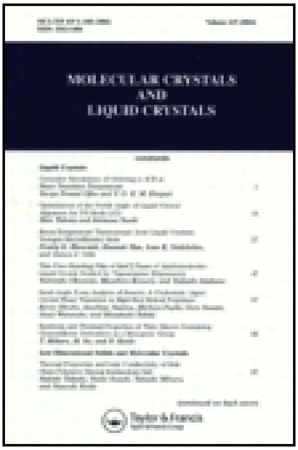


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Mesomorphic Transition Metal N_2O_2 Chelates

T. D. Shaffer [a] & K. A. Sheth [a]

[a] Department of Chemistry, University of Texas at Arlington, Arlington, Texas, 76019

To cite this article: T. D. Shaffer & K. A. Sheth (1989): Mesomorphic Transition Metal N_2O_2 Chelates, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 172:1, 27-39

To link to this article: http://dx.doi.org/10.1080/00268948908042148

Mol. Cryst. Liq. Cryst., 1989, Vol. 172, pp. 27–39
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Mesomorphic Transition Metal N_2O_2 Chelates

T. D. SHAFFER* and K. A. SHETH
Department of Chemistry, University of Texas at Arlington, Arlington, Texas 76019

(Received July 6, 1988)

The first class of transition metal N_2O_2 liquid crystals are reported. They are synthesized as the alkyl ethers of N,N′-bis(5-hydroxysalicylidene) ethylene diamine Mt^{II} complexes (Salen-Mt-n) containing either Cu^{II} or Ni^{II}. Both series were prepared with pentyl through nonyl alkane units. All complexes except Salen-Cu-5 exhibit liquid crystallinity. Decomposition controls the thermal behavior in the Salen-Cu-n complex series with degradation occurring several degrees above the clearing point. Smectic mesomorphism is found in all liquid crystalline chelates. The differences in the thermal characteristics between Salen-Cu-n and Salen-Ni-n chelates is attributed to the different electronic structures of the chelated metals. This behavior exemplifies the influence of the metal upon mesomorphic properties.

INTRODUCTION

Even after a hundred years of synthesis and characterization of liquid crystalline materials, nearly all of the chemical variants prepared have been organic in nature. The examples of organometallic liquid crystalline compounds containing main group elements have largely been prepared as analogs to purely organic systems.[1] Mesomorphic compounds containing transition metals are precious and few. The first known transition metal liquid crystal (TMLC) contained a ferrocene moiety.[2] Since then, four new class of TMLCs have been introduced: dithiene complexes of Ni, Pd, and Pt[3]; mono- and dinuclear cyclopalladated azo complexes[4]; keto-enol dionato Cu discotic complexes[5]; and the porphyrin and phthalocyanine complexes.[6]

In nearly all of these systems, some underlying molecular constraints are found. The introduction of the metal does not distort the required axial ratio of the molecule. In order to preserve this molecular character, the coordination geometry of the metal in the systems above should be square planar. Therefore, provided that the metal's coordination is consistent with an organic structure having a favorable axial ratio, some mesomorphic property might be observed.

Liquid crystals having paramagnetic properties and/or selective optical characteristics would prove interesting or even very useful. Since transition metals can offer these desirable traits, expansion of our understanding of TMLCs would be invaluable.

---

*To whom all correspondence should be addressed.

We now wish to report the first class of transition metal liquid crystalline N_2O_2 chelates. These TMLCs are based on ether derivatives of the well known N,N'-bis(salicylidene) ethylene diamine (salen)[7] complexes. Many studies involving the salen core have demonstrated the existence of square planar coordination in complexes with Cu^{II},Co^{II},Ni^{II}, and other transition metals. This feature permits all components of the molecule to lay within 1° of planarity. These molecular features make salen complexes ideal for the synthesis of TMLCs.

EXPERIMENTAL

A. Materials

2,5-Dihydroxybenzaldehyde (Lancaster Synthesis), ethylene diamine, nickel (II) acetate, and copper (II) acetate were used as received (Aldrich).

B. Techniques

^1H NMR were recorded from DMSO-d_6 solutions on a Varian EM 360 NMR spectrometer using TMS as an internal reference. Infrared spectra were either recorded from KBr pellets or KBr mixtures on a Perkin-Elmer 590-B spectrophotometer or a Digilab Model 40 FT-IR spectrophotometer using a diffuse reflectance accessory. Elemental analyses were performed on a Perkin-Elmer 2400 C,H,N analyzer. Thermal transitions were determined on a Du Pont 910 differential scanning calorimeter (DSC) equipped with a liquid nitrogen accessory and a Du Pont 9900 Thermal Analysis Station. Experiments were performed under nitrogen with scanning rates of 20 deg/min. Optical textures were observed and photographically recorded on a Leitz Laborlux microscope under cross polarization utilizing a Leitz 350 heating stage. Thermal gravimetric analyses (TGA) were run on a Du Pont 951 TGA unit.

