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Synthesis, spectral characterization and catalytic activity of cobalt(II) and nickel(II) complexes with new tetradentate Schiff base ligands

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Abstract
New Schiff base ligands containing N and O donor atoms were prepared by the condensation of orthophthalaldehyde and different ortho-nitro benzaldehyde. Further these ligands on reaction with Ni(II), Co(II) salts to produce respective Schiff base-metal complexes. All the new compounds have been well characterized by the analytical and spectral (IR, ^{1}H NMR, ^{13}C NMR & Mass) data.

Keywords: Schiff base, ligands, chiral diamines, Spectral characterization, Catalytic activity

Introduction
Design and synthesis of Schiff bases and their transition metal complexes is much attractive areas of current research round the globe owing to their catalytic applications in chemistry [1-7]. Metal complexes make these compounds effective as specific catalysts towards oxidation [8, 9], reduction [10, 11], hydrolysis [12], biological activity [13, 14, 15] and other transformations of organic and inorganic chemistry. A lot of synthetic paths to synthesis Schiff bases and their metal complexes have been expanded by many scientists in this field [16, 17]. Based on literature noteworthy research has been done on Schiff bases and their complexes [18, 19]; though it is noted that work in the synthesis, characterization, catalytic activity studies of Schiff bases exclusively derived from OPA and diamines and amino acids is inadequate [20, 21]. In this context new Schiff bases were designed and synthesized in ethanol medium with less reaction times and high product yields. The combination of medicinally valuable orthophthalaldehyde and respective diamines and amino acids is used to create an adaptable Schiff-base arrangement [22, 23, 24]. In extension of our continuing work is planned to synthesize and characterize the new Schiff base ligands containing N and O donor atoms and then these ligands on treating with Pd(II) salt to give respective Schiff base-metal complexes.

Synthesis of chiral Schiff base ligands
Materials
Ortho-phthalaldehyde (OPA), amino acids, ortho-nitro benzaldehyde and chiral diamines were acquired from Aldrich, USA and all other organic solvents, metal salts used in this study were of analytical grade products from Merck. The solvents were distilled by standard procedure before use. The water used in this study was essentially double distilled water. The purity of the ligands and the complexes prepared was checked by thin layer chromatography.
The new six Schiff base ligands have been synthesized and their structural characterization was carried out by physicochemical techniques such as elemental analysis, conductance, thermo gravimetric, magnetic susceptibility measurements and the spectroscopic techniques like UV-Visible (electronic), IR, mass [1],H NMR [13],C NMR. The physical data of these Schiff base ligands is given in the Table-1.1.

Synthesis of Schiff base (S1)
A solution of ortho-phthalaldehyde (1.70 g, 0.01268 mol) in absolute ethanol (20 mL) was added drop wise to a stirred solution of 1,2-diamino propane (0.94 g, 0.0126 mol) dissolved in warm absolute ethanol (10 mL) and the resulting solution was refluxed for 16 h (TLC checked). After the completion of the reaction the solution was concentrated on rotary evaporator and the ligand was precipitated by petroleum ether. The brown product is produced in 80% yield.
The ligand S1 was synthesized by treating 1, 2-diamino propane with ortho-phthalaldehyde in 1:1 ratio. The synthesis of S1 is shown in Scheme-1.1.

Scheme-1.1 Synthesis of S1

Table 1.1: Physical data of Schiff base ligands:

S.No.	Schiff base	M. P. (ºC)	Colour	Yield (%)
1	S1	110	Brown	80
2	S2	124	Yellow	82
3	A1	138	Green	85
4	A2	142	Yellow	78
5	S3	133	Brown	75
6	S4	141	Snuff	70

2.1 Characterization of chiral Schiff base ligands

The present aim of work is to synthesize a new N_4 and N_2O_2 donor Schiff bases. Six new Schiff base ligands were synthesized by the condensation of orthophthalaldehyde with different chiral 1, 2-diamines, amino acids, and ortho-amino benzaldehyde in different reaction conditions to get corresponding ligands S1, S2, A1, A2, S3 and S4.

All these newly synthesized ligands were well characterized ^{1}H, ^{13}C NMR and mass spectral analysis. Further these ligands were used for the synthesis of Schiff base metal complexes with Co(II) and Ni(II) ions.

Elemental analysis

The percentage of carbon, hydrogen and nitrogen of all these Schiff base ligands were experimentally determined by using CHN analyzer. The physical and analytical data (Table-2.1.1) of ligands is in good agreement with the proposed molecular formulae.

Mass spectral analysis

The mass spectra of ligands *viz*., S1 S2 and S3 showed the (M^{+}+Na) ion peaks at m/z 367,447, 401, where as A1, A2 and S4 ligands shows molecular ion peak at m/z 333,361, 419 (M^{+}+1) respectively. The spectra of the Schiff bases show characteristic molecular ion peaks at their expected m/z values confirming molecular formulas. The mass spectra of S1and A1 ligands were shown in respective Fig.2.1.1and 3.1.2.

Infrared spectral analysis

In IR spectra strong intensity band is appeared in the range of 1652-1631cm^{-1} which is attributed to $\upsilon_{C=N}$ provides a strong evidence for condensation of OPA with amine group [1]. The IR spectra of Schiff base ligands A1 and A2 shown broad a band at 2925cm^{-1} and 2943 cm^{-1} corresponding to -OH group [2] also contain characteristic band at1721 cm^{-1} and 1710 cm^{-1}(strong, very broad) belongs to free carboxyl group of amino acids [2] Aromatic stretching frequencies are observed for all the ligands in the range of 3062-3035 cm^{-1} and 1525-1471 cm^{-1} [2]. The selected infrared spectral data of all the ligands is presented in Table-2.1.2. The IR spectra of S1 and A1 are presented Fig.2.1.3 and 2.1.4 respectively.

^{1}H NMR spectral analysis:

The ^{1}H NMR spectra of six newly synthesized Schiff base ligands was recorded and the integral intensities of every signal were found to be in agreement with the number of different types of protons. All the ligands exhibited a singlet in the range of 8.72-8.10δ responsible to CH=N protons (2H) suggests that the condensation of OPA with amines [2] which was also confirmed by the absence of aldehydic proton peaks around 9.98 δ [1].In the spectra of Ligand S1 and S4 two peaks were observed for azomethine protons at different chemical shift values due to two chemically non-equalant environment where as Ligand S3 shown three peaks.

