## Cu(II) Complexes with 4,6-Bis(3,5-dimethyl-1*H*-pyrazole-1-yl)pyrimidine, 4-(3,5-dimethyl-1*H*-pyrazole-1-yl)-6-(3,5-diphenyl-1*H*-pyrazole-1-yl)pyrimidine: Synthesis and Catalytic Activity in Ethylene Polymerization Reaction

M. B. Bushuev<sup>a</sup>, V. P. Krivopalov<sup>b</sup>, N. V. Semikolenova<sup>c</sup>, Yu. G. Shvedenkov<sup>a</sup>, L. A. Sheludyakova<sup>a</sup>, G. G. Moskalenko<sup>b</sup>, L. G. Lavrenova<sup>a</sup>, V. A. Zakharov<sup>c</sup>, and S. V. Larionov<sup>a</sup>

> <sup>a</sup> Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

<sup>b</sup> Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia

<sup>c</sup> Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences,

pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

Received August 9, 2006

**Abstract**—The Cu(II) complexes with 4,6-bis(3,5-dimethyl-1*H*-pyrazole-1-yl)pyrimidine (L<sup>1</sup>) and 4-(3,5-dimethyl-1*H*-pyrazole-1-yl)-6-(3,5-diphenyl-1*H*-pyrazole-1-yl)pyrimidine (L<sup>2</sup>) of the composition  $Cu_2L^1Br_4$  and  $Cu_2L^2A_4$  (A = Cl, Br), respectively, were synthesized and studied by IR and magnetochemical methods. The molecular structure of the complexes is likely to be binuclear. In the presence of cocatalysts methylaluminoxane and triisobutylaluminium, the title complexes exhibit catalytic activity in the ethylene polymerization reaction.

DOI: 10.1134/S107032840708009X

The design of novel catalysts for different processes of chemical technology is a topical problem in modern chemistry. Of great practical importance are the syntheses and studies of new catalytic systems for the production of organic polymers with the desired properties [1, 2]. The extensive investigations are being performed today into the catalytic activity of the 3d transition metal complexes with the nitrogen-containing ligands, i.e., 2,6-bis(organylimino)pyridines,  $\alpha$ -diimines, and bis(benzimidazoles), which in combination with cocatalysts (organoaluminium compounds) catalyze the polymerization of olefins [1-17]. The catalytic activity of the Fe(II) and Co(II) complexes with 2,6-di(pyrazole-2-yl)- and 2,6-di(pyrazole-1-ylmethyl)pyridines in the presence of methylaluminoxane was reported in [18]. Previously [19], we synthesized and studied the Cu(II) chloride and bromide complexes with pyrazolylpyrimidine ligand, 2-(3,5-diphenyl-1H-pyrazole-1-yl)-4,6diphenylpyrimidine, and established their significant catalytic activity in the ethylene polymerization reaction in the presence of cocatalysts, methylaluminoxane (MAO) and triisobutylaluminium (TIBA). It has been shown for the first time that pyrazolylpyrimidine ligands (L) are promising reagents in the synthesis of transition metal complexes exhibiting catalytic properties. The molecules of compounds studied in [1-18]contain only one metal atom. However, a great number of catalytic reactions involve complexes containing several metal atoms [20]. The synthesis of binuclear and polynuclear complexes depends significantly on success in the synthesis of organic reagents, which can function as the polydentate bridging ligands. Such ligands include the earlier synthesized compound 4,6-bis(3,5-dimethyl-1*H*-pyrazole-1-yl)pyrimidine ( $L^1$ ) [21] and 4-(3,5-dimethyl-1*H*-pyrazole-1-yl)-6-(3,5diphenyl-1*H*-pyrazole-1-yl)pyrimidine ( $L^2$ ), whose synthesis is described in this work:



The binuclear complex Rh(I) with  $L^1$  containing diolefine was reported in [21]. The goal of this work was to synthesize  $L^2$  and Cu(II) complexes with  $L^1$  and  $L^2$  and to study the catalytic properties of the above complexes in the ethylene polymerization reaction.

## EXPERIMENTAL

The pure grade  $CuCl_2 \cdot 2H_2O$  and  $CuBr_2$ , MAO Witco Gm1H (Berghamen) (a solution in toluene with a total content of Al 1.8 mol/l), TIBA (a solution in heptane, commercial grade) were used. The reagents 4-hydrazino-6-chloropyrimidine and 4,6-dihydrazinopyrimidine were prepared by a known procedure [22] and [23], respectively.

