ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2174–2179. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © O.A. Turanova, G.I. Ivanova, L.G. Gafiyatullin, T.A. Ivanova, L.V. Mingalieva, A.N. Turanov, I.V. Ovchinnikov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 11, pp. 1878–1883.

Preparation and Liquid-Crystalline Properties of Mono- and Binuclear Complexes of Fe(III) with Pentadentate Schiff's Base

O. A. Turanova, G. I. Ivanova, L. G. Gafiyatullin, T. A. Ivanova, L. V. Mingalieva, A. N. Turanov, and I. V. Ovchinnikov

Kazan Physical Technical Institute, Kazan Scientific Center, Russian Academy of Sciences, ul. Sibirskii Trakt 10/7, Kazan, Tatarstan, 420029 Russia
e-mail: lightur@mail.ru

Received July 15, 2014

Abstract—Liquid-crystalline mono-and binuclear complexes of Fe(III) based on pentadentate Schiff's base, *N,N'*-bis(2-hydroxy-4-octadecyloxybenzyliden)-1,7-diamino-4-azaheptane, have been prepared for the first time. The effects of counterions of the binuclear complexes and of the monodentate ligand in the mononuclear complexes on formation of the mesophase as well as phase transitions temperatures and the range of the mesophase existence have been demonstrated. EPR studies have revealed the possibility of spin-crossover properties of the complexes.

Keywords: coordination compound, liquid crystal, synthesis
DOI: 10.1134/S1070363214110218

The special property of metallomesogens (coordination liquid crystals) to respond on weak external influence (magnetic, electric, temperature, optical, etc.) has significantly broadened the possibilities of their studies and extended their practical applications. Metallomesogens are used as templates of mesoporous materials [1–3], in production of monomolecular magnets [4], and in development of biomembranes, drug delivery systems and nanocomposites [5]. Furthermore, they are used for creation of information display systems [6–8], components of optical glass with defined properties [9], and as stationary phases in gas chromatography [10, 11].

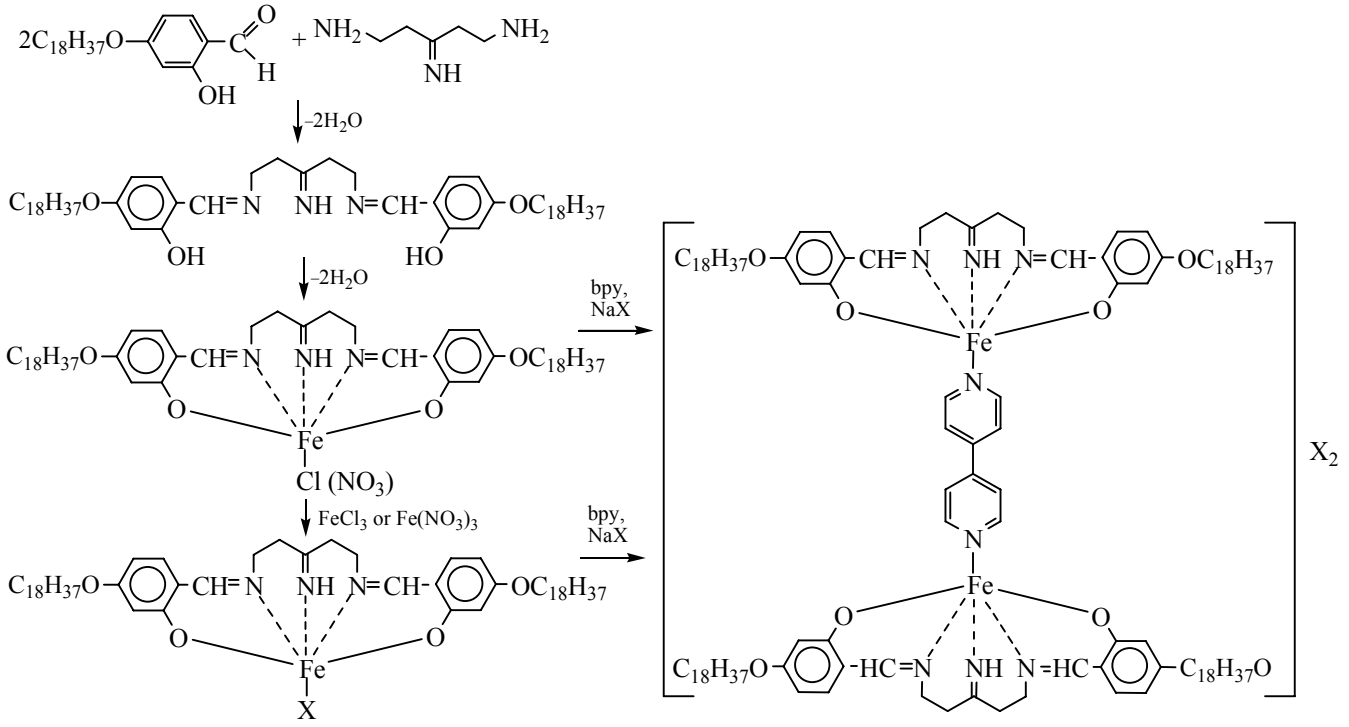
A key problem in development of metallomesogens is the connection between their molecular structure, supramolecular organization, and physico-chemical properties. Mesomorphism of coordination compounds is affected by nature of the ligand that defines the complex geometry as well as by electronic structure of the metal atom, conformation of the coordination core, and the supramolecular structure. Change of the above-listed parameters influences the liquid-crystal-line properties of coordination compounds.

