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# Complexes of Macroheterocyclic Compounds Derived from Substituted 1,2,4-Triazoles with Tetravalent Metals

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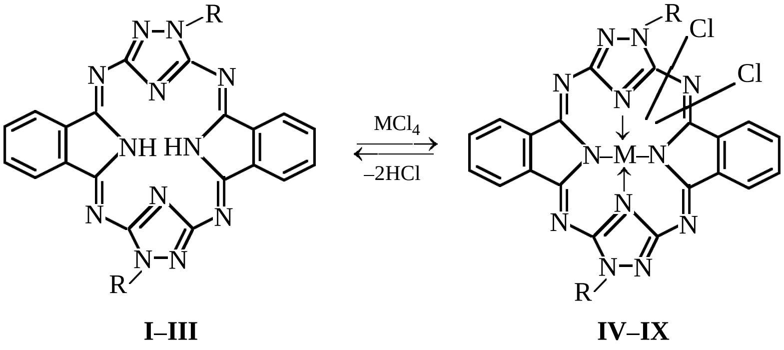
**Abstract**—Symmetrical marcoheterocyclic compounds derived from substituted 1,2,4-triazoles were reacted with tin(IV) and titanium(IV) chlorides to prepare the corresponding metal complexes. Macroheterocyclic compounds insoluble in organic solvents give mixtures of products on complex formation.

Metal complexes of macroheterocyclic compounds exhibit practically important properties. However, the information available at present relates mostly to complexes with divalent metals, such as Cu, Ni, Co, Zn, etc. In the present work we report on the synthesis of complexes with tetravalent metals (Sn and Ti).

Macroheterocyclic compounds **I** and **II** were prepared by known procedures [1]. As the starting diamine in the synthesis of compound **III** we used 1-decyl-1,2,4-triazole obtained by alkylation of guanazole [2] with decyl bromide in the presence of sodium methoxide. After purification, 1-decyl-1,2,4-triazole was reacted with *o*-phthalonitrile in ethylene glycol under reflux to obtain compound **III**. The electronic absorption spectrum of the product in chloroform (Fig. 1) contains three principal bands at 344, 358, and 379 nm, as well as a medium-intensity band at 368 nm and a shoulder at 349 nm. These data are consistent with data for a macroheterocyclic compound containing a 1-dodecyl-1,2,4-triazole fragment [3]. The IR spectrum of compound **III** (Fig. 2) displays a strong band at 3300 cm$^{-1}$, characteristic of stretching vibrations of the imino group. The absorption bands at 2920 and 2856 cm$^{-1}$ relate to stretching vibrations of alkyl C–H bonds [4].

The reactions of compounds **I**–**III** comprising substituted 1,2,4-triazole fragments with tin(IV) or titanium(IV) chlorides were used to prepare metal complexes **IV**–**IX**.



**I**–**III** **IV**–**IX**

R = H (**I, IV, VII**), Ph (**II, V, VIII**), Dec (**III, VI, IX**); M = Sn (**IV, VI**), Ti (**VII**–**IX**).

Complexes **IV**–**IX** as extra ligands contain two chlorine atoms which may locate on the same side or on opposite sides of the molecular plane, which is an important factor in the synthesis of sandwich structures. To explore this question, we performed quantum-chemical calculations for compound **IV** by the AM-1 method with full geometry optimization. The molecular model is represented in Fig. 3. The metal atom deviates from the plane defined by the four exo-

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† Deceased.

cyclic nitrogen atoms by 37.5°; this corresponds to a constant of this plane of 0.94 Å. The isoindole fragments deviate from this plane in opposite directions. The triazole fragments deviate from the macroring plane by 17°. The mean radius of the macroheterocyclic "window" is 1.97 Å. Therewith, the chlorine atoms locate symmetrically with respect to the metal atom and at the same distance from it (2.4 Å). This structure is quite suitable for the synthesis of sandwich compounds.

The principal electronic absorption bands of complexes **IV**, **V**, **VII**, and **VIII** are shifted slightly red compared with those of the parent heterocycles **I** and **II** [5] and are diffuse, which is probably associated with the presence of metal and is consistent with the theory of chromaticity of organic compounds. At the same time, compounds **VI** and **IX** give a new absorption band at 440 and 450 nm, respectively (Fig. 1). Introduction of long alkyl residues into macroheterocycle **III** allowed us to increase the solubility of the macrocycle as such and of its metal complexes in organic solvents, which made it possible to apply present-day purification techniques and to obtain a better resolved absorption spectrum.

