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New organometallic liquid crystals

I. Orthopalladated imine derivatives

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The synthesis, characterization and thermal behaviour of 12 dinuclear, orthopalladated complexes derived from Schiff's bases are reported. The complexes are of the type $[Pd_2(H\text{–}X)_2\{C_6H_3(OR)\text{–}C(Z){=}N\text{–}C_6H_4R'\}_2]$ (X = OAc, Cl, Br, SCN; Z = H, CH_3; $R' = OR, R$; $R = C_{10}H_{21}$) and ten of them exhibit ordered mesophases (S_C and S_A). The molecules were characterized structurally by I.R. and ^{1}H N.M.R. spectroscopy in order to elucidate the possible existence of isomers. The connection between their molecular structures and their mesogenic properties is discussed.

1. Introduction

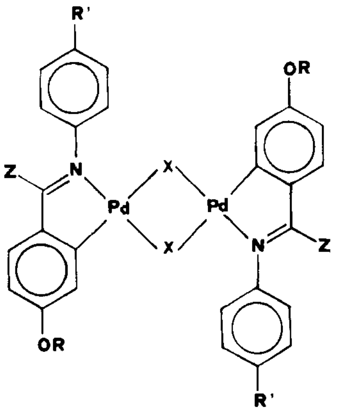
The synthesis of metal-containing liquid crystals has attracted increasing interest in the past few years. Most of the compounds of this kind so far described are coordination compounds in which the organic ligand is bound to the metal atom through a heteroatom; typical examples are provided by the salts of carboxylic acids [5, 6] or, more recently, by some coordination derivatives of copper [7, 8]. Mesogenic organometallic compounds containing a M–C bond are rarer [1–4].

Here we describe the synthesis and characterization of the mesogenic properties of 12 orthopalladated compounds derived from the Schiff's bases: 4-*n*-decyloxybenzylidene-4′-*n*-decylaniline (HL^1); 4,4′-di-*n*-decyloxybenzylideneaniline (HL^2); 4-*n*-decyloxy-α-methylbenzylidene-4′-*n*-decylaniline (HL^3). Four dinuclear derivatives of each of these ligands, having the structures shown in figure 1, have been synthesized. These provide a basis for studying the influence on the mesogenic properties of (*a*) the terminal chains; (*b*) the substitution on the imine-carbon; and (*c*) the nature of the X-bridges between the metallic centres.

2. Experimental

2.1. *Synthesis of the ligands*

The Schiff's bases were synthesized by acetic acid catalysed condensation of the corresponding substituted aldehyde and the respective substituted aniline in ethanol, as described elsewhere [9]. The Schiff's bases, which separated out on cooling, were filtered and purified by repeated recrystallization in ethanol until constant transition



	Z	*R*	*R'*
H-L¹:	H	n-$C_{10}H_{21}$	n-$C_{10}H_{21}$
H-L²:	H	n-$C_{10}H_{21}$	O-n-$C_{10}H_{21}$
H-L³:	CH_3	n-$C_{10}H_{21}$	n-$C_{10}H_{21}$

X :	OAc	Cl	Br	SCN
H-L¹	I a	I b	I c	I d
H-L²	II a	II b	II c	II d
H-L³	III a	III b	III c	III d

Figure 1. The structure of the dinuclear derivatives of the Schiff's bases.

temperatures were obtained. Their elemental analyses were satisfactory. Their transitional properties are

HL¹: $H_{21}C_{10}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_{10}H_{21}$
C 53·3°C (97·95 J/g) S_F 84·4°C (12·34 J/g)
S_A 89·1°C (19·16 J/g) I
HL²: $H_{21}C_{10}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}OC_{10}H_{21}$
C 102·3°C (82·22 J/g) S_C 110·9°C (17·41 J/g) I
HL³: $H_{21}C_{10}O{-}C_6H_4{-}C(CH_3){=}N{-}C_6H_4{-}C_{10}H_{21}$
C 65·4°C (122·72 J/g) I

2.2. *Synthesis of the complexes*

$Pd_2(H{-}OAc)_2L_2$. To a solution of 0·2 mmole of palladium acetate $Pd_3(OAc)_6$ in 20 ml of hot acetic acid was added the corresponding Schiff's base (0·6 mmole) and the mixture was refluxed for 10 min, until traces of black palladium began to appear. The complexes precipitated on cooling as yellow solids contamined with palladium. Once filtered they were dissolved in methylene dichloride, the traces of palladium were filtered off and the complexes were crystallized by evaporation and the addition of acetone.