Synthesis of L<sup>1</sup>. A mixture of 4,6-dihydrazinopyrimidine (2.20 g, 16 mmol) and acetylacetone (4.0 g, 40 mmol) was refluxed in 20 ml ethanol for 5 h. After cooling, the precipitate obtained was filtered off, washed with ethanol, and dried. The product yield was 3.90 g (93%). A high-resolution mass spectrum (the direct introduction of a sample to the ionic source): found m/z 450.1855 [M]<sup>+</sup>. For C<sub>31</sub>H<sub>22</sub>N<sub>4</sub> anal. calcd.: M = 450.1844. The <sup>1</sup>H NMR spectrum (200.13 MHz, CDCl<sub>3</sub>) is identical to that reported in [21].

Synthesis of 4-(3,5-diphenyl-1*H*-pyrazole-1-yl)-6-chloropyrimidine. A mixture of 4-hydrazino-6chloropyrimidine (1.44 g, 10 mmol) and dibenzoylmethane (2.40 g, 10 mmol) was refluxed in 25 ml ethanol for 12 h. The solvent was evaporated in a rotary evaporator and the residue was passed through a column with silica gel (CHCl<sub>3</sub>eluent) The product yield was 3.13 g (90%); mp = 143–144°C (from the hexane– benzene mixture, 1 : 1 v/v). A high-resolution mass spectrum: found *m*/*z* 332.0825 [M]<sup>+</sup>. For C<sub>19</sub>H<sub>13</sub>ClN<sub>4</sub> anal. calcd.: M = 332.0829. The <sup>1</sup>H NMR spectrum (200.13 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 8.50 (d, 1 H, *J* = 0.9 Hz, H(2)<sub>pyrimidine</sub>), 8.01 (d, 1 H, *J* = 0.9 Hz, H(5)<sub>pyrimidine</sub>), 7.97–7.88 (2 H, Ph), 7.52–7.35 (8 H, Ph), 6.80 (s, 1 H, H(4)<sub>pyrazole</sub>).

Synthesis of 4-hydrazino-6-(3,5-diphenyl-1*H*-pyrazole-1-yl)pyrimidine. A solution of 4-(3,5-diphenyl-1*H*-pyrazole-1-yl)-6-chloropyrimidine (5.0 g, 15 mmol) and 3 ml hydrazine hydrate in 30 ml ethanol was refluxed for 4 h. After cooling the solution to room temperature, the precipitate was formed. Then, the reaction mixture was diluted with twofold water quantity and cooled in a refrigerator for a night. The precipitate was filtered with suction and washed with water. The product yield was 4.80 g (98%). A high-resolution mass spectrum: found m/z 328.1440 [M]<sup>+</sup>. For C<sub>19</sub>H<sub>16</sub>N<sub>6</sub> anal. calcd.: M = 328.1436. A high-resolution mass spectrum of the minor component, 3,5-diphenyl-1*H*-pyrazole: found m/z 220.1007 [M]<sup>+</sup>. For C<sub>15</sub>H<sub>12</sub>N<sub>2</sub> anal. calcd.: M = 220.1000.

**Synthesis of L<sup>2</sup>.** A mixture of 4-hydrazino-6-(3,5diphenyl-1*H*-pyrazole-1-yl)pyrimidine (4.40 g, 13 mmol) and acetylacetone (2 g, 20 mmol) in 20 ml ethanol was refluxed for 5 h. The reaction mixture was cooled, the precipitate formed was filtered with suction, washed with ethanol, and the product was formed almost in quantitative yield; mp =  $161.5-163^{\circ}$ C. A high-resolution mass spectrum: found m/z 392.1752 [M]<sup>+</sup>. For C<sub>24</sub>H<sub>20</sub>N<sub>6</sub> anal. calcd.: M = 392.1749. The <sup>1</sup>H NMR spectrum (200.13 MHz, CDCl<sub>3</sub>),  $\delta$ , ppm: 8.55 (d, 1H, *J* = 1 Hz, H(2)), 8.40 (d, 1H, *J* = 1 Hz, H(5)), 8.10–7.92 (m, 2H, Ph), 7.51–7.32 (m, 8H. Ph), 6.82 (s 1H, H(4'')), 6.02 (s, 1H, H(4')), 2.70 (s, 3H, Me(5')), 2.30 (s, 3H, Me(3')).

