Binuclear and polynuclear transition metal complexes with macrocyclic ligands

5.* Novel complexes of asymmetric polydentate macrocyclic Schiff bases. Step-by-step synthesis

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Reactions of 2,6-bis(3-aminopropylaminocarbonyl)pyridine (**1**) with 4-*tert*-butyl-2,6-diformylphenol and 2,5-diformylpyrrole in the presence of $Ba(ClO_4)_2$ in EtOH afford barium complexes with asymmetric macrocyclic Schiff bases as soft and hard ligands. The reaction of compound **1** with $Cu(OCOCMe_3)_2$ involves closure of a tetrahydropyrimidine ring to give a mononuclear complex, which was structurally characterized by X-ray diffraction analysis.

Key words: complexes with macrocyclic ligands, X-ray diffraction analysis, NMR spectroscopy.

Our theoretical DFT study of binuclear complexes of transition metals with macrocyclic ligands showed[2] that some complexes of this type can bind to small low-reactivity molecules (H_2, O_2, CO, CO_2, CH_4, and $CH_2{=}CH_2$), activating them for further chemical conversions. Thus, they simulate the functions of active sites in some metal enzymes and are of considerable interest as potential components for novel catalytic systems. According to the theoretical analysis,[2] catalytically most active complexes meet the following requirements: (1) the cavity of its macrocyclic ligand should contain two different (electron-deficient early and electron-donor late) transition metals spaced at such a distance and mutually oriented in such a way to ensure their coherent effect on a substrate; (2) serving as an electron reservoir, the macrocyclic ligand should flexibly adjust the electron distribution by increasing or decreasing the electron density at each metal center as the system follows a particular reaction pathway; and (3) the geometry of the macrocyclic ligand should be adaptable to variations in the distance between the metals as a result of binding and transformations of substrates.

Selective and efficient binding of two dissimilar metal ions requires "soft" asymmetric macrocyclic ligands for a late transition metal ion and "hard" ones for an early transition metal ion. Several ligands of this type were described;[3] however, no general approaches to their synthesis have been developed to date. Known heterobinuclear complexes of transition metals with conjugated macrocyclic ligands are also few[4] and mostly contain symmetrical macrocycles. Methods for the template synthesis starting directly from dicarbonyl compounds and diamines, which are very effective in the assembly of symmetric macrocyclic Schiff bases and their complexes, are unsuitable for the preparation of asymmetric systems. In this situation, the following alternative approach seems to be most reasonable. Enlarged precursor units formed at the first step are then made to undergo closure into a macrocycle of the desired structure. Acyclic products of [1+1], [1+2], and [2+1] condensation of dicarbonyl compounds with diamines can be used as such units. A considerable number of such compounds were described;[5] some of them were synthesized by us earlier.[6]

A convenient precursor for the synthesis of asymmetric macrocycles by condensation with dicarbonyl compounds is the polydentate ligand **1**, which is prepared in quantitative yield[7] by the reaction of dimethyl pyridine-2,6-dicarboxylate with a tenfold excess (in equiv.) of 1,3-diaminopropane (Scheme 1).

Earlier,[7] ligand **1** was used to obtain two asymmetric mononuclear complexes **2** (Scheme 2).

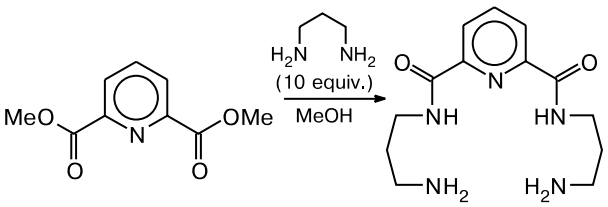
The coordination properties of compound **1** were not studied comprehensively; its mononuclear complex with

* For Part 4, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 326—331, February, 2004.

