Liquid crystalline heteronuclear complexes with a ferrocene-containing Schiff's base

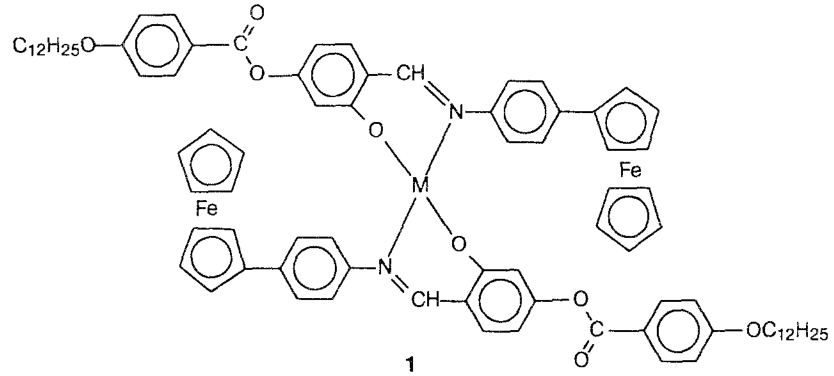
Yu. G. Galyametdinov,[a] *O. N. Kadkin,*[b]* *and A. V. Prosvirin*[a]

[a]*E. K. Zavoisky Kazan' Physical-Technological Institute, Russian Academy of Sciences,*
420029 Kazan', Tatarstan, Russian Federation.
Fax: +7 (843 2) 76 5075
[b]*Kazan' State Technological University,*
68 ul. K. Marksa, 420015 Kazan', Tatarstan, Russian Federation

A series of new heteronuclear complexes of a ferrocene-containing Schiff's base (LH) with Ni^{II}, Pd^{II}, $V^{IV}O$, and Fe^{III} as the central atoms has been obtained. PdL_2, VOL_2, FeL_2Cl, and $[FeL_2]_2O$ complexes manifest liquid-crystalline properties and NiL_2 is nonmesomorphic. The structures of the complexes synthesized have been established by magnetic measurements and IR and ESR spectroscopy. All of them except PdL_2 are paramagnetic. The antiferromagnetic exchange interactions have been observed in the Fe^{III} complexes. The correlation of liquid-crystalline properties with the geometry of the chelate centers is discussed.

Key words: ferrocene, Schiff's bases, coordination compounds; magnetism, paramagnetic liquid crystals.

Metal-containing liquid crystals attract the attention of investigators because they may be used as a basis for creating anisotropic media. High polarizability, low energetic levels of outer d-electrons, and the presence of the free d-orbitals of the transition metal atoms promote unusual electric, magnetic, and optical propreties[1,2] of molecules of metal-containing liquid crystals. Polynuclear and heteronuclear mesogenic complexes are of special interest, because an increase in the number of metal centers in one molecule and variation of their type make it more probable that additional physicochemical effects due to exchange processes between metal ions through the conjugated structure of the ligand, or directly, *i.e.*, in a cluster-type mode may occur.[3] Liquid crystals,[4] mesogenic derivatives,[5—9] and charge-transfer ferromagnetic complexes based on ferrocene derivatives[10] are well-known.



1

Recently, ferrocene-containing Schiff's bases and the first heteronuclear mesogenic Cu^{2+} complexes with nematic properties based on them[11,12] have been obtained. The present work opens a series of studies in the area of heteronuclear mesogenes based on coordination compounds with organometallic ligands, and deals with their synthesis, magnetic propreties, structure and its correlation with liquid-crystalline properties.

Compounds with an ML_2 type structure (M = Ni^{2+}, Cu^{2+}, Pd^{2+}, and VO^{2+}) (**1**) are obtained by the reaction of the corresponding ferrocene-containing Schiff's base LH with $M(OAc)_2$.

The reaction of LH with anhydrous $FeCl_3$ in dry benzene with subsequent addition of triethylamine affords the Fe^{3+} complex of the FeL_2Cl type (**2**).

