

Synthesis and Crystal Structure of the $[\text{Re}_2(\text{CH}_3\text{COO})_2\text{Cl}_4((\text{CH}_3)_2\text{NCOCH}_3)_2]$ Complex

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Abstract—Compound $[\text{Re}_2(\text{CH}_3\text{COO})_2\text{Cl}_4((\text{CH}_3)_2\text{NCOCH}_3)_2]$ is synthesized. The influence of parameters of the hydrothermal synthesis under elevated pressure on the yield of a target product and its molecular structure and physicochemical properties is studied. In the neutral complex with *cis*-arrangement of the bridging acetate and terminal chloride ligands with respect to the multiply bonded Re_2^{6+} complex-forming center, the Re–Re bond length is 2.2418(3) Å. Dimethylacetamide molecules are in the axial positions, the Re–O bond lengths being 2.304(3) and 2.321(4) Å. The influence of the donor ability of the axial substituents in analogous structures of the rhenium(III) binuclear clusters on the Re–Re and Re– L_{ax} bond lengths is analyzed.

INTRODUCTION

Complexes of rhenium(III) with the metal–metal quadruple bond containing the Re_2^{6+} binuclear fragment are of interest both from a theoretical viewpoint and in practical application for the low-temperature production of rhenium in CVD processes [1, 2].

A search for compounds suitable for production of metallic rhenium by the low-temperature method resulted in dirhenium *cis*-tetrahalodi- μ -carboxylates. The detailed study of their thermal destruction showed that these are the most suitable compounds for the production of metallic rhenium and its coatings. The thermal decomposition of binuclear dirhenium *cis*-tetrahalodi- μ -acetates is accompanied by *cis*–*trans* isomerization to form stable volatile *trans*- $[\text{Re}_2(\text{CH}_3\text{COO})_2\text{Cl}_4]$ cluster (I), which undergoes phase transitions (solid–gas–solid) without decomposition, can be easily transferred by an inert gas, and decomposes to metal in almost 100% yield [3].

Previously [2, 3], it has been shown that, among dirhenium(III) chloroacetates with a general formula $[\text{Re}_2(\text{CH}_3\text{COO})_2\text{Cl}_4\text{L}_2]$, where L is the axial ligand (for instance, *N,N*-dimethylacetamide (DMAA, II), H_2O (III), triphenylphosphineoxide (TPPO, IV), *N,N*-dimethylformamide (DMF, V), or pyridine (Py)), only the derivatives with H_2O and DMAA can eliminate axial ligands without decomposition of the binuclear complex under thermal destruction conditions. Therefore, it is important to study the atomic structure of complex II, to compare it with the available structural data for other compounds of this class, and to establish the influence of the axial substituent nature on the structures of the substances under study.

EXPERIMENTAL

Synthesis

Complex II was synthesized by the reduction of potassium perhenate in a mixture of glacial acetic acid and concentrated hydrochloric acid under an elevated hydrogen pressure. A weighed sample of KReO_4 (0.245 g, 0.85 mmol) was dissolved in a CH_3COOH – HCl (2 : 1 vol/vol) mixture. A quartz container with the reaction mixture was placed in a steel autoclave in which a hydrogen pressure of ~3 MPa was created. The autoclave was heated to 300°C and stored at this temperature for 4 h; the pressure in the autoclave increased to 59 MPa. The resulting brown-green reaction solution was filtered, and DMAA (1–2 ml) was immediately added, bringing about the equilibrium shift [4] toward

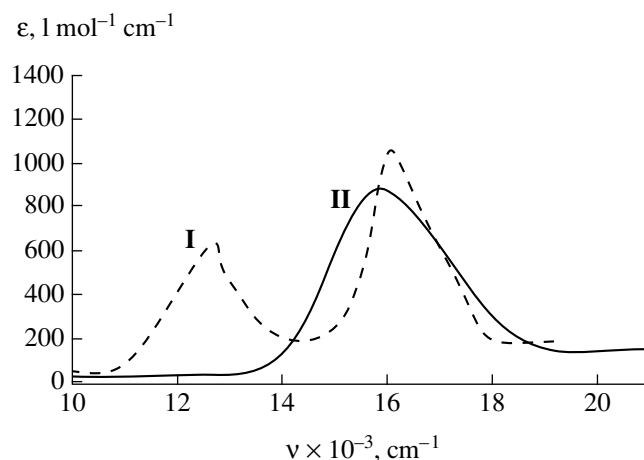


Fig. 1. Electronic absorption spectra of acetonitrile solutions of I and II.

the formation of complex **II**, which precipitated as well-faceted dark green crystals (0.299 g, 0.37 mmol). The high yield of the target product was achieved by optimization of the autoclave synthesis parameters according to [4, 5], upon changing the composition of the starting mixture of acids and by varying the heating temperature and time.

