

Mixed-Ligand Complexes. Part VII. Some Mixed Chelates of Cobalt (III)

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The following mixed chelates of cobalt(III) have been prepared and characterised: $[\text{Co}(\text{en})(\text{BigH})_2]^{3+}$ (en = ethylenediamine, BigH = biguanide), $[\text{Co}(\text{gly})(\text{BigH})_2]^{2+}$ (glyH = glycine), $[\text{Co}(\text{Pic})(\text{BigH})_2]^{2+}$ (PicH = picolinic acid), $[\text{Co}(\text{Lut})(\text{BigH})]^{2+}$ (LutH = pyridine 2,6 dicarboxylic acid), $[\text{Co}(\text{IDA})(\text{BigH})_2]^{2+}$ (IDAH₂ = iminodiacetic acid) and $[\text{Co}(\text{DMG})(\text{BigH})_2]^{2+}$ (DMGH₂ = dimethylglyoxime). A number of salts of each cation have been prepared and their ionic natures have been verified from conductance and equivalent weights. Electronic spectra reveal expected trends. Lutidinate anion and iminodiacetate anion behave as bidentates in the mixed chelates. Separation of diastereoisomers has been achieved for $[\text{Co}(\text{en})(\text{BigH})_2]^{3+}$ and $[\text{Co}(\text{Pic})(\text{BigH})_2]^{2+}$. The diastereoisomers of $[\text{Co}(\text{en})(\text{BigH})_2]^{3+}$ racemised in presence of iodide ion. The enantiomers of $[\text{Co}(\text{Pic})(\text{BigH})_2]^{2+}$ have been characterised.

WE report in this paper a study of several mixed chelates of cobalt(III) obtained by the action of ethylenediamine, glycine, picolinic acid, pyridine 2,6 dicarboxylic acid (lutidinic acid), iminodiacetic acid or dimethylglyoxime on cis-diammine bis(biguanide) cobalt(III) base. The abbreviations for the ligands are as in the abstract

Experimental

Biguanide acid sulphate¹, picolinic and lutidinic acids² were prepared by following standard procedures. Cis-diammine-bis(biguanide) cobalt(III) base was described earlier³.

Unless otherwise specified mixed ligand complex base was obtained by the reaction of the appropriate ligand on cis-diammine-bis(biguanide) base in aqueous medium on a steam bath. The complex base was then neutralised with appropriate acids to get the desired salts. The other salts were obtained by suitable double decomposition on the chloride salt.

Ethylenediaminebis(biguanide) cobalt(III) sulphate :

Cis-diammine bis(biguanide) cobalt(III) base (1 g.) and ethylenediamine (0.16 g.) were suspended in water (10-15 ml) and warmed on a steam bath till ammonia evolution ceased. The solution was neutralised with dilute H₂SO₄ to pH 7 and then treated with acetone (10-15 ml) in the cold. A red powder was filtered, redissolved in minimum volume of hot water and again precipitated with acetone in the cold. The final product was washed with acetone and air dried. (Found : Co, 11.6; N, 32.3; SO₄, 28.1; H₂O, 9.8%. Calcd. for $[\text{Co}(\text{en})(\text{BigH})_2](\text{SO}_4)_{1.5} \cdot 2.5 \text{H}_2\text{O}$: Co, 11.6; N, 33.0; SO₄, 28.3; H₂O, 8.9%.)

Ethylenediaminebis(biguanide) cobalt(III) iodide : (Found : N, 23.4; I, 54.3; H₂O, 1.6%. Calcd. for

$[\text{Co}(\text{en})(\text{BigH})_2]_3 \cdot 0.5 \text{H}_2\text{O}$: N, 23.7; I, 53.7; H₂O, 1.2 per cent.)

