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Metal Complexes of a Hexameric Network Tetrapyrazinoporphyrazine: II.[1] Complexing Sorption Properties

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Abstract — Coordination of metal ions from aqueous solutions with metal complexes of a hexameric network tetrapyrazinoporphyrazine was studied. These compounds are complexing sorbents; their equilibrium coordination capacity largely depends on the metal occupying the coordination cavity of the porphyrazine fragments and on the external factors: kind of salt being coordinated, solution acidity, etc.

Metal complexes of hexameric network tetrapyrazinoporphyrazine **I** contain various rigid cavities capable of coordination with metal ions: aza-24-crown-8 (“large” cavities, size ~8 Å), 1,9-dicarboxy⟨N_3-podand-3⟩, and 1,15-dicarboxy⟨N_5-podand-5⟩ [1]. The coordination activity of these fragments is provided by exocyclic porphyrazine and pyrazine nitrogen atoms containing lone σ-electron pairs. This fact provides prerequisites for development of polymeric complexing sorbents with the preset coordination capacity and selectivity, based on these compounds.

In a broader sense, variation of the degree of hetero substitution in the “primary surrounding” of the porphyrazine ring and its additional benz- and heterobenzannelation would provide formation of intramolecular cavities of various coordination capacities and of controllable size and geometry. This would allow development of complexing sorbents finely “tunable” to the required species (anions, cations, or neutral molecules).

On the other hand, when catalytically active metal porphyrazine fragments are combined in a common conjugated system, with additional coordination of metal ions with internal cavities of the non-porphyrazine (aza crown) nature and with terminal podand fragments, a synergistic effect can be expected (especially when macrocyclic complexes of different metals are combined within the same macromolecule). Thus, the systems under consideration also show promise for the development of catalysts of a preset activity.

The closest analogs of compounds **I** are polyphthalocyanines $(H_2Pc)_i$. Berezin and Shormanova studied their main physicochemical properties [2, 3]; in particular, they demonstrated the feasibility of purposeful synthesis of mono- and bimetallic complexes of $(H_2Pc)_i$ by treatment of these compounds in the solid phase with aqueous solutions of metal salts [4, 5]; the optimal conditions for the metallization of $(H_2Pc)_i$ with metal salts were found [6].

In this study, we examined the complexing sorption properties of metal complexes **Ia**–**Ic** of hexameric network tetrapyrazinoporphyrazine toward Cu^{2+}, Co^{2+}, and Fe^{2+}.

We found that, when the complexes $(PzcM)_6$ were kept in dilute (~1 g l^{-1}) aqueous solutions of bivalent metal salts $CuCl_2$, $FeBr_2$, and $Co(COOCH_3)_2$, the concentration of the corresponding cation gradually decreased to a certain constant value, with the formation of bimetallic, secondary complexes $(PzcM)^6 \cdot (M'A_2)_m$, where A is an anion. The counterions arranged perpendicular to the macroring plane are the anions present in the solution.

We failed to determine whether the metal ions are initially coordinated in the form of salts or hydroxides, because the subsequent thorough washing of the solid phase with water to remove physically sorbed (unbound) metal ions results in transformation of $(M'A_2)$ fragments into $[M'(OH)_2]$ by ion exchange; this is confirmed by the absence of halogens in $(PzcM)_6[Cu(A)_2]_m$ and $(PzcM)_6[Fe(A)_2]_m$.

The transformation of the starting $(PzcM)_6$ into $(PzcM)_6[M(OH)_2]_m$ is manifested in their X-ray dif-