In the case of ligand S2, all -CH_2 groups and chiral protons of cyclohexane were appeared as multiplates in the range of 2.21-1.15δ and 5.24δ. Schiff bases A1 and A2 have been shown a broad peak at ~11.0 δ corresponding to the –OH group of amino acids. Ligand S3 had shown a doublet peak at 1.42 δ corresponding to methyl group protons, multiplate in the range of 4.25-3.90δfor diastereotopic protons and multiplate at 3.55δ due to chiral proton. For ligand S4 multiplets appeared in the range of 2.18-1.52δ corresponding to methylene groups of cyclohexane and another at 5.28δ was owing to chiral protons [3, 4]. Multiplates exhibited in the range of 7.95-7.10δ were due to the aromatic protons [1]. The significant^{1}H NMR data of selected protons for all the ligands are given in Table-2.1.3. The ^{1}H NMR spectra of S1 and A1 are presented in Fig.2.1.5 and 2.1.6 respectively.

^{13}C NMR spectral analysis

The ^{13}C NMR spectra for all the ligands have been recorded and contain signal around 164.1-161.4δ indicating the presence of azomethine carbon [5] which indicating the condensation between OPA and amine group. All ligands have contained asymmetric carbons which were exhibited signals in the range of 74.2-
58.7δ. The spectra of ligands S1 and S3 shown a signal at 62.3-60.2δ corresponding to methylenic carbon adjacent to nitrogen atom, proves that the being there of N-CH_2 linkage [6]. The spectra of A1 and A2 ligands have been exhibited signals around ~175δ attributed to carboxyl carbon of amino acids [4, 7]. For all the ligands arylic carbons were appeared in the around 142.5-120.6 δ [8]. The ^{13}C NMR spectral data of all the ligands are

represented in Table-2.1.4. The ^{13}C NMR spectra of S1 and A1 are presented in Fig. 2.1.7and 2.1.8 correspondingly.

Conclusion

Based on elemental analysis, mass, IR, ^{1}H NMR and ^{13}C NMR spectral analysis condensation of orthophthalaldehyde with amine group, in the synthesis of new chiral Schiff base ligands, had been confirmed. In the above newly synthesized ligands S1, S2, S3 and S4 perform as N_4 donor systems where as A1 and A2 ligands acts as N_2O_2 donor systems.

Table-2.1.1: Physical data of Schiff base ligands.

S. No.	Schiff base	Molecular Formula	Analysis (%)Found (Calculated)			Mass
			C	H	N	
1.	S1	$C_{22}H_{24}N_4$	75.36(76.71)	6.98(7.02)	16.08(16.27)	367(M^++Na)
2.	S2	$C_{28}H_{32}N_4$	78.69(79.21)	7.54(7.60)	12.89(13.20)	447(M^++Na)
3.	A1	$C_{18}H_{24}N_2O_4$	64.58(65.04)	7.12(7.28)	8.36(8.43)	333(M^++1)
4.	A2	$C_{20}H_{28}N_2O_4$	65.69(66.64)	7.69(7.83)	7.65(7.77)	361(M^++1)
5.	S3	$C_{25}H_{22}N_4$	78.67(79.34)	5.74(5.86)	14.35(14.80)	401(M^++Na)
6.	S4	$C_{28}H_{26}N_4$	79.80(80.35)	6.15(6.26)	13.27(13.39)	419(M^++1)

Table-2.1.2: Infrared spectral data of Schiff base ligands

S. No.	Ligand	Selected IR bands (cm^{-1})			
		$\upsilon_{(C=N)}$	$\upsilon_{(OH)}$	$\upsilon_{(C=O)}$	Aromatic
1.	S1	1648	-	-	3039/1471
2.	S2	1643	-	-	3052/1485
3.	A1	1631	2925	1721	3035/1474
4.	A2	1636	2943	1710	3062/1525
5.	S3	1652	-		3054/1483
6.	S4	1645	.		3058/1495

Table-2.1.3: ^{1}H NMR spectral data of Schiff base ligands

S. No.	Schiff base	^{1}H NMR peak position (δ ppm)
1.	S1	8.25 (s, 2H, -N=CH), 8.10 (s, 2H, -N=CH), 7.90-7.62 (m, 8H, Ar-H), 4.12-3.96 (m, 4H, -CH_2-), 3.11 (m, 2H, -CH), 1.32 (d, 6H, -CH_3)
2.	S2	8.24 (s, 2H, -N=CH), 7.92-7.58 (m, 8H, Ar-H), 5.24 (m, 4H, -CH), 2.21-1.95 (m, 8H, -CH_2), 1.52-1.15 (m, 8H, -CH_2).
3.	A1	10.92 (s, 2H, -COOH), 8.68 (s, 2H, -N=CH), 7.78-7.46 (m, 4H, Ar-H), 3.84 (d, 2H, -CH-CO-), 2.32 (m, 2H, -C<u>H</u>-CH-CO-), 1.03 (d, 12H, -CH_3).
4.	A2	11.12 (s, 2H, -COOH), 8.72 (s, 2H, -N=CH), 7.85-7.41 (m, 4H, Ar-H), 4.18 (t, 2H, 2-CH-CO-), 1.98 (t, 4H, -CH_2-), 1.68 (m, 2H,-CH), 1.06 (d, 12H, -CH_3).
5.	S3	8.36 (s, 2H, -N=CH), 8.16 (s, 1H, -N=CH), 8.11 (s, 1H, N=CH), 7.95-7.12 (m, 12H, Ar-H), 4.25-3.90 (d, 2H, J = 6.0 Hz, CH_2), 3.55 (m, 1H, CH), 1.42(d, 3H, J = 5.3 Hz, CH_3).
6.	S4	8.41 (s, 2H, -N=CH), 8.20 (s, 2H, -N=CH), 7.83-7.10 (m, 12H, Ar-H), 5.28 (m, 2H, -CH), 2.18-1.95 (m, 4H,-CH_2-), 1.69-1.52 (m, 4H, -CH_2-).