C. Synthesis of N,N'-bis(5-hydroxysalicylidene) ethylene diamine (DH salen)

To a solution of 5.0 g (36 mmol) of 2,5-dihydroxybenzaldehyde in 25 ml of methanol a 10% methanolic solution of ethylene diamine (18 mmol) was added dropwise. Upon complete addition of the diamine solution, an orange precipitate formed. The suspension was heated to reflux and maintained there for 1–2 hours. The orange solids were collected by filtration of the cooled suspension. The product was recrystallized from a large volume of methanol. Yield: 4.6 g (84%); m.p. 241°C dec. ^1H-NMR (60 MHz, DMSO-d_6, TMS):$\delta = 9.2$ ppm (broad *s*, 2—O$\underline{H}$), 8.33 ppm (*s*, 2 —N=C$\underline{H}$—), 6.87 ppm (*m*, 6 aromatic H), 3.97 ppm (*s*, —C$\underline{H}_2$C$\underline{H}_2$—). IR (KBr pellet); 2840 cm^{-1} N=C—H stretch, 1620 cm^{-1} —C=N— stretch, 1235 and 1208 cm^{-1} —C—O— stretch, 965 and 955 cm^{-1} N=C—H deformation.

D. Synthesis of N,N'-bis(5-hydroxysalicylidene) ethylene diamine Mt^{II} complexes (Salen-Mt)

Both DH salen metal complexes were prepared from the acetate metal salts. An example is given below for the preparation of the salen Cu^{II}. The procedure for the salen Ni^{II} is essentially identical with the replacement of the appropriate metal salt.

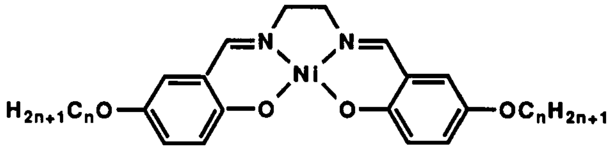
Under nitrogen, 3.00 g (9.9 mmol) of DH salen was dissolved into 50 ml of THF at reflux. Separately, 1.66 g of copper (ll) acetate was dissolved/suspended into 30 ml of ethanol. After adding this to the DH salen solution, two drops of piperidine were added. The solution turned from orange to a deep dark green. After refluxing for two hours, the suspension was cooled and poured into cold water. The dark precipitate was filtered and dried in vacuo. A forest green product was recovered. Yield: 3.08 g (85%); m.p. 317°C dec. IR: (KBr pellet): 1630 cm^{-1} C═N stretch, 1260 and 1250 cm^{-1} C—O stretch.

The salen Ni^{II} was prepared in 96% yield from DH salen and nickel (||) acetate. m.p.>400°C. IR (KBr pellet): 1630 cm^{-1} C═N stretch, 1300 and 1220 cm^{-1} C—O stretch.

E. Synthesis of the N,N′-bis(5-alkoxysalicylidene) ethylene diamine Mt^{II} complexes (Salen-Mt-n)

The syntheses of the Salen-Mt-n were carried out under a nitrogen or argon atmosphere in refluxing ethanol. Each reaction was continued for at least two days to ensure complete conversion. Shorter reaction times led to substantial amounts of mono alkylated product. All prepared compounds were purified by repeated crystallizations from toluene or toluene/heptane mixtures. Results for the Cu^{II} and Ni^{II} complexes are given in Tables I and II along with the elemental analysis data. An example of the reaction procedure is given for Salen-Cu^{II}-7. Salen-Cu^{II}, 0.509 g (1.4 mmol), was dissolved into 50 ml of refluxing ethanol. To this solution, 0.181 g (3.2 mmol) of KOH was added turning the solution a deep reddish-brown as the phenolate was formed. After phenolate formation, 0.787 g (4.3 mmol) of 1-bro-

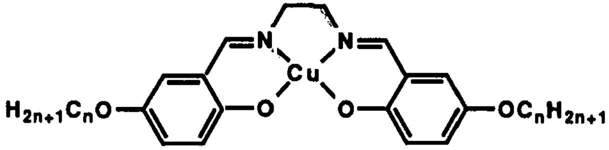
Table I
Elemental Analysis of 4,4′-Bisalkoxysalen- Ni^{II} complexes



n	Molecular Formula	Yield (%)	Elemental Anaylsis (Calc.)					
			C		H		N	
5	$C_{26}H_{34}N_2O_4Ni$	75	62.62	(62.81)	6.81	(6.84)	5.82	(5.81)
6	$C_{28}H_{38}N_2O_4Ni$	65	63.99	(64.03)	7.29	(7.24)	5.27	(5.29)
7	$C_{30}H_{42}N_2O_4Ni$	71	63.89	(65.13)	7.77	(7.59)	4.72	(5.06)
8	$C_{32}H_{46}N_2O_4Ni$	67	64.88	(66.12)	8.01	2)	4.60	(4.82)
9	$C_{34}H_{50}N_2O_4Ni$	73	66.54	(67.02)	8.22	(8.21)	4.49	(4.59)

