

Full Length Research Paper

Vitamin B₁₂ models: Synthesis and characterization of cyano bridged dicobaloximes and antimicrobial activity

Bakheit Mustafa Mohamed Salih and S. Satyanarayana*

Department of Chemistry, Osmania University, Hyderabad, 500007. Andhra Pradesh, India.

Accepted 15 June, 2009.

Reactions of the cyanide complexes of the type $\text{Co}(\text{CN})(\text{DH})_2\text{L}$ moiety (where L = thiourea, acetamide, formamide, semicarbazide, pyrazole and aniline; DH = dimethylglyoxime) with the corresponding benzyl(aqua)cobaloxime $\text{PhCH}_2\text{Co}(\text{DH})_2\text{OH}_2$ gives a series of homometallic cyano-bridged compounds of the type $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$. All these complexes have been synthesized and characterized by means of IR, LC/MS, ^1H , ^{13}C NMR and (C, H, N) analysis as well as their antimicrobial activities. The formation of cyanide bridge is evident from the IR spectra by the appearance of $\nu(\text{CN})$ shifts with respect to the mononuclear parent complex.

Key words: Cyano-bridged, bimetallic complexes, antimicrobial activity.

INTRODUCTION

It is well known that the cyanide ion can connect two metal ions as a bridging ligand. Linear cyanide-bridged bimetallic complexes of the type $\text{M}-\text{CN}-\text{M}$ have been extensively studied (Rigo and Turco, 1974; Davies et al., 1985; Mohan et al., 1987; Deeming and Proud, 1988; Darensbourg et al., 1996; Ramsharan and Dikshit, 1993). Cyanide-bridged, dinuclear transition metal compounds are widely used in the areas of electron delocalization and charge transfer studies (Zhou et al., 1990; Agnus et al., 1989; Burewicz and Haim, 1988; Chrisstofides et al., 1990; Scandola et al., 1993). The most successful and often the sole strategy for preparing these materials still consists in assembling building blocks, usually transition metal complexes, one having potential bridging ligands with another species possessing empty or available coordination sites. This ambidentate behavior is evident in cyanide compounds of the main group (Kawai and Kanetsaka, 1969) elements and transition metal complexes. The-cyano bridged dimetal systems have been of interest since the early recognition that ligand bridged complexes play an important role in inner-sphere electron transfer reaction (Paul and Alvin, 1976). For example; remarkable degrees of metal-metal electronic coupling can be observed across cyanide bridges (Scandola et al., 1993).

This synthetic strategy has been often utilized to provide a general route to synthesize neutral dinuclear

cyano-bridged complexes and this strategy consists in protecting the equatorial positions of the metal atoms with a planar pseudo macrocyclic group and carry out ligand substitution reactions on axial positions leading to bridge formation, thus avoiding undesired side reactions usually observed when preparing cyano-bridged complexes, such as $\text{cis} \rightarrow \text{trans}$, isomerization (Ribas et al., 1980; Ribas et al., 1979). In this study, we describe the synthesis of cyano-bridged dinuclear complexes formed from the reaction between the appropriate $\text{Co}(\text{CN})(\text{DH})_2\text{L}$ and $\text{PhCH}_2\text{Co}(\text{DH})_2\text{OH}_2$ fragment (DH = dimethylglyoxime).

