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Synthesis, Structure, and Electrochemical Properties of $[M(N\text{-}MeIm)_6]^{2+}$ (M = Ni, Co, Cu) Associated with $[HgCl_4]^{2-}$ [1]

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Abstract—Reaction of $Hg(NO_3)_2$ with 4 equivalent KI in water afford $K_2[HgI_4]$. By using $K_2[HgI_4]$ as the precursor, three new heterobimetallic compounds $[Ni(N\text{-}MeIm)_6][HgI_4]$ (**I**), $[Co(N\text{-}MeIm)_6][HgI_4]$ (**II**), and $[Cu(N\text{-}MeIm)_6][HgI_4]$ (**III**) have been characterized by elemental analysis, IR spectra, and the single-crystal X-ray crystallorgraphy analysis. Three complexes are isomorphous and crystallized in monoclinic symmetry space group $P2_1/c$. The coordination around each center metal(II) atom is octahedral with six nitrogen atoms of N-MeIm ligand. Each structure contains one tetrahedral $[HgI_4]^{2-}$ as an anion to balance the charge of the molecular. Thermogravimetry analysis indicates these complexes have the similar departure process and cyclic voltammogram exhibits a significant pair of redox peaks.

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INTRODUCTION

Small molecules with metal center have been widely studied as model complexes in the more complex biological systems of metalloproteins [1], because the structural geometries of the model complexes are often quite comparable to those in the proteins [2]. Imidazole and its derivatives, such as histamine, histidine, pilocarpine, and allantoin occurring in living organisms have been well studied to elucidate the interaction of the proteins with the metal ions or to model the biological systems including imidazole type bonding [3–6]. Many proteins and enzymes are known to contain active sites with multiple histidine residues bound to a metal center. The catalytic activity of enzymatic reactions involving Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, and Zn^{2+} ions has been found to depend on its tendency towards coordination and on the structure of the compounds [7]. Therefore, it is much more important to study the structure and physicochemical properties of metal complexes with ligands incorporating the imidazole ring [8].

N-Methylimidazole (N-MeIm), as a derivative of the imidazole, has been used as ligand in biological systems, e.g., one or more N-MeIm units bound to metal ions in copper- and ruthenium-containing complexes have been attracting considerable attention for their antitumor activity and ability to ligate radiosensitizing agents to DNA [9–11]. Such compounds are also increasingly being studied in coordination chemistry because of N-methylimidazole as a stronge donor ligand in transition metal compounds. N-MeIm also has been proved to be a useful displacing ligand other than halides from trivalent lanthanide metal centers [12]. However, these systems involve an anionic metal-halide component for charge balance has comparatively been neglected. Mercury(II) typically regarded, as a Lewis acid, readily forms $[HgI_4]^{2-}$ by accepting halide ions (I^-) from multiple donor sources [13]. In the recent paper, the $[HgI_4]^{2-}$ function as a halide ion donor with the lanthanide and transitional metals has been reported [14]. In this paper, we describe the syntheses, characterization, redox properties of a new series of $[M(N\text{-}MeIm)_6]^{2+}$ (M = Cu (**I**), Co (**II**), Ni (**III**)) associated with $[HgI_4]^{2-}$.

EXPERIMENTAL

Measurements. Elemental analyses for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer 240C elemental instrument. Thermal analysis was recorded on Shimadzu TGA-50 thermogravimetric analyzer. Cyclic voltammetric analysis was carried out on an Autolab/PGSTAT30 potentiostat. A glass carbon (2 mm diameter) working electrode, a platinum sheet counter electrode and a saturated calomel electrode reference were employed. FT-IR and electronic spectra were recorded on a PerkinElmer 2000 FT-IR and Shimadzu 3100 Uvi-Vis-NIR spectrometer, respectively.

All manipulations were carried out in air. All chemicals were of analytical reagent grade and used directly without further purification.

Synthesis of the precursor $K_2[HgI_4]$. ($Hg(NO_3)_2$ (0.324 g, 1 mmol) was dissolved in 10 mL water, and to this solution was added a solution of KI (0.332 g, 2 mmol) in 10 mL water. An orange precipitate was

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obtained, to this suspended solution was added KI (0.332 g, 2 mmol) in 10 mL of water, causing dissolution to a pale yellow solution.

