

Mixed Ligand Complexes of Co(III) with Biguanides & Nitric Oxide

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A number of cationic hexacoordinated complexes of cobalt(III) with biguanides and nitric oxide have been isolated and characterized on the basis of elemental analysis, conductance, spectral and magnetic moment data. The complexes prepared are of the types $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})]\text{X}_2$ and $[\text{Co}(\text{Hbg})_2(\text{NO})\text{X}']\text{X}''$ (where Hbg = biguanide or its derivative, X = ClO_4^- or $\frac{1}{2}\text{SO}_4^{2-}$, X' = halide or thiocyanate and X'' = Cl^- , Br^- , CNS^- or ClO_4^-). The complexes containing SO_4^{2-} as anion are stable in air in the solid state while other compounds are stable only in an atmosphere of nitrogen. Except the sulphate, all other compounds, even in dry state, are sensitive to diffused light.

A NUMBER of transition metal mixed ligand complexes involving biguanides and donors like H_2O , NH_3 , oxalate, thiosulphate and N'-amidinoisourea have been reported^{1,2}. In the majority of mixed ligand nitric oxide complexes of cobalt, oxidation state +2 of the latter is observed. However, other oxidation states have also been reported³⁻⁵. Nitric oxide can coordinate as NO , NO^+ or NO^- depending on the nature of the metal atom and the other ligands attached to it. If the already present ligand is π -acceptor, nitric oxide coordinates as NO^+ and stabilizes the lower oxidation states. If the ligand present is π -donor, nitric oxide coordinates as NO^- stabilizing the higher oxidation state. Since biguanide has filled π -orbital, which can overlap with vacant $p\pi$ or $d\pi$ orbitals of metal atom, delocalization of π -electrons can occur through the whole of metal ligand ring system favouring higher oxidation states of the metal atom. This has been corroborated by the preparation of a number of higher valent metal biguanide complexes such as $\text{Ag}(\text{III})$ ⁶, $\text{Pt}(\text{IV})$ ⁷ and $\text{Ru}(\text{III})$ ⁸ biguanides. Therefore, it is of interest to study the mixed ligand complexes of cobalt with biguanide and nitric oxide. The oxidation state of cobalt will be helpful in indicating the type of coordination exhibited by nitric oxide giving some qualitative information about the π -donor capacity of biguanide.

The general method for the preparation of complexes of the type $[\text{Co}(\text{R-Hbg})_2(\text{NO})\text{X}]\text{X}$ (Hbg = biguanide, X = Cl^- , Br^- or CNS^-) involved action of nitric oxide on $[\text{Co}(\text{R-Hbg})_2]\text{X}_2$ in methanol. The complexes $[\text{Co}(\text{R-Hbg})_2(\text{NO})\text{X}]\text{ClO}_4$ were isolated by the treatment of $[\text{Co}(\text{R-Hbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in acetone solution with lithium halide.

Materials and Methods

All experiments were carried out under nitrogen which was previously passed through alkaline pyro-

gallol solution to remove oxygen. The compounds $[\text{Co}^{\text{II}}(\text{Hbg})_2]\text{X}_2$ where X = Br^- , ClO_4^- , $\frac{1}{2}\text{SO}_4^{2-}$, were prepared following the methods described in the literature⁹. Nitric oxide was prepared and purified as per standard methods¹⁰. No precaution was taken to remove the traces of water from the solvents, since the reaction was not influenced by the presence or absence of water in the reaction media.

(Nitrosyl)(aquo)bis(biguanide)cobalt(III) perchlorate — Bis(biguanide)cobalt(II) perchlorate (2 g), prepared *in situ* from $[\text{Co}(\text{Hbg})_2](\text{OH})_2$ and NH_4ClO_4 , was suspended in oxygen-free methanol (25 ml). The suspension was purged with nitrogen and pure nitric oxide gas was bubbled through the suspension at the rate of 70 bubbles per minute for 2 hr when dark bluish violet crystals were formed. The passage of nitric oxide was discontinued and nitrogen was passed through the suspension for complete removal of unreacted nitric oxide. The crystals were filtered in a gooch crucible and washed with small portions of oxygen-free methanol under nitrogen. These were dried over sodium hydroxide in a desiccator in nitrogen atmosphere. The compounds were highly soluble in acetone, methanol and water. From the elemental analysis, the compound was characterized as $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)$.

(Halo)(nitrosyl)bis(biguanide)cobalt(III) perchlorate — The perchlorate complex, $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in acetone solution, on treatment with lithium halides gives bluish violet crystals, characterized as $[\text{Co}(\text{Hbg})_2(\text{NO})\text{X}]\text{ClO}_4$ where X = Cl^- , Br^- or I^- . The compounds were highly soluble in methanol and water. The chloro compound gave white precipitate of AgCl only on long standing and slight heating. The iodo complex is quite unstable and its detailed study was not possible.

