

A similar product was formed after 2 h when the amine (IVa) was heated in the nitrating mixture at 40-50°C or treated with nitric acid ( $d = 1.37$ ) at 50-60°C for 3-5 min.

When 0.24 g (1 mmole) of the nitrate (VIIIa) and 0.06 g (1.1 mmoles) of potassium hydroxide were heated in 4 ml of water for 2-3 min, a precipitate of the amine (IVa) was formed. The product formed colorless crystals; mp 305-306°C (from water). A mixed melting test with the authentic amine (IVa) did not give a melting-point depression.

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#### TEMPLATE SYNTHESIS OF METAL COMPLEXES OF 7,16-DISUBSTITUTED

#### DIBENZO[b,i][1,4,8,11]TETRAAZA[14]ANNULENES

#### FROM MALONIC ALDEHYDE ACETALS

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Metal complexes of 7,16-dialkyl- and 7,16-diphenyldibenzo[b,i][1,4,8,11]tetraaza[14]annulenes have been prepared by template condensation of o-phenylenediamine with 2-alkyl- and 2-phenyl-1,1,3,3-tetraethoxypropanes, respectively, in the presence of divalent metals salts. The effects of substituents in the meso-position and of the metal ion on the nature of the electronic and vibrational spectra of these metal complexes are discussed.

The chemistry of nitrogenous macroheterocycles has attracted increased research interest recently [1, 2]. Members of this class of chemical compounds are finding practical applications in new areas [3]. The bis(dimethylacetal) of malonaldehyde has been used successfully in the synthesis of unsubstituted (in the meso-position) nickel complexes of dibenzo[b,i] ×

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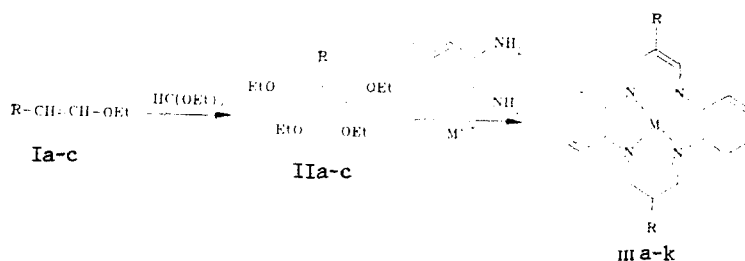
TABLE 1. Spectral Characteristics of Metal Complexes IIIa-k

Compound	Molecular formula	M <sup>++</sup>	Electronic spectrum, $\lambda_{\max}$ , nm (log $\epsilon$ )	IR spectrum, cm <sup>-1</sup>	Yield, %
IIIa	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> Ni	344	423 (4.80)	1330, 1460, 1473, 1574	89
IIIb	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> Ni	400	435 (4.82)	1335, 1460, 1478, 1596	68
IIIc	C <sub>30</sub> H <sub>22</sub> N <sub>4</sub> Ni	496	490 (4.92)	1332, 1462, 1480, 1590	51
IIId	C <sub>16</sub> H <sub>14</sub> CoN <sub>4</sub>	345	411 (4.77)	1330, 1460, 1471, 1575	87
IIIe	C <sub>22</sub> H <sub>22</sub> CoN <sub>4</sub>	401	415 (4.76)	1335, 1460, 1476, 1596	63
IIIf	C <sub>30</sub> H <sub>22</sub> CoN <sub>4</sub>	497	425 (4.64)	1330, 1462, 1480, 1596	48
IIIg	C <sub>16</sub> H <sub>14</sub> CuN <sub>4</sub>	349	406 (4.90)	1298, 1452, 1473, 1576	87
IIIh	C <sub>22</sub> H <sub>22</sub> CuN <sub>4</sub>	405	427 (4.83)	1306, 1458, 1480, 1592	65
IIIi	C <sub>30</sub> H <sub>22</sub> CuN <sub>4</sub>	501	433 (4.69)	1300, 1458, 1480, 1571	48
IIIj	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> Pd	393	385 (4.51)	1292, 1442, 1467, 1578	77
IIIk	C <sub>16</sub> H <sub>14</sub> HgN <sub>4</sub>	487			20

\*Mass spectrometric.

[1,4,8,11]tetraaza[14]annulene [4, 5]. Our goal in the present paper was to prepare corresponding metal complexes of 7,16-disubstituted dibenzo[b,i][1,4,8,11]tetraaza[14]annulenes and to study the effects of substituents in the malonaldehyde acetals and of various template metal ions on the condensation reaction itself and on the physicochemical properties of the resulting complexes.