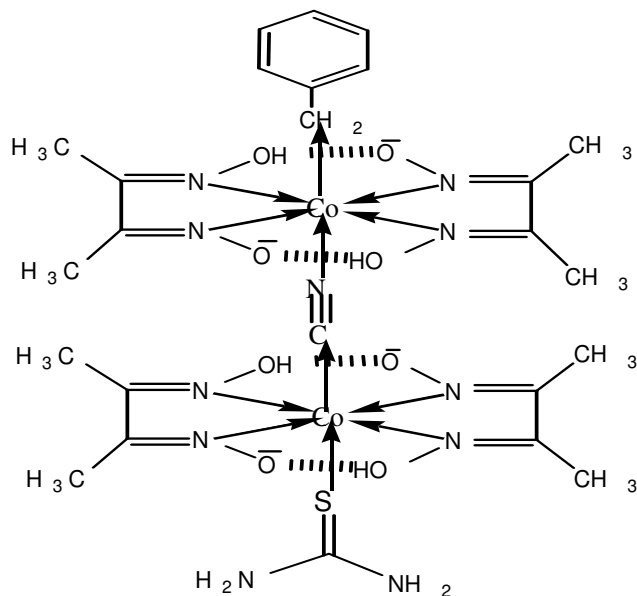
Experimental

All chemicals and solvents used for the synthesis were of reagent grade. Infrared spectra were recorded on Perkin-Elmer FTIR-1600 spectrophotometer in the range $4000-400\text{ cm}^{-1}$ as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a GE QE 300 NMR spectrometer at 25°C using a 5 mm broad band probe. Samples were prepared by dissolving 25-50 mmoles in $\text{DMSO}-d_6$. Elemental analyses were carried out using a Perkin-Elmer 2400 elemental analyzer.

Preparation of $\text{K}[\text{NCSCo}(\text{DH})_2\text{SCN}]$

This complex was prepared by the method of Ablov and Syrtsova (Ablov and Syrtsova, 1975; Crumbliss and Gaus, 1975) which was converted to $[\text{NH}_3\text{Co}(\text{DH})_2\text{SCN}]$ by treatment with concentrated NH_4OH as described by Crumbliss and Gaus (1976). This ammonia complex was treated with an equimolar amount of KCN dissolved in minimum amount of water to obtain the salt $\text{K}[\text{Co}(\text{CN})(\text{DH})_2\text{SCN}]$ in 80% yield. Then this potassium salt of cyano

*Corresponding author. E-mail: ssnsirasani@yahoo.com. Tel.: 91-40-23234231 or 09246521145.

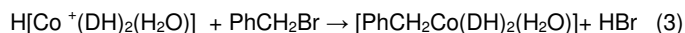
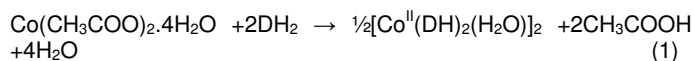


Structure 1. Cyano bridged benzyl thiourea dicobaloximes.

trans to SCN complex was dissolved in ethanol. To this an ethanolic solution of the ligand L (L= thiourea, acetamide, formamide, semicarbazide, pyrazole and aniline) was added. A slightly modified method of Crumbliss and Gaus (1976), Brown and Satyanarayana (1992) was used to prepare the above complexes.

Preparation of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{L}$

$\text{PhCH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}$ was prepared using the procedure of Brown et al (1972).



All manipulations were performed under minimal illumination due to photolability of the organo-cobalt bond and the solutions were covered with aluminum foil. $\text{PhCH}_2\text{Co}(\text{DH})_2\text{L}$ complexes were isolated by mixing 1:1 of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}$ and the base ligand in methanol. This mixture was heated at 40-50°C by constant stirring for 1-2 h. Then the minimum amount of distilled water was added, then the resulting precipitate of brown powder was filtered, washed with distilled water 95% methanol and ether and dried in vacuo (yields were 75-85%).

Preparation of cyano bridged dicobaloxime

Cyano bridged dicobaloxime was synthesized as follows²²: 2×10^{-4} moles of $\text{PhCH}_2\text{Co}(\text{DH})_2(\text{OH}_2)$ was dissolved in a minimum amount of chloroform at 40°C to give an orange solution, to this an equimolar concentration of the complex $\text{Co}(\text{CN})(\text{DH})_2\text{L}$ dissolved separately in a minimum amount of chloroform at 40°C is added. The two solutions were mixed and stirred constantly at 40-50°C for one hour. The solvent was removed under reduced pressure to give a yellow powder, which was washed with water and 90% of methanol, ether and dried in vacuo to give the product $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$

(Structure 1).

