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Syntheses, characterization and glass-forming properties of new bis[5-((4-ⁿdodecyloxyphenyl)azo)-*N*-(4-ⁿalkoxyphenyl)- salicylaldiminato]nickel (II) complex homologues

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Abstract

A series of bidentate Schiff base ligands, 5-((4-ⁿdodecyloxyphenyl)azo)-*N*-(4-ⁿalkoxyphenyl)-salicylaldimine (ⁿalkoxy = octyloxy, dodecyloxy, hexadecyloxy) homologues, have been synthesized and characterized by IR, NMR, mass spectroscopy and elemental analyses. Nickel (II) complexes of these ligands were synthesized and characterized by elemental analyses, ¹H NMR and IR spectroscopy. DSC measurements, X-ray powder diffraction experiments and optical polarizing microscopy studies indicated that the Ni complexes have a resistance to crystallization and give an amorphous glassy state but after annealing at room temperature for several days transform to an anisotropic glass.

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1. Introduction

In recent years, amorphous molecular materials or molecular glasses have attracted substantial interest due to their successful application in organic electroluminescent devices as well as photovoltaic, photochromic and resist materials [1]. These kinds of materials have excellent processability, transparency and isotropic properties [1a]. Low molecular weight organic compounds, polymers and molecularly doped polymer systems, which are able to form stable glasses with glass transition temperatures above room temperature have attracted great attention both from the scientific and application point of view [2,3].

Systematic studies on such stable low molecular weight organic compounds that readily form stable

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amorphous glasses above room temperature started in 1980 by Shirota [4]. Some molecular glasses based on twin molecules containing caracole, dihydrocarbazole, phenothiazine and naphthalimide have recently been reported by Braun and co-workers [5]. Moreover, Braun et al. [6] have reported low-molecular-weight glassy fulvalenes. Bazan et al. [7] have used the binaphtyl framework to synthesize glass-forming organic chromophores. Shirota et al. [8a] have reported 2,3-tetrakis[4-(*N*-2-naphthyl-*N*phenyl-amino)phenoxy]-substituted phthalocyanines as a novel class of amorphous molecular materials. McKeown et al. [8b] have described the syntheses and glass-forming properties of phthalocyanine-containing poly(aryl ether) dendrimers.

Azo-containing photochromic materials have been attracting a great deal of attention because of their potential technological applications to optical recording for data storage and optical switching [9]. For example, the azobenzene-based compounds, containing an

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azobenzene chromophore, 4-[di(biphenyl-4-yl)amino]azobenzene and 4,4'-bis[bis(4-*tert*-butylbiphenyl-4-yl)amino]-azobenzene have been used as photochromic amorphous molecular materials [10]. Other azobenzene-based amorphous molecular materials, with a spiro-linked bifluorene, have been synthesized and their photoinduced behavior such as optically induced birefringence, diffraction efficiency and surface relief gratings (SRGs) were investigated in relation to their unique molecular structures [11].

Based on our knowledge, only a few coordination or organometallic compounds have been reported as amorphous molecular materials. Platinum 5-fluorouridine green sulfate is a typical example of an amorphous coordination compound [12]. A polycrystalline sample of titanyl phthalocyanine was vacuum evaporated at ca. 10^{-5} Torr to form an amorphous thin film. Photovoltaic devices consisting of an amorphous thin film of titanyl phthalocyanine and N,N-dimethyl-3,4:9,10-perylenebis (dicarboximide), sandwiched between ITO and Au electrodes, demonstrated a response to light over the whole visible wavelength region from 400 to 900 nm [13]. Shirota and co-workers [8a] have synthesized copper and titanyl phthalocyanines containing triarylamine moieties. These compounds are soluble in common organic solvents and readily form stable amorphous glasses with high glass transition temperatures. Bazan and co-workers [14] have synthesized Iridium complexes with fluorene-modified phenylpyridine ligands that are resistant to crystallization and can be used in the fabrication of single layer light emitting diodes. It is worth mentioning that the introduction of a metal center into organic systems in order to form coordination or organometallic molecular materials can introduce extra parameters such as color, magnetism and birefringence in amorphous molecular materials. Besides the metal center can improve the electroluminescent properties of coordination molecular materials.