1066-5285/04/5302-0340

Scheme 1



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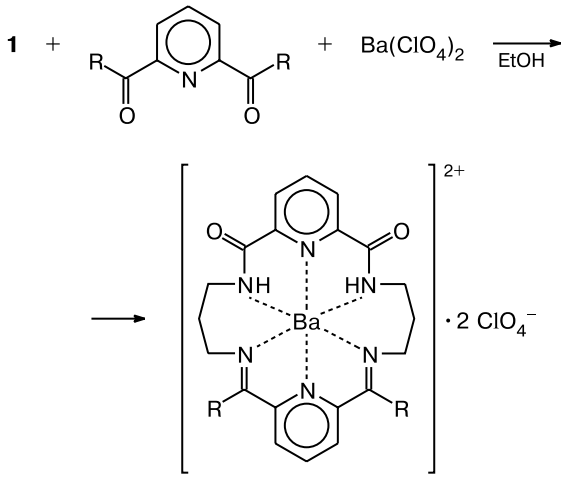
Scheme 2



2

R = H, Me

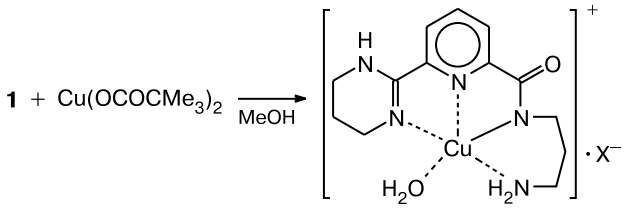
$Ni(ClO_4)_2$ (1 equiv.) is known only. In this complex, four N atoms are coordinated by the Ni atom in the cavity of the organic ligand, while the noncoordinated amino group makes an angle with the pyridine ring plane, being distant by >4 Å from the Ni atom (X-ray diffraction data).[7]

We found that compound **1** reacts with $Cu(OCOCMe_3)_2$ (2 equiv.) in MeOH to give a mononuclear complex of the corresponding pyrimidine **3a** as the result of intramolecular cyclization (Scheme 3). The structure of the complex was determined by MALDI-TOF* mass spectrometry and IR spectroscopy. Recrystallization of this complex from EtOH—THF—$CHCl_3$ results in anion exchange to give chloride **3b**.

The structure of complex **3b** was determined by X-ray diffraction analysis. The crystallographic data for complex **3b** are given in Table 1; the selected bond lengths and angles are listed in Table 2. Structure **3b** is built from complex cations and chloride anions linked in the crystal

* Matrix-assisted laser desorption ionization time-of-flight mass spectrometry.

Scheme 3



3a,b

X = Me_3CCO_2 (**a**), Cl (**b**)

by hydrogen bonds (Table 3) and interionic interactions. The structure of the complex cation is shown in Fig. 1. The coordination polyhedron of the Cu atom is a distorted square pyramid with four N atoms in its base (Cu—N 1.955(7) to 2.017(8) Å) and an apical water molecule (Cu—O 2.482(8) Å). The Cu atom and the water O atom are distant from the pyramid base of the four N atoms by 0.16 and 2.61 Å, respectively. The coordination bonds of copper with the N atoms form a system of conjugated rings, three of them being planar (two central five-membered and pyridine ones); the atoms of all the three rings are also virtually coplanar. The six-membered chelate ring exists in an envelope conformation with the C(12) atom deviating by 0.73 Å from the plane of the other five atoms. The tetrahydropyrimidine ring adopts a *gauche*-conformation, in which the C(2) and C(3) atoms deviate in opposite directions from the plane of the other four atoms (by 0.49 and 0.19 Å, respectively).

Table 1. Crystallographic parameters and a summary of data collection for complex **3b**

Parameter	Value
Molecular formula	$C_{13}H_{20}ClCuN_5O_2$
Space group	$P2(1)/c$
a/Å	12.17(4)
b/Å	16.59(5)
c/Å	7.921(19)
α/deg	90
β/deg	102.08(8)
γ/deg	90
V/Å^3	1563(8)
Z	4
d_{calc}/g cm^{-3}	1.603
Absorption factor/cm^{-1}	1.582
θ range/deg	1.71—32.05
Ranges of h, k, l indices	$-17 \le h \le 16$, $-9 \le k \le 23$, $-9 \le l \le 10$
Number of independent reflections	3063 ($R_{int} = 0.0938$)
GOOF (on F^2)	1.013
R ($I > 2\sigma(I)$)	$R_1 = 0.0781$, $wR_2 = 0.1986$
R (for all reflections)	$R_1 = 0.0967$, $wR_2 = 0.2044$

