



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol.5, No.4, pp 1502-1511, April-June 2013

Design, Synthesis, Structural Elucidation, DNA Cleavage, 3D Molecular Modelling and Antibacterial Activity of Binuclear Metal(II) Complexes Containing Salicylaldehydebased Schiff bases

E. Akila, M. Usharani and R. Rajavel*

Department of Chemistry, Periyar University, Salem-11, Tamilnadu, India.

*Corres. Author: akilachemphd@gmail.com Mobile: +91 9865094324; fax: +91 04272345124

Abstract: A binucleating tetradentate Schiff base ligand and its Cu(II), Ni(II) and VO(II) complexes derived from 1,5- diaminonapthalene and Salicylaldehyde have been synthesized. The complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility data, electronic, IR, ESR spectral data and 3D molecular modelling. On the basis spectroscopic studies, the Schiff base is dibasic tetradentate ligand having the composition M_2L_2 Where M = Cu(II), Ni(II) and VO(II). The UV–Vis, ESR, magnetic susceptibility data of the complexes suggest a square–planar geometry around the central metal ion except VO(II) complex which has square–pyramidal geometry. The 3D molecular modelling and analysis for bond lengths and bond angles have also been carried out for the Cu(II) complex to substantiate the proposed structure. The complexes show significant growth inhibitory activity against the bacteria like *Staphylococcus aureus, Escherichia coli, Bacillus subtilis* and *Klebsilla pneumonia* than the free ligands.

Keywords: 1, 5- diaminonapthalene, Salicylaldehyde, Antibacterial, Schiff base, 3D molecular modelling.

Introduction

Binucleating Schiff base metal complexes having unique electronic and spectroscopic signatures which offer a multitude of coordination geometries and mechanism of cytotoxic action which is related to DNA interaction and can also vary accordingly as the biological activity is strongly dependent on structure–activity relationship. Schiff bases are widely employed as ligands in coordination chemistry^{1, 2}. Schiff bases³ were still regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials. All these advantages make Schiff bases very good candidates in the effort to synthesize metal complexes of interest in bioinorganic chemistry, catalysis, encapsulation, transport, separation processes, and magneto chemistry⁴. In view of recent interest in the energetic of metal ligand binding in metal chelates involving N, O donor ligands, we started to study Schiff bases are well known to coordinate with various metal ligands involving an N₂O₂ donor atoms. Tetradentate Schiff bases are well known to coordinate with various metal ions forming stable compounds. Due to their importance in analytical and bioinorganic chemistry, complexes of tetra-coordinated (ONNO) Schiff bases and transition metals are extensively studied. Such complexes present many applications in catalysis and oxygen storage devices⁵. Many present antitumoral, antiviral and antibacterial activity⁶ and also used as mimetic systems for enzyme models⁷.

Schiff-base ligands derived from Salicylaldehyde and diamines have been widely applied in enantioselective cyclopropanation of styrenes, asymmetric aziridination of olefins⁸, enantioselective

epoxidation⁸, enantioselective ring opening of epoxides⁹, borohydride reduction of aromatic ketones⁹, asymmetric oxidation of methyl phenyl sulfide¹⁰, enantioselective oxidation of silyl enol¹¹ and trimethylsilylcyanation of benzaldehydes^{9, 12}. However, so far there have been few reports about the synthesis and application of Schiff-base ligands derived from 1, 5- diaminonapthalene and Salycilaldehyde. The reactions of these ligands with some transition metal ions in molar ratio (2:2, ligand: metal ion) were studied. The newly prepared metal complexes of these ligands were identified by different physico-chemical and spectroscopic techniques such as IR, UV–vis, ESR spectra and 3D molecular modelling, as well as the measurements of conductivity and magnetic moments at room temperature.

Experimental section

All the chemicals used were chemically pure and AR grade. Solvents were purified and dried according to standard procedures. Metal salts were purchased from Merck. 1, 5- diaminonapthalene and Salycilaldehyde were obtained from Aldrich. Other chemicals were also purchased from Merck and Aldrich.