In this work, we report the synthesis and investigation of glass-forming properties of new bis[5-((4-ⁿdodecyloxyphenyl)azo)-*N*-(4-ⁿalkoxyphenyl)-salicylaldiminato]nickel (II) complex homologues (see Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents used were supplied by Merck chemical company and used without further purification. 4-Alkoxynitrobenzene homologues were obtained by reaction between 4-nitrophenol with 1-bromoctan or 1-bromododecane in DMF as solvent and K_2CO_3 as base by refluxing for 3 h [15] and then crude 4-alkoxy nitrobenzene homologues were purified by recrystallization from ethanol. 4-Alkoxyaniline homologues prepared by reduction of the corresponding 4-alkoxynitrobenzene as described in the literature [16].

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 on a Finnigan-mat GC-MS-DS spectrometer model 8430. Infrared spectra were taken with a Bruker FT-IR spectrometer model vector 22, using KBr pellets in the 400-4000 cm⁻¹ range. The DSC thermograms of the compounds were obtained on a Mettler-Toledo DSC 822e module, which was calibrated with indium metal $(T = 156.6 \pm 0.3, \Delta H = 28.45 \pm 0.6 \text{ J g}^{-1})$. Samples of 2-5 mg in the solid form were placed in aluminum pans (40 μ l) with a pierced lid, and heated or cooled at a scan rate of 10 °C min⁻¹ under a nitrogen flow. TGA was carried out on a Mettler-Toledo TGA 851e at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. X-ray powder diffraction patterns were recorded on a Bruker D8 powder diffractometer (Cu Ka: 1.541 Å). The optical observations were made with a Zeiss polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage and Linkam THMS 93 programmable temperature-controller. ¹H NMR spectra were obtained in deutrated chloroform as solvent on a Bruker FT-NMR AC-400 (400 MHz) spectrometer. All chemical shifts are reported in δ (ppm) relative to tetramethylsilane as an internal standard.

2.3. Materials

5-(4-Dodecyloxyphenylazo)salicylaldehyde (1). This compound was prepared as described in the literature [17]. Yellow, yield 80%, m.p. 123 °C. MS *m*/*z* (relative intensity): 411.6 (M + 1,15), 410.6 (M, 45), 242.5 (M - C₁₂H₂₅, 25), 121.6 (M - C₁₂H₂₅OC₆H₄N₂, 100). *Anal.* Calc. for C₂₅H₃₄N₂O₃: C, 73.15; H, 8.35; N, 6.83. Found: C, 72.73; H, 8.14; N, 6.47%. ¹H NMR (400 MHz, CDCl₃) δ 11.26 (s, H-9), 10.02 (s, H-8), 8.15 (d, *J* = 2.8 Hz, H-3), 8.13 (dd, *J* = 2.9, 8.2 Hz, H-2), 7.89 (dd, *J* = 3.0, 7.9 Hz, H-4, H-7), 7.11 (d, *J* = 8.1 Hz, H-1), 7.01 (dd, *J* = 3.2, 7.9 Hz, H-5, H-6), 4.04 (t, *J* = 6.7 Hz, H-10), 1.84–0.87 (23H, alkyl chain).

3. Syntheses of the ligands

All homologue materials were prepared similarly. Thus, 0.026 mol of the related amine (4-alkoxy aniline) and 0.026 mol of $5-(4-^n$ dodecyloxyphenylazo)salicylaldehyde were dissolved in 100 ml absolute ethanol with a few drops of glacial acetic acid as a catalyst. The



solution was refluxed for 1 h and then left at room temperature. After cooling, the ligands were obtained as yellow micro crystals. The micro crystals were filtered off, washed with 15 ml of cold absolute ethanol and then recrystallized several times in ethanol–chloroform (1:3, v/v).

L12-8. Yellow, yield 85%. MS *m*/*z* (relative intensity): 614.8 (M + 1,15), 613.8 (M, 65), 443.7 (M - $C_{12}H_{25}$, 23), 324.7 (M - $C_{12}H_{25}OC_6H_4N_2$, 100). *Anal.* Calc. for $C_{39}H_{55}N_3O_3$: C, 76.30; H, 9.03; N, 6.85. Found: C, 76.0; H, 8.8; N, 6.6%. ¹H NMR (400 MHz, CDCl₃) δ 13.99 (s, H-9), 8.72 (s, H-8), 7.97 (dd, *J* = 3, 6.7 Hz, H-2), 7.95 (d, *J* = 6.7 Hz, H-3), 7.87 (dd, *J* = 3, 6.8 Hz, H-4, H-7), 7.30 (dd, *J* = 3.1, 7.9 Hz, H-5, H-6), 7.10 (d, *J* = 8.7 Hz, H-1), 6.99 (dd, *J* = 2, 8.9 Hz, H-13, H-15), 6.95 (dd, 1.9, 8.8 Hz, H-12, H-14), 4.03 (t, *J* = 6.5 Hz, H-10), 3.98 (t, *J* = 6.5 Hz, H-11), 1.85–0.86 (38H, alkyl chain).