Ethylenediaminebis(biguanide) cobalt (III) d-camphor-10-sulphonate : This was prepared as for the sulphate using a solution of d-camphor-10-sulphonic acid during neutralisation, evaporating on a steam bath and cooling in ice. (Found : Co, 5.4; N, 16.4; H₂O, 3.4 per cent. Calcd. for $[\text{Co}(\text{en})(\text{BigH})_2](\text{CS})_3 \cdot 2\text{H}_2\text{O}$: Co, 5.6; N, 16.0; H₂O, 3.4 per cent.)

Fractionation of ethylenediaminebis(biguanide) cobalt(III) d-camphor-10-sulphonate diastereoisomers : About 3 g of the sample was dissolved in cold water (70-80 ml) and the solution was fractionally crystallised. The first few fractions gave levo and the last few fractions gave dextro rotation. Found for the levo form : $[\alpha]_D = (-)150^\circ$; $[M]_D = (-)1590^\circ$ ($t = 30^\circ$); (Found : N, 15.8; H₂O, 4.2 per cent. Calcd. for $[\text{Co}(\text{en})(\text{BigH})_2](\text{CS})_3 \cdot 2.5\text{H}_2\text{O}$: N, 15.9; H₂O, 4.2 per cent.) Found for the dextro form : $[\alpha] = (+)150^\circ$; $[M]_D = (+)1590^\circ$ ($t = 30^\circ$); (Found : N, 15.6; H₂O, 4.1 per cent. Calcd. for $[\text{Co}(\text{en})(\text{BigH})_2](\text{CS})_3 \cdot 2.5\text{H}_2\text{O}$: N, 15.9; H₂O, 4.2 per cent.)

Glycinatobis(biguanide) cobalt (III) sulphate : Cis-diamminebis(biguanide) cobalt (III) base (1 g.) was treated with aqueous solution of glycine (0.21 g) on a steam bath. Afterwards the solution was neutralised with dilute H₂SO₄ in the cold and the resulting solution was repeatedly scratched with acetone to obtain a solid product. (Found : Co, 11.9; N, 30.1; SO₄, 19.4; H₂O, 14.0 per cent. Calcd. for $[\text{Co}(\text{gly})(\text{BigH})_2] \text{SO}_4 \cdot 4\text{H}_2\text{O}$: Co, 11.7; N, 30.7; SO₄, 19.1; H₂O, 14.3 per cent.)

Glycinatobis(biguanide) cobalt(III) chloride : The chloride salt was precipitated from solution by acetone. It was redissolved in minimum volume of water and reprecipitated by acetone. (Found : Co, 13.5; N, 36.6; Cl, 16.0; H₂O, 3.9 per cent. Calcd. for $[\text{Co}(\text{gly})(\text{BigH})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$: Co, 13.9; N, 36.5; Cl, 16.8; H₂O, 4.2 per cent.)

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Glycinatobis(biguanide) cobalt(III) iodide : (Found : N, 26.8; I, 43.0 per cent. Calcd. for $[\text{Co}(\text{gly})(\text{BigH}_2)]\text{I}_2$: N, 26.2; I, 43.2 per cent.)

Picolinatobis(biguanide) cobalt(III) sulphate : Cis-diamminebis(biguanide) cobalt(III) base (1 g.) was neutralised with dilute H_2SO_4 to pH 7. This solution was treated with picolinic acid (0.33 g) in the cold. After the evolution of ammonia slowed down, the solution was heated on a steam bath for a few minutes and then again neutralised with dilute H_2SO_4 to pH 7. On evaporation on a steam bath pale violet crystals of the complex sulphate were obtained. These were recrystallised from hot water (Found : Co, 12.2; N, 31.0; SO_4 , 20.1; H_2O , 1.5 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)]\text{SO}_4 \cdot 0.5\text{H}_2\text{O}$: Co, 12.1; N, 31.7; SO_4 , 19.7; H_2O , 1.8 per cent.)

Picolinatobis(biguanide) cobalt(III) chloride : (Found : Co, 12.3; N, 33.3; Cl, 14.8; H_2O , 3.6 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)]\text{Cl}_2 \cdot \text{H}_2\text{O}$: Co, 12.5; N, 32.7; Cl, 15.1; H_2O , 3.8 per cent.)