The Schiff's bases and structurally similar compounds have been the most widely used ligands in modern coordination chemistry. The long history of their application is due to vast diversity of the substituents in the azomethine ligands and, hence, a wide range of physico-chemical properties of the produced mono- and polynuclear coordination compounds [8, 12]. The thermotropic liquid-crystalline properties allow changing the supramolecular structure of the complexes by heating or cooling. In view of the above, such materials are promising molecular magnets with predefined properties to be used in the information recording devices.

Earlier, the variation of substituent nature in the ligands, nature of the bridging moieties, and the counter-ions has afforded a series of polynuclear complexes of Fe(III) with pentadentate Schiff's base studied in [13–21]. Many of the complexes revealed the spin-crossover properties [22]. Liquid-crystalline mono- and binuclear complexes of Fe(III) with a pentadentate have not been described in the literature so far.

In this work we prepared and studied mono- and binuclear complexes of Fe(III) with the pentadentate Schiff's base of the N_3O_2-donor type, revealing the liquid-crystalline properties; we further considered the influence of anions in the binuclear complexes and of

Scheme 1.



the monodentate ligand nature in the mononuclear complexes of their mesomorphism; and demonstrated the spin-crossover properties of the prepared compounds.

The binuclear complexes were prepared using the Scheme 1.

In order to prepare the compounds with potential mesogenic properties, long-chain alkoxy groups were introduced in the ligands. The pentadentate ligand H_2L was prepared via condensation of 4-octadecyloxy-substituted salicylic aldehyde with aliphatic diamine (2 : 1) in ethanol. The presence of long-chain substituent ($C_{18}H_{37}O$) in the *para*-position with respect to the C=N bond did not lead to liquid-crystalline properties of the ligands. That was due to high flexibility of the molecular skeleton of the Schiff's base.

The mononuclear precursors were prepared via complex formation of the pentadentate Schiff's base with Fe(III) chloride and nitrate. Complex compounds of Fe(III) with other monodentate ligands [FeLX] were prepared via interaction of the precursors with the corresponding sodium salts NaX (X = SCN, PF_6, BPh_4, SbF_6, or BF_4). Phase transitions temperatures of the compounds prepared for the first time are given in the table; it is to be seen that the nature of monodentate ligands noticeable influenced the temperature parameters of the mesophase.