Table 2. Selected bond lengths (d) and angles (ω) in complex **3b**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Cu(1)—N(3)	1.955(7)	N(3)—Cu(1)—N(4)	80.4(3)	N(1)—C(4)—C(5)	115.6(5)
Cu(1)—N(4)	1.974(7)	N(3)—Cu(1)—N(5)	167.3(2)	N(2)—C(4)—C(5)	119.0(5)
Cu(1)—N(5)	2.003(6)	N(4)—Cu(1)—N(5)	98.8(2)	N(3)—C(5)—C(6)	120.0(5)
Cu(1)—N(1)	2.017(8)	N(3)—Cu(1)—N(1)	79.4(2)	N(3)—C(5)—C(4)	110.5(5)
Cu(1)—O(2W)	2.482(8)	N(4)—Cu(1)—N(1)	159.5(2)	C(6)—C(5)—C(4)	129.5(6)
O(1)—C(10)	1.265(8)	N(5)—Cu(1)—N(1)	100.0(2)	C(7)—C(6)—C(5)	118.6(6)
N(1)—C(4)	1.318(8)	N(3)—Cu(1)—O(2W)	104.4(3)	C(6)—C(7)—C(8)	120.0(6)
N(1)—C(1)	1.478(8)	N(4)—Cu(1)—O(2W)	98.4(2)	C(7)—C(8)—C(9)	118.9(6)
N(2)—C(4)	1.333(8)	N(5)—Cu(1)—O(2W)	88.2(3)	N(3)—C(9)—C(8)	119.4(6)
N(2)—C(3)	1.475(8)	N(1)—Cu(1)—O(2W)	90.2(2)	N(3)—C(9)—C(10)	112.1(6)
N(3)—C(5)	1.330(8)	C(4)—N(1)—C(1)	119.1(5)	C(8)—C(9)—C(10)	128.3(6)
N(3)—C(9)	1.338(8)	C(4)—N(1)—Cu(1)	114.9(4)	O(1)—C(10)—N(4)	128.2(6)
N(4)—C(10)	1.324(8)	C(1)—N(1)—Cu(1)	125.7(4)	O(1)—C(10)—C(9)	119.0(6)
N(4)—C(11)	1.464(8)	C(4)—N(2)—C(3)	120.2(5)	N(4)—C(10)—C(9)	112.8(5)
N(5)—C(13)	1.510(9)	C(5)—N(3)—C(9)	122.7(5)	N(4)—C(11)—C(12)	111.6(5)
C(1)—C(2)	1.531(9)	C(5)—N(3)—Cu(1)	119.6(4)	C(13)—C(12)—C(11)	114.6(6)
C(2)—C(3)	1.516(9)	C(9)—N(3)—Cu(1)	117.6(4)	N(5)—C(13)—C(12)	112.5(6)
C(4)—C(5)	1.502(9)	C(10)—N(4)—C(11)	116.8(5)		
C(5)—C(6)	1.388(9)	C(10)—N(4)—Cu(1)	117.1(4)		
C(6)—C(7)	1.383(10)	C(11)—N(4)—Cu(1)	126.1(4)		
C(7)—C(8)	1.385(10)	C(13)—N(5)—Cu(1)	115.9(4)		
C(8)—C(9)	1.387(9)	N(1)—C(1)—C(2)	113.6(5)		
C(9)—C(10)	1.520(9)	C(3)—C(2)—C(1)	109.8(6)		
C(11)—C(12)	1.523(10)	N(2)—C(3)—C(2)	109.4(5)		
C(12)—C(13)	1.519(10)	N(1)—C(4)—N(2)	125.5(6)		

Table 3. Parameters of the D—H...A hydrogen bonds in compound **3b** (D and A denote donor and acceptor, respectively)