Picolinatobis(biguanide) cobalt(III) d-tartrate : A concentrated solution of picolinatobis(biguanide) cobalt(III) chloride was treated with a concentrated solution of sodium *d*-tartrate. On cooling in ice an oily product separated out. The supernatant liquid was decanted and the product was washed with ice-cold water and then scratched with acetone to obtain a solid product. (Found : Co, 10.5; N, 25.9; H_2O , 9.9 per cent. Calcd. $[\text{Co}(\text{Pic})(\text{BigH}_2)] \text{d-tart. } 3\text{H}_2\text{O}$: Co, 10.1; N, 26.4; H_2O , 9.2 per cent.)

Picolinatobis(biguanide) cobalt(III) d-camphor-10-sulphonate : To a concentrated solution of the chloride salt was added a concentrated solution of ammonium *d*-camphor-10-sulphate. The solution was evaporated on a steam bath to a small volume and cooled in a refrigerator overnight. The bulky voluminous precipitate was filtered, washed with ice-cold water, then with acetone and dried in air. (Found : Co, 6.7; N, 15.9; H_2O , 9.9 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)](\text{CS})_2 \cdot 5.5\text{H}_2\text{O}$, Co, 6.2; N, 16.3; H_2O , 10.5 per cent.)

Fractionation of picolinatobis(biguanide) cobalt(III) d-camphor-10-sulphonate diastereoisomers : 3 g of the salt was dissolved in cold water (300 ml) and was allowed to crystallise under a fan. The *levo* diastereoisomer crystallised first. Found for the *levo* form : $[\alpha]_D = (-)250^\circ$; $[M]_D = (-)2243^\circ$ ($t = 31^\circ$); (Found : N, 17.0; H_2O , 5.7 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)](\text{CS})_2 \cdot 3\text{H}_2\text{O}$: N, 17.1; H_2O , 6.0 per cent.) Found for the *dextro* form : $[\alpha]_D = (+)250^\circ$; $[M]_D = (+)2265^\circ$ ($t = 31^\circ$); (Found : N, 17.0; H_2O , 6.8 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)](\text{CS})_2 \cdot 3.5\text{H}_2\text{O}$, N, 16.9; H_2O , 6.9 per cent.)

The iodide salts of the optically active cations were prepared by triturating the diastereoisomers with saturated KI solution. The enantiomers were filtered, washed with ice cold water, acetone and air dried. Found for the *levo* enantiomer : $[\alpha]_D = (-)350^\circ$; $[M]_D = (-)2317^\circ$ ($t = 28^\circ$) (Found : N, 22.4; H_2O , 3.5 per cent. Calcd. for $[\text{Co}(\text{Pic})(\text{BigH}_2)]\text{I}_2 \cdot 1.5\text{H}_2\text{O}$, N, 23.2; H_2O , 4.0 per cent.) Found for the *dextro* enantiomer : $[\alpha]_D = (+)200^\circ$; $[M]_D = (+)1360^\circ$ ($t = 28^\circ$). (Found : N, 22.0; H_2O , 6.2 per cent. Calcd.

for $[\text{Co}(\text{Pic})(\text{BigH}_2)]\text{I}_2 \cdot 2.5\text{H}_2\text{O}$, N, 22.6; H_2O , 6.6 per cent.)

Dimethylglyoximatobis(biguanide) cobalt(III) sulphate : Cis-diammine bis(biguanide) cobalt(III) base (1 g) and dimethylglyoxime (0.36 g) were allowed to react in aqueous medium on a steam bath and the solution was afterwards neutralised with dilute H_2SO_4 to pH 7. The product thus obtained was dissolved in hot water. On cooling a yellow product separated which was rejected the filtrate concentrated to a small volume and treated with alcohol to a faint turbidity. On cooling in a refrigerator overnight yellow crystals of the pure mixed chelate were obtained. (Found : Co, 13.4; N, 37.2; H_2O , 5.8 per cent. Calcd. for $[\text{Co}(\text{DMG})(\text{BigH}_2)](\text{SO}_4)_{0.5} \cdot 1.5\text{H}_2\text{O}$: Co, 13.1; N, 37.5; H_2O , 6.0 per cent.)