Synthesis of  $Cu_2L^1Br_4$  (I). To a hot solution of  $CuBr_2$  (0.45 g, 2 mmol) in 15 ml ethanol, a hot solution of ligand  $L^1$  (0.28 g, 1 mmol) in 20 ml ethanol was added dropwise with stirring to give red-brown bulky precipitate. The mother solution with the precipitate was stirred for 1.5 h on heating, the precipitate was filtered with suction, washed with ethanol, and dried in air. The yield was 0.69 g (96%).

For C<sub>14</sub>H<sub>14</sub>Br<sub>4</sub>Cu<sub>2</sub>N<sub>6</sub>

anal. calcd., %:	C, 23.5;	Н, 2.3;	Cu, 17.8;	N, 11.8.
Found, %:	C, 22.5;	H, 2.6;	Cu, 17.8;	N, 11.4.

Synthesis of  $Cu_2L^2Cl_4$  (II) and  $Cu_2L^2Br_4$  (III). A hot solution of L<sup>2</sup> (0.20 g, 0.5 mmol) in 25 ml ethanol was added dropwise with heating to a hot solution of 1.5 mmol of the corresponding Cu(II) salt (0.26 g of  $CuCl_2 \cdot 2H_2O$ , 0.34 g of  $CuBr_2$ ) in 5–8 ml ethanol to give the precipitates (beige  $Cu_2L^2Cl_4$  and dark brown  $Cu_2L^2Br_4$ ). The mother solutions with the precipitates were stirred for 1–2 h with heating (the final volume of the solution was 8–10 ml), the precipitates were filtered with suction, washed with ethanol, and dried in air. The yield of II was 0.29 g (88%), the yield of III was 0.40 g (95%).

7.
5.
0.
1.

The Cu content in the complexes was determined by complexometric titration after decomposition of the sample in a mixture of concentrated  $H_2SO_4$  and  $HNO_3$ . The analysis for C, H, N was performed on Carlo Erba analyzer.

The IR spectra of the samples were measured on a Scimitar FTS 2000 spectrophotometer at 375–4000 cm<sup>-1</sup> (Nujol and fluorinated oil mulls) and on a BOMEM MB-102 spectrophotometer at 200–400 cm<sup>-1</sup> in polyethylene. A high-resolution mass spectrum was recorded on a Finnigan MAT-8200 spectrometer, electronic impact, 70 eV. The <sup>1</sup>H NMR spectra were recorded on the Bruker WP-200SY and AC-200 spectrometers.

The magnetic properties of the complexes were studied on a MPMS-5s SQUID-magnetometer (Quantum Design) at 2–300 K and external magnetic filed strength of about 5 kOe. The molar magnetic susceptibility ( $\chi$ ) was calculated with the account for atomic diamagnetism using Pascal additive scheme. The effective magnetic moment was calculated as  $\mu_{ef} = [(3k/N_A\beta^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$ , where k is the Boltzmann constant,  $N_A$  is the Avogadro number, and  $\beta$  is the Bohr magneton.

Estimation of catalytic properties in ethylene polymerization reaction. The verification of the catalytic activity of Cu(II) complexes in ethylene polymerization reaction was performed in a temperaturecontrolled reactor (0.2 1 in volume) equipped with a stirrer. MAO and TIBA were used as cocatalysts. The temperature and pressure of ethylele in the course of the reaction (1 h) were constant. The polyethylene (**PE**) powder obtained was dried in air and weighed.