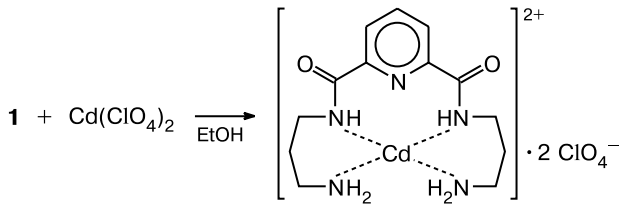
Bond	D—H	H...A	Angle DHA/deg	D...A	A
	Å			/Å	
O(2W)—H(2WA)	0.820	2.511	167.15	3.315	Cl(1)[a]
O(2W)—H(2WB)	0.610	—	—	—	—
N(2)—H(2A)	0.860	1.958	160.37	2.783	O(1)[b]
N(5)—H(5A)	0.900	2.456	176.00	3.355	Cl(1)[a]
N(5)—H(5B)	0.900	2.519	169.04	3.407	Cl(1)[c]

[a] Symmetry operation is $-x, -y, -z + 1$.
[b] Symmetry operation is $-x + 1, y - 1/2, -z + 3/2$.
[c] Symmetry operation is $x, y, z + 1$.

Condensation of compound **1** with 4-*tert*-butyl-2,6-diformylphenol in the presence of $Cd(ClO_4)_2$ afforded only mononuclear complex **4** in 63% yield (Scheme 4); being virtually insoluble in organic solvents, complex **4** immediately leaves the reaction zone and undergoes no further conversions.

Yet the desired condensation for the synthesis of an asymmetric macrocycle was carried out in the presence of barium ions. Diamide **1** reacts with 4-*tert*-butyl-2,6-diformylphenol in boiling EtOH in the presence of $Ba(ClO_4)_2$ to give barium complex **5** in 90% yield

Scheme 4



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(Scheme 5). Under analogous conditions, 2,5-diformylpyrrole affords complex **6** in 48% yield.

Complexes **5** and **6** were isolated as yellow powders insoluble in water and nonpolar organic solvents but moderately soluble in polar solvating solvents such as DMF or DMSO. The structures of complexes **5** and **6** were studied by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF and ESI* mass spectrometry, and IR spectroscopy and confirmed by elemental analysis data.

The MALDI-TOF mass spectrum of complex **5** contains the $[M - ClO_4]$ peak with m/z 588.4 (I_{rel} = ~10%). Partial loss of the counterion was observed in the ESI mass spectrum of complex **6** upon its fragmentation; the

* Electrospray ionization.

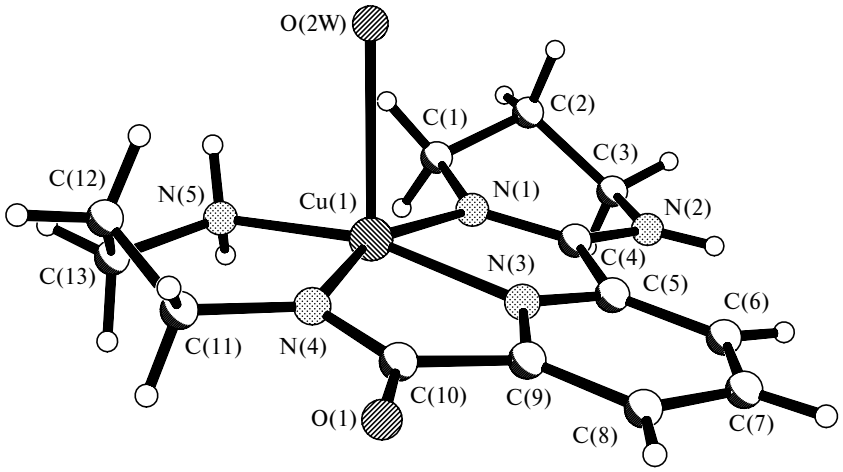
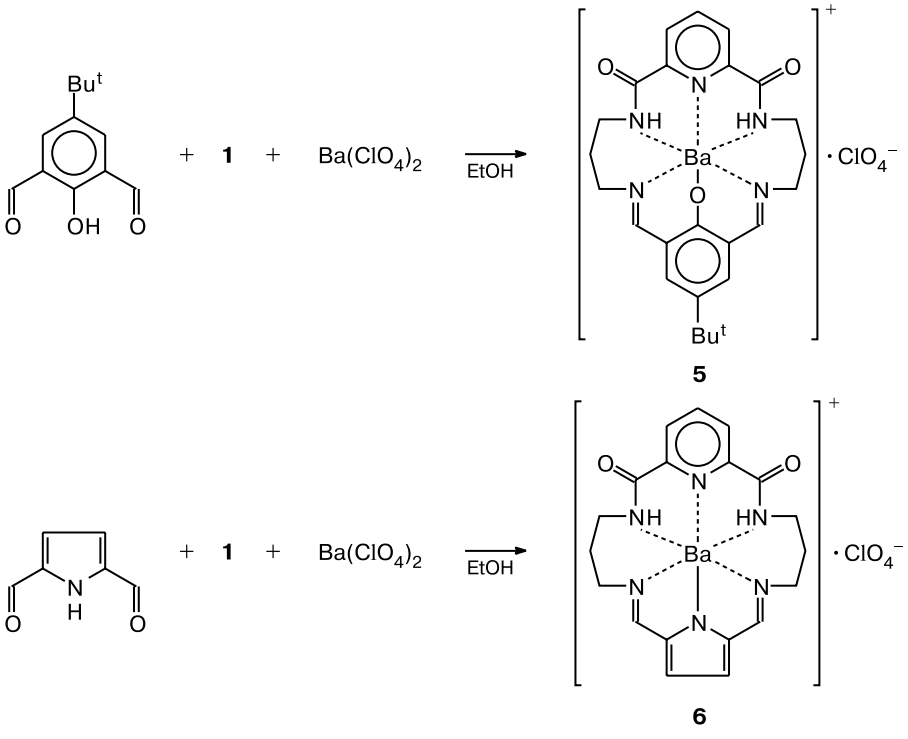


