ are also known in plenty.⁴ The attempt to separate octahedral disubstituted bis(biguanidinium) cobalt(III) salts into their optically active enantiomers have little been investigated.⁴⁻¹¹ In previous communication⁵ we have reported the resolution of dicyanobis (biguanidinium) cobalt(III) chloride into its optically active antipode using silver d-tartrate⁵.

II. Results and Discussion

The aerial oxidation of bis(biguanidinium) cobalt(II) hydroxide, $[\text{Co}(\text{BgH}^+)_2](\text{OH})_2$, in presence of stoichiometric proportion of α -picolinic acid ($\alpha\text{-picH}$) undergoes oxidative insertion of a picolinic acid forming octahedral complex $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})](\text{OH})_2$, which on neutralisation with dilute H_2SO_4 and concentration gave orange red crystals of complex sulphate $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{SO}_4 \cdot \text{H}_2\text{O}$. The different complex salts

$[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{X}_n \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, NO_3^- , $\frac{1}{2}\text{C}_2\text{O}_4^{2-}$, Br^- or I^- and $n = 2$ or 3) were prepared as orange

or orange red crystals on neutralising and concentration of base with appropriate acids. The water of crystallization of complexes were lost without change in colour of the complex salts below 120°C indicated uncoordinated nature of water molecules. The electrical conductance values of aqueous solutions of complex salts (Table-A) indicated ionic nature of anions. The complex salts are diamagnetic suggested low spin octahedral structure having oxidation state +3 for cobalt. The electronic absorption spectra of complex salts in aqueous solutions showed two spin allowed d-d transitions located at $360\text{-}355\text{ nm}$ ($\epsilon_{\text{max}} \sim 245$ to 260) and around $480\text{-}485\text{ nm}$ ($\epsilon_{\text{max}} 150\text{-}165$) attributable to $^1\text{A}_{1g} - ^1\text{T}_{1g}$ and $^1\text{A}_{1g} - ^1\text{T}_{2g}$ transitions in low spin octahedral field of Co(III) respectively. The optically active diastereoisomers of complex were separated as its d+ camphor sulphonate (CS⁻) by treating aqueous solution of complex sulphate $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{SO}_4 \cdot \text{H}_2\text{O}$, with calculated amount of $\text{Ba}(\text{CS})_2$. The concentration of d-camphorsulphonate salt slowly gave two-three fractions of Dextro-isomer of $[\text{Co}(\text{BgH}^+)_2(\alpha\text{-pic})]\text{CS}$.

pic)] (CS)₂·3H₂O. The third and fourth fraction gave impure mixture. The further concentration of mother liquor yielded pure leavo-rotatory isomer of [Co(BigH⁺)₂(α-pic)] (CS)₂·3H₂O. The optical rotation of double crystallized fraction of dextro sample of 0.02% aqueous solution in 4 decimeter tube at room temperature (28°C) showed optical rotation $[\alpha]_D^{28} = +2.35^\circ$ and $[M]_D = +2228^\circ$. Similarly the optical rotation of levo rotatory isomer was $[\alpha]_D^{28} = 250^\circ$ and $[M]_D = -2383^\circ$. The dextro isomer of diastereoisomer is less soluble then laero form. The dextro and laevo enantiomers of pure complex salts could not be isolated in pure form due to assymetric transformation of second order. The I.R. spectra of complex sulphate and complex chloride were recorded as KBr optics in the range 4000-625 cm⁻¹. The complex [Co(Big⁺H)₂(α-pic)]SO₄·H₂O showed a strong and broad band near 2800-3250 cm⁻¹ due to combination of ν(NH₂), (NH) and ν(H₂O) vibrations. The δ(=NH) and δ(NH₂) band was located at 1630 cm⁻¹ as a broad band, the ν(CO) of picolinate was located at 1665-70 cm⁻¹ as strong and broad band.¹² The ν(SO₄) of sulphate was located at 1105 cm⁻¹ as broad band similar to ionic sulphate group.¹³

III. Experimental

α-Picolinatobis (biguanidinium) cobalt(III)sulphate hydrate, [Co(BigH⁺)₂(α-pic)]SO₄·H₂O.