Materials and physical measurements

The elemental analysis were carried out with a Carlo-Erba 1106-model 240 Perkin Elmer analyzer. The solution conductivity measurements were performed to establish the charge type of the complexes. The complexes were dissolved in DMF and molar conductivities of 10^{-3} M of their solutions at 29 ^oC were measured with ELICO CM 185 conductivity Bridge. Infrared spectra were recorded on the Perkin Elmer FT-IR- 8300 model spectrometer using KBr disc and Nujol mull techniques in the range of 4000-400 cm⁻¹. Electronic absorption spectra in the UV-Visible range were recorded on Perkin Elmer Lambda -25 between 200-800 nm by using DMF as the solvent. The magnetic studies were carried out at room temperature on a Gouy balance calibrated with Hg [Co(SCN)₄]. EPR spectra were recorded on a Varian E–112 ESR spectrophotometer at X-band microwave frequencies for powdered samples at room temperature and for solution at 77 K, IIT-Bombay, Mumbai. The antibacterial activities of the compounds were determined by using the well diffusion method.

Preparation of binucleating tetradentate Schiff base ligand

The binucleating tetradentate Schiff base was prepared by condensation of diamine with appropriate aldehydes. 1, 5- diaminonapthalene (1 mmol) in 20 ml of ethanol was stirred with Salycilaldehyde (2 mmol) in 20 ml of ethanol for 4 hrs as shown in the scheme 1. The resulting yellow solid was separated and dried in vacuum. Yield: 80%.

Synthesis of binuclear Schiff base complexes

An ethanolic solution of the metal (II)chloride salts [Cu(II), Ni(II) and VO(II)] was added gradually to the ethanolic solution of the deprotonated ligand in the 2:2 molar ratio. The reaction mixture was stirred for 1 hr and then heated to reflux for 3 hrs as shown in the scheme 1. The complexes are soluble in DMF, DMSO producing intense color in their solution. After partial evaporation of the solvent, solid (65–75%) Schiff base complexes were separated and dried in vacuum. The analysis results are in good consistency with proposed formulas in **Table 1**.

Compounds	Color	Yield %	Melting Point	Calculated (Found) (%)			$(ohm^{-1}cm^2 mol^{-1})$	
			(°)	С	Η	Ν	Metal	
$(C_{24}H_{18}N_2O_2)$	Yellow	80	162	78.60 (78.58)	4.91 (4.93)	7.64 (7.62)		
$[Cu_2(C_{48}H_{32}N_4O_4)]$	Dark green	75	>250	67.36 (67.39)	3.74 (3.73)	6.54 (6.56)	14.86 (14.87)	15.21
$[Ni_2(C_{48}H_{32}N_4O_4)]$	Brown	70	>250	68.13 (68.14)	3.78 (3.80)	6.62 (6.63)	13.88 (13.87)	12.20
$[VO_2(C_{48}H_{32}N_4O_4)]$	Black	75	>250	69.41 (69.44)	3.85 (3.83)	6.74 (6.73)	12.26 (12.28)	17.40

Table 1. Physical properties of ligand and their binuclear Schiff base metal complexes



M= Cu, Ni & VO

Scheme 1 Synthesis of Schiff Base Ligand and its Complexes [M₂L₂]

The in vitro Antibacterial activity

The *in vitro* antibacterial activity of the ligand and the complexes were tested against the pathogenic bacteria like *Bacillus subtilis, Klebsiella pneumoniae, Escherichia coli* and *Staphylococcus aureus* by well diffusion method using nutrient agar as the medium¹³. *Streptomycin* was used as standard. The stock solution $(10^{-1} \text{ mol } \text{L}^{-1})$ was prepared by dissolving the compound in DMF and the solution was serially diluted to find minimum inhibitory concentration (MIC) values. In a typical procedure, a well was made on the agar medium with microorganisms in a petri plate. The well was filled with the test solution and the plate was incubated for 24 hrs for bacteria at 35°C. During the period, the test solution diffused and the growth of the inoculated microorganisms was affected. The inhibition zone was developed, at which the concentration was noted.