## **RESULTS AND DISCUSSION**

The starting reagents for the synthesis of pyrazolylpyrimidines  $L^1$  and  $L^2$ , i.e., 4,6-dihydrazinopyrimidine (2) and 4-hydrazino-6-chloropyrimidine (3), were obtained by the reaction of available 4,6-dichloropyrimidine (1) with hydrazine hydrate. Previously, ligand  $L^1$  was synthesized by two methods: a) by the interaction of 1 with the sodium salt of 3,5-dimethylpyrazole [21] and b) by cyclocondensation of 2 with acetylacetonate in a 10% HCl solution [23]. We prepared the above ligand using the latter method but with boiling in ethanol in a neutral medium. In the synthesis of 4-hydrazino-6-(3,5-diphenyl-1H-pyrazol-1-yl)pyrimidine (5) by the reaction of 4-(3,5-diphenyl-1H-pyrazole-1-yl)-6-chloropyrimidine (4) with hydrazine hydrate, the nucleofuge lability of 3,5-diphenyl-1H-pyrazole-2-yl group was observed, since a high-resolution mass spectrum of the product contained, in addition to the line of compound 5, the line due to the molecular ion of 3,5-diphenyl-1*H*-pyrazole ( $\sim$ 3%). The latter is registered as a major compound at the initial spectral recording, while the intensity ratio of the observed peaks of the ions agrees with the data of compound itself [24, 25]. The latter is inert as the subsequent stage of the synthesis of the ligand  $L^2$ . It was also reported recently that the heating of 2-(3,5-dimethylpyrazole-1-yl)-4-methyl-5-ethoxycarbonylpyrimidine with ethanol solution of hydrazine hydrate gave 2-hydrazino-4-methyl-5-ethoxycarbonylpyrimidine (in 82% yield) in the absence of both the product of pyrimidine ring recyclization and hydrazine of the starting compound [26].

The complex compounds **I**, **II** were synthesized by the reaction of Cu(II) salts with L in the ethanol solutions on heating. Taking into account the possible bridging functions of L<sup>1</sup> and L<sup>2</sup>, the molar ratios Cu : L = 2 : 1 and 3 : 1 were used in the synthesis. As follows from the chemical analysis data, the Cu : L ratio in compounds **I–III** is 2 : 1, which suggests the binuclear structure of the complexes. The following scheme of transformations was performed:



RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 33 No. 8 2007

Compound v(Cu-N) v(Cu-X) $(v + \delta)_{ring}$  $L^1$ 1594, 1571  $Cu_2L^1Br_4(I)$ 1611, 1542 260 244  $L^2$ 1589, 1558  $Cu_2L^2Cl_4$  (II) 1613, 1565, 1544, 1520 280313, 325  $Cu_2L^2Br_4$  (III) 1612, 1564, 1542, 1519 262 249

**Table 1.** The main vibration frequencies in IR spectra  $(cm^{-1})$ 

of ligands  $L^1$ ,  $L^2$ , and complexes **I**–**III** 

 Table 2. Optimal exchange parameters of complexes I–III

Compound	g	<i>J</i> , cm <sup>3</sup> /mol	σ	
$Cu_2L^1Br_4(I)$	$2.11\pm0.01$	$-5.5 \pm 0.1$	0.0184	
$Cu_2L^2Cl_4$ (II)	$2.12\pm0.01$	$-16.3 \pm 0.1$	0.00341	
$Cu_2L^2Br_4$ (III)	$2.06\pm0.01$	$-19.9 \pm 0.2$	0.00681	

Complexes **I–III** are stable in air. They are soluble in organic solvents, i.e., ethanol, MeCN, isopropyl alcohol, toluene,  $CH_2Cl_2$ ,  $CHCl_3$ , and their mixtures; the above complexes are insoluble in water.

Table 1 contains IR data for  $L^1$ ,  $L^2$ , **I–III**. The positions of the stretching-bending vibrations of heterocyclic rings in the spectra of complexes change noticeably as compared to the spectra of  $L^1$  and  $L^2$ , which indicated the coordination of the donor N atoms and molecules L. This agrees with the presence of the stretching vibrations of the Cu–N bonds in the low-frequency region. The spectra of the complexes also contain the bands due to the stretching vibrations of the bonds Cu–

Cl (I) and Cu–Br (I, III), for which the characteristic relationship is fulfilled v(Cu–Br)/v(Cu–Cl) = 0.77-0.80.

Complexes **I–III** have identical magnetic properties and therefore, the  $\mu_{eff}(T)$  and  $\chi(T)$  curves are plotted only for complex **III** (see in the figure). At room temperature, the  $\mu_{eff}$  values are equal to 2.59, 2.53, and 2.45  $\mu_B$  for **I**, **II**, and **III**, respectively. As the temperature is lowered, the  $\mu_{eff}$  values increase to indicate the predominant antiferromagnetic exchange interactions between the Cu<sup>2+</sup> ions.