Fig. 1. Structure of the mononuclear complex **3b** (according to X-ray diffraction data).

spectrum shows a peak with m/z 1099.6 (I_{rel} = 15%) corresponding to the dimeric mononuclear complex with one counterion. Complete or partial loss of the counterions during fragmentation is characteristic of all transition metal complexes with macrocyclic Schiff bases, irrespective of the ionization technique; it was observed by us earlier for similar systems.[8] However, the molecular ions of complexes **5** and **6** are mainly demetalated to give free macrocyclic ligand ions. The peaks of these ions (m/z 450.5 for **5** and m/z 367.2 for **6**) are most intense in both ESI and MALDI-TOF techniques. The ESI mass spectra of complexes **5** and **6** show rather intense (>40%) peaks for dimers of free asymmetric macrocycles, which were not observed previously for any of the investigated symmetrical macrocyclic Schiff bases or their complexes with transition metals.

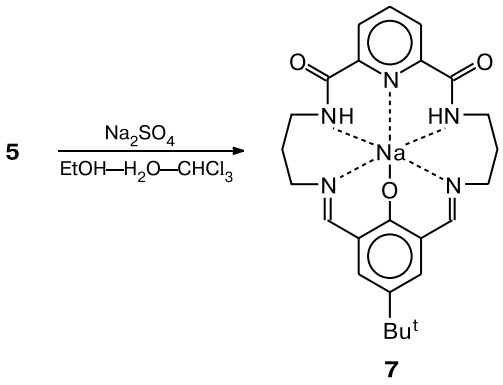
The barium ion is displaced from complex **5** by treating its suspension in EtOH with aqueous Na_2SO_4 to give a yellow sodium salt of asymmetric macrocyclic Schiff base **7** (Scheme 6). Unlike complex **5**, this salt is well soluble in

Scheme 5



water and thus is difficult to extract from aqueous solutions. The macrocyclic ligand entraps a sodium ion like a crown ether or cryptand, which makes base **7** perfectly soluble in polar organic solvents and moderately soluble in benzene and even colorize light petroleum. The sodium ion in complex **7** can be very easily replaced by transition metal ions. We obtained copper, nickel, and cobalt complexes, the structures and properties of which will be reported elsewhere.

Scheme 6



7

Hence, we synthesized barium and sodium complexes **5**—**7** with new asymmetric polydentate macrocyclic ligands, which open an attractive route to heterobinuclear complexes of transition metals.

