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Synthesis and Characterization of Nickel(II) Complexes of Nitrogen based Ligands of Type *N,N,N′,N′-tetrakis*(2-Pyridylmethyl)alkanediamine

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Hexadentate ligand of the type *N,N,N′,N′-tetrakis*(2-pyridylmethyl)alkanediamine (where alkane is butane (L_1), hexane (L_2) and octane (L_3) reacted with $Ni(ClO_4)_2·6H_2O$ (stoichiometry 1:1) in alcoholic solutions yielding mononuclear complexes of the type $[Ni(L)](ClO_4)_2·xH_2O$. The ligand L_1 reacted with $Ni(ClO_4)_2·6H_2O$ in ethanol medium to give a violet powder of $[Ni(L_1)](ClO_4)_2·3H_2O$. The other mononuclear nickel(II) complexes using L_2 and L_3 were synthesized in methanol solution to give violet powders of $[Ni(L_2)](ClO_4)_2·2H_2O$ and $[Ni(L_3)](ClO_4)_2·2H_2O$, respectively. All the three complexes were characterized by IR and elemental analysis. The X-ray crystallographic results for the purple crystals of $[Ni(L_1)](ClO_4)_2·3H_2O$ shows the octahedral geometry on the Ni(II) ions together with the tetrahedral perchlorate anions separated from the $[Ni(L_1)]^{2+}$ cation. The crystal structure data show monoclinic space group $P\ 2_1/c$; a = 17.1748(10), b = 9.8273(6), c = 17.8146(10) Å; α = 90º, β = 95.0200(10)º, γ = 90º; V = 2995.2(3) Å^3, Z = 4.

Keywords: Nickel complexes, *N,N,N′,N′-tetrakis*(2-pyridylmethyl)alkanediamine, Octahedral geometry, Crystallography.

INTRODUCTION

N,N,N′,N′-tetrakis(2-Pyridylmethyl)ethanediamine (tpen) is a hexadentate ligand and has shown the ability to react with compounds of the type $M(ClO_4)_2·6H_2O$ (M = Fe, Co, Ni, Cu) in 1:1 ratio in ethanol solution yielding the corresponding $[M(tpen)(ClO_4)_2]$ complexes [1]. The ligand forms very stable 1:1 metal complexes with most divalent metal ions of 1st row transition metals [2,3]. In biomedical studies, tpen has been used as polypyridyl ligand to chelate heavy metals [4]. It has also been used in studies measuring free cytosolic Ca^{2+} in *Ehrlich* and *Yoshida* "*Ascites Carcinomas*" [5]. Furthermore, tpen has been used in investigating the effect of iron chelating agents on toxicity of doxorubicin for MCF-7 Human breast cancer cells [6].

Chromium complexes of tpen have been synthesized by air oxidation of chromium(II) acetate and tpen in methanol-water mixture [7]. Addition of perchlorate ions precipitated $[Cr(tpen)(COOCH_3)](ClO_4)_2·H_2O$, which has been used as the starting material for the synthesis of a number of complexes including $[Cr(tpen)](ClO_4)_3$, $[Cr(tpen)(OH)](ClO_4)_2$ and *cis*-$[Cr(tpen)(OH)_2]ClO_4·3H_2O$. Characterization by single crystal structure determinantion has shown that these complexes are monomeric containing six-coordinated chromium (III) cations whereby all the six nitrogens of the potentially hexadentate tpen ligand are coordinated to the chromium. The coordination by only five nitrogen atoms is seen in $[Cr(tpen)(OCOCH_3)]^{2+}$ and $[Cr(tpen)(OH)]^{2+}$, the remaining coordination sites being occupied by oxygen atoms of the acetate and the hydroxide ligands. The divalent base $[Cr(tpen)(OH)]^{2+}$ is relatively stable in neutral solution but acidification leads to fast equilibration reaction between $[Cr(tpen)(OH_2)]^{3+}$ and $[Cr(tpen)]^{3+}$ which was characterised by stopped flow measurements. $[Cr(tpen)(OH)]^{2+}$ reacts slowly in basic aqueous solution to give *cis*-$[Cr(tpen)(OH)_2]^+$, while acidification of these solutions leads to the same hexamine/pentamine equilibrium mixture but by a considerably slower process. Part of this significant reactivity difference may be attributed to the conformation of the coordinated part of the ligand, which is similar in the hexamine and pentamine complexes, and markedly different in the tetramine complex. Furthermore in chromium(II) complexes of a hexadentate ligand like tpen (Fig. 1), there is steric crowding in the hexamine complex and this leads to the easy preparation of pentamine complexes with a wide variety of substituents and these comp-