Table II

Elemental Analysis of 4,4'-Bisalkoxysalen- Cu^{II} complexes



n	Molecular Formula	Yield (%)	Elemental Analysis (Calc.) C		H		N	
5	$C_{26}H_{34}N_2O_4Cu$	55	61.36	(62.20)	7.10	(6.77)	4.68	(5.58)
6	$C_{28}H_{38}N_2O_4Cu$	71	63.20	(63.45)	6.96	(7.17)	4.90	(5.28)
7	$C_{30}H_{42}N_2O_4Cu$	53	62.87	(64.56)	7.55	(7.53)	4.63	(5.02)
8	$C_{32}H_{46}N_2O_4Cu$	71	64.74	(65.58)	7.58	(7.85)	4.73	(4.78)
9	$C_{34}H_{50}N_2O_4Cu$	69	66.56	(66.49)	8.10	(8.14)	4.84	(4.56)

moheptane were added. The reaction was cooled after 48 hours and the precipitate was collected by filtration and washed with methanol. The clear dark filtrant was poured into water, precipitating the green product. After drying in vacuo, the product was recrystallized several times from toluene. Yield: 0.417 g (53%).

RESULTS AND DISCUSSION

As indicated in the introduction, the salen core offers a good deal of flexibility in synthesizing TMLCs. Substitution is most probably required at the 5,5′ positions to preserve the molecular symmetry necessary for liquid crystallinity. Diagram 1 outlines the generic synthetic pathway in preparation of the Salen-Mt-n complexes. For this initial study, only Cu^{II} and Ni^{II} complexes were prepared. The synthetic strategy presented is capable of good yields of the products (Table I and II). The last reaction in the sequence deserves some comment. Because of the electron withdrawing character of the metal complex, the reactivity of the phenolate seems to be substantially reduced. Consequently, reaction times (approximately 48 hours) must be extended beyond those normally required for Williamson etherification. Reaction times shorter than this yielded substantial quantities of monoalkylated product. Although not of interest here, this anomaly may point out the route to unsymmetrically substituted Salen-Mt-n complexes. We are currently pursuing this synthetic avenue.

The structures of the final products were confirmed by elemental analysis (Table I and II). In order to obtain analytically pure samples, it was necessary in some cases to recrystallize the products more than once. The analytically pure samples were used in thermal characterizations. Since these complexes are paramagnetic,

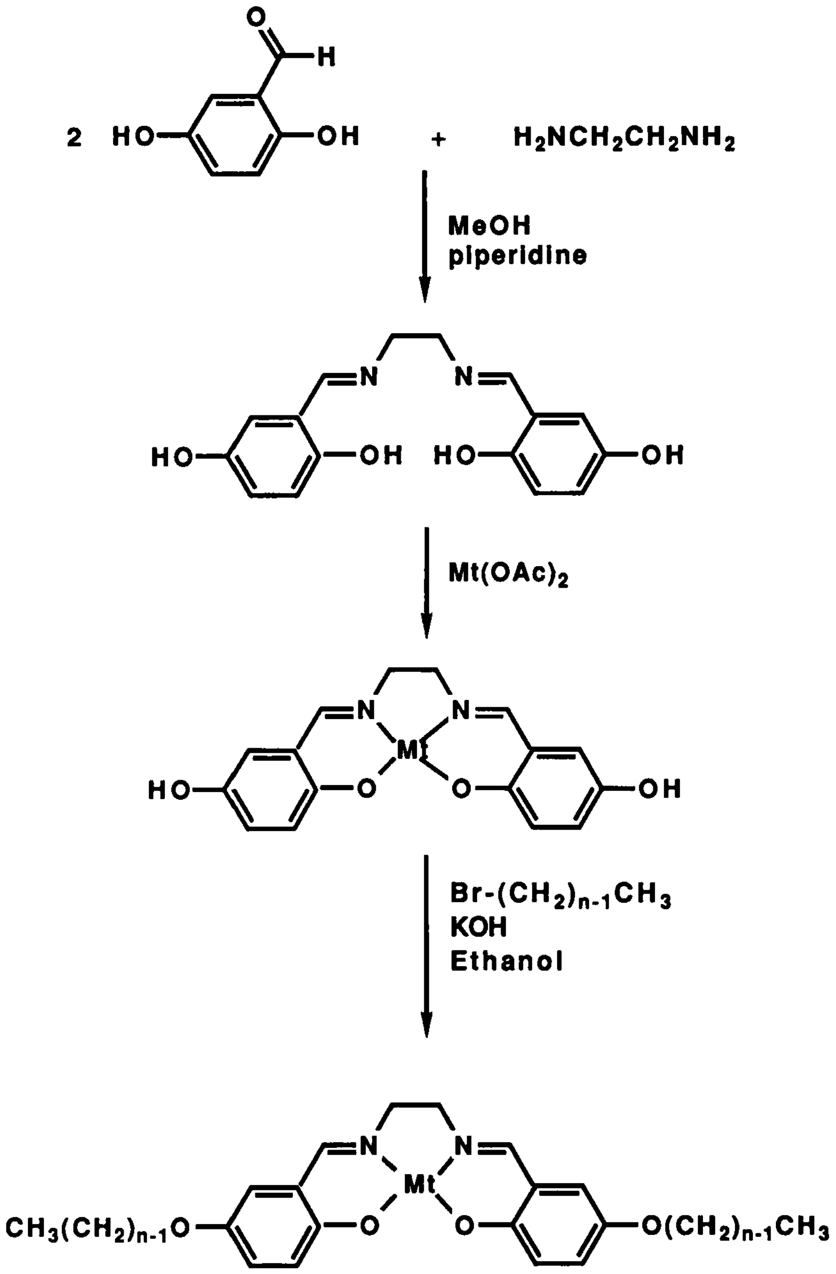


Diagram 1: Synthetic route in preparation of 4,4'-salen ethers (n: 5 - 9 ; Mt: Cu, Ni)

