Treatment of I and VII with Hydriodic and Hydrobromic Acids. Reaction mixtures from which 1,2,3,4-tetrahydroquinoxaline was isolated after evaporation and vacuum sublimation at 100°C (0.8 mm) were obtained by heating a solution of 0.32 g (2 mmole) of the dihydrobromide of I or the hydrobromide of VII in 6 ml of 56% HI in an ampul at 100°C for 6 h or in 10 ml of 48% HBr at 140°C for 60 h. In each case 0.12 g (48%) of a substance with mp 95°C was isolated. The characteristics of the compound obtained were in agreement with the data in [8].

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LITERATURE CITED

1. G. V. Shishkin and A. A. Gall', Khim. Geterotsikl. Soedin., No. 6, 827 (1980).
2. F. Cortese, Organic Syntheses, Collective Vol. 2, Wiley, New York (1943), p. 91.
3. G. R. Ramage and G. Trappe, J. Chem. Soc., No. 11, 4406 (1952).
4. M. A. Paul and F. A. Long, Chem. Rev., 57, 1 (1957).
5. L. B. Mrachkovskaya and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 6, 845 (1976).
6. S. M. McElvain and L. W. Bannister, J. Am. Chem. Soc., 76, 1126 (1954).
7. V. Beksha and Yu. Zh. Degutis, Zh. Org. Khim., No. 1, 1842 (1965).
8. The Sadtler Standard Spectra, Sadtler Research Laboratories, NMR Spectrum No. 18420; Infrared Grating Spectrum No. 12806.

DERIVATIVES OF 1,2,5,6,9,12-HEXAAZACYCLOTETRADECATETRAENE AND 1,2,5,6,9,14-HEXAAZACYCLOHEXADECAHEXAENE BASED ON 2,3-DIHYDRAZINOQUINOXALINE

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A bis(hydrazone) was synthesized by the reaction of 2,3-dihydrazinoquinoxaline with 3-methyl-1-phenyl-1H-pyrazole-4,5-dione. Treatment of the bis(hydrazone) with $POCl_3$ and Et_3N gave a dichloro diazo compound, from which macrocyclic metal chelates, viz., derivatives of 1,2,5,6,9,12-hexaazacyclotetradecatetraene and 1,2,5,6,9,14-hexaazacyclohexadecahexaene, were obtained by reaction with diamines in dimethylformamide in the presence of Pd(II) and Ni(II)salts.

2,3-Dihydrazinoquinoxaline has been described [1, 2], but little study has been devoted to it. Moreover, it holds promise as the starting compound in the synthesis of bis(diazo) macrocyclic systems by nucleophilic substitution of the halogen of the bis(diazo) compound by arylamino groups. The synthesis was carried out via the scheme.

Compound III was obtained initially by the reaction of I and II. The IR absorption band of the stretching vibrations of the carbonyl groups lies at 1675 cm^{-1}, while the absorption band of the stretching vibrations of the NH groups at 3100-3300 cm^{-1} is broadened markedly, which is characteristic for hydrazones with a strong intramolecular hydrogen bond [3]. A broad singlet of an NH proton involved in an intramolecular hydrogen bond is observed in the PMR spectrum at 14.3 ppm (Table 1). The identical character of the chemical shifts of the 5-H and 8-H protons of the quinoxaline ring, as well as the 2-H and 6-H and 3-H and 5-H protons of the N-phenyl rings, constitutes evidence for symmetry of the molecule and equivalence of the N-phenyl rings. It follows from these data that III probably exists in the Z,Z-bis(hydrazone) form.