Results and discussion

The binuclear Schiff base ligand prepared and reacts with transition metals Cu(II), Ni(II), and VO(II). The Schiff base ligand has been synthesized from 1, 5- diaminonapthalene and Salycilaldehyde in 1:2 mole ratio. The results of elemental analysis were in good agreement with those required by the proposed formulae given in Table 1. The data in consistent with the earlier reports support the proposed formulation of the binuclear complexes. The new binuclear complexes are stable, hygroscopic with higher melting points, insoluble in water, soluble in acetonitrile, chloroform, DMF and DMSO.

Conductivity studies

The binuclear complexes are dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at 30°C were measured. Table 1 shows the molar conductance values of the complexes. It is concluded from the results that the Cu(II), Ni(II), and VO(II) complexes have a molar conductivity in the range of 12.20 – 17.40 Ohm⁻¹cm²mol⁻¹, which indicates the non-ionic nature of these complexes and they are considered as non-electrolytes.

IR spectra

The IR data of the spectra of Schiff base and its complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may involve in chelation. Upon comparison it was found that the azomethine (C=N) stretching vibration is found in the free ligand at 1610 cm⁻¹. This band is shifted to lower wavenumbers (1598–1602 cm⁻¹) in the complexes indicating the participation of the azomethine nitrogen in coordination (M-N)¹⁴. The above data clearly indicate that the carbonyl groups of Salycilaldehyde have reacted with the amine groups of 1, 5- diaminonapthalene through the condensation of the metal atoms. Phenolic (C-O) stretching vibration band is observed at 1275 cm⁻¹ in the free ligand. On complexation this band is shifted to higher frequency in the range of 1290-1310 cm⁻¹ for all the Schiff base complexes which suggest that the carbonyl group is involved in coordination through deprotonation^{15, 16}. This is further supported by the disappearance of the OH in the range of 3300- 3440 cm⁻¹ in all the complexes. Accordingly, the ligand acts as a tetradendate chelating agent bonded. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 515-540cm⁻¹ and 455-480 cm⁻¹ which could be attributed to M-O, M-N respectively¹⁷. Thus from the IR spectra it is clear that the compounds may be bonded to the metal ions through the imine nitrogen.

Compounds	Free-OH	-C=N	C-0	M-O	M-N
$(C_{24}H_{18}N_2O_2)$	3340	1610	1275	-	-
$[Cu_2(C_{48}H_{32}N_4O_4)]$	-	1598	1293	515	460
$[Ni_2(C_{48}H_{32}N_4O_4)]$	-	1602	1290	535	480
$[VO_2(C_{48}H_{32}N_4O_4)]$	-	1600	1310	540	455

Table 2. Infrared spectroscopic data of the Schiff base ligand and its binuclear complexes

Electronic spectra

The UV-visible spectra are often very useful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and number of d-d transition peaks. The UV-vis spectra of the ligand and the complexes were recorded in DMF solution in the wavelength range from 200 to 800 nm. The two bands observed at 295 and 345 nm in the free ligand are reasonably accounted for * and n * transitions. The spectra of the complexes further display a bands in the range 415–455 which might be assigned to charge transfer transition from the ligand to metal ions (L M)¹⁸.

Further, the d-d transition of the complex showed a broad band centered at 530 nm for Cu(II) complex . This is due to ${}^{2}B_{1}g$ ${}^{2}A_{1}g$ transition¹⁹. The spectra of Ni(II) complex in the visible region at about 545 and 490 nm is assigned to ${}^{1}A_{1}g$ ${}^{1}A_{2}g$, ${}^{1}A_{1}g$ ${}^{1}B_{1}g$, transitions, suggesting an approximate square planar geometry of the ligand around the metal ions²⁰. The intense charge transfer band at 555 and 625 nm in VO(II) complex assigned to ${}^{2}B_{2}$ ${}^{2}A_{1}$, ${}^{2}B_{2}$ ${}^{2}E$ transitions. This is due to electron delocalization over whole molecule on complexation. Based on these data, a square planar geometry has been assigned to the complexes except VO(II) complex which has square pyramidal geometry. These values are comparable with other reported complexes²¹.