The product isolated is stable in air and well soluble in polar organic solvents, water, and inorganic acids. In an aqueous solution, complex **II** is slowly hydrolyzed with cleavage of the metal–metal bond and formation of the hydrated rhenium dioxide. When boiling in acetic acid, the substance under study is transformed into dirhenium(III) dichlorotetra- μ -acetate, while heating in hydrochloric acid produces dirhenium(III) octachloride $[\text{Re}_2\text{Cl}_8]^{2-}$. To isolate the latter in ~100% yield, the reaction mixture should contain a bulky organic cation.

Heating of complex **II** in an inert atmosphere or in vacuum results in the formation of volatile product **I**, which was identified using the data of electronic spectroscopy [2]. The electronic absorption spectra of solutions of complexes **I** and **II** are presented in Fig. 1. The spectral patterns of both substances are characterized by an absorption band attributed to the $\delta \rightarrow \delta^*$ electron transition [6] at 15 873 cm^{-1} for **II** and a doublet at 12 500 and 16 129 cm^{-1} for **I**.

X-ray Diffraction Analysis

The low-temperature (200 K) measurement from a needle-like crystal ($0.38 \times 0.095 \times 0.043$ mm in size) was carried out on a Stoe IPDS diffractometer (MoK_α radiation) equipped with an image plate detector. The lattice parameters at 293 K were determined from preliminary measurements. The crystallographic data, details of recording [7], and structure refinements [8] are presented in Table 1.

In the φ 0° – 180° range, 300 oscillation patterns with 3-min exposure were obtained. The distance from the crystal to the detector was 60 mm. The data were corrected for the Lorentz and polarization effects, and a numerical correction for absorption was applied (12 faces, $\mu = 11.1 \text{ mm}^{-1}$, $T_{\text{min/max}} = 0.3214/0.7072$). The unit cell parameters were refined by the least-squares method using angular parameters of 8000 reflections in the angle interval $4.8^\circ < 2\theta < 56.0^\circ$. No changes in the average intensity of reflections were observed during recording.

Systematic extinctions correspond to space groups $C2/c$ and Cc . The structure was solved by the direct methods (SHELXS97 [8]) in space group $C2/c$, and light atoms were found from the subsequent Fourier syntheses. Hydrogen atoms of the methyl groups were localized from the difference Fourier syntheses, and their positions were refined in the rider model with the isotropic temperature factors (equal to 1.5U) of the carbon atom bound to the H atom under study. The full-matrix least-squares refinement against F^2 was per-

Table 1. Crystallographic data and details of data collection for complex **II**

Parameter	Value
Formula	$\text{C}_6\text{H}_{12}\text{Cl}_2\text{NO}_3\text{Re}$
M	403.265
Crystal system, space group	Monoclinic, $C2/c$
Unit cell parameters at 200/293 K:	
a , Å	29.422(1)/29.623(7)
b , Å	10.9580(6)/11.015(3)
c , Å	14.2470(5)/14.378(3)
β , deg	97.560(5)/97.59(3)
V , Å ³	4553.4(4)/4650(2)
Z , $\rho(\text{calcd})$, g/cm^3	16, 2.353
$F(000)$	3008
$2\theta_{\text{max}}$, deg	55.94
Range of indices	$-38 \leq h \leq 38$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$
Number of reflections collected/independent ($I > 2\sigma(I)$)	19573/5146
Number of refined parameters	243
R -factors ($I > 2\sigma(I)$)	$R_1 = 0.0241$, $wR_2 = 0.0482$
R -factors (all data)	$R_1 = 0.0394$, $wR_2 = 0.0499$
GOOF against F^2 , weighing scheme	0.840, $w = [\sigma^2(F_o^2) + (0.024F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\text{max}}$	0.038
$\Delta\rho(\text{max})$, $\Delta\rho(\text{min})$, $e \text{ Å}^{-3}$	2.38 (0.8 Å from the Re(2) atom), –1.19

