Inorg. Chem. **1990**, *29*, 1177-1181

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Liquid Crystalline Copper(II) Complexes of *N*-Salicylideneaniline Derivatives. Mesomorphic Properties and a Crystal Structure

Naomi Hoshino,*[,1a] Hikari Murakami,[1a] Yoshio Matsunaga,[1a] Tamotsu Inabe,[1b] and Yusei Maruyama[1b]

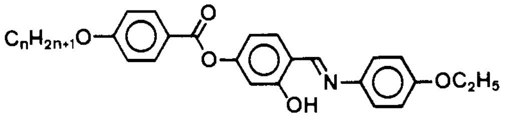
Received July 14, 1989

Homologous series of 3-hydroxy-4-(((4-ethoxyphenyl)imino)methyl)phenyl 4-alkoxybenzoates (L) and their copper(II) complexes (CuL_2) have been synthesized and thermally characterized. The ligands are highly stable mesogens displaying liquid crystalline phases over temperature ranges of 100–150 °C; homologues having hexyloxy to hexadecyloxy chains showed nematic phases and only the octadecyloxy homologue showed a smectic C phase below the nematic. The copper (II) complexes also proved to be mesogenic, with their melting points raised by 50–110 °C compared to the temperature of the ligands, and undecyloxy and higher homologues exhibited smectic C phases. The crystal structure of an analogous system, in which the 4-ethoxyphenyl groups are replaced by 4-*n*-hexylphenyl groups, has been solved. It crystallizes in the monoclinic space group $P2_1/c$, with $a = 21.995$ (8) Å, $b = 18.016$ (3) Å, $c = 14.957$ (4) Å, $\beta = 107.94$ (3)°, and $Z = 4$. The structure shows that the molecular shape is far from disklike, with both the *N*-phenyl and benzoyl groups twisted relative to the salicylidene moiety. A weak axial interaction involving a neighboring carbonyl oxygen to the copper center in the crystalline state has also been disclosed. These characteristics are discussed in relation to the mesophase structure of CuL_2.

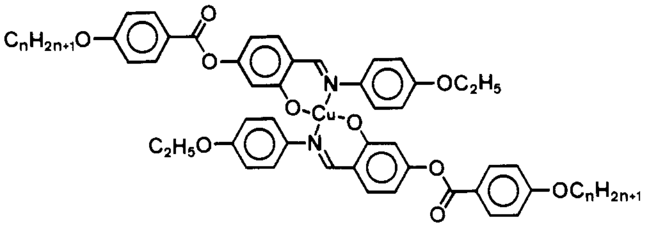
Introduction

Liquid crystalline materials containing metal ions (metallomesogens) are of interest to us in the following respects. While applications of existing materials have been increasingly elaborated, recent studies have also actively sought liquid crystals of a novel type that do not fit the conventional classification.[2,3] Calamitic and discotic mesophases are formed with rodlike and disklike molecules,[4,5] respectively, but incorporation of transition-metal ions into otherwise solely organic compounds will provide a means to alter the molecular shape beyond the range based on carbon and some heteroatoms owing to the diversity of metal coordination geometries. In addition, metallomesogens offer appealing prospects regarding optical, magnetic, and electrical properties.[6]

While examples of metallomesogens of various types are found in the literature,[7] we have chosen a well-known bis(*N*-phenylsalicylaldiminato)copper(II) framework primarily because of its molecular architecture, which is neither simply rodlike nor disklike, and because of the ease of introducing long-chain terminal groups on the periphery, and have undertaken a systematic study of several homologous series of complexes and ligands, searching for a molecular design principle for obtaining stable liquid crystalline phases with transition-metal complexes. Among the systems investigated to date are 3-hydroxy-4-(((4-ethoxyphenyl)imino)methyl)phenyl 4-alkoxybenzoates (L) and their copper(II) complexes, bis[4-((4-alkoxybenzoyl)oxy)-*N*-(4-ethoxyphenyl)salicylaldiminato]copper(II) (CuL_2), mesomorphic properties of which are reported in this paper. The crystal structure determination of an analogous system, bis[4-((4-butoxybenzoyl)oxy)-*N*-(4-*n*-hexylphenyl)salicylaldiminato]copper(II), was carried out in order to find correlations among molecular, crystal, and mesophase structures.



L



CuL_2

Results and Discussion

Mesomorphic Transitions. Table I summarizes the mesomorphic transition temperatures and enthalpy changes for the homologous series of L and CuL_2. Here K,[8] S_C, N, and I denote crystalline, smectic C, nematic, and isotropic liquid phases, respectively, and each homologue is designated by the number of carbon atoms in the terminal alkyl chains, *n*. All of the ligands of $n = 6$–16 melt around 105 °C, and the fluids display marble texture under a polarizing microscope. Considering also the typically rodlike shape of the molecules, the phase was identified as nematic. In the exceptional case of the $n = 18$ homologue, appearance of the nematic phase is preceded by the appearance of the smectic C phase. This was confirmed by the X-ray diffraction pattern showing an intense low-angle peak at 110 °C and only diffuse reflections at 155 °C. The magnitude of N–I transition enthalpies (1.1–1.9 kJ mol^{-1}) is in the known range.[9] The

---

(1) (a) Hokkaido University. (b) Institute for Molecular Science.