$Pd_2(\mu{-}Cl)_2L_2$. To a stirred solution of the corresponding acetate-bridged complex (0·2 mmole) in 30 ml of methylene dichloride was added to the stoichiometric amount (862 μl, 0·464 N) of a methanolic solution of hydrogen chloride (HCl/OAc = 1/1). After stirring at room temperature for 2 hours the solution was evaporated to dryness. Addition of acetone (15 ml) afforded the chloro-bridged complexes as yellow solids which were filtered, washed with acetone and dried.

$Pd_2(\mu{-}Br)_2L_2$. A suspension of 0·055 mmole of the corresponding chloro-bridged complex and 0·2 g of potassium bromide in methylene dichloride/acetone (20 ml/10 ml) was refluxed for 4 hours. The resulting suspension was evaporated to dryness. The complex was extracted in 20 ml of methylene dichloride and the insoluble potassium chloride and bromide were filtered off. Evaporation of the dichloromethane solution and addition of 10 ml of acetone gave the bromo-bridged complexes as yellow solids which were filtered, washed with acetone and air dried.

$Pd_2(\mu{-}SCN)_2L_2$. A suspension of 0·079 mmole of the corresponding chloro-bridged complex and 0·2 g of potassium thiocyanate in methylene dichloride/acetone (20 ml/10 ml) was stirred at room temperature for 1 day. The resulting yellow

suspension was filtered and the solid washed repeatedly with water and then with acetone, and air dried.

The analytical data, yields and molecular weights of the complexes synthesized are listed in table 1 and the relevant I.R. data are given in table 2.

2.3. *Techniques*

C, H and N analyses were performed with a Perkin-Elmer 240 B microanalyzer. I.R. spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. ^{1}H N.M.R. spectra were obtained with a Varian XL-200 instrument, operating at 200 MHz for ^{1}H, in deuterio chloroform solutions. Molecular weights were measured in chloroform solutions with a Knauer vapour pressure osmometer.

The textures of the mesophases were studied with a Reichert Thermovar polarizing microscope equipped with a heating stage. Transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-2 operated at a scanning rate of 5 K/min on heating. The apparatus was calibrated with indium (429·6 K; 28·4 J/g) and tin (505·06 K; 60·46 J/g) as standards.

3. Results and discussion

3.1. *Structure of the complexes*

The orthopalladation of azobenzenes, benzylamines and related derivatives is a well-known process and so are the structures of the resulting complexes [10]. All the complexes described here are dinuclear species containing two palladium centres linked by two bridging *X* groups. Each palladium atom completes its usual square-planar coordination with a N-imine atom and a σ bond to an ortho carbon in the phenyl ring.

Some relevant I.R. absorptions are given in table 2 and confirm the general structure of the complexes. Thus, $\nu(C=N)$ is in the typical range for orthometallated compounds [11]. $\nu(Pd-Cl)$ [12] and $\nu(SC=N)$ [13] are also in the typical ranges of a bridging situation for these groups. Although $\nu(C=O)$ for the acetato groups are difficult to assign because they are overlapped with $\nu(C=N)$ they are in the range of bridging or chelate acetato groups [14] and, since no chelate acetato groups are known in palladium complexes, a briding structure is proposed, which is confirmed by the molecular weights determined for the complexes (cf. table 1). $\nu(Pd-Br)$ frequencies for bridging situations are below the range of our spectrophotometer and so are not observed.

According to earlier X-ray structure determinations of related complexes [15] the five-membered palladiacycle, the phenyl ring and the donor atoms of the *X*-bridging groups are expected to lie in the same plane, whereas the other ring should be free to rotate around the N-ring bond.

The main structural differences between the complexes described here result from the nature of the bridging *X*-groups. When these are acetato groups they force the two square planes of each palladium atom to form a very closed dihedral angle [16] and the whole molecule is non-planar with an open book shape as shown in figure 2. In contrast thiocyanato bridges force a very strict coplanarity of the two square planes [17] and the whole molecule should be strictly planar, as shown in figure 3. Chloro and bromo bridges can yield either coplanar or angled dispositions of the two square planes around each palladium, depending on the nature of the other ligands in the

Table 1. Analytical data (calculated values in parentheses), yields and molecular weights (calculated values in parentheses).

