New Representatives of Promising Thermochromic Materials − Iron (II) Complexes with 1,2,4-Triazoles Possessing $^1A_1 \Leftrightarrow {}^5T_2$ Spin Transition

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Abstract

Iron (II) complexes with 1,2,4-triazoles are promising thermochromic materials. New complexes of iron (II) perrhenate and dodecahydro-closo-dodecaborate with 1,2,4-triazole (Htrz) and 4-amino-1,2,4-triazole (NH_2trz) of the composition $FeL_3A_n \cdot mH_2O$ ($n = 1, 2$; $m = 4, 5$) are synthesized and investigated. The compounds are studied by means of magnetochemicstry, XPA, electron and IR spectroscopy. Magnetochemical data show that the complexes possess $^1A_1 \Leftrightarrow {}^5T_2$ spin transition. The spin transition is accompanied by thermochromism (change of colour from pink to white).

INTRODUCTION

An urgent problem of the chemistry of inorganic materials is obtaining, investigation and application of thermochromes, which are substances that change colour while temperature changes. These compounds are of interest for the development of temperature indicators [1] and recording devices [2]. A substantial part of compounds exhibiting thermochromism is comprised by coordination compounds [3−6]. Special attention is attracted to the complexes in which colour can change reversibly and sharply. Such a character of thermochromism is exhibited by the coordination compounds of many classes. They include classical thermochromes Ag_2HgI_4, Cu_2HgI_4 and $PbHgI_4$ [6], complexes with aliphatic nitrogen-containing ligands [5], compounds with chlorocomplexes as anions [5, 7], compounds with $[Cr(NCS)_6]^{3-}$ anions [8].

Along with clearly exhibited thermochromic properties, coordination compounds of the mentioned classes have substantial disadvantages, for example, toxicity of some metals (Cr, Ni, Hg) or their high cost (Ag), potential danger (complexes of nickel (II), copper (II) having ClO_4^- anions), hygroscopic behaviour (compounds containing chlorocomplexes as anions). It is evident that a search for complexes of new classes is necessary in order to obtain thermochromes devoid of the mentioned disadvantages.

Promising thermochromes of a new class are iron (II) complexes with various nitrous heterocycles; change in their colour is connected with a reversible transition from low-spin state into high-spin one ($^1A_1 \Leftrightarrow {}^5T_2$). Among these complexes, the most interesting ones are iron (II) compounds with 1-substituted tetrazoles [9, 10], as well as with 1,2,4-triazole and its 4-substituted derivatives [11−17]. The properties of compounds obtained by rather simple procedures from low-toxic iron (II) salts make them very promising for practical application. The complexes are formed with high yield and are stable toward water vapour of the air. It is important that the compounds with the ligands indicated above exhibit easily observable colour change (pink $\Leftrightarrow$ white). Such a character of colour change is explained by the features of $d−d$ transitions for the $^1A_1$ and $^5T_2$

states of iron (II) in the ligand field, created by the coordinated 1-substituted tetrazoles, 1,2,4-tetrazole and its 4-substituted derivatives.

For the low-spin complexes of iron (II) with these ligands, the band of $d-d$ transition $^1A_1 \Leftrightarrow {}^1T_1$ is situated in the visible spectral region $\lambda = 520-550$ nm), which causes pink colouring of low-spin forms. High-spin white complexes formed as a result of thermally induced spin transition (ST) exhibit $d-d$ band related to $^5T_2 \Leftrightarrow {}^5E$ transition which is out of the visible spectral range ($\lambda = 770-920$ nm). For iron (II) complexes with 1-substituted tetrazoles, thermochromic transition pink $\Leftrightarrow$ white is observed at temperature points substantially below room temperature. From the practical viewpoint, the most interesting complexes are iron (II) complexes with 1,2,4-tetrazole (Htrz) and its 4-substituted derivatives (Rtrz).