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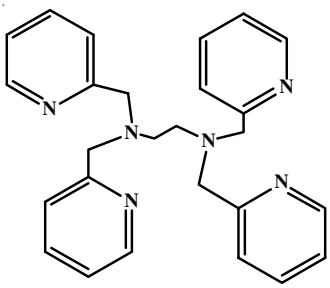


Fig. 1. Structure of *N,N,N′,N′-tetrakis*(2-pyridylmethyl)ethylenediamine (tpen)

lexes have biomimetic properties [8]. Kakoi *et al*. [9] reported that *N,N′-bis*(2-quinolylmethylidene)-1,2-diiminoethane and *N,N′*-(2-pyridylmethylidene)1,3-diimino-2,2-dimethylpropane have high extraction selectivity to Cu^{2+} ions.

According to Mascarenhas *et al*. [10], the crystal structure analysis of $[Ni(tpen)](ClO_4)_2 \cdot 2/3H_2O$ has been undertaken. This was done to facilitate possible explanation of the observed behaviour from the cyclic voltagram of $[Ni(tpen)](ClO_4)_2$ in acetonitrile, which showed the presence of Ni(III)/Ni(II) and Ni(II)/Ni(I) species in solution. From their findings the structure of $[Ni(tpen)](ClO_4)_2 \cdot 2/3H_2O$ consist of distorted perchlorate anions and water of crystallization. The molecule was shown to be lying on a crystallographic two fold axis which passes through the central Ni atom. Romerosa *et al*. [11] have managed to obtain a C(8)-Pd(II) purine complex from an N(7)-Pd(II) precursor. The X-ray analysis of N(7)-Pd(II) and C(8)-Pd(II) purine complexes showed that both structures consist of discrete essentially square planar neutral molecules. Earlier reports [12, 13] show that of all the recognised metal binding sites on DNA nucleobases, N(7) of the guanine is the preferred site by most of metals even though metallation at some donor sites are known. From the study of the coordination behaviour of ligand 3,4-*bis*(2-pyridylmethylthio)toluene with Cu^{2+} ions. The X-ray crystallography of the dinuclear complex $Cu_2L_2(ClO_4)_2$ shows that the complex resides about a two-fold axis and a Cu^{+} ion shows an irregular pseudo-tetrahedral geometry. This arises from the restricted bite angles of the chelating ligand that bridges the two metal ions in such a way that the thioether-S atoms and one pyridyl-N donors chelate one copper ion, the other pyridyl-N donor being connected to the other metal [14].

The aim of this work is to synthesize nickel complexes using other ligands of the same family as tpen. Nickel is among the palladium group metals (PGMs), which when complexed to these type of ligands have been shown to have various applications as anticancer properties, polymerization, catalytic properties, germicidal properties, antibacterial and fungicidal properties [2,3,12,13]. To have insight of how the nickel is bonding to these hexadentate ligands, the complete crystal structure analysis of Ni(2-pyridylmethyl)-1,4-butanediamine)$(ClO_4)_2 \cdot 3H_2O$ (A) has been undertaken together with other relevant analyses methods.