A special feature of the precursors, complexes of Fe(III) with the pentadentate Schiff's base, is that the only coordination site was labile and thus could be attacked by a bridging ligand to form the binuclear coordination compounds. 4,4'-bipyridine (bpy) was used as a bridging ligand. The coordination compounds were prepared be the general method modified for the long-chain compounds, via addition of equivalent amount of the bridging ligand in ethanol to a solution of precursor in the chloroform–ethanol 1 : 4 mixture containing a small excess of the NaX salt. The formed precipitate was filtered off, washed with ethanol and diethyl ether, and dried in vacuum. Structure and composition of the prepared compounds were elucidated taking advantage of elemental analysis, IR, and UV spectroscopy.

IR spectra revealed slight changes of the bands assigned to the N–H and C=N bonds. In particular, a strong band of C=N stretching was found at 1628 cm^{-1} in the ligand spectrum; it was shifted to 1606–1620 cm^{-1} upon the complex formation, pointing at coordination bonding of Fe(III) ion and the azomethine group. Spectra of all the complexes demonstrated narrower bands of N–H stretching, shifted to longer wavelength by 30–40 cm^{-1} as compared with the ligand spectrum. Disappearance of the O–H stretching

Phase transition temperatures of the ligand and the coordination compounds

Compound	Phase transition temperatures,[a] °C	ΔT, °C
H_2L	86.6	–
[FeLCl]	Cr 156 S 186 I	30
[FeL(NO_3)]	Cr 104 S 169 I	65
[FeL(SCN)]	Cr 155 S 191 I	36
[FeL(PF_6)]	Cr 171 S 210 I	39
[FeL(BPh_4)]	Cr 149 S 216 I	67
[FeL(SbF_6)]	Cr 125 S 169 I	44
[FeL(BF_4)]	Cr 159 S 216 I	57
[LFe(bpy)FeL](NO_3)$_2$	Cr 71 S 102 I	31
[LFe(bpy)FeL](SCN)$_2$	Cr 152 S 165 I	13
[LFe(bpy)FeL](PF_6)$_2$	Cr 144 S 181 I	37
[LFe(bpy)FeL](BPh_4)$_2$	Cr 90 I	–
[LFe(bpy)FeL](SbF_6)$_2$	Cr 106 S 137 I	31
[LFe(bpy)FeL](BF_4)$_2$	Cr 140 S 192 I	52

[a] Cr, crystalline phase; S, smectic mesophase; I, isotropic phase; ΔT, temperature range of mesophase existence.

band in the complexes spectra (3605 and 3686 cm^{-1} in the ligand) further confirmed the complex formation.

UV spectrum of the ligand solution in chloroform contained strong absorbance bands at λ_{max} 275, 307, and 386 nm. The band of charge transfer from the ligand to the metal was observed at 502–525 nm (mononuclear complexes) or at 525–550 nm (binuclear complexes), being indicative of stability of the formed coordination compounds in their solution [23].

Increasing of the molecule rigidity upon the complex formation as compared to the ligand resulted in the liquid-crystalline properties of the complexes (see table). Those properties were studied by multi-temperature polarization microscopy. The counter-ion nature noticeably affected the presence of the liquid-crystalline properties and on the temperature range of the mesophase existence (if any). The molecule "width" was significantly increased upon formation of the binuclear complexes, its "length" remaining the same. The suppression of geometrical anisotropy (the length to width ratio) of the binuclear complexes by more than two times as compared to the case of mononuclear complexes decreased the anisotropy of intermolecular interactions, the latter being an important factor of the liquid-crystalline state stability. That reason explained the less prominent ability of the binuclear complexes to form the liquid-crystalline phases. In the presence of a bulky counter-ion BPh_4 (323 $Å^3$ [24]), the liquid-crystalline properties of the binuclear complex vanished due to weaker intermolecular interaction. In the cases of mononuclear complexes, the nature and size of the monodentate ligand affected the mesophase stability range as well as the phase transitions temperatures. In the binuclear complexes, the range of the mesophase existence was narrowed.

