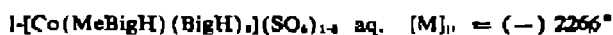


Mixed Ligand Complexes. Part II. Hetero Biguanide Co (III). and 1-Amidino-O-Ethyl Urea Bis Biguanide Cobalt (III) Complexes

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By the action of substituted biguanides on the *Cis* diammine bis biguanide Cobalt(III) base, a series of hetero biguanide Cobalt(III) complexes of the type, $[\text{Co}(\text{AA})(\text{BigH})_2]^{2+}$ (AA = methyl biguanide, ethyl biguanide or phenyl biguanide) have been synthesised and characterised. These give expected conductance values and equivalent weights. Absorption spectral studies reveal two ligand field bands around $28,000 \text{ cm}^{-1}$ and $20,000 \text{ cm}^{-1}$. A comparison reveals very close ligand field strength set by the substituted biguanides compared to biguanide itself.

The complexes, methyl biguanide bis biguanide Cobalt(III) and ethyl biguanide bis biguanide Cobalt(III) have been resolved through the fractionation of the Chloride-d-tartrate and the d-camphor-10-sulphonate. The sulphate salts of the pure optically active *levo* cations have been characterised. These have the following rotation characteristics:



The corresponding phenyl biguanide complex showed no evidence of undergoing any resolution at the Na-D-line.

A number of salts of the heterochelate, 1-amidino-O-ethylurea bis biguanide Cobalt(III) have also been synthesised, adequately characterised and resolved via chloride-d-tartrate. The pure 1-sulphate is characterised. Fractionation of the d-camphor 10-sulphonate provides the d-isomer. The rotation characteristics are:



This paper reports for the first time syntheses, characterisation and resolution of a number of hetero biguanide Cobalt(III) complexes and comes as an interesting extension of our programme on mixed-ligand complexes¹. Looking into the literature of metal biguanide complexes² it is clear that though much efforts have been lavished on homobiguanide complexes of a variety of transition metal ions, nothing has been done so far towards heterobiguanide complexes. In this report

1. Dutta and Sarkar. Papers in the series "Mixed Ligand Complexes", this *Journal*, under publication.
2. Rây, *Chem. Revs.*, 1961, 61, 313; Around 90 papers originating from his laboratory have been covered in this excellent review. For papers appearing after this review, Sen, *Science & Culture*, 1961, 27, 501, 502, 548; 1962, 28, 844; Ghosh and Sinha, this *Journal*, 1961, 38, 179; 1963, 40, 249; *J. Inorg. Nucl. Chem.*, 1964, 28, 1703; Rây, *J. Inorg. Nucl. Chem.*, 1965.

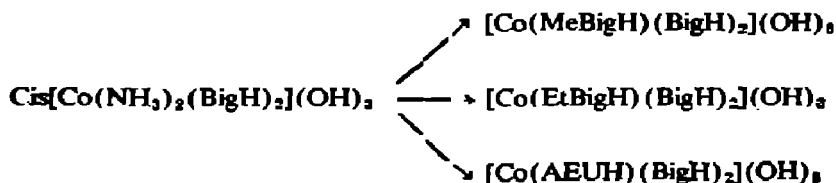
we describe the corresponding Cobalt(III) complexes, which furnish some interesting instance where the coordination sites around Cobalt(III) are occupied by differently substituted biguanides. Besides, 1-amidino-O-ethylurea, which has many similarities to biguanides with regard to complexing properties, has also been used to provide a heterochelate.

Tris biguanide Cobalt(III) was resolved³ through the fractional crystallisation of the Chloride-d-tartrate and a high yield of the levo isomer realised due to a second order asymmetric transformation.

This above tris biguanide Co(III) case has been claimed to be the first inorganic example by the authors. We have however noted, the tris biguanide case was not the first one. Much earlier tris oxalato chromium(III) has been resolved through strychnine in alcoholic medium giving primarily the dextro form and in aqueous solution, the levo form⁴. Besides the tris biguanide case a limited few are also known today e.g., the resolution of tris-o-phenanthroline Fe(III) antimonyl-d-tartrate giving a high yield of the levo isomer⁵ and the arsenic(V) Catechol complex⁶ again in alcohol through quinine etc. Recently a few substituted catecholates have also been found to give rise to a second order asymmetric transformation in alcohol⁷.

In this context we need to mention that the homochelates of phenyl biguanide Cobalt(III) chloride-d-tartrate was resolved earlier in a normal manner⁸, both the dextro and levo being obtained in nearly equal amounts, with no evidence towards asymmetric transformation. The homochelate tris (N^o-isopropyl N¹-p-chlorophenyl) biguanide Cobalt(III) also underwent apparently a normal resolution⁹.