Synthesis of [Ni(N-MeIm)][HgI_4] (I). To 10 mL of water were added $NiCl_2$ (0.129 g, 1 mmol), and N-MeIm (0.5 g, 6.1 mmol). This mixed solution was stired at room temperature for 1 h. To this solution was added $K_2[HgI_4]$ slowly with strring, producing a precipitate. The precipate was filtered, washed twice with water and dried in vacuo. A crystal suitable for X-ray diffraction was formed after dissolution in DMF at 36°C for 2 days. The yield was 91%.

For $C_{24}H_{36}N_{12}I_4HgNi$

anal. calcd., %:	C, 22.89;	H, 2.88;	N, 13.34.
Found, %:	C, 22.57;	H, 2.64;	N, 14.54.

IR spectrum (KBr; ν, cm^{-1}): 3431 m, 3116 s, 2924 w, 1654 v.s, 1531 s, 1517 sh, 1400 s,1371 sh, 1280 m, 1230 s, 1103 v.s, 1082 s, 1028 sh, 938 m, 828 m, 740 m, 664 s, 618 m, and 471 m.

Synthesis of [Co(N-MeIm)][HgI_4] (II) was carried out the same as that of **I** except for the use of $CoCl_2 \cdot 6H_2O$ instead of $NiCl_2$. The yield was 86%.

For $C_{24}H_{36}N_{12}I_4HgCo$

anal. calcd., %:	C, 22.88;	H, 2.88;	N, 13.34.
Found, %:	C, 22.35;	H, 2.53;	N, 14.26.

IR spectrum (KBr; ν, cm^{-1}): 3416 m, 3115 s, 2324 w, 1653 v.s, 1531 s, 1400 s, 1229 m, 1103 s, 1081 sh, 1027 sh, 937 m, 829 m, 742 m, 663 s, 618 m, and 476 m.

Synthesis of Cu(N-MeIm)][HgI_4] (III) was carried out the same as that of **I** except for the use of $CuCl_2$ instead of $NiCl_2$. The yield was 82%.

For $C_{24}H_{36}N_{12}I_4HgCu$

anal. calcd., %:	C, 22.80;	H, 2.87;	N, 13.29.
Found, %:	C, 21.95;	H, 2.45;	N, 14.05.

IR spectrum (KBr; ν, cm^{-1}): 3426 w, 3116 s, 2927 sh, 1653 v.s, 1531 s, 1415 s, 1373 sh, 1229 m, 1103 v.s, 1082 sh, 1027 sh, 938 m, 828 m, 740 m, 664 s, 618 m, and 476 w.

X-ray structure determination. The selected crystal was mounted on Enraf-Nonius CAD4/Mach3 diffractometer. Reection data were measured at 20°C using graphite monochromated MoK_α ($\lambda = 0.71073$ Å) radiation. The collected data were reduced by using the program SAINT. The structure was solved by direct methods and rened by full-matrix least-squares method on Fobs2 by using the SHELXTL software package [15]. All non-H atoms were anisotropically rened. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The summary of the key crystallographic information of compounds **I**–**III** are given in Table 1. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 894450 (**II**) and 894451 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Three novel heterobimetallic species [M(N-methylimidazole)$_6$]$^{2+}$ (M = Ni (**I**), Co (**II**), Cu (**III**)) associated with $[HgI_4]^{2-}$ as anion have been synthesized by reaction of metal salts $MCl_2 \cdot xH_2O$ with N-MeIm ligand and $K_2[HgI_4]$ under analogous conditions. $Hg(NO_3)_2$ was treated with KI in water to afford a yellow solution of $K_2[HgI_4]$ as a precursor. Free ligand N-MeIm and metal salts was stirred at room temperature for 1 h, then $K_2[HgI_4]$ solution was added slowly to afford a precipitate. After work up, three compounds was obtained in good yield. Complexes **I**–**III** are stable toward air and moisture, soluble in DMF, and insoluble in diethyl ether, hydrocarbon solvents and water.