Table 2. Coordinates and thermal parameters of atoms in structure **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}}(U_{\text{iso}}), \text{\AA}^2$
Re(1)	0.143378(6)	0.53847(2)	0.08949(1)	0.02631(5)
Re(2)	0.117817(7)	0.73136(2)	0.07925(2)	0.03438(6)
Cl(1)	0.21062(4)	0.5531(1)	0.1923(1)	0.0366(3)
Cl(2)	0.17344(5)	0.8376(1)	0.1768(1)	0.0474(4)
Cl(3)	0.10508(4)	0.4512(2)	0.2054(1)	0.0392(3)
Cl(4)	0.06597(5)	0.7382(1)	0.1891(1)	0.0475(4)
O(1)	0.1804(1)	0.5727(3)	−0.0204(3)	0.0353(8)
O(2)	0.1551(1)	0.7628(3)	−0.0301(3)	0.046(1)
O(3)	0.0892(1)	0.4883(3)	−0.0101(3)	0.0344(8)
O(4)	0.0647(1)	0.6793(3)	−0.0210(3)	0.0417(9)
O(5)	0.1662(1)	0.3428(3)	0.0593(3)	0.0406(9)
O(6)	0.0890(2)	0.9181(4)	0.0221(4)	0.082(2)
N(1)	0.1961(1)	0.1698(4)	0.0130(3)	0.035(1)
N(2)	0.0558(2)	1.0918(5)	−0.0205(6)	0.077(2)
C(1)	0.1788(2)	0.6778(5)	−0.0595(4)	0.039(1)
C(2)	0.2054(2)	0.7009(6)	−0.1394(5)	0.054(2)
H(2A)	0.1954	0.778	−0.170	0.08
H(2B)	0.2003	0.634	−0.185	0.08
H(2C)	0.2381	0.706	−0.115	0.08
C(3)	0.0612(2)	0.5680(5)	−0.0466(4)	0.038(1)
C(4)	0.0239(2)	0.5305(6)	−0.1232(4)	0.0491(2)
H(4A)	0.009	0.603	−0.153	0.07
H(4B)	0.001	0.481	−0.096	0.07
H(4C)	0.037	0.483	−0.171	0.07
C(5)	0.1510(2)	0.2960(5)	−0.1061(4)	0.045(1)
H(5A)	0.133	0.372	−0.108	0.07
H(5B)	0.131	0.229	−0.129	0.07
H(5C)	0.175	0.304	−0.146	0.07
C(6)	0.1715(2)	0.2706(4)	−0.0068(4)	0.031(1)
C(7)	0.2176(2)	0.1480(5)	0.1107(5)	0.049(2)
H(7A)	0.221	0.226	0.145	0.07
H(7B)	0.248	0.111	0.110	0.07
H(7C)	0.198	0.093	0.142	0.07
C(8)	0.2013(2)	0.0748(6)	−0.0558(5)	0.057(2)
H(8A)	0.182	0.093	−0.115	0.09
H(8B)	0.192	−0.004	−0.031	0.09
H(8C)	0.233	0.071	−0.067	0.09
C(9)	0.0891(3)	1.0822(8)	0.1374(6)	0.078(2)
H(9A)	0.061	1.106	0.162	0.12
H(9B)	0.108	1.154	0.133	0.12
H(9C)	0.106	1.023	0.180	0.12
C(10)	0.0767(3)	1.0221(6)	0.0341(7)	0.081(3)
C(11)	0.0401(3)	1.2145(6)	−0.0130(8)	0.089(3)
H(11A)	0.008	1.214	−0.001	0.13
H(11B)	0.042	1.258	−0.072	0.13
H(11C)	0.059	1.256	0.039	0.13
C(12)	0.0427(3)	1.0321(8)	−0.1212(6)	0.086(3)
H(12A)	0.058	0.952	−0.123	0.13
H(12B)	0.053	1.085	−0.170	0.13
H(12C)	0.009	1.022	−0.134	0.13

formed in the anisotropic approximation for all non-hydrogen atoms using the SHELXL97 program [8]. The structural data were tested with the PLATON 2002 program [9], revealing the absence of higher crystal symmetry or additional symmetry elements. No cavities that could be occupied by solvent molecules were found.