	Elect	tronic spectra	Geometry of the		
Compounds	*	n *	L M	d-d	complex
$(C_{24}H_{18}N_2O_2)$	295	345	-	-	-
$[Cu_2(C_{48}H_{32}N_4O_4)]$	269	360	415	530	Square planar
$[Ni_2(C_{48}H_{32}N_4O_4)]$	290	365	440	545, 490	
$[VO_2(C_{48}H_{32}N_4O_4)]$	275	370	455	555, 625	Square pyramidal

Table 3. Electronic Spectral data of Schiff base ligand and its metal complexes.

Magnetic properties

The magnetic moment values of binuclear metal complexes were carried out by room temperature. The magnetic moment of Cu(II) complex is 1.71.B.M. It lies below the spin only value. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ions no interaction between the metal centres²². The magnetic moment of the Ni(II) complex is diamagnetic in nature and square planar environment around the metal atom and it indicates there is no metal- metal interaction in Ni(II) centers. The room temperature value of VO(II) ion for the complex is 1.63.B.M. It has been observed that the µeff values indicate a single unpaired electron and is consistent with non-interacting metal centers or the absence of any strong magnetic interaction between the two VO(II) centers of the complexes.

ESR spectra

ESR spectra was used to identify coordination number, geometry of the complexes and also used to determine metal-ligand environment covalency. The room temperature EPR spectra of powdered samples were measured at X-band frequencies at 9.829475 GHZ. X-Band ESR spectra of $[Cu_2(C_{48}H_{32}N_4O_4)]$, were recorded in the solid state at 25°C^{23,24}.

The EPR-spectra of the copper(II) complex showed a sharp band, centered around $g_{iso} = 2.0013$. The g_{iso} lines are usually the results of either intermolecular spin exchange, which can broaden the lines or occupancy of the unpaired electron in a degenerate orbital in square planar geometry. This indicates that the two paramagnetic centers are equivalent and there is no super exchange interaction between the two metal centers .

3D Molecular modelling



Scheme 2 3D structure of [Cu₂(C₄₈H₃₂N₄O₄)].

The 3D molecular modeling of $[Cu_2(C_{48}H_{32}N_4O_4)]$ was carried out with the CS Chem 3D Ultra Molecular Modeling and Analysis Program as shown in the scheme 2. The details of bond lengths, bond angles as per the 3D structures (scheme 2) are given in Tables 4 and 5 respectively. Except only some cases, optimal values of both the bond lengths and the bond angles are given in the Tables along with the actual ones. The observed bond lengths and bond angles are close to the optimal values, and thus the proposed structure is square planar and is acceptable²⁵.

Atoms	Actual bond	Optimized	Atoms	Actual bond	Optimized
	length	bond length		Length	bond length
C(1)-C(2)	1.420	1.420	C(25)-C(29)	1.420	1.420
C(1)-C(6)	1.440	1.420	C(25)-H(78)	1.100	1.100
C(1)-H(85)	1.100	1.100	C(51)-C(52)	1.503	1.503
C(2)-C(3)	1.420	1.420	C(52)-H(68)	1.100	1.100
C(2)-H(90)	1.100	1.100	O(53)-Cu(57)	1.810	-
C(3)-C(4)	1.420	1.420	O(54)-Cu(57)	1.395	-
C(3)-N(21)	1.462	1.462	O(55)-Cu(58)	2.015	-

Table 4. Various bond length of Schiff base [Cu₂(C₄₈H₃₂N₄O₄)] complex.