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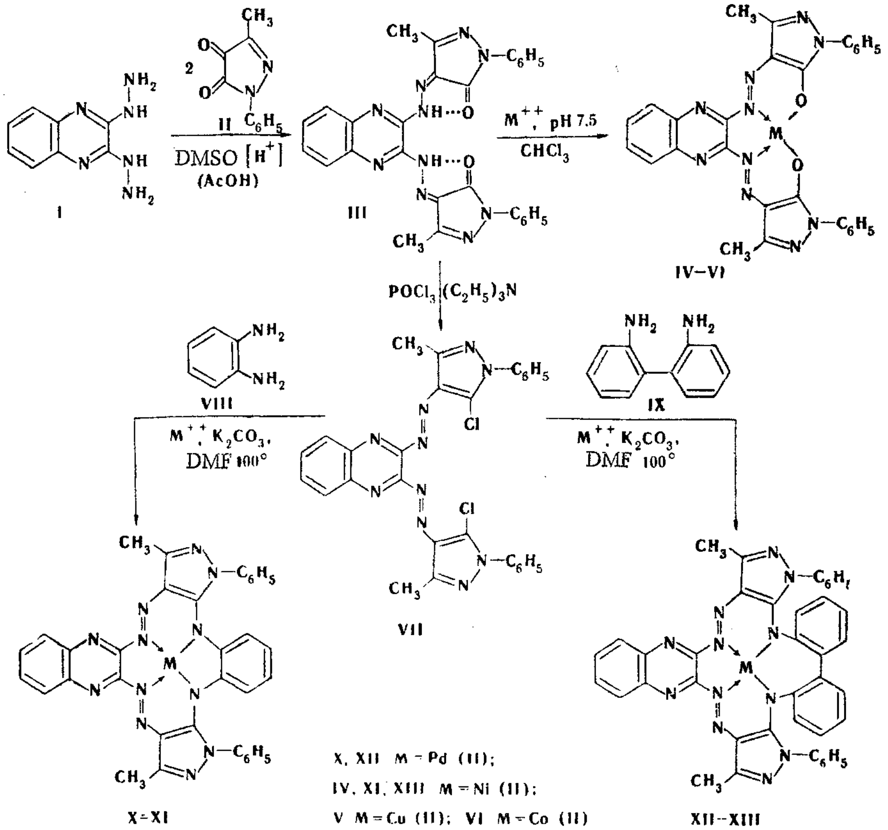
TABLE 1. PMR Spectra of III, VII, and X-XIII

Compound	Solvent (30°C)	δ, ppm							
		NH	CH_3 (pyrazole)	Protons of the N-phenyl ring			Protons of the quinoxaline ring, AA'BB'		Protons of the o-phenylenediamine (diaminobiphenylyl) ring, AA'BB'
				2-, 6-	3-, 5-	4-H	8-, 5-	7-, 6-H_2	
III	$CDCl_3$[a]	14,3^s (1H)	2,56s (6H)	7,98 m (2H)	7,46 m (2H)	7,1—7,2[c]	7,95 m (2H)	7,68m (2H)	
VII	$CDCl_3$[b]		2,56s (6H)	7,35—7,69 m			8,27 m (2H)	7,80m (2H)	
X	$CDCl_3$[a]		2,65s (6H)		7,19 s		7,87m (2H)	7,53m (2H)	6,25 node center
XI	$CDCl_3$[a]		2,68s (6H)	7,2—7,3 m			7,91m (2H)	7,52m (2H)	6,21 m (AA'), 6,42 m (BB ')
XII	$CDCl_3$[a]		2,62s (6H)	7,06—7,36m			8,07m (2H)	7,59m (2H)	6,64—7,36 m
XIII	$CDCl_3$[a]		2,60s (6H)	7,04—7,40m			8,08m (2H)	7,64 m (2H)	6,66—7,40 m

[a] Saturated solution. [b] 0.1 M $CDCl_3$. [c] The signals are overlapped by a strong signal from the solvent.



It is interesting that carmine-red crystals that turn orange when they are heated in the solid form or in solution are obtained in the reaction of I with II at room temperature after careful recrystallization of the product. The spectral characteristics of the red and orange forms in solution are identical, but the IR spectra in KBr differ. Thus, intensities of the bands of the C=O stretching vibrations (1675 cm^{-1}) and the out-of-plane deformation vibrations of the o-disubstituted benzene ring (756 cm^{-1}) are increased in the IR spectrum of the red form, and new intense or medium-intense bands appear at 1613, 1526, 1471, and 1110 cm^{-1}. The red form is evidently the E,Z-isomer.