(2) Kreuder, W.; Ringsdorf, H.; Herrmann-Schönherr, O.; Wendorff, J. H. *Angew. Chem.* **1987**, *99* (12), 1300–1303.

(3) Demus, D. *Mol. Crystl. Liq. Cryst.* **1988**, *165*, 45–84.

(4) Gray, G. W. In *Advances in Liquid Crystals, Vol. 2*; Brown, G. H., Ed.; Academic Press: New York, 1976; pp 1–72.

(5) Chandrasekhar, S. In *Advances in Liquid Crystals, Vol. 5*; Brown, G. H., Ed.; Academic Press: New York, 1982; pp 47–78.

(6) Piechocki, C.; Simon, J. *Nouv. J. Chim.* **1985**, *9*, 159.

(7) Copper(II) complexes related to our systems have been investigated: (a) Ghedini, M.; Armentano, S.; Bartolino, R.; Kirov, N.; Petrov, M.; Nenova, S. *J. Mol. Liq.* **1988**, *38*, 207–213. (b) Roviello, A.; Sirigu, A.; Iannelli, P.; Immirzi, A. *Liq. Cryst.* **1988**, *3*, 115–122. (c) Galyametdinov, Y. G.; Bikchantaev, I. G.; Ovchinnikov, I. V. *Zh. Obshch. Khim. SSSR* **1988**, *58*, 1326–1331. (d) Paschke, R.; Zaschke, H.; Mädicke, A.; Chipperfield, J. R.; Blake, A. B.; Nelson, P. G.; Gray, G. W. *Mol. Cryst. Liq. Cryst. Lett.* **1988**, *6*, 81–85. Copper(II) β-diketone complexes have been reported in, for instance: (e) Ohta, K.; Muroki, H.; Takagi, A.; Yamamoto, I.; Matsuzaki, K. *Mol. Cryst. Liq. Cryst.* **1986**, *135*, 247. (f) Chandrasekhar, S.; Ratna, B. R.; Sadashiva, B. K.; Raja, V. N. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 123–130. Some recent reports involve organometallic species: (g) Esteruelas, M. A.; Oro, L. A.; Sola, E.; Ros, M. B.; Serrano, J. L. *J. Chem. Soc., Chem. Commun.* **1989**, 55–56. (h) Marcos, M.; Ros, M. B.; Serrano, J. L. *Liq. Cryst.* **1988**, *3*, 1129–1136. (i) Adams, H.; Bailey, N. A.; Bruce, D. W.; Dhillon, R.; Dunmur, D. A.; Hunt, S. E.; Lalinde, E.; Maggs, A. A.; Orr, R.; Styring, P.; Wragg, M. S.; Maitlis, P. M. *Polyhedron* **1988**, *7*, 1861–1867.

(8) Solid-state polymorphism was observed for the $n = 7$, 9–11, 14, 16, and 18 homologues of L and the $n = 6$ and 7 homologues of CuL_2. Thermodynamic measurements were performed with both virgin crystals and annealed samples whenever double-melting behavior was detected on DSC thermograms.

(9) Demus, D.; Diele, S.; Grande, S.; Sackmann, H. In *Advances in Liquid Crystals, Vol. 6*; Brown, G. H., Ed.; Academic Press: New York, 1983; pp 1–107.

0020-1669/90/1329-1177$02.50/0 © 1990 American Chemical Society

Table I. Mesomorphic Transition Temperatures (°C) and Enthalpies (ΔH/kJ mol^{-1})^a for L and CuL$_2$

n	L							CuL$_2$						
	K_1^{b}		S_C		N		I	K		S_C		N		I^c
6	·	111			·	262	·	·	222			·	274	·
		(31)				(1.8)			(55)				-	
7	·	112			·	256	·	·	211			·	272	·
		(34)				(1.7)			(48)				-	
8	·	121			·	252	·	·	201			·	275	·
		(59)				(1.9)			(59)				-	
9	·	107			·	244	·	·	192			·	262	·
		(43)				(1.6)			(44)				-	
10	·	107			·	238	·	·	189			·	271	·
		(33)				(1.8)			(51)				-	
11	·	106			·	232	·	·	181	·	185	·	268	·
		(35)				(1.6)			(47)		(0.36)		-	
12	·	106			·	226	·	·	178	·	204	·	264	·
		(62)				(1.5)			(54)		(0.41)		-	
14	·	106			·	219	·	·	170	·	230	·	260	·
		(38)				(1.2)			(60)		(0.33)		-	
16	·	105			·	211	·	·	162	·	256			·
		(45)				(1.1)			(63)		(2.9)			
18	·	104	·	136	·	204	·	·	156	·	251			·
		(55)		(0.15)		(1.4)			(66)		(3.2)			

^{a}Values in parentheses. ^{b}Crystalline phase showing the highest melting point. ^{c}Onset of exothermic decomposition for the n = 6–14 homologues.