(Nitrosyl)(aquo)bis(biguanide)cobalt(III) sulphate — It was prepared by following the same method as for the corresponding perchlorate compound using bis(biguanide)cobalt(II) sulphate in place of perchlorate.

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(Hydroxo)(nitrosyl)bis(biguanide)cobalt(III) hydroxide — $[\text{Co}(\text{Hbg})_2](\text{OH})_2$ (0.5 g) was suspended in 15 ml of dry oxygen-free methanol. The suspension was purged with nitrogen for the complete removal of oxygen. Through this suspension, nitric oxide was bubbled for 3 hr when the colour of the contents turned bluish-violet. The excess nitric oxide was removed by purging with nitrogen. The bluish violet precipitate was filtered and dried over sodium hydroxide in nitrogen atmosphere. The compound was also prepared by reaction of $[\text{Co}(\text{BigH})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$ with barium hydroxide solution under N_2 .

(Chloro)(nitrosyl)bis(biguanide)cobalt(III) chloride — It was prepared by following the same method as for the perchlorate complex using ammonium chloride solution in place of ammonium perchlorate.

(Thiocyanato)(nitrosyl)bis(biguanide)cobalt(III) thiocyanate — The compound was prepared in the same way as the corresponding (chloro)(nitrosyl)bis(biguanide)cobalt(III) chloride compound except that ammonium thiocyanate was used in place of ammonium chloride. The thiocyanato compound resembles the chloro compound in physical and chemical properties.

The chloro, bromo and thiocyanato compounds were also prepared from the (nitrosyl)(aquo)bis(biguanide)cobalt(III) sulphate, $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$, by double displacement reactions with BaCl_2 , BaBr_2 and $\text{Ba}(\text{CNS})_2$ respectively.

Similar complexes with substituted biguanides such as methyl-, diethyl- and phenyl-biguanides have been prepared by following similar methods of preparation as those for the simple biguanide compounds. All the compounds along with their analytical data are listed in Table 1.

All the compounds of this series are light, air and heat sensitive. They were preserved and studied in dark at room temperature in an atmosphere of nitrogen.

The conductances were measured in methanolic solution of the compounds. The magnetic susceptibilities of the compounds were measured using a Guoy balance. The infrared spectra were recorded on a Beckman-IR 12 spectrophotometer.

Results and Discussion

(Nitrosyl)(aquo)bis(biguanide)cobalt(III) sulphate is fairly stable towards aerial oxidation. It is sparingly soluble in methanol and water. In the compounds of the type $[\text{Co}(\text{Hbg})_2(\text{NO})\text{X}]\text{ClO}_4$ (where $\text{X} = \text{Cl}, \text{Br}, \text{CNS}$), the presence of halide ions in the coordination sphere is indicated by the fact that the freshly prepared solution does not give any precipitate of silver halide with AgNO_3 solution. The aerial oxidation of nitrosyl group to NO_2 depends largely on the nature of the ligand in the *trans* position. $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$ remains unchanged for several weeks in the presence of diffused sunlight, while $[\text{Co}(\text{Hbg})_2(\text{NO})\text{Br}]\text{Br}$ gets oxidized within a few seconds on exposure to dry air. This trend is attributed to the strong electronegative character as well as lone pair participation of the halide ion *trans* to the nitrosyl group in the complex.

All the present complexes are diamagnetic in nature ($\mu_{\text{eff}} = +0.3$ to -0.5 BM). The diamagnetic nature of the compounds shows that all the complexes have central metal atom in the +3 oxidation state and probably the complexes have a bent Co-N-O group.

Compounds of the type $[\text{Co}(\text{Hbg})_2(\text{NO})\text{X}]\text{X}'$ behave as 1:1 electrolytes in methanol. This indicates the molecular formula as $[\text{Co}(\text{BigH})_2(\text{NO})\text{X}]\text{X}'$. The perchlorate compound behaves as a 1:2 electrolyte and hence it may be represented as $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$.

The infrared spectra (Table 2) of several of these complexes have been studied. A strong absorption at 1600 cm^{-1} indicates the presence

