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SYNTHESES AND PROPERTIES OF NITROSYLS OF COBALT N'-AMIDINOISOUREAS

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A number of nitrosyls of cobalt N'-amidinoisoureas of general formula $[\text{CoL}_2(\text{NO})(\text{H}_2\text{O})]$, $[\text{CoL}'_2(\text{NO})\text{Cl}]\text{Cl}$ and $[\text{CoL}'_2(\text{NO})(\text{H}_2\text{O})]\text{SO}_4$ (where L = N'-amidinoisourea, L' = O-alkyl-N'-amidinoisourea) have been synthesized and characterized. Physico-chemical properties of these complexes suggest the above formulations and indicate the presence of comparatively high electron density on the coordinated NO group.

INTRODUCTION

Stable complexes of biguanides and N'-amidinoisoureas are believed to possess a delocalized π -electron system in the metal chelate ring.^{1–5} These ligands are strongly π -basic in character⁶ and are known to stabilize higher oxidation states of the metal atoms^{7–9} due to L→M π -bonding. Biguanides and O-alkyl-N'-amidinoisoureas can form complex bases as well as salts^{4–8} (Figure 1) but simple N'-amidinoisourea is found incapable of forming complex salts probably due to intramolecular hydrogen bonding^{4,8,10} (Figure 1).

Nitrosyl is a versatile ligand and forms a large number of mixed ligand complexes with many transition metals^{11–18} due to its ability to accommodate appropriate electron density. The relative energies of the molecular orbitals in a six coordinated nitrosyl complexes undergo dramatic changes when m , the number of electrons in $[\text{M}(\text{NO})]^m$ moiety exceeds 6 in order to attain maximum stability.¹⁹ The molecular orbital diagram of $[\text{CoNo}]^8$ is different from that of $[\text{FeNO}]^6$. In the former the cobalt atom has a d^6 configuration with a lone pair residing in a nonbonding nitrogen orbital (sp^2 hybridized).¹⁹ In view of the above discussion it is certain that the electron distribution on coordinated NO will be greatly influenced by the nature of other ligands attached to the metal atom in the complex. In the present investigation, a number of cobalt nitrosyls have been synthesized and attempts have been made to obtain information regarding the extent of electron density on coordinated NO from a study of

their detailed physical and chemical properties. It is to be noted that Co(II) N'-amidinoisourea complexes have been used for homogeneous hydroformylation reaction with partial success²⁰ and the present nitrosyl complexes may be useful in organic nitrosation reactions like Fe(II) and Cu(II) nitrosyls.²¹

EXPERIMENTAL

All the reagents used were of analytical grade. The starting compounds were prepared and purified by recrystallization several times from water. The conductances of the solutions were measured in "Systronics, type 302" conductivity bridge. I.r. (from 400 cm^{-1} to 4000 cm^{-1} in KBr phase) and visible (from 350 to 1000 nm) spectra were taken in "Beckmann IR-12" and "Beckmann DB-G" spectrophotometers respectively. The magnetic susceptibilities were measured at two field strengths with Gouy type balance using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as calibrant. Thermal analyses were carried out in "Derivatograph, system Paulik, Paulik and Erdey" in the range 50°C to 450°C.

Preparation

a) The complex bases (compound 1–3, Table I) were prepared by taking a cold alkaline solution (100 ml, 10% NaOH) of the corresponding ligand normal sulphate (10 g) in a special apparatus provided with a Gooch crucible at the bottom. The solution was outgassed with hydrogen and an equimolar mixture of hydrogen and nitric oxide was passed through the solution for one hour. Oxygen free

