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Synthesis, characterisation and Biological importance of homobinuclear macrocyclic complexes with transition metal.

Chemistry

KEYWORDS: Homobinuclear; Macrocyclic ; cyclic voltammetry; biological activities

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ABSTRACT

New macrocyclic complexes of nickel with ligands L^1 1,7,10,16-tetraaza-2,6,11,15-tetraone-4,13-dithiacyclooctadecane, L^2 1,7,11,17-tetraaza-2,6,12,16-tetraone-4,14-dithia-cyclocosane, L^3 1,7,10, 13,19,22-Hexaaza-2,6,14,18-tetraone-4,16-dithia cyclotetracosane, L^4 1,7,14,20, tetraaza-2,6,15,19-tetraone-4,17, dithia tricyclo [22, 4, $O^{21,26}$, $O^{8,13}$] hexa cosa 8,10,12,21,23,25 hexene, L^5 1,7,13,19,25,26-Hexaaza-2,6,14,18 tetraone-4,16 dithia tricyclo [23, 3, 1, $1^{8,12}$] hexa cosa [8(26), 10, 12, 20(25), 22,24] hexane [ligands repoted earlier by us S.chandra, N.Gupta and R. Gupta Spectrochimica acta A, 63(2006) 587-593] have been synthesised and characterised. The bonding and stereochemistry of the complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, I.R. and uv-vis spectroscopy,. The magnetic and spectral data indicate square planar geometry for all the complexes. The antibacterial activities of the compounds were tested against S. fecalis and E. coli with different concentrations.

1. Introduction

Synthetic macrocycles are a growing class of compounds with varying chemistry with a wide range of different molecular topologies and sets of donor atoms [1,2]. Transition metal complexes have received much attention as catalyst in oxidation and epoxidation processes [3,4]. Systematic investigation to understand the structural, spectroscopic and redox properties of Ni(II) ion in a set of 13-membered amide-based macrocyclic ligands have been done [5]. Nickel(II) complexes with the macrocyclic schiff base ligand were synthesised for spectroscopic studies, electrochemical behaviours and 1D supramolecular structure [6]. New binuclear complexes of macrocycles, having a reactive peripheral thioketo functional group [7] has been prepared. Mononuclear, binuclear Ni(II) and hetereobinuclear Zn(II), Ni(II) complexes derived from lateral macrobicyclic tricompartmental ligands embracing three different donor sets(i) O_2N_2 from ether oxygens and tertiary amine nitrogens (ii) O_2N_2 from tertiary amine nitrogens and phenolic oxygens (iii) O_2N_2 from phenolic oxygens and azomethine nitrogens is also reported [8]. Macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard-soft donor character and versatile coordination behaviour.[9,10] Azatype ligands appear as very promising to be used as antifertile, antibacterial, antifungal and or other biological properties [11-15]. In this paper we report an efficient route for the synthesis of new series of nickel(II) binuclear macrocyclic complexes by template condensation.

2. Experimental

All chemicals used were of AR grade and were purchased from Sigma Chemical Co., U.S.A., E. Merck, Germany or Sarabhai Merck Company, India. Ethanol used was of analytical grade procured from S.D. Fine Chemicals Pvt. Ltd. It was dried by storing over clean, dried sodium wire, refluxed for 30 min and distilled using a double-walled condenser at 78 C.

2.1 Preparation of the complexes

All the complexes were prepared by template synthesis as the yield of the ligand is very low. To hot ethanolic solution of diamine, ethanolic solution of metal salt were added for binuclear nickel complexes. The precipitate formed get readily dissolved and then to it an ethanolic solution of thiodiglycolic acid was added. The resultant solutions were refluxed for 5-9h at 79-80C. On cooling at room temperature, colored complexes precipitate out. The products were filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}. The reaction was attempted with chlorate, nitrate, thiocyanate and sulphate of nickel.