When Cis diamine bis biguanide Cobalt(III) base is treated with methyl biguanide, ethyl biguanide (at pH 7) or 1-amidino-o-ethylurea there occurs evolution of ammonia leading to the formation of the co-responding Cobalt(III) heterochelate bases. Treatment with dilute acids and/or metathetic reactions leads to the



isolation of a number of salts of the complex cations. In the case of the tris biguanide Cobalt(III) chloride, $[\text{Co}(\text{BigH})_3]\text{Cl}_3$, treatment with one mole of silver-d-tartrate and evaporation to dryness had led to the isolation of the tris biguanide

3. Rây and Dutta, *this Journal*, 1941, 18, 289.
4. Warner, *Ber.* 1912, 45, 3061 as cited by Basolo in Bailar, "Chemistry of the Coordination Compounds".
5. Dwyer and Gyafas, *J. Proc. Roy. Soc., N. S. Wales*, 1960, 83, 263.
6. Rosenheim and Plato, *Ber.* 1925, 58, 2000.
7. Larkins and Jones, *Inorg. Chem.*, 1963, 2, 143.
8. Siddhanta, Dutt and Rây, *this Journal*, 1960, 27, 641.
9. Spacn *et al.*, *Chem. Abst.*, 1962, 57, 410.

Cobalt(III) chloride-d-tartrate. We have, however, found that treatment of the aqueous solution of the tris-chloride with an excess of sodium-d-tartrate, always provided glistening crystals of the hetero biguanide Cobalt(III) chloride-d-tartrate instead of the pure d-tartrate.

TABLE I

Measurement of conductance in aqueous solution at 36°C.

- | 1. $[\text{Co}(\text{MeBigH})(\text{BigH})_2]\text{Cl}_2$
Dilutions (in litres) | 64 | 128 | 256 | 512 | 1024 |
|--|--------|--------|--------|--------|--------|
| Λ^v | 124.2 | 124.3 | 151.0 | 158.0 | 169.6 |
| Λ^∞ | 156.42 | 147.11 | 170.59 | 172.50 | 180.60 |
- Λ^∞ (Mean) = 165.44, Molar conductance = 495.32 mhos. $\text{cm}^2 \text{mole}^{-1}$.
- $[\text{Co}(\text{PhBigH})(\text{BigH})_2]\text{Cl}_2 \cdot 2.5 \text{H}_2\text{O}$, Molar conductance = 439.31 mhos. $\text{cm}^2 \text{mole}^{-1}$.
 - $[\text{Co}(\text{EtBigH})(\text{BigH})_2]\text{Cl}_2 \cdot 2.2\text{H}_2\text{O}$, Molar conductance = 517.8 mhos. $\text{cm}^2 \text{mole}^{-1}$.
 - $[\text{Co}(\text{AEUH})(\text{BigH})_2]\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$, Molar conductance = 445 mhos. $\text{cm}^2 \text{mole}^{-1}$.

The Λ^∞ values were calculated by Walden formula $\Lambda^\infty = \Lambda^v (1 + .692 \times n_1 \times n_2 \times v^{-1})$
 Where Λ^v = the equivalent conductance at a definite dilution.
 v = dilution in litres, n_1 & n_2 the valencies of the ions.

The complex chlorides gave expected values of molar conductance, provided the prevailing temperature was taken into consideration¹⁰. Besides the equivalent weights of the chloride and the nitrate-salts agree well with the values obtained from analytical results.

TABLE II

Determination of Equivalent weights.

Complex	Equivalent weight	
	Required	Found
1. $[\text{Co}(\text{MeBigH})(\text{BigH})_2]\text{Cl}_2$	160	155
2. $[\text{Co}(\text{MeBigH})(\text{BigH})_2](\text{SO}_4)_{1.5} \cdot 5\text{H}_2\text{O}$	203	203
3. $[\text{Co}(\text{PhBigH})(\text{BigH})_2]\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$	199	174
4. $[\text{Co}(\text{PhBigH})(\text{BigH})_2](\text{SO}_4)_{1.5} \cdot 5\text{H}_2\text{O}$	223	216
5. $[\text{Co}(\text{EtBigH})(\text{BigH})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	176	170
6. $[\text{Co}(\text{AEUH})(\text{BigH})_2](\text{SO}_4)_{1.5} \cdot \text{H}_2\text{O}$	183	161
7. $[\text{Co}(\text{AEUH})(\text{BigH})_2]\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	168	159

Next we completed the absorption spectral measurements and found out that as usual the complexes exhibit two ligand field absorption bands, one around 28,000 cm^{-1} and the other around 20,000 cm^{-1} . For comparison, the spectra of tris biguanide chloride is also given. This would show that the substituted biguanides and the amidino-*o*-ethylurea set a very close ligand field around Cobalt(III) as does biguanide itself.