Compounds		N	C	H	(Yield per cent)	Molecular weight
Ia	$Pd_2(OAc)_2L^1_2$	2·05 (2·13)	63·10 (63·87)	8·23 (8·12)	60	1260 (1282·8)
IIa	$Pd_2(OAc)_2L^2_2$	2·16 (2·18)	65·69 (65·46)	8·19 (8·37)	75	1291 (1314·8)
IIIa	$Pd_2(OAc)_2L^3_2$	2·01 (2·13)	65·59 (65·89)	7·95 (8·45)	80	1315 (1310·8)
Ib	$Pd_2(Cl)_2L^1_2$	2·13 (2·21)	62·59 (62·45)	7·53 (7·94)	88	1215 (1234·8)
IIb	$Pd_2(Cl)_2L^2_2$	2·06 (2·26)	64·12 (64·07)	8·02 (8·15)	90	1253 (1266·8)
IIIb	$Pd_2(Cl)_2L^3_2$	2·07 (2·21)	64·61 (64·55)	8·09 (8·28)	93	1250 (1262·8)
Ic	$Pd_2(Br)_2L^1_2$	2·40 (2·06)	57·97 (58·37)	7·17 (7·42)	86	1302 (1324·8)
IIc	$Pd_2(Br)_2L^2_2$	2·40 (2·11)	59·68 (59·78)	7·51 (7·60)	84	1321 (1356·8)
IIIc	$Pd_2(Br)_2L^3_2$	2·56 (2·07)	60·27 (60·31)	7·79 (7·74)	75	1315 (1352·8)
Id	$Pd_2(SCN)_2L^1_2$	4·21 (4·26)	61·35 (62·13)	7·33 (7·67)	92	1317 (1308·8)
IId	$Pd_2(SCN)_2L^2_2$	4·58 (4·37)	63·47 (63·68)	7·56 (7·86)	93	1325 (1340·8)
IIId	$Pd_2(SCN)_2L^3_2$	3·82 (4·28)	63·63 (64·15)	7·66 (8·00)	93	1340 (1264·8)

Table 2. Relevant I.R. data for the complexes.

Compounds		ν_1†/cm^{-1}	ν_2†/cm^{-1}	ν_3†/cm^{-1}	ν_4†/cm^{-1}	ν_5†/cm^{-1}	(SCN)/cm^{-1}	ν(Pd–Cl)/cm^{-1}
Ia	$Pd_2(OAc)_2L_2^1$	1605	1590	1570	1540	1500		
IIa	$Pd_2(OAc)_2L_2^2$	1610	1590	1575	1540	1500		
IIIa	$Pd_2(OAc)_2L_2^3$	1610			1540‡	1500		
Ib	$Pd_2(Cl)_2L_2^1$	1605		1580	1535	1500		250
IIb	$Pd_2(Cl)_2L_2^2$	1600		1570	1540	1500		244
IIIb	$Pd_2(Cl)_2L_3^2$			1570	1550	1500		245
Ic	$Pd_2(Br)_2L_2^1$	1605	1590	1575	1545	1500		
IIc	$Pd_2(Br)_2L_2^2$			1580	1540	1500		
IIIc	$Pd_2(Br)_2L_2^3$			1570	1545	1500		
Id	$Pd_2(SCN)_2L_2^1$	1600		1575	1535	1490	2130	
IId	$Pd_2(SCN)_2L_2^2$	1605		1580	1540	1500	2145	
IIId	$Pd_2(SCN)_2L_2^3$			1570	1540		2125	

†Overlap of (C=N), (C=C) and (C=O) absorptions precludes unequivocal assignment of these bands.
‡Broad band between 1610 cm^{-1} and 1540 cm^{-1}.

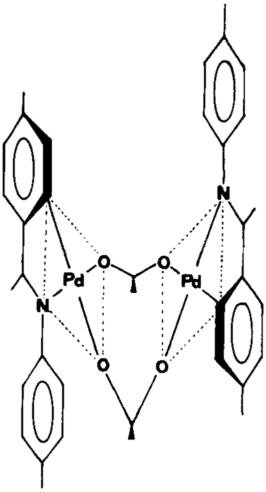


Figure 2. The non-planar open book structure of the aceto-bridged complex.