Preparation of binuclear Ni^{2+} complexes with L^1 ligand (L^1 1,7,10,16-tetraaza-2,6,11,15-tetraone-4,13-dithiacyclooctadecane)

To hot ethanolic solution of ethylene diamine (2 mmol; 0.158 gm), ethanolic solution (1 mmol and 2 mmol) of metal salt were added for mono and binuclear nickel complexes respectively. The precipitate formed get readily dissolved and then to it an ethanolic solution (2 mmol; 0.376 gm) of thiodiglycolic acid was added. The resultant solution was refluxed for 6-9h at 79-80C. On cooling at room temperature, colored complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

Preparation of binuclear Ni^{2+} complexes with L^2 ligand (L^2 1,7,11,17-tetraaza-2,6,12,16-tetraone-4,14-dithia-cyclocosane)

To hot ethanolic solution of 1,3-diamino propane (2 mmol; 0.17 gm), ethanolic solution (1 mmol and 2 mmol) of metal salt were added for mono and binuclear nickel complexes respectively. The precipitate formed get readily dissolved and then to it an ethanolic solution (2 mmol; 0.376 gm) of thiodiglycolic acid was added. The resultant solution was refluxed for 5-9h at 79-80C. On cooling at room temperature, colored complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

Preparation of binuclear Ni^{2+} complexes with L^3 ligand ($L^3$1,7,10,13,19,22-Hexaaza-2,6,14,18-tetraone-4,16-dithia cyclo-tetracosane)

To hot ethanolic solution of Diethylene triamine (2 mmol; 0.19 gm), ethanolic solution (1 mmol; 2 mmol) of metal salt were added for mono and binuclear nickel complexes respectively. The precipitate formed get readily dissolved and then to it an ethanolic solution (2 mmol; 0.376 gm) of thiodiglycolic acid was added. The resultant solution was refluxed for 4-8h at 79-80C. On cooling at room temperature, colored complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

Preparation of binuclear Ni^{2+} complexes with L^4 ligand (L^4 1,7,14, 20, tetraaza-2,6,15,19-tetraone-4,17, dithia tricyclo [22, 4, $O^{221,26}$, $O^{8,13}$] hexa cosa 8,10,12,21,23,25 hexene) To hot ethanolic solution of o-phenylene diamine (2 mmol; 0.216 gm), ethanolic solution (1 mmol and 2 mmol) of metal salt were added for mono and binuclear nickel complexes respectively. The precipitate formed get readily dissolved and then to it an ethanolic solution (2 mmol; 0.376 gm) of thiodiglycolic acid was added. The resultant solution was refluxed for 6-9h at 79-80C. On cooling at room temperature colored complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

Preparation of binuclear Ni^{2+} complexes with L^5 ligand (L^5 1,7,13,19,25,26-Hexaaza-2,6,14,18 tetraone-4,16 dithia tricyclo [23, 3, 1, $1^{8,12}$] hexa cosa [8(26), 10, 12, 20(25), 22,24] hexene)

To hot ethanolic solution of 2,6-diaminopyridine (2 mmol; 0.22 gm), ethanolic solution (1 mmol and 2 mmol) of metal salt were added for mono and binuclear nickel complexes respectively. The precipitate formed get readily dissolved and then to it an ethanolic solution (2 mmol; 0.376 gm) of thiodigylcolic acid was added. The resultant solution was refluxed for 6-9h at 79-80C. On cooling at room temperature colored complex was precipitated out. It was filtered,

washed with cold ethanol and dried under vacuum over P_4O_{10}.

2.2 Physical measurements

IR spectra were recorded on a Perkin Elmer 137 instrument in KBr pellets. Microanalyses (C, H and N) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini – 1240 spectrophotometer. The molar conductance was measured on an Elico conductivity bridge (type CM82T). Magnetic moment measurements (Gouy balance) were made at room temperature using $CuSO_4$ $5H_2O$ as callibrant. Antimicrobial activity The in vitro antimicrobial (antibacterial) activities of these complexs were tested using paper disc diffusion method .The chosen strains were G(+) Streptococcus fecalis and G(-) Escherichia coli.

3. Result and Discussion

3.1 Molar conductance

The molar conductance measurements (Table 1) in DMSO show that all the complexes except those with sulphate anions are 1:2 electrolytes and they may be formulated as $[Ni_2LX_2]X_2$ and others with sulphate anions are found to be non-electrolytes and may be formulated as $[Ni_2L(SO_4)_2]$. Thus the complexes may be formulated as homobinuclear complexes respectively. In square-planar complexes, all the electrons in 3d orbitals of Ni^{2+} ion are paired up and as such the complexes are diamagnetic.

Table 1.Molar conductance and elemental analysis data of binuclear nickel(II) complexes.

