

Synthesis And Physico-Chemical Investigations On Some Bis(Carbodithioato)Nitrosyl Complexes Of Cobalt(I)

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Abstract: Some bis(carbodithioato)nitrosyl complexes of cobalt(I) of the general formula $[Co(NO)(L)_2]$ ($L = 4\text{-MPipzcdt}$, 4-EtPipzcdt , $Morphcdt$ and $Pipcdt$) have been prepared and characterized by elemental analysis, molar conductance, mass, infrared, NMR (1H , ^{13}C and ^{15}N) and solution electronic absorption spectra and room temperature field dependent magnetic susceptibility measurements. The complexes are diamagnetic corresponding to cobalt(I), a d^8 system. The ligand $4\text{-MPipzcdtNa.H}_2\text{O}$ and its cobalt(I) nitrosyl complex have also been screened against some pathogenic bacteria, viz. *Escherichia coli*, *Salmonella typhi*, *Enterobacter*, *Pseudomonas aeruginosa*, *Shigella flexneri*, *S.Epidermidis* and *Salmonella typhimurium*, for assaying their antimicrobial activity.

Keywords: Heterocyclic carbodithioate, Cobalt(I), Nitric oxide, Magnetic, Spectra.

I. Introduction

A large number of transition metal complexes with various aliphatic, aromatic and heterocyclic dithiocarbamate ligands have been reported¹. Dithiocarbamates are an important class of ligands, being capable of stabilising transition metals in a wide range of oxidation states. In by far the vast majority of instances, they act merely as non-sterically demanding ancillary ligands.^{2,3} It is however, becoming increasingly clear that under certain circumstances the ligand can behave in a non-innocent fashion³ (addition of dithiocarbamates to unsaturated ligands and insertion of unsaturated groups into metal-sulphur bond(s) of dithiocarbamates).² The major advantage of using the small bite-angle of dithiocarbamate moiety as a stabilising chelating ligand, is its unique property to remain intact under a variety of reaction conditions.^{4,5} The ability of the dithiocarbamate ligands (innocent ligand) to stabilize cobalt in its low oxidation state in conjugation with π -acid ligand, i.e. nitrosyl (non-innocent ligand) has been explored in the present study with heterocyclic carbodithioate ligands. Intense interest in the chemistry and biochemistry of NO and their derivatives such as metal nitrosyl complexes is because of the strategies of these complexes to deliver NO to biological targets on demand.^{6,7} The role of biomimicry in metal nitrosyl complex systems is based on the fact they undergo one electron oxidation and reduction processes.⁸ NO, 'Molecule' of the Year, 1992, had also been proclaimed as a fundamental player in the fields of mammalian bioregulation, immunology and neuroscience. This has further stimulated intense interest in the chemistry and biochemistry of derivatives of metal nitrosyl complexes.⁹ Such type of derivatives have been studied much in detail for iron metal ion while the electronic description of cobalt complexes has not been probed as effectively as those of their iron analogues.

II. Experimental

Material and Methods

All the chemicals used were of analytical reagent grade and used as such.

III. Preparation Of Ligands:

Sodium 4-methylpiperazine-1-carbodithioatemonohydrate (4-MPipzcdtNa.H₂O), sodium 4-ethylpiperazine-1-carbodithioatemonohydrate (4-EtPipzcdtNa.H₂O) and sodium morpholine carbodithioate monohydrate (MorphcdtNa.H₂O):

Heterocyclic secondary amine (1-methylpiperazine: 1.15 g; 11.5 mmol, 1-ethylpiperazine: 1.31 g; 11.5 mmol and morpholine: 1.0 g; 11.5 mmol) in ethanol (15ml) was cooled to 5^oC. To this cooled solution, carbon disulphide (0.87 g; 11.5 mmol) was slowly added with stirring. A cream coloured (in case of 1-MPipz and 1-EtPipz) and white coloured (in case of morpholine) solid carbodithioic acid separated immediately. It was filtered, washed with ethanol and diethyl ether and air dried. To the solid carbodithioic acid, viz. 4-methylpiperazine-1-carbodithioic acid (4-MPipzcdtH), 4-ethylpiperazine-1-carbodithioic acid (4-EtPipzcdtH) and morpholinecarbodithioic acid (MorphcdtH) (1.08 g; 6.13 mmol, 1.16 g; 6.13 mmol and 1.0 g; 6.13 mmol respectively) was added sodium hydroxide (0.24 g; 6.13 mmol) dissolved in minimum quantity of water (2 ml). This resulting solution was filtered and the filtrate was evaporated to dryness on water bath. The solid sodium