10. Jones, "Elementary Coordination Chemistry", Prentice Hall, 1964, p. 254.

TABLE III

Absorption spectral characteristics.

Complex	Band II			Band I		
	λ Max	W. number	Molar ϵ	λ Max	W. number	Molar ϵ
1. [Co(MeBigH)(BigH) ₂]Cl ₂	350-355	28600-28100	220	475	21100	235
2. [Co(EtBigH)(BigH) ₂]Cl ₂	350-355	28600-28100	265	480	20800	275
3. [Co(PhBigH)(BigH) ₂](SO ₄) _{1.5}	355	28200	275	480	20800	210
4. [Co(AEUH)(BigH) ₂]Cl ₂	355	28100	210	475	21100	225
5. [Co(BigH) ₃]Cl ₂	350-355	28000-28200	220	475	21100	235

The resolution studies show that the chloride-d-tartrates as prepared in this work (Vide Experimental) get fractionated to a considerable extent right during the preparation. Thus the crop (about 50-60% of the total theoretical yield) is distinctly levorotatory, which on further fractionation provide the pure levorotatory isomer (in about 85% of the above yield). Thus the technique of the resolution, we have adopted, provides a partial resolution and a quicker route to obtain a good yield of the pure levo isomer. Some impure dextrofraction may be collected from the original mother liquor on long standing. This, however, has not been investigated in much details. This resolution behaviour was observed in all the three cases, namely, of methylbiguanide bisguanide Cobalt(III) and the corresponding ethylbiguanide and 1-amidino-O-ethyl urea complexes.

TABLE IV

Complex	Specific Rotation	Molar Rotation	Temperature
1. [Co(MeBigH)(BigH) ₂]d-tart $\frac{\text{Cl}}{4.5\text{H}_2\text{O}}$	(-) 365°	(-) 2328°	30°C.
2. [Co(MeBigH)(BigH) ₂](SO ₄) _{1.5} $\frac{\text{Cl}}{3.5\text{H}_2\text{O}}$	(-) 390°	(-) 2266°	30°C.
3. [Co(EtBigH)(BigH) ₂]d-tart $\frac{\text{Cl}}{4\text{H}_2\text{O}}$	(-) 375°	(-) 2411°	30°C.
4. [Co(EtBigH)(BigH) ₂](SO ₄) _{1.5} $\frac{\text{Cl}}{3.5\text{H}_2\text{O}}$	(-) 385°	(-) 2291°	30°C.
5. [Co(AEUH)(BigH) ₂]d-tart $\frac{\text{Cl}}{4.5\text{H}_2\text{O}}$	(-) 337°	(-) 2197°	27°C.
6. [Co(ABUH)(BigH) ₂](SO ₄) _{1.5} $\frac{\text{Cl}}{3\text{H}_2\text{O}}$	(-) 375°	(-) 2197°	27°C.
7(a) d[Co(BigH) ₃]d-tart $\frac{\text{Cl}}{5\text{H}_2\text{O}}$	(+) 340°	(+) 2161°	31°C.
(b) [Co(BigH) ₃]d-tart $\frac{\text{Cl}}{5\text{H}_2\text{O}}$	(-) 335°	(-) 2129°	31°C.
8. d & l [Co(BigH) ₃](SO ₄) _{1.5} $\frac{\text{Cl}}{3.5\text{H}_2\text{O}}$	(±) 362.5°	(±) 2062°	31°C.

For the dextro methyl biguanide bis biguanide Cobalt(III) Camphor sulpho-
nate, $[\alpha]_D = (+) 143^\circ$; $[M]_D = (+) 1530^\circ$. For the dextro methyl biguanide
bis biguanide Cobalt(III) Iodide $[\alpha]_D = (+) 155^\circ$; $[M]_D = (+) 1150^\circ$. For
the ethyl biguanide bis biguanide Cobalt(III) camphor sulpho-
nate, $[\alpha]_D = (+) 150^\circ$; $[M]_D = (+) 1720^\circ$. For the dextro 1-amidino-O-ethyl urea bis bigua-
nide Cobalt(III) Camphor sulpho-
nate $[\alpha]_D = (+) 150^\circ$; $[M]_D = (+) 1734^\circ$.
The Iodide salt of the dextro ethyl biguanide bis biguanide Cobalt(III) cation and
the dextro 1-amidino-o-ethyl urea bis biguanide Cobalt(III) cation gave practically
no rotation.

Optical rotations were measured in a student model Carl Zeiss Polarimeter,
giving reading upto $\pm 0.05^\circ$. Accuracy of the above rotation values are limited be-
cause of only moderate accuracy that the Polarimeter offered and also because
of the limitations offered by the coloured Cobalt(III) solutions (0.06-0.1%
solution).