Dimethylglyoximatobis(biguanide) cobalt(III) chloride : (Found : Co, 14.5; Cl, 9.0 per cent. Calcd. for $[\text{Co}(\text{DMG})(\text{BigH}_2)]\text{Cl}$, Co, 14.4; Cl, 8.6 per cent)

Dimethylglyoximatobis(biguanide) cobalt(III) d-camphor-10-sulphonate : (Found : N, 23.0; H_2O , 15.0 per cent. Calcd. for $[\text{Co}(\text{DMG})(\text{BigH}_2)](\text{CS}) \cdot 6\text{H}_2\text{O}$, N, 22.4; H_2O , 15.1 per cent.)

Lutidinatobis(biguanide) cobalt(III) sulphate : Cis-diamminebis(biguanide) cobalt(III) base (1 g) was treated with lutidinic acid (0.44 g) in cold water (10–12 ml) and heated on a steam bath. The reaction product was neutralised with dilute H_2SO_4 to pH 7, and was recrystallised from a large volume of water. (Found : Co, 10.8; N, 28.8; SO_4 , 8.8; H_2O , 13.0 per cent. Calcd. for $[\text{Co}(\text{Lut})(\text{BigH}_2)](\text{SO}_4)_{0.5} \cdot \text{Co}$, 10.8; N, 28.3; SO_4 , 8.8; H_2O , 13.2 per cent.)

Lutidinatobis(biguanide) cobalt(III) chloride : (Found : Co, 11.6; N, 30.2; Cl, 6.7; H_2O , 11.0 per cent. Calcd. for $[\text{Co}(\text{Lut})(\text{BigH}_2)]\text{Cl} \cdot 3\text{H}_2\text{O}$, Co, 11.5; N, 30.0; Cl, 6.8; H_2O , 10.5 per cent.)

Lutidinatobis(biguanide) cobalt(III) nitrate : (Found : Co, 10.5; N, 30.3; H_2O , 11.8 per cent. Calcd. for $[\text{Co}(\text{Lut})(\text{BigH}_2)]\text{NO}_3 \cdot 3.5\text{H}_2\text{O}$: Co, 10.7; N, 30.6; H_2O , 11.4 per cent.)

Lutidinatobis(biguanide) cobalt(III) d-tartrate : (Found : Co, 10.4; H_2O , 10.0 per cent. Calcd. for $[\text{Co}(\text{Lut})(\text{BigH}_2)](\text{tart})_{0.5} \cdot 3\text{H}_2\text{O}$: Co, 10.7; H_2O , 9.8 per cent.)

Lutidinatobis(biguanide) cobalt(III) d-camphorsulphonate : (Found : Co, 8.2; N, 21.5; H_2O , 10.2 per cent. Calcd. for $[\text{Co}(\text{Lut})(\text{BigH}_2)](\text{CS}) \cdot 4\text{H}_2\text{O}$: Co, 8.1; N, 21.2; H_2O , 9.9 per cent.)

Iminodiacetatobis(biguanide) cobalt(III) chloride : Cis diammine bis(biguanide) cobalt(III) base (2 g) was suspended in water (20 ml) and was treated with a saturated solution of sodium iminodiacetate (1.2 g) and triturated for an hour at room temperature. The resultant mixture was neutralised with dilute HCl and cooled in ice. Crystals were washed with ice cold water and alcohol and air dried (Found : Co, 12.9; N, 34.4; Cl, 8.3; H_2O , 5.0 per cent. Calcd. for $[\text{Co}(\text{IDA})(\text{BigH}_2)]\text{Cl} \cdot 1.5\text{H}_2\text{O}$: Co, 13.0; N, 34.0; Cl, 7.8; H_2O , 5.9 per cent.)