Table-2.1.4: ^{13}C NMR spectral data of Schiff base ligands:

S. No.	Schiff base	^{13}C NMR peak position (δ ppm)
1.	S1	163.1 (4C, -N=CH-), 141.7-132.5 (12C, Aromatic), 62.3 (2C, =N-CH_2-), 60.1 (2C, =N-CH-), 18.5 (2C, -CH_3).
2.	S2	163.7 (4C, -N=CH-), 140.2-130.2 (12C, Aromatic),73.8 (4C, =N-CH-), 28.6 (4C, -CH-<u>C</u>H_2-CH_2-), 23.9 (4C, -CH_2-<u>C</u>H_2-CH_2-),
3.	A1	175.3(2C,-CO-OH),161.4(2C,-N=CH-),142.5-128.3(6C, Aromatic),73.5(2C,=N-<u>C</u>H-CO-),30.2(2C,-<u>C</u>H-CH_3),19.1(4C,-CH3).
4.	A2	176.1 (2C, -CO-OH), 162.2 (2C, -N=CH-), 140.2-131.4 (6C, Aromatic), 72.8(2C, =N-<u>C</u>H-CO-), 31.3(2C, -<u>C</u>H-CH_3), 22.4 (2C, -CH-<u>C</u>H_2-CH-), 20.2(4C, -CH3).
5.	S3	164.1 (4C, -N=CH-), 142.5-121.8 (18C, Aromatic), 60.2(1C,-CH_2-N=), 58.7 (1C,=N-CH-), 20.8 (1C, -CH_3).
6.	S4	163.3 (4C, -N=CH-), 141.5-120.6 (18C, Aromatic), 74.2(2C,-CH-N=), 28.6 (2C,-CH-<u>C</u>H_2-CH_2-), 25.1 (2C, -CH_2-<u>C</u>H_2-CH_2-).

3.3. Characterization of Schiff base Co(II) complexes

In general Co(II) ion has d^7configuration, always forms complexes which constitutes different coordination numbers with octahedral and tetrahedral geometries [90]. Complexes having octahedral geometry exhibits colors such as purple (or) wine red on the other hand tetrahedral complexes show blue color. Though, square planar and trigonalbipyramidal geometries are also possible for few complexes.

a. Elemental analysis

$CoCl_2.6H_2O$ was used to synthesize six new Schiff base Co(II) complexes and carbon, hydrogen and nitrogen percentages have been determined. In all newly synthesized Schiff base complexes percentage of cobalt also estimated with the help of literature method [14]. The elemental data of all complexes represented in Table-3.3.1.

b. Mass spectral analysis

The proposed molecular formula of Co(II) complexes was confirmed by the mass spectral analysis by comparing their molecular formula weights with m/z values. The mass spectra contain molecular ion peaks at m/z (M^+) 474 (for comp-2.1), 554 (for comp-2.2), 461 (for comp-2.3), 471 (for comp-2.4), 508 (for comp-2.5) and 548(for comp-2.6). This data is in good agreement with the respective molecular formulae. The mass spectra of $[Co(S1)Cl_2]$ (Complex-2.1)and $[Co(A1)(H_2O)_2].2H_2O$ (Complex-2.3) are presented in Fig.3.3.3 and 3.3.4, respectively.

c. Infrared spectral analysis

To understand the binding nature of Co(II) ion with Schiff bases in newly formed complexes, infrared spectral studies were carried out and compared with corresponding Schiff bases. The azomethine($\upsilon_{C=N}$) band shifted towards lower side about 35-40 cm^{-1}, is appeared with medium intensity in the range of 1607-1622 cm^{-1}[15, 16] which supports the coordination of ligand to the metal ion which also further confirmed by a medium intensity band at 536-522 cm^{-1} responsible to metal nitrogen bond(υ_{M-N}) [17].

In the Schiff base complexes2.3 and 2.4 two bands observed in the range of 1593-1586 & 1381-1362 assignable to symmetric and asymmetric vibrations of carboxylate ion suggesting the coordination of the carboxylate oxygen to the metal atom which also confirmed by the disappearance of a band in the range of 2943-2925 cm^{-1} is due to υ_{OH}.A medium intensity band found in the far IR region of 436-428 cm^{-1} corresponding to metal oxygen bond(υ_{M-O}) is also supports the above fact [16, 17].A broad band around 3400 cm^{-1} is due to the presence of water molecule and additional to this a band in the range of 752-736 cm^{-1} attribute to rocking mode of water molecules which confirming the coordination of water molecules to metal centre which is a non-ligand band. In the case of complexes *viz*., 2.1, 2.2, 2.2.5, 2.6 a medium intensity band found at 338-326 cm^{-1} is evidence for metal-chloride bonds in trans manner [9].There were no significant changes observed for aromatic ring frequencies in all the complexes (Table-3.3.4).The IR spectra of $[Co(S1)Cl_2]$(Complex-2.1), $[Co(A1)(H_2O)_2].2H_2O$ (Complex-2.3) represented Fig.3.3.5 and 3.3.6 respectively.

d. Thermal analysis

The thermogravimetric analysis of all Co(II) complexes was carried out by taking >10 mg of the compound. The TG-DTA curves of Co(II) complex of ligand A1 is presented in Fig.3.3.8.

The water molecules present in complexes classified in to two categories which are lattice and the coordinated water. These two types of water molecules bonded in complex in different manner hence needs variety of temperature range to evaporate. The water present at lattice of the complex evaporates at lower temperature when compared to the water in coordination with directly to central metal atom. Above fact could help to identify the water molecules present at different locations of the complex. In general evaporation of lattice water takes place in the range of 70-130^{o}Cwhereasapproximately 150-220 ^{o}C or above requires for coordinated water.

In the thermograms of all the complexes except 2.3 and 2.4 no peak was observed in the range of 70-130^{o}C indicating the absence of lattice water molecules. It was also supported by the DTA studies which revealed that no of endothermic peak was found in the above temperature range. There was no weight loss found in the temperature range of 150-200^{o}C and the DTA curve representing absence of endothermic peak in this range confirming that the coordinated water molecules were not present in these complexes.

In contrast Schiff base complexes 2.3 and 2.4 were shown initial peak in the range of 70-130 ^{0}C owing to presence of lattice water which was also supported by endothermic peak found in the same temperature range in curve of DTA. The percentage weight loss in this temperature range indicates that there are two water molecules in Co(II) complex of A1 and one water molecule in Co(II) complex of A2 as lattice water. Further another weight loss also observed at 150-220 ^{0}C responsible to coordinated water molecules, later it was confirmed by DTA curve in which endothermic appeared at same temperature range. The percentage weight loss in this temperature range indicates that there are two coordinated water molecules in the complexes 2.3 & 2.4.