As a three-carbon dicarbonyl synthon for the synthesis of metal complex derivatives of different dibenzotetraazaannulenes we used bis(diethylacetals) malonic (IIa), ethylmalonic (IIb), and phenylmalonic aldehydes (IIc), which were prepared by treatment of the enol ethers Ia-c with ethyl orthoformate in the presence of boron trifluoride etherate [6].



I, II a R=H, b R=Et, c R=Ph; III a,d,g,j,k R=H; b,e,h R=Et, c,f,i R=Ph; a-c M=Ni, d-f M=Co, g-i M=Cu, j M=Pd, k M=Hg

The metal complexes IIIa-k were synthesized according to the procedure reported in [4].

In order to study the effect of different template ions on the course of the cyclization reaction, we used various salts (acetates, chlorides, and nitrates) of nickel, cobalt, copper, palladium, mercury, calcium, lead, and barium. Nickel, cobalt, and copper complexes (IIIa-i), as well as the palladium complex (IIIj), were obtained in fair to excellent yields, and differed little from one another with the same R groups (Table 1). Attempts to prepare calcium, barium, and lead complexes from various acetals II were unsuccessful. The mercury complex IIIk could be isolated only in 20% yield, which is considerably lower than the yields obtained for the corresponding nickel, cobalt, and copper complexes. The results obtained in these syntheses can be explained in terms of ligand field theory and taking into account the geometric sizes of the metal ions [2].

The course of the ring closure step depends to a large degree on the nature of the substituent in the meso-position of acetals II. Nickel, cobalt, and copper complexes of the unsubstituted dibenzotetraazaannulene, compounds IIIa, d, g, were synthesized in 87-89% yield. The formation of the corresponding 7,16-disubstituted metal complexes proceeded less successfully. Acetal IIb gave complexes in 63-68% yield, while acetal IIc gave complexes in 48-51% yield.

The IR spectra of metal complexes III (Table 1), in agreement with the data reported in [7, 8], contain a strong absorption band in the 1460-1480 cm<sup>-1</sup> region, which has been assigned to C=C and C=N stretching vibrations in the macrocyclic skeleton, as well as a weak

band in the 1590-1610  $\text{cm}^{-1}$  region, which has been assigned to C=C stretching vibrations in the aromatic rings. The spectra also contain a characteristic Ar-N-C bending vibration band at 1290-1330  $\text{cm}^{-1}$ . The formation of N-M bonds is indicated qualitatively by the absence of absorption in the 3200-3350  $\text{cm}^{-1}$  region, which is characteristic of N-H bonds in secondary amines.

The electronic spectra of metal complexes III contain several peaks, with the main peak located at 410-490 nm and with a molar extinction coefficient on the order of tens of thousands (Table 1). This intense absorption reflects a  $\pi \rightarrow \pi^*$  transition in the macroheterocycle and charge transfer from the metal ion to the ligand [7]. Depending on the nature of the substituents present and on the metal ion, the position of the main absorption maximum can vary widely. Metal complexes IIIb, e, and h absorb at higher wavelength, for instance, than their unsubstituted analogs IIIa, d, and g, apparently due to the electron-donating effect of the ethyl substituents. An even greater bathochromic shift is observed in metal complexes IIIc, f, and i. The occurrence of such a shift provides qualitative evidence for the assumption that the phenyl substituents are located in the same plane as the macroheterocycle skeleton, forming one continuous and planar  $\pi$ -electron system. The marked hypsochromic shift of the main absorption band in compound IIIk is apparently due to disruption of the coplanarity of the molecule, which in turn arises from an unsuitable "fit" of the geometric sizes of the mercury ion and of the dibenzotetraazaannulene cavity.

#### EXPERIMENTAL

IR spectra were recorded on a UR-10 spectrophotometer using KBr pellets. Electronic spectra were measured on a Specord UV-Vis spectrophotometer using solutions in DMF. Mass spectrometric molecular-weight determinations were made on a JEOL GMS D-3 mass spectrometer. The results of C, H, N, and Me elemental analysis agreed with the calculated values.

Dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinatonicel(II) (IIIa). A mixture of 1.1 g (5 mmol) of 1,1,3,3-tetraethoxypropane, 0.58 g (5 mmol) of o-phenylenediamine, and 0.67 g (2.5 mmol) of nickel acetate tetrahydrate (II) in 50 ml water was refluxed for 4 h. The reaction mixture was cooled to 20°C and the resulting precipitate was filtered and washed with dilute methanol (1:1). Yield 0.77 g.

Compounds IIIb-k were obtained in an analogous manner, and consisted of finely crystalline dark orange, dark purple, or black powders, mp >300°C.

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