

Mixed-Ligand Complexes : Part V. Cobalt (III) Heterochelates with Ethylenedibiguanide

R. L. Dutta and Ila Mallik

A series of Cobaltic heterochelates have been prepared by the action of O-phenanthroline, 4,4'-dipyridyl, biguanide or glycine on diamine ethylene-dibiguanide Cobalt(III) hydroxide sulphate. The complexes are all quite soluble and have been characterised by conductance and equivalent weight measurements. The electronic absorption spectra reveal two ligand field bands representing the transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. The ligands obey their expected position in the spectrochemical series.

Partial characterisation of the levorotatory biguanide ethylene-dibiguanide Cobalt(III) d-camphor-sulphonate diastereoisomer has been made.

As studies were progressing in our Laboratory on the mixed ligand complexes of Cobalt(III) having two bidentate biguanide ligands¹, we thought this might be worthwhile to undertake a programme on quadridentate functioning biguanides. The literature does not have any record of a Cobaltic heterochelate containing such a polydentate biguanide. Nor are such examples common with other quadridentate ligands².

While looking for a synthetic route to such Cobaltic heterochelates containing the quadridentate ethylenedibiguanide, we found that a diamine ethylene-dibiguanide Cobalt(III) hydroxide sulphate had already been reported³. The quadridentate ethylenedibiguanide, among other aspects, has stabilised tripositive silver in the form of a four coordinated cationic complex, with an extraordinarily high stability constant and also tri- and tetrapositive manganese in the form of first-ever examples of cationic complexes of manganese to be stabilised by nitrogen donor ligands^{4,5}.

1. Dutta and Sarkar, papers in the series "Mixed-Ligand Complexes", Part I-VI, this *Journal* under publication.
2. See for example, (a) Kyuno, Boucher and Bailar, *J. Amer. Chem. Soc.*, 1965, **87**, 4461.
(b) Legg and Cooke, *Inorg. Chem.*, 1965, **4**, 1576.
3. Ray, *Z. anorg. Chem.*, 1960, **308**, 133.
- 4(a) Ray and Chakravarty, this *Journal*, 1944, **21**, 47.
(b) Sen, Ghosh and Ray, *ibid.*, 1950, **27**, 619.
(c) Sen and Ray, *ibid.*, 1953, **30**, 519.
5. Ray and Ray, this *Journal*, 1958, **35**, 595, 601.

The diamine ethylenedibiguanide Cobalt(III) hydroxide sulphate is not known whether it is a *cis* or a *trans* derivative. In any case, we found that when the substance was taken in aqueous solution and treated with bases, such as *O*-phenanthroline or $\alpha\alpha'$ -dipyridyl, there was no immediate evolution of ammonia. On warming on a water bath, ammonia was disengaged and a dark red solution resulted. On concentrating to a small volume and neutralising, the cations could be isolated. Both the heterochelate cations, namely, *O*-phenanthroline ethylenedibiguanide Cobalt(III) and $\alpha\alpha'$ -dipyridyl ethylenedibiguanide Cobalt(III) have been isolated in the form of a limited number of salts, such as sulphate, chloride and iodide. The salts are far more soluble than the corresponding bis biguanide Cobalt(III) complexes. Conductance measurements are indicative of the tri-univalent nature of the cations, although somewhat higher values are recorded due to a high room temperature. Besides, the equivalent weights were also determined by the ion exchange technique pursued in our Laboratory.^{1,6}

On treating the diamine base with biguanide around *pH* 8 on a steam bath once again there occurred evolution of ammonia and the bidentate biguanide slipped into the coordination zone. The heterobiguanide cation, biguanide ethylenedibiguanide Cobalt(III) was isolated in the form of sulphate, chloride and the iodide. Here too, the solubility was much larger than the other heterobiguanide Cobalt(III) complexes reported earlier from our Laboratory. The conductance and equivalent weights were also studied and found to be giving expected values. With a view to studying the resolution characteristics of the complex, we did isolate the salt with *d*-camphor sulphonate as the anion. Our attempts to isolate the chloride-*d*-tartrate or the pure *d*-tartrate did not materialise, an oily product being obtained. The camphor sulphonate was fractionated and a crop (about 7%) was collected which showed a *levo* rotation $[\alpha]_D = -135^\circ$ and the other fractions were all impure and showed very little rotation. Compared to similar heterobiguanide systems reported earlier, the first crop is believed to be substantially impure. The yield, poor as it was, discouraged us very much to pursue further studies in this context.

