Syntheses, characterization and mesomorphic properties of new bis(alkoxyphenylazo)-substituted *N*,*N*′ salicylidene diiminato Ni(II), Cu(II) and VO(IV) complexes

Kamellia Nejati*[a] **and Zolfaghar Rezvani**[b]

[a] *Department of Chemistry, Payam Noor University-Tabriz center, Emamieh, Hakim nezami street, Tabriz, Iran. E-mail: nejati_k@yahoo.com*
[b] *Department of Chemistry, Faculty of Science, Azarbaijan University of Tarbiat Moallem, Tabriz, Iran*

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A series of tetradentate Schiff base ligands *N*,*N*′-bis[5-(4-n-alkoxy)phenylazosalicylidene]alkyldiamine-(n-alkoxy = butyloxy, octyloxy) homologues based on 1,2 diaminoethane and 1,3 diaminopropane have been synthesized and characterized by IR, NMR and mass spectroscopy. For all the ligands the nickel(II), copper(II) and oxovanadium(IV) complexes have been synthesized and characterized by elemental analyses and IR spectroscopy. The thermal behavior of these compounds was examined by differential scanning calorimetry (DSC) and polarizing microscopic observations. None of the Schiff-base ligands and butoxy containing complexes exhibit liquid crystalline properties but the octyloxy containing metal complexes show a smectic A mesophase.

1 Introduction

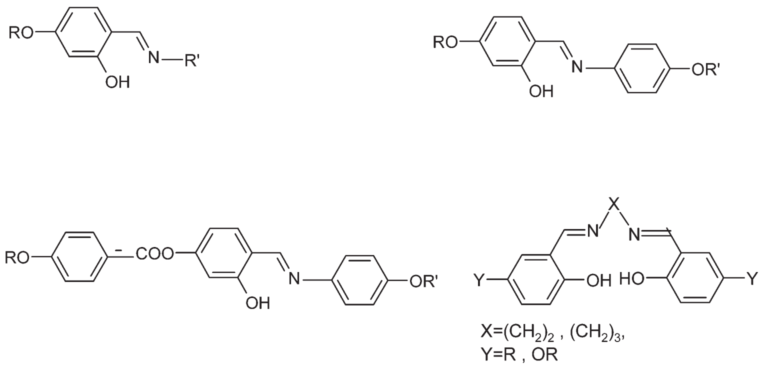
Investigation of metallomesogens is one of the most promising areas in the field of liquid crystal research.[1–6] This interest has been stimulated by the potential applications of metal-containing liquid crystals.[7–9] Much of this attention on the synthesis and study of metallomesogens is due to the perceived advantages of combining the properties of liquid crystal systems with those of transition metals.[10–12] Bidentate and tetradentate salicylaldimine-based ligands (see Scheme 1) have been widely used in the synthesis of metallomesogens. The majority of these compounds described in the literature contain Cu(II), Ni(II), Ag(I), Pt(II), Pd(II), VO(IV), lanthanide or actinide[13] as the central metal ion.

Recently, some metallomesogens containing isomerizable azo moieties such the azo-substituted calixarenes containing WO(IV),[14] calamitic Cu(II) complexes of {1-[4′-(4″-hexyloxyphenylazo)phenyl-3-alkylamino-2-en-1-ones},[15] and rodlike bis(alkylphenylazo) substituted *N*,*N*-salicylidinediiminato Ni(II), Cu(II) and VO(IV) complexes, have been reported.[16] Sudhadevi and co-workers[17] reported the azopyridine containing silver mesogens. We recently reported the synthesis and liquid crystal character of Cu(II) bis(chelates) based on azo-linked bidentate salicylaldimine.[18] Only a few data are available from the literature about metallomesogens containing the phenylazo fragment. In continuation of our interest we reported herein the synthesis and investigation of liquid crystalline behavior of symmetric tetradentate azo-linked *N*,*N*-salicylidinediiminato Ni(II), Cu(II) and VO(IV) complexes (Scheme 2).