EXPERIMENTAL

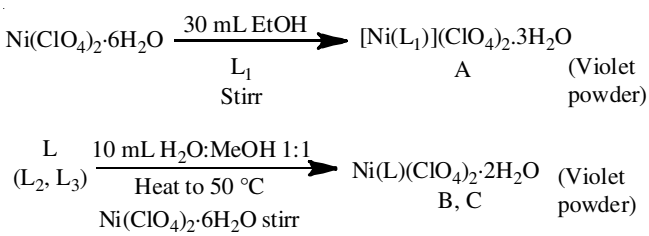
The chemicals *viz*. 2-pyridylmethylchloride, dichloromethane, methanol, chloroform, hexane, sodium hydroxide and sodium perchlorate were supplied by Rochelle Chemicals while cetyltrimethylammonium bromide (CTAB), anhydrous magnesium sulphate, anhydrous sodium sulphate, nickel(II) perchlorate hexahydrate, dimethylsulphoxide (DMSO) and acetonitrile were supplied by Sigma-Aldrich, USA.

The infrared spectra for all the synthesized ligand and its complexes were recorded in solid state using KBr pellets on a Shimadzu Hyper IR system FT-IR 8700 spectrophotometer (Japan) in the range 4000-400 cm^{-1}. The CHN elemental analyses for the complexes were done using the Vario EL CHNOS Elemental analyzer (Germany). All the samples were analyzed in solid state. Each analysis was done in triplicate and the average was obtained and reported. The melting points were recorded on a Stuart Scientific SMP1 melting point apparatus (U.K.). The Bruker-APEX DUO 4K-CCD diffractometer was used for the structural determination. The frames were intergrated with Bruker SAINT Software package. Using OLEX 2 the structure was solved with SHELXS structure solution programme using Direct methods and refined with SHELXTS refinement package using least square minimisation.

Synthesis of ligands: The ligands, *N,N,N′,N′-tetrakis*(2-pyridylmethyl)-1,4-butanediamine (L_1), *N,N,N′,N′-tetrakis*(2-pyridylmethyl)-1,6-hexanediamine (L_2) and *N,N,N′,N′-tetrakis*(2-pyridylmethyl)-1,8-octanediamine (L_3) were synthesized by modified literature methods [15,16].

Syntheses of nickel complexes:

Ni(2-Pyridylmethyl)-1,4-butanediamine)$(ClO_4)_2 \cdot 3H_2O$ (A): The complex was synthesized following a similar procedure as described in literature [1]. In brief, 0.1810 g (0.4 mmol) of ligand *N,N,N′,N′-tetrakis*(2-pyridylmethyl)-1,4-butanediamine was added to a stirred ethanolic solution (30 mL) containing 0.1463 g (0.4 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ (light green). The resulting violet precipitate was filtered by suction and washed with ice cold water (**Scheme-I**). This product was found to be soluble in acetonitrille and gave a yield of 71%. The melting point was found to be between 284-286 ºC.



Scheme-I: Reaction scheme for the synthesis of complexes **A**, **B** and **C**

Ni(2-Pyridylmethyl)-1,6-hexanediamine)$(ClO_4)_2 \cdot 2H_2O$ (B) and Ni(2-Pyridylmethyl)-1,8- octanediamine)$(ClO_4)_2 \cdot 2H_2O$ (C): These were synthesized following a procedure as described by Toftlund *et al*. [14]. In brief, 1:1 methanol: water solution (10 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.1829 g, 0.5 mmol) was heated to 50 ºC and the ligand (0.5 mmol, 0.2403 g for L_2 and 0.2544 g for L_3) was added whilst stirring. The violet solution was slowly cooled to room temperature and the precipitated nickel(II) complex was filtered off and washed with ice-cold water. The powder was then air dried giving a yield of 71% for complex B and 62% for complex C. The violet powdery

products showed solubility in DMSO and acetonitrile and had melting point of 274-278 ºC and 268-272 ºC, respectively (**Scheme-I**).