We synthesized for the first time compounds of the composition $Fe(Rtrz)_3A_n \cdot mH_2O$ (R = H, NH_2, et, pr; A = BF_4^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, SO_4^{2-}, SiF_6^{2-}; n = 1, 2; m = 0–2) [12, 13, 15–17]. Work aimed at the synthesis of the complexes of various Fe(II) salts with 4-amino-1,2,4-triazole were continued by some authors. Complexes of the composition $Fe(NH_2trz)_3A_2$ were synthesized, in which A = 1-naphthalenesulphonate (1-ns), 4-amino-1-naphthalenesulphonate(4-NH_2-1-ns), 4-hydroxy-1-naphthalenesulphonate (4-OH-1-ns), 2-naphthalenesulphonate (2-ns), 6-hydroxy-2-naphthalenesulphonate (6-OH-2-ns) [18], p-toluenesulphonate (tos) [19], $CH_3SO_3^-$ [20].

Investigation of complexes by means of magnetic susceptibility, electron, IR, EXAFS and Mossbauer spectroscopy showed that they have polynuclear structure due to the bidentate bridging group Rtrz. The ligand is coordinated to the neighbouring Fe (II) ions by N_1, N_2 atoms of heterocycle with the formation of polymeric chain. Such a method of coordinating provides strong cooperative interactions between the electron subsystem of Fe (II) ions and the phonon system of the lattice, which in turn leads to a sharp spin transition $^1A_1 \Leftrightarrow {}^5T_2$ and thermochromism connected with this transition. It was discovered that the transition temperature is substantially affected by the composition of compounds, in particular the nature of ligand and anion, as well as by the presence and number of crystallization water

molecules. This allowed obtaining thermochromic materials with transition temperatures within a broad range (lower, near and much higher than room temperature). It was interesting to broaden the mentioned set of complexes by synthesizing new compounds of iron (II) with Htrz and NH_2trz containing ReO_4^- and $B_{12}H_{12}^{2-}$ anions. The ReO_4^- anion is an example of anions containing metal atom; $B_{12}H_{12}^{2-}$ represents anions of cluster structure. No data on Fe (II) complexes with nitrogen-containing heterocycles containing these anions are available from literature.

EXPERIMENTAL

For the synthesis, the following reagents were used: $FeSO_4 \cdot 7H_2O$ recrystallized from aqueous solution acidified with H_2SO_4; $NaReO_4$ of analytically pure grade (ch.d.a.); KOH of chemically pure grade (kh.ch.); 1,2,4-triazole recrystallized from isopropanol, with T_{melt} = 121 °C (reference data: T_{melt} = 121 °C [21]); 4-amino-1,2,4-triazole synthesized using a procedure close to that described in [22], with T_{melt} = 82–83 °C (according to the data reported in [23], T_{melt} = 82–83 °C); ascorbic acid of medical grade (med). The salt of dodecahydro-closo-dodecaborate(2-)triethylammonium $[NH(C_2H_5)_3]_2B_{12}H_{12}$ was obtained *via* the reaction conducted at 140–160 °C in high-melting hydrocarbons [24]:

$$2(C_2H_5)_3N \cdot BH_3 + B_{10}H_{14}$$
$$\rightarrow [NH(C_2H_5)_3]_2B_{12}H_{12} \downarrow + 3H_2 \uparrow$$
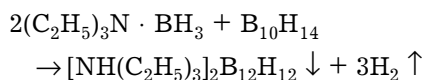
Synthesis of $Fe(Htrz)_3(ReO_4)_2$ (I). 2 mmol (0.56 g) of $FeSO_4 \cdot 7H_2O$ (with 0.1 g of ascorbic acid added) and 4 mmol (1.09 g) of $NaReO_4$ were separately dissolved in 5 ml of H_2O under heating with water bath. The solutions were mixed and cooled; a cooled solution of 12 mmol (0.83 g) of Htrz in 5 ml of ethanol was added. After mixing the solutions, a pink precipitate was formed. It was filtered and washed with water several times. Both this substance and the substances II–IV were dried in the air. The yield was 60 % of theoretical. Determined, %: C 10.2; H 1.8; N 16.1; Fe 7.7. For $C_6H_9FeN_9O_8Re_2$, calculated, %: C 9.4; H 1.2; N 16.5; Fe 7.3.