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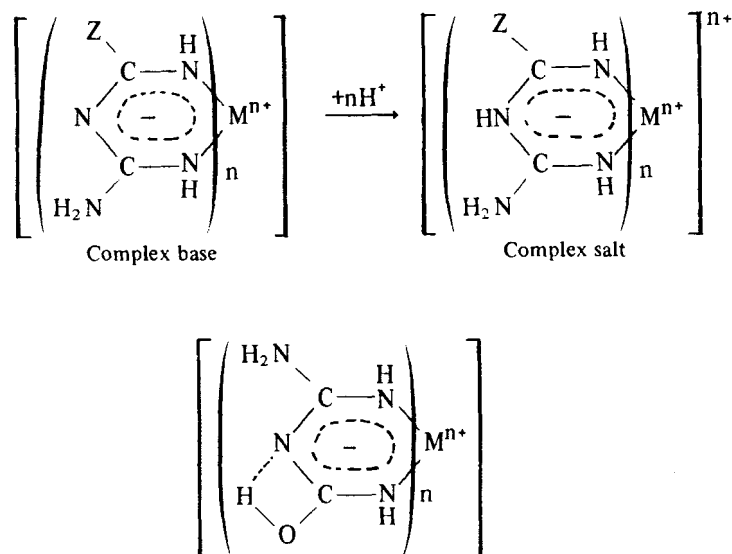


FIGURE 1
 Metal N'-amidinoisourea (base)
 Z = NH-Alkyl (N-alkylbiguanide)
 Z = O-Alkyl (O-alkyl-N'-amidinoisourea)

cobalt sulphate solution (10%, 20 ml) at 0° C was added and the gas mixture (H₂ + NO) was bubbled for five hours after the initial yellow precipitate of Co(II) complex²² turned completely into pink with no further visual change. The pink suspension was flushed thoroughly with hydrogen, filtered, washed with cold distilled water and finally dried over sodium hydroxide pellets under hydrogen atmosphere. These compounds were also prepared in ammoniacal methanol medium (10%, NH₃) or shaking the corresponding sulphates or chlorides with 10% sodium hydroxide solution.

b) The nitrosyl chlorides (compounds 4 and 5, Table I) were generally prepared by the use of ammoniacal solution (100 ml, 1% NH₃) of the corresponding ligand normal chloride (10 g). The passage of hydrogen and nitric oxide was done similar to that of previous method. After the addition of cobalt chloride solution, the gas mixture (H₂ + NO) was bubbled through the yellow suspension of Co(II) complexes²² for nearly four hours when pink crystals separated out. These were filtered, washed and dried as described under a).

c) In the preparation of nitrosyl sulphates (compounds 6 and 7, Table I), ligand normal chlorides and cobalt chloride were replaced by the corresponding sulphates in the procedure b). Other

conditions were maintained same as those described in the previous paragraph.

All these nitrosyl complexes were synthesized under hydrogen or nitrogen atmosphere below 25° C.

d) For the isolation of nitro-derivatives (compounds 8,9,10 and 11, Table I), an aqueous solution of the corresponding nitrosyl complex was subjected to aerial oxidation for 48 hours at room temperature (25° C). The resulting orange-red solution was filtered and evaporated under reduced pressure over calcium chloride. Orange red crystals separated out which were washed with cold water and dried over calcium chloride.

The nitrosyl complexes are generally deep violet in colour, slightly soluble in polar solvents (e.g. H₂O, CH₃OH, dimethylformamide etc.) and insoluble in nonpolar solvents (e.g. benzene). They form stable solutions at 0° C which decompose at higher temperatures. Both the solubility and stability in aqueous solutions are increased in the presence of basic reagents i.e., NH₃, NaOH, NH₂-NH₂ etc. The compounds either in solid state or in solution decompose instantaneously in the presence of acids. The sulphates and chlorides do not show any sign of decomposition when dry while the bases decompose under this condition.