Crystal growth of complex A: Complex A, Ni(2-pyridylmethyl)-1,4-butanediamine)$(ClO_4)_2 \cdot 3H_2O$ was dissolved in minimum amount of acetonitrile. The resulting violet solution was then left for solvent evaporation and concentrated for several days until purple crystals formed. A purple cube-like specimen of $C_{28}H_{36}Cl_2N_6NiO_{11}$ of approximate dimensions 0.18 mm × 0.20 mm × 0.21 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured and solved accordingly with the data given in Table-1.

TABLE-1
CRYSTAL DATA COLLECTION AND
REFINEMENT PARAMETERS FOR COMPLEX **A**

Identification code	Complex **A**
Chemical formula	$C_{28}H_{36}N_6O_{11}NiCl_2$
Formula weight	762.24
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.18 mm × 0.20 mm × 0.21 mm
Crystal habit	Purple cube
Crystal system	Monoclinic
Space group	P121/c1
Unit cell dimensions	a = 17.1748(10) Å, α = 90°
	b = 9.8273(6) Å, β = 95.0200(10) °
	c = 17.8146(10) Å, γ = 90°
Volume	2995.2(3) Å^3
Z	4
Density (calculated)	1.690 Mg/cm^3
Absorption coefficient	0.901 mm^{-1}
F(000)	1584

A total of 1988 frames were collected. The total exposure time was 5.52 h. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 44649 reflections to a maximum θ angle of 28.29º (0.75 Å resolution), of which 7420 were independent (average redundancy 6.017, completeness = 99.8%, R_{int} = 4.08%, R_{sig} = 2.90%) and 6283 (84.68%) were greater than 2σ (F^2). The final cell constants of a = 17.1748(10) Å, b = 9.8273(6) Å, c = 17.8146(10) Å, β = 95.0200(10)º, volume = 2995.2(3) Å^3, are based upon the refinement of the XYZ-centroids of 9857 reflections above 20 σ(I) with 4.983° < 2θ < 56.32°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.887. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8355 and 0.8532.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\,2_1/c\,1$, with $Z = 4$ for the formula unit, $C_{28}H_{36}Cl_2N_6NiO_{11}$. The final anisotropic full-matrix least-squares refinement on F^2 with 406 variables converged at R_1 = 3.67%, for the observed data and ωR^2 = 10.17% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.894 e$^-$/Å^3 and the largest hole was –0.511 e$^-$/Å^3 with an RMS deviation of 0.076 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.690 g/cm^3 and F (000), 1584 e$^-$.

RESULTS AND DISCUSSION

A cream white crystalline powder of ligands were agreed well with the characterization data of already reported for these ligands L_1, L_2 and L_3 [15,16]. A 1:1 molar reaction of nickel(II) perchlorate and the ligands L_1, L_2 and L_3 produced violet powders complexes A, B and C with yields of 71%, 71% and 62%, respectively. A decrease in the melting points was observed from complexes A to B and to C as the complex size increases due to the changing chain length of ligands. The melting point showed this trend because apart from the chain length increase leading to increased flexibility and easy rotation of the bonds, there is bound to be more disorderliness in the structure as the chelate forms. This results in few atom to atom van der Waals forces leading to lower melting point.

The IR spectra of the compounds showed absorption bands at around 3411 cm^{-1} and 3413 cm^{-1} correspond to the -OH in the structure of the complex due to the water of hydration. This was a newly formed peak upon complexation as compared to the spectrum of the free ligand. Another peak characteristic of the perchlorate ion in all the three complexes appeared at around 1100 cm^{-1} (broad) and 626 cm^{-1} (weak), due to asymmetric stretching and δ-bending frequencies, respectively, of the perchlorate ion (Table-2). A weak band around 920 cm^{-1} observed for each of the complexes, is characteristic of symmetric perchlorate ion. However, there was a peak characteristic of the pyridyl nitrogen which appeared at 765 cm^{-1} and it was of reduced intensity as compared to the free ligand. This is an evidence that the nitrogen in the ring was involved in the bonding with the nickel(II) ion. The results obtained by elemental analysis for C, H and N showed a closer correlation to these nickel complexes as shown in Table-2. The results showed that complex A showed similar coordination as a mononuclear complex Ni(tpen)-$(ClO_4)_2 \cdot 2/3H_2O$, which was observed in literature [1]. Similarly, complexes B and C also gave violet powders as previously observed earlier [10,17].