The IR spectra of **I**–**III** are quite similar, which provides support to the characterization of the product by identifying the vibration of the ligands surrounding the central transition metal. The absorption frequencies of the aromatic hydrogen atoms C–H of 1-MeIm are located in the 3132–2937 cm^{-1} in all IR spectra. Vibrations corresponding to ν(C=N) of the coordinated imidazole ring appeared at ~1653 cm^{-1} suggesting the coordination of the ligand N-MeIm through imidazole nitrogen [16].

The structures of **I**–**III** were determined by single-crystal X-ray diffraction. Selected bond distances and angles for compound **III** are summarized in Table 2. The molecular structure of **III** is listed in Fig. 1, as well as a perspective view of the crystal packing in the unit cells is showed in Fig. 2. The crystal structure of the compounds **I** and **II** are similar to that of **III** with the M^{2+} (Ni, Co and Cu) atoms coordinated by six 1-methylimidazolium groups. Every single-crystal structure contains a $[HgI_4]^{2-}$ anion.

For complex **III**, the Cu atom is in an distorted octahedral environment formed by six N atoms of 1-methylimidazolium moieties. The bond distances involved in this octahedral geometry (Cu(1)–N(2), Cu(1)–N(4), and Cu(1)–N(6)) are the most close to the regular octahedron [17]. The Cu–N bond distances fall in the range of 2.118(10)–2.152(11) Å. These values are comparable to those reported elsewhere [18]. The Hg–I lengths are in the range from 2.776(4) to 2.797(4) Å and the IHgI angles vary within the range from 105.45(16)° to 110.58(12)°. As indicated in packing diagram in Fig. 2, the tetrahedral HgI_4^{2-} was linked not only by the electrostatic forces but also by the C–H···I hydrogen bonds. One $[HgI_4]^{2-}$ anion connects with one neighboring CH_3 of the $[M(N\text{-MeIm})]^{2+}$

Table 1. Crystallographic data and experimental details for complexes **II** and **III**

Parameter	Value	
	II	**III**
Formula weight	1259.77	1264.38
Color	Pink	Blue
Space group	$P2_1/c$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
a, Å	9.5000(19)	9.5445(19)
b, Å	19.964(4)	20.153(4)
c, Å	20.379(4)	20.244(4)
β, deg	99.91(3)	99.80(3)
V, Å^3	3807.4(13)	3837.1(13)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.198	2.189
μ, mm^{-1}	7.739	7.801
F(000)	2332	2340
θ Range, deg	2.03–25.00	1.44–25.00
Reflection collected	7131	15475
Independent reflections, R_{int}	6702 ($R_{int} = 0.0623$)	6723 ($R_{int} = 0.0821$)
Reflections with $I > 2\sigma(I)$	3120	5109
Number of parameters	355	367
GOOF	1.022	1.186
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0704$, $wR_2 = 0.1720$	$R_1 = 0.0899$, $wR_2 = 0.1899$
R indices (all data)	$R_1 = 0.1781$, $wR_2 = 0.2240$	$R_1 = 0.1140$, $wR_2 = 0.2010$
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−1.28/2.52	−1.225/1.656

Table 2. Selected bond lengths (Å) and bond angles (deg) for **II** and **III**

Bond	d, Å	
	II	**III**
M(1)–N(1)	2.31(9)	2.146(11)
M(1)–N(3)	2.14(5)	2.118(10)
M(1)–N(5)	2.11(4)	2.152(11)
Hg(1)–I(1)	2.791(5)	2.8012(17)
Hg(1)–I(2)	2.789(5)	2.7949(16)
Hg(1)–I(3)	2.783(5)	2.7795(17)
Hg(1)–I(4)	2.789(5)	2.7968(15)
Angle	ω, deg	
	II	**III**
N(3)M(1)N(1)	95(2)	88.6(4)
N(5)M(1)N(1)	90(2)	88.4(4)
N(3)M(1)N(5)	86.5(17)	90.1(4)
I(1)Hg(1)I(2)	109.2(2)	105.23(7)
I(1)Hg(1)I(3)	110.85(19)	109.84(6)
I(2)Hg(1)I(4)	109.78(19)	110.48(6)
I(3)Hg(1)I(4)	110.00(19)	110.56(5)

groups forming the weak C–H···I hydrogen bonds (distances 3.248(2) Å and angles 128°) [19].

