Russian Journal of General Chemistry, Vol. 75, No. 6, 2005, pp. 980–984. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 6, 2005, pp. 1036–1040. Original Russian Text Copyright © 2005 by Korzhenevskii, Markova, Efimova, Koifman, Krylova.

## Metal Complexes of a Hexameric Network Tetrapyrazinoporpyrazine: I. Synthesis and Identification

A. B. Korzhenevskii\*, L. V. Markova\*\*, S. V. Efimova\*\*, O. I. Koifman\*, and E. V. Krylova\*\*

\* Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia \*\* Ivanovo State University of Chemical Technology, Ivanovo, Russia

Received February 2, 2004

**Abstract**—Metal complexes of a hexameric network tetrapyrazineporpyrazine were synthesized by template polycyclotetramerization of pyrazine-2,3,5,6-tetracarboxamide in an urea melt in the presence of a corresponding metal acetate; irrespective of the metal, the polymerization degree of the polymeric ligand does not exceed six. A method for structural assessment of such compounds was proposed.

Unique properties of phthalocyanines have stimulated research into the synthesis of polymers containing azaporphyrin macrocycles [1-3], and by now several types of such compounds [4, 5] have been described. Among them, polymers with continuous conjugation over the entire macromolecule I have attracted the greatest interest, as in this case a unique-in-size  $\pi$ -electron system is formed. Its presence opens ample opportunities for practical use of these substances. Such polymers form a basis for design of technically valuable materials combining specific physicochemical properties of high-molecular compounds with chemical and thermal stability, catalytic activity, electrophysical, and other parameters characteristic of phthalocyanines.



Extensive work in this field has been concerned exclusively with polyphthalocyanines as the simplest representatives of polytetraarenoporphyrazines. At the same time, it is known that aza substitution [6] and benzo fusion [7] in the periphery of the phthalocyanine molecule enhance stability, catalytic activity, semiconductor and other properties of its metal complexes and serve as one the main ways to creating new highly effective materials.

In this connection profound structural modification of polyphthalocyanines is also of interest. The presence of rigid aza-crown fragments differing in size, geometry, and number of aza atoms would essentially differentiate such polymers from polyphthalocyanines. Directed introduction of a certain number of nitrogen atoms which possess lone electron pairs in the periphery of controlled-size intramolecular cavities would be expected to provide selective complex derivatives. Nevertheless, polymers based on azaphthalo- and azanaphthalocyanines has not only been studied, but are also unknown. The present work is devoted to development of synthetic approaches to metal complexes of a hexameric network polytetrapyrazineporphyrazine (PzcM)<sub>n</sub> **IIa–IIc**. Such polymeric macro= molecules contain no hydrogen atoms (except for terminal groups) and can be considered as an intermediate stage in passing from organic to inorganic polymers. Furthermore, coordination-active fragments of various nature coexist in the composition of the macromolecule: porphyrazine, rigid aza-8-crown24, 1,9-dicarboxy $\langle N_3$ -podand-3 $\rangle$ , 1,15-dicarboxy(N5podand-5, and terminal groups.

To obtain  $(PzcM)_n$ , we made use of a scheme whose final stage involved of template polycyclo-



 $M = Cu(2^+)$  (a),  $Co(2^+)$  (b),  $Fe(2^+)$  (c).

tatramerization of pyrazine-2,3,5,6-tetracarboxamide **VI** in an urea melt in the presence of a corresponding

metal acetate and a catalytic amount of ammonium molybdate.



Products **IIa–IIc** are finely crystalline hygroscopic substances of black color with a metal shine. They do not melt up to 300°C and are insoluble in water and most organic solvents but give brightly colored solutions in DMF, DMSO, and concentrated sulfuric acid.

most intricate problems in the chemistry of such compounds, as the majority of classical methods for structural assessment of low- and high-molecular organic compounds appear unsuitable for this purpose.