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carbodithioate thus obtained was stored in a calcium chloride desiccator. 4-MPipzcdtNa.H₂O, Yield: 92 %, Decomposition temp. 268 °C, *Anal. Calcd.* for C₆H₁₃N₂S₂ONa (%) : C, 33.33; H, 6.02; N, 12.96; S, 29.43. Found: C, 33.66; H, 6.51; N, 12.52; S, 29.56. 4-EtPipzcdtNa.H₂O, Yield: 93 %, Decomposition temp. 242 °C, *Anal. Calcd.* for C₇H₁₅N₂S₂ONa (%) : C, 36.52; H, 6.65; N, 12.17; S, 27.83. Found: C, 36.74; H, 6.52; N, 12.21; S, 27.54. MorphcdtNa.H₂O, Yield: 90 %, Decomposition temp. 290 °C, *Anal. Calcd.* for C₅H₁₀O₂NS₂Na (%) : C, 29.55; H, 4.92; N, 6.89; S, 31.52. Found: C, 29.10; H, 4.98; N, 6.53; S, 31.10.

Sodium piperidine carbodithioate dihydrate (PipcdtNa.2H₂O):

Piperidine (0.977 g; 11.5 mmol) in ethanol (15 ml) was cooled to 5 °C. To this cooled solution carbon disulphide (0.87 g; 11.5 mmol) was added slowly with stirring when white solid separated. To this solid was added sodium hydroxide (0.46 g; 11.5 mmol) dissolved in minimum quantity of water (4 ml). The resulting solution was filtered and the filtrate was evaporated to dryness on water bath. The product was stored in a calcium chloride desiccator. PipcdtNa.2H₂O, Yield: 90 %, Decomposition temp. 214 °C, *Anal. Calcd.* for C₆H₁₄O₂NS₂Na (%) : C, 32.88; H, 6.39; N, 6.39; S, 29.22. Found: C, 32.93 ; H, 6.55; N, 5.99; S, 29.87.

IV. Preparation of the complexes:

[Co(NO)(L)₂] (L = 4-MPipzcdt, 4-EtPipzcdt, Morphcdt and Pipcdt):

A solution of Co(ClO₄)₂.6H₂O (0.040 g; 1.09 mmol) in 120 µl of carefully degassed ethanol was cooled to 0 °C in an ice bath and saturated with purified nitric oxide gas*. A cooled solution of (0.0472 g; 0.218 mmol for 4-MPipzcdtNa.H₂O, 0.0502 g; 0.218 mmol for 4-EtPipzcdtNa.H₂O, 0.0442 g; 0.218 mmol for MorphcdtNa.H₂O and 0.0478 g; 0.218 mmol for PipcdtNa.H₂O) in 80 µl of degassed ethanol was added to it immediately in a single lot and the mixture was stirred for 20 minutes while keeping it in the ice bath. The excess nitric oxide was removed from the system by passing nitrogen gas through the solution until no further brown fumes were observed, this stage was reached in about 2-4 minutes. The brown precipitates were obtained. Centrifugation was done to avoid losses of the complex. It was washed several times with degassed ethanol using centrifugation technique and dried in CaCl₂ desiccator. [Co(NO)(4-MPipzcdt)₂], Yield: 60 %, Decomposition temp. 240 °C, *Anal. Calcd.* for CoC₁₂H₂₂N₅S₄O (%) : C, 32.80; H, 5.01; N, 15.94; S, 29.15; Co, 13.43. Found: C, 32.91; H, 5.15; N, 15.91; S, 28.98; Co, 13.39. [Co(NO)(4-EtPipzcdt)₂], Yield: 62 %, Decomposition temp. 227 °C, *Anal. Calcd.* for CoC₁₄H₂₆N₅S₄O (%) : C, 35.97; H, 5.56; N, 14.98; S, 27.40; Co, 12.63. Found: C, 36.10; H, 5.48; N, 14.89; S, 27.55; Co, 12.31. [Co(NO)(Morphcdt)₂], Yield: 61 %, Decomposition temp. 262 °C, *Anal. Calcd.* for CoC₁₀H₁₆N₃S₄O₃ (%) : C, 29.05; H, 3.87; N, 10.16; S, 30.99; Co, 14.28. Found: C, 29.56; H, 3.81; N, 10.09; S, 30.74; Co, 14.31. [Co(NO)(Pipcdt)₂], Yield: 62 %, Decomposition temp. 190 °C, *Anal. Calcd.* for CoC₁₂H₂₀N₃S₄O (%) : C, 35.20; H, 4.88; N, 10.26; S, 31.29; Co, 14.42. Found: C, 34.97; H, 4.82; N, 10.21; S, 31.27; Co, 14.38.

*Sulphuric acid (50%) was added dropwise to a solution of 10g of KNO₂ and 5g of KI in 35ml of H₂O. The gas was washed with 90% sulphuric acid and purified by passing it through three traps of 50% KOH solution.