TABLE I

Conductance measurements in aqueous solution at 36°.

1. $[\text{Co}(\text{O-phen})\text{Et}(\text{BigH})_2]\text{Cl}_2 \cdot 3.5 \text{H}_2\text{O}$				
Dilution (in litres)	128	256	512	1024
Λ°	128	145	165	161
Λ°	151.5	163.8	180.1	171.4
Λ° (mean)	166.7	$\Lambda^\circ = 500.1 \text{ mhos. cm}^2 \text{ mole}^{-1}$		
2. $[\text{Co}(\text{dipy})\text{Et}(\text{BigH})_2]\text{Cl}_2 \cdot 2.5\text{H}_2\text{O}$	$\Lambda^\circ = 505.8 \text{ mhos. cm}^2 \text{ mole}^{-1}$			
3. $[\text{Co}(\text{BigH})\text{Et}(\text{BigH})_2]\text{Cl}_2$	$\Lambda^\circ = 509.1 \text{ mhos. cm}^2 \text{ mole}^{-1}$			
4. $[\text{Co}(\text{gly})\text{Et}(\text{BigH})_2]\text{SO}_4 \cdot 1.5\text{H}_2\text{O}$	$\Lambda^\circ = 328 \text{ mhos. cm}^2 \text{ mole}^{-1}$			

* $\text{Et}(\text{BigH})_2$ designates one molecule of ethylenedibiguanide.

6. Dutta and Syamal, this *Journal*, under publication.

Glycine reacts with diamine hydroxide sulphate at the temperature of a steam bath disengaging ammonia and producing the permanganate violet hetero-chelate, glycine ethylenedibiguanide Cobalt(III) ion, being isolated as the sulphate salt. Conductance showed this to be bi-bivalent salt⁷. The equivalent weight as determined by the ion exchange technique came within the expected spread of the theoretical value. (cf. Tables I & II).

TABLE II

Equivalent weight measurements.

Complex	Found	Required
1. [Co(O-phen)Et(BigH) ₂]Cl ₂ · 3.5 H ₂ O	220	213
2. [Co(O-phen)Et(BigH) ₂](SO ₄) _{1.5} · 4.5 H ₂ O	221	230
3. [Co(dipy)Et(BigH) ₂](SO ₄) _{1.5} · 6H ₂ O	240	231
4. [Co(dipy)Et(BigH) ₂]Cl ₂ · 2.5 H ₂ O	209	198
5. [Co(BigH)Et(BigH) ₂](SO ₄) _{1.5} · 4H ₂ O	210	200
6. [Co(gly)Et(BigH) ₂](SO ₄) _{1.5} · 1.5H ₂ O	250	242

The electronic absorption spectra of all these systems (Table III) have been recorded within the range 320 m μ to 550 m μ and compared with the similar complexes reported earlier in this series. There is a close resemblance in the spectra of all these complexes and a qualitative spectrochemical series is obeyed.



TABLE III

Electronic absorption spectral data.

Complex	Band II		Molar ϵ	Band I		Molar ϵ
	λ max. (m μ)	W. number ν (cm ⁻¹)		λ max. (m μ)	W. number ν (cm ⁻¹)	
[Co(O-phen)Et(BigH) ₂](SO ₄) _{1.5}	335	30,000	800	480-496	20,800-20,200	74
[Co(BigH)Et(BigH) ₂]Cl ₂	355	28,200	220	480-490	20,800-20,400	220
[Co(dipy)Et(BigH) ₂](SO ₄) _{1.5}				480-490	20,800-20,400	175
[Co(gly)Et(BigH) ₂]SO ₄	360	27,800	326	515-530	19,400-18,900	175

With a view to extend such studies we conceived of preparing similar hetero-chelates containing meta-phenylene-dibiguanide as the quadridentate functioning ligand. Although the trans diamine metaphenylenedibiguanide Cobalt(III) salts⁸

7(a) Jones, "Elementary Coordination Chemistry", Prentice Hall, 1964, p. 254.

(b) Dhar, *Z. anorg. Chem.*, 1913, **80**, 43 as cited in Quagliano *et al.*, *Inorg. Chem.*, 1963, p. 286.

8. Ray and Das Sarma, *this Journal*, 1949, p. 138.

have been described long back, all our efforts failed to obtain a material of reasonably crystalline nature. In our hands, the method always produced a sticky mass which could not be crystallised.