2 Experimental

2.1 Reagents

All reagents and solvents were used as supplied by Merck chemical company. In order to prepare the 4-alkoxyaniline homologues, 4-alkoxynitrobenzene homologues were obtained by standard etherification of 4-nitrophenol[19] and reduced as described in the literature.[20]



Scheme 1

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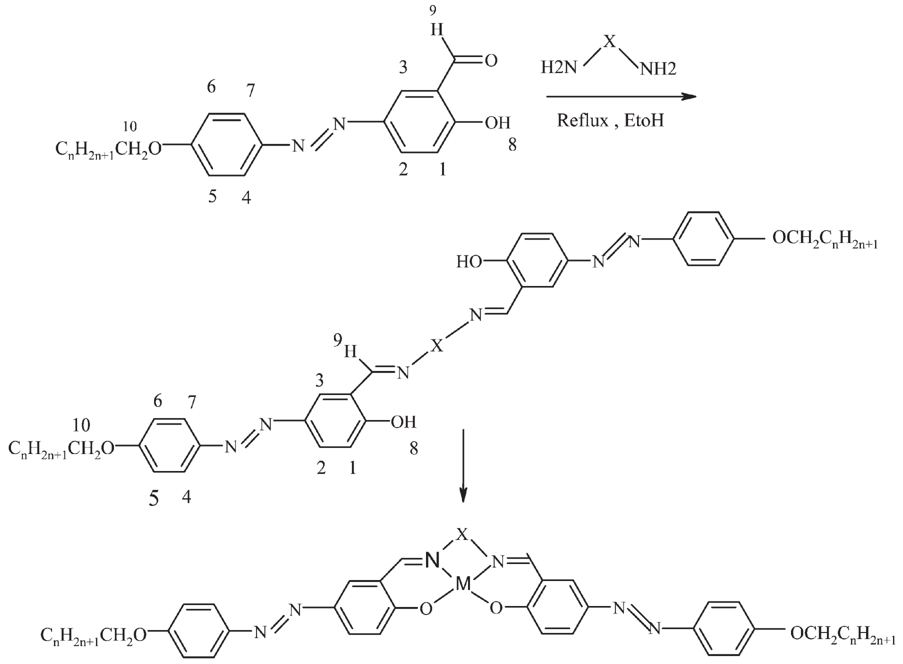

Compound No.	n	X	M
1a	3	-	-
1b	7	-	-
2a	3	$(CH_2)_2$	-
2b	7	$(CH_2)_2$	-
3a	3	$(CH_2)_3$	-
3b	7	$(CH_2)_3$	-
4a	3	$(CH_2)_2$	Cu
4b	3	$(CH_2)_2$	Ni
4c	3	$(CH_2)_2$	VO
5a	3	$(CH_2)_3$	Cu
5b	3	$(CH_2)_3$	Ni
5c	3	$(CH_2)_3$	VO
6a	7	$(CH_2)_2$	Cu
6b	7	$(CH_2)_2$	Ni
6c	7	$(CH_2)_2$	VO
7a	7	$(CH_2)_3$	Cu
7b	7	$(CH_2)_3$	Ni
7c	7	$(CH_2)_3$	VO

Scheme 2

2.2 Physical measurements

Elemental (C, H and N) analyses were carried out on a Perkin-Elmer automatic equipment model 240B. Electron impact (70 eV) mass spectra were recorded with a Finnigen-mat GC-MS-DS spectrometer model 8430. Infrared spectra were recorded with a FT-IR Bruker, vector 22 spectrometer from KBr pellets in the 400–4000 cm^{-1} range. Transition temperatures and enthalpy changes were determined using a Mettler TA4000 system linked to a DSC-11 differential scanning calorimeter, which was calibrated with indium. The optical observations were made with a Leitz Orthoplan-Pol polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage. A flow of liquid nitrogen was used for the cooling. The heating or cooling rates were 10 K min^{-1}. NMR spectra were measured in $CDCl_3$ and $(CD_3)_2SO$ as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si.

2.3 Materials

All homologue materials were prepared in similar manners.

1a, *5-(4-Butoxyphenylazo)salicylaldehyde*. 5-(4-butoxyphenylazo)salicylaldehyde was obtained as described elsewhere.[18] Yellow. Yield 75%. Mp 131 °C. ^{1}HNMR δ 11.27(s,H^8), 10.02(s,H^9), 8.17(d,H^3), 8.14(dd,H^2), 7.91(dd,H^{4,7}), 7.11(d,H^1), 7.01(dd,H^{5,6}), 4.05(t,H^{10}), 1.81(p, O–C–CH_2), 1.51(q, O–C–C–CH_2) 1(t, CH_3).

1b, *5-(4-Octyloxyphenylazo)salicylaldehyde*. Yellow. Yield 80%. Mp 126 °C. ^{1}HNMR δ 11.27(s,H^8), 10.02(s,H^9), 8.18(d,H^3), 8.14(dd,H^2), 7.91(dd,H^{4,7}), 7.10(d,H^1), 7.01 (dd,H^{5,6}), 4.05(t,H^{10}), 1.81–1.00 (15H, alkyl chain).