Antimicrobial activity

Anti-microbial activities of the dibridged cyanocobaloximes were determined *in vitro* using different microorganisms by the standard serial dilution method. All the bacterial cultures were maintained in nutrient broth at 37°C. The culture was inoculated into nutrient broth and incubated for 18 h at 37°C. The culture was then given three passages before it was used to determine minimum bactericidal concentration. All the complexes were tested for their antibacterial activity by the zone of inhibition assay. For this purpose, filter paper discs of 5 mm diameter were prepared from Whatman No.1 filter paper; 15 $\mu\text{mol/L}$ solutions of dimetallic complexes dissolved in methanol were added. At the end of the incubation period, the zones of the inhibitions were measured.

RESULTS AND DISCUSSION

Spectral analysis

In this paper we have reported the complexes of the type $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$ (were L = thiourea, acetamide, formamide, semicarbazide, pyrazole and aniline). The electronic spectra of cyano bridged dicobaloximes in methanol solution exhibit a weak absorption band at 22624cm^{-1} , where as strong absorption appears at 22624cm^{-1} in the $\text{PhCH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}$. The disappearance of peak at 22624cm^{-1} confirms the replacement of H_2O during the formation of dinuclear bridged cobaloximes. The UV- visible absorption maximum of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{L}$ is 22624cm^{-1} . This is assigned to cobalt-carbon ($\text{PhCH}_2 \rightarrow \text{Co}$) sigma bond similar visible absorption maximum is present in the electronic spectra of the cyano bridged dinuclear cobaloximes at 22624cm^{-1} with very low intensity, thus one of the cobalt centers in the cyano bridged binuclear cobaloximes must simultaneously be coordinated by PhCH_2 and a trans donor ligand (L). This can be true if these complexes possess the -CN- linkage isomeric structure (1) where one side cobalt is coordinated to PhCH_2 and the other coordinated to atom of (N, O or S) donor ligand (L) and both the cobalt's bridged through -CN- ligand. Therefore we should expect the spectrum of the bridged dicobaloximes to be approximately the sum of the monomeric benzyl and cyano cobaloximes.

Infrared spectra

The cyano-bridged complexes were synthesized by reacting stoichiometric amounts of two different complementary mononuclear complexes, one containing the terminal cyano group and the other a weakly coordinated water molecule. The infrared spectra of each of these cyano-bridged complexes have been characterized in the solid state as pressed solid KBr disks. The infrared spectra of the products show no absorptions attributed to coordinated H_2O , this proves that it is the H_2O ligand in

Table 1. IR spectral data of $\text{Co}(\text{DH})_2\text{CN}(\text{L})$ and the $\nu(\text{C}\equiv\text{N})$ of dibridged cobaloxime complexes.

Complex	(C=N)*	$\nu(\text{C}\equiv\text{N})^{**}$	NO	CH ₃	OH	C=N	Co-N
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{TU}$	2107.2	2174	1229	1326	1772	1557	511
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{FA}$	2108.3	2175	1232	1324	1707	1560	512
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{AC}$	2108.0	2138	1232	1364	1684	1558	513
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{SC}$	2108.3	2127	1283	1379	1656	1555	511
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{PY}$	2112.5	2170	1235	1367	1680	1557	513
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{AL}$	2109.4	2142	1232	1336	1705	1542	510

Recorded as KBr discs and values in cm^{-1} , where $(\text{DH})_2$ dimethyl glyoxime, TU = thio urea, FA = formamide AC = acetamide, SC = semicarbazide, PY = pyrazole, AL = alanine. $\nu(\text{C}\equiv\text{N})^*$ of monomer, $\nu(\text{C}\equiv\text{N})^{**}$ of dimer.

Table 2. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data of cyano bridged benzyl ligand dicobaloximes.