Of extreme importance for identifying and studying the structure and properties of our prepared  $(PzcM)_n$ is that, unlike completely insoluble metal complexes

Identification of polyporphyrazines is one of the is that, unlik RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 75 No. 6 2005 981

(PzcM) <sub>n</sub>	λ <sub>max</sub>	, nm	DzoM	$\lambda_{max}$ , nm		
	H <sub>2</sub> SO <sub>4</sub>	DMSO	r zem	H <sub>2</sub> SO <sub>4</sub>	DMSO	
$(PzcCu)_n$ $(PzcCo)_n$ $(PzcFe)_n$	690 690 700	658 641 656	PzcCu PzcCo PzcFe	648 643 620	629 612 628	

Table 1. Positions of the long-wave maxima in the electronic absorption spectra of  $(PzcM)_n$  and  $PzcM^a$ 

<sup>a</sup> Data of [6].

of network polyphthalocyanines with continuous conjugation over the entire macromolecule, they are soluble (up to  $10^{-5}$  base mol/l) in concentrated acids owing to the great number of potential protonation centers. This allows electronic absorption spectroscopy to be applied for structural assessment of porphyrazine polymers.

The electronic absorption spectra of  $(PzcM)_n$  in concentrated  $H_2SO_4$  and DMSO contain a long-wave maximum at 650-700 nm and sharply enhanced absorption in the violet and UV ranges. Table 1 compares the positions of the long-wave absorption maxima of the synthesized compounds with those of the Q bands of the corresponding monomers.

The visible parts of the electronic absorption spectra of the polymeric and low-molecular metalcomplexes are generally similar, which may be considered as evidence for the presence of porphyrazine fragments in the synthesized compounds. At the same time, there are some notable differences in the spectral patterns of the polymers and monomers: The first absorption band of the former is shifted bathochromically and simultaneously decreases in intensity and broadens. Such changes in the absorption electronic spectra can be interpreted as evidence in favor of the polymeric nature of the porphyrazine-containing substance and of a certain increase in the electron density of the basic chromophore.

The IR spectra of  $(PzcM)_n$  are ill-resolved, implying polymeric structures. On the other hand, the fact that the IR spectra of compounds **IIa–IIc** are fully identical points to similarity of these compounds irrespective of the nature of the metal (M–N absorption bonds are beyond the measurement range).

It is readily shown that the elemental composition and equivalent molecular weight of  $(PzcM)_n$  (fraction of the molecular weight corresponding to one terminal group) are uniquely related to their structure and polymerization degree. Terminal groups in  $(PzcM)_n$ are undoubtedly carboxylic after repeated acid treatment and reprecipitation from a solution in concentrated H<sub>2</sub>SO<sub>4</sub> during their isolation and purification (this is indirectly proved by the elemental analysis, Table 2). This fact allows us to use simple procedures to determine the number of terminal groups and calculate the equivalent molecular weights of the polymers.

Compound	п	М	Found, %		Calculated, %			Number of	Equivalent molecular weight		
			С	N	Ma	С	N	Ma	terminal groups	calculated	found
(PzcCu) <sub>n</sub>	1	935.5				41.05	23.94	6.78	8	116.9	<b></b>
	2	1615				41.61	26.01	7.83	12	134.6	
	4	2718				42.38	28.84	9.34	16	169.9	
	6	3821	42.66	30.00	10.09	42.71	30.04	9.97	20	191.1	194.6
	8	4924				42.89	30.71	10.31	24	205.2	
$(PzcCo)_n$	1	931				41.24	24.06	6.34	8	116.4	
	2	1606				41.84	26.15	7.35	12	133.8	
	4	2700				42.67	29.03	8.74	16	168.8	
	6	3794	43.37	30.01	9.12	43.02	30.26	9.33	20	189.7	190.4
	8	4888				43.21	30.93	9.66	24	203.7	
(PzcFe) <sub>n</sub>	1	928				41.38	24.14	6.03	8	116.0	
	2	1600				42.00	26.25	7.00	12	133.3	
	4	2688				42.86	29.17	8.33	16	168.0	
	6	3776	43.17	30.26	8.63	43.22	30.40	8.90	20	188.8	191.3
	8	4864	<u> </u>	L		43.42	31.09	9.21	24	202.7	L

Table 2. Calculated and experimental characteristics of metal complexes of hexameric network tetrapyrazineporphyrazine

For correct analyses, samples of the synthesized polymers were dried in a vacuum under thermogravimetric control (until weight loss and the endothermic effect at 100–150°C were no longer observed).