Synthesis of $Fe(NH_2trz)_3(ReO_4)_2$ (II). 2 mmol (0.56 g) of $FeSO_4 \cdot 7H_2O$ (with 0.1 g of ascorbic acid added) and 2 mmol (0.52 g) of $Ba(NO_3)_2$ were dissolved separately in 5 ml of water under heating with water bath. Precipitation of $BaSO_4$ was performed; the solution with the precipitate was stored for 3 h. The $BaSO_4$ precipitate was filtered; an aqueous solution of 4 mmol (1.09 g) of ReO_4 and a solution of 12 mmol (1.014 g) of NH_2trz in 5 ml of ethanol were added to the $Fe(NO_3)_2$ solution. Immediately after mixing, white precipitate was formed; after cooling, it was filtered and washed several times with water and ethanol. The yield was 75 % of theoretical. Determined, %: C 9.1; H 1.2; N 21.0; Fe 6.7. For $C_6H_{12}FeN_{12}O_8Re_2$, calculated, %: C 8.9; H 1.5; N 20.8; Fe 6.9.

Synthesis of $Fe(Htrz)_3B_{12}H_{12} \cdot 4H_2O$ (III) and $Fe(NH_2trz)_3B_{12}H_{12} \cdot 5H_2O$ (IV). In order to transfer the poorly soluble salt of dodecahydro-closo-dodecaborate(2-)triethylammonium into solution, we mixed 3 mmol (1.02 g) of $[NH(C_2H_5)_3]_2B_{12}H_{12}$ and 6.5 mmol (0.36 g) of KOH in 10 ml of water, and heated the solution till complete removal of triethylamine. The resulting $K_2B_{12}H_{12}$ solution was neutralized till pH 7 by adding several drops of acetic acid solution. 2 mmol (0.56 g) of $FeSO_4 \cdot H_2O$ (with 0.1 g of ascorbic acid added) was dissolved in 5 ml of H_2O on heating with water bath. The $K_2B_{12}H_{12}$ and $FeSO_4$ solutions were mixed; a solution of 16 mmol of the ligand (1.10 g Htrz or 1.34 g NH_2trz) in 5 ml of ethanol was added. After mixing the solutions, a white precipitate was formed. It was treated similarly to the synthesis of I. The yield was 70–80 % of theoretical. For III, determined, %: C 14.9; H 5.9; N 25.4; Fe 12.2.. For $C_6H_{29}FeN_9O_4B_{12}$, calculated, %: C 15.1; H 6.1; N 26.4; Fe 11.7. For IV, determined, %: C 15.8; H 5.2; N 30.5; Fe 11.3. For $C_6H_{34}FeN_{12}O_5B_{12}$, calculated, %: C 13.3; H 6.3; N 31.1; Fe 10.3.

Elemental analysis for C, H, N was performed with Carlo-Erba 1106 instrument at the Laboratory of Microanalysis of the NIOCh, SB RAS. X-ray phase analysis (XPA) was performed with PHILIPS-PW1700 diffractometer (CuK_α radiation, Ni filter, scintillation detector, step 0.015°, 2θ measurement range of 5 to 30 °C). Measurements were performed at room temperature, silicon powder was used as an external standard ($\alpha = 5.4309$ Å). Magnetic susceptibility of polycrystalline samples of complexes was measured by Faraday procedure within the temperature range of 78–400 K. Effective magnetic moment (μ_{ef}) was calculated using the equation $\mu_{ef} = 8\chi_{M'}T)^{1/2}$, where $\chi_{M'}$ is the molar magnetic susceptibility corrected for diamagnetism. The heating (cooling) rate within the ST region was ~0.2 K/min. When examining magnetic properties of the samples of complexes, removal of the crystallization water was performed in vacuum till constant mass. The diffuse reflection spectra (DRS) were recorded at room temperature with Unicam 700 A spectrophotometer. The IR adsorption spectra were recorded with Specord 75 IR spectrophotometer within the spectra region of 400–3600 cm^{-1} and with M-80 spectrophotometer within the range of 200–400 cm^{-1}. The curves of thermal analysis of the complexes containing water were recorded with Paulic–Paulic–Erday derivatograph in the air in quartz crucibles. The heating rate was 2.5 °C/min, reference: Al_2O_3; weighed portion: 50 mg.