* 2KNO₂ + KI + H₂SO₄ → K₂SO₄ + 2NO↑ + I₂

Elemental analyses

Carbon and hydrogen analyses were performed on an automatic Coleman-33 Analyser while nitrogen was analysed by Kjeldahl's method. The cobalt metal was determined volumetrically by EDTA method using murexide indicator while sulphur was determined gravimetrically as barium sulphate.

V. Physical measurements

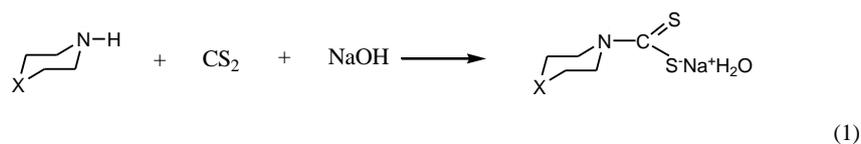
NMR spectra of the ligands 4-RPipzcdtNa.H₂O (R= M, Et) and their complexes and ¹³C and ¹⁵N spectra for [Co(NO)(4-MPipzcdt)₂] were recorded on av500 MHz spectrophotometer using (CD₃)₂SO as solvent and TMS as an internal standard. Infrared spectra of all the ligands and complexes were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4000-600 cm⁻¹ region. Infrared spectra of all the complexes were recorded as nujol mull with cesium chloride plates as windows in the 600-200 cm⁻¹ region. The mass spectra of DMSO:ACN (2 mg/10 ml) solution of the complex, i.e. [Co(NO)(4-MPipzcdt)₂] was recorded on an Agilent LCMS (6300) Ion-Trap mass spectrometer by Electron spray ionization (ESI) source having temperature of 300 °C using EMD ion detector. Molar conductance measurements (10⁻³ M DMSO solutions) were made at 25 ± 1 °C using Elico Conductivity Bridge type CM-82T. Solution (ethanol) electronic absorption spectra of the complexes with solvent as the reference, in quartz glass cells were recorded on Cary 100 Bio UV-Visible recording Spectrophotometer (range 900-200 nm) and Shimadzu UV-Visible 1700 recording spectrophotometer (range 1100-200 nm). Field dependent magnetic susceptibilities of the complexes were also measured on a Vibrating Sample Magnetometer PAR-155 (model-152).

In Vitro Antimicrobial Activity Screening:

As a preliminary screening for antimicrobial activity, compounds were tested against pathogenic bacterial strains: *Escherichia coli*, *Salmonella typhi*, *Enterobacter*, *S.Epidermidis*, *Psuedomonas aeruginosa*, *Shigella flexneri* and *Salmonella typhimurium*. Stock solutions (1000 µg/ml) of the ligand, (4-MPipzcdtNa.H₂O) and its metal complex were prepared in DMSO. Quantitative antibacterial activities of the compounds were determined using 2-fold serial dilution method. MIC was considered minimum inhibitory concentration of test compound that inhibited visible growth of bacteria after 24 h incubation at 37 °C. Uniform volume (125 µL) of nutrient broth was dispensed in all the wells of 8 rows of 96 Well Cell Culture Plate. Pure DMSO (125 µL) as blank solvent was taken in the first column of the culture plate. Afterwards 125 µL (1000 µg/ml conc.) of the solution of the test sample was added to the second well of all the seven rows of the culture plate except the eighth row (resultant concentration of test sample = 500 µg/mL). Serial dilution method was applied to the remaining wells of all the seven rows, so as to achieve the serial concentrations, viz. 250 µg/mL, 125 µg/mL, 62.5 µg/mL, 31.25 µg/mL, 15.62 µg/mL, 7.81 µg/mL, 3.90 µg/mL, 1.95 µg/mL, 0.975 µg/mL and 0.486 µg/mL in each row. Uniform volume of inoculum (10 µL) of particular test organism was added to each row except for the control (blank) which receives only the nutrient broth and DMSO. The eighth row of the culture plate was used for the reference drug, i.e. Penicillin. The inoculated culture plates covered with lids were incubated at 37°C for 20-24 hr in shaker at 162 rpm. The growth was compared with that of control culture by measuring the absorbance at 620 nm after 20-24 hr on Shimadzu-1700 UV-Vis spectrophotometer. The results were compared with that of Penicillin, a standard broad-spectrum antibiotic for bacterial strains. Blank tests have shown that DMSO in the preparation of the test solution does not affect the results.

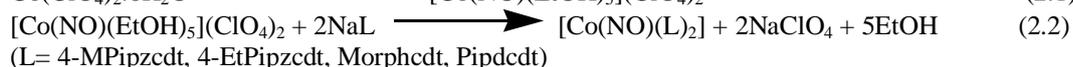
VI. Results and Discussion

Sodium carbodithioate ligands of heterocyclic secondary amines were obtained according to the (Equation.1).