Complexes IV-VI, which were found to be only slightly soluble, were obtained in the reaction of bis(hydrazone) III with the cations of divalent metals. Intense isotope peaks of molecular ions are recorded in their mass spectra, while fragment ions are virtually absent.

TABLE 2. Electronic Spectra of Solutions of III, IV, VII, and X-XIII in $CHCl_3$

Compound	λ_{max}, nm (lg ε)
III	250 i (4,53); 325 i (4,20); 357 (4,36); 423 (4,54)
VII	326 (4,59); 346 i (4,56); 355 i (4,55)
X	250 (4,61); 284 (4,42); 395 (4,37); 412 (4,43); 451 (4,49); 481 (4,45); 512 (4,53); 542 i (4,15); 610 i (3,54); 657 i (3,26)
XI	250 (4,59); 290 (4,46); 312 i (4,25); 372 (4,25); 408 (4,25); 453 i (4,50); 485 (4,41); 525 sh (4,34); 618 i (3,77)
XII	250 i (4,62); 268 (4,57); 392 i (4,30); 424 (4,34); 495 (4,54)
XIII	266 (4,59); 395 i (4,25); 422 (4,28); 499 (4,49)
IV	251 (4,49); 352 (4,33); 456 (4,37); 518 (4,34); 545 i (4,26)

Dichloro bis(diazo) compound VII was obtained by treatment of III with phosphorus oxychloride and triethylamine. The IR spectrum of VII does not contain an absorption band in the region of C=O stretching vibrations, the intensity of the stretching vibrations of the C⩵C/C⩵N bonds at 1600, 1540, and 1504 cm^{-1} is weakened markedly. The chemical shifts of the 5-H and 8-H protons of the quinoxaline rings in the PMR spectrum of this compound are identical but are shifted ~0.3 ppm as compared with III to weak field. The ^{13}C NMR spectrum confirms its structure and constitutes evidence for the symmetrical character of the molecule (see the experimental section). The ratio of the intensities of the isotope peaks in the mass spectrum of VII confirms the presence of two chlorine atoms.

Macrocyclic metal chelates X-XIII were obtained by the reaction of dichloro bis(diazo) compound VII with diamines VIII and IX under template conditions. The IR spectra of these compounds do not contain absorption bands of NH stretching vibrations at 3100-3500 cm^{-1}. The PMR spectra of solutions of X-XIII in $CDCl_3$ consist of two AA'BB' systems of spectra of the protons of two symmetrical o,o'-disubstituted benzene rings that arise from the quinoxaline and o-phenylenediamine (diaminobiphenylyl) rings, a singlet of protons of the CH_3 groups, and a multiplet of the N-phenyl rings. Close coincidence of all of the transitions is observed in the electronic absorption spectra (Table 2) in chloroform for XII and XIII, whereas in the case of the X-XI pair the long-wave transition of X is located more in the red region than in the case of XI. The addition of pyridine to solutions of X-XIII does not lead to a shift of λ_{max} in the electronic absorption spectra, which indicates the absence of a tendency to undergo axial ligation. The compounds do not liberate a metal ion under the influence of concentrated mineral acids, and this characterizes their great stability. Six isotope peaks of molecular ions are observed in the mass spectra of macrocyclic metal chelates X and XII, and from the distribution of their intensities one can form a judgment regarding the presence of a Pd atom in the molecules; five isotope peaks of the molecular ions are present in the mass spectra of XI and XIII, and the ratio of their intensities confirms the presence of an Ni atom. Fragmentation under the influence of electron impact is not observed.

EXPERIMENTAL

The IR spectra of solutions of the compounds in $CHCl_3$ and of KBr pellets were recorded with a UR-20 spectrometer. The electronic spectra were obtained with a Unicam SP-100A spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-100-12 spectrometer with tetramethylsilane as the internal standard. The mass spectra of I-VII, XII, and XIII were obtained with an MS-702 mass spectrometer; the mass spectra of X and XI were obtained with a Varian Mat CH-6 mass spectrometer with a source with electron impact with direct introduction of the samples into the ionization region. The purity of the compounds was monitored by thin-layer chromatography (TLC) on Silufol UV-254.