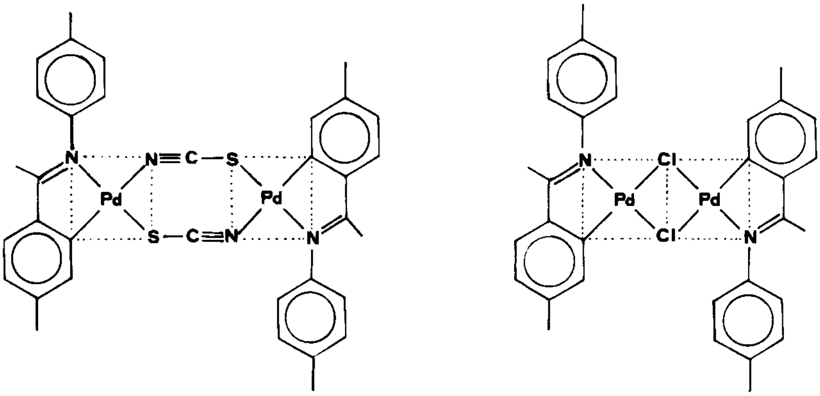


Figure 3. The planar structure for the thiocyanato- and chloro-bridged complexes.

complex, but in our case the whole molecule is expected to be planar [18–20]; the lack of strain would determine, anyway an average planar shape both in solution or under melting conditions. The *X*-bridges also determine the distance between the palladium centres and, consequently, between the alkyl chains. In the planar molecules this distance should increase in the order Cl < Br < SCN (see figure 3). In addition the possibility of isomerism in the complexes has to be considered. For the complexes with symmetric bridging groups the only possibility of steroisomerism results from the two possibilities of coordinating the orthometallated ligands, which give rise to the two isomers trans and cis, represented in figure 4. In the non-planar molecules Ia, IIa and IIIa each isomer should consist of a 1 : 1 mixture of two enantiomers, which are indistinguishable in the ^{1}H N.M.R. spectra. ^{1}H N.M.R. spectra of complexes Ia, IIa and IIIa (table 3) show only one singlet for the acetato groups thus discounting the cis isomer in which both acetato groups are inequivalent. Consequently, we assign the trans geometry to the parent complexes with bridging acetato groups and also to their Cl and Br derivatives for which ^{1}H N.M.R. spectroscopy reveals the presence of only one isomer in solution. For X = SCN the ^{1}H N.M.R. spectra reveal that besides the

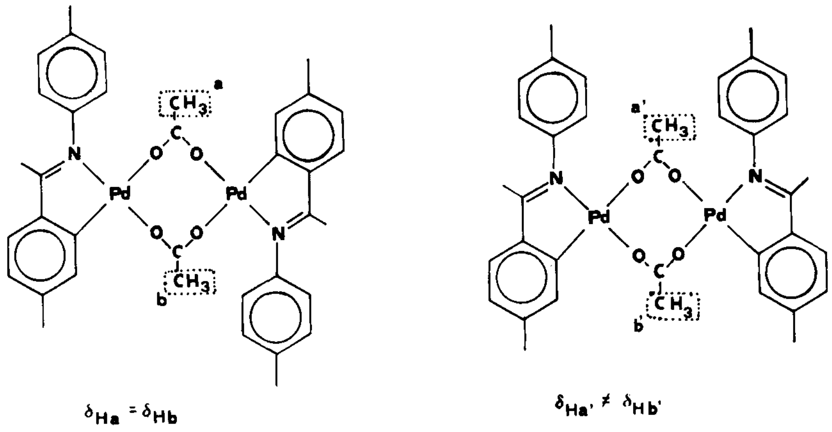


Figure 4. The cis and trans isomers for the aceto-bridged complexes.

Table 3. ^1H N.M.R. data for the complexes.

Compounds	CH_3COO^-	$-C(X)=N-$†		
$Pd_2(OAc)_2L^1_2$	1·80 (s)	7·47 (s)		
$Pd_2(OAc)_2L^2_2$	1·88 (s)	7·46 (s)		
$Pd_2(OAc)_2L^3_2$	1·49 (s)	1·92 (s)		
$Pd_2(Cl)_2L^1_2$		7·79 (s)		
$Pd_2(Cl)_2L^2_2$		7·78 (s)		
$Pd_2(Cl)_2L^3_2$		2·06 (s)		
$Pd_2(Br)_2L^1_2$		7·82 (s)		
$Pd_2(Br)_2L^2_2$		7·79 (s)		
$Pd_2(Br)_2L^3_2$		2·03 (s)		
$Pd_2(SCN)_2L^1_2$		7·92 (s)	7·88 (s)‡	7·78 (s)
$Pd_2(SCN)_2L^2_2$		7·89 (s)	7·85 (s)	7·75 (s)
$Pd_2(SCN)_2L^3_2$		2·10 (s)	2·07 (s)	2·00 (s)

† X = H for L^1, L^2; $X = CH_3$ for L^3.