L12-12. Yellow, yield 87%. MS *m*/*z* (relative intensity): 670.7 (M + 1,13), 669.7 (M, 60), 500.6 (M - $C_{12}H_{25}$, 25), 380.5 (M - $C_{12}H_{25}OC_6H_4N_2$, 100). *Anal.* Calc. for $C_{43}H_{63}N_3O_3$: C, 78.02; H, 9.59; N, 6.35. Found: C, 77.8; H, 9.4; N, 6.2%. ¹H NMR (400 MHz, CDCl₃) δ 13.99 (s, H-9), 8.73 (s, H-8), 7.97 (dd, *J* = 3, 6.8 Hz, H-2), 7.95 (d, *J* = 2.9 Hz, H-3), 7.88 (dd, *J* = 3, 6.9 Hz, H-4, H-7), 7.31 (dd, *J* = 3.0, 7.8 Hz, H-5, H-6), 7.11 (d, *J* = 8.8 Hz, H-1), 7.00 (dd, *J* = 1.9, 8.9 Hz, H-13, H-15), 6.95 (dd, 1.9, 8.8 Hz, H-12, H-14), 4.04 (t, *J* = 6.6 Hz, H-10), 3.99 (t, *J* = 6.5 Hz, H-11), 1.85– 0.87 (46H, alkyl chain).

L12-16. Yellow, yield 87%. MS m/z (relative intensity): 726.8 (M + 1,12), 725.8 (M,63), 556.7 (M - C₁₂H₂₅, 26), 433.7 (M - C₁₂H₂₅OC₆H₄N₂, 100). *Anal.* Calc. for C₄₇H₇₁N₃O₃: C, 78.62; H, 9.97; N, 5.85. Found: C, 77.1; H, 9.5; N, 5.5%. ¹H NMR (400 MHz,

CDCl₃) δ 13.99 (s, H-9), 8.73 (s, H-8), 7.97 (dd, J = 3, 6.8 Hz, H-2), 7.95 (d, J = 6.8 Hz, H-3), 7.89 (dd, J = 3, 6.8 Hz, H-4, H-7), 7.30 (dd, J = 3.0, 7.6 Hz, H-5, H-6), 7.12 (d, J = 8.8 Hz, H-1), 7.00 (dd, J = 1.9, 8.8 Hz, H-13, H-15), 6.96 (dd, 2.0, 8.7 Hz, H-12, H-14), 4.04 (t, J = 6.6 Hz, H-10), 3.99 (t, J = 6.5 Hz, H-11), 1.85–0.87 (54H, alkyl chain).

Syntheses of the nickel complexes. The nickel complexes were prepared in a similar manner as described by Nejati et al. [17]. Thus, a solution of 4 mmol of Ni(CH₃COO)₂·4H₂O in 10 ml of ethanol was added to an ethanol–chloroform (1:1 v/v) solution containing 8 mmol of ligand, and the resulting solution was refluxed for 2 h. The obtained solution was left at room temperature. The nickel complexes were obtained as yellow-green micro crystals. The micro crystals were filtered off, washed with absolute ethanol and then recrystallized in ethanol–chloroform (1:3 v/v).

Ni12-8. Yellow-green, yield 80%. *Anal.* Calc. for $C_{78}H_{108}N_6O_6Ni$: C, 72.94; H, 8.48; N, 6.54. Found: C, 72.4; H, 8.0; N, 6.2%. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, H-8), 7.97 (dd, J = 2.9, 6.9 Hz, H-2), 7.94 (d, J = 6.6 Hz, H-3), 7.84 (dd, J = 3, 6.8 Hz, H-4, H-7), 7.28 (dd, J = 3.1, 7.9 Hz, H-5, H-6), 7.13 (d, J = 8.5 Hz, H-1), 7.00 (dd, J = 2, 8.8 Hz, H-13, H-15), 6.93 (dd, 1.9, 8.7 Hz, H-12, H-14), 4.24 (t, J = 6.1 Hz, H-11), 4.02 (t, J = 6.5 Hz, H-10), 1.81–0.84 (76H, alkyl chain).