The nitro compounds form stable solutions in

TABLE I
Analytical, conductance and magnetic data

Compound	Colour	Found						Calculated						Λ_{1024} S.cm ² mol ⁻¹	
		%M	%N	%C	%Cl/SO ₄	%M	%N	%C	%Cl/SO ₄	%M	%N	%C	%Cl/SO ₄		μ_{eff} B.M.
1. [Co(aiu) ₂ (NO)(H ₂ O)]	Pink	18.96	40.68	15.48	—	19.06	40.78	15.53	—	19.06	40.78	15.53	—	diamagnetic	—
2. [Co(maiuH) ₂ (NO)(OH)] OH	Pink	16.59	35.45	20.45	—	16.61	35.50	20.29	—	16.61	35.50	20.29	—	diamagnetic	—
3. [Co(eaiuH) ₂ (NO)(OH)] OH	Pink	15.40	32.89	25.04	—	15.39	32.91	25.07	—	15.39	32.91	25.07	—	diamagnetic	—
4. [Co(maiuH) ₂ (NO)Cl] Cl	Pink	15.06	32.20	18.36	18.09	15.04	32.15	18.37	18.11	15.04	32.15	18.37	18.11	diamagnetic	114.4 ^a
5. [Co(eaiuH) ₂ (NO)Cl] Cl	Pink	13.98	30.06	22.84	16.89	14.04	30.02	22.87	16.91	14.04	30.02	22.87	16.91	diamagnetic	86.2 ^b
6. [Co(maiuH) ₂ (NO)(H ₂ O)] SO ₄	Bluish violet	13.58	28.99	16.54	22.10	13.55	28.97	16.55	22.08	13.55	28.97	16.55	22.08	diamagnetic	—
7. [Co(eaiuH) ₂ (NO)(H ₂ O)] SO ₄	Bluish violet	13.98	30.06	20.72	16.89	12.75	27.23	20.74	20.74	12.75	27.23	20.74	20.74	diamagnetic	—
8. [Co(maiuH) ₂ (NO ₂)Cl] Cl	Orange red	14.38	30.81	17.52	17.61	14.44	30.87	17.65	17.41	14.44	30.87	17.65	17.41	diamagnetic	120.2 ^a
9. [Co(eaiuH) ₂ (NO ₂)Cl] Cl	Orange red	13.52	28.90	21.95	16.15	13.51	28.91	22.03	16.29	13.51	28.91	22.03	16.29	diamagnetic	116.5 ^a
10. [Co(maiuH) ₂ (NO ₂)(H ₂ O)] SO ₄	Red	12.92	27.91	15.92	21.32	13.05	27.95	15.97	21.29	13.05	27.95	15.97	21.29	diamagnetic	112.8 ^a
11. [Co(eaiuH) ₂ (NO ₂)(H ₂ O)] SO ₄	Red	12.15	26.31	20.12	20.11	12.30	26.31	20.04	20.04	12.30	26.31	20.04	20.04	diamagnetic	116.8 ^a

aiu = N'-amidinoisourea, maiuH = O-methyl-N'-amidinoisourea (protonated), eaiuH = O-ethyl-N'-amidinoisourea (protonated).

^a In water at 0°C.

^b In methanol at 0°C.

water-methanol below 25°C and are less susceptible to acids than the corresponding nitrosyls.

RESULTS AND DISCUSSION

The nitrosyl chlorides are 1:1 electrolytes in water-methanol at 0°C and the former precipitates only one chloride ion per molecule with silver nitrate solution. All these compounds undergo aerial oxidation to produce the corresponding nitrocomplexes. The preparation of the nitrosyl complexes, therefore, were carried out under nonoxidizing atmosphere such as hydrogen or nitrogen.

The nitro-complexes are however, more stable and can be crystallised from aqueous or very dilute alkaline solutions. Absence of any precipitate with nitron reagent and their decomposition on boiling with dilute acids liberating NO₂ suggest the formulations as in Table I.

Comparison of i.r. bands of the nitrosyls with those of Co(III) complexes²² shows the appearance of strong new peaks in the region 1600 cm⁻¹ to 1550 cm⁻¹ which have been assigned to ν NO. Bands at \approx 1700 cm⁻¹ and \approx 1300 cm⁻¹ assigned to ν N-C-N and ring vibrations respectively^{9, 22} are shifted to lower frequency regions. This may be attributed to the electron density drift from the chelate ring to the NO group. For the nitro-complexes, strong new peaks in the range 1300 cm⁻¹–1400 cm⁻¹ are assigned to ν NO₂.²³

Electronic spectra of these complexes suggest them to be trans octahedral with d⁶ configuration of the cobalt atom (Table II). Only the nitrosyl com-

plexes and not the corresponding nitro-derivatives show charge transfer spectra (Table II). The blue shift of π - π^* bands in these complexes is probably due to lowering of π -level¹ caused by the flow of π -electron density from chelating ligands to NO via the metal atom.