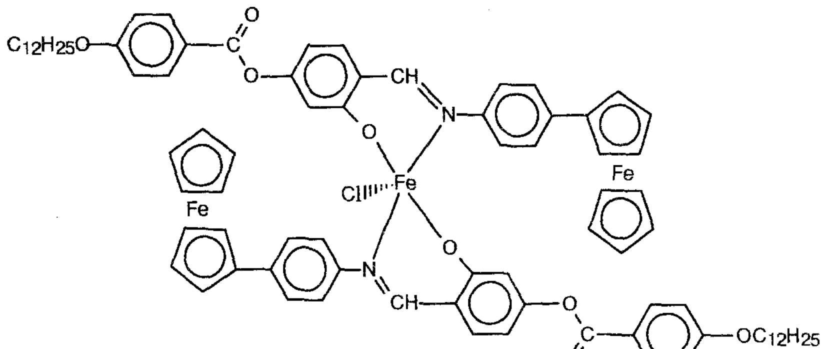
The μ-oxocomplex of Fe^{3+} with the general formula $[FeL_2]_2O$ (**3**) is obtained by passing moist air through a mixture of the same reagents.

$$2\,FeCl_3 + 4\,LH + 6\,Et_3N \xrightarrow{[H_2O]} [FeL_2]_2O + 6\,Et_3N\cdot HCl$$

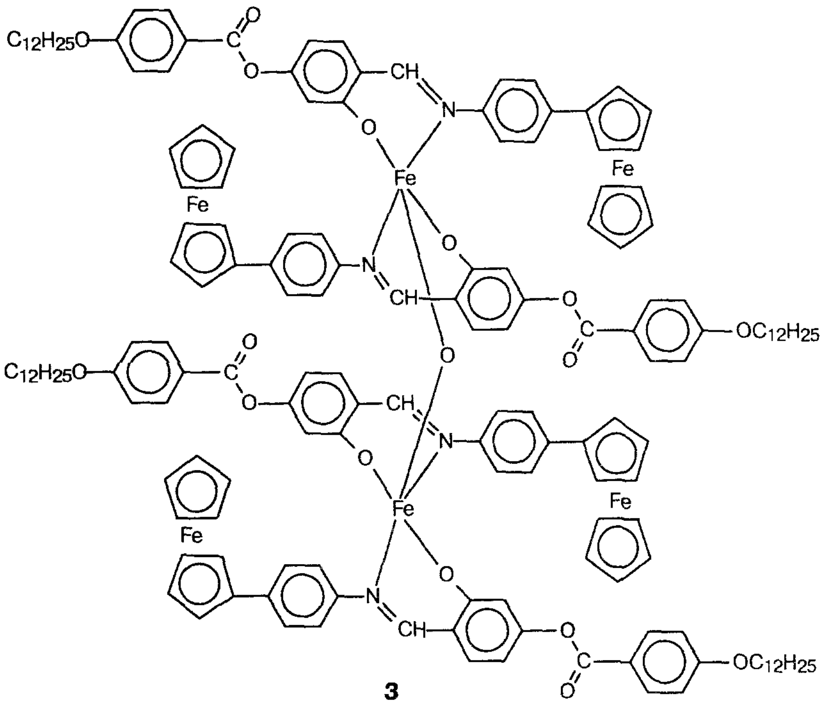
3

The composition and structure of the synthesized compounds **1—3** were confirmed by elemental analysis data, magnetic susceptibility measurements, and IR and ESR spectra.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 941—945, May, 1994.



2



3

Thermooptical studies using a polarization microscope demonstrated that PdL_2, VOL_2, $[FeL_2]_2O$ and CuL_2 possess a nematic phase, FeL_2Cl possesses smectogenic properties, and NiL_2 is nonmesomorphic (Table 1). The temperatures of the phase transitions increase in the order Cu^{2+}—VO^{2+}—Pd^{2+}, and VOL_2 has a monotropic mesophase. The same regularities have been observed for mesogenic complexes of these metals with other Schiff's bases.[2,14]

The IR and ESR spectroscopy data and magnetic susceptibility measurements of the complexes obtained (Table 2), and earlier investigations of mesogenic complexes of these metals with ferrocene-free Schiff's bases[2,12] allow us to draw some conclusions about the structure of their chelate centers and also to relate their mesogenic properties to the geometry of the coordination environment of the metal.