C(4)-C(5)	1.420	1.420	O(56)-Cu(58)	1.231	-
C(4)-C(7)	1.420	1.420	C(26)-C(51)	1.337	1.337
C(5)-C(6)	1.420	1.420	C(26)-H(69)	1.100	1.100
C(5)-C(10)	1.420	1.420	C(27)-C(36)	1.337	1.337
C(6)-H(86)	1.100	1.100	C(27)-H(75)	1.100	1.100
C(7)-C(8)	1.420	1.420	C(28)-C(44)	1.337	1.337
C(7)-H(88)	1.100	1.100	C(28)-H(72)	1.100	1.100
C(8)-C(9)	1.442	1.420	C(29)-C(30)	1.420	1.420
C(8)-H(83)	1.100	1.100	C(29)-C(34)	1.503	1.503
C(9)-C(10)	1.420	1.420	C(30)-C(31)	1.503	1.503
C(9)-H(84)	1.100	1.100	C(30)-O(55)	1.355	1.355
C(10)-N(22)	1.462	1.462	C(31)-C(32)	1.337	1.337
C(11)-C(12)	1.420	1.420	C(31)-H(76)	1.100	1.100
C(11)-C(16)	1.437	1.420	C(32)-C(33)	1.586	1.503
C(11)-H(81)	1.100	1.100	C(32)-H(62)	1.100	1.100
C(12)-C(13)	1.420	1.420	C(33)-C(34)	1.337	1.337
C(12)-H(89)	1.100	1.100	C(33)-H(61)	1.100	1.100
C(13)-C(14)	1.420	1.420	C(34)-H(77)	1.100	1.100
C(13)-N(23)	1.462	1.462	C(35)-C(36)	1.503	1.503
C(14)-C(15)	1.420	1.420	C(35)-C(40)	1.337	1.337
C(14)-C(17)	1.420	1.420	C(35)-O(54)	1.355	1.355
C(15)-C(16)	1.420	1.420	C(36)-C(37)	1.503	1.503
C(15)-C(20)	1.420	1.420	C(37)-C(38)	1.420	1.420
C(16)-H(82)	1.100	1.100	C(37)-H(74)	1.100	1.100
C(17)-C(18)	1.420	1.420	C(38)-C(39)	1.484	1.420
C(17)-H(87)	1.100	1.100	C(38)-H(60)	1.100	1.100
C(18)-C(19)	1.519	1.420	C(39)-C(40)	1.503	1.503
C(18)-H(79)	1.100	1.100	C(39)-H(59)	1.100	1.100
C(19)-C(20)	1.420	1.420	C(40)-H(73)	1.100	1.100
C(19)-H(80)	1.100	1.100	C(41)-C(42)	1.590	1.420
C(20)-N(24)	1.462	1.462	C(41)-C(46)	1.503	1.503
N(21)-C(27)	1.462	1.462	C(41)-H(65)	1.100	1.100
N(21)-Cu(57)	1.846	-	C(42)-C(43)	1.420	1.420
N(22)-C(25)	1.462	1.462	C(42)-H(70)	1.100	1.100
N(22)-Cu(58)	1.846	-	C(43)-C(44)	1.503	1.503
N(23)-C(28)	1.462	1.462	C(43)-H(71)	1.100	1.100
N(23)-Cu(57)	1.846	-	C(44)-C(45)	1.503	1.503
N(24)-C(26)	1.462	1.462	C(45)-C(46)	1.337	1.337
N(24)-Cu(58)	1.445	-	C(45)-O(53)	2.646	1.355
C(46)-H(66)	1.100	1.100			
C(47)-C(48)	1.420	1.420			
C(47)-C(52)	1.420	1.420			
C(47)-H(67)	1.100	1.100			
C(48) - C(49)	1.592	1.503			
C(48)-H(63)	1.100	1.100			
C(49)-C(50)	1.337	1.557			
C(49)-H(64)	1.100	1.100			
C(50) - C(51)	1.503	1.503			
U(30) - U(36)	1.335	1.335			