‡ Minor isomers, less than 10 per cent for L^1 and L^2 and 20 per cent for L^3.

main isomer there are very small quantities of other isomers, possibly resulting from the different possibilities of coordination of two assymmetric SCN groups relative to each other and to the C,N-orthopalladiacycle. Existence of isomers in these complexes is observed by ^1H N.M.R. in the signals from H (for ligands I and II) and CH_3 (for ligand III) linked to the carbon atom of the central imine group (see table 3). According to the usual antisymbiotic behaviour of palladium [21] we suggest that the structure of figure 5 (A) is the most likely one for the predominant isomer.

3.2. *Mesogenic behaviour*

Table 4 shows the transition temperatures and enthalpies for the complexes synthesized. As we can see, all of the compounds with the exception of the acetato-bridged complexes show enantiotropic mesophases. The chloro-bridged complexes of the HL^1 and HL^2 ligands show two mesophases, S_C and S_A, whereas the remainder only exhibit one mesophase, S_A.

Table 4. Thermal and thermodynamic data for the complexes.

Compound	Transition	Temperature/°C	Enthalpy/kJ mole^{-1}
$Pd_2(OAc)_2L_2^1$	C–I	169·9	41·88
	I–S_A	160·0	—
$Pd_2(Cl)_2L_2^1$	C–C′	95·0	26·74
	C′–S_C	112·4	3·25
	S_C–S_A	135·0†	—
	S_A–I	237·6 (dec.)	
$Pd_2(Br)_2L_2^1$	C–S_A	102·6	32·45
	S_A–I	241·2	10·63
$Pd_2(SCN)_2L_2^1$	C–C′	159·2	24·89
	C′–S_A	166·6	26·04
	S_A–I	219·6	
$Pd_2(OAc)_2L_2^2$	C–I	192·4	56·22
$Pd_2(Cl)_2L_2^2$	C–C′	124·2	15·14
	C′–S_C	132·7	3·15
	S_C–S_A	220·0†	
	S_A–I	242·8	
$Pd_2(Br)_2L_2^2$	C–S_A	161·6	32·61
	S_A–I	239·0 (dec.)	
$Pd_2(SCN)_2L_2^2$	C–C′	126·9	4·09
	C′–S_A	201·8	35·08
	S_A–I	226·4 (dec.)	
$Pd_2(OAc)_2L_2^3$	C–I	214·3	56·44
$Pd_2(Cl)_2L_2^3$	C–C′	91·2	5·86
	C′–C″	136·0	13·35
	C″–S_A	142·8	18·53
	S_A–I	246·0	14·73
$Pd_2(Br)_2L_2^3$	C–S_A	130·7	44·56
	S_A–I	235·9	14·02
$Pd_2(SCN)_2L_2^3$	C–S_A	217·8	41·45
	S_A–I	229·8	11·21

† Optical microscopic data.

Low angle X-ray diffraction measurements on the complex $Pd_2(\mu\text{–}Br)_2L_2^1$ show the characteristic bands of a smectic A mesophase. The solid obtained by cooling is very interesting because its structure is also smectic A. We shall continue these structural studies using the X-ray synchroton at Lure (Orsay) to determine more precisely the environment of the palladium atom and other structural features.

The mesophases observed for these organometallic complexes show a higher viscosity than the similar organic mesogenic compounds. This property is specially sensitive to temperature, and a gradual variation from fusion to isotropization is observed.

In the acetato-bridged complexes we have only observed a monotropic S_A mesophase in the complex with HL^1 ligand, whereas the other two complexes are not mesomorphic. This difference in thermal behaviour can be understood by considering the lack of planarity of the molecule. In the rest of the complexes the whole molecule is planar and this molecular geometry allows adequate packing to produce mesogenic behaviour.