- 1-MPipz : X= N-CH₃
- 1-EtPipz : X= N-CH₂CH₃
- Morph : X= O
- Pipd : X= CH₂

Nitrosyl complexes with empirical formula [Co(NO)(L)₂] (L=4-MPipzcdt, 4-EtPipzcdt, Morphcdt and Pipdcdt) deduced from elemental analysis data were synthesized following the reactions¹⁰ (Equation 2.1, 2.2).



All the complexes do not melt but decompose between (190-290 °C).The complexes are sparingly soluble in ethanol, have some solubility in methanol and are fairly soluble in DMSO.

Molar Conductance Studies:

The 10⁻³ M DMSO solution of complexes exhibits molar conductance values between (15-24 ohm⁻¹ cm² mol⁻¹) (Table-1) which reveal non-electrolytic and, therefore, non-conducting nature of all the complexes.

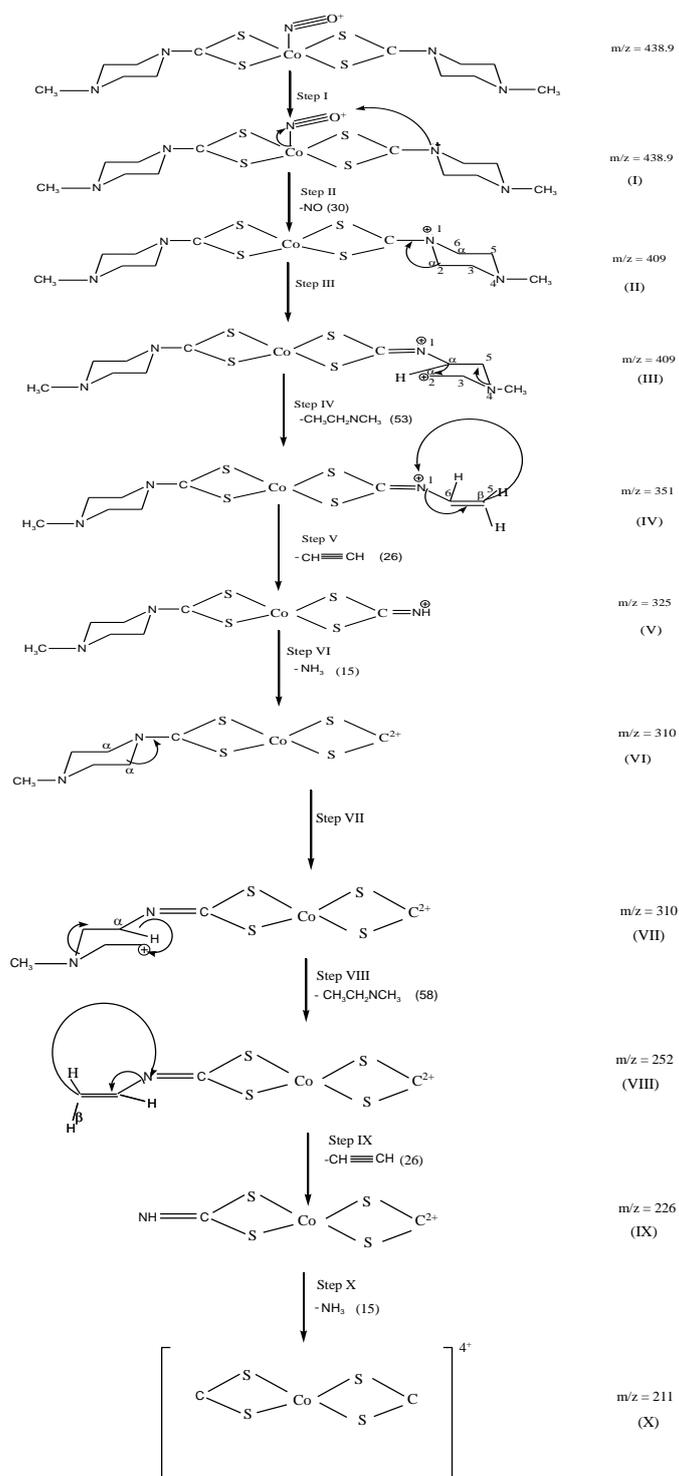
Mass Spectra:

An interesting fragmentation pattern for the complex, as illustrated in Scheme-1 reveals the presence of molecular ion peak due to [Co(NO)(4-MPipzcdt)₂]⁺ of m/z=438.9 (53.1 %). ⁵⁹Co isotope has 100% natural abundance.