The resolution of the d-camphor sulpho-
nate diastereoisomer is normal offer-
ing both dextro and levo rotatory fraction, the levo diastereoisomer appearing
first. However, our attempts to prepare the iodide salt by triturating with con-
centrated NaI or KI solution gave in the case of methyl biguanide complex on
iodide salt with poor optical activity ($[\alpha]_D = +155^\circ$) and in the case of the ethyl
biguanide there was practically no rotation. This rapid loss of optical activity in the
case of ethyl biguanide complexes calls for detailed study of the racemization
reactions. However, these types of examples are not entirely uncommon in the
literature¹¹⁻¹³. The 1-amidino-O-ethylurea case is also comparable.

We would now compare the resolution studies with all the other tris biguanide
Cobalt(III) complexes that have been resolved. It is thus observed that the
substitution of one biguanide by methyl biguanide or ethyl biguanide does not
retain the property of exhibiting the second order transformation with respect to
the chloride-d-tartrate diastereo isomers. Besides, the resulting heterochelates
have rotation values which are indicative of a greater asymmetry introduced in the
complex, though somewhat lower than what is observed in tris phenyl biguanide
Cobalt(III) system⁹. In tris biguanide Cobalt(III) as well as the present cases,
the levo rotatory chloride-d-tartrate form the less soluble fraction. The diastereo-
isomers as also the optically active complex sulphate were quite stable in solution
around 30°C , since no racemisation took place even on standing for days together.
The samples also did not undergo any racemisation in the solid crystalline state
when these were heated in 120°C for several hours.

Phenyl biguanide also reacted with cis diamine bis biguanide Cobalt(III)
forming the corresponding heterochelates. The complex had a trend to turn
oily, so that we did not spend much efforts for isolation of a number of salts.

11. Waller *et al.*, *Ibid.*, 1965, 27, 2371.

12. Celap *et al.*, *Inorg. Chem.*, 1965, 4, 1494.

13. *Inorg. Syntheses*, Part VI, p. 65:

However, we wish to record that our efforts to resolve and separate the diastereoisomers of the phenyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate did not prove successful in so far as the sodium-d-line was concerned.

EXPERIMENTAL

Biguanide acid sulphate, methyl biguanide acid sulphate, ethyl biguanide acid sulphate and phenyl biguanide hydrochloride were all prepared by following standard procedures^{13, 14}. The 1-amidino-O-ethylurea has been prepared as described elsewhere¹⁵.

Cis-diamine bis biguanide Cobalt(III) base was prepared as will be described later¹⁶.

1. *Methyl biguanide bis biguanide Cobalt(III) sulphate*: Methyl biguanide acid sulphate (.72 gm.) was dissolved in water (20 ml.) and neutralised with 6N NaOH till faintly alkaline. This methyl biguanide solution was added to a suspension of cis diamine bis biguanide Cobalt(III) base (1 gm.) in water (10 ml.). There was immediate evolution of ammonia, and the mixture was digested on a steam bath till free from ammonia. It was then neutralised to pH 6.5-7 with dilute H₂SO₄. The complex sulphate separated readily and was cooled thoroughly in ice. This was recrystallised from hot water, washed with alcohol and air dried. {Found: Co, 9.8; N, 34.6; SO₄, 24.1; H₂O (at 120°C) 14.8%; [Co(BigH)₂(MeBigH)](SO₄)_{1.5} 5H₂O requires, Co, 9.7; N, 34.5; SO₄, 23.7 and H₂O, 14.8% }.

2. *Methyl biguanide bis biguanide Cobalt(III) chloride*: Methyl biguanide (.72 gm.) was dissolved in hot water (about 20 ml.) and treated with BaCl₂ (.75 gm.) in water (10 ml.). BaSO₄ was filtered off and the filtrate neutralised with 6N NaOH till faintly alkaline. This was then added to a suspension of cis diamine bis biguanide Cobalt(III) base (1 gm.) in water (5-6 ml.) and digested on a steam bath when all the ammonia was expelled, the solution was neutralised with dilute HCl when the yellow chloride salt of the complex began to separate out. The solution was further concentrated, cooled thoroughly in ice and the product recrystallised from hot water. The chloride salt was obtained as yellow powder. {Found: Co, 12.4; N, 42.9; Cl, 22.2%; [Co(MeBigH)(BigH)₂]Cl₂ requires, Co, 12.3; N, 43.7; Cl, 22.1% }.

3. *Methyl biguanide bis biguanide Cobalt(III) iodide*: Methyl biguanide bis biguanide Cobalt(III) chloride (1 gm.) was dissolved in a minimum volume of hot water, and treated with a concentrated solution of KI (3-4 ml.). There was an immediate precipitation of the yellow iodide salt of the complex. It was treated as usual. {Found: Co, 7.6; N, 28.5; I, 50.0%; [Co(MeBigH)(BigH)₂]I₃ requires, Co, 7.8; N, 27.8; I, 50.4% }.