Table 1. Liquid-crystalline properties of compounds obtained and geometric parameters of their molecules

Compound	Transition points /°C		Calculated geometric parameters[a] of molecules		
	C—N[b]	N(C)—i[b]	l/Å	d/Å	l/d
LH	154	165	38	6	6.3
CuL_2	214	223	53	10	5.3
NiL_2	—	245(decomp.)	43	27	1.6
PdL_2	271	275	53	10	5.3
VOL_2	[240][c]	243	53	10	5.3
FeL_2Cl	195(S)[d]	205(i)	53	10	5.3
$[FeL_2]_2O$	155	232	58	14	4.2[e]

[a] Abbreviations: *l* — molecular length, *d* — molecular width, *l*/*d* — ahisotropy. [b] Mesophase types: C — crystalline, N — nematic, i — isotropic. [c] Monotropic phase transition. [d] Smectic phase. [e] Calculated for parallel orientation of ligands.

Table 2. Spectral data and magnetic properties of compounds synthesized

Compound	IR, ν/cm^{-1}				ESR spectral parameters		μ_{eff}/μ_B (300 K)
	C=O	C=N	Ph—O	M—O,M—N	g_0	A_0/Oe	
LH	1733	1623	1266	—	—	—	0
CuL_2	1732	1608	1308	538;520;450	2.11	64.5	2.46
NiL_2	1740	1612	1312	552;528;440	1.80	480	3.6
PdL_2	1722	1611	1308	624;552;438	—	—	0
VOL_2	1733	1612	1295	606;526;452	1.98	87.4	1.94
FeL_2Cl	1740	1608	1310	592;535; 440	2.10. 4.30	—	5.69
$[FeL_2]_2O$	1730	1610	1310	590;532;436	4.30	—	2.31

In the IR spectra of ligands, the bands of valent vibrations of the following bonds are present: C=O (1730 cm^{-1}), C=N and C=C (1620—1500 cm^{-1}), Ph—O (1260 cm^{-1}), and a broad band at *ca.* 2850 cm^{-1} which corresponds to valent vibrations of the OH group. When the complex is formed, the absorption band of the OH group disappears, and the bands of the valent vibrations of the C=N bond are shifted in 10—15 cm^{-1} to low-frequency region, and for valent vibrations of the Ph—O bond a *ca.* 40 cm^{-1} high-frequency shift is observed. Some new bands appear at 400—600 cm^{-1} that were assigned by us as vibrations of the M—O and M—N bonds. The frequencies of the valent vibrations of the C=O bond and the vibrations of the ferrocenyl group (492 and 478 cm^{-1}) are not changed by complex formation. Thus, the coordination of the metal ion involves the O atom of the hydroxyl group and the N atom of the azomethine group.

Measurements of the magnetic susceptibility (μ_{eff}) of the complexes obtained demonstrate that CuL_2, NiL_2, VOL_2, FeL_2Cl, and $[FeL_2]_2O$ are paramagnetic and PdL_2 is diamagnetic (see Table 2). For the Ni^{II} complex μ_{eff} = 3.78 μ_B, which corresponds to its high spin state due to the tetrahedral structure of its chelate center.[14] The singlet state of the diamagnetic Pd^{II} complex implies that it is planar, which is characteristic of palladium complexes with Schiff's bases.[14] The Fe^{III} complexes are high-spin complexes according to the measurements; the small value of μ_{eff} and the deviations from the Curie's law observed for $[FeL_2]_2O$ point to an exchange interaction between the magnetic nuclei in this compound, which is known to be normal for oxygen-bridged Fe^{III} complexes.[15]

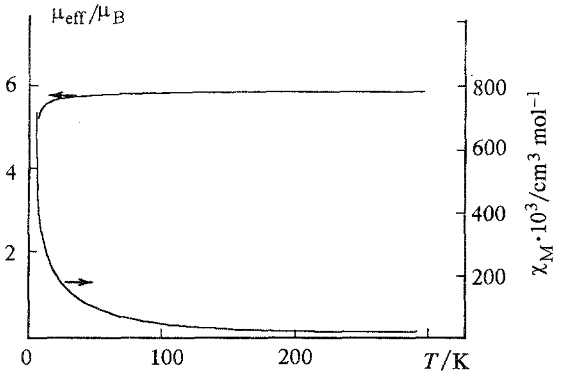
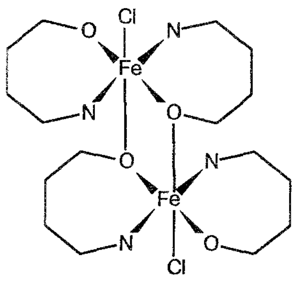