Compound	^1H NMR (δ ppm)				^{13}C NMR			
	NH ₂ /OH	CH ₃	CH ₃ *	Aromatic protons	(C≡N) of bridged complex	(C=N) of oxime	CH ₃	CH ₃ *
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{TU}$	NH ₂ = 8 OH = 11.5	1.97	1.99	6.76-8.30	125	154	11.68	12.53
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{FA}$	NH ₂ = 8.1 OH = 11.6	1.95	2.2	6.80-8.36	127	153.4	10.4	10.66
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{AC}$	NH ₂ = 7.6 OH = 10.9	1.98	2.1	6.77-8.31	129	154	9.8	11.2
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{SC}$	NH ₂ = 7.7 OH = 11.4	2.05	2.2	6.82-8.22	130	152	10.6	12.4
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{PY}$	NH ₂ = 7.4 OH = 11.6	1.98	2.3	6.75-8.26	128	151.4	12.0	13.1
$\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{AL}$	NH ₂ = 7.6 OH = 11.2	2.1	1.98	6.82-8.20	124	153.6	11.4	11.88

CH₃ of benzyl cobaloxime, CH₃* of cyano cobaloxime.

$\text{PhCH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}$ that substituted in the dinuclear combination reaction. In these dimetallic complexes, the $\nu(\text{C}\equiv\text{N})$ stretching frequency shifted to higher energies by about 12-40 cm^{-1} compared to the parent mononuclear cyano-cobalt complexes (Mohn Rao and Rymmai, 2001). Though, such shifts to higher energy have been usually attributed to the kinematic effect of constraining the CN motion by N coordination to the second metal fragment (Dows and Walmarth, 1961). An examination of the IR data (Table 1) shows that the $\nu(\text{C}\equiv\text{N})$ is highest, when the ligand is weaker donor in $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$ complexes. The reason that the bridging cyano ligands vibrates at a higher frequency than the terminal ligands may be attributed to stabilization of the (occupied) σ^*2s antibonding orbital of the bridging CN^- ligand through overlap with the Co orbitals, thus strengthening the CN bond (Bernhardt et al., 2004). In addition, a regular decrease in the $\nu(\text{C}\equiv\text{N})$ is expected as the basicity of ligand L increases. This behavior is taken here as a justification for the formulation of these dimers as cyano-bridged dicobaloximes. There is no other major difference in the infrared spectra of the reactants and the products and this has been found to be a general phenomenon.

^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra

^1H NMR spectra (Figure 1) have been determined for the dicobaloximes $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$. These data are given in Table 2. The resonances due to 12 equivalent protons of the equatorial dimethylglyoxime ligands at each of the cobalt centers of the bridged complexes are observed. ^1H NMR spectra shows a peak around 1.98-2.3 ppm for the appropriate mononuclear cobaloximes $\text{CNC}(\text{DH})_2\text{L}$ compared to $(\text{DH})_2$ methyl protons δ (1.98-2.3) ppm and where as the dimethylglyoxime methyl protons of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{H}_2\text{O}$ resonance at (1.95-2.1) ppm. ^1H NMR spectra for the axial benzyl (PhCH_2) ligand were obtained in the region δ (6.7-7.3) ppm attributable to the aromatic proton which appear almost at the same position as in the respective ligand.

The CH_2 protons of benzyl were observed in the range of 5.2 ppm in almost all of these dimer complexes. In the free ligand of amides ($\text{O}=\text{CNH}_2$) and thioamides ($\text{S}=\text{CNH}_2$) the position of NH_2 resonance occurs at about 5.7 ppm which is shifted to down field in these metal complexes due to resonance of lone pair on NH_2 with $\text{C}=\text{O}$ and $\text{S}=\text{O}$. In the complexes $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$