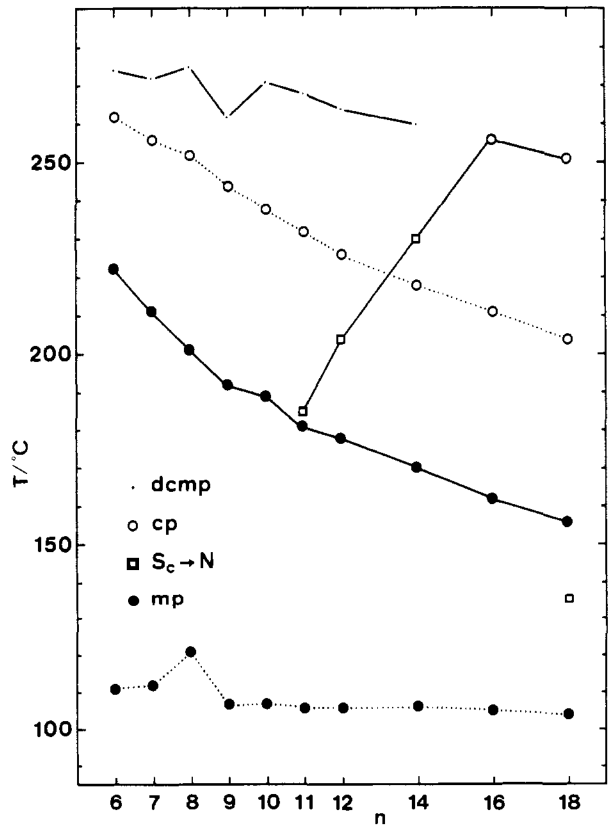


Figure 1. Plots of mesomorphic transition temperatures vs terminal alkyl chain length (n) for L (dotted line) and CuL$_2$ (solid line).

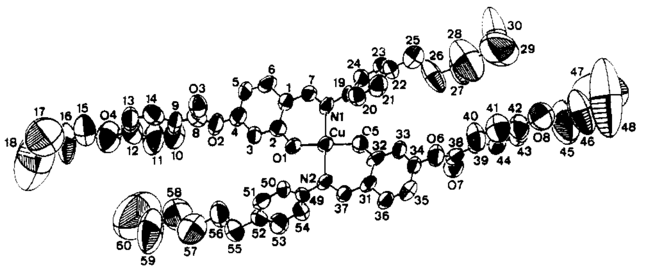


Figure 2. ORTEP drawing for bis[4-((4-butoxybenzoyl)oxy)-N-(4-n-hexylphenyl)salicylaldiminato]copper(II). The letter C for carbon atoms is omitted from the atomic numbering scheme for clarity.

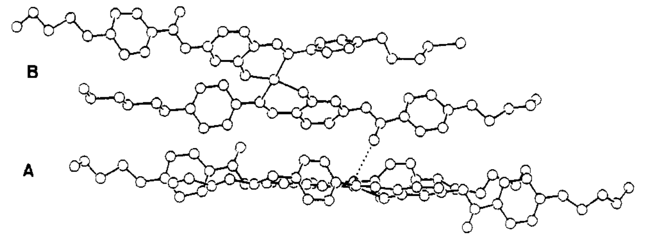


Figure 3. Ball-and-stick representation showing weak axial coordination (dotted line) of a carbonyl oxygen to the neighboring copper center.

phase persists up to temperatures between 204 °C (n = 18) and 262 °C (n = 6), giving wide temperature ranges of nematic appearance. The ligands are thus highly mesogenic, which should be advantageous for furnishing liquid crystalline properties to metal complexes.

Table I shows that the copper(II) complexes are indeed mesogenic, and Figure 1 gives a graphic comparison of their phase behavior to that of the ligands. The melting points are raised by 50 °C (n = 18) to 110 °C (n = 6) upon complex formation and so seem the clearing points (though undetermined for the n = 6–14 homologues due to thermal decomposition). It should be noted that an increased number of homologues yield the smectic C phase. The optical texture of the phase was a blurred Schlieren pattern, similar to that of the nematic phase, but concentric arcs were clearly visible in some domains. The $S_C \rightarrow N$ (n = 11, 12, 14) and $S_C \rightarrow I$ (n = 16, 18) transitions were detectable both by optical means and on DSC thermograms, although the magnitude of these transition enthalpies is relatively small compared with literature values.[9] An X-ray diffraction pattern indicative of a lamella structure also supported the identification (vide infra).

Thus, incorporation of a metal center into the molecule of L leads to a more ordered mesophase of CuL$_2$. The change clearly involves one in molecular geometry; CuL$_2$ is more symmetric than L, having long alkyl chains on both ends. Greater polarity of the coordination bonds in CuL$_2$ should also enhance transverse intermolecular association and promote smectic phases. The fact that the smectic C phase is particularly favored may be related to the symmetrical molecular structure,[10] but coordinating interaction with the metal center as found in the crystalline state (vide infra) may contribute to the formation of this tilted polymorph.

Molecular and Crystal Structures. Single-crystal X-ray structure analysis was performed at room temperature for a copper complex that corresponds to the n = 4 homologue of CuL$_2$ with its ethoxy groups replaced by n-hexyl groups. This compound also shows the nematic phase above 223 °C. Figure 2 shows the molecular structure together with the atomic numbering scheme. Table II summarizes atomic positional parameters for non-hydrogen atoms. The molecule is nearly centrosymmetric, but actually the whole molecule is crystallographically independent. The structure has not been resolved for possible disorder involving different conformations of terminal alkyl chains, but it is sufficient for characteristic features related to the mesomorphism to be drawn.