Table III

Thermal Properties of the 4,4'-Bisalkoxysalen-Cu^{II} complexes

n	Mesophases and Thermal Transition Temperatures (°C)[a]													
	Heating							Cooling						
5	k	279	dec.											
6	k	124	s	278			I	k	68	s	245			I
7	k	102	s	235			I	k	--	s	224			I
8	k	122	s	245			I	k	--	s	231			I
9	k	110	s	253	s_2	269	I	k	78	s	201	s_2	212	I

a: k, crystalline; s, low temperature smectic mesophase; s_2, higher temperature smectic mesophase; I, isotropic; dec., decomposition.

FT-IR was the only other tool available for us for structural assessment. Monitoring of the phenol absorptions confirmed their absence in the prepared complexes.

Thermal characterization of the Salen-Mt-n complexes was performed with DSC and optical microscopy. The results of these experiments are listed in Tables III and IV. Each series of complexes yielded mesomorphic compounds. Because the metal is the distinguishing and controlling feature in the series of complexes, we will discuss each separately.

Salen complexes containing Cu^{II} were prepared to contain pentyl to nonyl alkane units (Table III). Decomposition, unfortunately, dominates the thermal behavior of these complexes. Only Salen-Cu-5 did not exhibit mesomorphic behavior, but decomposed on melting. All other Salen-Cu complexes prepared exhibited enan-

Table IV

Thermal Properties of the 4,4'-Bisalkoxysalen-Ni^{II} complexes

n	Mesophases and Thermal Transition Temperatures (°C)[a]																
	Heating											Cooling					
5	*k*	*69*	*k_2*	*97*	T_g	135	s	236	n	251	I	T_g	<—	s	220	n	237	I
6			*k*	*91*	T_g	72	s	218			I	T_g	<—	s	205			I
7			k	116			s	201			I	k	56	s	180			I
8			k	70			s	196			I	k	58	s	175			I
9	*k_1*	*55*	k_2	73			s	185	s_2	288	I	k_2	60	s	162	s_2	283	I

a: *k*, *k_1*, crystalline from solution crystallization (observed only on the first heating cycle); k, k_2, crystalline; T_g, second order transition; s, low temperature smectic mesophase; s_2, higher temperature smectic mesophase; I, isotropic; n, nematic.

tiotropic mesomorphism, provided that decomposition could be controlled. In all cases, decomposition begins to occur shortly above the clearing point (5–10 degrees); thus, only in experiments where short isothermal periods are maintained in the isotropic melt were we successful in reproducing the transitions upon cooling. In dynamic TGA experiments, the degradation temperature was recorded only as high as 315°C. The melting/crystallization transition seems to be most sensitive to the decomposition process. Evidence of this is found in Salen-Cu-7 and 8 (Table III). Even though short isotherms were used in DSC experiments, we were unsuccessful at limiting the degree of degradation. Only an isotropic-anisotropic transition was observed on cooling. When heating these samples again, only the clearing point was observed. Salen-Cu-6 and 9 also exhibited this behavior, but only on a longer time scale. Multiple cycling of the experiment was required before enough decomposition occurred to duplicate the phenomenon observed in Salen-Cu-7 and 8.

Optical microscopy confirmed the thermal characteristics described above. The copper complexes can be observed in their mesomorphic state for extended periods below decomposition temperatures. The textures observed are indicative of smectic mesophases. An example texture is shown in Figure 1 for Salen-Cu-7 at 217°C. As the degree of degradation in the Salen-Cu complexes increases, regions of isotropic, visually darkened material appeared. After this occurred to even a small degree, the samples could be cooled to room temperature, forming a frozen mesophase.