The elemental analyses and equivalent molecular weights of compounds **IIa–IIc** are given in Table 2. These data show that our developed procedure allowed us to synthesize metal complexes of a hexameric henwork tetrapyrazineporphyrazine with an average polymerization degree of  $\sim 6$ .

## EXPERIMENTAL

The electronic absorption spectra of  $\sim 10^{-5}$  M solutions of substances in corresponding solvents were recorded on a Perkin-Elmer Lambda-20 spectrophotometer in 10-mm quartz rectangular cells.

Mixture III of 2,3-diaminophenazine and 2amino-3-hydoxyphenazine. A solution of 406 g of FeCl<sub>3</sub>·6H<sub>2</sub>O in 750 ml of distilled water was added with stirring to a solution of 54 g of ophenylenediamine in 2 l of distilled water acidified with 84 ml of HCl ( $\rho$  1.19 g cm<sup>-3</sup>). The reaction mixture was held for one day at 20°C and 1 atm, then the resulting precipitate was filtered off, washed with 0.3 N HCl to remove FeCl<sub>3</sub>, and dried up at 60°C. A reddish brown powder of the mixture of practically equal amounts of 2,3-diamino-phenazine and 2-amino-3-hydoxyphenazine was obtained with a near-quantitative yield and used in the further synthesis without separation into individual components.

Pyrazine-2,3,5,6-tetracarboxylic acid (IV). To a suspension of 19.5 g of mixture **III** in a solution of 12.5 g of KOH in 1 l of water, 158 g of  $KMnO_4$  was added in small portions with stirring at 70-80°C. The mixture was stirred for 4 h more and separated by filtration. The precipitate of MnO<sub>2</sub> was washed with hot water up to a negative reaction of washins for  $FeSO_4$ . The combined filtrate was evaporated until crystallization began and acidified with HCl (p 1.19 g cm<sup>-3</sup>) to pH 2–3. After cooling, a pale yellow finely crystalline powder of the target reaction product formed and was isolated by filtration. It is soluble in water, alcohol, and acetone; yield 21 g (91%), mp 198°C {published data: mp 198–199°C [8]}. Found, %: C 38.87; H 1.63; N 10.76. C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>8</sub>. Calculated, %: C 37.50; H 1.56; N 10.94.

Tetramethyl pyrazine-2,3,5,6-tetramethylcarboxylate (V). A solution of 10 g of acid IV in 100 ml of methanol was saturated by dry hydrogen chloride at cooling. The reaction mixture was left to stand for one day and diluted with water. A precipitate formed and was filtered off, washed, and dried in air to obtain 7.5 g (67%) of compound V as a yellow crystalline powder readily soluble in alcohols and acetone and insoluble in water, mp 180°C {published data: mp 181–183°C [8]}. Found, %: C 50.95; H 4.72; N 10.16.  $C_{12}H_{12}N_2O_8$ . Calculated, %: C 51.43; H 4.28; N 10.00.

**Pyrazine-2,3,5,6-tetracarboxamide (VI).** A suspension of 10 g of ester V in 200 ml of anhydrous methanol was saturated at room temperature within one hour with dry ammonia and left to stand for one day. The reaction mixture was separated by filtration, the precipitate was triturated with water, squeezed, and dried at 150°C to obtain 6 g (96%) of compound VI as a yellow finely crystalline powder insoluble in water and organic solvents, mp 390°C {published data: mp 390°C [8]}. Found, %: C 38.78; H 3.10; N 33.79.  $C_8H_8N_6O_4$ . Calculated, %: C 38.09; H 3.17; N 33.33.