The overall molecular shape is lathlike rather than disklike due to the twist of all of N-phenyl and benzoyl moieties relative to

---

(10) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210–5221.

Table II. Final Atomic Coordinates for Non-Hydrogen Atoms of Bis[4-((4-butoxybenzoyl)oxy)-*N*-(4-*n*-hexylphenyl)salicylaldiminato]copper(II)

atom	x	y	z
Cu	−0.0109	0.1514	0.3774
O1	−0.0677	0.1331	0.2559
O2	−0.1734	0.0186	−0.0323
O3	−0.1009	0.0202	−0.1081
O4	−0.3635	−0.0261	−0.4347
O5	0.0215	0.1559	0.5106
O6	0.1581	0.2597	0.7903
O7	0.0895	0.2357	0.8664
O8	0.3638	0.2243	1.1916
N1	0.0388	0.0563	0.3816
N2	−0.0477	0.2560	0.3698
C1	−0.0318	0.0113	0.2304
C2	−0.0723	0.0767	0.2008
C3	−0.1179	0.0776	0.1102
C4	−0.1254	0.0161	0.0516
C5	−0.0864	−0.0472	0.0796
C6	−0.0434	−0.0498	0.1629
C7	0.0187	0.0080	0.3172
C8	−0.1564	0.0167	−0.1080
C9	−0.2110	0.0044	−0.1885
C10	−0.2714	0.0025	−0.1857
C11	−0.3240	−0.0125	−0.2636
C12	−0.3082	−0.0189	−0.3479
C13	−0.2494	−0.0136	−0.3598
C14	−0.1999	0.0000	−0.2739
C15	−0.3590	−0.0306	−0.5293
C16	−0.4330	−0.0328	−0.5958
C17	−0.4259	−0.0378	−0.6824
C18	−0.4749	0.0042	−0.7192
C19	0.0892	0.0395	0.4628
C20	0.1414	0.0853	0.4912
C21	0.1886	0.0729	0.5702
C22	0.1889	0.0086	0.6247
C23	0.1387	−0.0364	0.5961
C24	0.0896	−0.0229	0.5176
C25	0.2411	−0.0074	0.7107
C26	0.2341	0.0427	0.7872
C27	0.2830	0.0239	0.8953
C28	0.3389	0.0503	0.9095
C29	0.4159	0.0521	1.0311
C30	0.3879	−0.0111	1.0239
C31	0.0147	0.2859	0.5338
C32	0.0416	0.2133	0.5663
C33	0.0883	0.2058	0.6565
C34	0.1061	0.2657	0.7087
C35	0.0805	0.3389	0.6823
C36	0.0338	0.3483	0.5950
C37	−0.0304	0.3003	0.4406
C38	0.1442	0.2413	0.8670
C39	0.2051	0.2364	0.9485
C40	0.2622	0.2535	0.9409
C41	0.3164	0.2530	1.0224
C42	0.3073	0.2294	1.1078
C43	0.2475	0.2100	1.1115
C44	0.1949	0.2153	1.0304
C45	0.3674	0.2324	1.2850
C46	0.4387	0.2421	1.3429
C47	0.4692	0.1911	1.4162
C48	0.5117	0.2354	1.4339
C49	−0.0920	0.2801	0.2837
C50	−0.1520	0.2920	0.2826
C51	−0.2011	0.3102	0.1979
C52	−0.1793	0.3181	0.1177
C53	−0.1170	0.3066	0.1241
C54	−0.0709	0.2878	0.2070
C55	−0.2302	0.3365	0.0228
C56	−0.2573	0.2662	−0.0291
C57	−0.3076	0.2938	−0.1344
C58	−0.3336	0.2305	−0.1864
C59	−0.3786	0.2703	−0.2906
C60	−0.3959	0.2095	−0.3384

the salicylidene units. Relevant torsional angles between benzene rings are as follows: C1–C6 vs C19–C24, 56.0 (6)°; C1–C6 vs C9–C14, 68.1 (6)°; C31–C36 vs C49–C54, 78.1 (5)°; C31–C36 vs C39–C44, 83.1 (6)°. Furthermore, the copper coordination geometry is not precisely planar. The two chelate planes, (Cu, N1, O1) and (Cu, N2, O5), make a torsional angle of 21.9 (4)°. Table III summarizes bond length and angle data.

Figure 3 shows the spacial arrangement of two molecules, A and B, which are related by the *c* glide symmetry element of space group $P2_1/c$. It should be noted here that atom O7(B) is located near the fifth coordination site of Cu(A). The distance between them is 3.04 (1) Å, short enough to be regarded as weak axial coordination. Molecular packing diagrams are presented in Figure 4. The projection onto the (010) plane (Figure 4a) shows that the molecules form tilted layers parallel to the *bc* plane. When viewed along their long molecular axes (Figure 4b), the molecules upon melting could be easily imagined to rotate around these axes and start to translate in this direction, giving a nematic liquid crystal.

Structures of the Mesophases. Assuming similar factors determine packing forces for CuL_2 ($n = 4$), the nematogenic behavior of the lower homologues of CuL_2 may be explained in a similar manner. The analogy may be further extended to the higher homologues (n = 11–18), and it is speculated that the layer crystal lattice is retained for a while after the alkyl chains have melted until the molecules start to slide along each other at the $S_C \rightarrow N$ or $S_C \rightarrow I$ transition.