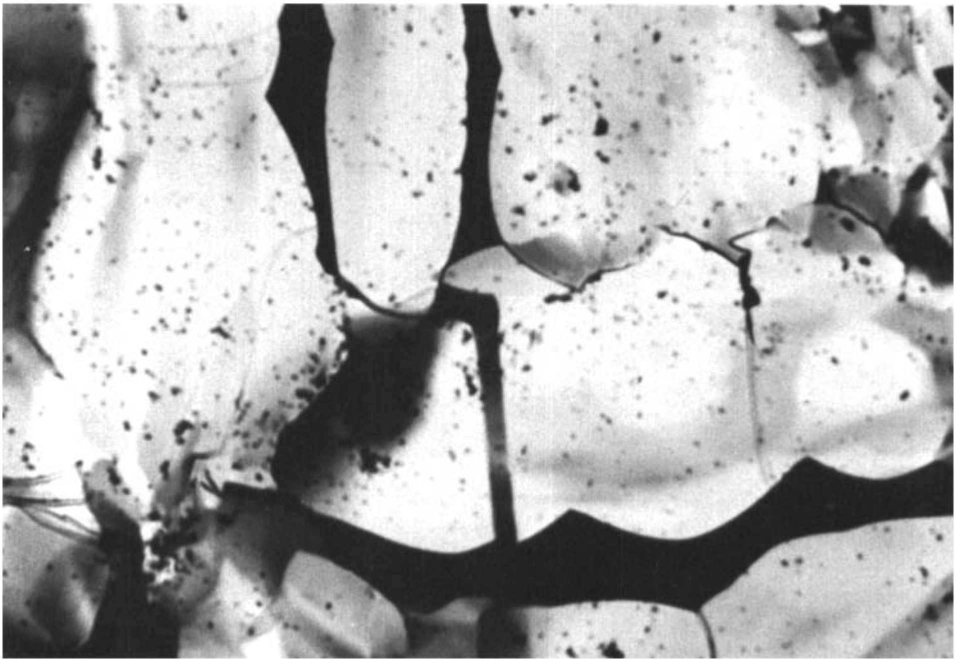


FIGURE 1 Optical polarization micrographs of Salen-Cu-7 mosaic smectic texture at 217°C (heating cycle, 150×).

See COLOR PLATE I.

This is consistent with the DSC data, which do not show a crystallization transition under equivalent conditions. If decomposition is allowed to proceed, the entire sample will become dark and lose its mesomorphic properties.

Salen-Ni-n complexes were prepared to contain pentyl to nonyl alkane units. All of the Salen-Ni-n complexes exhibited enantiotropic mesomorphism (Table IV). Unlike their copper counterparts, these complexes are thermally stable to approximately 350°C, well above isotropization temperatures. Some anomalous behavior is observed in Salen-Ni-5 and 6 complexes. A set of DSC thermograms is shown for Salen-Ni-6 in Figure 2. On heating a fresh sample, the melting and the clearing point transitions are observed. After the first heating, only mesomorphic transitions are observed. Optical microscopy reveals a frozen mesomorphic texture at room temperature after similar sample treatment. This suggests that the second order transition signifies the existence of a glassy phase which prevents crystallization on cooling cycles. Similar observations are made with Salen-Ni-5. Nickel complexes with longer alkyl spacers do not exhibit this behavior.

The mesophases shown by these nickel complexes are smectic. Salen-Ni-5 is the only exception, revealing a nematic phase in addition to its smectic phase. Examples of the observed textures are shown in Figure 3 for Salen-Ni-5, 6, and 9, respectively.

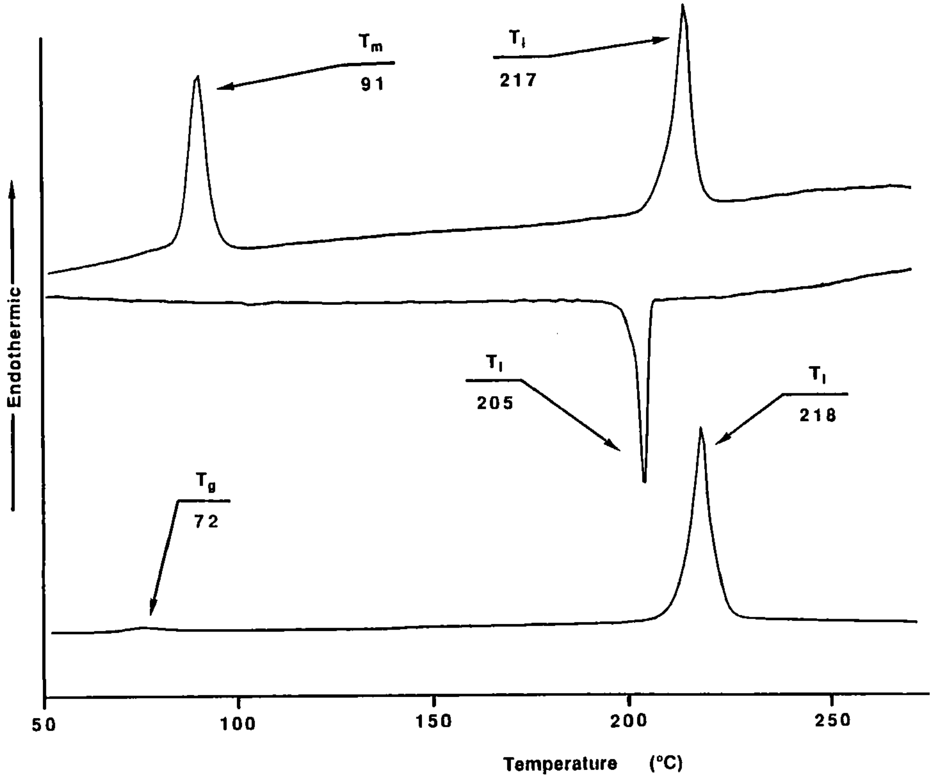
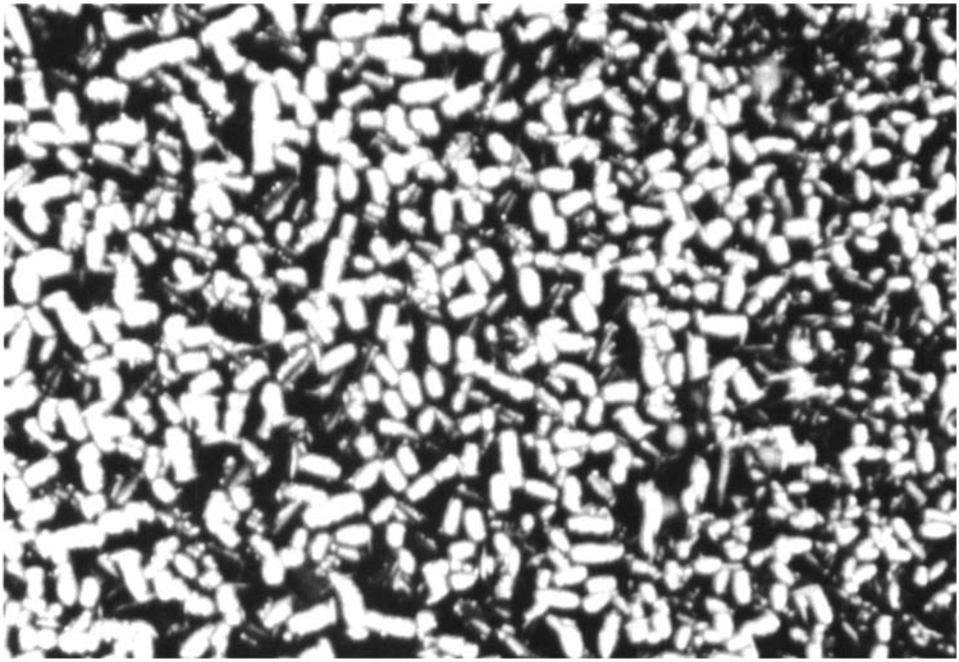