(Figure1) shows the mass fragmentation pattern of ions. The ionization resulting into monocation radical formation leaves positive charge on the nitrogen atom. This is followed by Co-NO bond cleavage wherein nitrogen of NO takes away alongwith its lone pair of electrons as well as radical electron from the nitrogen of the ring (Step-II) and cation (II) is formed. This is in consonance with the fact that nitrosyl ligand is formally regarded sometimes as NO⁺, sometimes as NO⁻, but is usually eliminated as stable neutral oxide, NO (ligands with formal charge can be eliminated as stable neutral molecule comparatively easily).¹¹ The cation (II) fragmentation starts with cleavage of the α-bond, shift of the electron density and formation of a double bond between this nitrogen atom and the carbon atom of the dithiocarbamate group, such that obtained cation (III) and the cation (II) have the same relations of m/z = 409 (19.14 %) but with different structures. The cation (IV), m/z= 351(15.95 %) for complex, is a result of intermolecular rearrangement prior to fragmentation, involving migration of the α-hydrogen atom across the six member heterocyclic ring of 4-MPipzcdt ligand, followed by

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simultaneous cleavage of 4-5 bond. Then cation (IV) get generated consequence upon loss of the $\text{CH}_3\text{CH}_2\text{NCH}_3$ fragment. Next step involves the movement of the β -hydrogen atom, alongwith the bond electron pair to the nitrogen atom of cation (IV), followed by cleavage of the 1-6 bond. This is facilitated by stabilization of the resulting highly pronounced peak at $m/z=325$ (100 %). This intensive ion (V) represents the base peak of the complex. Formation of cation (V), occurs upon elimination of ethyne. In the next step ion (VI) corresponding to peak at $m/z=310$ (1.06 %) corresponds to the fragmentation of ammonia and formation of cation (VI). The mass ion peak at $m/z=310$ indicates the elimination of one of the heterocyclic rings of 4-MPipzcdt ligand. Afterwards exactly same fragmentation behaviour has been observed for the second heterocyclic ring of 4-MPipzcdt ligand from the cation (II) (Step-III), exhibiting intermediate ions at $m/z=252$ (72.3 %), $m/z=226$ (19.14 %) and $m/z=211$ (2.12 %), with the formation of cation, i.e. $[\text{Co}(\text{CS}_2)_2]^{4+}$, $m/z=211$ as the apparent final product.¹²



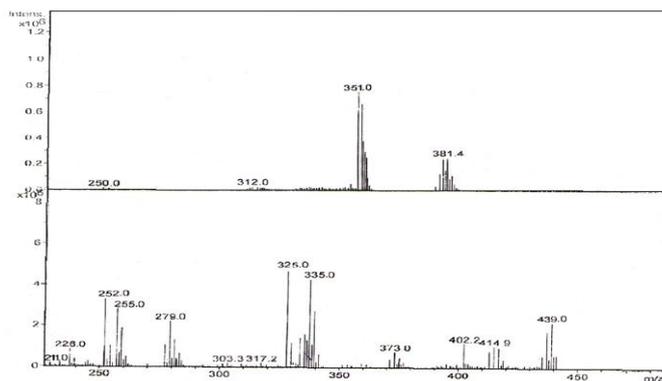


Figure 1 : Mass spectrum of [Co(NO)(4-MPipzcdt)₂]

VII. Infrared Spectral Studies:

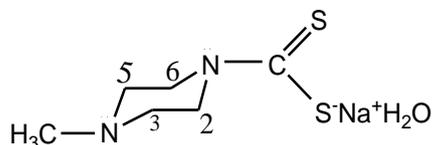
In all the cobalt nitrosyl carbodithioates the $\nu(\text{C}=\text{N})$ band has been observed at higher energies around (1489-1500 cm^{-1}) in comparison to free ligands (1450-1467 cm^{-1}) (Table-1). The rise in C-N stretching frequency has been attributed to a considerable double bond character of the $\text{C}=\text{N}$ bond in the complexes.¹³ Observation of two bands in the region 960-1015 cm^{-1} (separated by less than 20 cm^{-1}) for the antisymmetric ν_a (SCS) vibration and one band for the symmetric ν_s (SCS) stretch in the region 663-686 cm^{-1} (Table-1) in the IR spectra of complexes, suggest the unsymmetrical chelating bidentate mode of coordination to the metal ion.¹⁴ In the far-IR spectra of the complexes, additional bands in the 366-360 cm^{-1} region as compared to the free ligands, ascribable to the $\nu(\text{Co-S})$ stretching mode have been observed.^{15, 16} In addition all the complexes exhibit three peaks in the region 291-315 cm^{-1} , because of (Co-NO) absorptions possibly reflecting the threefold Co-N-O disorder corresponding to bent Co-NO binding mode¹⁷ (in contrast for the M-NO stretching region, the complexes exhibit a single sharp peak for the ordered linear M-NO group). For the free intermediate, i.e. [Co(NO)(EtOH)₅](ClO₄)₂ (Equation 2.2) (obtained by passing NO through degassed ethanolic solution of Co(ClO₄)₂.6H₂O), the ν_{NO} appears at 1687 cm^{-1} as a strong band, while this band has shifted to lower energy in the complexes [Co(NO)(cdt)₂] because of the increased electron density due to the carbodithioate ligand, which results into the increased back bonding from metal to the NO⁺ and weakening of the N≡O bond. The band in the complexes, lie in the range 1657-1639 cm^{-1} which is the range for the bent NO ligand. Such an observation has earlier been made for [Co(NO)(S₂CNMe₂)₂] being elucidated using X-ray crystallography study.^{8, 17, 18} The complex also exhibits ν_{NO} at 1630 cm^{-1} , for its bent Co-NO linkage.