RESULTS AND DISCUSSION

The compounds of iron (II) were isolated from water-ethanol solutions using a substantial excess of the ligand (L : Fe = 6–8). This is explained by the fact that at lower L : Fe ratio, along with the main reaction products, the compounds of different stoichiometry are also isolated. The compounds I–III exhibit thermochromism: on heating, the pink colour of I changes for white; on cooling, the white colour of II and III changes for pink; the colour of complex IV within the temperature range of 78–350 K remains white. The compounds I–IV, similarly to the major part of iron (II) complexes with 1,2,4-triazoles, synthesized earlier, are stable for a long time when stored in the air at room temperature.

The presence of crystallization water in the complexes II and IV is confirmed by the IR spectroscopic data (the region of 3400–3600 cm^{-1}) and elemental analysis. Water content was determined using the data of thermal analysis. The temperature of the start of mass loss on

the TG curves of complexes is 50−70 °C. According to the XPA data, the compounds I−IV are crystalline but poorly crystallized.

Magnetochemical investigation of compounds I−IV showed that I−III possess $^1A_1 \Leftrightarrow {}^5T_2$ ST (Fig. 1, *a−c*). It is noteworthy that, unlike III, complex IV remains in the high-spin state within the temperature range of 78−350 K, though the difference between them is due only to the amino group appearing in the position 4 of 1,2,4-triazole. It is possible that the
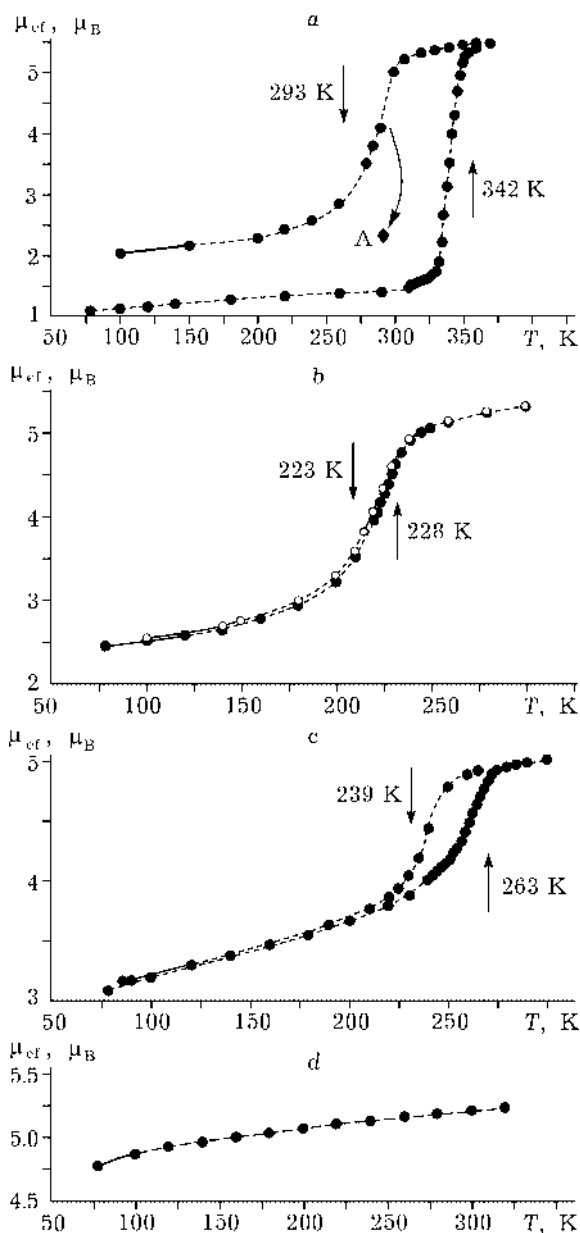

