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Complexes of Macroheterocyclic Compounds Having 2,3-Dicyanopyrazine Fragments

M. A. Kulikov, N. R. Neustroeva, Yu. G. Vorob'ev, and R. P. Smirnov

Ivanovo State University of Chemical Engineering, Ivanovo, Russia

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Abstract—Cobalt(II), copper(II), and nickel(II) complexes of macroheterocyclic compounds on the basis of 2,3-dicyanopyrazine were synthesized, and their IR and UV spectra were examined.

Up to now vast data have been accumulated on the synthesis of coordination compounds derived from macroheterocycles containing 1,3-diiminoisoindole fragments and various aromatic amine residues. Early studies of Russian authors [1, 2] dealt with the synthesis and investigation of physical and chemical properties of unsubstituted coordination compounds with ligands having variable dentacity. In the recent years much attention was given to the synthesis and applied properties of coordination compounds having various alkyl moieties, which are soluble in organic solvents [3, 4].

Our research is focused on symmetrical coordination compounds in which benzene fragments of the diiminoisoindole moieties are replaced by pyrazine rings. According to our preliminary results, the presence of heteroatoms in the conjugation system strongly affects properties of the linear chromophore. The complexes were prepared by reaction of macroheterocycles **I** and **II** with the corresponding metal acetates in boiling butanol. Initial compounds **I** and **II** were synthesized by reaction of 2,3-dicyanopyrazine with 2,6-diaminopyridine and *m*-phenylenediamine, respectively, in a high-boiling solvent; also, their synthesis was accomplished through three-unit compounds [5].

As expected, complex formation resulted in reduced solubility of the products which were purified from impurities by extraction with acetone and methanol. According to the data of elemental analysis (Table 1), the obtained complexes were crystal hydrates containing two molecules of water.

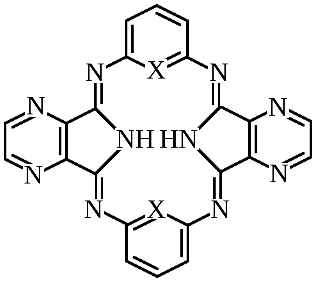
The IR and electronic absorption spectra of the complexes were compared with those of the free ligands. Like phthalocyanine, most vibrations of macroheterocyclic molecules are not characteristic. They correspond to vibrations of the molecular skeleton as a whole rather than of particular groups of atoms. However, some vibrations intrinsic to all the synthesized macroheterocycles and their complexes may be distinguished (Table 2). These include stretching vibrations of double C=C and C=N bonds and single C–C and C–N bonds in the pyrazine (or pyridine) fragments [6]. Absorption bands belonging to vibrations of double bonds shift only slightly in going from ligand **I** to complexes **III**–**V**. The observed changes result from increased rigidity of the complexes, as

Table 1. Metal complexes **III–VIII**

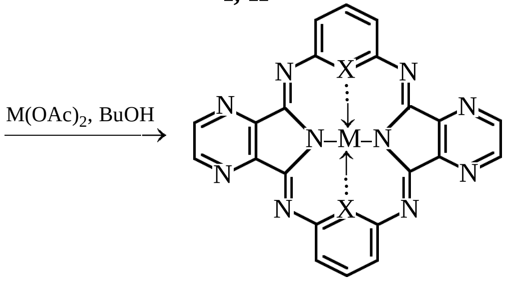
Comp. no.	Yield, %	Metal, %		Formula	λ_{max}, nm
		found	calculated		
III	85	11.0	11.85	$C_{24}H_{12}CuN_{10}$	408, 430
IV	91	10.8	11.03	$C_{24}H_{12}CoN_{10}$	408, 429
V	87	10.8	11.03	$C_{24}H_{12}N_{10}Ni$	408, 428
VI	92	11.3	11.81	$C_{22}H_{10}CuN_{12}$	385
VII	88	10.3	11.00	$C_{22}H_{10}CoN_{12}$	388
VIII	85	11.6	11.00	$C_{22}H_{10}N_{12}Ni$	386