Study of the magnetic properties of the prepared liquid-crystalline compounds will be reported separately. As an example confirming the spin-crossover properties (S 1/2–5/2), the illustrations demonstrate data on the temperature-dependence EPR spectra (Fig. 1) and integral intensity of the low-field (high-spin S 5/2) component with *g*-factor of 4.2 (Fig. 2) in the case of the [LFe(bpy)FeL](BPh_4)$_2$ complex. The incomplete spin transition was observed at 300–130 K. Indeed, in the absence of spin transition the integral intensity of the high-spin component should have followed the Curie's law, increasing with temperature. The observed opposite trend evidenced about the decreasing number of high-spin complexes upon cooling [25].

To conclude, this work was the first to demonstrate the preparation of liquid-crystalline mono- and binuclear complexes of Fe(III) with the pentadentate Schiff's base of the N_3O_2-donor type. The suggested strategy allows changing the phase transition temperatures and the temperature-rage of mesophase existence by variation of the counter-ion nature in the binuclear complexes and of the monodentate nature in the mononuclear complexes. That will aid in developing of the materials organized at the supramolecular level, bearing peculiar magnetic and optical properties.

EXPERIMENTAL

Mesophases texture and the phase transitions temperatures were determined using a Boëtius polarization microscope equipped with temperature control unit (±0.1°C). IR spectra of the ligands and their complexes with Fe(III) were recorded at 4000–400 cm^{-1} in Vaseline oil at room temperature using a Bruker-JFS66V/S spectrometer. UV spectra of the

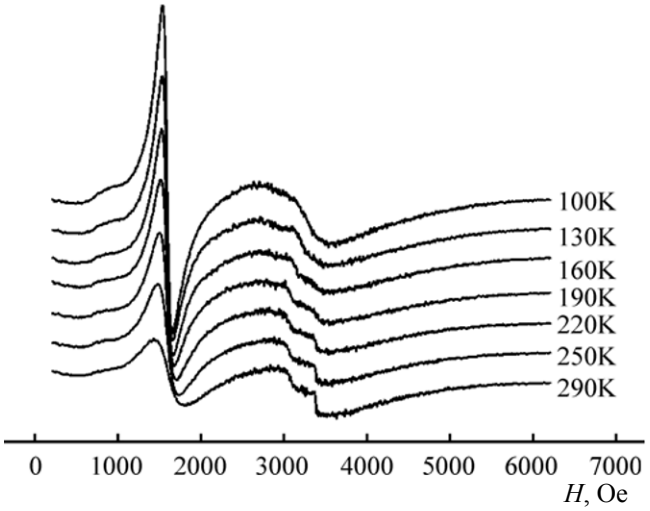


Fig. 1. EPR spectra of compound $[(L)Fe(bpy)Fe(L)](BPh_4)_2$. (ν = 9.43 GHz).

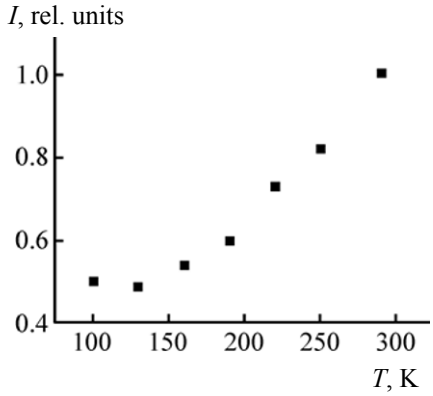


Fig. 2. Integral intensity of the high-spin centers signals in $[(L)Fe(bpy)Fe(L)](BPh_4)_2$ as function of temperature.

solutions in chloroform [$c = (1–5) \times 10^{-3}$ mol/L] were recorded at room temperature using a Varian Cary 100 spectrophotometer. EPR spectra were recorded using a Bruker EMXplus spectrometer in the X-range at 100–300 K. All the used compounds and solvents were purified by recrystallization or distillation, their final physical properties coincided with the corresponding reference data.