The crystal structure determination reveals that complex A consists of $[Ni(L_1)]^{2+}$ cations which are well separated from the perchlorate anions show a normal tetrahedral coordi-nation with uncoordinated water of crystallization as shown in Fig. 2. The complex molecule lies on a crystallographic two-fold axis which passes through the central atom Ni1. A perspective view of complex A with the atom numbering schemes is shown in Fig. 2 (hydrogen atoms are omitted for clarity). Selected bond lengths and angles are reported in Tables 3 and 4, respectively.

Ni1 has octahedral coordination geometry. From Table-3, the bond distances between the Ni1 atom and the pyridine nitrogen atoms are very close to each other with a mean value of 2.1065 Å, but the Ni1-N2 and Ni1-N4 (N2 and N4 = N_{alph}) distances of 2.2071 and 2.1340 Å, respectively with a mean value of 2.17055 Å are slightly higher than those with the pyridine nitrogens. These findings are in line with the reported data from literature [8,11]. The pyridine nitrogen-nickel bond lengths are slightly shorter and are on the same axis, perpendicular to the longer amine nitrogen-nickel bonds, indicative

TABLE-2
ELEMENTAL ANALYSIS DATA AND KEY IR BANDS (cm^{-1}) OF NICKEL(II) COMPLEXES OF NITROGEN BASED LIGANDS OF TYPE *N,N,N',N'-tetrakis*(2-PYRIDYLMETHYL)ALKANEDIAMINE

Name	Assignment	Frequency (cm^{-1})	Ref.	Elemental analysis (%)
Ni(2-pyridylmethyl)1,4-butane diamine] $(ClO_4)_2 \cdot 3H_2O$ (**A**)	ν(O-H)	3411	[18]	C: 43.96 (44.00) H: 5.16 (4.98) N: 10.91 (11.00)
	ν(C-H)	2943	[19]	
	ν ring (C=N and C=C) mode **8b**	1616	[10,20]	
	ν ring (C=N and C=C) mode **19b**	1450	[18]	
	ν_{asym} (ClO_4)	1101	[10,20]	
	ν ring breathing mode	761	[10,20]	
	δ (ClO_4)	626	[18]	
	ν(Ni-N)	298	[19]	
	δ(N-Ni-N)	216	[19]	
Ni(2-pyridylmethyl)-1,6-hexane diamine] $(ClO_4)_2 \cdot 2H_2O$ (**B**)	ν(O-H)	3413	[18]	C: 47.20 (47.53) H: 5.12 (5.28) N: 10.71 (11.09)
	ν(C-H)	2933	[19]	
	ν ring (C=N and C=C) mode **8b'**	1618	[10,20]	
	ν ring (C=N and C=C) mode **19b**	1450	[18]	
	ν_{asym} (ClO_4)	1097	[10,20]	
	ν (ring breathing) mode **1'**	763	[10,20]	
	δ(ClO_4)	626	[18]	
	ν(Ni-N)	296	[19]	
	δ(N-Ni-N)	233	[19]	
Ni(2-pyridylmethyl)1,8-octane diamine] $(ClO_4)_2 \cdot 2H_2O$ (**C**)	ν(O-H)	3411	[18]	C: 48.63 (48.88) H: 5.24 (5.60) N: 10.37 (10.69)
	ν(C-H)	2925	[19]	
	ν ring (C=N and C=C) mode **8b'**	1608	[10,20]	
	ν ring (C=N and C=C) mode **19b**	1446	[18]	
	ν_{asym} (ClO_4)	1091	[10,20]	
	ν (ring breathing)	765	[10,20]	
	δ (ClO_4)	624	[18]	
	ν (Ni-N)	290	[19]	
	δ (N-Ni-N)	268	[19]	