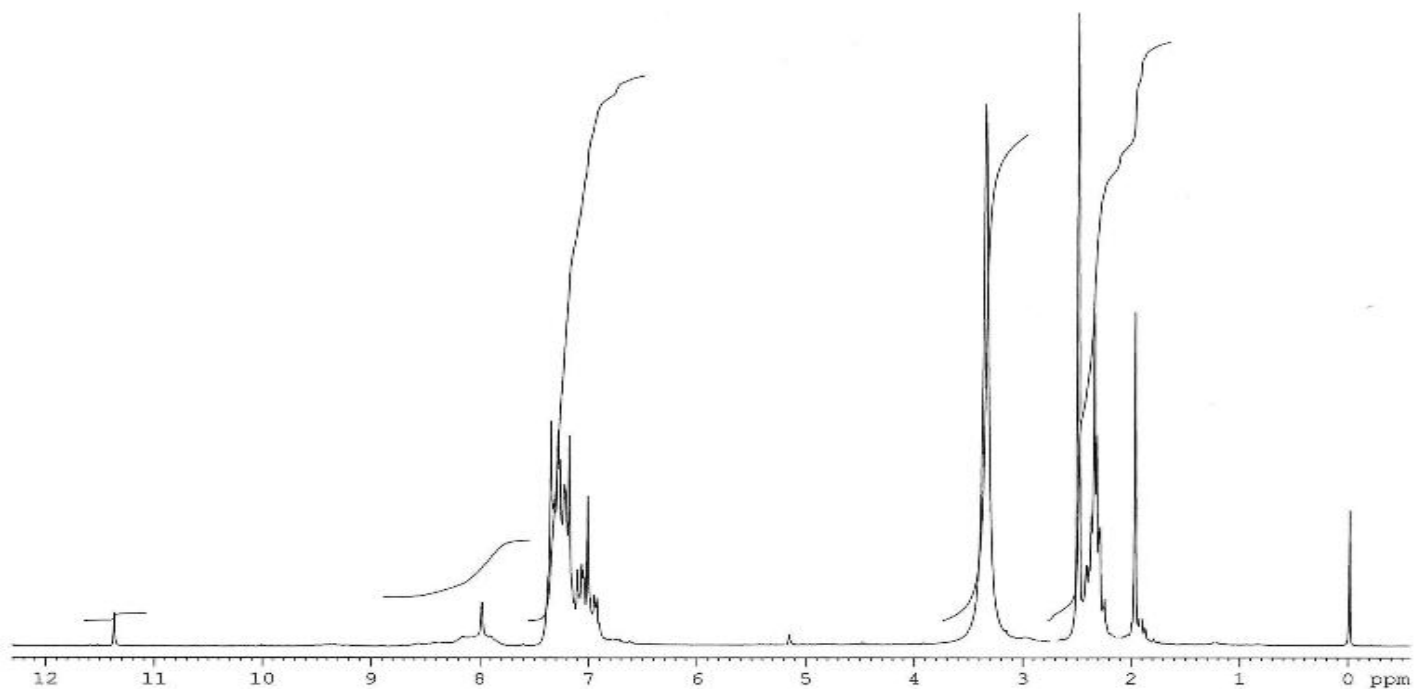


Figure 1. ^1H NMR spectrum of $\text{PhCH}_2 \text{Co}(\text{DH})_2\text{CN}(\text{DH})_2\text{TU}$ complex in $\text{DMSO-}d_6$.