***N,N'*-Bis(2-hydroxy-4-octadecyloxybenzyliden)-1,7-diamino-4-azaheptane (H_2L).** 1,7-Diamino-4-azaheptane (0.064 g, 0.49 mmol) was added dropwise upon stirring to a solution of 4-octadecyloxy-2-hydroxybenzaldehyde (0.38 g, 0.98 mmol) in ethanol, and the mixture was heated during 5 min at a water bath upon stirring. The formed grey-green precipitate was twice recrystallized from ethanol. Yield 88%, mp 88°C. IR spectrum, ν, cm^{-1}: 3645, 3605 (O–H), 3437 (N–H), 1628 (CH=N), 1574, 1469 (Ar), 722 [$(CH_2)_nO$]. Found, %: C 76.80; H 11.00; N 4.89. $C_{56}H_{97}N_3O_4$. Calculated, %: C 76.80; H 11.09; N 4.80.

Complex [FeLCl]. The ligand (0.20 g, 0.23 mmol) solution in anhydrous benzene was slowly added upon stirring to a solution of anhydrous iron(III) chloride (0.037 g, 0.23 mmol) in the same solvent. The reaction mixture was stirred during 20 min; then 0.046 g (0.46 mmol) of freshly distilled triethylamine was added dropwise, and the mixture was incubated at 80°C during 15 min. The formed triethylammonium hydrochloride was filtered off the hot mixture. The filtrate was evaporated to 1/3 of the volume, and hexane was added. Violet precipitate formed upon cooling was filtered off, washed with hexane, and dried in vacuum. Yield 75%. IR spectrum, ν, cm^{-1}: 3477 (N–H), 1606 (CH=N), 1532, 1464 (Ar), 722 [$(CH_2)_nO$], 425 (Fe–N). found, %: C 69.28; H 10.00; N 4.10. $C_{56}H_{95}ClFeN_3O_4$. Calculated, %: C 69.67; H 9.85; N 4.35.

Complex [FeLNO$_3$] was prepared similarly using $Fe(NO_3)\cdot 9H_2O$ instead of anhydrous $FeCl_3$. Yield 80%, dark-red powder. Calculated, %: C 67.80; H 9.59; N 5.65. $C_{56}H_{95}FeN_4O_7$. Found, %: C 67.25; H 9.61; N 5.60.

Mononuclear complex [FeLX] (X = SCN, PF_6, BPh_4, SbF_6, BF_4). Excess of the corresponding salt (KSCN, $NaBPh_4$, $NaSbF_6$, or $AgBF_4$ in ethanol or KPF_6 in the minimal amount of water) was added to a suspension of the precursor in ethanol. The mixture was heated at a water bath at 60°C during 15 min upon stirring. The precipitate formed upon cooling was filtered off, washed with cold ethanol, hexane, or diethyl ether, and dried in vacuum. In the case of $AgBF_4$, hot solution should have been filtered of the formed AgCl. The precipitate formed upon the filtrate cooling was washed with cold ethanol and dried in vacuum.

[FeL(SCN)]. Yield 62%, dark-red powder. Found, %: C 69.38; H 9.58; N 5.60. $C_{57}H_{95}FeN_4O_4S$. Calculated, %: C 69.30; H 9.63; N 5.67.

[FeL(PF_6)]. Yield 65%, dark-red powder. Found, %: C 62.32; H 8.91; N 3.93. $C_{56}H_{95}F_6FeN_3O_4P$. Calculated, %: C 62.57; H 8.85; N 3.91.

[FeL(BPh_4)]. Yield 70%, black powder. Found, %: C 76.48; H 9.18; N 3.33. $C_{80}H_{115}BFeN_3O_4$. Calculated, %: C 76.92; H 9.21; N 3.37.

[FeL(SbF_6)]. Yield 63%, dark-red powder. Found, %: C 58.00; H 8.19; N 3.35. $C_{56}H_{95}F_6FeN_3O_4Sb$. Calculated, %: C 55.68; H 8.15; N 3.61.

[FeL(BF_4)]. Yield 70%, dark-red powder. Found, %: C 65.98; H 9.43; N 4.08. $C_{56}H_{95}BF_4FeN_3O_4$. Calculated, %: C 66.14; H 9.35; N 4.13.