Complexes	M.W. Calc. (Found)	Molar cond. $^1cm^2$ mol^1	Colour	Yield %	M.Pt. C	Elemental analysis Calc. (Found)			
						Mn	C	H	N
$[Ni_2L_1(NO_3)_2](NO_3)_2$ $Ni_2C_{12}H_{20}N_6S_2O_{10}$	716 (715.72)	237	Green	69	213	16.75 (16.79)	20.11 (20.19)	2.79 (2.83)	15.64 (15.71)
$[Ni_2L_1(SO_4)_2]$ $Ni_2C_{12}H_{20}N_4S_3O_8$	660 (659.53)	18	Green	65	198	18.18 (18.27)	21.81 (21.87)	3.03 (3.12)	8.48 (8.53)
$[Ni_2L_1(SCN)_2](SCN)_2$ $Ni_2C_{14}H_{20}N_6S_4O_4$	580 (579.62)	235	Purple	63	199	20.68 (20.73)	33.10 (33.17)	3.44 (3.51)	19.31 (19.39)
$[Ni_2L_2(NO_3)_2](NO_3)_2$ $Ni_2C_{14}H_{24}N_6S_2O_{10}$	744 (743.83)	239	Green	58	203	16.12 (16.19)	22.58 (22.63)	3.22 (3.29)	15.05 (15.12)
$[Ni_2L_2(SO_4)_2]$ $Ni_2C_{14}H_{24}N_4S_3O_8$	908 (907.69)	21	Green	75	207	13.21 (13.27)	18.50 (18.57)	2.64 (2.71)	9.25 (9.29)
$[Ni_2L_2(SCN)_2](SCN)_2$ $Ni_2C_{16}H_{24}N_6S_4O_4$	728 (727.91)	240	Purple	73	201	16.48 (16.53)	30.50 (30.59)	3.29 (3.31)	15.38 (15.41)
$[Ni_2L_3(NO_3)_2](NO_3)_2$ $Ni_2C_{16}H_{30}N_8S_2O_{10}$	802 (801.75)	249	Green	62	195	14.96 (14.99)	23.94 (23.99)	3.74 (3.79)	17.45 (17.52)
$[Ni_2L_3(SO_4)_2]$ $Ni_2C_{16}H_{30}N_6S_3O_8$	746 (745.61)	15	Green	57	193	16.08 (16.13)	25.73 (25.78)	4.02 (4.09)	11.26 (11.31)
$[Ni_2L_3(SCN)_2](SCN)_2$ $Ni_2C_{18}H_{30}N_8S_4O_4$	730 (729.69)	237	Purple	72	197	16.43 (16.47)	29.58 (29.63)	4.10 (4.17)	19.17 (19.24)
$[Ni_2L_4(NO_3)_2](NO_3)_2$ $Ni_2C_{20}H_{20}N_6S_2O_{10}$	812 (811.77)	247	Green	69	217	14.77 (14.82)	29.55 (29.59)	2.46 (2.53)	13.79 (13.83)
$[Ni_2L_4(SO_4)_2]$ $Ni_2C_{20}H_{20}N_4S_3O_8$	756 (755.81)	17	Light Green	59	211	15.98 (16.07)	31.74 (31.79)	2.64 (3.77)	7.40 (7.49)
$[Ni_2L_4(SCN)_2](SCN)_2$ $Ni_2C_{22}H_{20}N_6S_4O_4$	796 (795.78)	238	Violet	63	213	15.07 (15.14)	36.18 (36.21)	2.51 (2.58)	14.07 (14.13)
$[Ni_2L_5(NO_3)_2](NO_3)_2$ $Ni_2C_{18}H_{18}N_8S_2O_{10}$	814 (813.79)	234	Green	73	210	14.74 (14.81)	26.53 (26.62)	2.21 (2.27)	17.19 (17.27)
$[Ni_2L_5(SO_4)_2]$ $Ni_2C_{18}H_{18}N_6S_3O_8$	758 (757.82)	23	Algae Green	78	212	15.83 (15.89)	28.49 (28.53)	2.37 (2.39)	11.08 (11.13)
$[Ni_2L_5(SCN)_2](SCN)_2$ $Ni_2C_{20}H_{18}N_8S_4O_4$	862 (861.71)	242	Leafy Green	76	211	13.92 (13.97)	30.62 (30.68)	2.08 (2.12)	16.24 (16.29)