X-ray diffraction measurements were performed for the nematic phase of $n = 10$ and smectic C phase of n = 14, 16, and 18 homologues of CuL_2 (Table IV). The diffraction pattern for the latter commonly consisted of a sharp low-angle peak (and its secondary reflection) corresponding to the layer thickness (d_l) and a diffuse outer reflection giving average lateral separation (d_t). Molecular length was calculated by assuming an all-trans conformation for polymethylene chains added to the above crystal structure for the $n = 4$ analogue (C18–C48 = 33.1 Å), and this led to an estimate of the tilt angle of 50 ± 2° for these homologues. The fact that the phase changes directly to either the nematic or isotropic liquid phase (without going through the smectic A phase) may be related to these large tilt angles.[11]

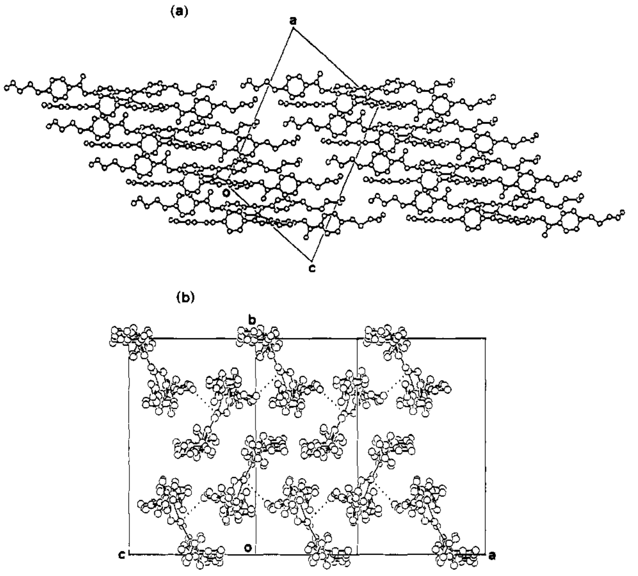


Figure 4. Ball-and-stick representation showing molecular packing projected onto (a) the (010) plane and (b) the (101) plane.

The X-ray diffraction patterns of the crystalline phases of these compounds at room temperature are quite complex, but those measured at elevated temperatures have a common feature that is reminiscent of the smectic C phase (Table IV). The pattern

---

(11) De Vries, A. *J. Phys. Paris* **1975**, *36*, C1-1–C1-11.

Table III. Selected Bond Lengths (Å) and Angles (deg) in Bis[4-((4-butoxybenzoyl)oxy)-*N*-(4-*n*-hexylphenyl)-salicylaldiminato]copper(II)

Cu–O1	1.190 (8)	N2–C49	1.42 (1)
Cu–O5	1.899 (8)	C1–C2	1.46 (2)
Cu–N1	2.02 (1)	C1–C6	1.46 (2)
Cu–N2	2.04 (1)	C1–C7	1.43 (2)
O1–C2	1.29 (2)	C2–C3	1.42 (2)
O2–C4	1.37 (2)	C3–C4	1.39 (2)
O2–C8	1.30 (2)	C4–C5	1.41 (2)
O3–C8	1.22 (2)	C5–C6	1.31 (2)
O4–C12	1.48 (2)	C22–C25	1.46 (2)
O4–C15	1.45 (3)	C31–C32	1.46 (2)
O5–C32	1.31 (1)	C31–C36	1.43 (2)
O6–C34	1.40 (2)	C31–C37	1.46 (2)
O6–C38	1.32 (2)	C32–C33	1.43 (2)
O7–C38	1.21 (2)	C33–C34	1.32 (2)
O8–C42	1.47 (2)	C34–C35	1.44 (2)
O8–C45	1.38 (4)	C35–C36	1.40 (2)
N1–C7	1.27 (2)	C38–C39	1.51 (2)
N1–C19	1.40 (1)	C52–C55	1.55 (2)
N2–C37	1.29 (2)		
O1–Cu–O5	159.9 (5)	O3–C8–C9	126 (2)
O1–Cu–N1	94.2 (4)	C8–C9–C10	124 (2)
O1–Cu–N2	88.5 (4)	C8–C9–C14	117 (2)
O5–Cu–N1	88.8 (4)	O4–C12–C11	115 (2)
O5–Cu–N2	91.9 (4)	O4–C12–C13	117 (2)
N1–Cu–N2	170.2 (5)	N1–C19–C20	120 (1)
Cu–O1–C2	130.5 (8)	N1–C19–C24	123 (1)
C4–O2–C8	117 (1)	C21–C22–C25	122 (2)
C12–O4–C15	125 (2)	C23–C22–C25	121 (2)
Cu–O5–C32	130.0 (8)	C32–C31–C36	119 (1)
C34–O6–C38	116 (1)	C32–C31–C37	124 (1)
C42–O8–C45	129 (2)	C36–C31–C37	117 (1)
Cu–N1–C7	119.8 (8)	O5–C32–C31	188 (1)
Cu–N1–C19	119.0 (8)	O5–C32–C33	122 (1)
C7–N1–C19	120 (1)	C31–C32–C33	120 (1)
Cu–N2–C37	121.0 (8)	C32–C33–C34	119 (1)
Cu–N2–C49	118.8 (8)	O6–C34–C33	118 (1)
C37–N2–C49	120 (1)	O6–C34–C35	117 (1)
C2–C1–C6	116 (1)	C33–C34–C35	125 (1)
C2–C1–C7	123 (1)	C34–C35–C36	119 (1)
C6–C1–C7	121 (1)	C31–C36–C35	119 (1)
O1–C2–C1	121 (1)	N2–C37–C31	128 (1)
O1–C2–C3	120 (1)	O6–C38–O7	121 (1)
C1–C2–C3	119 (1)	O6–C38–C39	109 (1)
C2–C3–C4	120 (1)	O7–C38–C39	129 (2)
O2–C4–C3	117 (1)	C38–C39–C40	123 (1)
O2–C4–C5	122 (1)	C38–C39–C44	113 (1)
C3–C4–C5	121 (1)	O8–C42–C41	118 (2)
C4–C5–C6	120 (1)	O8–C42–C43	121 (2)
C1–C6–C5	123 (1)	N2–C49–C50	117 (1)
N1–C7–C1	131 (1)	N2–C49–C54	118 (1)
O2–C8–O3	124 (1)	C51–C52–C55	117 (1)
O2–C8–C9	110 (1)	C53–C52–C55	122 (1)