Binuclear complex [LFe(bpy)FeL](BPh_4)$_2$. A solution of 4,4'-bipyridine (0.008 g, 0.05 mmol) in ethanol was added upon stirring to a suspension of the precursor [FeLCl] (0.1 g, 0.1 mmol) in ethanol. The mixture was heated at 60°C during 10 min and filtered. A small excess of sodium tetraphenylborate (0.042 g, 0.125 mmol) in ethanol was added to the filtrate. Depending on the counter-ion nature, crystals were formed immediately or within several hours. They were filtered off, washed with hexane, and dried in vacuum. Yield 55%, black powder. IR spectrum, ν, cm^{-1}: 3485 (N–H), 1603 (CH=N), 1530, 1461 (Ar), 1146, 891, 742, 628, 612 (BPh_4); 723 [$(CH_2)_nO$], 426 (Fe–N). Found, %: C 77.02; H 8.89; N 4.25. $C_{170}H_{238}B_2Fe_2N_8O_8$. Calculated, %: C 76.92; H 8.97; N 4.22.

The other binuclear complexes described in this work were prepared similarly using the corresponding inorganic salts.

[LFe(bpy)FeL](NO_3)$_2$. Yield 52%, dark-red powder. Found, %: C 68.08; H 9.28; N 6.48. $C_{122}H_{198}Fe_2N_{10}O_{14}$. Calculated, %: C 68.48; H 9.26; N 6.55.

[LFe(bpy)FeL](SCN)$_2$. Yield 50%, dark-red powder. Found, %: C 65.89; H 7.84; N 7.68. $C_{124}H_{198}Fe_2N_{12}O_{14}S_2$. Calculated, %: C 66.02; H 8.78; N 7.45.

[LFe(bpy)FeL](PF_6)$_2$. Yield 44%, dark-red powder. Found, %: C 63.77; H 8.44; N 4.95. $C_{122}H_{198}F_{12}Fe_2N_8O_8P_2$. Calculated, %: C 63.54; H 8.59; N 4.86.

[LFe(bpy)FeL](SbF_6)$_2$. Yield 49%, red powder. Found, %: C 58.99; H 7.72; N 4.33. $C_{122}H_{198}F_{12}$·$Fe_2N_8O_8Sb_2$. Calculated, %: C 58.89; H 7.96; N 4.51.

[LFe(bpy)FeL](BF_4)$_2$. Yield 42%, dark-red powder. Found, %: C 66.54; H 9.10; N 5.21. $C_{122}H_{198}B_2F_8Fe_2N_8O_8$. Calculated, %: C 66.91; H 9.05; N 5.12.

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (project no. 12-03-97090-r_povolzh'e_a).