14. Ray and Chakravarty, *this Journal*, 1941, 18, 609.

15. Dutta and Ray, *this Journal*, 1959, 36, 499.

16. Dutta and Sarkar, *this series*, under publication.

4. *Methyl biguanide bis biguanide Cobalt(III) nitrate*: A concentrated solution of Methyl biguanide bis biguanide Cobalt(III) chloride in hot water was treated with a concentrated solution of NaNO_3 . On cooling in a refrigerator overnight it gave the bright red crystals and these were collected as usual. [Found: Co, 10.8; N, 45.3%; $[\text{Co}(\text{MeBigH})(\text{BigH})_2](\text{NO}_3)_3$ requires, Co, 10.5; N, 45.0%].

5. *Methyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate*: Methyl biguanide (2.4 gm.), BaCl_2 (2.5 gm.) and cis diamine bis biguanide Cobalt(III) base (3.5 gm.) were treated as above, and after neutralisation with dilute HCl, more water was added to dissolve the separated product at the steam bath temperature (about 80 ml.) and this was filtered directly into a saturated solution of sodium-d-tartrate. There appeared readily crystals of the chloride-d-tartrate salt of the complex in the form of shining red needles. It was cooled in ice for half an hour, filtered and washed with alcohol and air dried. [Found: Co, 9.3; N, 32.5; Cl, 5.3; H_2O (120°C) 12.9%; $[\text{Co}(\text{BigH})_2(\text{MeBigH})\text{d-tart} \cdot 4.5\text{H}_2\text{O}$ requires, Co, 9.2; N, 32.9; Cl, 5.5; and H_2O 12.6%].

This above product was found to be substantially levorotatory. $[\alpha]_D^{25} = (-) 285^\circ$.

6. *Methyl biguanide bis biguanide Cobalt(III) d-camphor sulphonate*: Methyl biguanide bis biguanide Cobalt(III) chloride (1 gm) was dissolved in a minimum volume of hot water and was added to a solution of excess ammonium d-camphor-10-sulphonate with stirring. There was an immediate precipitation of the camphor sulphonate salt and after digestion on a steam bath for about 5 minutes, it was filtered, washed with cold water and air dried. [Found: Co, 5.2; N, 18.3; H_2O , (at 120°C) 6.5%; $[\text{Co}(\text{MeBigH})(\text{BigH})_2](\text{CS})_3 \cdot 4\text{H}_2\text{O}$ requires, Co, 5.1; N, 18.3; H_2O , 6.3%].

Fractionation of the chloride-d-tartrate diastereoisomer: Methyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate (4 gm.) was dissolved in water at room temperature (35°C), (about 400 ml.) to form almost a saturated solution and then allowed to evaporate slowly under a fan. The crops collected were all levorotatory and the yield of the levo isomer was above 85% of the starting chloride d-tartrate. Found for the levo diastereoisomer: $[\alpha]_D^{25} = (-) 365^\circ$ $[\text{M}]_D^{25} = (-) 2328^\circ$ ($t=30^\circ\text{C}$); [Found: Co, 9.3; N, 32.6; Cl, 6.0; H_2O (at 120°C) 12.6%; $[\text{Co}(\text{MeBigH})(\text{BigH})_2]\text{d-tart} \cdot 4.5\text{H}_2\text{O}$ requires, Co, 9.2; N, 32.9; Cl, 5.5; H_2O , 12.6%].

Fractionation of the d-camphor-10-sulphonate diastereoisomer: Methyl biguanide bis biguanide Cobalt(III) Camphor sulphonate (4 gm.) was dissolved in water at 35°C (450 ml.) to make an almost saturated solution. It was allowed to evaporate under a fan. The first few crops collected gave levo rotation and after two more fractions with poor rotations, the final two crops gave dextro rotations. The levo and dextro fractions at the two ends were mixed separately and

refractionated. The rotation values are indicative of not having arrived at the purest fractions. Found for the dextro diastereoisomer: $[\alpha]_D = (+) 143^\circ$ $[M]_D = (+) 1530^\circ$ ($t=30^\circ\text{C}$). $\{$ Found: Co, 5.5; N, 19.4%; $[\text{Co}(\text{MeBigH})(\text{BigH})_2](\text{CS})_2$ requires, Co, 5.5; N, 19.6% $\}$.

The sulphate salt of the levo complex cation and the iodide salt of the dextro complex cation were prepared by triturating the levo chloride-d-tartrate diastereoisomer and the dextro-d-camphor-10-sulphonate diastereoisomer with saturated $(\text{NH}_4)_2\text{SO}_4$ and NaI respectively.