2,3-Dihydrazinoquinoxaline (I) was obtained by the method in [2], and its constants were in agreement with the data in [1, 2]. 3-Methyl-1-phenyl-1H-pyrazole-4,5-dione (II) was obtained by the methods in [4, 5]; according to the data in [4] and [5], this compound had mp 119 and 120-121°C, respectively.

2,4-Dihydro-5-methyl-2-phenyl-3H-pyrazole-3,4-dione 4-Bis(quinoxaline-2,3-diylhydrazone) (III). A) A 0.48-g (2.5 mmole) sample of I was dissolved by heating on a water bath and stirring in 12 ml of dimethyl sulfoxide (DMS). The solution was cooled to room temperature, a solution of 0.94 g (5 mmole) of II in 8 ml of DMSO was added dropwise, and 0.05 g

(0.3 mmole) of p-toluenesulfonic acid was added. The mixture was stirred at room temperature for 5 h, after which the precipitate was removed by filtration, washed with water, dried in a vacuum desiccator, and recrystallized from dimethylformamide (DMF) (or pyridine) to give 0.71 g (53%) of carmine-red needles.

B) The bis(hydrazone) was similarly obtained in acetic acid after reaction for 2 h. The yield was 0.76 g. The product was soluble in chloroform, DMF, and DMSO, less soluble in benzene and alcohols, soluble in hot aqueous alkalis, and insoluble in water and had mp 277-278°C. IR spectrum (in $CHCl_3$), ν, cm^{-1}, ε ($liters\text{-}mole^{-1}\text{-}cm^{-1}$): 1675 (850), 1617 sh (245), 1600 (590), 1570 i (870), 1555 (1240), and 1505 (870). Found %: C 63.5; H 4.2; N 26.3; M 530. $C_{28}H_{22}N_{10}O_2$. Calculated %: C 63.4; H 4.2; N 26.4; M 530.5.

2,3-Bis(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)quinoxaline (VII). A 20-ml (~0.22 mole) sample of phosphorus oxychloride was added with stirring to 2.65 g (5 mmole) of III, after which 1.5 ml (15 mmole) of triethylamine was added dropwise, and the mixture was refluxed for 8 h. A total of 10 ml of phosphorus oxychloride was removed by vacuum distillation, and the residue was cooled and poured with stirring over 100 g of crushed ice. The aqueous mixture was neutralized to pH 6-7 with 1 N NaOH solution, and the precipitate was removed by filtration, washed with water, dried, and recrystallized from isopropyl alcohol (or benzene) to give 1.71 g (60%) of light-orange needles with mp 178-179°C that were soluble when they were heated with many organic solvents but insoluble in aqueous alkalis and water. ^{13}C NMR spectrum in $CDCl_3$, δ (ppm): quinoxaline ring: 5-, 8-C_2 (130.21), 6-, 7-C_2 (130.74), 9-, 10-C_2 (137.49), 2-, 3-C_2 (153.44); pyrazole ring: CH_3 (14.97), C—Cl (131.63), C—N (135.55), C—CH_3 (143.85); phenyl ring: 1-C (141.71), 2-, 6-C_2 (124.88), 3-, 5-C_2 (129.23), 4-C (129.00). IR spectrum: 1600 (218), 1540 (145), and 1504 cm^{-1} (175). Found %: C 59.2; H 3.6; Cl 12.6; N 24.5; M 566 (by mass spectrometry with respect to the first isotope peak). $C_{28}H_{20}Cl_2N_{10}$. Calculated %: C 59.3; H 3.6; Cl 12.5; N 24.7; M 567.4.