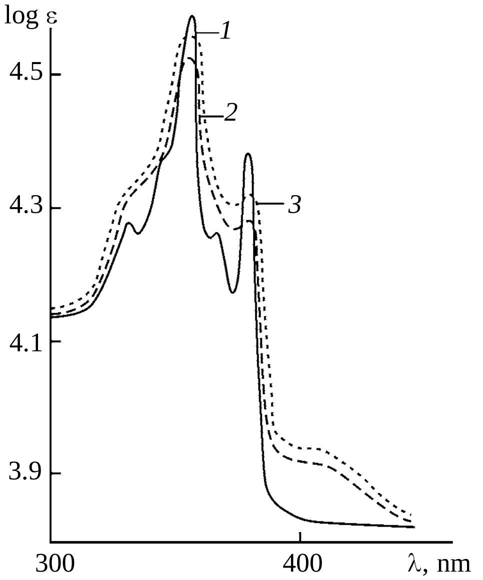

**Fig. 1.** Electronic absorption spectra of (*1*) macroheterocycle **III** and complexes (*2*) **VI** and (*3*) **IX**.

The IR spectra of the resulting metal-free macrocycles and their complexes (Fig. 2) show common absorption bands at 760, 1040, 1104, 1304–1316, 1408, and 1500–1504 $\mathrm{cm}^{-1}$, which points to a common macroheterocyclic system (shown with compounds **III** and **IV**). At the same time, some dif-