Table 1: Some coordinatively diagnostic features of infrared spectra (cm^{-1}) and molar conductance values, Λ_m ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of various carbodithioate ligands and their cobalt nitrosyl complexes.

Sr. No.	Compound	$\nu(\text{N-H})/(\text{O-H})$	$\nu(\text{C-H})$ (H ₃ C-N or H ₃ C ₂ -N)	$\nu(\text{C}=\text{N})$	$\nu_a(\text{SCS})$	$\nu_s(\text{SCS})$	$\nu(\text{N}=\text{O})$	$\nu(\text{Co-S})$	$\nu(\text{Co-N})$	Λ_m
1.	4-MPipzcdtNa.H ₂ O	3460-3160 b,s	2808 s	1455 s	989 s, 971 m	686 w	-	-	-	-
2.	4-EtPipzcdtNa.H ₂ O	3465-3160 b,s	2818 s	1460 s	997 s, 1015 m	680 w	-	-	-	-
3.	MorphcdtNa.H ₂ O	3415-3310 b,s	-	1450 s	980 s, 996 m	678 w	-	-	-	-
4.	PipcdtNa.2H ₂ O	3400-3160 b,s	-	1467 s	964 s, 982m	670 w	-	-	-	-
5.	[Co(NO)(4-MPipzcdt) ₂]	-	2859 s	1491 s	985 s, 968 m	679 w	1649	365	296, 302, 313	20
6.	[Co(NO)(4-EtPipzcdt) ₂]	-	2865 s	1495 s	995 s, 1012 m	672 w	1639	366	298, 305, 315	19
7.	[Co(NO)(Morphcdt) ₂]	-	-	1489 s	973 s, 991 m	671 w	1655	363	295, 300, 310	24
8.	[Co(NO)(Pipcdt) ₂]	-	-	1500 s	960 s, 977m	663 w	1657	360	291, 295, 307	15

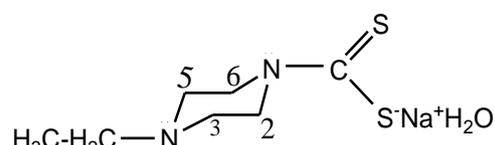
Proton NMR Spectra:

The free ligands, viz. 4-MPipzcdtNa.H₂O and 4-EtPipzcdtNa.H₂O (a,b) in their proton NMR spectra exhibit the resonance signals: two overlapping triplets due to 2,6 and 3,5 -CH₂ protons of the heterocyclic rings of 1-MPipz at δ 3.70-3.74 ppm and 1-EtPipz at δ 2.46 ppm of the corresponding carbodithioate ligands, (Table-2). Methyl of H₃C-N< group of 4-MPipzcdtNa.H₂O has been observed to exhibit a singlet at δ 2.93 ppm. The protons of -CH₃ and -CH₂ moieties of H₃C-CH₂-N< group in 4-EtPipzcdtNa.H₂O have appeared as a triplet at δ 0.97-1.01 ppm and as a quartet at δ 2.35-2.40 ppm respectively. Another broad band at δ 4.28 ppm and δ 4.25 ppm has also been observed in both the carbodithioate ligands. This has been attributed due to the lattice water.



(4-MPipzcdtNa.H₂O)

(a)



(4-EtPipzcdtNa.H₂O)

(b)

In the ¹H NMR spectra of the complexes, [Co(NO)(4-RPipzcdt)₂] (Figure.2) separate triplets due to 2,6 methylene at (δ 3.73-4.00 ppm when R=M; δ 2.49-2.72 ppm when R=Et) and 3,5 methylene at (δ 3.05-3.20 ppm when R=M; δ 1.81-1.96 ppm when R=Et) have been observed on the downfield and upfield sides respectively in comparison to the free ligands (Table-2). Resolution of the two above said signals in the ¹H NMR spectra of the complexes under study in comparison to the free ligands may result because of the hindered rotation of the S₂C=N group of the 4-MPipzcdt and 4-EtPipzcdt ligands.¹⁹ Upon coordination as the partial positive charge on the nitrogen increases and hence the C=N vibrational frequencies, [Co(NO)(4-EtPipzcdt)₂] (1495 cm⁻¹) > [Co(NO)(4-MPipzcdt)₂] (1491cm⁻¹), the deshielding of the N-bonded methylene protons in the complexes under study also increases,^{16,20} indicating coordination of the 4-RPipzcdt ligand to the metal ion has been found to cause a deshielding of 2,6 methylene protons and a downfield shift has been observed, while the upfield shift of 3,5 methylene protons inferred increase in electron density because of drainage of the charge from the electron releasing nature of the methyl group of H₃C-N< in [Co(NO)(4-MPipzcdt)₂] and ethyl group of H₃C-CH₂-N< in [Co(NO)(4-EtPipzcdt)₂].