Iminodiacetatobis(biguanide) cobalt(III) nitrate : Found : Co, 12.8; N, 35.3; H_2O , 3.7 per cent. Calcd.

for $[\text{Co}(\text{IDA})(\text{BigH}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$: Co, 12.6; N, 35.6, H_2O , 3.8 per cent).

Iminodiacetatobis(biguanide) cobalt(III) iodide: (Found: Co, 10.8; N, 27.7; I, 23.0; H_2O , 6.5 per cent. Calcd. for $[\text{Co}(\text{IDA})(\text{BigH}_2)_2]\text{I} \cdot 2\text{H}_2\text{O}$: Co, 10.7; N, 27.8; I, 22.9; H_2O , 6.5 per cent).

Iminodiacetatobis(biguanide) cobalt(III) bromide: (Found: Co, 12.3; N, 31.8; Br, 16.4; H_2O , 3.6 per cent. Calcd. for $[\text{Co}(\text{IDA})(\text{BigH}_2)_2]\text{Br} \cdot \text{H}_2\text{O}$, Co, 12.1; N, 31.6; Br, 16.4; H_2O , 3.6 per cent)

Iminodiacetatobis(biguanide) cobalt(III) d-camphor-10-sulphonate: (Found: Co, 8.9; N, 22.9; H_2O , 7.8 per cent Calcd for $[\text{Co}(\text{IDA})(\text{BigH}_2)_2](\text{CS})_3 \cdot 3\text{H}_2\text{O}$: Co, 8.7; N, 22.8; H_2O 8.0 per cent.)

Experimental Procedures: Cobalt was estimated as anhydrous cobalt sulphate, anions by usual methods and nitrogen by semi-micro combustion technique Water of crystallisation was determined at 120°

Measurements for absorption spectra were made with a Hilger Uvispek spectrophotometer.

Equivalent weight was determined by running an aqueous solution of the complex through a bed of cation exchanger (amberlite IR-120) in H^+ form and titrating the acid in the eluate with standard NaOH.

Results and Discussion

Molar conductances of the aqueous solutions (at 32°) of the chloride or the iodide salts of the mixed chelates indicate⁴ a tri-univalent character for $[\text{Co}(\text{en})(\text{BigH}_2)_2]^{3+}$ (460 ohms⁻¹ cm² mole⁻¹), a bi-univalent character for $[\text{Co}(\text{gly})(\text{BigH}_2)_2]^{2+}$ (288 ohms⁻¹ cm² mole⁻¹) and $[\text{Co}(\text{Pic})(\text{BigH}_2)_2]^{2+}$ (296 ohms⁻¹ cm² mole⁻¹) and a uni-univalent character for $[\text{Co}(\text{Lut})(\text{BigH}_2)_2]^+$ (157 ohms⁻¹ cm² mole⁻¹), $[\text{Co}(\text{IDA})(\text{BigH}_2)_2]^+$ (145 ohms⁻¹ cm² mole⁻¹) and $[\text{Co}(\text{DMG})(\text{BigH}_2)_2]^+$ (150 ohms⁻¹ cm² mole⁻¹) complex ions.

$(\text{BigH})_2\text{Cl}$ as a bidentate dibasic acid ligand (Equivalent weight: Found 405; Calcd. 409).