Fig. 1. Temperature dependence of molar magnetic susceptibility and magnetic moment of the FeL_2Cl (**2**) complex.

Comparison of the ESR spectral parameters of NiL_2, VOL_2, and previously synthesized CuL_2[11,12] (see Table 2) with those of the analogous complexes of these metals with Schiff's bases[2,13] demonstrates that the geometry of their coordination centers are identical. Hence, the chelate center of VOL_2 is a tetragonal pyramid with the oxygen atom at its apex, CuL_2 has a planar or quasi-planar structure, and the tetrahedral geometry of NiL_2 is confirmed.

The ESR spectral parameters of FeL_2Cl (see Table 2) allow one to conclude that two types of complexes exist in the sample. The ratio of integral intensities of the ESR lines indicates that the percentage of the complex with g = 2 in a polycrystalline sample is 91 %, and that of the complex with g = 4.3 is 9 %. We believe that the first type complex consists of molecular chains bonded through the Cl atoms by weak antiferromagnetic exchange. The fact that the value of the exchange integral J = −0.25 cm^{-1} calculated from the temperature dependence of magnetic susceptibility (Fig. 1) is significantly lower than that found for structure **A**, where the bonding into dimers occurs through the oxygen atoms of the Ar—O$_M$ group and J = −5 to 8 cm^{-1} (*cf.* Ref. 16), also attests to this fact. Binding into chains can also explain the smectic properties of the FeL_2Cl complex (in contrast to the other complexes), since it favors packing of the molecules in smectic layers. Apparently, the signal with g = 4.3 belongs to non-bonded molecules.



A

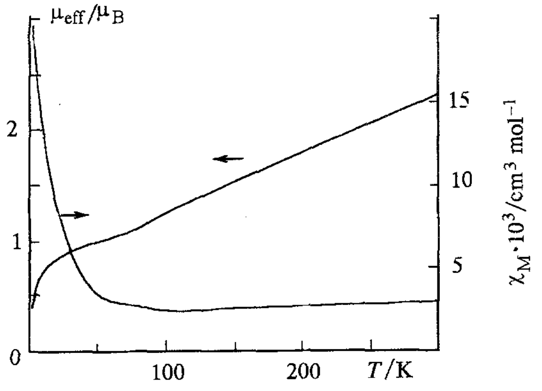


Fig. 2. Temperature dependence of molar magnetic susceptibility and magnetic moment of the $[FeL_2]_2O$ (3) complex.

The occurence of liquid-crystalline properties in the studied compounds is in accordance with the geometric and structural criteria of the mesomorphism of metallomesogenes.[2] In Table 1, the results of theoretical calculations of the geometric parameters of molecular anisotropy obtained by modeling their geometry using the method of atom-atomic potentials are presented. In planar or quasi-planar configurations of the chelate centers in molecules of CuL_2, PdL_2, VOL_2, FeL_2Cl and $[FeL_2]_2O$ complexes there is significant geometric anisotropy and simultaneously liquid-crystalline properties appear. In tetrahedral configuration of the chelate center, *e.g.*, in the NiL_2 complex, the l/d ratio is small and liquid-crystalline properties are absent.

Mathematical analysis of the temperature dependence of the magnetic susceptibility of $[FeL_2]_2O$ (Fig. 2) shows that it can be described by the Van Vlek equation for a dimer, $S_1 = S_2 = 5/2$, with the exchange parameter $J = -98\ cm^{-1}$. Using the J value and the known empirical correlations,[15] we approximate the Fe—O—Fe angle as 160—170°. Evidently, a value of the Fe—O—Fe angle close to 180° is especially favorable for the conformation of the molecule with parallel orientation of the ligands, which is necessary for the formation of the nematic phase present in the complex. In the case of smaller angles, steric hindrances for the realization of this conformation are possible, and the other conformation with crossed ligands is characterized by low anisometry.