Fig. 1. The $\mu_{эф}(T)$ dependence for complexes: $Fe(Htrz)_3(ReO_4)_2$ (*a*), $Fe(NH_2trz)_3(ReO_4)_2$ (*b*), $Fe(Htrz)_3B_{12}H_{12}$ (*c*) and $Fe(NH_2trz)_3B_{12}H_{12}$ (*d*).

TABLE 1

Temperatures of direct and reverse ST and the width of hysteresis loop for complexes I, II, and for dehydrated complex III

Compound	$T_c\uparrow$	$T_c\downarrow$	ΔT_c
$Fe(Htrz)_3(ReO_4)_2$	342	293	49
$Fe(NH_2trz)_3(ReO_4)_2$	228	223	5
$Fe(Htrz)_3B_{12}H_{12}$	263	239	24

ST in IV occurs below 78 K (see Fig. 1, *d*). Temperature points of the direct ($T_c\uparrow$) and reverse ($T_c\downarrow$) transitions, as well as the width of hysteresis loop (ΔT_c) are shown in Table 1. Attention should be paid to the fact that for the complex I at the mentioned heating (cooling) rate, the curve of $\mu_{ef}(T)$ dependence on cooling passes substantially higher than the curve obtained on heating.

Measurements performed after 18 h (for example, point A in Fig. 1, *a*) showed that m_{ef} values decrease, and the curve of $\mu_{ef}(T)$ dependence for cooling comes close to the curve obtained for heating. This is likely to be explained by kinetic hindrance during the transition from high-spin (HS) form to low-spin (LS) one in the low temperature region. Within the row of complexes I−III, compound I is most interesting since it is one more compound having the high-temperature ST ($T_c\uparrow > 293$ K). The analysis of the characteristics of ST in iron (II) complexes with Htrz and NH_2trz shows that they are substantially dependent on the composition of the complex compound (CC), which noticeably affects not only T_c but also the width of hysteresis loop. Similarly to the previously investigated compounds, as a rule, $T_c\uparrow$ of the complexes of Fe(II) with 1,2,4-triazole are higher than $T_c\uparrow$ of Fe(II) complexes with 4-amino-1,2,4-triazole; in Fe(II) complexes with NH_2trz, the transition is not so sharp as in the CC with unsubstituted Htrz.

It should be noted that substantial residual paramagnetism is observed in the compounds II and III at 78 K (see Fig. 1, *b, c*). The transitions are rather sharp but not complete; the curves of $\mu_{ef}(T)$ dependencies point to substantial residual content of the HS forms of complexes. The fraction of Fe_{HS}, calculated using the equation $\alpha_{HS} = \mu^2_{ef} / \mu^2_{ef}(Fe_{HS})$, is 0.22 and

TABLE 2

Basic vibrational frequencies in the IR spectra of complexes I–IV

Compound	R_{ring}, cm^{-1}	$\nu(N^4-NH_2)$, cm^{-1}	Absorption bands of anions, cm^{-1}	τ_2, cm^{-1}	$\nu(Fe-N)$, cm^{-1}
Htrz	1530, 1540			640	
Fe(Htrz)$_3$(ReO$_4$)$_2$	1505, 1525		910, 291	625	302
Fe(Htrz)$_3$B$_{12}$H$_{12}$ · 4H$_2$O	1505, 1525		2470	620	263
atrz	1520, 1530	1190, 1205		610	
Fe(atrz)$_3$(ReO$_4$)$_2$	1540, 1550	1210, 1215	910, 291	615	251
Fe(atrz)$_3$B$_{12}$H$_{12}$ · 5H$_2$O	1540, 1550	1210, 1215	2480	615	242, 251

0.37 for II and III, respectively; therefore, a substantial part of iron (II) atoms dos not pass into the LS state. A possible reason for large α_{HS} can be the existence of two structurally non-equivalent forms of complexes, one of which does not take part in the ST process. Such an example was discovered for the CC of Fe(II) tetrafluoroborate with 1-methyltetrazole of the composition [FeL$_6$](BF$_4$)$_2$ [25].