[1,16,17,22-Tetrahydro-3,14-dimethyl-1,16-diphenylbenzo[j]dipyrazolo[4,3-g:3',4'-m]quinoxalino[2,3-c][1,2,5,6,9,12]hexaazacyclotetradecatetraenato(2-)-N^5,N^{12},N^{17},N^{22}]palladium (X). A solution of 0.18 g (1 mmole) of $PdCl_2$ in 50 ml of DMF and 0.27 g (2 mmole) of K_2CO_3 were added to a solution of 0.57 g (1 mmole) of VII and 0.11 g (1 mmole) of o-phenylenediamine in 50 ml of DMF, and the mixture was stirred at 100-110°C for 5 h. The course of the reaction was monitored by TLC (elution with benzene). A total of 70 ml of DMF was removed by vacuum distillation, and the residue was diluted with 200 ml of water. The aqueous mixture was heated to the boiling point and cooled, and the precipitate was removed by filtration, dried, and purified by column chromatography on L 40/100 silica gel [elution with chloroform–acetone (20:1)]. Evaporation and recrystallization of the residue from benzene gave 0.25 g (35%) of shiny, very fine, dark-red needles that were soluble in chloroform, DMSO, DMF, concentrated H_2SO_4, and hot benzene, less soluble in alcohols, and insoluble in water and melted above 350°C. IR spectrum: 1598 (277), 1589 (261), 1566 (590), 1559 i (545), and 1501 (237). Found %: C 57.8; H 3.4; N 23.7; residue 15.0; M 702 (with respect to the first isotope peak). $C_{34}H_{24}N_{12}Pd$. Calculated %: C 57.7; H 3.4; N 23.8; Pd 15.0; M 707.0.

[1,16,17.22-Tetrahydro-3,14-dimethyl-1,16-diphenylbenzo[j]dipyrazolo[4,3-g:3',4'-m]quinoxalino[2,3-c][1,2,5,6,9,12]hexaazacyclotetradecatetraenato(2-)-N^5,N^{12},N^{17},N^{22}]nickel (XI). This compound was obtained under conditions similar to those used to prepare X, except that $(CH_3COO)_2Ni \cdot 4H_2O$ was used as the metal salt. At the end of the reaction, the mixture was vacuum distilled to dryness, and the residue was diluted with water. The solid material was removed by filtration, dried, and dissolved by heating in 200 ml of chloroform. The chloroform solution was filtered, the chloroform was removed by distillation to dryness, and the residue was recrystallized from benzene to give 0.2 g (30%) of dark-violet needles that had the same solubility as X and melted above 350°C. IR spectrum: 1594 (505), 1568 (838), 1559 i (335), and 1498 (458). Found %: C 62.0; H 3.6; N 25.4; residue 9.0; M 658. $C_{34}H_{24}N_{12}Ni$. Calculated %: C 61.9; H 3.7; N 25.5; Ni 8.9; M 659.3.

[1,16,17,26-Tetrahydro-3,14-dimethyl-1,16-diphenyldibenzo[j,l]dipyrazolo[4,3-g:3',4'-o]quinoxalino[2,3-c][1,2,5,6,9,14]hexaazacyclohexadecahexaento(2-)-N^5,N^{12},N^{17},N^{26}]palladium (XII). A 0.3-g (2 mmole) of K_2CO_3 and 0.18 g (1 mmole) of $PdCl_2$ in 50 ml of DMF were added to a solution of 0.57 g (1 mmole) of VII and 0.18 g (1 mmole) of 2,2'-diaminobiphenyl in 30 ml of DMF, and the mixture was stirred at 100°C for 5 h. The DMF was removed by distillation to dryness, and the residue was diluted with water. The aqueous mixture was heated to the boiling point, and the precipitate was removed by filtration, washed with water, dried, and dissolved in 70 ml of chloroform. The chloroform solution was applied to a column filled with L 40/100 silica gel [elution with benzene—CCl_4—acetone (10:5:1)]. Evaporation of the solvent and recrystallization of the residue from benzene gave 0.19 g (24%) of dark-brown needles that had the same solubility as X and melted above 350°C. IR spectrum: 1603 (206), 1565 (238), and 1498 cm^{-1} (222). Found %: C 61.4; H 3.7; N 21.4; residue 13.7; M 778. $C_{40}H_{28}N_{12}Pd$. Calculated %: C 61.3; H 3.6; N 21.5; Pd 13.6; M 783.1.