Thermal analysis of the nitrosyl complexes reveal complete decomposition of the bases between ca 110°C–150°C while small endothermic changes observed in case of sulphates and chlorides in the range ca 150°C–175°C are due to loss of (H₂O + NO) and NO respectively. Co-ordination of water molecules in the sulphates is suggested by their dehydration at higher temperatures. Residues left at 175°C contain mainly Co(III) N'-amidinoisoureas with some unidentified decomposed products.

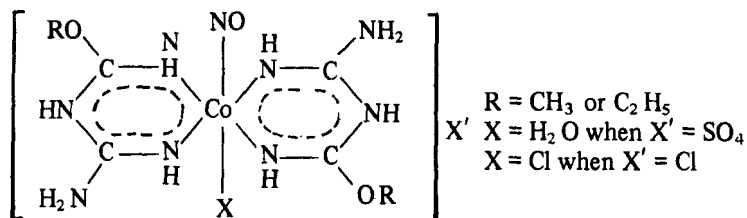
The stabilities of the nitrosyls towards bases (e.g. OH⁻, NH₃, NH₂–NH₂ etc.) and their instantaneous decomposition in presence of acids or oxidising agents (i.e. H⁺, O₂, H₂O₂ etc.) indicate the presence of comparatively high electron density on the coordinated NO group. This is also supported by spectral and magnetic data (Table I). Further on the basis of the physicochemical properties of these nitrosyl complexes containing [Co(NO)]⁸ species discussed above, it may be concluded that cobalt atom possesses d⁶ configuration with a lone pair residing on the nonbonding orbital of sp² hybridised nitrogen atom.¹⁹ The splitting of ¹A_{1g} → ¹T_{1g} band in the electronic spectra of these complexes (Table II) suggest the presence of Co(III) with trans configuration (Figure 2). The NO group is suggested to be bent, but the M-N-O angle could not, however, be determined due to lack of X-ray crystallographic data.

TABLE II
Electronic spectral data

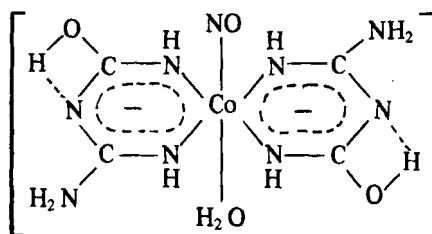
Compound	¹ A _{1g} $\xrightarrow{\nu_1}$ ¹ T _{1g} cm ⁻¹	¹ A _{1g} $\xrightarrow{\nu_2}$ ¹ T _{2g} cm ⁻¹	ν_3 C.T. spectra ^a cm ⁻¹	$\pi \xrightarrow{\nu_4} \pi^*$ cm ⁻¹
1. [Co(maiuH) ₂ (NO)(OH)]OH	16940 (2.23) 19610 (2.22)	26680 (2.28)	38910 (3.82)	46290 (4.12)
2. [Co(maiuH) ₂ (NO)Cl]Cl	16920 (2.25) 19580 (2.21)	26530 (2.27)	38850 (3.75)	46280 (4.08)
3. [Co(eaiuH) ₂ (NO)(OH)]OH	16900 (2.24) 19650 (2.25)	26480 (2.29)	38940 (3.85)	46400 (4.13)
4. [Co(eaiuH) ₂ (NO)Cl]Cl	16890 (2.23) 19610 (2.24)	26580 (2.28)	38920 (3.81)	46250 (4.15)
5. [Co(maiuH) ₃]Cl ₃	20500 (2.24)	27350 (2.28)	—	43480 (4.28)

Figures in the parenthesis indicate ϵ values.

^a Charge transfer spectra.



Co(III) O-alkyl-N'-amidinoisourea



Co(III) N'-amidinoisourea

FIGURE 2

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