Thus, for the first time polynuclear complexes of Fe^{III}, Pd^{II}, and V^{IV} with a ferrocene-containing ligand that possesses liquid-crystalline properties have been obtained. The μ-oxocomplex of Fe^{III} is the first example of liquid crystals that include six Fe atoms in different oxidation states. The synthesized complexes exibit liquid-crystalline properties with a planar structure of the chelate center, and the presence of the ferrocenyl fragment does not exert a significant effect. Comparison of the properties of the compounds obtained with those of the analogous complexes with alkoxy substituents (instead of ferrocenyl substituents)[17,18] shows that the ferrocenyl group is nematogenic and resembles the methoxyl group in this respect.

Experimental

The composition of the synthesized complexes was confirmed by elemental analysis data. Phase transition points and the types of mesophases were established with a polarization microscope equipped with Boetius-type heating stage. The IR spectra were recorded on a Specord 75 IR spectrophotometer in CCl_4 in KBr cells. Magnetic susceptibilities of the complexes were measured at 4.2—300 K using liquid helium for cooling in a 1.5 kOe magnetic field. The ESR studies were carried out at 4.2—300 K on RE-1306 and ER 200E-SRC spectrometers.

The ligand LH was obtained according to the published procedure.[12] Dry solvents were used for recrystallization.

Bis{4-ferrocenyl-*N*-[4-(4-dodecyloxybenzoyloxy)salicylidene]phenyliminato}nickel(II). A solution of LH (0.250 g, 0.36 mmol) and $Ni(OAc)_2$ (0.033 g, 0.18 mmol) in butanol was stirred for 15 min with heating. The yellow precipitate was filtered off, washed with ethanol, and recrystallized from butanol. The complex (0.24 g, 98 %) was obtained. Found (%): C, 70.23; H, 5.97; N, 2.01. $C_{84}H_{92}Fe_2N_2NiO_8$. Calculated (%): C, 70.65; H, 6.49; N, 1.96.

Bis{4-ferrocenyl-*N*-[4-(4-dodecyloxybenzoyloxy)salicylidene]phenyliminato}palladium(II). A mixture of LH (0.078 g, 0.1 mmol) and $Pd(OAc)_2$ (0.012 g, 0.05 mmol) was dissolved in dioxane. After addition of ethanol, a yellow precipitate was formed. Recrystallization from butanol gave 0.070 g (95 %) of the complex. Found (%): C, 69.17; H, 6.37; N, 1.85. $C_{84}H_{92}Fe_2N_2O_8Pd$. Calculated (%): C, 68.37; H, 6.28; N, 1.90.

Bis{4-ferrocenyl-*N*-[4-(4-dodecyloxybenzoyloxy)salicylidene]phenyliminato}oxovanadium(IV). Solutions of $VOSO_4$ (0.5 g, 3.05 mmol) and NaOAc (0.5 g, 6.1 mmol) in EtOH were mixed under Ar, the precipitate of Na_2SO_4 was filtered off. A solution of LH (4 g, 6 mmol) in butanol was added to the filtrate. The yellow precipitate was filtered off, washed with ethanol, and recrystallized from butanol. The complex (4.2 g, 96 %) was obtained. Found (%): C, 69.93; H, 6.38; N, 1.86. $C_{84}H_{92}Fe_2N_2O_9V$. Calculated (%): C, 70.24; H, 6.46; N, 1.95.

Bis{4-ferrocenyl-*N*-[4-(4-dodecyloxybenzoyloxy)salicylidene]phenyliminato}chloroiron(III) (2). Solutions of anhydrous $FeCl_3$ (0.0076 g, 0.047 mmol) and LH (0.064 g, 0.094 mmol) in dry benzene were mixed. Triethylamine (0.0095 g, 0.094 mmol) was added to the resulting black mixture, and the reaction mixture was refluxed for 15 min. The residue was filtered off, and after cooling of the filtrate and addition of hexane, a dark brown precipitate was formed. Recrystallization from a benzene—ethanol mixture gave 0.045 g (66 %) of the complex. Found (%): C, 70.23; H, 6.18; Cl, 2.67; N, 1.89. $C_{84}H_{92}ClFe_3N_2O_8$. Calculated (%): C, 69.07; H, 6.35; Cl, 2.43; N, 1.92.