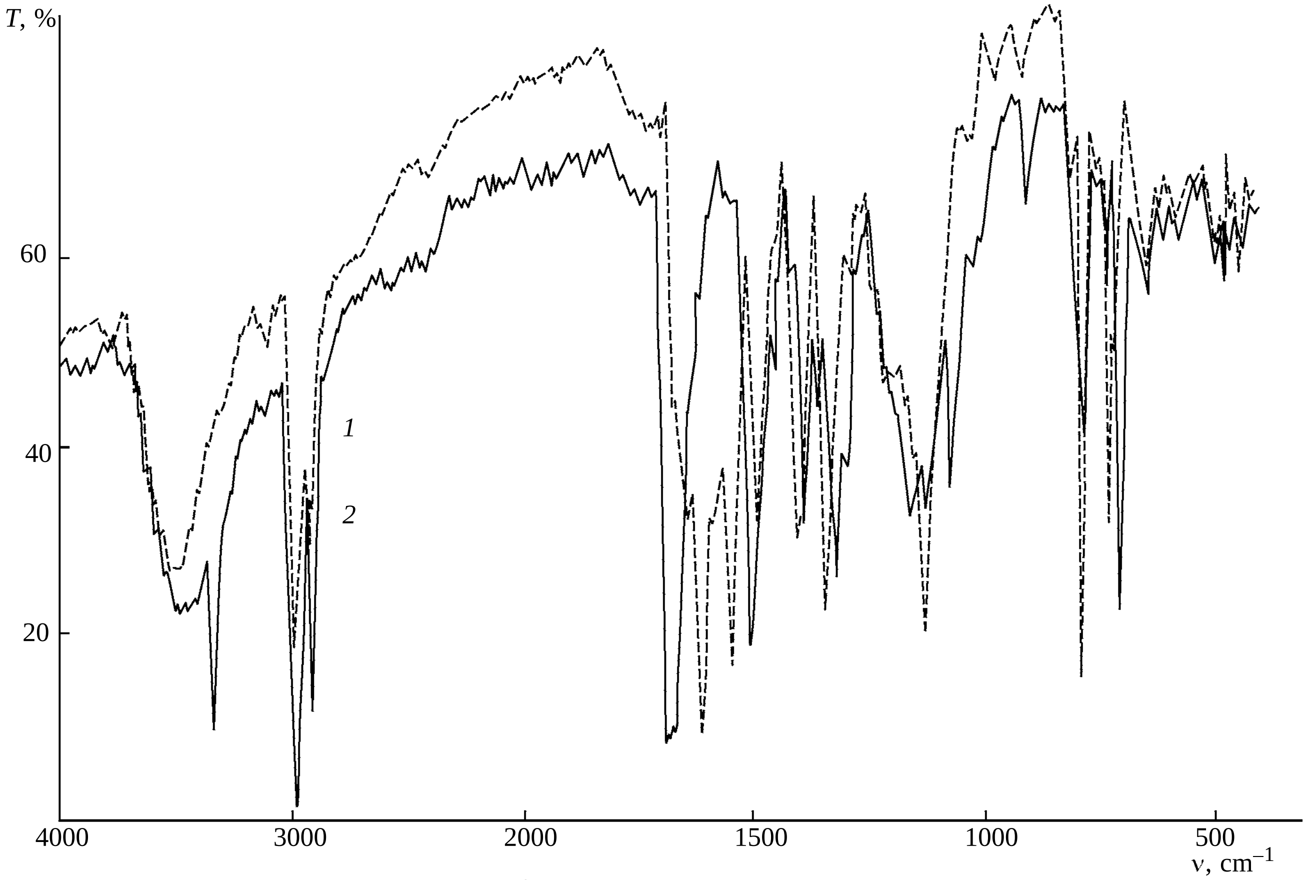

**Fig. 2.** IR spectra of (*1*) macroheterocycle **III** and (*2*) complex **VI**.

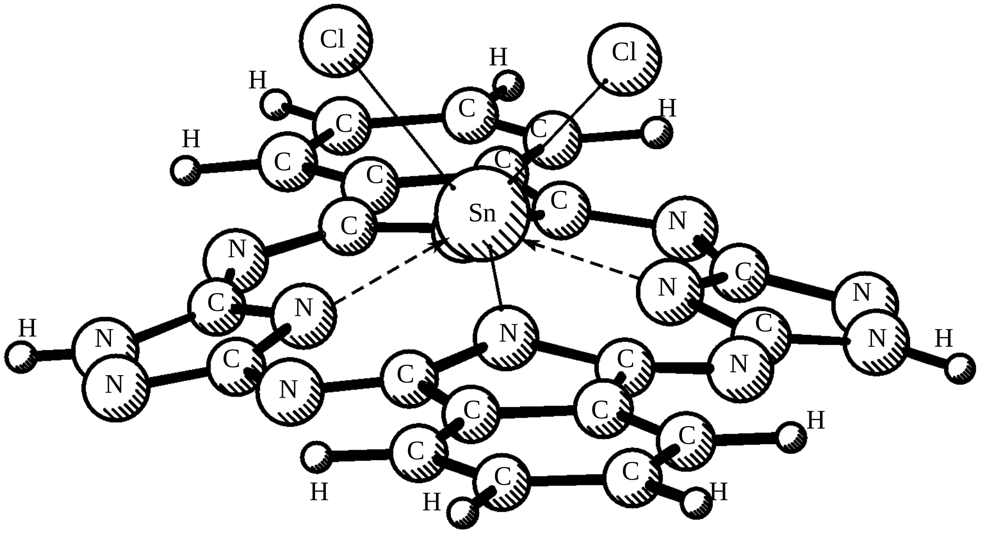

**Fig. 3.** Calculated molecular model of complex **IV**.

ferences can be noted. Thus, for instance, complexes **VI**–**IX** give no band at 3300 $\mathrm{cm}^{-1}$, characteristic of stretching vibrations of the imino group. As shown in [3], in going from a metal-free compound to a complex, the absorption band at 1660–1670 $\mathrm{cm}^{-1}$, characteristic of imino C=N stretching vibrations, shifts to 1550–1580 $\mathrm{cm}^{-1}$. Thus, the corresponding band for complex **VI** is at 1580 $\mathrm{cm}^{-1}$ and for the metal-free compound **III**, at 1668 $\mathrm{cm}^{-1}$.

Upon isolation of complexes **IV**, **V**, **VII**, and **VIII**, derived from macrocycles **I** and **II**, we, probably, have a mixture of the starting and final products, since the IR spectra of the isolated materials show not only new bands at 1560 $\mathrm{cm}^{-1}$, but also imino C=N bands at 1660 $\mathrm{cm}^{-1}$, while slightly weaker.

As shown by electronic and IR spectroscopy and atomic absorption analysis, complexes **VI** and **IX** are individual compounds.