All the complexes exhibited a decomposition curve at around 300 ^{0}C due to loss of organic moiety which also confirmed by appearing of exothermic peak in the DTA curve. Above 500^{o}C all decomposition curves attribute to oxidation of metal to metal oxide.

e. Conductance measurements:

All Co(II) complexes were subjected to molar conductance studies by using dichloromethane as solvent [18]. The very low conductance values indicating non-electrolytic behavior nature of the complexes (Table-3.3.6).

f. Magnetic properties

The magnetic moment values (Table-3.3.6) of all the Co(II) complexes were determined by magnetic susceptibility measurements [19, 20]. These are in the range of 4.83-5.05 B.M. and suggesting the octahedral

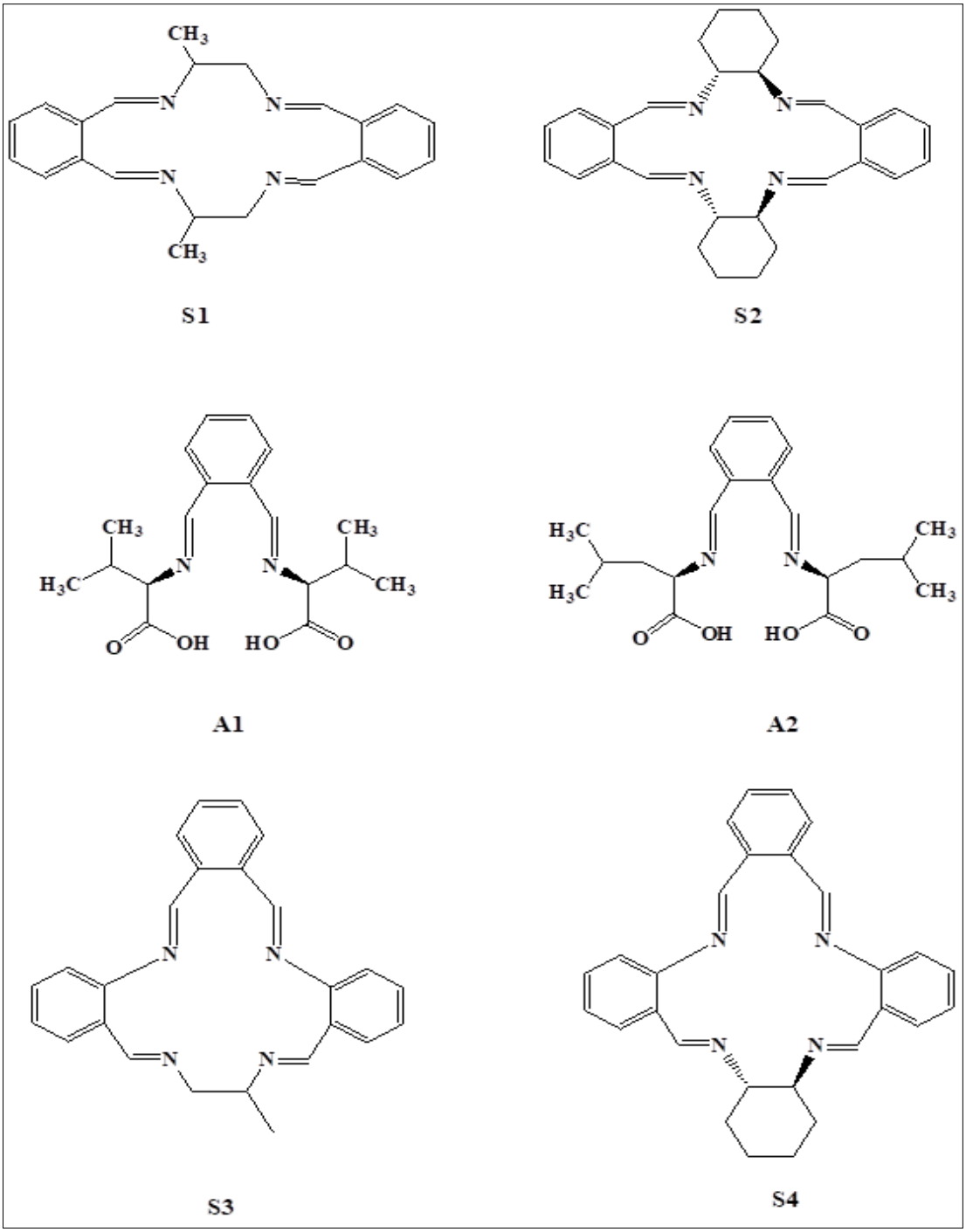
geometry for all the complexes. The magnetic properties depend on the ground and excited states of the metal complexes. The magnetic moment values of Co(II) complexes found to be higher than spin only value and representing the angular momentum value involvement.

g. Structures of the complexes:

On the basis of analytical and spectral data, octahedral structures have been tentatively proposed for all the Schiff base cobalt(II) complexes (Scheme-3.3).

1. Conclusions

Schiff base Co(II) complexes were synthesized by treating $CoCl_2.6H_2O$ with the six Schiff bases individually. In Cobalt(II) complexes of all the ligands(except 2.3 & 2.4)were coordinate through four nitrogen atoms of C=N group, in complexes-2.3, 2.4 ligands coordinates to the metal ion through two nitrogen atoms of C=N group and two oxygen atoms of carboxylic acid groups of amino acids by deprotonation. All the complexes were shown to have non-electrolytic nature. Octahedral structures were proposed to for all the complexes based on elemental and spectral data.