The coordinates of atoms and their temperature factors for structure **II** are presented in Table 2. The interatomic distances and bond angles are presented in Table 3.

RESULTS AND DISCUSSION

Complex **II** is characterized by *cis*-arrangement of the bridging acetate and terminal chloride ligands with respect to the quadruple-bonded Re_2^{6+} complex-forming center (Fig. 2). The framework of the complex possesses a mirror pseudoplane, whereas two independent DMAA molecules are linked by the inversion pseudo-center localized between the rhenium atoms.

The Re–Re bond length is 2.2418(3) Å. The axial positions of the rhenium polyhedra are occupied by the oxygen atoms of the DMAA molecules (Re–O_{ax} 2.304(3) and 2.321(4) Å). The complex molecule is characterized by the completely screened conformation of equatorial ligands (Fig. 3); the Cl–Re–Re–Cl torsion angles involving *cis*-Cl atoms are 0.33(6)° and 0.78(5)°. The oxygen atoms of the axial DMAA molecules are shifted from the axis of the Re–Re bond, and the ReReO_{ax} angles are 165.6(1)° and 163.3(1)°. Both organic molecules are shifted from the axis of the Re–Re bond toward the carboxylate bridges to form a hindered conformation: the O_{eq}–Re–Re–O_{ax} torsion angles lie within 42.6(4)°–44.8(4)°, and the O(5)–Re(1)–Re(2)–O(6) angle is equal to 0.8(7)°. The ReO_{ax}C angles in the amide group are nonlinear (142.7(3)° and 151.6(6)°). The angles between the planes of non-hydrogen atoms of the carboxylate groups and DMAA molecules vary within 28.8(3)°–55.8(2)°. The angle between the conjugation planes of the organic molecules is 9.1(3)°. The absence of a rigidly linear axial ligand indicates a substantial role of weak interactions in the complex structure. The characteristics of the most important intra- and intermolecular hydrogen contacts in structure **II** are presented in Table 4.

As has already been mentioned in [3], a necessary condition for the *cis*–*trans* isomerization and formation of a volatile rhenium compound by the thermal decomposition of *cis*-[Re₂(CH₃COO)₂Cl₄L₂] is the preliminary removal of the axial substituent, i.e., the cleavage of the Re–L bond. The published data [11–13] for the *cis*-[Re₂(CH₃COO)₂Cl₄L₂] complexes (**II**, **III**–**V**) (Table 5) indicate the following tendency: the Re–O_{ax} bond length decreases and the Re–Re bond length increases with an enhancement of the donor ability of the axial ligand. For example, the Re–O_{ax} bond length in hydrate **III** is maximum and equals 2.50 Å, whereas

Table 3. Bond lengths and bond angles in structure **II**

Bond	<i>d</i> , Å	Angle	ω, deg
Re(1)–Re(2)	2.2418(3)	O(1)Re(1)O(3)	87.9(1)
Re(1)–Cl(1)	2.307(1)	O(1)Re(1)O(5)	80.3(1)
Re(1)–Cl(3)	2.324(1)	O(3)Re(1)O(5)	80.9(1)
Re(1)–O(1)	2.055(4)	O(1)Re(1)Cl(1)	88.6(1)
Re(1)–O(3)	2.065(3)	O(3)Re(1)Cl(1)	167.2(1)
Re(1)–O(5)	2.304(3)	O(5)Re(1)Cl(1)	86.40(9)
O(5)–C(6)	1.256(6)	O(1)Re(1)Cl(3)	166.2(1)
		O(3)Re(1)Cl(3)	88.6(1)
		O(5)Re(1)Cl(3)	86.0(1)
		Cl(1)Re(1)Cl(3)	91.89(5)
		Re(2)Re(1)O(5)	165.6(1)
		Re(1)O(5)C(6)	142.7(3)
Re(2)–Cl(2)	2.317(1)	O(2)Re(2)O(4)	87.3(2)
Re(2)–Cl(4)	2.325(2)	O(2)Re(2)O(6)	78.0(2)
Re(2)–O(2)	2.048(4)	O(4)Re(2)O(6)	78.0(2)
Re(2)–O(4)	2.055(3)	O(2)Re(2)Cl(2)	88.0(1)
Re(2)–O(6)	2.321(4)	O(4)Re(2)Cl(2)	165.8(1)
O(6)–C(10)	1.215(8)	O(6)Re(2)Cl(2)	87.9(1)
		O(2)Re(2)Cl(4)	166.0(1)
		O(4)Re(2)Cl(4)	88.3(1)
		O(6)Re(2)Cl(4)	88.1(2)
		Cl(2)Re(2)Cl(4)	93.11(5)
		Re(1)Re(2)O(6)	163.3(1)
		Re(2)O(6)C(10)	151.6(6)

