(C=C). The mass spectra were taken on an MAT-212 mass spectrometer at 70 eV with injection at 180°C. The temperature of the ionization chamber was 250°C.

CONCLUSIONS

The effect of the nature of the acyl substituent on the direction and extent of fragmentation of triethylacylgermanes upon electron impact was elucidated.

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LIQUID CRYSTAL COMPLEXES OF COPPER WITH SCHIFF BASES

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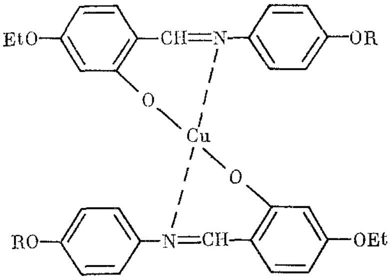
Most of the reported thermotropic liquid crystals are organic diamagnetic compounds [1]. However, communications have recently appeared on the preparation of liquid crystal metal complexes which display paramagnetic properties such as the complexes of copper with β-diketones [2] and phthalocyanine [3]. The preparation of mesomorphic derivatives of ferrocene has also been reported [4].

We have obtained paramagnetic liquid crystals which are complexes of copper with Schiff bases of the general type.*



where R = Me (Ib), Bu (IIb), C_5H_{11} (IIIb), C_6H_{13} (IVb), C_7H_{15} (Vb), and C_8H_{17} (VIb).

The starting Schiff bases (Ia)-(VIa) given in Table 1 also display liquid crystal properties.

The copper Schiff base complexes were synthesized by heating these bases in absolute ethanol with cupric acetate. These complexes form green-brown complexes and, with the exception of (Ib), have several melting points corresponding to phase transitions, which is a characteristic of liquid crystals. The temperatures and thermodynamic parameters of the phase transitions of the compounds studied found by polythermal microscopy and calorimetry are given in Table 1, which shows that the liquid crystal properties of these complexes are evident at temperatures higher than those for the starting ligands but in a rather broad range.

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*The first representatives of this class were reported in our previous work [5, 6].

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TABLE 1. Thermodynamic Parameters for the Phase Transitions of Schiff Bases (Ia)-(VIa) and Their Copper Complexes (Ib)-(VIb)

Compound	C–S(D) *			C (S)-N			I		
	T, °C	ΔH, kcal/mole	ΔS·10^{-3}, kcal/mole·°K	T, °C	ΔH, kcal/mole	ΔS·10^{-3}, kcal/mole·°K	T, °C	ΔH, kcal/mole	ΔS·10^{-3}, kcal/mole·°K
(Ia)	–	–	–	117	7,66	19,8	128	0,16	0,40
(Ib)	–	–	–	–	–	–	195,4	6,60	1,41
(IIa)	–	–	–	97,5	7,19	19,5	140,6	0,25	0,61
(IIb) †	165	–	–	–	–	–	170	–	–
(IIIa) ‡	–	–	–	91,0	7,55	20,7	129,4	0,22	0,54
(IIIb) ‡	155,2	5,22	12,2	–	–	–	174,1	1,37	3,06
(IVa) ‡	89,5	7,47	20,6	87,9	0,09	0,26	135,0	0,30	0,73
(IVb)	148,9	8,14	19,3	–	–	–	179,0	1,85	4,09
(Va)	90	10,08	27,9	98	0,06	0,16	131,4	0,24	0,60
(Vb)	135,6	5,59	13,7	–	–	–	170,8	1,39	3,08
(VIa) ‡	86	7,36	20,6	–	–	–	131,4	0,32	0,79
(VIb)	131,7	7,51	18,6	–	–	–	179,1	1,59	3,52

*Phases: C) crystalline; S) smectic; D) discoidal; N) nematic I) isotropic liquid.

†Polythermal microscopy data.

‡C^2-C polymorphic transitions: IIIa) 32.7°; IIIb) 136.3°; IVa) 30.5°; VIa) 79.1°C.

The mesophase texture in the complexes is similar to the "fingerprint" texture noted for the discoidal mesophase [7].

All the complexes obtained are paramagnetic compounds with spin $S = {}^1/_2$ corresponding to d^8 electron configuration of the central cupric ion. The magnetic resonance parameters ($g_0 = 2.114$, $A_0^{Cu} = 62 \cdot 10^{-4}$ cm^{-1}; $g_\parallel = 2{,}229$; $g_\perp = 2{,}056$; $A_\parallel^{Cu} = 162 \cdot 10^{-4}$ cm^{-1}; $A_\perp^{Cu} = 15 \cdot 10^{-4}$ cm^{-1}), measured using the ESR spectra of the complexes in diamagnetic solvents are typical for square planar complexes of copper with Schiff bases [8].