Regarding the transition temperatures (cf. figure 6), the melting points of the complexes with the same intermetallic central core behave similarly to the free ligands: lower temperatures for the complexes with HL^1 (imines derived from an aldehyde with

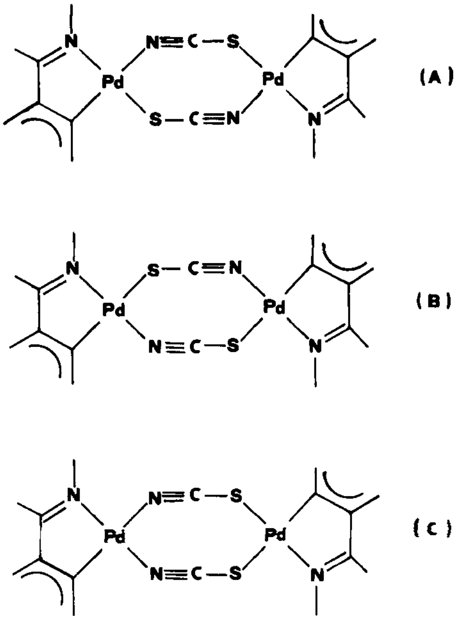


Figure 5. Possible structures for the thiocyanato-bridged complex.

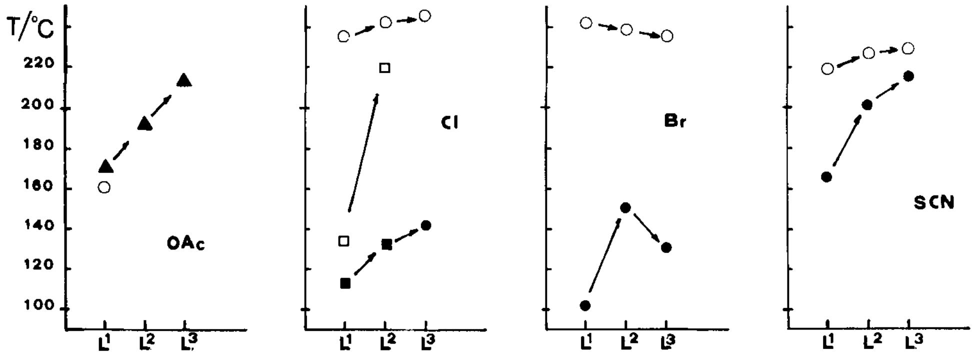


Figure 6. Plot of transition temperatures versus the nature of the ligand.

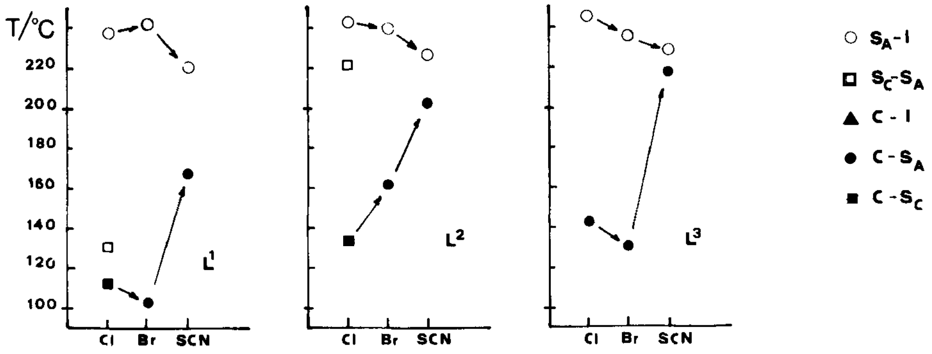


Figure 7. Plot of transition temperatures versus the bridging group.

alkyl and alkoxy groups as terminal chains), than for the complexes with HL^2 (imines derived from an aldehyde with alkoxy terminal chains on both sides). On the other hand the melting temperatures are lower for complexes of imines derived from an aldehyde than for complexes of imines derived from a ketone. There is, however, one exception in the bromo-complexes, where the compound with the HL^2 ligand has a higher melting point than the complex of HL^3 (see figure 6). In the clearing temperatures the same behaviour is observed and the bromo-bridged complexes show again a reversed behaviour.

Finally, figure 7 shows that for the same ligand the acetato- and thiocyanate-bridged complexes exhibit, in general, the highest melting points, whereas chloro- and bromo-bridged complexes have lower melting temperatures. Transition temperatures to the isotropic liquid show a reversed behaviour, the thiocyanate-bridged complexes exhibiting the lowest clearing temperatures.

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