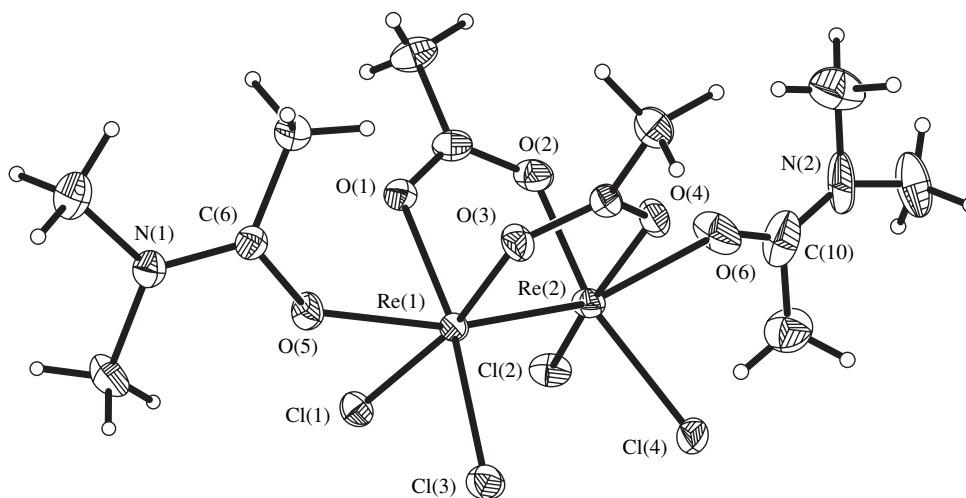


Fig. 2. Molecular structure of **II** (30% probability ellipsoids are shown).

it decreases to 2.36 Å in the derivatives with TPPO (**IV**) and DMF (**V**). This explains the most favorable (among the *cis*-[Re₂(CH₃COO)₂Cl₄L₂] complexes) thermal destruction with elimination of water molecules at 160–180°C in complex **III**.

However, the highest yield in the syntheses of the volatile rhenium compounds (80–90%) was observed

for the dirhenium *cis*-tetrachlorodi-μ-acetate complex with both H₂O (**III**) and DMAA (**II**) molecules. During heating in an inert atmosphere, these axial substituents are completely removed below the sublimation temperature and do not react on heating with the main part of the [Re₂(CH₃COO)₂Cl₄] complex. Other substituents (TPPO in **IV**, DMF in **V**) are not completely removed and partially interact on heating with the starting compound, which decreases sharply the yield (to 40–50%) of the volatile product.

It is of interest that the similar lability of the axial ligand in complexes **II** and **III** does not correlate with different donor abilities of the axial substituents and, correspondingly, with the Re–O_{ax} distances. At much higher (as compared to that of water molecules) nucleophilicity of DMAA molecules, the latter cannot form stable hydrogen bonds, which, probably, explains the unusually easy thermal destruction of complex **II**.

Table 4. Characteristics of hydrogen bonds in structure **II**

D–H...A	Distance, Å			D–H...A, angle, deg
	D–H	H...A	D...A	
C(11)–H(11A)...O(4) ⁱ	0.96	2.51	3.389	152
C(2)–H(2B)...Cl(1) ⁱⁱ	0.96	2.75	3.691	165
C(5)–H(5A)...O(3)	0.96	2.41	3.205	140
C(7)–H(7A)...O(5)	0.96	2.29	2.663	102
C(12)–H(12A)...O(6)	0.96	2.18	2.618	106

Note: Symmetry operators: ⁱ $-x, -y, 1-z$; ⁱⁱ $x, 1-y, -1/2+z$.