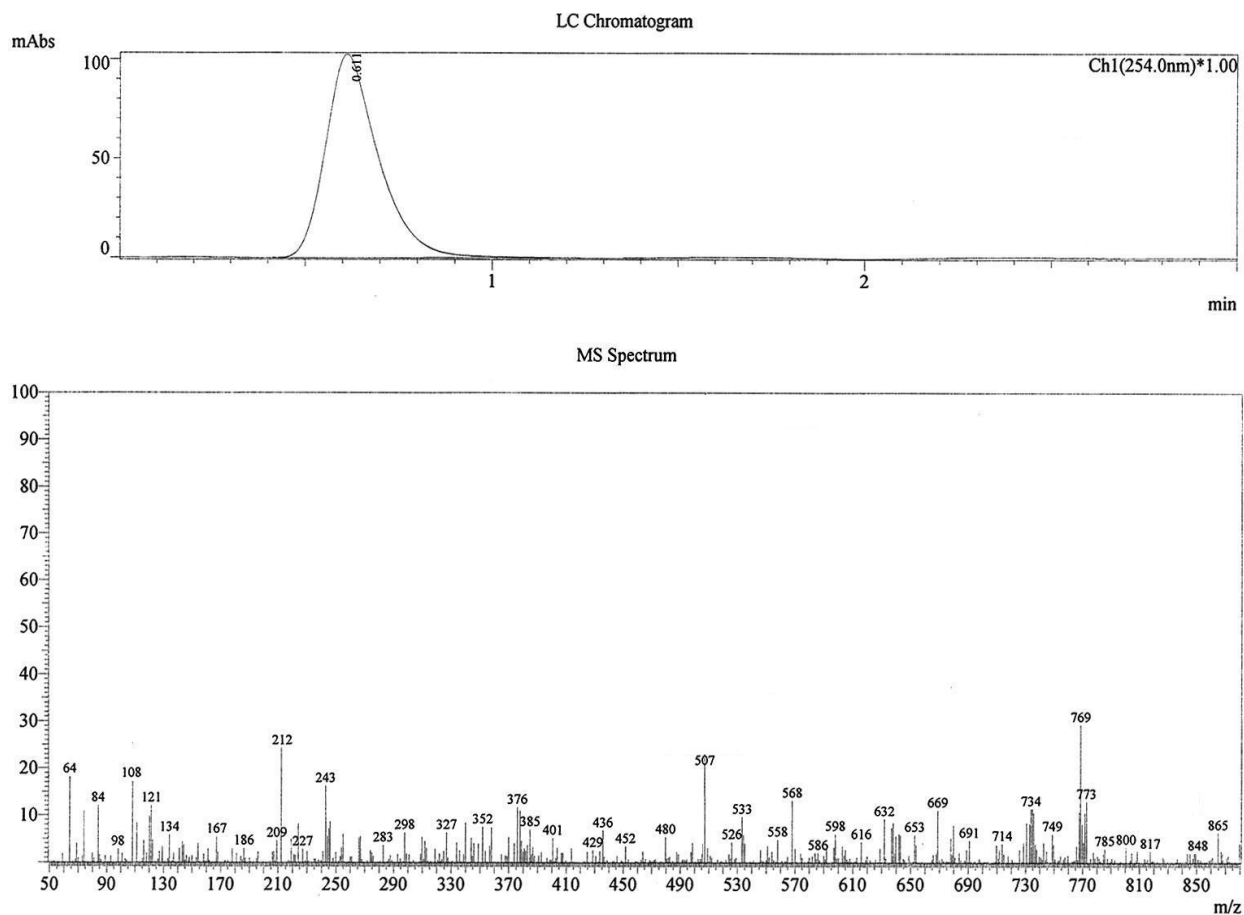


Figure 2. LC/MS analysis of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{SC}$.

Table 3. Analytical data of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$ complexes.