EXPERIMENTAL

Ethylenedibiguanide hydrogen sulphate⁹ and biguanide sulphate¹⁰ were prepared according to published procedures. Diamine ethylenedibiguanide hydroxide sulphate was also obtained by following a known method⁹.

1. *O-phenanthroline ethylenedibiguanide Cobalt(II) Sulphate*: Diamine ethylenedibiguanide Cobalt(III) hydroxide sulphate 4-hydrate (hereinafter called "diamine compound") (1 g.) was dissolved in water (15 ml.) and treated with *O-phenanthroline* (0.4 g.) and the mixture warmed on a steam bath till evolution of ammonia ceased. The solution was then neutralised with dilute H₂SO₄, concentrated further and allowed to cool. The red crystals were filtered, washed with spirit and dried in air. Recrystallisation was effected from a small volume of water using about 2 gm. of the crude salt. {Found: Co, 8.7; N, 24.9; SO₄, 20.4 H₂O (by loss at 120°), 12.0%; [Co(*O-phen*)Et(BigH)₂](SO₄)_{1.5} 4.5 H₂O requires, Co, 8.5; N, 24.3; SO₄, 20.8; H₂O, 11.7%}.

2. *O-phenanthroline ethylenedibiguanide Cobalt(III) Chloride*: The diamine compound (5 g.) was dissolved in water (50 ml.) and treated with *O-phenanthroline* (2 g.). The mixture was digested on a steam bath till there was no further evolution of ammonia. The solution was neutralised with dilute HCl and treated with aqueous barium chloride dihydrate (2.5 g.). The mixture was digested further, filtered and filtrate concentrated to a small volume and cooled to obtain red crystals of the chloride salt, which were further purified by recrystallisation from a small volume of hot water. {Found: Co, 9.0; N, 26.2; Cl, 16.6 and H₂O (at 120°), 10.3%; [Co(*O-phen*)Et(BigH)₂]Cl₃ 3.5 H₂O requires, Co, 9.3; N, 26.4; Cl, 16.8 and H₂O, 10.0%}.

3. *O-phenanthroline ethylenedibiguanide Cobalt(III) Iodide*: The iodide salt was obtained by the addition of KI to a concentrated aqueous solution of the chloride salt obtained *in situ* by the above method. {Found: Co, 6.8; N, 20.0; I, 43.4; H₂O (at 120°) 3.1%; [Co(Et(BigH)₂)(*O-phen*)]I₃ H₂O requires, Co, 6.8; N, 19.4; I, 44.0; H₂O, 2.8%}.

4. *αα'-dipyridyl ethylenedibiguanide Cobalt(III) Sulphate*: This was obtained as for the *O-phenanthroline* complex, using dipyridyl (.32). {Found: Co, 8.5; N, 24.2; SO₄, 20.1; H₂O (at 120°) 14.8%; [Co(dipy)Et(BigH)₂](SO₄)_{1.6} 6H₂O requires, Co, 8.5; N, 24.2; SO₄, 20.7; H₂O, 15.5%}.

9. *Inorg. Syntheses*, Vol. VI, p. 75.

10. *Ibid.*, Vol. VI, p. 65.

5. $\alpha\alpha'$ -dipyridyl ethylenedibiguanide Cobalt(III) Chloride : The diamine compound (2.5 g.) and dipyridyl (.8 g.) were suspended in water (about 40 ml.) and warmed on a steam bath till ammonia evolution ceased. The solution was neutralised with dilute HCl and treated with barium chloride dihydrate (1.5 g.) solution. After digestion the barium sulphate was filtered off, the solution further concentrated, cooled and treated with acetone (about 10 ml.) and left overnight in a refrigerator. The shining red crystals were collected and washed with acetone and dried in air. Found : Co, 9.9 ; N, 28.4 ; Cl, 18.3 ; H₂O (at 120°) 7.6% ; [Co(dipy)Et(BigH)₂]Cl₂ · 2.5H₂O requires, Co, 10.0 ; N, 28.3 ; Cl, 17.9 ; H₂O, 7.6%.

6. $\alpha\alpha'$ -dipyridyl ethylenedibiguanide Cobalt(III) Iodide : The chloride solution as obtained above was treated with KI, warmed to obtain a clear solution and was allowed to crystallise slowly thus furnishing red crystals. Found : Co 7.2 ; N, 21.0 ; I, 46.7% ; [Co(dipy)Et(BigH)₂]₂I₂ requires, Co, 7.1 ; N, 20.4 ; I, 46.3%.