As expected for cobalt (III) complexes⁵ all the above chelates exhibit band I (${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$) (Table 1). The higher energy band (${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$) in some cases could not be located due to their getting mixed up with ligand transitions. Insofar as the first band is concerned the complexes conform to the usual expected positions of the ligands in the spectrochemical series. The first bands of $[\text{Co}(\text{en})(\text{BigH}_2)_2]^{3+}$, $[\text{Co}(\text{gly})(\text{BigH}_2)_2]^{2+}$ and $[\text{Co}(\text{Pic})(\text{BigH}_2)_2]^{2+}$ also obey Jorgensen's rule of average environment⁶. Since cobalt(III) complexes are all consistently six coordinate and since data are not available for cobalt(III) complexes containing bidentate iminodiacetate or monodentate biguanide, the rule cannot be extended to $[\text{Co}(\text{IDA})(\text{BigH}_2)_2]^+$ or to $[\text{Co}(\text{Lut})(\text{BigH}_2)_2]^+$. It is certain that in order to maintain six coordination one of the coordinated ligands must be exhibiting flexidentate character in these complexes. Interesting in this connection is the similarity in the electronic spectra of the members of the pair glycinatobis(biguanide) cobalt(III) and iminodiacetatobis(biguanide) cobalt(III) and of the pair lutidinobis(biguanide) cobalt(III) and picolinatobis(biguanide) cobalt(III). The similarity in the spectra of these pairs of mixed chelates offers one conclusion that lutidinic acid, a potentially tridentate ligand as in six coordinate $[\text{Ag}^{\text{II}}(\text{Lut})(\text{LutH}_2)]\text{H}_2\text{O}^7$ and $[\text{VO}^{\text{II}}(\text{Lut})(\text{H}_2\text{O})_2]^{3+}$, effectively behaves as the bidentate picolinic acid. Similarly iminodiacetic acid, a tridentate ligand as in $[\text{VO}(\text{IDA})(o\text{-phen})]^{3+}$ and $[\text{Co}(\text{IDA})(\text{dien})]^{3+}$ (dien-diethylenetriamine), behaves like the bidentate glycine.

The diastereoisomers of $[\text{Co}(\text{en})(\text{BigH}_2)_2](\text{CS})_3$ and of $[\text{Co}(\text{Pic})(\text{BigH}_2)_2](\text{CS})_2$ have been separated through fractional crystallisation from water. On treating the *dextro* and *levo* diastereoisomers of $[\text{Co}(\text{en})(\text{BigH}_2)_2]$

TABLE 1. ELECTRONIC SPECTRA OF COBALT(III) MIXED CHELATES IN AQUEOUS MEDIUM

Complex	Band I (kK)		Band II (kK)	Reference
	Observed	Predicted by rule of average environment		
$[\text{Co}(\text{en})_3]^{3+}$	21.3 (72.5)	—	29.4 (65)	11
$[\text{Co}(\text{gly})_3]$	19.2 (158)	—	26.7 (141)	11
$[\text{Co}(\text{Pic})_3]$	19.4 (148)	—	26.5 (174)	11
$[\text{Co}(\text{BigH}_2)_3]^{3+}$	21.1 (235)	—	28.4 (220)	12
$[\text{Co}(\text{en})(\text{BigH}_2)_2]^{3+}$	20.9 (165)	21.16	28.6 (155)	This study
$[\text{Co}(\text{gly})(\text{BigH}_2)_2]^{2+}$	20.4 (150)	20.46	27.5 (175)	"
$[\text{Co}(\text{Pic})(\text{BigH}_2)_2]^{2+}$	20.6 (130)	20.52	—	"
$[\text{Co}(\text{Lut})(\text{BigH}_2)_2]^+$	20.5 (165)	—	—	"
$[\text{Co}(\text{IDA})(\text{BigH}_2)_2]^+$	20.5 (163)	—	27.0 (sh)	"
$[\text{Co}(\text{DMG})(\text{BigH}_2)_2]^+$	21.7 (210)	—	—	"

Figures in parentheses indicate the molar extinction coefficients.

The equivalent weights of some of these ions are close to the values deduced on the basis of analyses and conductance. Dimethylglyoxime, known as a bidentate monobasic acid, functions in $[\text{Co}(\text{DMG})$

$(\text{CS})_3$ with sodium iodide there was rapid loss of optical activity so that the enantiomers could not be obtained. However, enantiomers of $[\text{Co}(\text{Pic})(\text{BigH}_2)_2]^{2+}$ have been obtained as iodide salt, though

the *dextro* salt was impure. Attempts to separate the diastereoisomers of $[\text{Co}(\text{Lut})(\text{BigH})_2](\text{CS})$ and $[\text{Co}(\text{IDA})(\text{BigH})_2](\text{CS})$ met with no positive results.

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