S. No	Complex $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$ Where L=	Formula (Mol.wt)	Found (cal) %		
			C	H	N
1	Thiourea	$\text{Co}_2\text{C}_{25}\text{H}_{39}\text{N}_{11}\text{O}_8\text{S}$	38.44	4.95	19.65
	NH_2CSNH_2	771	(38.91)	(5.05)	(19.97)
2	Acetamide	$\text{Co}_2\text{C}_{26}\text{H}_{40}\text{N}_{10}\text{O}_9$	41.21	5.17	18.13
	CH_3CONH_2	754	(41.37)	(5.30)	(18.46)
3	Semicarbazide	$\text{Co}_2\text{C}_{25}\text{H}_{40}\text{N}_{12}\text{O}_9$	38.12	5.12	21.41
	$\text{NH}_2\text{CONHNH}_2$	770	(38.96)	(5.19)	(21.81)
4	Formamide	$\text{Co}_2\text{C}_{25}\text{H}_{38}\text{N}_{10}\text{O}_9$	40.40	4.96	18.49
	HCONH_2	740	(40.54)	(5.13)	(18.91)
5	Pyrazole	$\text{Co}_2\text{C}_{27}\text{H}_{39}\text{N}_{11}\text{O}_8$	42.27	4.87	20.06
	$\text{H}_4\text{N}_2\text{C}_3$	763	(42.46)	(5.11)	(20.18)
6	Alanine	$\text{Co}_2\text{C}_{27}\text{H}_{42}\text{N}_{10}\text{O}_{10}$	40.91	5.16	18.26
	$\text{CH}_3\text{CH}_2\text{NH}_2\text{COOH}$	784	(41.32)	(5.35)	(17.85)

*Calculated values in parenthesis.

where L is acetamide, formamide and thiourea the signals at 7.7, 8.4 and 8.12 ppm respectively with a base peak at 769 m/z (Figure 2) and some are in the pyrazole complex observed that the electron donation from $\text{N} \rightarrow \text{Co}(\text{III})$ leads to pronounced deshielding of the proton adjacent to the N-2 nitrogen (Saha and Bhattacharyya, 1976). Pyrazole H_4 signal is at 6.4 ppm in the free ligand and it is slightly shifted to upfield when compared to the free ligand position, because of the loss in aromaticity due to the withdrawal of electron density from N-2 to $\text{Co}(\text{III})$ and as a result ring protons experience a higher shielding effect. When pyrazole coordinates to $\text{Co}(\text{III})$, C3-H and C5-H signals separate and give signals at 7.7 and 6.9 ppm respectively. In case of alanine, NH_2 signal observed at 5.6 ppm and shifted lightly to down field 6.2 ppm as compared to the free ligand.

It is well known that ^{13}C chemical shifts are essential for structural verification and elucidation of organometallic molecules. ^{13}C NMR of $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{L}$ showed signals for the equatorial methyls and the equatorial oxime carbons, in addition it gives a very broad and prominent resonance attributed to the bridged cyanide carbon with resonance appeared at about 124-130 ppm, which is definitely assignable to the bridged cyanide carbon (Table 2). The broadness of the ^{13}C resonance of CN^- is generally attributed to the quadrupolar relaxation by the ^{59}Co nucleus ($I = 7/2$) (Rajeshwar et al., 1999). The sharp resonances at about 12.5 ppm is due to the equatorial methyl groups and the resonance appeared at 154 ppm is attributed to the oxime carbons.

Elemental analysis

The most common type of elemental analysis is for carbon, hydrogen and nitrogen (CHN analysis). The elemental analysis of a compound is particularly useful in determining the empirical formula of the compound that

contains the smallest set integer ratios for the elements in the compound that gives the correct elemental composition by mass. The analytical data for the synthesized complexes presented in (Table 3).

LC/MS analysis

In the LCMS there is only one peak observed in all of these selected dimeric complexes having the exact average molecular weight of the analyzed compounds which suggesting the formation of only one complex. By using LC/MS analysis, it is possible to make structural predictions from the mass difference of the molecular ion and fragment ions seen in a mass spectrum. These compounds are typically dominated by a single ion that corresponds to the molecular weight of the complex which is protonated in the positive ion mode $(\text{M}+\text{H})^+$ or deprotonated in the negative ion mode $(\text{M}-\text{H})^-$ such as $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{SC}$ with a molecular weight of 770 m/z in the negative ion mode will result in a spectrum giving the exact molecular weight of the analyzed complexes.