Table 2. ¹H NMR spectral data, δ(ppm) for sodium 4-methylpiperazine-1-carbodithioate monohydrate, sodium 4-ethylpiperazine-1-carbodithioate monohydrate and their cobalt nitrosyl complexes.

Sr. No.	Compound	(3,5-)CH ₂ (2,6-)CH ₂	CH ₂ (C ₂ H ₅)	CH ₃ & CH ₃ (C ₂ H ₅)
1.	4-MPipzcdtNa.H ₂ O	3.70-3.74(t,8H:2,3,5,6-H ₂)	-	2.93 (s,3H)
2.	4-EtPipzcdtNa.H ₂ O	2.46 (t,8H : 2,3,5,6-CH ₂)	2.35-2.4(q,2H)	0.97-1.01 (t,3H)
3.	[Co(NO)(4-MPipzcdt) ₂]	3.05-3.20 (t,4H) 3.73- 4.00 (t,4H)	-	3.0-3.05 (s,3H)
4.	[Co(NO)(4-EtPipzcdt) ₂]	1.81-1.96 (t,4H) 2.49-2.72 (t,4H)	2.36-2.4(q,2H)	0.98-1.09 (t,3H)

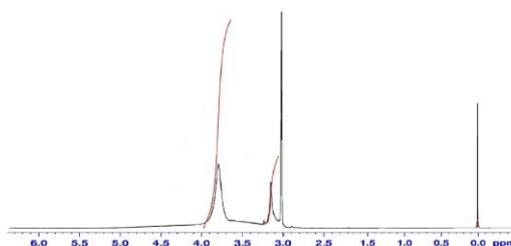


Figure 2 : ¹H NMR spectrum of [Co(NO)(4-MPipzcdt)₂]

¹³C NMR Spectra:

¹³C NMR spectrum of the complex (Figure 3) exhibits a sharp signal at δ 193.07 ppm due to >NCS₂, i.e. thiocarboxylato carbon, indicating coordination of sulphur atoms to the cobalt metal ion. This range of ¹³C signal for >NCS₂ group for its binding to the metal ion has also been reported by Rehman et al.²¹ ¹³C NMR signals due to 2,6-methylene (-CH₂) carbon atoms at δ 40.37-40.53 ppm, 3,5-methylene (-CH₂) carbon atoms at δ 40.04-40.21 ppm and CH₃ carbon at δ 39.71-39.87 ppm have also been observed to lie in the range for the respective carbon atoms of the heterocyclic ring.^{16,22} (Table-3).

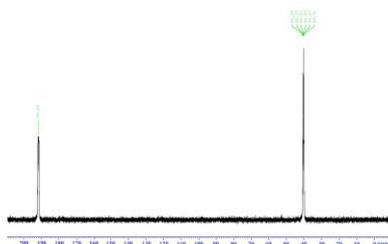


Figure 3: ¹³C NMR spectrum of [Co(NO)(4-MPipzcdt)₂]

¹⁵N NMR Spectra:

Generally, ¹⁵N chemical shifts in NO⁻ species are significantly more deshielded than those in NO⁺ systems, δ_N for NO⁻ in M-N-O systems ranging from about 950 to 350 ppm and for NO⁺ systems from about 200 to -110 ppm⁸.

In the present complex, i.e. Co(NO)(4-MPipzcdt)₂ we have observed a band (Figure 4) at δ 202.57 ppm corresponding to ¹⁵N NMR of NO⁺ group (Table-3). Nitrogen atoms of the heterocyclic rings of 4-MPipzcdt ligand i.e. (>S-C-N) have appeared at 106.25 ppm while CH₃-N< at 53.11 ppm which were in accordance with the range reported for the N atoms by Joan Mason et al.²³

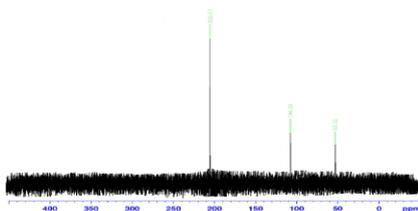
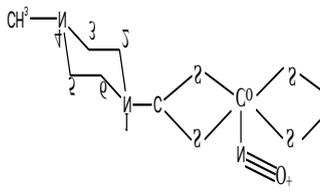


Figure 4 : ¹⁵N NMR spectrum of [Co(NO)(4-MPipzcdt)₂]

Table 3. ¹³C and ¹⁵N NMR spectral data, δ(ppm) for Bis(4-methylpiperazine-1-carbodithioato)nitrosonium cobalt(I).