The  $\chi(T)$  curves of the complexes are characterized by the maxima (see in the figure, b). The observed magnetic behavior is typical of the compounds, whose exchange clusters consist of even number of the paramagnetic centers with the same spin. We analyzed the relations obtained using the isotropic spin-Hamiltonian in terms of the approach suggested in [27]. The twocenter exchange cluster was used for approximation and the "monomer impurity" effect [28], which takes into account the powdered state of the samples. The obtained optimal parameters of the effective g-factor of the  $Cu^{2+}$  ions, the exchange interaction (J), and the standard deviation values ( $\sigma$ ) are listed in Table 2. The theoretical curves corresponding to the above parameters agree well with the experimental curves (shown in the figure in dotted line is the theoretical curve for complex **III**). If g-factor is taken to be 2.1 on the basis of the data obtained, then the theoretical value of  $\mu_{\text{eff}}$  calculated for two practically noninteracting Cu<sup>2+</sup> ions with the spin S = 1/2 will be 2.57  $\mu_B$ , which is in a good agreement with the experimental data for complexes I-III synthesized at room temperature.

On the basis of the results obtained we suggest that the most probable variant of the structure of complexes I-III is the following. The complexes have the molecular binuclear structure: the tetradentate cyclic-bridging ligands (molecules L) are coordinated by two Cu atoms through the N atoms of pyrazole and pyrimidine rings:



The coordination surrounding of the Cu atoms is completed to a distorted tetrahedral surrounding by the halide ions as in the case of the Cu(II) chloride and bromide complexes with the analogous pyrazolylpyrimidine ligands [19, 29]. Estimates of the catalytic activity of complexes **I–III** in the ethylene polymerization reaction are given in Table 3. Under indicated conditions, complexes **I–III** show appreciable activity in the ethylene polymerization that noticeably exceeds the activity of the



The temperature dependence of (a)  $\mu_{eff}$  and (b)  $\chi$  of the  $Cu_2L^2Br_4$  complex.

previously studied  $\alpha$ -diimine complex of Cu(II) (Table 3). For complexes I–III, as for the Cu(II) chloride and bromide complexes with 2-(3,5-diphenyl-1*H*pyrazole-1-yl)-4,6-diphenylpyrimidine [19], TIBA turned somewhat more efficient cocatalyst than MAO. Note that in the presence of the same cocatalysts, the catalytic activity of complexes I–III does not almost depend on the nature of the anion or substituents (Me, Ph) in a pyrazole ring.

Thus, it has been shown for the first time that the synthesized binuclear Cu(II) complexes with pyrazolylpyrimidine ligands exhibit catalytic activity in the ethylene polymerization reaction.

## REFERENCES

- 1. Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, vol. 103, no. 1, p. 283.
- Bianchini, C., Giambastiani, G., Rios, I.G., et al., *Coord. Chem. Rev.*, 2006, vol. 250, nos. 11–12, p. 1391.
- 3. Sun, W.-H., Zhang, D., Zhang, S., et al., *Kinet. Catal.*, 2006, vol. 47, no. 2, p. 278.
- Britovsek, G.J.P., Gibson, V.C., Kimberley, B.S., et al., *Chem. Commun.*, 1998, no. 7, p. 849.
- 5. Britovsek, G.J.P., Bruce, M., Gibson, V.C., et al., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 38, p. 8728.
- 6. Svejda, S.A., Johnson, L.K., and Brookhart, M., J. Am. Chem. Soc., 1999, vol. 121, no. 45, p. 10634.
- 7. Ivancheva, N.I., Badaev, V.K., Oleinik, I.I., et al., *Dokl. Akad. Nauk*, 2000, vol. 374, no. 5, p. 648.
- Talzi, E.P., Babushkin, D.E., Semikolenova, N.V., et al., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 165 [*Kinet. Catal.* (Engl. Transl.), vol. 42, no. 2, p. 147].
- Schmidt, R., Welch, M.B., Knudsen, R.D., et al., J. Mol. Catal. A: Chem., 2004, vol. 222, nos. 1–2, p. 17.
- 10. Gibson, V.C., Tomov, A., Wass, D.F., et al., *Dalton Trans.*, 2002, no. 11, p. 2261.
- 11. Stibrany, R.T., Schulz, D.N., Kacker, S., and Patil, A.O., *PCT Int. Appl.*, 1999.
- 12. Helldörfer, M., Backhaus, J., and Alt, H.G., *Inorg. Chim. Acta*, 2003, vol. 351, no. 1, p. 34.
- 13. Baugh, L.S., Sissano, J.A., Kacker, S., et al., *J. Polymer. Sci.*, *A*, 2006, vol. 44, no. 6, p. 1817.
- 14. Britovsek, G.J.P., Gibson, V.C., Hoarau, O.D., et al., *Inorg. Chem.*, 2003, vol. 42, no. 11, p. 3454.
- 15. Nakayama, Y., Sogo, K., Yasuda, H., and Shiono, T., J. *Polymer. Sci.*, *A*, 2005, vol. 43, no. 15, p. 3368.
- Ionkin, A.S. and Marshall, W.J., *Organometallics*, 2004, vol. 23, no. 13, p. 3276.