Ni12-12. Yellow-green, yield 85%. *Anal.* Calc. for $C_{86}H_{124}N_6O_6Ni$: C, 74.26; H, 8.95; N, 6.02. Found: C, 73.9; H, 8.6; N, 5.8%. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, H-8), 7.97 (dd, J = 3, 6.8 Hz, H-2), 7.93 (d, J = 6.7 Hz, H-3), 7.85 (dd, J = 2.9, 6.7 Hz, H-4, H-7), 7.27 (dd, J = 3.0, 7.8 Hz, H-5, H-6), 7.12 (d, J = 8.3 Hz, H-1), 7.01 (dd, J = 2.1, 8.6 Hz, H-13, H-15), 6.94 (dd, 2, 8.5 Hz, H-12, H-14), 4.24 (t, J = 6.1 Hz, H-11), 4.02 (t, J = 6.5 Hz, H-10), 1.82–0.82 (92H, alkyl chain).

Ni12-16. Yellow-green, yield 80%. *Anal.* Calc. for $C_{94}H_{140}N_6O_6Ni$: C, 74.82; H, 9.35; N, 5.57. Found: C, 74.4; H, 8.9; N, 5.2%. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, H-8), 7.96 (dd, J = 3, 6.9 Hz, H-2), 7.92 (d, J = 6.8 Hz, H-3), 7.84 (dd, J = 3, 6.8 Hz, H-4, H-7), 7.28 (dd, J = 3.0, 7.7 Hz, H-5, H-6), 7.13 (d, J = 8.1 Hz, H-1), 7.02 (dd, J = 2.2, 8.5 Hz, H-13, H-15), 6.95 (dd, 2, 8.6 Hz, H-12, H-14), 4.23 (t, J = 6.2 Hz, H-11), 4.01 (t, J = 6.4 Hz, H-10), 1.83–0.81 (108H, alkyl chain).

4. Results and discussion

4.1. Synthesis

The Schiff base ligands were synthesized in a four-step process, in which the hydroxy group in 4-nitrophenol is first replaced by an alkoxy chain followed by reduction of nitro group to an amine. In the third step, salicylaldehyde is coupled with the diazonium chloride obtained from the 4-dodecyloxyaniline and finally the Schiff base ligands were obtained by reaction of 5-(4-dodecyloxyphenylazo)salicylaldehyde with an appropriate 4-alkoxyaniline (Scheme 1) by refluxing in absolute ethanol, using a few drops of acetic acid as a catalyst. The Schiff-bases, 2a-2c, were purified by repeated crystallization in an ethanol/chloroform mixture. The 5-(4-ndodecyloxyphenylazo)salicylaldehyde and ligand homologues were characterized by IR, ¹H NMR, mass spectroscopy and elemental analyses. The Ni complexes were characterized by C, H, N elemental analyses, ¹H NMR and IR spectroscopy. Some physical and characterization data for the ligands and the complexes are given in the experimental section and selected IR data are reported in Table 1. The IR spectra of the nickel complexes show that the stretching frequency of the C=N bond was shifted to lower wavenumbers (ca. 15 cm⁻¹) in comparison with the free ligand after coordination. This shift is due to the reduction of the double bond character of the C=N bond, which is caused by the coordination of nitrogen to the metal center and is in agreement with the results obtained from the other similar complexes described previously [17–19]. On the other hand, the disappearance of the OH band of the free ligands in the spectra of the metal complexes indicates that the OH group has been deprotonated and coordinates to the metal ion as $-O^-$. In addition, a comparison of the ¹H NMR spectra of the ligands and the Ni complexes indicates that the proton signal corresponding to the OH group of the free ligands has disappeared in the nickel complexes and a large shielding occurrs for the imine proton H-8 ($\Delta \delta = \delta_{\text{ligand}} - \delta_{\text{complex}} = 0.7$ ppm). Based on these observations and elemental analyses results, we concluded that the Schiff-base ligands are coordinated to the metal center as bidentate (N-O) ligands in a 2:1 ratio.

Table 1												
Selected	IR	data	for	the	Schiff	base	ligands	and	the	metal	compl	lexes

Compound	$v (\mathrm{cm}^{-1})$								
	O–H	C-H (aromatic)	C-H (aliphatic)	C=N	C-O (etheric)	C=O			
1	3185(br, m)	3070-75(m)	2950-2850(s)		1241-4(s)	1663(s)			
L12-m	3445-60(br, m)	3050-55(m)	2950-2865(s)	1625-30(s)	1250-80(s)				
Ni12-m		3040-47(m)	2922-2848(s)	1615-18(s)	1240-48(s)				

s, strong; m, medium; br, broad.