Complex	Ring Carbon				Substituent Carbon		
	C-2	C-6	C-3	C-5	>N-CH ₃ (C)	>S ₂ CN (C)	
 [Co(NO)(4-MPipzcdt) ₂]	δ40.37-40.53		δ40.04-40.21		δ39.71-39.87	δ 193.07	
	Ring Nitrogen					NO ⁺ (N)	
	N-1		N-4		δ 202.57		
	δ 106.25		δ 53.11				

Magnetic Study:

Room temperature and magnetic field dependent magnetic susceptibility measurements of the cobalt nitrosyl carbodithioate complexes, exhibit magnetic moment values in the range 0.02 B.M – 0.08 B.M. The μ_{eff} values lying near to zero and their non-variation with the increasing/decreasing strength of the magnetic field reveal diamagnetic nature of the complexes. The magnetic study further predicts that metal, i.e. cobalt is in +1 oxidation state, which correspond to a d^8 system. The diamagnetism arises because of the pairing of electron spins in the low lying molecular orbitals of the complex with electronic configuration $(d_{xy})^2, (d_z)^2, (d_{yz})^2$ & $(d_{xz})^2$ in a low-spin distorted square pyramidal geometry.²⁴

Electronic Spectra:

The electronic absorption spectra of the complexes, with bent $\{M(NO)\}^8$ and different basal carbodithioate ligands has been explained using the orbital ordering due to Paul A.Duffin et al.²⁴ and Joan Mason et al.²³ Thus, the low spin (singlet state) will have the electronic configuration $(d_{xy})^2, (d_z)^2, (d_{yz})^2, (d_{xz})^2$. This configuration would leave the $\pi^*(NO)$ group orbitals unoccupied. Ethanolic solution electronic absorption spectra of the complexes exhibit four bands which fall in the regions (I) 11,813-11,715 cm^{-1} , (II) 13,741-13,685 cm^{-1} , (III) 15,420-15,330 cm^{-1} and (IV) 20,422-20,361 cm^{-1} . These have been assigned to the transitions, i.e. $d_{xz} \rightarrow \pi^*NO$, $d_{yz} \rightarrow \pi^*NO$, $d_z^2 \rightarrow \pi^*NO$ and $d_{xy} \rightarrow \pi^*NO$ respectively. A d-d band corresponding to the transition $d_{xy} \rightarrow d_{x^2-y^2}$ has also been observed in the range 30,687-30,634 cm^{-1} . These electronic spectral band assignments reveal that the low spin cobalt(I) d^8 complexes with $\{Co(NO)\}^8$ under study, have square pyramidal geometry.

Biological Studies:

Antimicrobial studies of free ligand, 4-MPipzcdtNa.H₂O and its complex, $[Co(NO)(4-MPipzcdt)_2]$ against the pathogenic bacteria, *Escherichia coli*, *Salmonella typhi*, *Enterobacter*, *Psuedomonas aeruginosa*, *Shigella flexneri*, *S.Epidermidis* and *Salmonella typhimurium* using the agar dilution method gave MIC (minimum inhibitory concentration) values in the range 125-500 $\mu\text{g/mL}$ and 31.25-125 $\mu\text{g/mL}$ respectively (Table-4) and reveal them to be moderate antibacterial agents. A decrease in the MIC value upon complexation or the high activity of the cobalt complexes surmounting that of free ligands showed that complexation of the organic ligand and nitrosonium ion to cobalt ion substantially enhances the activity against the pathogenic microbial strains.

Table 4. Antimicrobial activity of some of the compounds.

Compound	Minimum Inhibitory Concentration ($\mu\text{g/mL}$)						
	<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Enterobacter</i>	<i>Staphylococcus epidermidis</i>	<i>Psuedomonas aeruginosa</i>	<i>Shigella flexneri</i>	<i>Salmonella typhimurium</i>
4-MPipzcdtNa.H ₂ O	500.00	125.00	250.0	500.00	250.00	500.0	125.00
$[Co(NO)(4-MPipzcdt)_2]$	62.50	31.25	31.25	125.00	31.25	62.50	62.50
DMSO	—	—	—	—	—	—	—
Penicillin	—	—	—	—	—	—	—

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Scheme Caption:

Scheme 1: Showing fragmentation pattern of [Co(NO)(4-Mpipzcdt)₂]

Figure Captions:

Figure 1 : Mass spectrum of [Co(NO)(4-MPipzcdt)₂].

Figure 2 : ¹H NMR spectrum of [Co(NO)(4-MPipzcdt)₂].

Figure 3 : ¹³C NMR spectrum of [Co(NO)(4-MPipzcdt)₂].

Figure 4 : ¹⁵N NMR spectrum of [Co(NO)(4-MPipzcdt)₂].