(a) Found for the levo, $[\alpha]_D = (-) 390^\circ$, $[M]_D = (-) 2266^\circ$ ($t=30^\circ\text{C}$). $\{$ Found: Co, 10.0; N, 36.5; SO_4 , 25.1; H_2O , 10.3%; $[\text{Co}(\text{BigH})_2(\text{MeBigH})(\text{SO}_4)_{1.5} \cdot 3.5\text{H}_2\text{O}$ requires, Co, 10.1; N, 36.1; SO_4 , 24.7; H_2O , 10.8% $\}$.

(b) Found for the dextro $[\alpha]_D = (+) 155^\circ$ $[M]_D = (+) 1170^\circ$. $\{$ Found: Co, 8.0; 28.1; I, 51.0%; $[\text{Co}(\text{BigH})_2(\text{MeBigH})\text{I}]_2$ requires, Co, 7.8; N, 27.8; I, 50.4% $\}$.

It is worth mentioning that though the resolution of the camphor sulphonate diastereoisomer is normal, the molar rotation values offered are poor. The same is the case with the iodide salt prepared from it. It is difficult to prepare sulphate salt from the camphor sulphonate diastereoisomer.

7. *Ethyl biguanide bis biguanide Cobalt(III) sulphate*: Ethyl biguanide sulphate (.76 gm.) was dissolved in water (10 ml.) and was treated with NaOH till just alkaline. This alkaline solution of Ethyl biguanide was added to that of the diammine bis biguanide Cobalt(III) base (1 gm. in 10 ml.) and was digested on a steam bath to free it from ammonia. On neutralisation with dilute H_2SO_4 , the sulphate salt began to separate out. It was recrystallised from hot water, washed with alcohol and air dried. $\{$ Found: Co, 9.4; N, 35.0; SO_4 , 24.0; H_2O (at 120°C) 12.0%; $[\text{Co}(\text{BigH})_2(\text{EtBigH})_2(\text{SO}_4)_{1.5} \cdot 4\text{H}_2\text{O}$ requires, Co, 9.7; N, 34.7; SO_4 , 23.7; and H_2O 11.9% $\}$.

8. *Ethyl biguanide bis biguanide Cobalt(III) chloride*: This was obtained as yellow crystals by following the procedure adopted for the methylbiguanide complex. $\{$ Found: Co, 11.1; N, 40.0; Cl, 20.2; H_2O (at 120°) 7.0%; $[\text{Co}(\text{EtBigH})(\text{BigH})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ requires, Co, 11.1; N, 39.6; Cl, 20.0; H_2O 6.8% $\}$.

9. *Ethyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate*: This was also obtained like the methylbiguanide chloride-d-tartrate. $\{$ Found: Co, 9.4; N, 32.8; H_2O (at 120°C), 11.0%; $[\text{Co}(\text{EtBigH})(\text{BigH})_2]\text{d-tart} \cdot 3\text{H}_2\text{O}$ requires, Co, 9.1; N, 32.6; H_2O , 11.2% $\}$.

10. *Ethyl biguanide bis biguanide-d-camphor-10-sulphonate*: This was prepared as for the methylbiguanide derivative. $\{$ Found: Co, 5.3; N, 18.4; H_2O (at 120°C), 6.2%; $[\text{Co}(\text{EtBigH})(\text{BigH})_2](\text{CS})_2 \cdot 4\text{H}_2\text{O}$ requires, Co, 5.1; N, 18.1; H_2O , 6.2% $\}$.

Fractionation of the chloride-d-tartrate diastereoisomer: Ethyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate (4 gm.) was dissolved in water (about 350 ml.) at room temperature, 30°C to form an almost saturated solution, and allowed to crystallise under a fan. All the crops collected showed levo rotation. The yield of the pure levo rotatory fraction was about 85% of the starting chloride-d-tartrate. Found for the levo diastereoisomer: $[\alpha]_D = (-) 375^\circ$ $[M]_r = (-) 2411^\circ$. ($t=30^\circ\text{C}$). Found: Co, 9.2; N, 33.0; H₂O (at 120°C) 11.9%: $[\text{Co}(\text{EtBigH})(\text{BigH})_2]_d\text{-tart } 4\text{H}_2\text{O}$ requires, Co, 9.1; N, 32.6; H₂O, 11.2%.

The sulphate salt of the optically active cation was prepared by triturating the chloride-d-tartrate diastereoisomer with saturated ammonia sulphate solution. Found for the levo sulphate salt: $[\alpha]_D = (-) 385^\circ$; $[M]_r = (-) 2291^\circ$ ($t=30^\circ\text{C}$). Found: SO₄, 23.8; H₂O (at 120°C) 10.9%; $[\text{Co}(\text{BigH})(\text{BigH})_2(\text{EtBigH})](\text{SO}_4)_{1.5} 3.5\text{H}_2\text{O}$ requires, SO₄, 24.2; H₂O, 10.6%.