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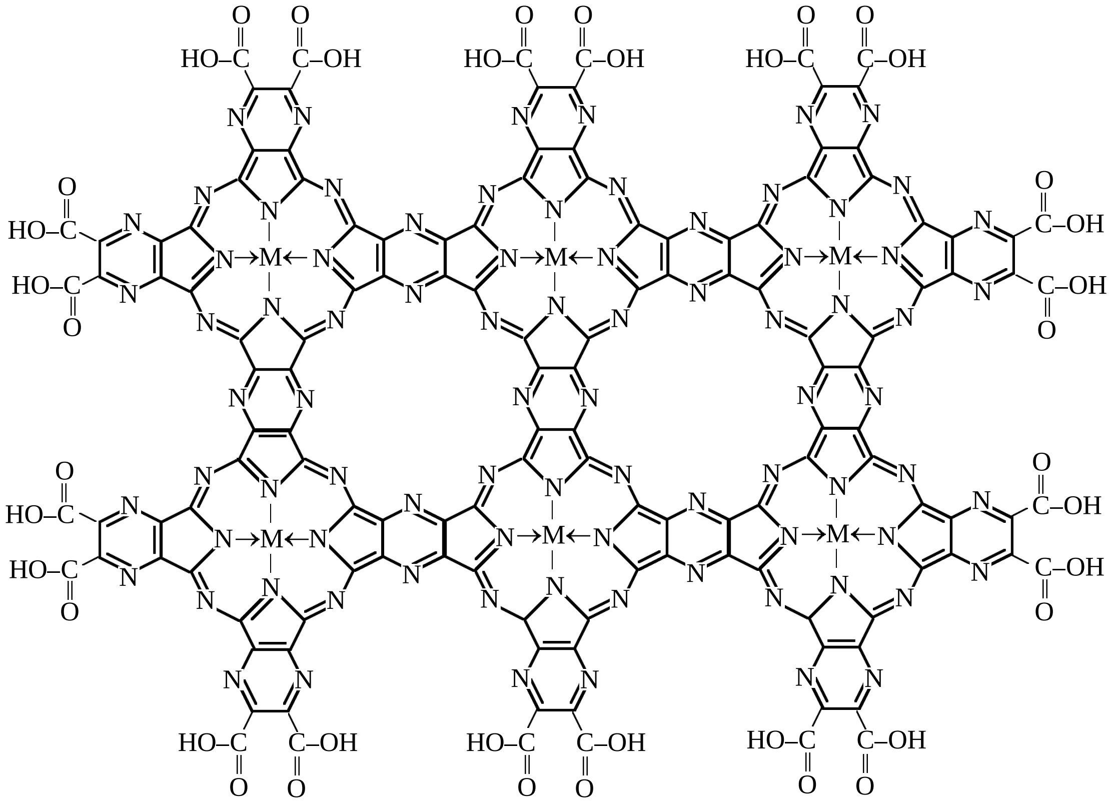
[1] For communicarion I, see [1].



Ia–Ic

$(PzcM)_6$ (**I**), M = Cu (**a**), Cu (**b**), Fe (**c**).

fraction patterns (Fig. 1) and IR spectra. The diffraction patterns of $(PzcM)_6[M(OH)_2]_m$ differ essentially from those of $(PzcM)_6$ and are not superpositions of the diffraction patterns of the starting hexamer and metal salt. It should be noted that the diffraction patterns of $(PzcM)_6$ do not change on keeping the compounds in distilled water.

Appearance of a system of sharp reflections in the diffraction patterns of the "bimetallic" complexes, as well as better resolution and higher intensity of certain bands in their IR spectra, suggest that the salt coordination makes the hexamer structure more ordered.

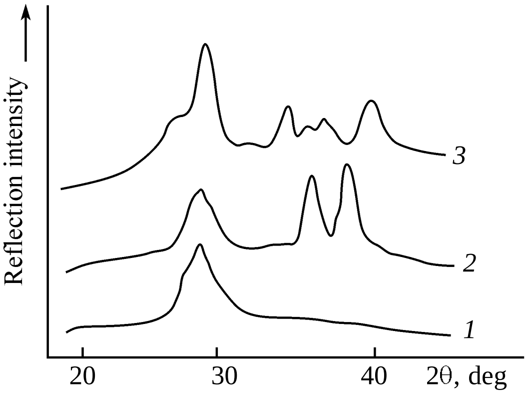


Fig. 1. Diffraction patterns of (*1*) $(PzcCu)_6$, (*2*) $(PzcCu)_6[Cu(OH)_2]_4$, and (*3*) $(PzcCu)_6[Co(OH)_2]_{10}$.

Apparently, metal ions are sorbed from solutions with $(PzcM)_6$ molecules by formation of coordination bonds between the metal ions and aza groups: σ-donor with respect to the metal and, possibly, also π-donor (π-dative) with respect to the ligand.

The sorption by salt formation with the terminal carboxy groups of the complexing sorbent should be ruled out in our case, because weakly basic carboxy groups are capable of ion exchange only in alkaline solutions, whereas the sorption capacity of $(PzcM)_6$ reaches a maximum at pH ~5 and decreases at lower acidities (Fig. 2).

Since the sorption is provided exclusively by the coordination bonds, the secondary metal complexes formed in the process, in contrast to the primary porphyrazine complexes, are unstable in more acidic solutions in which the aza atoms are protonated. The reversibility of the sorption is very favorable when using $(PzcM)_6$ for recovery of metal ions from solutions.