The DRS of complex I exhibits one band with λ = 540 nm, which can be assigned to the d–d transition $^1A_1 \rightarrow {}^1T_1$ in the strong octahedral distorted lignad field, FeN$_6$ centre. The DRS of complexes II–IV contain one band within the region of 850–900 nm, related to the d–d transition $^5T_2 \rightarrow {}^5E$ in weak octahedral distorted ligand field, which is characteristic of high-spin complexes of Fe(II) with triazoles.

The IR spectra of complexes (Table 2) contain the bands of mixed stretching and bending vibrations of triazole cycles within the region of 1510–1550 cm^{-1}, which are shifted by 10–15 cm^{-1} toward lower frequencies (for complexes with Htrz) or higher frequencies (for complexes with NH$_2$trz), compared to the positions of these bands in the spectra of ligands. This is the evidence of the coordination of nitrogen atoms of Htrz and NH$_2$trz cycles to metal [26].

The spectrum of Htrz in the region of 600–700 cm^{-1} contains two bands of torsion vibrations of the ring: τ_1 at 680 cm^{-1} and τ_2 at 650 cm^{-1}. The spectra of complexes I and III exhibit one band at 625 cm^{-1} (τ_2), which points to bidentate bridging coordination of Htrz by N$_1$, N$_2$ atoms of the cycle (C_{2v} symmetry) [11].

For making conclusions concerning the mode of coordination of NH$_2$trz, more informative analysis is the one of the position of absorption band of the exocyclic bond $\nu(N-N)$ of this ligand. These bands are observed in the spectra of II and IV complexes at 1210 and 1215 cm^{-1}, respectively, and are shifted to higher frequencies with respect to the spectrum of non-coordinated NH$_2$trz (a doublet 1190, 1205 cm^{-1}). Such a shift also points to the N$_1$, N$_2$ coordination of NH$_2$trz [27].

Absorption bands of anions are observed in the spectra of complexes; these bands are not split, which is the evidence of the absence of strong distortions of the symmetry of anions and therefore confirms their outer-sphere position.

The spectrum of complex I in the region of stretching vibrations metal – ligand (200–400 cm^{-1}) contains the band $\nu(Fe-N)$ at 302 cm^{-1}; the spectra of compounds II–IV have a band at 251 cm^{-1}. Such a position of $\nu(Fe-N)$ is characteristic of the compounds of Fe(II) with 1,2,4-triazoles in which Fe(II) at room temperature is in low-spin (I) or high-spin (II–IV) state.

Taking into account the whole set of data accumulated by us, including those obtained in the present study, we can range the compounds in the following rows of the dependence of $T_c\uparrow$, K on anion for dehydrated compounds FeL$_3$A$_n$ (n = 1,2): B$_{12}$H$_{12}^{2-}$ (263) < ClO$_4^-$ (266) < Cl$^-$ (337) < ReO$_4^-$ (342) < NO$_3^-$ (355) < SiF$_6^{2-}$ (~380*) < BF$_4^-$ (397) for Fe(Htrz)$_3$A$_n$ and NCS$^-$ (190) < ClO$_4^-$ (210) < ReO$_4^-$ (228) < SiF$_6^{2-}$ (254) < I$^-$ (280) < Br$^-$ (312) < BF$_4^-$ (335) < NO$_3^-$ (342) < Cl$^-$ (355) ≈ SO$_4^{2-}$ (355) for Fe(NH$_2$trz)$_3$A$_n$.

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*T_c value is close to the temperature of the start of the complex's decomposition.