Syntheses of the ligands. 0.013 mole of related diamine and 0.026 mole of 5-(4-alkoxyphenylazo)salicylaldehyde were condensed by refluxing in 100 ml of absolute ethanol for 1 h. The solution was left at room temperature. The ligands were obtained as yellow micro crystals. The micro crystals were filtered off, washed with 15 ml of absolute ethanol and then recrystallized from ethanol–chloroform(1 : 3, v/v).

2a. Yellow. Yield 90%. Mp 215 °C. ^{1}HNMR δ 13.91 (s,H^8), 8.48(s,H^9), 7.94(dd,H^2), 7.90–7.82(H^{3,4,7}), 7.06(d,H^1), 6.98(d,H^{5,6}), 4.02(t,H^{10}), 3.78(s, =N–CH$_2$), 1.84 (p, O–C–CH$_2$),1.55(q, O–C–C–CH$_2$) 0.89(t, CH$_3$).

2b. Yellow. Yield 85%. Mp 210 °C. ^{1}HNMR δ 13.90 (s,H^8), 8.49(s,H^9), 7.93(dd,H^2), 7.91–7.81(H^{3,4,7}), 7.05(d,H^1), 6.99(d,H^{5,6}), 4.03(t,H^{10}), 3.78(s, =N–CH$_2$), 1.83–0.90(30H, alkyl chain).

3a. Yellow. Yield 87%. Mp 158 °C. ^{1}HNMR δ 13.92 (s,H^8), 8.47(s,H^9), 7.94(dd,H^2), 7.91–7.82(H^{3,4,7}), 7.05(d,H^1), 6.99(d,H^{5,6}), 4.02(t,H^{10}), 3.79(s, =N–CH$_2$), 2.18(m, =N–C–CH$_2$), 1.85 (p, O–C–CH$_2$), 1.57(q, O–C–C–CH$_2$) 0.91(t, CH$_3$).

3b. Yellow. Yield 91%. Mp 152 °C. ^{1}HNMR δ 13.90(s,H^8), 8.48(s,H^9), 7.94(dd,H^2), 7.91–7.81(H^{3,4,7}), 7.06(d,H^1), 6.98(d,H^{5,6}), 4.02(t,H^{10}), 3.78(s, =N–CH$_2$), 2.17(m, =N–C–CH$_2$), 1.85–0.90 (30H, alkyl chain).

Syntheses of the copper and nickel complexes. Copper and nickel complexes were prepared in a similar manner. A solution of 0.004 mole of Ni(OAc)$_2$·4H$_2$O or Cu(OAc)$_2$·H$_2$O in 10 ml of ethanol was added to an ethanol–chloroform(1 : 1 v/v) solution containing 0.004 mole of ligand and refluxed for 2 h. The obtained solution was left at room temperature. Copper complexes were obtained as brown micro crystals, and nickel complexes were obtained as green micro crystals. The micro crystals were filtered off, washed with absolute ethanol and then recrystallized from ethanol–chloroform (1 : 3 v/v).

4a. Brown. Yield 80%. Anal. Calcd for $C_{36}H_{38}N_6O_4Cu$: C, 63.39; H, 5.57; N, 12.32. Found: C, 63.16; H, 5.33; N, 12.18%.

4b. Green. Yield 85%. Anal. Calcd for $C_{36}H_{38}N_6O_4Ni$: C, 63.84; H, 5.61; N, 12.41. Found: C, 63.66; H, 5.30; N, 12.25%.

5a. Brown. Yield 75%. Anal. Calcd for $C_{37}H_{40}N_6O_4Cu$: C, 63.84; H, 5.75; N, 12.07. Found: C, 63.61; H, 5.49; N, 11.86%.

5b. Green. Yield 86%. Anal. Calcd for $C_{37}H_{40}N_6O_4Ni$: C, 64.28; H, 5.79; N, 12.16. Found: C, 64.03; H, 5.54; N, 11.94%.

6a. Brown. Yield 74%. Anal. Calcd for $C_{44}H_{54}N_6O_4Cu$: C, 66.54; H, 6.80; N, 10.59. Found: C, 66.39; H, 6.50; N, 10.47%.

6b. Green. Yield 75%. Anal. Calcd for $C_{44}H_{54}N_6O_4Ni$: C, 66.94; H, 6.85; N, 10.65. Found: C, 66.73; H, 6.55; N, 10.40%.

7a. Brown. Yield 80%. Anal. Calcd for $C_{45}H_{56}N_6O_4Cu$: C, 66.87; H, 6.93; N, 10.40. Found: C, 66.68; H, 6.65; N, 10.22%.

7b. Green. Yield 78%. Anal. Calcd for $C_{45}H_{56}N_6O_4Ni$: C, 67.27; H, 6.97; N, 10.46. Found: C, 66.95; H, 6.69; N, 10.24%.