Scheme-2.1: Tentative structures of Schiff base ligands

Table-3.3.1: Analytical data of Co (II) metal complexes

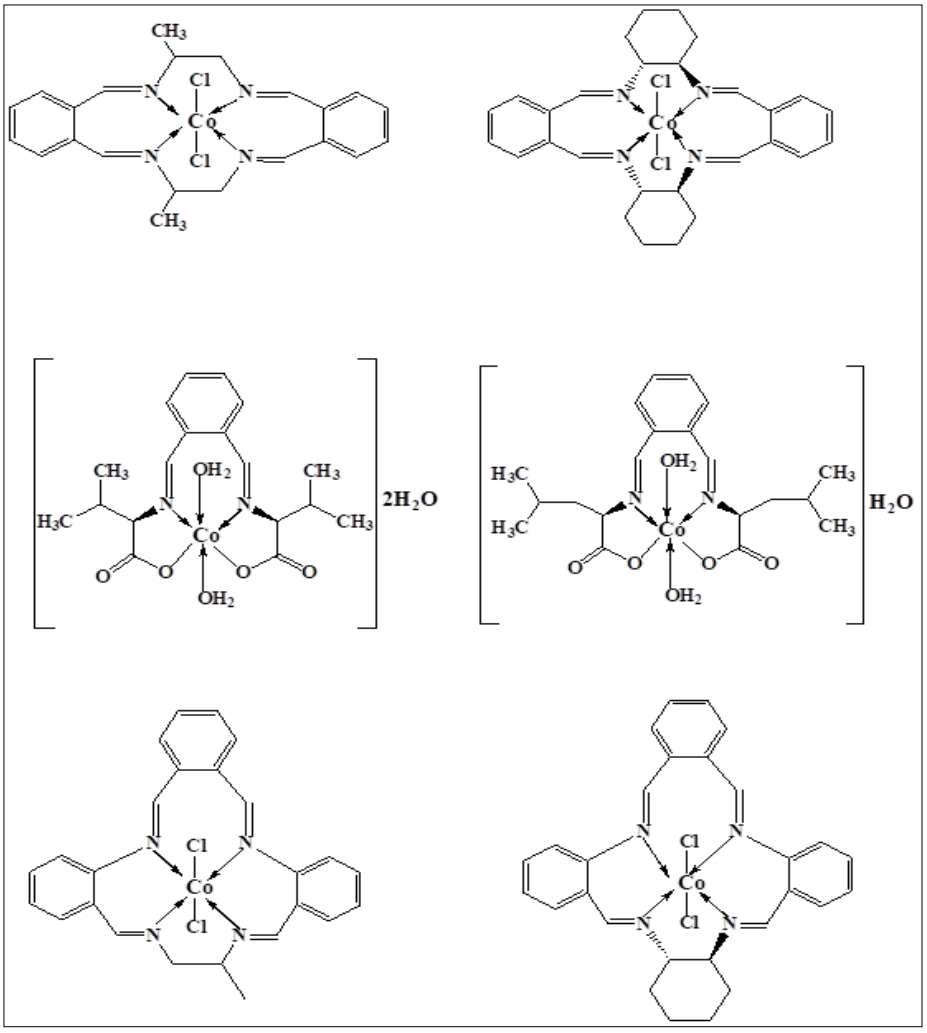
Sr. No.	Co(II) Complex	Molecular Formula	Analysis (%) Found (Calculated)			
			C	H	N	Co
2.1	$[Co(S1)Cl_2]$	$C_{22}H_{24}Cl_2N_4Co$	55.48 (55.71)	5.04(5.10)	11.56(11.81)	12.32(12.43)
2.2	$[Co(S2)Cl_2]$	$C_{29}H_{35}Cl_2N_4Co$	60.90(61.17)	6.15(6.20)	9.74(9.84)	10.21(10.35)
2.3	$[Co(A1)(H_2O)_2].2H_2O$	$C_{18}H_{30}N_2O_8Co$	46.81(46.86)	6.51(6.55)	6.02(6.07)	12.74(12.77)
2.4	$[Co(A2)(H_2O)_2].H_2O$	$C_{20}H_{32}N_2O_7Co$	50.92(50.96)	6.78(6.84)	5.91(5.94)	12.48(12.50)
2.5	$[Co(S3)Cl_2]$	$C_{25}H_{22}Cl_2N_4Co$	59.01(59.07)	4.32(4.36)	11.01(11.02)	11.51(11.59)
2.6	$[Co(S4)Cl_2]$	$C_{28}H_{26}Cl_2N_4Co$	61.28(61.33)	4.71(4.78)	10.18(10.22)	10.71(10.75)

Table-3.3.4: Infrared spectral data of Schiff base Co(II) complexes.

S. No.	Co(II) complex	Selected IR bands (cm^{-1})					
		υ(C=N)	υ(COO-) asym/sym	υ(Co-H_2O)	υ(Co-N)	υ(Co-O)	υ(Co-Cl)
2.1	$[Co(S1)Cl_2]$	1611	-	-	522	-	326
2.2	$[Co(S2)Cl_2]$	1618	-	-	536	-	335
2.3	$[Co(A1)(H_2O)_2].2H_2O$	1607	1593, 1381	752	524	428	-
2.4	$[Co(A2)(H_2O)_2].H_2O$	1612	1586, 1362	736	528	436	-
2.5	$[Co(S3)Cl_2]$	1622	-	-	531	-	338
2.6	$[Co(S4)Cl_2]$	1613	-	-	534	-	327

Table 3.3.6: Molar conductance and magnetic moment data of Schiff base Co(II) complexes.

Sr. No.	Co(II) complex	$\Lambda_M(\Omega^{-1} cm^2 mol^{-1})$	μ_{eff} (B. M.)
2.1.	$[Co(S1)Cl_2]$	12.5	4.98
2.2.	$[Co(S2)Cl_2]$	16.4	5.01
2.3.	$[Co(A1)(H_2O)_2].2H_2O$	9.3	5.03
2.4.	$[Co(A2)(H_2O)_2].H_2O$	15.5	4.92
2.5.	$[Co(S3)Cl_2]$	11.3	5.05
2.6.	$[Co(S4)Cl_2]$	13.2	4.83



Scheme 3.3: Tentative structures of Schiff base Co(II) complexes

Characterization of Schiff base Ni(II) complexes

The Ni(II) complexes of d^8 electronic configuration generally categorized in to three classes:1) octahedral paramagnetic complexes of hexa coordination 2) tetrahedral paramagnetic complexes of tetra coordination 3) square planar diamagnetic complexes of tetra coordinated. Among complexes with octahedral and some tetrahedral Ni(II) geometries exhibits generally violet, green or, light green while red, yellow or brown colors in the case of square planar geometry [21].

a. Physical and analytical data

A new series of Ni(II) complexes were synthesized by the reacting $NiCl_2.6H_2O$ with Schiff base ligands individually. The percentages of carbon, hydrogen and nitrogen in all the complexes were obtained by using CHN analyzer and the percentage of nickel metal in Ni(II) complexes was acquired by using standard method [14]. The physical and analytical data represented in Table-3.4.1 is in good agreement with the proposed molecular formulae.