FIGURE 2 Differential scanning calorimetry thermograms for Salen-Ni-6 at 20°C/min. a) first heating of a fresh sample crystallized from solution; b) first cooling scan of the sample sample; c) second (and subsequent) heating scans.



See COLOR PLATE II.

(a)

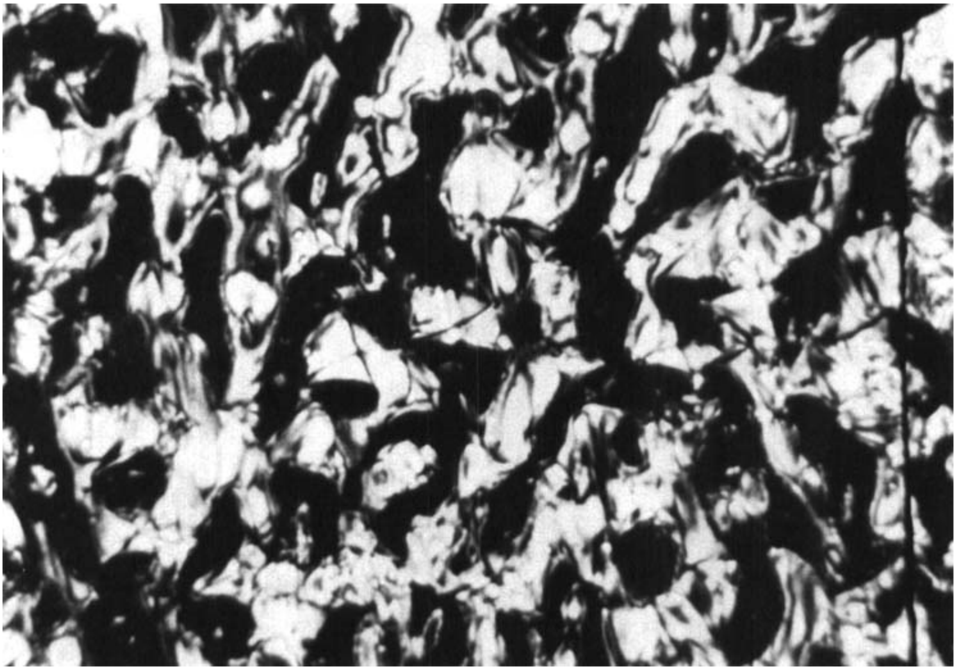
FIGURE 3 Optical polarization micrographs of Salen-Ni-n complexes. a) smetic texture of Salen-Ni-5 at 190°C (heating cycle, 150×); b) focal conic texture of Salen-Ni-6 at 175°C (cooling cycle, 150×); c) simple fan-shaped texture in Salen-Ni-9 at 190°C (cooling cycle, 150×); d) mosaic texture with paramorphic grain boundaries in Salen-Ni-9 at 125°C (cooling cycle, 150×, same section as in figure 3c).