About 0.1 milli mole of [Co(BigH⁺)₂](OH)₂⁵ was suspended in 100 ml water and treated with 0.1 milli mole of α-picolinic acid (α-picH) and air was passed for two hours when orange yellow coloured solution was formed. The solution was neutralised with dilute H₂SO₄ and concentrated to 25-30 ml when orange red crystal of complex sulphate was separated gradually on cooling over night. The product was collected on Buchner funnel washed with aqueous ethanol and dried in air.

[Co(BigH⁺)₂(α-pic)]X₂ × nH₂O [X = Cl⁻, Br⁻, I⁻, NO₃⁻ or $\frac{1}{2}$ C₂O₄ and n = 2,4 or 6).

The complex salts were obtained by neutralising the above base [Co(Big⁺H)₂(α-pic)](OH)₂. With appropriate acid and obtained as orange or orange yellow crystals or concentration and cooling. The results of elemental analysis and physical data are given in Table A.

Diastereoisomeric dl(±)[Co(Big⁺H)₂(α-pic)](CS)₂·3H₂O (CS=d + camphorsulphonate).

About 0.02 milli mole of [Co(BigH⁺)₂(α-pic)]SO₄·H₂O was dissolved in 50 ml hot water and treated with 0.02 milli mole of barium salt of d-camphor sulphonate dissolved in 30 ml hot water. The mixed solution was digested on a steam bath and BaSO₄ was separated by filtration. The filtrate was concentration when less soluble dextro-isomer separated gradually. The first two fractions were recrystallised to get pure dextro isomers from the monks liquor after three fractions of crystallisation; the laevo isomers of [Co(BigH⁺)₂(α-pic)](CS)₂·3H₂O was obtained on evaporation.

Table – A

	Complex Salt	Elemental analysis found (Cal)			Electrical conductance $\Lambda_{\infty} \text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$	Electron absorption band (nm) with assignment
		Metal %	Nitrogen %	Anions %		
1	[Co(BigH ⁺) ₂ (α-pic)]Cl ₂ ·4H ₂ O	11.25 (11.16)	29.60 (29.22)	13.46 (13.45)	140.3	360, 485 nm
2	[Co(BigH ⁺) ₂ (α-pic)]SO ₄ ·H ₂ O	11.98 (11.84)	30.82 (30.97)	19.01 (19.31)	12704	355, 480
3	[Co(BigH ⁺) ₂ (α-pic)]Br ₂ ·2H ₂ O	10.06 (10.18)	—	27.47 (27.59)	142.5	360, 385
4	[Co(BigH ⁺) ₂ (α-pic)]I ₂ ·2H ₂ O	8.62 (8.76)	—	37.46 (37.71)	141.1	355, 480
5	[Co(BigH ⁺) ₂ (α-pic)]C ₂ O ₄ ·2H ₂ O	11.72 (11.85)	—	17.32 (17.35)	128.2	360, 485
6	[Co(BigH ⁺) ₂ (α-pic)](NO ₃) ₂ ·6H ₂ O	9.62 (9.58)	24.86 (25.11)	19.67 (20.16)	148.4	355, 480
7	d(+)[Co(BigH ⁺) ₂ (α-pic)](CS) ₂ ·6H ₂ O	6.21 (6.18)	16.14 (16.16)	—	—	360, 485

8	$l(-)[Co(BigH^+) _2(\alpha - pic)](CS)_2 \cdot 6H_2O$	6.26 (6.18)	16.22 (16.16)	—	—	360, 485
9	$d(+)[Co(BigH^+) _2(\alpha - pic)]SO_4 \cdot H_2O$	11.91 (11.84)	—	19.12 (19.31)	—	355, 480

Acknowledgements

First two authors R.K. Prasad and Bina Rani are thankful to UGC (ERO) Kolkata for the Award of Minor Research Project and special thanks are due to Prof. L.K. Mishra, Retd. Prof. of Chemistry, Patna Science College for taking his interest in the work.

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