b. Mass spectral analysis

The mass spectra of Schiff base Ni(II) complexes exhibited molecular ion peaks at m/z (M^+) 474 (for comp-3.1), 554 (for comp-3.2), 461 (for comp-3.3), 471 (for comp-3.4), 508 (for comp-3.5) and 548 (for comp-3.6). This data is in good agreement with the respective molecular formulae. The mass spectra of $[Ni(S1)Cl_2]$ (3.1) and $[Ni(A1)(H_2O)_2].2H_2O$ (3.3) complexes are presented in Fig.3.4.1 and 3.4.2.

c. Infrared spectral analysis

The infrared spectra of Ni(II) complexes obtained and characteristic stretching frequencies were compared with the spectra of corresponding ligands. In the spectra of all complexes the characteristic stretching frequency of C=N was found in the range of 1622-1612 cm^{-1} and it is down field shift of 30-45 cm^{-1} when compared to their ligands supports the coordination of metal ion to ligand. It is also confirmed by a non-ligand band [15] in the range of 536-525 cm^{-1} is due to M-N.

The symmetric and asymmetric stretching modes of carboxylate ion's observed at 1590-1588 & 1379-1360 respectively for complexes of A1 & A2 ligands are evidence for the coordination of Ni(II) ion to oxygen atom of carboxylate [16, 23]. It is also inferred by disappear of band in the between 2943-2925 cm^{-1} (υ_{OH}) and a band in the range of 440-433 cm^{-1} is responsible to stretching frequency [15] of M-O. These complexes contains water is revealed by a broad band around ~3400 cm^{-1} and confirmed by a band found in the range of 757-740 cm^{-1}because of stretching frequency of water molecules indicates the coordination of metal ion to water molecules.

In the case of all complexes (except 3.3 & 3.4) a medium intensity band observed in range of 335-322 cm^{-1} is corresponding to coordination between metal ion and chlorides in trans manner [22].

There are no significant changes are observed for the aromatic ring frequencies in all complexes. The selected infrared stretching frequencies are given in Table-3.4.2 and spectra of $[Ni(S1)Cl_2]$ (complex-3.1), $[Ni(A1)(H_2O)_2].2H_2O$ (complex-3.3)represented Fig.3.4.3 and 3.4.4.

d. Structures of the complexes

All these observations suggest octahedral geometry for the all complexes. On the basis of experimental data the tentative structures (Scheme-3.4) have been proposed.

e. Conclusions

In the present study, six new Nickel(II) complexes were synthesized by the treatment of $NiCl_2.6H_2O$ with six new Schiff base ligands separately.

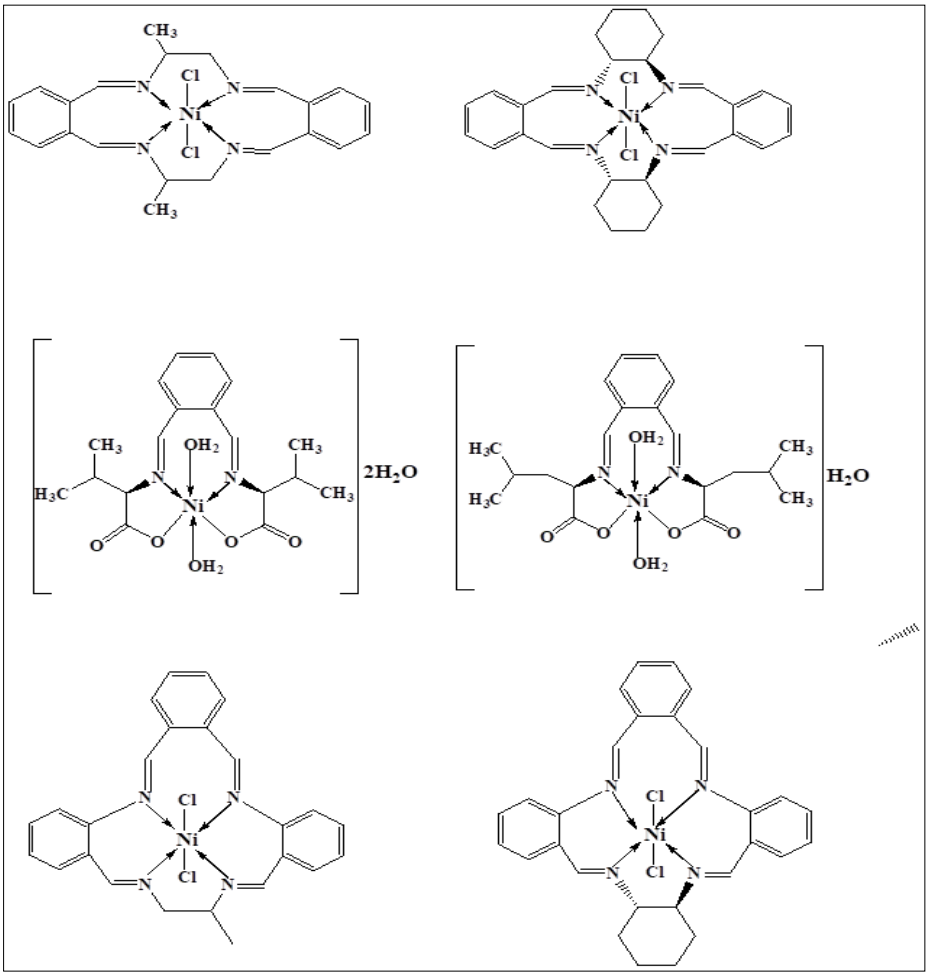
In nickel (II) complexes of all the ligands (except 3.3 & 3.4) were coordinate through four nitrogen atoms of C=N group, in complexes-3.3, 3.4 ligands coordinates to the metal ion through two nitrogen atoms of C=N group and two oxygen atoms of carboxylic acid groups of amino acids by deprotonation. All the complexes were shown to have non-electrolytic nature. Based on the elemental and spectral data octahedral geometry has been assigned for all the complexes.