Syntheses of the oxovanadium(IV) complexes. 0.004 mol of VO(acac)$_2$ was added to 70 ml of dichloromethane hot solution containing 0.004 mol of ligand and a few drops of triethylamine and refluxed for 1 h. The resulting yellow precipitate was collected by filtration and washed with dichloromethane and ether and recrystallized from ethanol–chloroform (1 : 3 v/v).

4c. Brownish green. Yield 85%. Anal. Calcd for $C_{36}H_{38}N_6O_5V$: C, 63.07; H, 5.55; N, 12.26. Found: C, 62.88; H, 5.34; N, 12.04%.

5c. Brownish green. Yield 80%. Anal. Calcd for $C_{37}H_{40}N_6O_5V$: C, 63.52; H, 5.72; N, 12.02. Found: C, 66.43; H, 5.51; N, 11.88%.

6c. Brownish green. Yield 85%. Anal. Calcd for $C_{44}H_{54}N_6O_5V$: C, 66.25; H, 6.77; N, 10.54. Found: C, 66.14; H, 6.49; N, 10.38%.

7c. Brownish green. Yield 78%. Anal. Calcd for $C_{45}H_{56}N_6O_5V$: C, 66.59; H, 6.90; N, 10.36. Found: C, 66.37; H, 6.72; N, 10.10%.

3 Result and discussion

3.1 Synthesis

The 5-(4-alkoxyphenylazo)salicylaldehyde homologues (**1a,b**), Schiff-base ligand homologues (**2a,b, 3a,b**) and related metal complexes were obtained in good yields and purity. Aldehyde and ligand homologues were characterized by IR and ^{1}H NMR spectroscopy and complexes were characterized by C, H, N elemental analysis and IR spectroscopy. Some physical and characterization data for ligands and complexes are given in the experimental section and some selected IR data are reported in Table 1. For the IR spectra of metal complexes, $\upsilon_{C=N}$ shifted to lower wavenumbers by 10–30 cm^{-1} upon coordination. On the other hand, the disappearance of the OH band of free ligands in metal complexes indicates that the OH group has been deprotonated and connected to the metal ion as –O$^-$. On the basis of these observations it can be concluded that the Schiff-base ligands are coordinated to metal atoms as tetradentate ONNO ligands.

It is well known that the Ni(II) coordination geometry in salen type ligands is usually square planar.[21,22]

We recently reported the crystal structure of [bis(5-phenylazo salicylaldehyde)-trimethylendiiminato] copper(II)[23] which has a similar ONNO coordination environment to that of the title complex of this work. However it is suggested that the Cu(II) coordination is square planar or nearly square planar from its similar coordination environment to a recently reported copper(II) complex.[21,22,24]

VO complexes with salen type ligands can give rise either to monomeric structure[25–27] with square pyramidal coordination geometry or to polymeric structures[26–29] with [V=O···V=O] interactions which afford a distorted octahedral geometry. However on the basis of the position of the V=O band in IR spectra[25–31] we can distinguish between the monomeric or polymeric nature of these complexes. In this work, the VO complexes with –CH$_2$CH$_2$– bridge show $\upsilon_{V=O}$ at 995.93 cm^{-1}, according to which result, a square pyramid coordination is assigned to the salen derivative. In the case of complexes

Table 1 Selected IR data for Schiff base ligands and metal complexes

	v/cm^{-1}						
Compound	O–H	C–H (aromatic)	C–H (aliphatic)	C=N	C–O (etheric)	C=O	V=O
1(a,b)	3185 (br,m)	3055(m)	2952, 2866(s)	–	1239(s)	1660	—
2(a,b)	3420 (br,m)	3040(m)	2955, 2872(s)	1637(s)	1248(s)	—	—
3(a,b)	3441 (br,m)	3060(m)	2965, 2871(s)	1634(s)	1247(s)	—	—
(4,6)a	—	3042(m)	2925(s)	1626(s)	1250(s)	—	—
(4,6)b	—	3055(m)	2955, 2870(s)	1618(s)	1249(s)	—	—
(4,6)c	—	3047(m)	2936, 2869(s)	1620(s)	1255(s)	—	995(s)
(5,7)a	—	3037(m)	2924(s)	1616(s)	1252(s)	—	—
(5,7)b	—	3050(m)	2923, 2834(s)	1630(s)	1250(s)	—	—
(5,7)c	—	3066(m)	2 2935,2864(s)	1620(s)	1248(s)	—	842(s)

s: strong, m: medium

with the trimethylene bridge (see Scheme 2), $\upsilon_{V=O}$ appeared at 842.91 cm^{-1} which indicated a polymeric structure with an octahedral coordination for the vanadyl complex. These results are similar to the bis(alkylphenylazo)-*N*,*N* salicylidendiiminato VO(IV) complexes, as reported by Iolinda Aiello and co-workers.[16]