3.2 IR Spectra

The IR spectra of the complexes do not show any band around 3400 cm^{1} indicating the absence of free primary diamine and hydroxyl of carboxyl group, which suggests the complete condensation of keto group with amino group [16-17]. Appearance of four new bands in the IR spectra, in the region 16141676, 1548-1587, 1226-1272, 619769 cm^{1}, which are corresponding to amide I [f (C=O)], amide II [(CN)] + (NH)], amide III [(NH)] and amide IV [(C=O)], respectively [19-21]. Another band appears in the IR spectrum at 1456 cm^{1} is due to pyridine ring, supporting the macrocyclic nature of the ligand. The bands at 730770 cm^{1} and 1413-1445 cm^{1} are due to the presence of phenyl ring in the macrocycle [18] (Table 4).The appearance of a band at 3188- 3437 cm^{1} may be attributed to [(NH)] of secondary amino group, which is further supported by the presence of a medium intensity band in the range 406-455 cm^{1}.The infrared spectra of nitrato complexes of Ni(II) display medium intensity bands in the region at 1406-1468, 1245-1276 and 930-989 cm^{1}, which are assigned to $_{5,2}$ and , respectively. This suggests the unidentate coordinated behaviour of both nitrate groups with centrally located Ni(II) metal ion [21, 17]. IR spectra of sulphato complexes display bands in the region at 1123-1137, 1003-1009 cm^{1}, which suggest the unidentate coordination behaviour of both sulphate groups. Coordination of both SCN group is also confirmed from infrared spectra [22], which shows a strong band at 2087 cm^{1}. This show that coordination occur through N-atom of SCN group (Fig. 1-2).

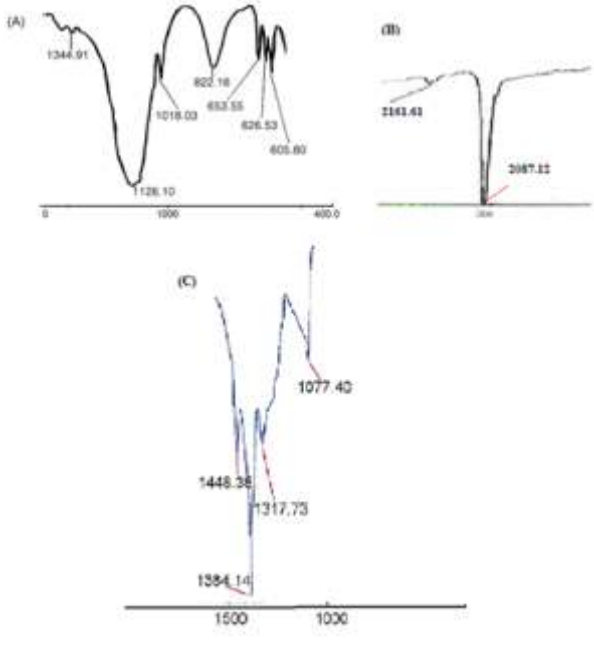


Fig.1 IR spectral bands due to anions (a) Coordinated SO_4^{2-} (a) Coordinated NO_3^{-} (a) Coordinated SCN^{-}

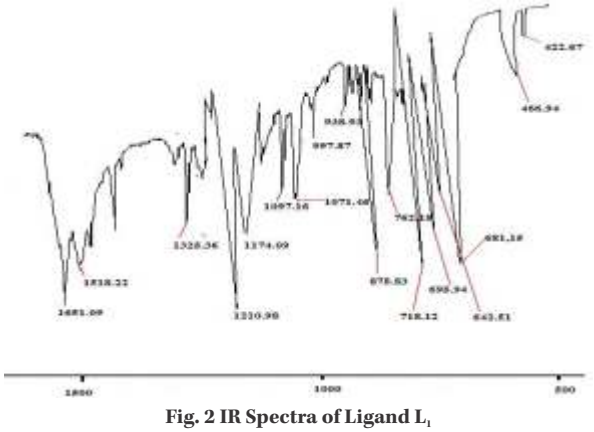


Fig. 2 IR Spectra of Ligand L_1

3.3 UV Spectra

Square planar binuclear complexes of Ni(II) [23, 24] exhibit a strong absorption band in the visible region between 15,00020,000 cm^{1} and 23,00030,000 cm^{1} which are referred to $_{2}$ and $_{3}$. Certain square planar amine complexes also exhibit a low energy band near 11000 cm^{1} which is very weak and is probably a spin forbidden transition. The first major band near (20,000 cm^{1}) is assigned to $^{1}B_{1g}$ ® #B_{2g} ($_{2}$) and the second major band to the $^{1}B_{1g}$ ® #$^{1}A_{1g}$ (n_3) (Table 3). These values suggests the square planar geometry of the complexes.