Table-3.4.1: Analytical data of Ni (II) metal complexes:

Sr. No.	Ni(II) Complex/ Molecular Formula	Analysis (%) Found (Calculated)			
		C	H	N	Ni
3.1	$[Ni(S1)Cl_2]$ $C_{22}H_{24}Cl_2N_4Ni$	55.70 (55.74)	5.08 (5.10)	11.71 (11.82)	12.32 (12.38)
3.2	$[Ni(S2)Cl_2]$ $C_{28}H_{32}Cl_2N_4Ni$	60.61 (60.68)	5.72 (5.82)	10.05 (10.11)	10.51 (10.59)
3.3	$[Ni(A1)(H_2O)_2].2H_2O$ $C_{18}H_{30}N_2O_8Ni$	46.82 (46.88)	6.51 (6.56)	6.04 (6.07)	12.64 (12.73)
3.4	$[Ni(A2)(H_2O)_2].H_2O$ $C_{20}H_{32}N_2O_7Ni$	50.93 (50.98)	6.81 (6.85)	5.21 (5.95)	12.05 (12.46)
3.5	$[Ni(S3)Cl_2]$ $C_{25}H_{22}Cl_2N_4Ni$	59.05 (59.10)	4.25 (4.36)	11.01 (11.03)	11.32 (11.55)
3.6	$[Ni(S4)Cl_2]$ $C_{28}H_{26}Cl_2N_4Ni$	61.21 (61.35)	4.65 (4.78)	10.15 (10.22)	10.65 (10.71)

Table-3.4.2: Infrared spectral data of Schiff base Ni(II) complexes.

S. No.	Ni(II) complex	Selected IR bands (cm^{-1})					
		υ(C=N)	υ(COO-) asym/sym	υ(Ni-H_2O)	υ(Ni-N)	υ(Ni-O)	υ(Ni-Cl)
3.1	$[Ni(S1)Cl_2]$	1613	-	-	525	-	322
3.2	$[Ni(S2)Cl_2]$	1622	-	-	534	-	340
3.3	$[Ni(A1)(H_2O)_2].2H_2O$	1612	1590, 1379	757	528	433	-
3.4	$[Ni(A2)(H_2O)_2].H_2O$	1614	1588, 1360	740	532	440	-
3.5	$[Ni(S3)Cl_2]$	1622	-	-	529	-	333
3.6	$[Ni(S4)Cl_2]$	1619	-	-	536	-	335



Scheme-3.4: Tentative structures of Schiff base Ni(II) complexes

Results and discussion

In the present investigations, six new Schiff base ligands were synthesized by condensation of ortho-phthalaldehyde with different amines and amino acids in alcohol medium. By using these Schiff bases new hexa coordinated Schiff base Co(II)and Ni(II) complexes were synthesized by treating $CoCl_2 \cdot 6H_2O$, with N_2O_2 and N_4 donor Schiff base ligands separately and all the complexes are stable in air and soluble in ethanol. The percentages of carbon, hydrogen and nitrogen were determined experimentally using CHN analyzer. The physical and analytical data (Table-1) for the newly synthesized compounds is in good agreement with the proposed molecular formulae.

References

1. Holm RH, O'Connor MJ. The stereochemistry of bis-chelate metal(II) complexes. Prog Inorg Chem. 1971;14:241-401.
2. Oki AR, Hodgson DJ. Synthesis, characterization and catalytic properties of manganese(III) Schiff base complexes. Inorg Chim Acta. 1990;170(1):65-73.
3. Singh K, Barwa MS, Tyagi P. Synthesis and characterization of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with Schiff base derived from 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine. Eur J Med Chem. 2007;42(3):394-402.
4. Singh HL, Singh JB, Sachedva H. Synthesis, spectroscopic and antimicrobial studies of lead (II) complexes of Schiff bases derived from amino acids and isatins. Spectrosc Lett. 2013;46(4):286-296.
5. Vigato PA, Tamburini S, Bertolo L. The development of compartmental macrocyclic Schiff bases and related polyamine derivatives. Coord Chem Rev. 2007;251(11-12):1311-1492.
6. El-Boraey HA, Abdel-Rahman RM, Atia EM, Khalid EM, Hilmy H. Spectroscopic, thermal and toxicity studies of some 2-amino-3-cyano-1,5-diphenylpyrrole containing Schiff bases copper (II) complexes. Cent Eur J Chem. 2010;8(4):820-833.
7. Sohrab E, Loft-Ali S, Karim-Nezhad G, Sahar K. Electrochemical behavior of N2SO Schiff-base Co(II) complexes in non-aqueous media at the surface of solid electrodes. Int J Electrochem Sci. 2009;4:846-854.
8. Priya NP, Arunachalam S, Manimaran A, Muthupriya D, Jayabalakrishnan C. Mononuclear Ru(III) Schiff base complexes: synthesis, spectral, redox, catalytic and biological activity studies. Spectrochim Acta A Mol Biomol Spectrosc. 2009;72(3):670-676.
9. Seyedi SM, Sandaroos R, Zohuri GH. Novel cobalt(II) complexes of amino acids-Schiff bases catalyzed aerobic oxidation of various alcohols to ketones and aldehyde. Chin Chem Lett. 2010;21(11):1303-1306.
10. Himeda Y, Komatsuzaki NO, Sugihara H, Arakawa H, Kasuga K. Transfer hydrogenation of a variety of ketones catalyzed by rhodium complexes in aqueous solution and their application to asymmetric reduction using chiral Schiff base ligands. J Mol Catal A Chem. 2003;195(1-2):95-100.