Table 5. Main bond lengths (Å) for some dirhenium(III) chloroacetates and donor numbers (DN_{SbCl_5}) according to Gutman [10] for axial substituents

Compound	Re–Re	Re–O _{ax}	DN_{SbCl_5}	References
[Re ₂ (CH ₃ COO) ₂ Cl ₄ (H ₂ O) ₂] (III)	2.224(2)	2.50(2) 2.51(2)	18.0	[11]
[Re ₂ (CH ₃ COO) ₂ Cl ₄ (TPPO) ₂] (IV)	2.236(2)	2.36(2)	23	[12]
[Re ₂ (CH ₃ COO) ₂ Cl ₄ (DMF) ₂] (V)	2.239(2)	2.36(2) 2.35(2)	26.6	[13]
[Re ₂ (CH ₃ COO) ₂ Cl ₄ (DMAA) ₂] (II)	2.2418(3)	2.304(3) 2.321(4)	27.8	This work

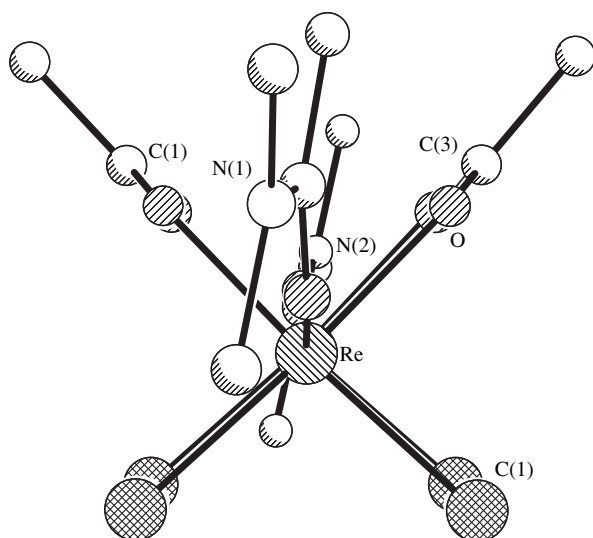


Fig. 3. Projection of binuclear complex **II** along the Re–Re bond (hydrogen atoms are not shown).

REFERENCES

1. *Vapor Phase Deposition*, Powell, K., Ed., New York: Wiley, 1968.
2. Shtemenko, A.V., Bovykin, B.A., Shram, V.P., *et al.*, *Zh. Neorg. Khim.*, 1985, vol. 30, no. 12, p. 3085.
3. Shtemenko, A.V., Matrosov, A.S., and Tikhonov, V.I., *Vopr. Khim. Khim. Tekhnol.*, 2000, no. 2, p. 24.
4. Golovaneva, I.F., Bovykin, B.A., Shtemenko, A.V., *et al.*, *Zh. Neorg. Khim.*, 1987, vol. 32, no. 2, p. 387.
5. Shtemenko, A.V., Kotel'nikova, A.S., Bovykin, B.A., and Golovaneva, I.F., *Zh. Neorg. Khim.*, 1986, vol. 31, no. 2, p. 399.
6. Shtemenko, A.V., Golichenko, A.A., and Kozhura, O.V., *Vopr. Khim. Khim. Tekhnol.*, 2000, no. 2, p. 21.
7. Stoe & Cie, *X-RED (Version 1.19) and IPDS Software (Version 2.92)*, Darmstadt (Germany): Stoe & Cie, 1999.
8. Sheldrick, G.M., *SHELXS97 and SHELXL97. Programs for the Solution and Refinement of Crystal Structures*, Gottingen (Germany): Univ. of Gottingen, 1997.
9. Spek, A.L., *PLATON99. Multipurpose Crystallographic Tool*, Utrecht (Netherlands): Univ. of Utrecht, 2002.
10. Gutman, V., *Coordination Chemistry in Non-Aqueous Solutions*, Vienna: Springer, 1968.
11. Koz'min, P.A., Surazhskaya, M.D., and Kuznetsov, V.G., *Zh. Strukt. Khim.*, 1970, vol. 11, no. 2, p. 313.
12. Kotel'nikova, A.S., Misailova, T.V., Koz'min, P.A., *et al.*, *Koord. Khim.*, 1977, vol. 3, no. 1, p. 127.
13. Surazhskaya, M.D., Larina, T.B., Koz'min, P.A., *et al.*, *Koord. Khim.*, 1978, vol. 4, no. 9, p. 1430.