Textures from Salen-Ni-9 are especially clear, with a fan-shaped focal conic texture.

The exact nature of the smectic phases observed in both nickel and copper complexes is unconfirmed. We are currently pursuing both X-ray analysis and miscibility studies for these determinations; therefore, we will reserve speculation on this point.

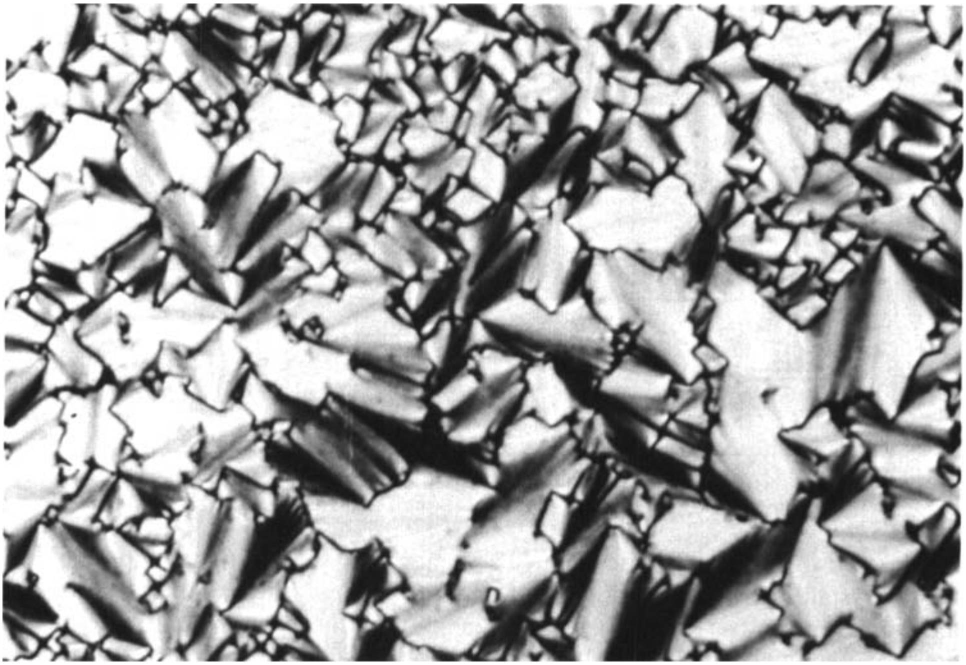
The properties of Salen-Mt-n complexes at first seem curious, until one considers their structure. The organic ligand in the complex remains almost completely unchanged from one transition metal complex to the other. Only the chemistry (that is the eletronic structure) of the metal changes from one complex to the next, so one can envision the *simple* replacement of one metal for another, altering the thermal properties. This scenario seems to exist under the present study.

Copper in its 2^+ state prefers an octahedral coordination shell. By distortion of its atomic orbital (and therefore its energetics), it often adopts a square planar coordination with an overextended d_z^2 orbital. This phenomenon is known as the Jahn-Teller distortion.[8] As a result, most Cu^{II} square planar coordination compounds exhibit a propensity for strong axial interactions. In the present systems, copper may interact with a neighboring molecule through this axial coordination. As such, oxygen in the neighbor may serve as the ligand. This arrangement is



See COLOR PLATE III. (b)

See COLOR PLATE IV. (c)



See COLOR PLATE V.

(d)

conceptualized in Diagram 2. Here only a one pair interaction is shown, but this need not be the only interaction. One can envision a second coordination below the plane of the first salen molecule. This molecular arrangement may create a crystal structure that maintains a higher order than in the Ni series. As such, the melting temperature is increased and directs the formation of higher order smectic melts. Unfortunately, the copper's diameter is bordering on excessive for the salen core. Additionally, the strain found in the axial ligand arrangement (Diagram 2) accelerates the lowering of thermal stability.

Nickel in its 2^+ state, however, may adopt a square planar coordination without the orbital reorganization found in Cu^{II} complexes. This feature usually excludes nickel from participating in axial chemistry. As such, we do not expect or observe intermolecular ligation in the Salen-Ni-n complexes. This is primarily seen in the increased thermal stability of the nickel compounds. An additional contribution arises from the more favorable atomic diameter of nickel in the salen core. Given the above explanation, the smectic mesomorphism observed in Salen-Ni-n complexes must then be attributed almost entirely to the molecular shape of the salen structure. If this supposition is valid, then other salen complexes with different metals should exhibit mesomorphism similar to the compounds studied here. In essence, this system introduces mesomorphic control by the metal's, and *not* the chelate's structure.