Similarly, complex **I** and **II** are also coordinated by six N atoms of 1-methylimidazol and form a qusi-octahedral environment. The Co–N and Ni–N distances are range from 2.142(14) to 2.30(3) and 2.14(3) to 2.21(3) Å, respectively. Every crystal structure consists of one $[HgI_4]^{2-}$ anion as well as hexakis(*N*-methylimidazole) metal cation. The Hg–I lengths are ranged from 2.776(4) to 2.797(4) Å for complex **II** and 2.7796(17) to 2.8000(17) Å for complex **III**, which are good agreement with the corresponding length for complex **I**. According to the packing diagram of the structure **II** and **III**, the $[HgI_4]^{2-}$ was surrounded by the cation $[M(N\text{-}MeIm)]^{2+}$. The $[HgI_4]^{2-}$ of the two complexes are also forming the weak hydrogen bond with the neighboring CH_3.

To probe the thermal stability, the thermogravimetry analysis (TGA) was performed on these synthesized complexes. As indicated by the TG curve shown in Fig. 3, the structure remained stable almost up to ~200°C for complex **I**–**III**. On further heating, a three-step weight loss was observed for these complex-

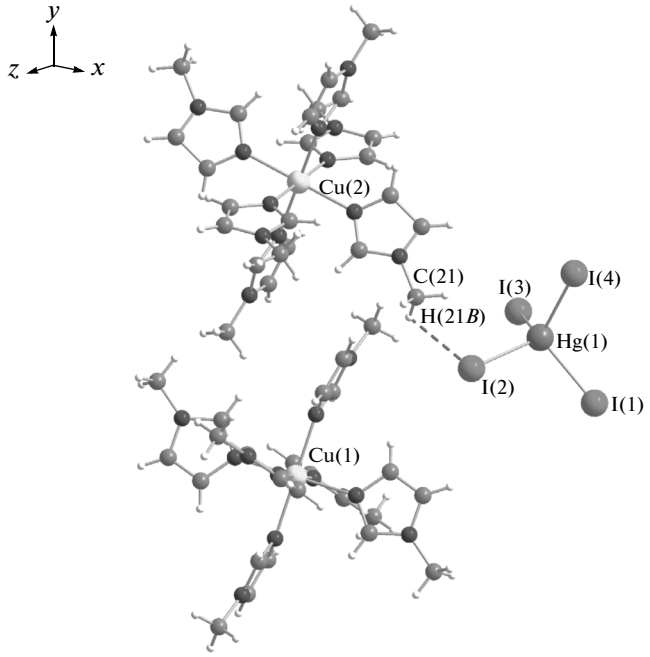

Fig. 1. The molecular structure of complex **III**.

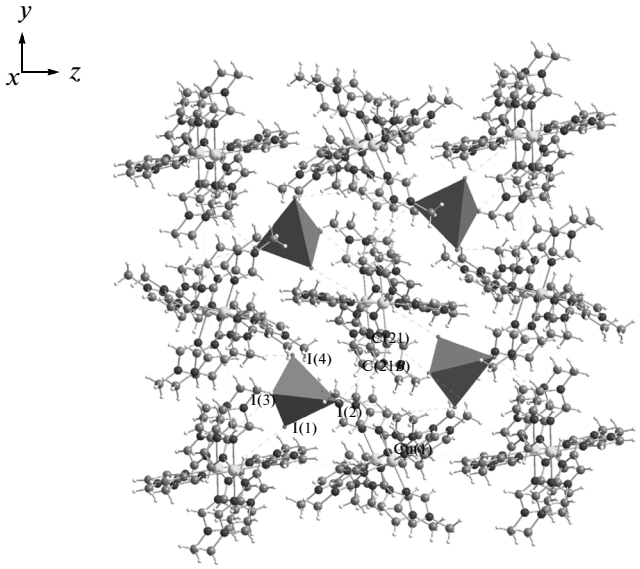

Fig. 2. Packing diagram of complex **III** with hydrogen bonds.