## EXPERIMENTAL

The IR spectra were measured on a Specord M-80 spectrophotometer (4000–400 $\mathrm{cm}^{-1}$) in KBr. The electronic absorption spectra were obtained on a Specord M-40 spectrophotometer (300–700 nm) in DMF.

The metal contents were determined by flame-ionization spectroscopy on a Saturn device.

Quantum-chemical calculations were performed by the HYPERCHEM-4 program.

**3,5-Diamino-1-decyl-1,2,4-triazole.** A mixture of 100 ml of methanol, 2.32 g of metallic sodium, and 10 g of 3,5-diamino-1,2,4-triazole was stirred under reflux for 1 h. Decyl bromide, 24.5 g, was then added dropwise over the course of 2 h and the mixture was refluxed for 6 h and poured into 500 ml of cold water. The oil layer was collected from the water surface and steamed until the condensate no longer smelled of decyl bromide. The hot residue was poured into 500 ml of cold water. The precipitate was filtered off and dried at room temperature to obtain a pale-yellow powderlike substance, 73%, mp 75–78°C; the substance is insoluble in acetone and readily soluble in acetone, chloroform, and diethyl ether. IR spectrum, ν, $\mathrm{cm}^{-1}$: 2920, 2848, 1648, 1488, 1448, 1376, 1088. Found, %: C 60.3; H 10.5; N 29.2. $C_{12}H_{25}N_5$. Calculated, %: C 60.1; H 10.8; N 29.1.

2,4,5,7,16,18,19,21,29,30,31,32-Dodecaazaheptacyclo[$20.6.1.1^{3,6}.1^{8,15}.1^{17,20}.0^{9,14}.0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (**I**) and 5,19-diphenyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[$20.6.1.1^{3,6}.1^{8,15}.1^{17,20}.0^{9,14}.0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (**II**) were prepared by the procedure in [1].

**5,19-Didecyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[$20.6.1.1^{3,6}.1^{8,15}.1^{17,20}.0^{9,14}.0^{23,28}$]-dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (III).** A solution of 10 g 3,5-diamino-1-decyl-1,2,4-triazole and 5.4 g of phthalonitrile in 100 ml of ethylene glycol predried by azeotropic distillation. The mixture was stirred for 8 h under reflux. The precipitate that formed was filtered off, washed with water, twice recrystallized from 120 ml of DMF, and dried at 100–120°C to obtain a reddish-brown substance, 20%, mp 215–217°C; the substance is readily soluble in chloroform, benzene, and methanol and insoluble in acetone and water. Electronic absorption spectrum, $\lambda_{\max}$, nm (log ε): 344

(4.27), 349, 358 (4.56), 368, 379 (4.35). IR spectrum, ν, cm$^{-1}$: 3296, 2920, 2856, 1668, 1616, 1488, 1456, 1444, 1372, 1344, 1300, 1096, 1056, 888, 768, 720. Found, %: C 68.3; H 7.8; N 23.9. $C_{40}H_{52}N_{12}$. Calculated, %: C 68.5; H 7.5; N 24.0.

**Metal complexes IV, V, VII, and VIII.** A mixture of 1.19 mmol of macroheterocycle **I** or **II**, 3.57 mmol of tin or titanium chloride, and 30 ml of dry nitrobenzene was stirred under reflux for 6 h. The precipitate was filtered off, washed with benzene and acetone, and suspended in 10% hydrochloric acid. The precipitate was filtered off, washed with distilled water to Cl$^{-}$-free washings ($AgNO_3$ test), dried at 110°C, and purified by treatment with acetone.

**29,31-Dichlorotin-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (IV),** yield 68%, does not melt up to 450°C. Dark brown substance; sparingly soluble in DMF and pyridine and insoluble in other organic solvents. Electronic absorption spectrum, $\lambda_{max}$, nm: 352, 367, 402. IR spectrum, ν, cm$^{-1}$: 1648, 1560, 1364, 1304, 1184, 1100, 1044, 764. Found, %: C 47.5; H 3.6; Cl 4.3; N 34.0; Sn 10.6. $C_{20}H_{10}Cl_2N_{12}Sn$. Calculated, %: S 39.5; H 1.7; Cl 11.7; N 27.6; Sn 19.5.