Analytical data for bimetallic complexes of hexameric network tetrapyrazinoporphyrazine

Bimetallic complex	*M* [a]	Found, %			Calculated M', %
		M in $(PzcM)_6$	M + M'	M'	
$(PzcCu)_6[Cu(OH)_2]_4$	4211	10.09	15.36	6.21	6.02
$(PzcCu)_6[Co(OH)_2]_{10}$	4750		20.48	12.37	12.40
$(PzcCu)_6[Fe(OH)_2]_{10}$	4719.5		20.17	12.00	11.83
$(PzcCo)_6[Cu(OH)_2]_8$	4574	9.12	18.85	11.28	11.11
$(PzcCo)_6[Co(OH)_2]_{10}$	4723		19.97	12.64	12.47
$(PzcCo)_6[Fe(OH)_2]_2$	3973.7		11.75	3.04	2.81
$(PzcFe)_6[Cu(OH)_2]_6$	4361	8.63	15.84	8.37	8.74
$(PzcFe)_6[Co(OH)_2]_{10}$	4705		19.02	12.09	12.52
$(PzcFe)_6[Fe(OH)_2]_{10}$	4674.5		19.08	12.11	11.95

[a] (M) Molecular weight.

The compositions of $(PzcM)_6[M'(OH)_2]_m$ (see table) were found by determining the content of metal M in the starting $(PzcM)_6$, total content M and M' in the samples of the secondary metal complexes, and the content of M in the $(PzcM)_6$ samples regenerated by desorption of $M'A_2$ (acid washing). All the analyses were preceded by thorough washings, until the wash waters became free of ions to be removed, and by drying to constant weight in a vacuum on heating.

The table shows that the compositions of the compounds $(PzcM)_6[M(OH)_2]_m$ are different depending on the parameters of the coordination sphere of M' and of the coordination centers of $(PzcM)_6$. The dependence of the results of the solid-phase metallization on the kind of the incorporated ion was already noted for phthalocyanine [7].

We studied the kinetics of complexing sorption of copper and cobalt ions with $(PzcCu)_6$ from aqueous solutions of $CuSO_4$ and $Co(COOCH_3)_2$, respectively, and examined the dependence of the equilibrium specific coordination capacity of these complexing sorbents on the initial salt concentration and solution acidity. The isotherms shown in Fig. 3 indicate that the time in which the equilibrium coordination capacity *E* is attained is virtually independent of the kind and concentration of the ion being coordinated, which suggests the diffusion control of the process. At 20°C, the equilibrium is attained in ~5 h.

The independence of the coordination rate on the Cu^{2+} concentration in solution is due to the low diffusion constant or to a decrease in the equilibrium coordination capacity with a decrease in pH of $CuSO_4$ solution from 5.1 ($[Cu^{2+}]$ 1 g l^{-1}) to 4.7 ($[Cu^{2+}]$ 4 g l^{-1}). Furthermore, with increasing acidity, the hexamer matrix may become denser.

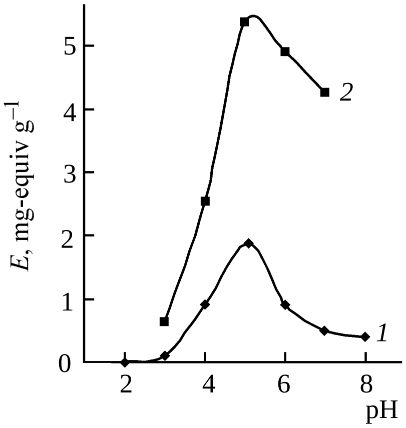


Fig. 2. Equilibrium specific coordination capacity of $(CuPzc)_6$ at 20°C for various ions as a function of solution acidity: (*1*) Cu^{2+}, $C^0_{Cu^{2+}}$ 1 g l^{-1}; (*2*) Co^{2+}, $C^0_{Co^{2+}}$ 1 g l^{-1}.

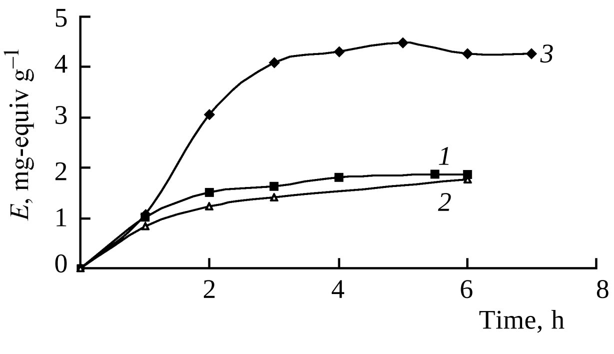


Fig. 3. Isotherms of complexing sorption of metal ions from aqueous solutions with $(PzcCu)_6$ at 20°C: (*1*) Cu^{2+} from $CuSO_4$ solution, $[Cu^{2+}]_0$ 1 g l^{-1}; (*2*) Cu^{2+} from $CuSO_4$ solution, $[Cu^{2+}]_0$ 4 g l^{-1}; and (*3*) Co^{2+} from $Co(COOCH_3)_2$ solution, $[Co^{2+}]_0$ 1 g l^{-1}.