REFERENCES

1. Gimenez R., Lydon, D.P., and Serrano, J.L., *Current Opinion in Solid State and Materials Science*, 2002, vol. 6, no. 6, p. 527.
2. Zhao, D., Huo, Q., Feng, J., Chmelka, B.F., and Stucky, G.D., *J. Am. Chem. Soc*., 1998, vol. 120, p. 6024. DOI: 10.1021/ja974025i.
3. Polarz, S., Regenspurger, R., and Hartmann, J., *Angew. Chem. Int. Ed*., 2007, vol. 46, p. 2426. DOI: 10.1002/anie.200602262.
4. Terazzi, E., Jensen, T.B., Donnio, B., Buchwalder, K., Bourgogne, C., Rogez, G., Heinrich, B., Gallani, J., and Piguet, C., *Dalton Trans*., 2011, vol. 40, p. 12028. DOI: 10.1039/C1DT10908A.
5. Oriol, L. and Serrano, J.L., *Angew. Chem. Int. Ed*., 2005, vol. 44, p. 6618. DOI: 10.1002/anie.200501880.
6. Giroud-Goodwing, A.M. and Maitlis, P.M., *Angew. Chem. Int. Ed*., 1991, vol. 30, p. 375. DOI: 10.1002/anie.199103751.
7. Tantrawong, S. and Styring, P., *Liquid Crystals*, 1997, vol. 22, no. 1, p. 17. DOI: 10.1080/026782997209621.
8. Garnovskii, A.D. and Vasil'chenko, I.S., *Russ. Chem. Rev*., 2002, vol. 71, p. 943. DOI: 10.1070/RC2002v071n11ABEH000759.
9. Hadson, S.A. and Maitlis, P.M., *Chem. Rev*., 1993, vol. 93, p. 861. DOI: 10.1021/cr00019a002.
10. Binnemans, K. and Moors, D., *J. Mater. Chem*., 2002, vol. 12, p. 3374. DOI: 10.1039/B206810A.
11. Chen, J.-L. and Liu, C.-Y., *J. Chromatog. (A)*, 2007, vol. 1161, nos. 1–2, p. 269. DOI: 10.1016/j.chroma.2007.05.084.
12. Garnovskii, A.D., *Koord. Khim.*, 1993, vol. 191, no. 5, p. 394.
13. Boca, R., Fukuda, Y., Gembicky, M., Hezchel, R., Jarosciak, R., Linert, W., Renz, F., and Yuzurihara, J., *Chem. Phys. Lett*., 2000, vol. 325, p. 411. DOI: 10.1016/S0009-2614(00)00701-6.
14. Ohta, S., Yoshimura, C., Matsumoto, N., Okawa, H., and Ohyoshi, A., *Bull. Chem. Soc. Japan*, 1986, vol. 59, p. 155. DOI: org/10.1246/bcsj.59.155.
15. Hayami, S., Inoue, K., and Maeda, Y., *Mol. Cryst. Liq. Cryst*., 1999, vol. 335, p. 573. DOI: 10.1080/10587259908028898.
16. Hayami, S., Inoue, K., Osaki, S., and Maeda, Y., *Chem. Lett*., 1998, vol. 27, no. 10, p. 987. DOI: org/10.1246/cl.1998.987.
17. Kitashima, R., Imatomi, S., Yamada, M., Matsumoto, N., and Maeda, Y., *Chem. Lett*., 2005, vol. 34, no. 10, p. 1388. DOI: org/10.1246/cl.2005.1388.
18. Nihei, M., Shiga, T., Maeda, Y., and Oshio, H., *Coord. Chem. Rev*., 2007, vol. 251, p. 2606. DOI: 10.1016/j.ccr.2007.08.007.

19. Visinescu, D., Pascu, G.I., Andruh, M., Magull, J., and Roesky, H.W., *Inorg. Chim. Acta*, 2002, vol. 340, p. 201. DOI: 10.1016/S0020-1693(02)01043-5.
20. Zein, S. and Borshch, S.A., *J. Am. Chem. Soc*., 2005, vol. 127, p. 16197. DOI: 10.1021/ja054282k.
21. Hayami, S., Hosokoshi, Y., Inoue, K., Einaga, Y., Sato, O., and Maeda, Y., *Bull. Chem. Soc. Japan*, 2001, vol. 74, p. 2361. DOI: org/10.1246/bcsj.74.2361.
22. *Spin Crossover in Transition Metal Compounds,* Gutlich, P. and Goodwin, H.A. Berlin: Springer-Verlag, 2004, vol. 2, p. 261. DOI: 10.1002/(SICI)1099-0682 (199912)1999:12<2117::AID-EJIC2117>3.0.CO;2-P.
23. Sour, A., Boillot, M-L., Riviere, E., and Lesot, P., *Eur. J. Inorg. Chem*., 1999, no. 12, p. 2117. DOI: 10.1002/ (SICI)1099-0682(199912)1999:12<2117::AID-EJIC2117> 3.0.CO;2-P.
24. Mingos, D.M.P. and Rohl, A.L., *Inorg. Chem*., 1991, vol. 30, no. 19, p. 3769. DOI: 10.1021/ic00019a039.
25. Ovchinnikov, I.V., Ivanova, T.A., Turanova, O.A., Ivanova, G.I., Mingalieva, L.V., and Sukhanov, A.A., *Russ. J. Coord. Chem.,* 2013, vol. 39, p. 598. DOI: 0.1134/S107032841308006X.