During the preparation of this manuscript, a communication appeared on work which utilized Salen-Cu^{II} complexes in liquid crystalline polymers (LCP).[9] The

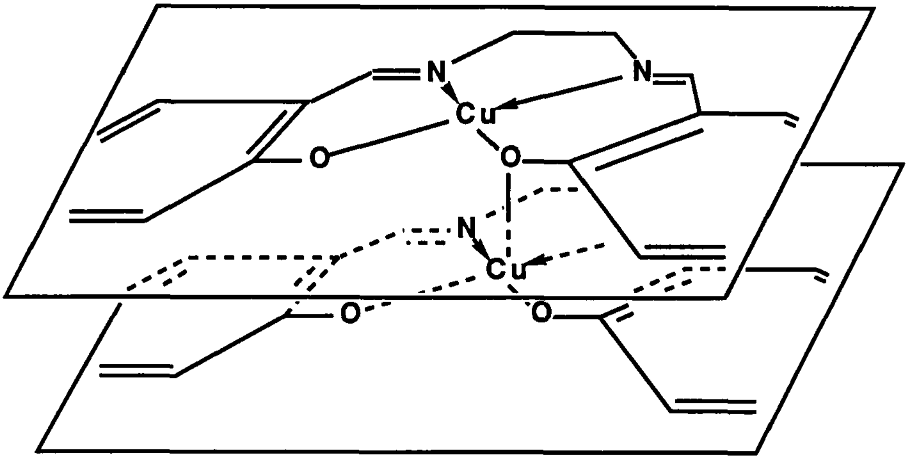


Diagram 2: Possible axial ligand interaction in Cu^{II} Salen Complexes

authors reported several "unexplained" phenomena, such as the enhancement of liquid crystallinity by incorporation of Salen-Cu^{II}. We wish to offer the results of the work reported in this paper as explanation to the phenomena observed. In order to unequivocally demonstrate the ability of Salen-Mt^{II} complexes to induce liquid crystalline behavior in a polymer it is necessary to prepare a polymer using Salen-Cu^{II} (or any Salen-Mt^{II}) complex as the sole mesogen in the polymer. Our attempts to date are negative, having only prepared infusible, unmeltable polymers. This aspect of Salen-Mt^{II} we are continuing to pursue.

Finally, we have demonstrated that N,N′-bis(5-alkoxysalicylidene) ethylene diamine Mt^{II} complexes containing either Cu^{II} or Ni^{II} exhibit mesomorphic melts. As such, they represent the first examples of mesomorphic N_2O_2 complexes. These complexes can be easily synthesized, and may contain any transition metal that may show square planar coordination. The mesomorphism nearly always observed in the prepared complexes is smectic in nature. Copper complexes were limited in their thermal behavior by decomposition. The regulation of this decomposition was necessary for the full characterization of these complexes.

ACKNOWLEDGEMENTS

We wish to thank the Defense Advanced Projects Agency (DARPA) University Research Initiative administered by the Office of Naval Research and the Welch Foundation for their support of this work.

REFERENCES

1. a) W. R. Young, I. Haller, D. C. Green, *Mol. Cryst. Liq. Cryst.*, **13**, 305 (1971). b) W. R. Krigbaum, J. C. Poirier, M. J. Costello, *Mol. Cryst. Liq. Cryst.*, **20**, 133 (1973).
2. J. Malthete, J. Billard, *Mol. Cryst. Liq. Cryst. (Lett.)*, **34**, 117 (1976).
3. a) A. M. Giroud, U. T. Mueller-Westerhoff, *Mol. Cryst. Liq. Cryst. (Lett.)*, **41**, 11 (1977); b) A. M. Giroud, *Ann. Phys.*, **3**, 147 (1978); c) A. M. Giroud, A. Nazzal, U. T. Mueller-Westerhoff,

Mol. Cryst. Liq. Cryst. (Lett.), **56**, 225 (1980); d) U. T. Mueller-Westerhoff, *Mol. Cryst. Liq. Cryst. (Lett.)*, **56**, 249 (1980).

4. a) B. J. Bulkin, R. K. Rose, A. Santoro, *Mol. Cryst. Liq. Cryst.*, **43**, 53 (1977); b) M. Ghedini, M. Longeri, R. Bartolino, *Mol. Cryst. Liq. Cryst.*, **84**, 207 (1982); c) M. Ghedini, S. Licoccia, S. Armentano, *Mol. Cryst. Liq. Cryst.*, **108**, 269 (1984).
5. a) A. M. Giroud-Godquin, J. Billard, *Mol. Cryst. Liq. Cryst.*, **66**, 147 (1981). b) A. M. Giroud-Godquin, J. Billard, *Mol. Cryst. Liq. Cryst.*, **97**, 287 (1983).
6. J. W. Goodby, P. S. Robinson et.al., *Mol. Cryst. Liq. Cryst. (Lett.)*, **56**, 303 (1980).
7. a) C. J. O'Connor, D. P. Freyberg, E. Sinn, *Inorg.Chem.*, **18**, 1077 (1979); b) Gruber, Harris, Sinn, *Inorg. Chem.*, **7**, 268 (1968). c) Gruber, Harris, Sinn, *J. Inorg. Nucl. Chem. Lett.*, **3**, 495 (1967). d) Sinn, *Inorg. Chem.*, **15**, 366 (1976), etc.
8. a) J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 374, (1978); b) F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 678, (1980).
9. J. S. Moore, S. I. Stupp, *Polym. Bull.*, **19**, 251 (1988).