EXPERIMENTAL

The polythermal studies were carried out using a polarization microscopie equipped with a Boëtius heating table manufactured in the German Democratic Republic. The calorimetric measurements were performed on a Perkin-Elmer DSC-2 scanning microcalorimeter at scanning rates from 1 to 2.5 deg/min. The ESR spectra were obtained on an RE-1306 spectrometer.

Samples of the starting Schiff bases were obtained according to our previous work [9].

{(4-Ethoxy-2-hydroxy-N-4-pentyloxyphenyl)benzaldiminato} Cu(II) (IIIb). A sample of 0.12 g (0.55 mmole) cupric acetate in 50 ml absolute ethanol was added to 0.37 g (1.1 mmole) 4-ethoxy-2-hydroxybenzal-4'-amyloxyaniline (IIIa) in 50 ml hot absolute ethanol. The mixture was heated for 1 h. The brick red precipitate was filtered off, washed with water, and recrystallized from hexane and ethanol to yield 0.32 g (80%) (IIIb). Found, %: C 66.94; H 6.82; N 3.95; Cu 8.86. $C_{40}H_{48}O_6N_2Cu$. Calculated, %: C 67.04; H 6.70; N 3.91; Cu 8.94. IR spectrum (ν, cm^{-1}): 1608 (C=N); 1324 (C–O$_{Cu}$).

TABLE 2. Yields and Elemental Analysis Data for Copper Schiff Base Complexes

Compound	Yield, %	Found, %			Chemical formula	Calculated, %		
		C	H	N		C	H	N
(Ia)	86	63,48	5,33	4,70	$C_{32}H_{32}O_6N_2Cu$	63,57	5,30	4,64
(IIb)	84	66,15	6,42	4,23	$C_{38}H_{44}O_6N_2Cu$	66,28	6,39	4,07
(IIIb)	80	66,94	6,82	3,95	$C_{40}H_{48}O_6N_2Cu$	67,04	6,70	3,91
(IVb)	79	67,54	7,05	3,86	$C_{42}H_{52}O_6N_2Cu$	67,74	6,99	3,76
(Va)	82	68,31	7,36	3,71	$C_{44}H_{56}O_6N_2Cu$	68,39	7,25	3,63
(VIb)	80	68,85	7,51	4,52	$C_{46}H_{60}O_6N_2Cu$	68,91	7,49	3,49

Products (Ib), (IIb), (IVb), and (Vb) were obtained by analogy. Their yields and elemental analysis data are given in Table 2.

CONCLUSIONS

A synthesis is reported for paramagnetic copper complexes of Schiff bases possessing liquid crystal properties.

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MECHANISM FOR THE REACTION OF TRIETHYLGERMANE WITH DIALKYLMERCURY COMPOUNDS

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The reaction of triethylgermane with diethylmercury in the absence of oxygen leads to bis(triethylgermyl)mercury (I), which is the first representative of a new class of compounds with a bond between mercury and a group IVB element [1]. In subsequent work [2, 3], we showed that the hydride method for the synthesis of compounds with a metal—metal bond is a promising approach and, for example, this method gave high yields of the following compounds:

$$\begin{gathered} n\mathrm{Et_3MH} + \mathrm{Et}_n\mathrm{M'} \rightarrow n\mathrm{C_2H_6} + (\mathrm{Et_3M})_n\mathrm{M'} \\ \mathrm{M} = \mathrm{Si, Ge, Sn};\ \mathrm{M'} = \mathrm{Hg, Cd, Zn, Se, Te, Tl, Sb, Bi};\ n = 2, 3. \end{gathered} \tag{1}$$

Bychkov et al. [4] proposed that reaction (1) proceeds by electrophilic substitution [4].

We have shown that the reaction of Et_3GeH with Et_2Hg or t-Bu_2Hg is inhibited by benzophenone. In the case of such inhibition, an ESR signal is detected at 50°C for the $Ph_2\dot{C}OGeEt_3$ radical (II). The same stable radical was obtained in our study of the photochemical reaction of (I) with benzophenone in benzene. The replacement of Et_2Hg by t-Bu_2Hg in the reaction with Et_3GeH leads to a sharp increase in the reaction rate and the temperature for the onset of the reaction may be reduced from 120° to 20°C [1, 5]. We also established that the reaction of Et_2Hg with Et_3GeH is initiated by atmospheric oxygen even at 20°C. All these findings which are difficult to explain within the framework of the mechanism proposed by Bychkov et al. [4] are in good accord with a radical chain S_H2 reaction mechanism

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