7. $\alpha\alpha'$ -dipyridyl ethylenedibiguanide Cobalt(III) Nitrite : Obtained as for the iodide salt using sodium nitrite instead of potassium iodide. Found : Co, 9.1 ; N, 35.5 and H₂O (at 120°) 1.5% ; [Co(dipy)Et(BigH)₂](NO₂)₂ · 0.5H₂O requires, Co, 10.0 ; N, 35.7 ; H₂O, 1.5%.

8. Biguanide ethylenedibiguanide Cobalt(III) Sulphate : The diamine compound (2.5 gm.) was suspended in water (15 ml.) and treated with a neutralised (NaOH) solution of biguanide acid sulphate (1.2 gm. in 30 ml. water). The mixture was warmed on a steam bath till entire amount of ammonia was lost. The solution was then neutralised with dilute H₂SO₄, filtered, concentrated to about 20 ml. and allowed to cool slowly. The deep orange red crystals were filtered, washed with alcohol and dried in air. Found : Co, 9.6 ; N, 35.1 ; SO₄, 25.0 ; H₂O, 12.5% ; [Co(BigH)Et(BigH)₂](SO₄)_{1.5} · 4H₂O requires, Co, 9.8 ; N, 35.0 ; SO₄, 24.0 ; H₂O, 12.0%.

9. Biguanide ethylenedibiguanide Cobalt(III) Chloride : The above sulphate salt (2 gm.) was dissolved in water and treated with an aqueous solution of barium chloride (.8 gm.). After filtering off the barium sulphate, the solution was concentrated to a small volume and allowed to crystallise. The crystals were washed with spirit and dried in air. Found : Co, 12.2 ; N, 43.0 ; Cl, 21.3% ; [Co(BigH)Et(BigH)₂]Cl₂ requires, Co, 12.0 ; N, 42.7 ; Cl, 21.7%.

10. Biguanide ethylenedibiguanide Cobalt(III) d-camphor-10-Sulphonate : This was obtained by treating concentrated aqueous solution of the above complex chloride with that of ammonium d-camphor-10-sulphonate in the cold, when shining crystals separated. These were filtered and washed with acetone. Found : Co, 5.3 ; N, 18.65 ; H₂O (at 120°) 4.8% ; [Co(BigH)Et(BigH)₂](CS)₂ · 3H₂O requires, Co, 5.2 ; N, 18.5 ; H₂O, 4.7%.

11. *Biguanide ethylenedibiguanide Cobalt(III) Iodide*: Obtained as shining red crystals following earlier procedures. {Found: Co, 7.9; N, 27.0; I, 50.8%; [Co(BigH)Et(BigH)₂]₂I₃ requires, Co, 7.7; N, 27.4; I, 50.0%}.

12. *Glycinate ethylenedibiguanide Cobalt(III) Sulphate*: The diamine compound (2.5 g.) and glycine (0.4 g.) were taken in water (30 ml.) and heated on a steam bath till ammonia evolution ceased. The solution was concentrated, cooled and scratched with acetone. The oil that separated first, turned into a crystalline powder. The powder was dried in a desiccator for a few days and the hard mass was dissolved in almost boiling water (70 ml.). The filtered bluish-violet solution was concentrated (30-40 ml.) on a steam bath when shining crystals started appearing. The mixture was sufficiently cooled and the permanganate violet crystals collected. These were washed with spirit and dried over CaCl₂. {Found: Co, 11.9; N, 31.8; SO₄, 19.6; H₂O (at 120°) 5.9%; [Co(gly)Et(BigH)₂]₂SO₄. 1.5 H₂O requires, Co, 12.1; N, 31.8; SO₄, 19.8; H₂O, 5.5%}.

EXPERIMENTAL METHODS

Cobalt was estimated as anhydrous Cobalt(II) sulphate, nitrogen by the combustion technique and the anions by common procedures. Equivalent weights have been determined by our ion-exchange technique. Electronic spectra were recorded in Hilger Uvispek Spectrophotometer and conductance with a Phillips conductivity bridge.

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INORGANIC CHEMISTRY LABORATORY,
THE UNIVERSITY OF BURDWAN,
BURDWAN, WEST BENGAL (INDIA).

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