Table IV. Layer Spacings (d/Å) for CuL_2 from X-ray Powder Diffraction

	crystalline phase				mesophase		
n	d_1	d_2	d_3	T, °C	d_l	d_t	T, °C
10	27.4	4.5	4.4	170	35.6[a]	4.9[a]	195
14	34.2	4.5	4.3	130	41.6	4.7[a]	190
16	33.7	4.4	4.3	130	42.9	4.9[a]	190
18	35.6	4.5	4.3	130	44.6	4.7[a]	190

[a] Peak of a diffuse reflection in the nematic phase for n = 10 and in the smectic C phase for n = 14, 16, and 18 homologues.

typically contains three intense peaks, the first of which (the largest spacing) must correspond to a longitudinal periodic array (d_1). Sharpness of the other two peaks, d_2 and d_3, indicates that the lateral arrangement remains in order. It should be noted, however, that a similar pattern is recognized with the n = 10 homologue, which is nematogenic. Therefore, how far the layer lattice persists seems to depend more on the size of the alkyl chains, and n = 11 is around the limit in the present case. Results with other systems having different molecular designs will be compared in forthcoming publication.

Table V. Crystallographic Data for Bis[4-((4-butoxybenzoyl)oxy)-*N*-(4-*n*-hexylphenyl)salicylaldiminato]-copper(II)

formula $C_{60}H_{68}N_2O_8Cu$	space group $P2_1/c$
fw 1008.76	T = 24 °C
a = 21.995 (8) Å	λ = 0.71073 Å
b = 18.016 (3) Å	ρ_{calcd} = 1.188 g cm^{-3}
c = 14.957 (4) Å	ρ_{obsd} = 1.23 g cm^{-3}
β = 107.94 (3)°	μ(Mo Kα) = 4.38 cm^{-1}
V = 5638 (3) Å^3	$R(F_o)$ = 0.091
Z = 4	$R_w(F_o)$ = 0.088

Experimental Section

Materials. All of the ligand homologues and their copper(II) complexes were prepared in similar manners. Typical synthetic procedures are described below.

***p*-Alkoxybenzoic Acids.** Literature methods[12,13] for alkylating *p*-hydroxybenzoic acid can be extremely tedious, particularly if the alkyl chain is tetradecyl or longer. Therefore we have developed a new facile, high-yield, one-pot synthesis. The conventional ethanol/water solvent and KOH as a base were replaced by dimethyl sulfoxide and potassium *tert*-butoxide, respectively, and the reaction was carried out under a nitrogen atmosphere. Desired product was obtained in 60–70% yield after a few hours of reaction time at room temperature and several recrystallizations of the crude material from acetic acid, ethanol, and then toluene; this solvent efficiently removed a major byproduct, alkyl *p*-alkoxybenzoate.

Ligands. Equimolar amounts of 2,4-dihydroxybenzaldehyde and *p*-phenetidine were condensed by refluxing for a couple of hours in benzene with a Dean-Stark trap attached to the vessel. Resulting 4-ethoxy-*N*-(2,4-dihydroxybenzylidene)aniline was isolated by filtration and subjected to esterification without purification. DCC esterification was patterned after the method of Hassner and Alexanian[14] using an appropriate benzoic acid. Resulting esters were recrystallized several times from 2:1 ethanol/chloroform until constant melting points were obtained. Yields: 40–70%. Anal. Found (calcd) for $C_{34}H_{43}NO_5$ (n = 12): C, 74.92 (74.83); H, 8.04 (7.94); N, 2.78 (2.57).