	Actual	Ontimized		Actual	Ontimized
Atoms	bond	bond	Atoms	bond	bond angle
1 toms	angle	angle	rtoms	angle	bonu angie
C(2)-C(1)-C(6)	119.533	120.000	C(11)-C(16)-C(15)	118.830	120.000
C(2)- $C(1)$ - $H(85)$	120.001	120,000	C(11) - C(16) - H(82)	120.015	120,000
C(6)-C(1)-H(85)	120.001	120.000	C(15)-C(16)-H(82)	120.014	120.000
C(1)-C(2)-C(3)	120,000	120,000	C(14)-C(17)-C(18)	120,000	120,000
C(1)- $C(2)$ - $H(90)$	119 998	120.000	C(14)-C(17)-H(87)	119 998	120.000
C(3)-C(2)-H(90)	120,000	120.000	C(18)-C(17)-H(87)	119 998	120.000
C(2)- $C(3)$ - $C(4)$	119 998	120,000	C(17)-C(18)-C(19)	116 101	120,000
C(2)- $C(3)$ - $N(21)$	120.000	120.000	C(17) - C(18) - H(79)	120.010	120.000
C(4)- $C(3)$ - $N(21)$	120.000	120.000	C(19)-C(18)-H(79)	120.010	120.000
C(3)-C(4)-C(5)	120.000	120.000	C(18)-C(19)-C(20)	114.387	120.000
C(3)-C(4)-C(7)	119.998	120.000	C(18)-C(19)-H(80)	120.015	120.000
C(5)-C(4)-C(7)	119.998	120.000	C(20)-C(19)-H(80)	120.015	120.000
C(4)- $C(5)$ - $C(6)$	119,998	120.000	C(15)-C(20)-C(19)	119.998	120.000
C(4)- $C(5)$ - $C(10)$	119.998	120.000	C(15)-C(20)-N(24)	120.000	120.000
C(6)-C(5)-C(10)	119.998	120.000	C(19)-C(20)-N(24)	120.000	120.000
C(1)-C(6)-C(5)	118.597	120.000	C(3)-N(21)-C(27)	121.998	124.000
C(1)- $C(6)$ - $H(86)$	120.005	120.000	C(3)-N(21)-Cu(57)	117.999	-
C(5)-C(6)-H(86)	120.001	120.000	C(27)-N(21)-Cu(57)	119.998	-
C(4)-C(7)-C(8)	120.000	120.000	C(10)-N(22)-C(25)	121.998	124.000
C(4)- $C(7)$ - $H(88)$	120.000	120.000	C(10) - N(22) - Cu(58)	117.999	-
C(8)-C(7)-H(88)	119,998	120.000	C(25)-N(22)-Cu(58)	119.998	-
C(7)-C(8)-C(9)	119.225	120.000	C(13)-N(23)-C(28)	121.998	124.000
C(7)- $C(8)$ - $H(83)$	120.010	120.000	C(13)-N(23)-Cu(57)	117.999	-
C(9)- $C(8)$ - $H(83)$	120.010	120.000	C(28)-N(23)-Cu(57)	119.998	-
C(8)-C(9)-C(10)	119.417	120.000	C(20)-N(24)-C(26)	144.073	124.000
C(8)-C(9)-H(84)	120.015	120.000	C(20)-N(24)-Cu(58)	121.003	-
C(10)-C(9)-H(84)	120.012	120.000	C(26)-N(24)-Cu(58)	94.919	-
C(5)-C(10)-C(9)	119.998	120.000	N(22)-C(25)-C(29)	119.000	119.000
C(5)-C(10)-N(22)	120.000	120.000	N(22)-C(25)-H(78)	120.500	113.500
C(9)-C(10)-N(22)	119.998	120.000	C(29)-C(25)-H(78)	120.500	120.000
C(12)-C(11)-C(16)	119.671	120.000	N(24)-C(26)-C(51)	119.000	119.000
C(12)-C(11)-H(81)	120.010	120.000	N(24)-C(26)-H(69)	120.498	113.500
C(16)-C(11)-H(81)	120.010	120.000	C(51)-C(26)-H(69)	120.500	120.000
C(11)-C(12)-C(13)	120.000	120.000	N(21)-C(27)-C(36)	119.000	119.000
C(11)-C(12)-H(89)	119.998	120.000	N(21)-C(27)-H(75)	120.498	113.500
C(13)-C(12)-H(89)	119.998	120.000	C(36)-C(27)-H(75)	120.500	120.000
C(12)-C(13)-C(14)	119.998	120.000	N(23)-C(28)-C(44)	119.000	119.000
C(12)-C(13)-N(23)	119.998	120.000	N(23)-C(28)-H(72)	120.500	113.500
C(14)-C(13)-N(23)	120.000	120.000	C(44)-C(28)-H(72)	120.498	120.000
C(13)-C(14)-C(15)	120.000	120.000	C(25)-C(29)-C(30)	120.000	120.000
C(13)-C(14)-C(17)	119.998	120.000	C(25)-C(29)-C(34)	119.998	120.000
C(15)-C(14)-C(17)	119.998	120.000	C(30)-C(29)-C(34)	119.998	120.000
C(14)-C(15)-C(16)	119.998	120.000	C(29)-C(30)-C(31)	120.000	120.000
C(14)-C(15)-C(20)	120.000	120.000	C(29)-C(30)-O(55)	124.298	124.300
C(16)-C(15)-C(20)	119.998	120.000	C(31)-C(30)-O(55)	115.700	124.300
C(30)-C(31)-C(32)	119.998	120.000	C(52)-C(47)-H(67)	119.998	120.000
C(30)-C(31)-H(76)	119.998	120.000	C(47)-C(48)-C(49)	119.877	120.000
C(32)-C(31)-H(76)	119.998	120.000	C(47)-C(48)-H(63)	120.059	120.000
C(31)-C(32)-C(33)	120.001	120.000	C(49)-C(48)-H(63)	120.059	120.000
C(31)-C(32)-H(62)	120.000	120.000	C(48)-C(49)-C(50)	119.596	120.000
C(33)-C(32)-H(62)	119.996	120.000	C(48)-C(49)-H(64)	120.001	120.000
C(32)-C(33)-C(34)	120.001	120.000	C(50)-C(49)-H(64)	119.998	120.000