We recently reported the crystal structure of bis-[5-((4-"propyloxyphenyl)azo)-N-("-pentyl-salicylaldiminato)] Ni(II) [20], which has a similar coordination environment to that of the title complex of this work. In these kinds of complexes, the Schiff base ligands have an approximately *trans*-planar configuration around the Ni central ion and the structure is square planar. Therefore, we propose that the Ni(II) complexes have square planar or nearly square planar coordination geometry.





4.2. Glass formation

The thermal stability of these materials was checked by thermogravimetric analysis (TGA) at first. All other thermal characterizations were then carried out below the decomposition temperature. Glass forming properties of the Schiff base ligands and the related Ni(II) complexes were studied by differential scanning calorimetry, polarizing optical microscopy (POM) observations utilizing a heating-cooling stage and X-ray diffraction (XRD). The transition temperatures of the ligands and the complexes were measured by DSC. Fig. 1(a)–(c)



Fig. 2. DSC thermograms of: (a) Ni12-8, (b) Ni12-12 and (c) Ni12-16, heating and cooling rate: 10 K min⁻¹.

shows the DSC curves of the ligands. The thermal behaviors of the ligands were similar as it is apparent from the DSC curves; therefore we describe here the behavior of compound L12-12 as a representative. In the first heating scan, L12-12 showed four endothermal peaks at 99.1, 102.9, 114.3 and 120.5 °C (Fig. 1(b)). In the second heating scan, four endothermal peaks at 98.1, 101.0, 113.4 and 120.2 °C were observed. When the isotropic melt of L12-12 was cooled at a cooling rate of 10 K min⁻¹, two exothermal peaks at 108.7, and 99.5 °C were observed (see Fig. 2). The powder XRD patterns of L12-12 recorded at room temperature prior to heating and after cooling from the isotropic liquid indicated a typical crystalline phase. Therefore, the peaks at 120.5 °C (in the first and second heating scan) are attributed to melting, the peak at 108.7 °C on the cooling step due to crystallization and other peaks may be related to solid-solid phase transitions. The melting peak is narrow and the enthalpy of fusion amounts to 40 kJ mol⁻¹. Such a high value of the enthalpy of fusion is in agreement with the presence of a perfect crystalline state of the compound as found by X-ray analyses [3a]. Melting to the isotropic liquid and crystallization of the isotropic liquid of L12-12 are confirmed by polarizing optical microscopy and are in agreement with the DSC measurements. On the basis of these observations we can conclude that, due to little difference between melting and crystallization temperatures, the Schiff base ligands do not have a tendency towards supercooling and do not form a glassy state. The tendency of Ni(II) complexes towards glass formation was analyzed using differential scanning calorimetry, POM and XRD. We here again describe the glass-forming behavior of Ni12-12 as a representative; because the other complexes behave similarly. When a polycrystalline sample of Ni12-12 obtained by recrystal-



Fig. 3. X-ray diffraction patterns of Ni12-12; (a) virgin sample crystallized from ethanol/chloroform, (b) after heating the sample above the melting point and cooling to room temperature.



Fig. 4. Optical texture of **Ni12-12** after annealing the isotropic glass phase at room temperature for 7 days between crossed polarizers.

lisation from ethanol/chloroform (1:1 v/v) was heated, two endothermic peaks at 90 and 150 °C due to solidsolid transition and melting were observed. In the cooling cycle no exothermal peaks were observed. When the isotropic liquid was cooled down at the same cooling rate by DSC under polarizing microscopy, a transparent glass was formed via a supercooled liquid. When the amorphous glass sample was again heated, a glass transition phenomenon was observed at 64 °C. On further heating above the glass transition, an exothermic peak was observed at 120 °C due to crystallization producing the same crystals obtained by recrystallization from solution, which melted at 150 °C. Fig. 3 shows the XRD patterns of Ni12-12. The powder XRD pattern from virgin crystals of Ni12-12 (Fig. 3(a)) indicates a crystalline state. In order to determine the amorphous

state of Ni12-12, the XRD pattern of a sample upon cooling from the isotropic liquid was recorded at room temperature. The XRD pattern of Ni12-12 after cooling from the isotropic liquid is given in Fig. 3(b). No sharp Bragg peaks were observed in the diffraction pattern of Ni12-12 and only a broad diffraction hump was observed, indicating an amorphous state. The crystallization process of Ni12-12 was confirmed by XRD. XRD patterns of Ni12-12 after annealing the amorphous material at 120 °C for 30 min. and virgin sample are similar, which indicates that the two crystalline phases are identical. Moreover, the high value of the enthalpy of fusion of Ni12-12 (29.9 kJ mol⁻¹) is in agreement with the presence of a perfect crystalline state of Ni12-12 as confirmed by the X-ray analyses.