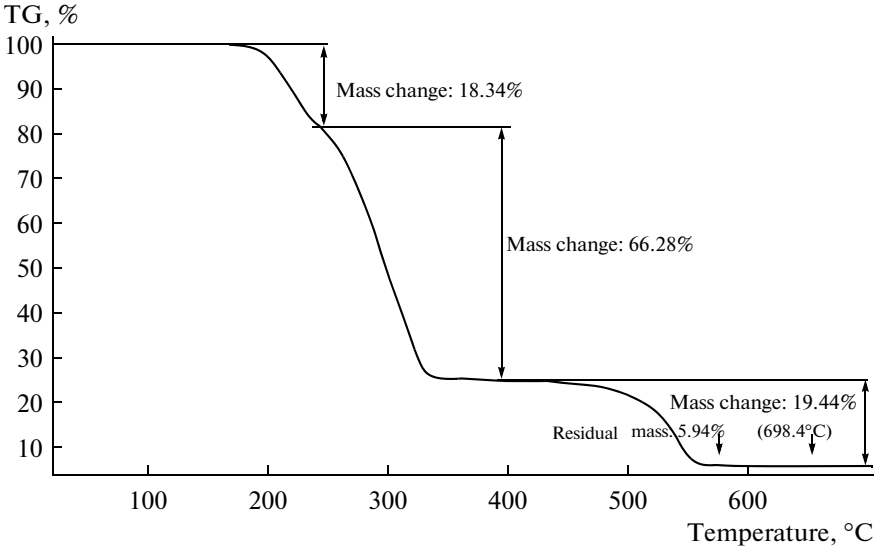

Fig. 3. Thermal analyses curves of complex **I**.

es. In complex **I**, the initial weight loss between 180 and 240°C should correspond to the departure of three 1-methylimidazole ligands. The observed weight loss (18.34%) was slightly lower than the expected value (calcd. 19.55%). The second step, occurring between 260 and 340°C with a weight loss of 56.28%, should be attributed to the anion of $[HgI_4]^{2-}$ (calcd. 56.22%). The third step (the weight loss of 19.44%) also attributed to another three 1-methylimidazole ligands. Finally, the weight loss of 94.06% suggests that the residue may be Cu atom (found 5.94%, calcd. 5.02%). For complex **II** and **III**, the similar weight loss process was found. However, the observed total weight loss (89.53%) for complex **III** was much lower than the expected value (calcd. 94.93%). Maybe, it was due to the retention of carbon in the solid residue [20].

The redox chemistry of compounds **I**–**III** was investigated by cyclic voltammetry (CV) in a 0.1 M DMF solution of $(Bu_4N)(PF_6)$ under an inert atmospheres. A three-electrode system containing a glassy carbon

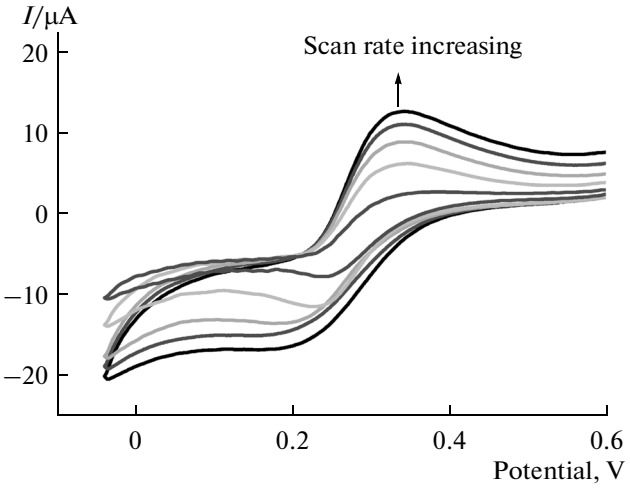

Fig. 4. The cyclic voltammogram of complex **I** (0.1 M in DMF) at the different scan rates (from inner to outer: 50, 100, 150, 200, 300 mV s^{-1}).