Metal complexes of hexameric network tetrapyrazineporphyrazine IIa–IIc. A thoroughly ground mixture of 7.56 g of amide VI, 20 g of carbamide, and 0.2 g of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> was slowly heated with stirring to 170°C. When the reaction mixture became dark, a thoroughly ground mixture of 0.5 g  $(NH_4)_2MoO_4$ , 2.5 g of carbamide, and 18 mmol of an anhydrous metal salt (2.42 g of CuCl<sub>2</sub>, 2.59 g of FeC<sub>2</sub>O<sub>4</sub>, or 2.34 g CoCl<sub>2</sub>) was added, and the mixture was heated at 200°C for 3 h with stirring. Then a thoroughly ground mixture of 0.05 g of  $(NH_4)_2MoO_4$ , 5 g of carbamide, and 9 mmol of an anhydrous metal salt (1.41 g of  $CuCl_2$ , 1.29 g  $FeC_2O_4$ , or 1.17 g  $CoCl_2$ ) was added, and the melt was stirred for 1.5 1/2 at 200°C until it solidified, after which 10 g of carbamide was added. The mixture liquefied and was stirred for 1.5 h at 200°C and then cooled. The greenish black melt was treated with hot water up to colorless extracts and washed sequentially with 5% HCl, hot water, and acetone to colorless filtrates. The dry powder was dissolved in a 20-fold amount of concentrated sulfuric acid, filtered on a Schott filter no. 3, and reprecipitated onto ice. The precipitate was filtered off, washed sequentially with hot water up to a neutral filtrate and with acetone, and dried in a vacuum oven at 200°C (2.7 kPa) to obtain compounds **IIa–IIc** as finely crystalline, nonmelting, hygroscopic powders of black color with a metal shine, insoluble in organic solvent. Yield: **IIa** 3.9 g (58%), **IIb** 3 g (45%), and **IIc** 2.8 g (42%).

The equivalent molecular weights of the polymers were determined by potentiometric back titration with 0.05 N HCl solutions of samples prepared by keeping 0.1 g of  $(PzcM)_n$  in 20 ml of 0.05 N NaOH for 12 h. In parallel, a control experiment was carried out. An accurate weighed portion of a substance was held in an aliquot amount of distilled water for 12 h. The precipitate was isolated by filtering and washed with water ( $2 \times 20$  ml). The filtrate and washings were combined and titrated with 0.05 N NaOH.

The equivalents (E, g) were calculated by the following equation:

$$\mathbf{E} = \frac{G}{\left(V_1 - \frac{V_1^1 G}{g}\right)N_1 k_1 - V_2 N_2 k_2}$$

Here G and g are the weight of the sample and control sample, respectively, g;  $V_i$ ,  $N_i$ , and  $k_i$ , volume (1), normality, and correction factor (i = 1 for alkali and i = 2 for acid), respectively.

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 03-03-96472).

## REFERENCES

- Marvell, C.S. and Rassweiler, J.H., J. Am. Chem. Soc., 1958, vol. 80, no. 5, p. 1197.
- 2. Marvell, C.S. and Martin, M.W., J. Am. Chem. Soc., 1958, vol. 80, no. 24, p. 6600.
- Drinkard, W.C. and Bailar, J.C., J. Am. Chem. Soc., 1959, vol. 81, no. 18, p. 4795.
- 4. Berlin, Å.Å. and Sherle, A.I., Usp. Khim., 1979, vol. 48, no. 11, p. 2087.
- Koifman, O.I. and Ageeva, T.A., in Uspekhi khimii porfirinov (Advances in Porphyrin Chemistry), St. Petersburg: Nauchno-Issled. Inst. Khimii, S.-Peterb. Gos. Univ., 2001, vol. 3, pp. 260–283.
- Berezin, B.D., Klyuev, V.N., and Korzhenevskii, A.B., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1977, vol. 20, no. 3, p. 357.
- Korzhenevskii, A.B., Markova, L.V., Koifman, O.I., and Panova, M.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1990, vol. 33, no. 10, p. 73.
- Begland, R.W., Hartter, D.R., Donald, D.S., Cairneross, A., and Sheppard, W.A., *J. Org. Chem.*, 1974, vol. 39, no. 5, p. 1235.