A STUDY OF METAL COMPLEXES OF MACROHETEROCYCLIC COMPOUNDS CONTAINING TRIAZINE [SIC] RESIDUES

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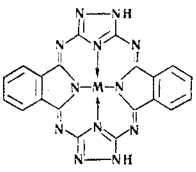
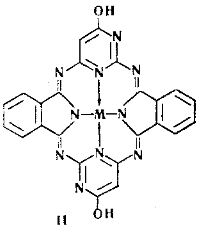
The reaction of macroheterocyclic compounds containing guanazole and pyrimidine residues with metal salts have given complex compounds of copper, nickel, cobalt, cadmium, and zinc, and their properties have been studied. The introduction of the metal atom into the "window" of the macrocycle leads to the appearance of new electronic transitions not characteristic for the ligand. The influence of the metal on the chromophoric system of the macroheterocycle has been elucidated by IR spectroscopy.

Continuing investigations begun previously [1–3], macroheterocyclic compounds (macrocycles) containing triazine [sic] residues and differing from porphyrazine by the fact that the two diagonally opposite pyrrole systems are replaced by two other nitrogen-containing 5- and 6-membered rings (1, 2, 4-triazole or pyrimidine) have been prepared and studied. It was also of interest to study the possibility of the formation of complexes of these macrocycles and the stabilization of the molecules through the replacement of the hydrogen atoms of the imino groups by ions of bivalent metals (M):



I



II

$M = Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}$

Such complexes are formed by the reaction of a macroheterocyclic compound with metal salts, as is shown by the elementary analysis of the reaction products (Table 1) and the absence of absorption bands in the IR spectra in the 3360 cm^{-1} region that is characteristic for the vibrations of the imino group [4].

The question of the influence of the nature of the metal ion on the chromophoric systems of the macroheterocyclic compounds is an extremely interesting one. The entry of a metal into the "window" of the macrocycle (compounds I and II) causes some change in the absorption spectra. In the absorption spectra of the Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} derivatives (Figs. 1 and 2), in addition to the absorption band at 350 nm characteristic for the metal-free compound, there is a new band in the 400 nm region that does not correspond to the ligand. Thus, in the spectrum of the copper complex of compound I there is an absorption maximum at 410 nm and in the spectrum of the copper complex of II one at 415 nm. Thus, the introduction of a metal into the "window" of the macrocycle leads to a bathochromic effect, as in the case of the dipyridyldiisoindole macrocycle [5].

The first absorption band of the macrocycles I and II in the 350 nm region is apparently due to electronic transitions in the individual isoindole nuclei. The introduction into the "window" of the macroheterocyclic compound of an ion of a metal with a covalent nature is accompanied by the formation of a σ-bond because of the filling of the $3d4s4p^2$ (Cu, Ni, Co) and $4d4s4p^2$ (Zn) levels of the ion with the electrons of the unbound electron pairs of the intracyclic nitrogen atoms.

Table 1

Properties of Metal Complexes of the Macroheterocyclic Compounds

Complex	Mp, °C	Color of the substance	Empirical formula	M, % found	M, % calculated	Yield, %
Complexes with I						
Copper	Does not melt below 500	Brown	$C_{20}H_{10}N_{12}Cu$	13.3; 13.4	13.2	86
Nickel	" "	Orange	$C_{20}H_{10}N_{12}Ni$	12.7; 12.9	12.5	84
Zinc	" "	Orange	$C_{20}H_{10}N_{12}Zn$	13.4; 13.3	13.2	85
Cobalt	" "	Brown	$C_{20}H_{10}N_{12}Co$	12.4; 12.5	12.5	87
Cadmium	" "	Orange	$C_{20}H_{10}N_{12}Cd$	21.1; 21.2	21.0	88
Complexes of II						
Copper	Does not melt below 400	Cherry-red	$C_{24}H_{12}N_{10}O_2Cu$	11.9; 11.0	11.8	62
Nickel	" "	Dark brown	$C_{24}H_{12}N_{10}O_2Ni$	10.8; 10.9	11.0	65

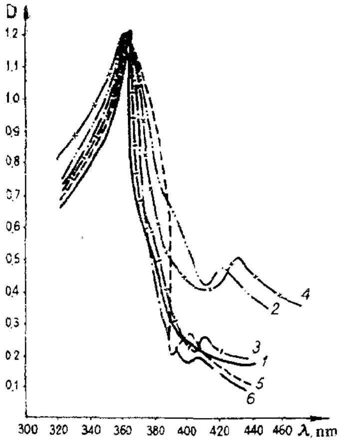


Fig. 1. Electronic absorption spectra of complexes of the macrocycle I in pyridine: 1) macrocycle not bound into a complex; 2) Cu(I); 3) Co(I); 4) Ni(I); 5) Zn(I); 6) Cd(I).

Fig. 2. Electronic absorption spectra of complexes of the macrocycle II in pyridine: 1) macrocycle not bound into a complex; 2) Cu(II); 3) Ni(II).