Table 2. Characteristic absorption bands (ν, cm^{-1}) in the IR spectra of metal complexes **III–VIII**

Comp. no.	Pyrazine rings		Macroring			
	C=C, C=N	C–H	C–N, C=N	C–C, C–N	C–N	N–M
III	1560, 1624	2900	1176, 1296, 1340, 1624	620	1340, 1396	480, 548
IV	1548, 1604	2900	1176, 1340, 1640	620	1340, 1370	500, 520
V	1550, 1620	2880	1175, 1345, 1625	615	1340, 1380	485, 510
VI	1576, 1632	2880	1150, 1660, 1680	605	1400	468, 552
VII	1576, 1664	2900	1144, 1320, 1600, 1620, 1680	615	1360, 1400	485, 552
VIII	1580, 1670	2900	1148, 1590, 1620, 1682	610	1365, 1380	472, 555



I, II



III–VIII

III, X = N, M = Cu; **IV**, X = N, M = Co; **V**, X = N, M = Ni; **VI**, X = CH, M = Cu; **VII**, X = CH, M = Co; **VIII**, X = CH, M = Ni.

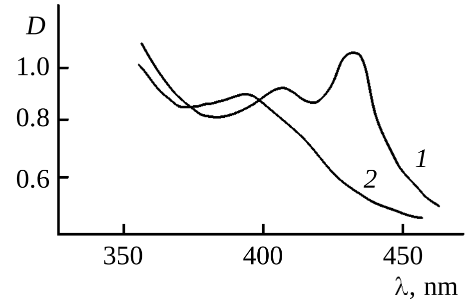
compared to free ligands **I** and **II**. Broad absorption bands in the region of 2900 cm^{-1}, corresponding to stretching vibrations of C–H bonds, almost do not change their position. Presumably, these bands are overlapped by OH absorption due to crystallization water [7]. The absence of νNH bands at about 3400 cm^{-1} and the presence of νN–M absorption at 460–550 cm^{-1} confirm the formation of metal complexes.

Structures **III–V** and **VI–VIII** are characterized by different modes of coordination of the macroring to the central metal ion. In complexes **III–V** protons of the isoindole imino groups are replaced by metal with formation of new N–M bonds through population of vacant orbitals of the metal ion by unshared electron pairs on the pyridine nitrogen atoms (*dsp*^{2} hybridization of the central atom). A small red shift of the long-wave absorption maximum is observed in going from ligand **I** to complexes **III–V** (Table 1; see figure). No shift of the absorption maxima occurs upon formation of complexes **VI–VIII**, and the long-wave maximum decreases in intensity. These data suggest that the coordination entity in **III–V** has a more favorable planar structure.

Complexes **VI–VIII** lack dative N→M bonds, so that planar structure of the coordination entity therein is less probable. The red shift of the long-wave absorption maxima in the electronic spectra of **III–V** does not exceed 4 nm, in contrast to known carbon analogs for which the corresponding shift attains 30–50 nm [1]. Presumably, the metal-induced polarization of the isoindole fragment is compensated by polarization caused by the electron-acceptor effect of the nitrogen atoms. The blue shift of the long-wave absorption maximum in the spectra of complexes **VI–VIII** is even smaller. This may be due to variation of their geometric structure toward reduced coplanarity.

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord M-40 spectrophotometer in *N*,*N*-dimethyl-



Electronic absorption spectra of complexes (*1*) **IV** and (*2*) **VII** in dimethylformamide.

formamide. The IR spectra were recorded on a Specord M-80 instrument in KBr.

General procedure for synthesis of complexes III–VIII. Macroheterocyclic compound **I** or **II**, 0.00011 mol, and appropriate metal acetate, 0.0003 mol, were added to 10 ml of butanol, and the mixture was refluxed for 12 h under vigorous stirring. The mixture was cooled, the precipitate was filtered off and washed with a 5% solution of ammonia to remove excess metal salt, and impurities were removed by extraction with acetone and methanol. The products were brown powders with various tints which did not melt below 400°C.

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