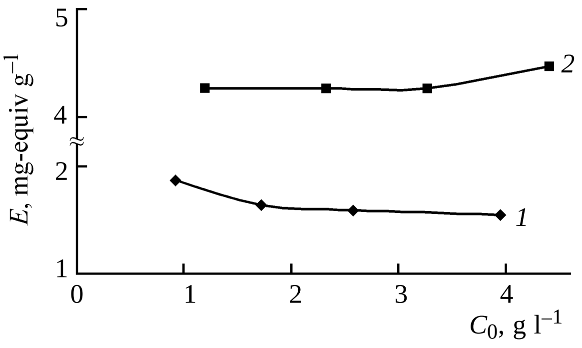


Fig. 4. Equilibrium specific coordination capacity of $(CuPzc)_6$ at 20°C as a function of the initial coordination of the ion being coordinated: (*1*) Cu^{2+} and (*2*) Co^{2+}.

The equilibrium specific coordination capacity of $(PzcCu)_6$ for Cu^{2+} (1.87 mg-equiv g^{-1}), attained at pH 5.1, suggests that each "large" cavity accommodates one copper ion. Contrastingly, the equilibrium specific coordination capacity for Co^{2+} (4.48 mg-equiv g^{-1}), attained in a $Co(COOCH_3)_2$ solution with $[Co^{2+}]_0$ 1 g l^{-1} at pH 7.3, suggests the cobalt coordination not only in "large" cavities, but also with a part of the $\langle N_5$-podand-5$\rangle$ fragment.

Figure 4 shows that the equilibrium specific capacity of $(PzcCu)_6$ for Cu^{2+} decreases with an increase in the initial Cu^{2+} concentration. This trend is due to higher acidity of more concentrated $CuSO_4$ solution, which is clearly confirmed by the dependence of the specific coordination capacity of this complexing sorbent on the solution acidity at a constant Cu^{2+} concentration. As the solution acidity is increased relative to the optimum, the coordination capacity decreases owing to dissociation of the secondary metal complexes. A decrease in the capacity at pH > 5 is apparently due to changes in the state of the ion being sorbed in the solution.

In contrast to the system $(PzcCu)_6$–Cu^{2+}, for the system $(PzcCu)_6$–Co^{2+} the equilibrium specific coordination capacity of the complexing sorbent is virtually independent of the initial cobalt concentration in the solution (Fig. 4), which is due to the buffer properties of the salt used [in the entire examined range of $Co(COOCH_3)_2$ concentrations, pH varies from 7.3 to 7.1]. However, the equilibrium specific coordination capacity of $(PzcCu)_6$ for the Co^{2+} ion is very sensitive to the solution acidity (Fig. 2). As in the case of Cu^{2+}, this dependence has a maximum at pH ~5. Under these conditions, the equilibrium specific coordination capacity (5.37 mg-equiv g^{-1}) corresponds to the accommodation of one cobalt ion in each "large" cavity and each of the six $\langle N_5$-podand-5$\rangle$ fragments.

The different equilibrium specific coordination capacities of $(PzcCu)_6$ for the Cu^{2+} and Co^{2+} ions and their different dependences on the solution acidity indicate that the complexes of the polymeric ligand with Co^{2+} are more stable than those with Cu^{2+}.

Our results show that, despite the similar kinetic pattern, the thermodynamics of the coordination of the Cu^{2+} and Co^{2+} ions are essentially different, which creates prerequisites for the development of complexing sorbents selective to various ions. The aim of the further studies is to find an optimum of the coordination selectivity for each ion in various ion mixtures.

EXPERIMENTAL

Metal complexes of hexameric network tetrapyrazinoporphyrazine were prepared, purified, and identified according to [1].

The coordination properties of $(PzcM)_6$ were determined by placing an accurately weighed portion (0.05–0.2 g) of the finely ground complexing sorbent, preliminarily dried to constant weight at 150°C, in 50 ml of a solution of a metal salt with a known concentration of the metal being coordinated. The mixture was stirred on a magnetic stirrer for a required time, after which a solution sample was taken, and the current metal ion concentration in the solution was determined after filtration through a Schott filter no. 3. The specific coordination capacity was calculated from the difference between the initial and current concentrations, and the maximal constant value of this parameter was assumed to be the equilibrium specific coordination capacity.

To obtain the diffraction patterns, finely dispersed polycrystalline samples of the "bimetallic" complexes were densely packed in a polyvinyl chloride cell, and the patterns were taken on a DRON-3 diffractometer in the reflection mode (CuK_α radiation, Ni filter, differential discriminator).

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