Table 2

Positions of the Absorption Bands of the Metal Complexes of Macroheterocyclic Compounds

Compound	Electron transitions			
	I		II	
	λ_{max}, nm	D	λ_{max}, nm	D
H_2Mcc	355	1.2	—	—
CuMcc (I)	353	1.2	415	0,44
NiMcc (I)	353	1,22	425	0.48
CoMcc (I)	353	1,15	405	0,25
CdMcc (I)	353	1.14	402	0.22
ZnMcc (I)	355	1.2	400	0.25
H_2Mcc	350	0,84	—	—
CuMcc (II)	350	0.94	410	0.80
NiMcc (II)	365	0,98	420	0.60

It could be expected that the coordination of the molecules of compounds I and II with the central ions would lead to the appearance of a new chromophore, as in the case of phthalocyanine. However, the absorption spectra of the complexes in the UV, visible, and IR regions show that the expected phenomena do not occur.

Apparently, on coordination with insufficiently "rigid" ligands the central ion changes their geometrical configuration. This leads to a stabilization of the π-system of the macrocycle, as has been shown by X-ray structural analysis of a complex of the dipyridyldiisoindole macrocycle [6]. In this case, in accordance with chromaticity theory [7, 8], a bathochromic effect arises.

The similarity of the IR spectra of the initial compounds and the metal complexes I and II in the 700–1900 cm^{-1} region shows that the nature of the central metal atom has no fundamental influence on the spectrum, but that it does cause a shift in some bands (734 → 746 cm^{-1}; 865 → 870 cm^{-1}; 1639 → 1378 cm^{-1}; 1640 → 1660 cm^{-1}) in the high-frequency region on passing from one metal–macrocycle complex to another in the sequence Cu, Ni, Co, Cd. These bands apparently relate to the vibrations of the groups of atoms connected to the central metal atom.

The introduction of a metal leads not only to a change in the spectra but also to a change in the chemical properties of the molecule. The metal complexes of the macroheterocyclic compounds have a considerably enhanced temperature stability (they do not melt below 400° C) and a lower solubility in organic solvents as compared with the metal-free compounds, and they are stable to the action of acids.

EXPERIMENTAL

Macroheterocyclic compounds giving the complexes I containing 1, 2, 4-triazole residues. A mixture of 2.9 g of guanazole (3, 5-diamino-1, 2, 4-triazole) and 4.3 g of diiminoisoindoline in 80 ml of butanol was heated at the boil for 20 hr. The precipitate that had deposited was filtered off and washed with methanol. Yield 64% of a substance not melting below 400° C. Found, %: C 56.8, 56.4; H 3.8, 3.8; N 39.7, 39.4. Calculated for $C_{20}H_{12}N_{12}$, %: C 57.1; H 2.85; N 40.0. 40.0. The substance was red-brown. It dissolved in conc H_2SO_4 with decomposition. It did not dissolve in organic solvents except for pyridine and α-chloronaphthalene, in which it dissolved on heating.

Macroheterocyclic compounds giving the complexes II containing a pyrimidine residue. A mixture of 0.8 g of dimethoxydiiminoisoindoline and 0.6 g of 2, 4-diaminochloropyrimidine with 30 ml of redistilled trichlorobenzene was heated to the boil for 20 hr. The precipitate that had deposited was filtered off and washed with water and ethanol. Yield 67%. The substance did not melt below 400° C. Found, %: C 61.8, 61.9; H 2.9, 3.0; N 30.0, 30.5. Calculated for $C_{24}H_{12}N_{10}O_2$, %: C 60.7; H 2.9; N 29.5. The substance was brown and did not dissolve in α-chloronaphthalene, dimethylformamide, or pyridine, but dissolved in sulfuric acid with decomposition.

Metal complexes I. With stirring, 0.8 g of a macroheterocyclic compound, an equivalent amount of anhydrous metal chloride, and a solvent were heated at the boil under reflux for 3 hr. The precipitate that deposited was filtered off, washed with water until chloride ion was no longer present and then with methanol, dried, and weighed, and the yield and melting point were determined and an elementary analysis was performed. The figures obtained are given in Table 1.

The synthesis of the metal complexes II was carried out similarly. For this purpose, 0.5 g of the macroheterocyclic compound, and an equivalent amount of metal acetate were taken and the solution was heated for 3.5 hr (Table 1).

The metal complexes were insoluble in benzene and its homologs in the cold and on heating. They did not dissolve in halogen-substituted benzenes, nitrobenzene, or aniline. They were sparingly soluble in pyridine and chloronaphthalene in the cold and somewhat more soluble on heating. They dissolved partially in alcohols—butanol, pentanol.

They dissolved in conc H_2SO_4 with decomposition. Under the action of weak mineral acids in the cold they underwent no change and were not demetallated. On dilution of the solution with cold water, they were recovered unchanged.

The absorption spectra were measured on an SF-4 spectrophotometer in pyridine solution at 22-24° C in the ultraviolet and visible parts of the spectrum. The IR spectra were measured in the 700–3800 cm^{-1} region on a UR-10 spectrophotometer.

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