11. Reddy V, Patil N, Reddy T, Angadi SD. Synthesis, characterization and biological activities of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes with Schiff base derived from 3-(4-chlorophenoxymethyl)-4-amino-5-mercapto-1,2,4-triazole. E-J Chem. 2008;5(3):529-538.
12. Chakraborty H, Paul N, Rahaman ML. Catalytical activities of Schiff bases aquo complexes of Cu(II) in the hydrolysis of amino acid esters. Transit Met Chem. 1994;14:524-526.
13. Mohamed GG, Omar MM, Ibrahim AA. Biological activity studies on metal complexes of novel tridentate Schiff base ligand: spectroscopic and thermal characterization. Eur J Med Chem. 2009;44(12):4801-4812.
14. Raman N, Raja SJ, Sakthivel A. Transition metal complexes with Schiff-base ligands 4-aminoantipyrine based derivatives. J Coord Chem. 2009;62(4):691-709.
15. Hussain N, Joshi P, Bhandari A, Dangi R, Khanam R, Talesara GL. Synthesis, biological evaluation and electrochemical studies of Cu (II) and Ni (II) complexes of N',N''-1,2-diphenylethane-1,2-diylidenedibenzohydrazide. Int J Pharm Sci Drug Res. 2010;2(4):272-274.
16. Abdalrazaq EA, Ramadane OMA, Numa KSA. Synthesis and characterization of dinuclear metal complexes stabilized by tetradentate Schiff base ligands. Am J Appl Sci. 2010;7(5):628-633.
17. Geeta B, Shravankumar K, Reddy PM, Ravikrishna E, Sarangapani M, Reddy KK, *et al*. Binuclear cobalt(II), nickel(II), copper(II) and palladium(II) complexes of a new Schiff-base as ligand: synthesis, structural characterization, and antibacterial activity. Spectrochim Acta A Mol Biomol Spectrosc. 2010;77(5):911-915.
18. Holm RH, Solomon EI. Preface: Biomimetic inorganic chemistry. Chem Rev. 2004;104(2):347-348.
19. Geeta B, Reddy PM, Rani KS, Hu A, Ravinder V. Synthesis, characterization and biological evaluation of mononuclear Co(II), Ni(II), Cu(II) and Pd(II) Complexes with new N2O2 Schiff base ligands. Chem Pharm Bull (Tokyo). 2011;59(2):166-171.
20. Reddy PM, Prasad AVSS, Rohini R, Ravinder V. Catalytic reduction of pralidoxime in pharmaceuticals by macrocyclic Ni(II) compounds derived from orthophthalaldehyde. Spectrochim Acta A Mol Biomol Spectrosc. 2008;70(4):704-712.
21. Shanker K, Rohini R, Ravinder V, Reddy PM, Ho YP. Ru(II) complexes of N4 and N2O2 macrocyclic Schiff base ligands: their antibacterial and antifungal studies. Spectrochim Acta A Mol Biomol Spectrosc. 2009;73(1):205-211.
22. Reddy PM, Prasad AVSS, Shanker K, Ravinder V. Synthesis, spectral studies and antibacterial activity of novel macrocyclic Co(II) compounds. Spectrochim Acta A Mol Biomol Spectrosc. 2007;68(4):1000-1006.
23. Bharati N, Sharma SS, Naqvi F, Azam A. Bioorg Med Chem. 2003;11(13):2923-2929.
24. Shakir M, Chishti HTN, Chingsubam P. Spectrochim Acta A Mol Biomol Spectrosc. 2006;64(2):512-519.
25. Shakir M, Varkey SP, Hameed PS. J Chem Res. 1993;(11):442.
26. Wiles DM, Gingras BA, Suprunchuk T. Can J Chem. 1967;45(5):469-473.
27. Jeewoth T, Bhowan MG, Wah HLK. Transit Met Chem. 1999;24(4):445-448.
28. Chandra S, Kumar R, Singh R. Spectrochim Acta A Mol Biomol Spectrosc. 2006;65(1):215-220.
29. Sheshagiri NR, Raghava NR. Indian J Chem. 1977;15A:652.
30. Yang H, Sun WH, Li Z, Wang L. Synth Commun. 2002;32(15):2395-2402.
31. Colthup NB, Daly LH, Wiberley SE. Introduction to Infrared and Raman Spectroscopy. New York: Academic Press; 1964.
32. Nikolaev AV, Logvinenko VA, Myachina LI. Thermal Analysis. New York: Academic Press; 1969. Vol. 2.
33. Allan JR, Veitch TM. J Therm Anal. 1983;27(1):3-8.
34. Rama AK, Shah JR. Indian J Chem. 1981;20A:142.
35. Okawa H, Nishio J, Ohba M, Tadokoro M, Matsumoto N, Koikawa M, *et al*. Inorg Chem. 1993;32(13):2949-2953.
36. Ryan DE. Anal Chem. 1950;22(4):599-600.
37. Geary WJ. Coord Chem Rev. 1971;7(1):113-152.
38. Colak AT, Tumer M, Serin S. Transit Met Chem. 2000;25(2):200-205.
39. Kneubühl FK. J Chem Phys. 1960;33(4):1074-1078.
40. Sallam SA. Transit Met Chem. 2006;31(1):46-55.
41. Satyanarayana DN. Electronic Absorption Spectroscopy and Related Techniques. Hyderabad: Universities Press; 2001.
42. Ballhausen CJ. Introduction to Ligand Field Theory. New York: McGraw-Hill; 1962.
43. Jahn HA, Teller E. Proc R Soc Lond A. 1938;164(917):117-131.
44. Anita R, Somanath M, Nibedita N, Alekha Kumar S, Tungabidya M. Chin Chem Lett. 2016;27(6):891-896.
45. Orgel LE. An Introduction to Transition-Metal Chemistry: Ligand-Field Theory. 2nd ed. London: Wiley; 1966.
46. van Soest MD. Inorg Chem. 1972;11(1):151-155.
47. Stephens FS. J Chem Soc A. 1969;883-889.
48. Lever ABP. Inorganic Electronic Spectroscopy. Amsterdam: Elsevier; 1968.
49. Sands RH. Phys Rev. 1955;99(4):1222-1226.
50. Rosenberg RC, Root CA, Bernstein PK, Gray HB. J Am Chem Soc. 1975;97(8):2092-2096.
51. Kivelson D, Neiman R. J Chem Phys. 1961;35(1):149-155.
52. Griffith WP. Platinum Met Rev. 2003;47(4):175-183.
53. Anna MZ, Jacques M. Tetrahedron Lett. 2007;48(38):6738-6741.
54. Quagliano JV, Fujita J, Franz G, Phillips DJ, Walmsley JA, Tyree SY. J Am Chem Soc. 1961;83(18):3770-3773.
55. Ivanova BB, Mayer-Figge H. J Coord Chem. 2005;58(8):653-661.
56. Ivanova BB, Arnaudov MG, Mayer-Figge H. Polyhedron. 2005;24(13):1624-1630.
57. Shakir M, Nasman OSM, Varkey SP. Polyhedron. 1996;15(2):309-317.
58. Ilhan S. J Coord Chem. 2008;61(22):3634-3644.
59. Chohan ZH, Praveen M. Appl Organomet Chem. 2001;15(7):617-625.
Tzschach A, Jurkschat K, Zschunke A, Mügge C, Altenbrunn B, Leopardi CP, *et al*. J Chem Crystallogr. 1985;15(5):423-429.