Table 2. Electronic Spectral bands (cm^{1}) and Magnetic moment (B.M.) of Binuclear Ni(II) complexes

Complexes	Spectral bands in cm^{1}
$[Ni_2L_1(NO_3)_2](NO_3)_2$	10892, 15453, 24532
$[Ni_2L_1(SO_4)_2]$	10993, 16932, 24939
$[Ni_2L_1(SCN)_2](SCN)_2$	11005, 18792, 23592
$[Ni_2L_2(NO_3)_2](NO_3)_2$	11047, 18979, 23789
$[Ni_2L_2(SO_4)_2]$	10972, 18999, 23889
$[Ni_2L_2(SCN)_2](SCN)_2$	10837, 19000, 24601
$[Ni_2L_3(NO_3)_2](NO_3)_2$	10852, 17331, 23890
$[Ni_2L_3(SO_4)_2]$	10871, 17605, 23975
$[Ni_2L_3(SCN)_2](SCN)_2$	10869, 16959, 23594
$[Ni_2L_4(NO_3)_2](NO_3)_2$	11049, 16779, 24692
$[Ni_2L_4(SO_4)_2]$	11008, 16997, 25000
$[Ni_2L_4(SCN)_2](SCN)_2$	11032, 18899, 24987

3.6 Antibacterial activity

Results of antibacterial screening as shown in Fig. 3 indicate that the metal complexes inhibit higher antibacterial activity than controlled one.

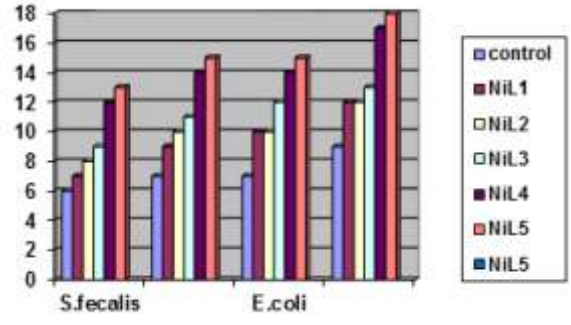


Fig. 3 Antibacterial activities shown by the complexes

6. Conclusion

Homobinuclear complexes of nickel were synthesised and characterised by various physico-chemical techniques. The overall geometry around respective metal ion has been drawn on the basis of spectral, magnetic moment, elemental analysis, molar conductance, magnetic susceptibility measurement, I.R studies, the following structures may be proposed for the complexes (Figs. 4 to 8).

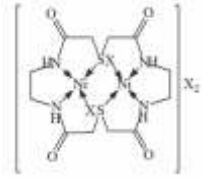


Fig. 4. Complexes with ligand L_1, X = Cl^{-}, NO_3^{-}, SCN^{-}, ½So_4^{-}

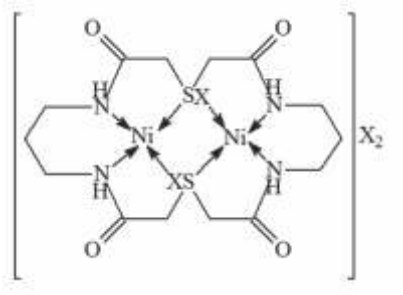


Fig. 5. Complexes with ligand L_2, X = Cl^-, NO_3^-, SCN^-, ½So_4-

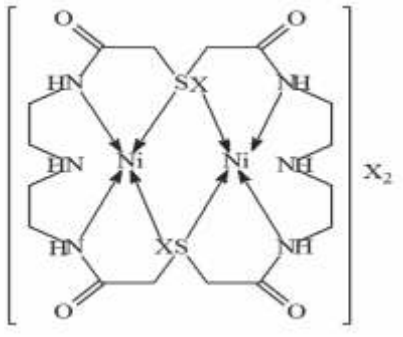


Fig. 6. Complexes with ligand L_3, X = Cl^-, NO_3^-, SCN^-, ½So_4-

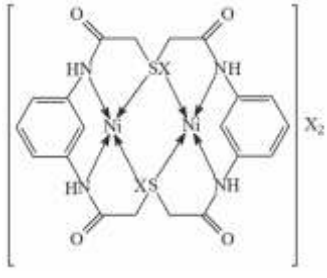


Fig. 7. Complexes with ligand L_4, X = Cl^-, NO_3^-, SCN^-, ½So_4-

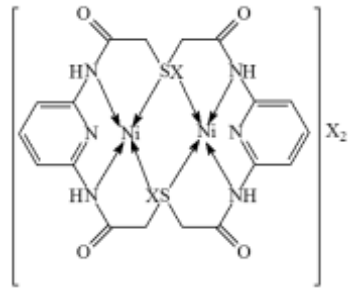


Fig. 8. Complexes with ligand L_5, X = Cl^-, NO_3^-, SCN^-, ½So_4-

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