(The elemental analysis results in brackets are the calculated figures)

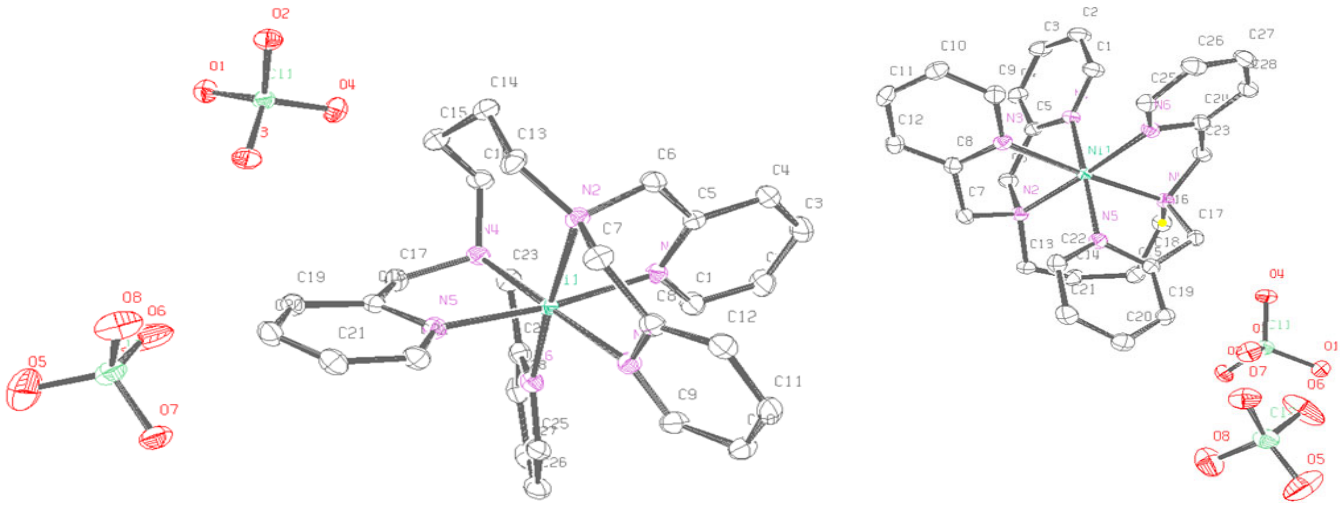


Fig. 2. Ortep drawings of the ClO_4^- nions and the $[Ni(tbn)]^{2+}$ cation showing atoms labelling scheme

of distortion from normal octahedral geometry. This distortion can be ascribed to the different types of nitrogen bound to the nickel atom. The crystal structure shows that the two amine nitrogens have typical Ni-N(amine) bond lengths while the two imine nitrogens which are trans to the amine ones, have longer bond lengths, typical of Ni-N(pyridine) bond lengths (Table-3). These observations are in line with those obtained by Neumann *et al*. [21]. The two pyridine rings *trans* to the amine nitrogens lie in the same plane while the other two pyridine rings occupy the axial positions and lie perpendicular to each other. These observations suggest that the axial pyridines anti-bonding orbitals experience greater degree of backbonding from the nickel's d_{xz} and d_{yz} orbitals than the other two equatorial pyridines, hence the distortion.