3.2 Mesomorphism

The mesomorphic properties of the Schiff ligands and related Cu(II), Ni(II) and VO(IV) complexes have been investigated by polarizing microscopic observations using a heating–cooling stage. The phase transition temperature and enthalpy data were obtained by Differential Scanning Calorimetry (DSC). None of the Schiff-base ligands, despite the two mesogenic alkoxyphenylazo fragments they contain, exhibit liquid crystalline properties. All ligands clearly melted and transformed into isotropic liquids as seen optically. The melting points of the ligands decrease with either increasing bridge size or alkyl chain length. On the basis of the literature data we propose that this behaviour results from the *transoid N*,*N* conformation of Schiff base ligands (see Scheme 2) which stabilizes a stepped molecular geometry that prevents mesomorphism.[16] This behavior is similar to that of the tetradentate Schiff base ligands *N*,*N*′-bis[5-(4′-n-alkyl)phenylazosalicylidene]alkyldiamine and *N*,*N*′-bis[5-(4′-n-alkoxy-5′-fluoro)salicylidene]ethylenediimine as reported by Iolinda Asello and co-workers[16] and A. B. Blake and co-workers[22] respectively.

Copper(II), nickel(II) and oxovanadium(IV) complexes of Schiff Base ligands (except **7c**, see Scheme 2), containing octyloxy substitution, exhibit liquid crystalline character as seen optically. Metal complexation of Schiff base ligands induces the mesomorphism because the *transoid N*,*N* conformation of Schiff base ligands is converted to the rod like molecular shape (see Scheme 2) upon complexation.[16]

Optical, thermal and thermodynamic data for metal complexes are shown in Table 2. These metal complexes show enantiotropic smectic A mesophase which has been identified in optical microscopy by the typical batonnet texture[32] on cooling from the isotropic liquid. A typical microscopic picture from S_A mesophase for complex **6a** is illustrated in Fig. 1. All the metal complexes described undergo a considerable amount of decomposition near the transition to the isotropic liquid phase which has been detected by exothermic peaks in the DSC trace and optical observations.

Mesogens containing the alkoxy or alkyl-substituted salen core and incorporating Cu(II),[21–33] Ni(II),[21,22,24] and VO(IV)[28] were previously reported.

These complexes represent further examples of a mesomorphic complex derived from a non-mesogenic ligand.

Table 2 Transition temperatures and enthalpy changes of copper(II), nickel(II) and oxovanadium(IV) complexes

Compound	Transision[a]	T^b/°C	δH^b/kJ mol^{-1}
6a	K–S_A	295	16.21
	S_A–I^c (dec.)	317	
6b	K–S_A	292	17.25
	S_A–I^c (dec.)	312	
6c	K–S_A	303	18.23
	S_A–I^c (dec.)	321	
7a	K–S_A	230	14.36
	S_A–I^c (dec.)	255	
7b	K–S_A	239	15.29
	S_A–I^c (dec.)	261	
7c	K–I^c (dec.)	380	

[a] K: Crystal, S_A : Smectic A, I: Isotropic liquid. [b] Data obtained from first DSC cycle. [c] Microscopic data.

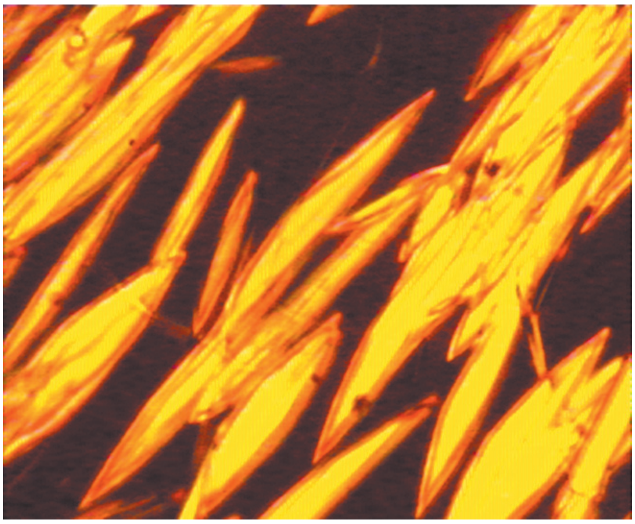

Fig. 1 Batonnet texture of **6a** at 315 °C, which was obtained with a polarizing microscope on cooling from the isotropic liquid.

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