TABLE 1 — ANALYTICAL AND CONDUCTANCE DATA

Compounds	Found (%)				Calc. (%)				λ_{M}
	M	N	SO_4	X	M	N	SO_4	X	
$[\text{Co}(\text{Hbg})_2(\text{NO})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$	13.81	35.67	—	16.02	13.30	35.63	—	16.33	—
$[\text{Co}(\text{Hbg})_2(\text{NO})(\text{CNS})]\text{CNS}$	14.42	44.42	—	—	14.25	44.71	—	—	85.21 ^a
$[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$	14.44	38.00	23.55	—	14.54	38.02	23.65	—	111.3 ^b
$[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$	11.73	30.32	—	—	11.61	30.34	—	—	152.78 ^b
$[\text{Co}(\text{Hbg})_2(\text{NO})\text{Cl}]\text{ClO}_4$	13.94	38.42	—	8.32	13.80	36.20	—	8.24	69.345 ^a
$[\text{Co}(\text{Hbg})_2(\text{NO})\text{Br}]\text{ClO}_4$	12.61	32.61	—	17.00	12.52	32.73	—	16.98	—
$[\text{Co}(\text{MeHbg})_2(\text{NO})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$	12.83	33.34	—	15.3	12.78	33.92	—	15.17	85.71 ^a
$[\text{Co}(\text{MeHbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$	11.47	30.00	—	—	11.22	29.30	—	—	80.76 ^a
$[\text{Co}(\text{MeHbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$	13.67	35.00	22.00	—	13.60	35.56	22.13	—	—
$[\text{Co}(\text{MeHbg})_2(\text{NO})\text{Cl}]\text{ClO}_4$	13.23	35.62	—	—	13.00	35.56	—	—	—
$[\text{Co}(\text{MeHbg})_2(\text{NO})\text{CNS}]\text{CNS}$	11.21	33.72	—	—	10.99	33.96	—	—	—
$[\text{Co}(\text{DietHbg})_2(\text{NO})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$	11.02	28.11	—	12.9	10.81	28.25	—	12.82	—
$[\text{Co}(\text{DietHbg})_2(\text{NO})\text{CNS}]\text{CNS}$	11.45	34.81	—	22.43	11.35	35.08	—	22.33	—
$[\text{Co}(\text{DietHbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$	11.39	29.54	18.67	—	11.37	29.78	18.53	—	—
$[\text{Co}(\text{DietHbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$	9.61	24.81	—	—	9.57	25.00	—	—	171.25 ^b
$[\text{Co}(\text{DietHbg})_2(\text{NO})\text{Cl}]\text{ClO}_4$	10.93	28.45	—	6.62	10.96	28.64	—	6.60	—
$[\text{Co}(\text{PhHbg})_2(\text{NO})\text{Cl}]\text{Cl}$	12.14	31.54	—	14.33	12.13	31.69	—	14.48	88.25 ^a
$[\text{Co}(\text{PhHbg})_2(\text{NO})\text{CNS}]\text{CNS}$	12.94	39.43	—	—	12.82	39.63	—	—	83.01 ^a
$[\text{Co}(\text{PhHbg})_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$	12.92	33.53	20.81	—	12.88	33.65	20.99	—	—
$[\text{Co}(\text{PhHbg})_2(\text{NO})(\text{H}_2\text{O})](\text{ClO}_4)_2$	10.56	27.32	—	—	10.53	27.54	—	—	167.03 ^b

X = Cl, Br or CNS, a = in methanol, b = in water.

TABLE 2—INFRARED SPECTRAL DATA AND ASSIGNMENTS OF BANDS

(Hbg) ₂ SO ₄	[Co(Hbg) ₂ (NO) (CNS)]CNS	[Co(Hbg) ₂ (NO)Cl] Cl	[Co(Hbg) ₂ (NO) (H ₂ O)]SO ₄	[Co(Hbg) ₂ (NO)Cl] ClO ₄	Assignments
3540 vs	3490 vs, 3400 vs	3500 vs, 3430 vs	3460 vs, 3340 vs	3450 vs, 3425 vs	ν N-H
3170 vs	3200 vs, 3020 vs	3250 vs	3230 vs	3230 vs	ν CNS (coordinated)
—	2065 vs, 2050 vs	—	—	—	ν N-C-N
1650 s	1685 s	1680 s	1650 s	1675 s	ν NO
—	1610 s	1605 s	1625 s	1615 s	ν N-C-N
1560 s	1545 s	1555 s	1540 s	1535 s	—
1230 s	1280 s	1280 s	—	1360 s	ν SO ₄
1135 s	—	—	—	—	NH bending
760 s	775 s	780 s	770 s	775 s	NH wagging
720 s	725 s	720 s	725 s	720 s	

s = strong, vs = very strong.

of NO⁻ coordination in the complex since a band in the region 1500-1700 cm⁻¹ is expected for the coordinated NO⁻ group¹¹. The oxidation product of the compound [Co(Hbg)₂(NO)Cl]Cl gives a compound similar in all respects to *trans*-[Co(Hbg)₂(NO₂)Cl]Cl. The nitrosyl biguanide compounds have been assigned *trans* configurations.

The thiocyanate complex [Co(Hbg)₂(NO)]CNS shows a strong band at 2065 cm⁻¹ due to coordinated CNS⁻ group. This indicates that the thiocyanate complex has similar configuration as the halide complexes.

From all these studies it appears that the nitrosyl group is coordinated as NO⁻ in the biguanide complexes of cobalt. It can be concluded that ligand (biguanide) to metal π -donor capacity (L→M) is strong enough to push the electron density from

the metal to the antibonding molecular orbital of nitric oxide which in turn coordinates as NO⁻ and Co-N-O bond becomes bent.

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