**29,31-Dichlorotin-5,19-diphenyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (V),** yield 68%, does not melt up to 450°C. Brown substance, sparingly soluble in DMF and pyridine and insoluble in other organic solvents. Electronic absorption spectrum, $\lambda_{max}$, nm: 352, 371, 394. IR spectrum, ν, cm$^{-1}$: 1664, 1580, 1596, 1500, 1408, 1304, 1100, 1016, 762, 616. Found, %: S 56.0; H 3.9; Cl 4.3; N 27.7; Sn 8.1. $C_{32}H_{20}Cl_2N_{12}Sn$. Calculated, %: C 50.4; H 2.6; Cl 9.4; N 22.0; Sn 15.6.

**29,31-Dichlorotitanium-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (VII),** yield 81%, does not melt up to 450°C. Brown substance, sparingly soluble in DMF and pyridine and insoluble in other soluble. Electronic absorption spectrum, $\lambda_{max}$, nm: 332, 352, 367. IR spectrum, ν, cm$^{-1}$: 1648, 1560, 1364, 1304, 1184, 1100, 1044, 764, 688. Found, %: C 54.2; H 3.0; Cl 4.6; N 36.4; Ti 1.8. $C_{20}H_{10}Cl_2N_{12}Ti$. Calculated, %: C 44.7; H 1.9; Cl 13.2; N 31.3; Ti 8.9.

**29,31-Dichlorotitanium-5,19-diphenyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (VIII),** yield 81%, does not melt up to 450°C. Brown substance, sparingly soluble in DMF and pyridine and insoluble in other organic solvents. Electronic absorption spectrum, $\lambda_{max}$, nm: 352, 371, 394. IR spectrum, ν, cm$^{-1}$: 1664, 1580, 1596, 1500, 1408, 1304, 1100, 1016, 762, 616. Found, %: S 63.0; H 4.3; Cl 1.9; N 28.5; Ti 2.3. $C_{32}H_{20}Cl_2N_{12}Ti$. Calculated, %: C 55.6; H 2.9; Cl 10.3; N 24.3; Ti 6.9.

**Metal complexes VI and IX.** Macrocycle **III**, $7.13 \times 10^{-4}$ mol, tin or titanium tetrachloride, $21.4 \times 10^{-4}$ mol, and 30 ml of 1-chloronaphthalene were stirred at 200°C for 20 h. After cooling, the reaction mixture was diluted with heptane. The precipitate that formed was washed with acetone and purified by treatment with acetone.

**29,31-Dichlorotin-5,19-didecyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (VI),** yield 44%, does not melt up to 300°C. Brown substance; moderately soluble in hot chloroform, readily soluble in DMF, and insoluble in acetone and water. Electronic absorption spectrum, $\lambda_{max}$, nm: 275, 359 (4.5), 379 (4.27), 440 (3.9). IR spectrum, ν, cm$^{-1}$: 2920, 2856, 1580, 1512, 1468, 1376, 1312, 1100, 888, 760, 704. Found, %: S 54.2; H 5.3; Cl 8.0; N 19.2; Sn 13.3. $C_{40}H_{50}Cl_2N_{12}Sn$. Calculated, %: C 54.0; H 5.6; Cl 8.5; N 18.9; Sn 13.0.

**29,31-Dichlorotitanium-5,19-didecyl-2,4,5,7,16,18,19,21,29,30,31,32-dodecaazaheptacyclo[20.6.1.$1^{3,6}$.$1^{8,15}$.$1^{17,20}$.$0^{9,14}$.$0^{23,28}$]dotriaconta-1,3,6(32),7,9,11,13,15,17,20(30),21,23,25,27-tetradecaene (IX),** yield 44%, does not melt up to 300°C. Brown substance; moderately soluble in hot chloroform, readily soluble in DMF, and insoluble in acetone and water. Electronic absorption spectrum, $\lambda_{max}$, nm: 280, 360 (4.54), 380 (4.31), 450 (3.94). IR spectrum, ν, cm$^{-1}$: 2920, 2856, 1580, 1511, 1470, 1376, 1310, 1100, 888, 762, 706. Found, %: S 59.0; H 5.3; Cl 8.1; N 6.2; Ti 6.4. $C_{40}H_{50}Cl_2N_{12}Ti$. Calculated, %: C 58.8; H 6.1; Cl 8.5; N 20.6; Ti 6.0.

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