Experimental

NMR spectra were recorded on a Bruker DPX-300 instrument at 24 °C. IR spectra were recorded on Specord M80 (KBr pellets) and UR-2 spectrometers (Nujol). MALDI-TOF mass spectra were recorded on a Bruker Reflex 3 instrument in the positive ion mode (UV laser at $\lambda = 337$ nm); ESI mass spectra were recorded on a Finnigan MAT LCQ instrument. Unless otherwise specified, Aldrich chemicals were used.

Synthesis of complexes 3a,b. A solution of compound **1** (279 mg, 1 mmol) and $[Cu(OCOCMe_3)_2]_2(EtOH)_2$ [9] (266 mg, 1 mmol) in 20 mL of MeOH was refluxed for 2 h. On cooling, the solution was concentrated to 1.5—2 mL, and water (2 mL) was added. The precipitate of $Cu(OCOCMe_3)_2$ that formed was filtered off, the filtrate was evaporated to dryness, and the residue was recrystallized from a mixture of 95% EtOH (1.5 mL) and THF (5 mL) to give **[6-(3-aminopropylaminocarbonyl)-2-(3,4,5,6-tetrahydropyrimidin-2-yl)pyridino]copper trimethylacetate (3a)** (358 mg, 78%). MALDI-TOF MS, *m/z*: 261.7 $[L + H]^+$, 323.7 $[LCu]^+$. Crystals of **[6-(3-aminopropylaminocarbonyl)-2-(3,4,5,6-tetrahydropyrimidin-2-yl)pyridino]copper chloride (3b)** for X-ray diffraction analysis were obtained by the recrystallization of compound **3a** from 95% EtOH—THF in the presence of $CHCl_3$.

[2,6-Bis(3-aminopropylaminocarbonyl)pyridino-*N*,*N*′,*N*″,*N*‴]cadmium(II) diperchlorate (4). A solution of compound **1** (391 mg, 1.4 mmol) in 30 mL of anhydrous EtOH was added to a solution of $Cd(ClO_4)_2 \cdot 4H_2O$ (536.2 mg, 1.4 mmol) in 70 mL of anhydrous EtOH. The reaction mixture containing a yellow precipitate was refluxed for 2 h. Filtration of the hot solution gave complex **4** (279.7 mg). On cooling, an additional amount (239.7 mg) of this complex was filtered off. The total yield of **4** was 519.4 mg (63%). ^{1}H NMR (DMF-d_7), δ: 1.80 (br.m, 4 H, 2 CH_2); 3.83, 4.30 (both m, 4 H each, 4 CH_2); 8.00 (m, 3 H, 3 CH). ^{13}C NMR (DMF-d_7), δ: 28.6, 36.8, 38.3, 125.2, 140.4, 149.3, 164.9. IR (KBr), ν/cm^{-1}: 625, 1100 (ClO_4), 1650 (C=O), 2960 (CH), 3360 (NH).

[11-*tert*-Butyl-26-hydroxy-2,20-dioxo-3,7,15,19,25-pentaazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),7,9,11,13(26),14,21,23-octaeno]barium perchlorate (5). 4-*tert*-Butyl-2,6-diformylphenol[10] (420 mg, 2 mmol) was dissolved in 20 mL of hot anhydrous EtOH. To the solution, solid $Ba(ClO_4)_2 \cdot 3H_2O$ [11] (800 mg, 2 mmol) and a solution of compound **1** (560 mg, 2 mmol) in 50 mL of anhydrous EtOH were added. The reaction mixture was refluxed for 2 h. The precipitate that formed was separated by filtering the hot solution. An additional amount of the complex was filtered off from the cooled mother liquor. The yield of **5** was 1.219 g (90%), m.p. >350 °C. ^{1}H NMR (DMSO-d_6), δ: 1.20 (s, 9 H, 3 Me); 1.94 (br.q, 4 H, 2 CH_2, J = 4.8 Hz); 3.64 (br.q, 8 H, 4 CH_2, J = 5.7 Hz); 7.61 (s, 2 H, 2 CH); 8.08 (m, 3 H, 3 CH); 8.54 (s, 2 H, 2 CH=N); 9.32 (br.s, 2 H, 2 NH). ^{13}C NMR (DMSO-d_6), δ: 30.7, 31.7, 33.7, 37.1, 57.3, 120.5, 124.0, 128.5, 139.2, 139.8, 148.6, 159.4, 161.3, 163.1. Found (%): C, 43.50; H, 4.23; N, 10.27. $C_{25}H_{30}BaClN_5O_7$. Calculated (%): C, 43.82; H, 4.41; N, 10.22. MALDI-TOF MS, *m/z*: 451.3 $[L + 2H]^+$, 588.4 $[LBa + 3H]^+$, 899.4 $[2L + H]^+$. ESI MS, *m/z*: 450.5 $[L + H]^+$, 899.4 $[2L + H]^+$. IR (KBr), ν/cm^{-1}: 650, 1100 (ClO_4), 1700 (C=O), 2950 (CH), 3360 (NH).