[1,16,17,26-Tetrahydro-3,14-dimethyl-1,16-diphenyldibenzo[j,l]dipyrazolo[4,3-g:3',4'-o]-quinoxalino[2,3-c][1,2,5,6,9,14]hexaazacylohexadecahexaenato(2-)-N^5,N^{12},N^{17},N^{26}]nickel (XIII). This compound was obtained under conditions similar to those in the preparation of XII, except that $(CH_3COO)_2Ni \cdot 4H_2O$ was used as the metal salt. Workup gave 0.15 g (20%) of dark-brown needles that had the same solubility as X and melted above 350°C. IR spectum: 1599 (230), 1558 (270), and 1492 cm^{-1} (234). Found %: C 65.4; H 3.9; N 22.8; residue 7.9; M 734. $C_{40}H_{28}N_{12}Ni$. Calculated %: C 65.3; H 3.8; N 22.8; Ni 8.0; M 735.4.

2,3-Bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)quinoxalinato(2-)-O,N,N',O'-nickel (IV). A solution of 0.26 g (1 mmole) of $(CH_3COO)_2Ni \cdot 4H_2O$ was added to a solution of 0.53 g (1 mmole) of III in 100 ml of $CHCl_3$, after which the pH was brought up to 7.5 with stirring at room temperature by means of 40% NaOH solution. After shaking for 2 h, the layers were separated, and the organic layer was washed with water, dried with Na_2SO_4, applied to a column filled with SiO_2, and eluted with chloroform—acetone (10:1). The brownish-red zone was collected, and the solvent was removed by evaporation at room temperature to give 0.28 g (47%) of brownish-red rhombic crystals. During an attempt to crystallize the product with heating, it became virtually insoluble and melted above 300°C. IR spectrum: 1624 (640) and 1600 cm^{-1} (1300). Found %: C 57.2; H 3.5; N 23.8; residue 9.9; M 586 (with respect to the first isotope peak). $C_{28}H_{20}N_{10}NiO_2$. Calculated %: C 57.3; H 3.4; N 23.8; Ni 10.0; M 587.2.

2,3-Bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)quinoxalinato(2-)-O,N,N',O'-copper (V). This compound was obtained under conditions similar to those in the preparation of IV, except that $(CH_3COO)_2Cu \cdot H_2O$ was used as the metal salt. Workup gave 0.27 g (45%) of brown crystals that had the same solubility as IV and melted above 300°C. Found %: C 56.8; H 3.5; N 23.6; residue 10.7; M 591. $C_{28}H_{20}CuN_{10}O_2$. Calculated %: C 56.8; H 3.4; N 23.7; Cu 10.7; M 592.1.

2,3-Bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalinato(2)-O,N,N',O'-cobalt (VI). This compound was obtained under conditions similar to those in the preparation of IV, except that $(CH_3COO)_2Co \cdot 4H_2O$ was used as the metal salt. Workup gave red-brown crystals (44%) that had the same solubility as IV and melted above 300°C. Found %: C 57.3; H 3.4; N 23.8; residue 10.1; M 587. $C_{28}H_{20}CoN_{20}O_2$. Calculated %: C 57.2; H 3.4; N 23.8; Co 10.0; M 587.4.

LITERATURE CITED

1. K. Asano, Yakugaku Zasshi, 78, 729 (1958).
2. V. M. Dziomko, K. A. Dunaevskaya, and K. E. Kalinina, Zh. Org. Khim., 8, 161 (1972).
3. Yu. P. Kitaev (ed.), The Chemistry of Hydrazones [in Russian], Moscow (1977), p. 196.
4. F. Sachs and H. Barschall, 35, 1437 (1902).
5. West German Patent No. 1181057; Chem. Abstr., 62, P2865e (1964).