Copper(II) Complexes. Two millimoles of an appropriate ligand was dissolved in a 30–60-mL quantity of a hot methanol/benzene mixture and to this was added 30 mL of a hot methanolic solution of 1.1 mmol of cupric acetate dihydrate. The yellowish ligand solution turned brown, and the product gradually precipitated while the mixture was stirred for 1 h under mild heating conditions. The resulting solid was collected by filtration and washed extensively with methanol. Recrystallization from 1:1 ethanol/chloroform yielded brown thin flaky (fibrous for the n = 7 homologue as an exception) microcrystals. Yields: 50–70%. Anal. Found (calcd) for $C_{68}H_{84}N_2O_{10}Cu$ (n = 12): C, 70.82 (70.84); H, 7.35 (7.34); N, 2.61 (2.43).

Physical Measurements. Mesomorphic transition temperatures and enthalpy changes were determined by using Rigaku Thermoflex and Rigaku TAS100 differential scanning calorimeters. The heating or cooling rate was 5 K min^{-1}. X-ray powder diffraction measurements were made with a Rigaku RAD IVB automated diffractometer. A temperature-controlled sample holder used in this study has been described elsewhere.[15]

X-ray Crystal Structure Determination. The complex was prepared as described above except for the use of *p*-*n*-hexylaniline, which replaced *p*-phenetidine, and single crystals for X-ray analysis were obtained as brown platelets by slow evaporation of a 1:2 methanol/chloroform solution. Crystal data and relevant information are summarized in Table V. An automated Rigaku AFC-5R diffractometer with graphite-monochromatized Mo Kα radiation was used for data collection. Twenty-five reflections with 20° < 2θ < 27° were used to determine the lattice parameters. Intensity data were collected in the region 2° < 2θ < 60° in θ–2θ mode at a scan rate of 6° min^{-1} and width of $(1.2 + 0.5 \tan \theta)°$. Intensities of three standard reflections (hkl = $2\bar{1}6$, $3\bar{1}6$, 515) monitored every 100 measurements varied no more than 3%. A total of 2986 independent reflections with $|F_o| > 3\sigma(F_o)$ were used for structural analysis.

The structure was solved by first locating the copper atom from a Patterson map and then finding other atoms by repeating difference

---

(12) Ikeda, M.; Hatakeyama, T. *Mol. Cryst. Liq. Cryst.* **1976**, *33*, 201–212.

(13) Neubert, M. E.; Laskos, S. J., Jr.; Maurer, L. J.; Carlino, L. T.; Ferrato, J. P. *Mol. Cryst. Liq. Cryst.* **1978**, *44*, 197–210.

(14) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475–4478.

(15) Inoue, N.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 90.

Fourier synthesis. Block-diagonal least-squares refinement for all of the 71 non-hydrogen atoms with anisotropic temperature factors converged to $R = 0.105$. Addition of calculated hydrogen atoms with isotropic thermal parameters to the refinement gave the final R values, $R = 0.091$ and $R_w = 0.088$ (weighting scheme: $1/w = \sigma^2 + (0.015|F_o|)^2$). The UNICS III computer program system at the Institute for Molecular Science (IMS) was used throughout.

Acknowledgment. This work was supported by Grant-in Aid for Scientific Research No. 63740328 from the Ministry of Education, Science, and Culture of Japan. The assistance of Chikako Nakano of IMS and support by the IMS Joint Studies Program (1988–1989) for the X-ray crystal structure determination are gratefully acknowledged.

Supplementary Material Available: Tables SI and SII, listing atomic positional parameters and anisotropic temperature factors (3 pages); listings of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination, associé au CNRS (UA 416), Université Louis Pasteur, F-67070 Strasbourg Cédex, France

Stepwise Synthesis and Reactivity of $Ph_2PCH_2PPh_2$-Stabilized Mixed-Metal Clusters Containing Three or Four Different Metals

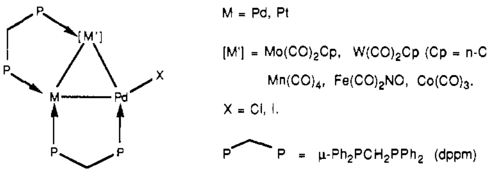
Pierre Braunstein,* Claude de Méric de Bellefon, and Michel Ries