μ-Oxo-bis(bis{4-ferrocenyl-*N*-[4-(4-dodecyloxybenzoyloxy)salicylidene]phenyliminato}iron(III)) (3). Solutions of $FeCl_3$ (0.02 g, 0.12 mmol) and LH (0.1 g, 0.24 mmol) in dry benzene were mixed. Triethylamine (0.09 g, 0.96 mmol) was added, and the mixture was refluxed for 15 min while moist air was passed through it. After removal of the precipitate of triethylamine hydrochloride, hexane was added to the chilled mixture, and the dark red precipitate was filtered off, dried *in vacuo* over P_2O_5, and recrystallized from a benzene—ethanol mixture. The complex (0.084 g, 78 %) was obtained.

Found (%): C, 70.55; H, 6.83; N, 1.73. $C_{168}H_{184}Fe_6N_4O_{17}$. Calculated (%): C, 70.40; H, 6.47; N, 1.95.

References

1. C. Piechocki and J. Simon, *Nov. J. Chim.*, 1985, **9,** 159.
2. I. V. Ovchinnikov, I. G. Bikchantaev, and Yu. G. Galyametdinov, *Izv. Akad Nauk SSSR, Ser. Fiz.*, 1989, **53,** 1870 [*Bull. Acad. Sci. USSR, Ser. Phys.*, 1989, **53** (Engl. Transl.)].
3. V. A. Kogan, O. A. Zelentsov, A. S. Osipov, and A. S. Burlov, *Usp. Khim.*, 1979, **48**, 1208 [*Russ. Chem. Rev.*, 1979, **48**, 645 (Engl. Transl.)].
4. J. Malthete and J. Billard, *Mol. Cryst. Liq. Cryst.*, 1976, **34,** 117.
5. J. C. Bhatt, B. M. Fung, K. M. Nicholas, and C.-D. Poon, *J. Chem. Soc., Chem. Commun.*, 1988, 1439.
6. M. A. Khan, J. C. Bhatt, B. M. Fung, K. M. Nicholas, and E. Wachtel, *Liq. Cryst.*, 1989, **5**, 285.
7. P. Singh, M. D. Raush, and R. W. Lenz, *Liq. Cryst.*, 1991, **9**, 19.
8. R. Deschenaux and J.-L. Marendaz, *J. Chem. Soc., Chem. Commun.*, 1991, 909.
9. N. J. Thompson, J. W. Goodby, and K. J. Toyne, *Liq. Cryst.*, 1993, **13**, 381.
10. J. S. Miller, A. J. Epstein, and W. A. Reiff, *Chem. Rev.*, 1988, **88**, 201.
11. Yu. G. Galyametdinov, O. N. Kadkin, and I. V. Ovchinnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2462 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2235 (Engl. Transl.)].
12. Yu. G. Galyametdinov, O. N. Kadkin, and I. V. Ovchinnikov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 402 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 316 (Engl. Transl.)]
13. Yu. G. Galyametdinov, I. G. Bikchantaev, and I. V. Ovchinnikov, *Zh. Obshch. Khim.*, 1988, **58**, 1326 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
14. G. V. Panova, N. K. Vikulova, and V. M. Potapov, *Usp. Khim.*, 1980, **49**, 1234 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].
15. M. Atanasov, V. S. Angelov, and J. Mayer, *J. Mol. Struct. Teochem.*, 1989, **187,** 23.
16. M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1973, **9**, 311.
17. J. L. Serrano, P. Romero, M. Marcos, and P. J. Alonso, *J. Chem. Soc., Chem. Commun.*, 1990, 859.
18. M. Marcos, P. Romero, J. L. Serrano, J. Barbera, and A. M. Levelut, *Liq. Cryst.*, 1990, **7**, 251.

Received November 29, 1993;
in revised form January 14, 1994