[2,19-Dioxo-3,7,14,18,24,25-hexaazatricyclo[18.3.1.1^{9,12}]pentacosa-1(24),7,9,11,13,20,22-heptaeno]barium perchlorate (6) was obtained analogously from 2,5-diformylpyrrole (250 mg, 2 mmol). The yield of **6** was 423 mg (48%), m.p. >350 °C. ^{1}H NMR (DMF-d_7), δ: 1.95 (m, 4 H, 2 CH_2); 3.53, 3.62 (both q, 4 H each, 4 CH_2, J = 5.7 Hz); 6.57 (s, 2 H, 2 CH); 8.20 (m, 3 H, 3 CH); 9.23 (br.s, 2 H, 2 NH). ^{13}C NMR (DMF-d_7), δ: 31.5, 38.1, 58.7, 114.3, 124.8, 133.7, 139.8, 150.0, 152.8, 164.4. MALDI-TOF MS, *m/z*: 727.2 $[2L - 3H]^+$, 733.2 $[2L + 2H]^+$. ESI MS, *m/z*: 367.2 $[L + 2H]^+$, 733.4 $[2L + 2H]^+$, 1099.6 $[2(LBa)ClO_4 - 4H]^+$. IR (KBr), ν/cm^{-1}: 665, 1100 (ClO_4), 1700 (C=O), 2925 (CH), 3350 (NH).

[11-*tert*-Butyl-26-hydroxy-2,20-dioxo-3,7,15,19,25-pentaazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),7,9,11,13(26),14,21,23-octaeno]sodium (7). A suspension of complex **5** (100 mg, 0.15 mmol) in 75 mL of 95% EtOH was treated with a solution of Na_2SO_4 (213 mg, 1.5 mmol) in 25 mL of water. The resulting solution contained some precipitate. The product was extracted with $CHCl_3$ (75 mL). The organic layer was separated, dried over K_2CO_3, and evaporated to dryness. The yield of **7** was 7.6 mg (10%). Found (%): C, 62.54; H, 7.17; N, 13.27. $C_{25}H_{30}N_5NaO_3 \cdot C_2H_6O$. Calculated (%): C, 62.65; H, 7.01; N, 13.53. ESI MS, *m/z*: 450.3 $[L + H]^+$.

X-ray diffraction analysis of complex 3b. The X-ray diffraction experiment for complex **3b** followed a standard procedure[12] with a Bruker AXS SMART 1000 diffractometer fitted with a CCD detector (λ-Mo radiation, graphite monochromator, T = 293 K, ω scan mode, scan step 0.3°, frame exposure time 30 s, $2\theta_{max} = 60°$). A semiempirical absorption correction was ap-

plied.[13] The structure was solved by the direct method with the SHELXS97 program[14] and refined by the least-squares method with the SHELXL97 program[15] in the full-matrix anisotropic approximation (the H atoms were fixed with $U_H = 0.08$ Å^2). The crystallographic data for complex **3b** are given in Table 1; the selected bond lengths and angles are listed in Table 2.

We are grateful to the staff members of the Crystallographic Center (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) and the Russian Foundation for Basic Research (Project No. 00-03-32807) for the possibility of using the SMART diffractometer to collect experimental material.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-32101 and 03-03-06588mas).

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Received July 17, 2003;
in revised form October 28, 2003