Received August 2, 1989

The reactions of the carbonylmetalate anions $[m]^- = [Co(CO)_4]^-$, $[Fe(CO)_3NO]^-$, $[Mn(CO)_5]^-$, $[Mo(CO)_3Cp]^-$, and $[W(CO)_3Cp]^-$ with the trinuclear clusters $[PdMCoX(CO)_3(dppm)_2]$ (M = Pd, Pt; X = Cl, I; dppm = μ-$Ph_2PCH_2PPh_2$), $[Pd_2FeI(CO)_2NO(dppm)_2]$, $[Pd_2MnCl(CO)_4(dppm)_2]$, $[PdMMoCpCl(CO)_2(dppm)_2]$, and $[PdMWCpCl(CO)_2(dppm)_2]$ occur by substitution of the Pd-bound halide by the carbonylmetalate anions. As a result of Pd–m bond formation, they afford $[Pd_2Co_2(CO)_7(dppm)_2]$ (**3a**), $[Pd_2Mn_2(CO)_9(dppm)_2]$ (**10**), and new tetranuclear clusters $[PdMCoFe(CO)_6(NO)(dppm)_2]$ (M = Pd, **4a**; M = Pt, **4b**), $[PdMCoMn(CO)_8(dppm)_2]$ (M = Pd, **5a**; M = Pt, **5b**), $[PdPtCoMoCp(CO)_6(dppm)_2]$ (**6b**), $[Pd_2FeCo(CO)_6(NO)(dppm)_2]$ (**8**), $[PdMMoCoCp(CO)_6(dppm)_2]$ (M = Pd, **13a**; M = Pt, **13b**), and $[Pd_2WCoCp(CO)_6(dppm)_2]$ (**14**). These clusters possess a metalloligated triangular framework PdMM′m, with three (M = Pd) or four (M = Pt) different metals, the Pd, M, and M′ atoms constituting the triangle and m belonging to the metalloligand. The stepwise syntheses used in this work have led to the isolation of two pairs of positional isomers: $[PdPtCoMoCp(CO)_6(dppm)_2]$ (**6b**), $[PdPtMoCoCp(CO)_6(dppm)_2]$ (**13b**) and $[Pd_2CoFe(CO)_6(NO)(dppm)_2]$ (**4a**), $[Pd_2FeCo(CO)_6(NO)(dppm)_2]$ (**8**), respectively, which do not interconvert and present interesting spectroscopic (IR, NMR) features. The substitution of the halide of $[PdMCoX(CO)_3(dppm)_2]$ was shown to depend on the nature of (i) the halide (Cl vs I), (ii) the incoming carbonylmetalate anion $[m]^-$, and (iii) the solvent used for the reaction. The lability of the exocyclic Pd–m bond has been studied with respect to the nature of both the endocyclic metals (Pd, M, and M′) and the exocyclic metal m. These studies reveal that (i) the space available for coordination at the Pd center decreases in the order [M′] = $Co(CO)_3 \gg Mo(CO)_2Cp$, (ii) the Pd–m bond is less labile when M = Pd than when M = Pt, and (iii) the steric hindrance of the metalloligand increases in the sequence of m = $Co(CO)_4 \leq Fe(CO)_3NO \ll Mn(CO)_5 \ll Mo(CO)_3Cp \approx W(CO)_3Cp$.

Introduction

In previous papers, we have described the syntheses of molecular mixed-metal clusters whose structures are characterized by a triangular metal core of which two edges are bridged by a $Ph_2PCH_2PPh_2$ (dppm) ligand.[1-3] Among them, clusters containing a halide ligand are of particular interest as potential precursors of higher nuclearity clusters, e.g., by substituting the halide with various carbonylmetalate anions.



This would, in principle, allow the systematic access to tetranuclear metalloligated clusters, containing three (M = Pd) or four (M = Pt) different metal atoms, stabilized by dppm ligands. Other methods have led to systematic syntheses of multimetallic clusters.[4] We describe in this paper comparative studies on the reactivity of various carbonylmetalates toward such halogeno clusters as a function of the nature of their constitutive metals. A preliminary communication on part of this work has appeared.[3a]

Results

Syntheses. In order to facilitate comparisons between related molecules, these will be presented according to the nature of their triangular core PdMM′. For clarity, the metal carbonyl fragments are written in square brackets, e.g. [M′] and [m], and the corresponding metal atoms without.

1. Clusters with a PdMCo Core (M = Pd, Pt). The red-brown trinuclear cluster $[Pd_2CoCl(CO)_3(dppm)_2]$ (**1a**) reacts immediately with 1 equiv of $Na[Co(CO)_4]$ in solvents such as THF or Et_2O, to give quantitative yields of the deep green tetranuclear cluster $[Pd_2Co_2(CO)_7(dppm)_2]$ (**3a**) (eq 1) whose crystal structure has been determined previously.[1a,b] When the reaction of eq 1 is carried out with $K[Fe(CO)_3NO]$, $Na[Mn(CO)_5]$, or $Na[Mo(CO)_3Cp]$, it affords the new tetranuclear clusters $[PdMCoFe(CO)_6(NO)(dppm)_2]$ (**4a**, M = Pd; **4b**, M = Pt), $[PdMCoMn(CO)_8(dppm)_2]$ (**5a**, M = Pd; **5b**, M = Pt), or [PdMCoMoCp-

---

(1) (a) Braunstein, P.; Jud, J.-M.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 180. (b) Braunstein, P.; de Méric de Bellefon, C.; Ries, M.; Bouaoud, S.-E.; Grandjean, D.; Fischer, J. *Inorg. Chem.* **1988**, *27*, 1327. (c) Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *Inorg. Chem.* **1988**, *27*, 1338.

(2) (a) Braunstein, P.; Jud, J.-M.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1983**, 5. (b) Braunstein, P.; de Méric de Bellefon, C.; Ries, M.; Fischer, J. *Organometallics* **1988**, *7*, 332.

(3) (a) Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *J. Organomet. Chem.* **1984**, *262*, C14. (b) Braunstein, P.; Kervennal, J.; Richert, J.-L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 768. (c) Braunstein, P.; Ries, M.; de Méric de Bellefon, C.; Dusausoy, Y.; Mangeot, J.-P. *J. Organomet. Chem.* **1988**, *355*, 533.

(4) (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (c) Bruce, M. I. *J. Organomet. Chem. Libr.* **1985**, *17*, 399. (d) Bruce, M. I. *J. Organomet. Chem.* **1983**, *257*, 417. (e) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 40, p 763.

0020-1669/90/1329-1181$02.50/0 © 1990 American Chemical Society