working electrode, a Ag/Ag^+ reference electrode, and a Pt wire counter electrode was used for all measurements. The plots of the CV for complex **I** was depicted in Fig. 4. The nickel complex [Ni(N-MeIm)][HgI_4] is redox active and exhibits a quasi-reversible one-electron oxidation wave at $E_{1/2} = 0.276$ V vs. SCE, which is assigned as metal-centered Ni^{2+}/Ni^{3+} oxidation [21]. Furthermore, the peak potential changes gradually using a scan rate of 50–300 mV s^{-1}; the cathodic peak potential shifts to the negative direction and the corresponding anodic peak potential shifts to the positive direction. The peak-to-peak separations between the corresponding anodic and cathodic peaks increase, which reveals that the redox process of **I** is surface-controlled [22]. No redox signals of $[HgI_4]^-$ for three compounds were detected because the iodine was present [23]. The CV of Co and Cu compounds also exhibit a significant pair of redox peaks in the potential range (−0.15 to 0.3 V). For the Co compound, there was a quasi-reversible one-electron oxidation wave at $E_{1/2} = 0.175$ V which may be ascribed to a one-electron oxidation of Co(II) → Co(III), whereas an irreversible oxidation wave appeared at 0.102 V for the Cu compound was assigned to the oxidation of Cu(I) → Cu(II).

REFERENCES

1. Ibers, J.A. and Holm, R.H., *Science*, 1980, vol. 209, p. 223.
2. Harding, M.M., *Acta Crystallogr.*, *D*, 2001, vol. 57, p. 401.
3. Cheruzel, L.E., Cecil, M.R., Edison, S.E., et al., *Inorg. Chem.*, 2006, vol. 45, p. 3191.
4. Parkin, G., *Chem. Rev.*, 2004, vol. 104, p. 699.
5. Flint, D.H. and Allen, R.M., *Chem. Rev.*, 1996, vol. 96, p. 2315.
6. Cheruzel, L.E., Cecil, M.R., Edison, S.E., et al., *Inorg. Chem.*, 2006, vol. 45, p. 3191.
7. Gillard, R.D., *Inorg. Chim. Acta Rev.*, 1967, vol. 6, p. 69.
8. Kurdziel, K. and Glowiak, T., *Pol. J. Chem.*, 1998, vol. 72, p. 2181.
9. Clarke, M.J., Jansen, B., Marx, K.A., and Kruger, R., *Inorg. Chim. Acta*, 1986, vol. 124, p. 13.
10. Keppler, B.K., *Metal Complexes in Cancer Chemotherapy*, Weinheim (Germany): VCH, 1993, vol. 429, p. 85.
11. McNamara, M. and Clarke, M.J., *Inorg. Chim. Acta*, 1992, vol. 195, p. 175.
12. Moulton, B. and Zaworotko, M.J., *Curr. Opin. Solid State Mater. Sci.*, 2002, vol. 6, p. 117.
13. Huebner, L., Korko, A., Emge, T., and Brennan, J., *Inorg. Chem.*, 2004, vol. 43, p. 5659.
14. Maharaj, F., Russell, V., Chow, H., et al., *CrystEngComm*, 2003, vol. 5, p. 285.
15. Sheldrick, G. and Egert, E., *SHELXS/PATSEE Structure Solution Package*, Göttingen (Germany): Institut für Anorganische Chemie der Universität, 1992.
16. Arifa, M., Nazir, S., Iqbal, M.S., and Anjum, S., *Inorg. Chim. Acta*, 2009, vol. 362, p. 624.
17. Latif Abuhijleh, A. and Woods, C., *Inorg. Chem. Commun.*, 2002, vol. 5, p. 269.
18. Forbes, T.Z. and Sevov, S.C., *Inorg. Chem.*, 2009, vol. 48, p. 6873.
19. Liu, Q., Li, H., Zhao, X., et al., *Inorg. Chim. Acta*, 2011, vol. 376, p. 437.
20. Lv, Y., Jiang, Z., Chen, J., et al., *J. Inorg. Organomet. Polym.*, 2011, vol. 21, p. 223.
21. Ding, Y., Gao, D.S., Li, S.D., et al., *Russ. J. Coord. Chem.*, 2009, vol. 35, p. 663.
22. Lv, Y.K., Zhan, C.H., Jiang, Z.G., and Feng, Y.L., *Inorg. Chem. Commum.*, 2010, vol. 13, p. 440.
23. Bildstein, B., Malaun, M., Kopacka, H., et al., *J. Organomet. Chem.*, 1998, vol. 552, p. 45.