Fractionation of the d-camphor-10-sulphonate diastereoisomer: Ethyl biguanide bis biguanide Cobalt(III) camphor sulphonate (4 gm.) was dissolved in water (about 400 ml.) to form an almost saturated solution. It was then allowed to crystallise under a fan.

Of the five crops collected the first two and last two crops gave equal giving dextro rotation. The middle fractions were of lower values and evidently impure. The first few and the last few crops were again mixed separately and the best fractions that we could obtain was the following one: Found for the dextro diastereoisomer: $[\alpha]_D = (+) 150^\circ$, $[M]_r = (+) 1720^\circ$ ($t=30^\circ\text{C}$). Found: Co, 4.8; H₂O (at 120°C) 5.4%; $[\text{Co}(\text{EtBigH})(\text{BigH})_2](\text{CS})_3 3.5\text{H}_2\text{O}$ requires, Co, 5.1, H₂O, 5.4%.

The levorotatory fractions are not included as the rotations were poorer compared to the pure chloride-d-tartrate obtained earlier.

The Iodide salt of the dextro-cation was obtained by the trituration of the dextro-diastereoisomer with a saturated solution of NaI. But surprisingly it gave practically no rotation values. This fast loss of rotation calls for a detailed study of the racemisation process.

11. *1-amidino-O-ethyl urea bis biguanide sulphate**: Cis diamine bis biguanide Cobalt(III) base (1 gm.) was suspended in water (20 ml.) and was treated with 1-amidino-O-ethyl urea (.51 gm.) dissolved in water (5-6 ml.). This was digested on a water bath till free from ammonia. The clear solution was then neutralised with dilute H₂SO₄ in the cold to pH 7, and then concentrated on a steam bath till precipitate began to separate out. It was cooled in ice when the yellow sulphate salt separated out. It was filtered, recrystallised from small volume of hot water, washed with acetone and air dried. Found: Co, 10.75; N, 35.7; SO₄, 25.9%; $[\text{Co}(\text{BigH})_2(\text{AEUH})](\text{SO}_4)_{1.5} \text{H}_2\text{O}$ requires, Co, 10.7; N, 35.6; SO₄, 26.1%.

* AEUH will represent one molecule of 1-amidino-o-ethyl urea

12. *1-amidino-O-ethyl urea bis biguanide Cobalt(III) chloride*: 1-amidino-O-ethyl urea sulphate (.51 gm.) was dissolved in water (10 ml.) and was treated with a solution of Barium chloride (.75 gm.) in water and digested on a steam bath. BaSO₄ was filtered off and the solution was added to that of Cis diamine bis biguanide Cobalt(III) base in water (10 ml.) and digested on a steam bath till free from ammonia and then neutralised with dilute HCl and concentrated to 5-6 ml. and cooled. The yellow powdery product was further purified by recrystallisation from a small volume of water. Found Co, 12.0; N, 39.3; Cl, 21.3; H₂O, 1.6%; [Co(BigH)₂(AEUH)]Cl₃. 0.5H₂O requires, Co, 11.7; N, 38.9; Cl, 21.0; H₂O, 1.7%.

13. *1-amidino-O-ethyl urea bis biguanide Cobalt(III) chloride d-tartrate*: The complex chloride (1 gm.) was dissolved in a minimum volume of hot water and added directly into a saturated solution of sodium d-tartrate and cooled. The chloride-d-tartrate salt separated in the form of red needles. These were filtered, washed with ice cold water and air dried. Found: Co, 9.3; N, 31.0; Cl, 5.6; H₂O (at 120°C) 13.3%; [Co(BigH)₂(AEUH)]^{Cl}d-tart 5H₂O requires, Co, 8.9; N, 29.6; Cl, 5.3; H₂O, 13.6%.

The racemic form gave a rotation of $[\alpha]_D = (-) 270^\circ$.

Fractionation of the diastereoisomer: 1-amidino-O-ethylurea bis biguanide Cobalt(III) chloride-d-tartrate (4 gm.) was dissolved in water (about 300 ml.) at room temperature and allowed to crystallise under a fan. All the fractions collected were levorotatory. The yield was above 75% of the starting chloride d-tartrate. Found for the Levo diastereoisomer: $[\alpha]_D = (-) 337^\circ$ $[M]_D = (-) 2197^\circ$ (t=27°C). Found: Co, 8.7; Cl, 5.0; H₂O (at 120°C) 12.4%; [Co(BigH)₂(AEUH)]^{Cl}d-tart 4.5H₂O requires, Co, 9.0; Cl, 5.4; H₂O, 12.4.