The strain in $[[Ni(L_1)]^{2+}$ is enough to also distort the octahedral geometry. The N-Ni-N angles in the faces N1-N2-N3 and N4-N5-N6 are all acute. But as expected, the N-Ni-N angles outside of these faces are all obtuse. The overall strain in this

TABLE-3
SELECTED BOND LENGTHS (Å) FOR NICKEL COMPLEX **A**

Ni1-N5	2.0831(17)	Ni1-N1	2.1027(16)
Ni1-N6	2.1173(18)	Ni1-N3	2.1228(18)
Ni1-N4	2.1340(17)	Ni1-N2	2.2071(17)
N1-C5	1.339(3)	N1-C1	1.353(3)
N2-C6	1.492(3)	N2-C7	1.493(3)
N2-C13	1.506(3)	N3-C9	1.353(3)
N3-C8	1.349(3)	N4-C23	1.486(3)
N4-C16	1.497(3)	N4-C17	1.494(2)
N5-C22	1.347(3)	N5-C18	1.347(3)
N6-C25	1.342(3)	N6-C24	1.353(3)

TABLE-4
SELECTED BOND ANGLES (°) FOR NICKEL COMPLEX **A**

N5-Ni1-N1	173.00(7)	N5-Ni1-N6	91.71(7)
N1-Ni1-N6	93.50(7)	N5-Ni1-N3	101.29(7)
N1-Ni1-N3	82.40(7)	N6-Ni1-N3	100.04(7)
N5-Ni1-N4	81.72(7)	N1-Ni1-N4	94.82(7)
N6-Ni1-N4	77.73(7)	N3-Ni1-N4	176.36(7)
N5-Ni1-N2	93.73(6)	N1-Ni1-N2	80.95(6)
N6-Ni1-N2	174.32(6)	N3-Ni1-N2	80.49(7)
N4-Ni1-N2	101.45(7)	O4-Cl1-O3	109.96(10)
C5-N1-Ni1	115.81(13)	C1-N1-Ni1	126.13(14)
C6-N2-C7	109.11(16)	C6-N2-C13	109.84(16)
C7-N2-C13	103.17(16)	C6-N2-Ni1	108.54(12)
C7-N2-Ni1	102.09(12)	C13-N2-Ni1	123.05(12)
C9-N3-C8	117.46(18)	C9-N3-Ni1	127.58(15)
C8-N3-Ni1	113.11(14)	C23-N4-C16	106.96(16)
C23-N4-C17	108.35(16)	C16-N4-C17	110.58(16)
C23-N4-Ni1	104.07(12)	C16-N4-Ni1	118.50(13)
C17-N4-Ni1	107.83(12)	C22-N5-C18	118.55(17)
C22-N5-Ni1	126.87(14)	C18-N5-Ni1	114.21(13)
C25-N6-C24	118.24(18)	C25-N6-Ni1	129.40(15)
C24-N6-Ni1	112.13(14)	N1-C1-C2	123.2(2)
N1-C1-H1	118.4	C2-C1-H1	118.4

nickel complex is given by the angle N5-Ni1-N3 = 101.29º as shown in Table-4. This angle is in plane of the butanediamine ring and is the most strained angle in the octahedral geometry. The rigidity of the pyridyl arms causes ring strain in the relatively planar chelate rings containing pyridine nitrogen atoms. The $[Cl(1)O_4]^-$ and the $[Cl(2)O_4]^-$ show normal tetrahedral geometry.

Conclusion

The complexes of nickel were synthesized and spectroscopically characterized. The yields of the complexes were satisfactory. These mononuclear octahedral nickel complexes gave yields between 62% and 72% and all the spectral data were in agreement with the expected results. All the nickel complexes prepared, attempts to grow good crystals failed except for one nickel complex A. This restricted the analysis by X-ray crystallography for the other nickel complexes B and C. From the X-ray crystallography, the mononuclear nickel complex A was found to be coordinated by six nitrogen atoms of ligand (L_1) making a slightly distorted octahedral structure.

Supplementary data: Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fizkarlsruhe.de/request_for_deposited_data.html) on quoting the CSD 431272.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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