Antimicrobial activity

These dinuclear metal complexes were explored with the evaluation of their antimicrobial activity against Gram positive and Gram-negative *Escherichia coli*. Double strength nutrient broth and dextrose broth (Pharmacopoeia of India; Ministry of Health Department, 1996) were employed for bacterial growth. The Minimum Inhibitory Concentrations (MIC) were determined by means of standard serial dilution method (Cappucino and Sherman, 1999) and diameter of inhibition zone were about (14-17) mm which indicates that all these metal complexes are promising candidates for novel antibacterial activity against pathogenic bacteria *E. coli* (Figure 3).

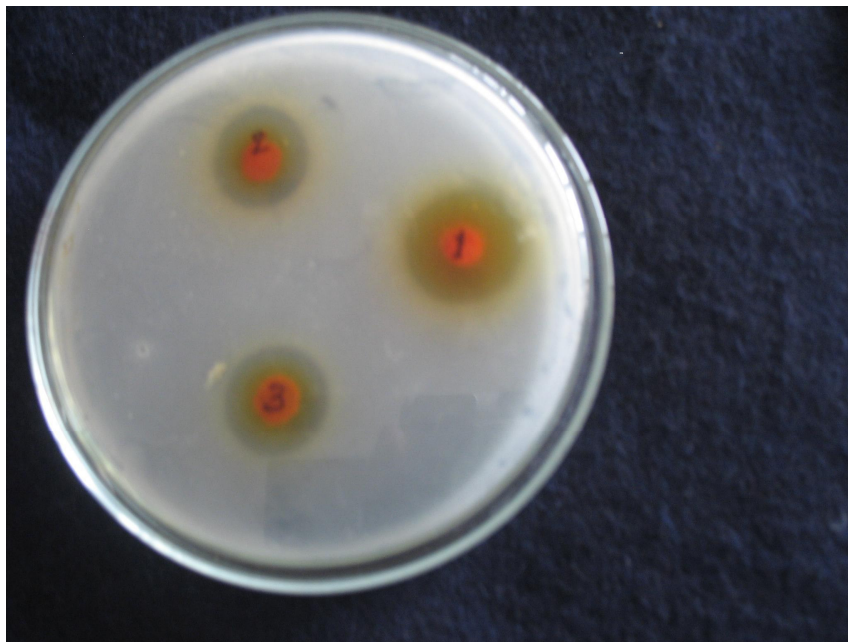


Figure 3. Antimicrobial activity of different dimer complexes based on the disc diffusion assay.

1. $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{TU}$.
2. $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{SC}$.
3. $\text{PhCH}_2\text{Co}(\text{DH})_2\text{CNC}(\text{DH})_2\text{PY}$.

1-comment 1: Is this formula correct- 2SCN ligand? Yes it is right to write as 2SCN
 2-what does $1\frac{1}{2}\text{H}^+ + 1\frac{1}{2}\text{H}^-$ signify in eq 2? To balance the equation after reduction of Co^{II} to Co^{I} by addition of sodium borohydride.

The values indicate that most of the dimer complexes have higher antimicrobial activity than their monomer complexes (12-15) mm. Such increased activity of the dimer complexes can be explained on the basis of chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism (Dharmaraj et al., 2001).

TG analysis

TGA/DTG analysis, the complexes of cobaloximes show a weight loss at around 135°C that is due to the physically absorbed water. The mass loss observed in the TG curve for the second decomposition at around 275°C suggesting that, both the ligand molecules were eliminated in this step and forming polymeric intermediate product. Finally, at a temperature of about 553°C the intermediate product is further decomposed to give

Co_3O_4 as the final residue (Das and Dash, 1985; Mohapatra and Dash, 1987).

Conclusion

Cyano bridged complexes were isolated successfully by reacting cyanide complexes with benzyl (aquo) complex in methanol to form a neutral compound in a system where ($\text{C}\equiv\text{N}$) is bridging between two similar metals Co-CN-Co- where both C-bonded and N-bonded groups at the same

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