Complex	Conditions			DE vield a	Activity,
	cocatalyst	$p_{C_2H_4}$ , atm	<i>T</i> , °C	r E yield, g	kg PE/(mol Cu h atm)
$\overline{Cu_2L^1Br_4\left(I\right)}$	MAO	10	35	0.96	48.0
	TIBA	10	35	1.39	69.5
$Cu_2L^2Cl_4$ (II)	MAO	10	35	1.04	52.0
	TIBA	10	35	1.29	64.5
$Cu_2L^2Br_4$ (III)	MAO	10	35	1.13	56.5
	TIBA	10	35	1.18	59.0
Cu(α-diimine)Cl <sub>2</sub> [10]**	MAO	4.5	25	0.4	4.5

Table 3. Catalytic activity of complexes I-III in the ethylene polymerization reaction\*

Notes: \* Polymerization conditions: 70 ml of toluene (heptane),  $c_{\text{Cu}} = 3 \times 10^{-5} \text{ mol/l}$ , molar ratio Al<sub>cocat</sub>/Cu = 500.

\*\* The data of [10] are listed for comparison ( $c_{\text{Cu}} = 2.0 \times 10^{-4} \text{ mol/l}$ ).

- 17. Ionkin, A.S., Marshall, W.J., Adelman, D.J., et al., *Organometallics*, 2006, vol. 25, no. 12, p. 2978.
- 18. Karam, A.R. and Catari, E.L., López-Linares, F. et al., *Appl. Catal.*, *A*, 2005, vol. 280, no. 2, p. 165.
- 19. Bushuev, M.B., Krivopalov, V.P., Semikolenova, N.V., et al., *Koord. Khim.*, 2006, vol. 32, no. 3, p. 208 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 3, p. 199].
- 20. Kukushkin, Yu.N., *Reaktsionnaya sposobnost' koordinatsionnykh soedinenii* (Reactivity of Coordination Compounds), Leningrad: Khimiya, 1987.
- 21. Uson, R., Oro, L.A., Esteban, M., et al., *Polyhedron*, 1984, vol. 3, no. 2, p. 213.
- 22. Postovskii, I.Ya. and Smirnova, N.B., *Dokl. Akad. Nauk SSSR*, 1966, vol. 166, no. 5, p. 1136.
- 23. Twomey, D., Proc. Roy. Irish Acad., 1974, B74, no. 4, p. 37.

- 24. Krasnoshchek, A.P., Khmel'nitskii, R.A., Polyakova, A.A., and Grandberg, I.I., *Zh. Org. Khim.*, 1968, vol. 4, no. 4, p. 689.
- 25. Junk, T., Catallo, W.J., and Elguero, J., *Tetrahedron Lett.*, 1997, vol. 38, no. 36, p. 6309.
- 26. Danagulyan, G.G. and Mkrtchyan, A.D., *Khim. Zh. Armenii*, 2005, vol. 58, nos. 1–2, p. 70.
- Ovcharenko, I.V., Shvedenkov, Yu.G., Musin, R.N., and Ikorskii, V.N., *Zh. Strukt. Khim.*, 1999, vol. 40, no. 1, p. 36.
- Rakitin, Yu.V. and Kalinnikov, V.T., *Sovremennaya magnetokhimiya* (Modern Magnetochemistry), St. Petersburg: Nauka, 1994.
- 29. Peresypkina, E.V., Bushuev, M.B., Virovets, A.V., et al., Acta Crystallogr. Sect. B: Struct. Sci., 2005, vol. 61, no. 2, p. 164.