CONCLUSION

Thus, representative rows of thermochrome complexes of iron (II) with 1,2,4-triazole and 4-amino-1,2,4-triazole have been synthesized by present. The changes in the colour of these compounds depending on their composition is observed within a broad temperature range, including the region near and above room temperature, which is promising for their practical application.

REFERENCES

1 S. P. Gvozdev, A. A. Erunova, *Izv. vuzov. Khimiya i khim. tekhnologiya*, 5 (1958) 154.

2 O. Kahn, J. Krober, C. Jay, *Adv. Mater.*, 4, 11 (1992) 718.

3 J. H. Day, *Chem. Rev.*, 68, 6 (1968) 649.

4 K. Sone, Y. Fukuda, Inorganic Thermochromism, Springer-Verlag, Berlin, 1987.

5 D. R. Bloomquist, R. D. Willett, *Coord. Chem. Rev.*, 47, 1−2 (1982) 125.

6 M. Meyer, *J. Chem. Educ.*, 20 (1943) 145.

7 S. V. Larionov, Z. A. Savelyeva, G. V. Romanenko, *Koordinats. khimiya*, 28, 2 (2002) 89.

8 T. G. Cherkasova, V. S. Cherkasov, E. S. Tatarinova, *ZhNKh*, 39, 9 (1994) 1483.

9 P. L. Franke, J. G. Haasnoot, A. P. Zuur, *Inorg. Chim. Acta*, 59, 1 (1982) 5.

10 P. Gutlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed.*, 33, 20 (1994) 2024.

11 J. G. Haasnoot, G. Vos, W. L. Groeneveld, *Z. Naturforsch.*, 32B, 12 (1977) 1421.

12 L. G. Lavrenova, V. N. Ikorskiy, V. A. Varnek *et al.*, *Koordinats. khimiya*, 12, 2 (1986) 207.

13 L. G. Lavrenova, S. V. Larionov, *Ibid.*, 12, 2 (1986) 207.

4 J. G. Haasnoot, *Coord. Chem. Rev.*, 200−202 (2002) 131.

15 L. G. Lavrenova, O. G. Shakirova, Yu. G. Shvedenkov *et al.*, *Koordinats. khimiya*, 25, 3−4 (1999) 208.

16 L. G. Lavrenova, E. V. Kirillova, V. N. Ikorskiy *et al.*, *Ibid.*, 27, 1 (2001) 51.

17 L. G. Lavrenova, O. G. Shakirova, V. N. Ikorskiy *et al.*, *Ibid.*, 29, 1 ((2003) 24.

8 P. J. Koningsbruggen, Y. Garcia, E. Codjovi *et al.*, *J. Mater. Chem.*, 7, 10 (1997) 2069.

19 E. Codjovi, L. Sommier, O Kahn, *New. J. Chem.*, 20 (1996) 505.

20 R. Bronisz, K. Drabent, P. Polomka *et al.*, Conf. Proc. "ICAME-95", Bologna, 1996, Vol. 50, p. 11.

21 K. T. Potts, *Chem. Rev.*, 61, 2 (1961) 108.

22 R. M. Herbst, J. A. Garrison, *J. Org. Chem.*, 18 (1953) 872.

23 Sintezy organicheskikh preparatov, in B. A. Kazanskiy (Ed.), Izd-vo inostr. lit., Moscow, 1952, vol. 3, p. 56.

24 N. N. Greenwood, J. H. Morris, *Proc. Chem. Soc.*, (1963) 338.

25 P. Poganiuch, S. Decurtins, P. Gutlich, *J. Amer. Chem. Soc.*, 112, 9 (1990) 3270.

26 L. G. Lavrenova, I. A. Baydina, V. N. Ikorskiy *et al.*, *ZhNKh*, 37, 3 (1992) 630.

27 V. P. Sinditskiy, V. I. Sokol, A. E. Fogelsang *et al.*, *Ibid.*, 32, 8 (1987) 1950.