Table 5. Various bond angle of Schiff base $[Cu_2(C_{48}H_{32}N_4O_4)]$ complex.

C(32)-C(33)-H(61)	119.998	120.000	C(49)-C(50)-C(51)	120.000	120.000
C(34)-C(33)-H(61)	119.998	120.000	C(49)-C(50)-O(56)	115.700	124.300
C(29)-C(34)-C(33)	120.000	120.000	C(51)-C(50)-O(56)	124.299	124.300
C(29)-C(34)-H(77)	119.998	120.000	C(26)-C(51)-C(50)	120.000	120.000
C(33)-C(34)-H(77)	120.000	120.000	C(26)-C(51)-C(52)	119.998	120.000
C(36)-C(35)-C(40)	120.000	120.000	C(50)-C(51)-C(52)	119.998	120.000
C(36)-C(35)-O(54)	124.298	124.300	C(47)-C(52)-C(51)	120.000	120.000
C(40)-C(35)-O(54)	115.698	124.300	C(47)-C(52)-H(68)	120.000	120.000
C(27)-C(36)-C(35)	120.000	120.000	C(51)-C(52)-H(68)	119.998	120.000
C(27)-C(36)-C(37)	119.998	120.000	C(45)-O(53)-Cu(57)	77.696	-
C(35)-C(36)-C(37)	119.998	120.000	C(35)-O(54)-Cu(57)	125.696	-
C(36)-C(37)-C(38)	120.000	120.000	C(30)-O(55)-Cu(58)	107.891	-
C(36)-C(37)-H(74)	119.998	120.000	C(50)-O(56)-Cu(58)	90.645	-
C(38)-C(37)-H(74)	119.998	120.000	N(21)-Cu(57)-N(23)	109.470	-
C(37)-C(38)-C(39)	116.340	120.000	N(21)-Cu(57)-O(53)	109.472	-
C(37)-C(38)-H(60)	121.407	120.000	N(21)-Cu(57)-O(54)	102.350	-
C(39)-C(38)-H(60)	121.407	120.000	N(23)-Cu(57)-O(53)	109.470	-
C(38)-C(39)-C(40)	121.825	120.000	N(23)-Cu(57)-O(54)	121.093	-
C(38)-C(39)-H(59)	118.592	120.000	O(53)-Cu(57)-O(54)	104.413	-
C(40)-C(39)-H(59)	118.592	120.000	N(22)-Cu(58)-N(24)	132.023	-
C(35)-C(40)-C(39)	120.000	120.000	N(22)-Cu(58)-O(55)	84.770	-
C(35)-C(40)-H(73)	119.998	120.000	N(22)-Cu(58)-O(56)	53.049	-
C(39)-C(40)-H(73)	119.998	120.000	N(24)-Cu(58)-O(55)	121.918	-
C(42)-C(41)-C(46)	118.034	120.000	N(24)-Cu(58)-O(56)	143.065	-
C(42)-C(41)-H(65)	126.013	120.000	O(55)-Cu(58)-O(56)	93.865	-
C(46)-C(41)-H(65)	115.952	120.000			
C(41)-C(42)-C(43)	110.255	120.000			
C(41)-C(42)-H(70)	127.919	120.000			
C(43)-C(42)-H(70)	121.822	120.000			
C(42)-C(43)-C(44)	120.000	120.000			
C(42)-C(43)-H(71)	120.000	120.000			
C(44)-C(43)-H(71)	119.998	120.000			
C(28)-C(44)-C(43)	119.998	120.000			
C(28)-C(44)-C(45)	120.000	120.000			
C(43)-C(44)-C(45)	119.998	120.000			
C(44)-C(45)-C(46)	119.998	120.000			
C(44)-C(45)-O(53)	125.499	124.300			
C(46)-C(45)-O(53)	114.501	124.300			
C(41)-C(46)-C(45)	120.000	120.000			
C(41)-C(46)-H(66)	119.998	120.000			
C(45)-C(46)-H(66)	119.998	120.000			
C(48)-C(47)-C(52)	120.000	120.000			
C(48)-C(47)-H(67)	120.000	120.00			