Upon cooling the isotropic liquid of the nickel complexes, only a black field under POM was observed throughout the cooling process even when the temperature reached below -20 °C, which confirms the existence of the amorphous state. However, anisotropic glass phases were found while annealing samples for a long time. When the samples were annealed at room temperature for several days, a schlieren optical texture was formed. Fig. 4 shows the photomicrograph of Ni12-12 as an example, indicating the formation of a discotic nematic (N_d) mesophase [21]. To further confirm the structure of the mesophase, we carried out XRD experiments. The XRD pattern obtained exhibits only a peak in the small angle area and a broad halo with a wide angle (Fig. 5). On the basis of these observations we can conclude that an anisotropic glass has been formed. Formation of a discotic nematic mesophase in the Ni complexes is in agreement with the discotic structure of the complexes [22]. Thermodynamic data for the Schiff-base ligands and the related Ni complexes are tabulated in Table 2.



Fig. 5. X-ray diffraction pattern after annealing Ni12-12 at room temperature for 7 days.

Table 2	
Thermal transitions and thermodynamic data of the ligands and the Ni complexes, heating and cooling rate: 10 $^{\circ}$ C min ⁻¹	

Compound	Phase transitions (°C) and corresponding enthalpies (kJ mol ⁻¹ , in parentheses) ^a						
	First heating scan	First cooling scan	Second heating scan				
L12-8	K104.0,105.5(2.7) ^b K107.7(7)K118.2(61.3)I	I112.3(59.3)K99.4(15.1)K	K102.4(16.7)K116.7(58.70)				
L12-12	K99.1,102.9 ^b (18.6)K114.3(21.3)K120.5(26.9)I	I108.7(56.0)K99.5(14.5)K	K98.1,99.6,101.1 ^b (10.6)K113.4(17.0)K120.2(40.30)I				
L12-16	K104.9,108.1 ^b (6.1)K113.4(31.3)I	I107.7(34.6)K102.2(10.7)K	K107.1(10.9)K112.0(33.7)I				
Ni12-8	K86.8(8.5),105.1(11.6) ^b ,160.8(35.6)I		G65.1 ^c ,126.4(-24.2)K159.4(33.3)I				
Ni12-12	K73.4(16.1),83.2(0.2),149.1(29.9)I		G66.5°,119.9(-19.7)K147.7(25.8)I				
Ni12-16	K107.7(9.7),136.2(41.5)I		G58.1 ^c ,83.7(-19.3)K107.7(1.0)K135.1(39.4)				

^a K, crystal; G, glass; I, isotropic.

^b Overlapped with a previous transition.

^c Glass transition.

From the above results, it is apparent that the Schiff base ligands do not show any tendency towards glass formation and go to a crystalline phase when cooled from the isotropic liquid, but the related Ni(II) complexes have a great tendency for glass forming and after several days change to an anisotropic glassy state. Some structural requirements such as non-planarity of molecular structure, bulkiness and weight of substitutions and number of conformers of the molecule in the fluid state are responsible for glass formation in organic compounds. Furthermore, the enlargement of molecular size is an important factor for the achievement of the stability of a glassy state [1a]. On the other hand, another requirement is that the molecular system should have a weak tendency towards crystallization despite strong intermolecular attractions [5]. From a structural point of view, the nickel complex is essentially non-planar. It is well known that azobenzene and its p,p'-substituted derivatives are essentially planar, but the azomethine part of the structure is non-planar. As the X-ray analyses indicates in the crystalline state, in this kind of compound, the two benzene rings (phenylimine and salicylidenic ring) are twisted with respect to the azomethine group plan [23]. The Ni(II) complexes, in comparison with the ligands, have all of the structural requirements to form a glassy state. It is notable that the phenomenon of polymorphism, which is observed for the Ni(II) complexes and suggests the existence of different conformers, is responsible for the formation of the glassy state [1a].

5. Conclusion

In this work, we have prepared a series of nickel complex homologues derived from $5-((4-^nalkoxyphenyl)azo)-N-(4-^nalkoxyphenyl)-salicylaldimine homologues. For the first time, we report the glass forming properties of azo-containing salicylaldimine complexes of nickel. While the Schiff base ligands do not show any glass forming properties, the nickel complexes have a resistance to crystallization and form a glassy state.$

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