The sulphate salt of Levo complex entity was prepared by triturating the chloride-d-tartrate with a concentrated solution of ammonium sulphate. Found for the levo sulphate: $[\alpha]_D = (-) 375^\circ$ $[M]_D = (-) 2197^\circ$ (t=27°C). Found: Co, 9.8; SO₄, 25.0; H₂O, 9.5%; [Co(BigH)₂(AEUH)](SO₄)_{1.5} 3H₂O requires, Co, 10.0; SO₄, 24.5; H₂O, 9.2%.

14. *1-amidino-O-ethyl urea bis biguanide Cobalt(III) camphor sulphonate*: A concentrated solution of 1-amidino-O-ethyl urea bis biguanide Cobalt(III) chloride in hot water was added to a solution of ammonium d-camphor-10-sulphonate and when there was an immediate precipitation of the camphor sulphonate salt of the complex, it was digested on a steam bath for a few minutes and then filtered off, washed with cold water and air dried. Found: Co, 5.3; N, 17.1; H₂O, (at 120°C) 6.1%; [Co(BigH)₂(AEUH)](CS)₁ 4H₂O requires, Co, 5.1; N, 16.9; H₂O, 6.2%.

Fractionation of the diastereoisomer: 1-amidino-O-ethyl urea bis biguanide Cobalt(III) d-camphor-10-sulphonate (4 gm.) was dissolved in cold water and allowed to crystallise under a fan. Several crops were collected showing normal

resolution behaviour. The dextro crops were further fractionated, yielding a maximum $[\alpha]_D = (+) 150^\circ$; $[M]_D = (+) 1734^\circ$. This compared to the d-tartrate, was still impure. (Attempts to prepare the iodide salt was not undertaken as in a number of such similar systems, investigated in our Laboratory, total loss of rotation occurred during trituration with a concentrated KI or NaI solution). Found for the dextro: $[\alpha]_D = (+) 150^\circ$; $[M]_D = (-) 1734^\circ$, ($t=27^\circ\text{C}$). Found: N, 17.3; H_2O (at 120°C), 6.2%; $[\text{Co}(\text{BigH})_2(\text{AE}(\text{H}))](\text{CS})_2 \cdot 4\text{H}_2\text{O}$ requires, N, 16.9; H_2O , 6.2%.

Found for the levo: $[\alpha]_D = (-) 143^\circ$; $[M]_D = (-) 1640^\circ$, ($t=27^\circ\text{C}$). Found: N, 17.1; H_2O , 5.5%; $[\text{Co}(\text{BigH})_2(\text{AE}(\text{H}))](\text{CS})_2 \cdot 3.5\text{H}_2\text{O}$ requires, N, 17.0; H_2O , 5.4%.

15. *Phenyl biguanide bis biguanide Cobalt(III) chloride*: Cis diamine bis biguanide Cobalt(III) base was suspended in water (about 10 ml.) and to it was added an alkaline solution of phenyl biguanide hydrochloride and digested on a steam bath and when all the ammonia was out, it was neutralised with dilute HCl and evaporated to a small volume. On cooling yellow products began to separate out. They were treated as usual. Found: Co, 10.6; N, 36.7; Cl, 18.4; H_2O (at 120°C), 4.3%; $[\text{Co}(\text{PhBigH})(\text{BigH})_2\text{Cl}_2] \cdot 2.5\text{H}_2\text{O}$ requires, Co, 10.0; N, 35.7; Cl, 18.0; H_2O 7.6%.

16. *Phenyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate*: Phenyl biguanide bis biguanide Cobalt(III) chloride (1 gm.) was dissolved in a minimum volume of hot water (5-6 ml.) and it was added to a saturated solution of Sodium-d-tartrate. The solution on cooling in ice gave an oily product. The mother liquor was decanted off and the oily product was washed twice with ice cold water and then scratched with acetone to obtain a crystalline product, which was dried over CaCl_2 . Found: Co, 8.3; Cl, 4.0; H_2O (at 120°C) 7.6%; $[\text{Co}(\text{PhBigH})(\text{BigH})_2]_d\text{-tart} \cdot 3\text{H}_2\text{O}$ requires, Co, 8.7; Cl, 5.2; H_2O , 8.0%.

Fractionation of the Chloride-d-tartrate diastereoisomer: Phenyl biguanide bis biguanide Cobalt(III) chloride-d-tartrate (4 gm.) was dissolved in water (about 40 ml.) and allowed to crystallise under a fan. No product separated out. It was subjected to fractional precipitation by the gradual addition of acetone. The oil that separated out was scratched repeatedly with acetone to obtain crystalline powder. Several such crops were obtained with no rotation at the Sodium-D-line.

All the experimental techniques have been described in the earlier part.