Antibacterial activity



Scheme 3 Antibacterial activity of Schiff base ligand and their binuclear complexes.

	Diameter of inhibition zone (mm)							
Compounds	Staphylococcus	Bacillus Cereus	Escherichia coli	Pseudomonas				
	Aureus mm	mm	mm	AeruginosaMm				
$(C_{24}H_{18}N_2O_2)$	8	10	7	10				
$[Cu_2(C_{48}H_{32}N_4O_4)]$	21	22	23	24				
$[Ni_2(C_{48}H_{32}N_4O_4)]$	22	17	19	23				
$[VO_2(C_{48}H_{32}N_4O_4)]$	20	21	20	22				
Streptomycin(standard)	25	26	24	26				

Table 6. Antibacterial activity of ligand and its complexes.

The biological activity of the Schiff base ligand and their complexes were tested against the bacteria because bacteria can achieve resistance to antibiotics through biochemical and morphological modifications²⁶. The organisms used in the present investigations included *Staphylococcus aureus, Bacillus subtilis* (as Grampositive bacteria) *Escherichia coli, Klebsilla pneumonia*(as Gram-negative bacteria). The well diffusion agar technique was used to assess the antibacterial activity of the synthesized complexes. The results of the bactericidal screening of the synthesized compounds are recorded in Table 6. The remarkable activity of the Schiff base ligand may be arise from the hydroxyl groups, which may play an important role in the antibacterial activity, as well as the presence of four imine groups which imports in elucidating the mechanism of transformation reaction in biological systems.

The activity of the Schiff base ligand and their complexes increases as the concentration increases because it is a well known fact that concentration plays a vital role in increasing the degree of inhibition. The results indicate that the complexes show more activity than the ligand against same microorganisms under identical experimental conditions this would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane ²⁷ and can be explained by Tweedy's chelation theory²⁸. Chelation will enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of the cell membrane²⁹ and jamming the metal binding sites on enzymes of microorganisms. *Streptomycin* was used as standard antibiotics and was used to compare the synthesized complexes with the standard shown by Table 5. The minimum inhibitory concentration (MIC) values of the investigated compounds are also summarized in Table 5. From the table, the observed MIC values indicate that the complexes have higher antibacterial activity. The increase in antibacterial activity is due to the faster diffusion of metal complexes as a whole shown in scheme 3. Such increased activity of metal complexes can be explained by the chelation theory³⁰.

Conclusion

The binucleating tetradentate Schiff base ligand is synthesized from 1, 5- diaminonapthalene and Salycilaldehyde. It acts as a N_2O_2 type ligand and forms stable complexes with transition metal ions such as Copper(II), Nickel(II), and Oxovanadium(IV). The ligand and its complexes are characterized using spectral and

analytical data. Based on the reported structural characterization investigations results, square planar and square- pyramidal binuclear structures are proposed. The bond length and bond angle values of 3D molecular modeling and analysis proposed the $[Cu_2(C_{48}H_{32}N_4O_4)]$ complex is square planar geometry. The metal complexes have higher antibacterial activity than the free ligand by the chelation theory.

Acknowledgement

Financial support from Department of Science and Technology(DST), New Delhi, is gratefully acknowledged.

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