$\frac{1-(\alpha-\text{Cyano-2,3-dimethoxybenzyl})-3,5-\text{diphenyl-2-pyrazoline (IIIc).}}{\text{from the salt (Ic). Yield 35\%, mp 187°C. IR spectrum, cm⁻¹: 1675, 2280.} Mass spectrum: 397 (10.0), 222 (21.2), 221 (100.0), 176 (23.2), 116 (24.7), 115 (57.6), 104 (44.4), 103 (77.5), 91 (67.2), 77 (36.2).}$

1-(1-Ethoxycarbonylprop-1-en-2-yl)-3-methyl-5-phenyl-2-pyrazoline (VI). A solution of 3 g (3.5 mmole) of the salt (IVa) in 15 ml of absolute pyridine was left to stand for 2 h. Then the pyridine was evaporated off and the residual mass was treated with 10 ml of water and extracted with chloroform (3 × 10 ml). The extract was dried with sodium sulfate, the solvent was evaporated off, and the residue was recrystallized from hexane. The constants and yield of the substance are given in Table 1.

<u>3-Methyl-l-(4-oxopent-2-en-2-yl)-5-phenyl-2-pyrazoline (VII)</u>. This was obtained similarly from salt (Vc) (see Table).

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FUNCTIONALIZED DERIVATIVES OF DIBENZO[c,j]DIPYRAZOLO-

[3,4-f:3',4'-m][1,2,5,8,9,12]HEXAAZACYCLOTETRADECINATE

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A number of derivatives of dibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecinate with peripheral nitro, amino, and acetylamino groups have been synthesized.

Functionalized derivatives of macroheterocyclic compounds are of interest in connection with the broad possibilities of obtaining from them "picket fence" [1, 2], capped [3, 4], cyclophane (binuclear) homo- and heterobinuclear [5, 6], and other superstructures [7-9], and also spin-labeled [10], oligo peptide [11], and polymeric [12] derivatives and systems covalently bound to the surface of a solid [13] or to an organic polymer [14].

In order to obtain such structures from tetraazatetradecine systems condensed with hetarene rings, we have performed the synthesis of diamino derivatives of substituted dibenzodipyrazolohexaazacyclotetradecinates (the first model system). Out of the various possible methods of synthesizing the diamino derivatives we chose the method of selectively reducing nitro groups in the corresponding dinitro derivatives in order to obtain aminonitro compounds, which are of independent interest and also permit the comparison of a number of physicochemical characteristics to be performed.

The diazotization of 2-bromo-5-nitroaniline (I) followed by azo coupling with 5-amino-3methyl-1-propylpyrazole (II) led to the isolation of the azo compound (III), the template selfcyclization of which [15] yielded new macrocyclic compounds — derivatives of dibenzo[c,j]dipyrazolo[3,4-f:3',4'-m][1,2,5,8,9,12]hexaazocyclotetradecinate (IV-VI):

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IV, V, VI $R=R^1=NO_2$; IV M=Pd; V M=Ni; VI M=Cu, VII $R=NO_2$, $R^1=NH_2$, M=Ni; VIII $R=NO_2$, $R^1=NHCOCH_3$, M=Ni; IX-XI $R=R^1=NH_2$; IX M=Pd; X M=Ni; XI M=Cu; XII $R=R^1=NHCOCH_3$, M=Ni

For the selective reduction of the peripheral nitro groups and the retention of the azo groups in the macrocyclic system a suitable reducing agent proved to be sodium sulfide. The reaction was carried out in dioxane or pyridine. Depending on the time of performing the reaction, macrocyclic compounds with one (VII, $R = NO_2$, $R^1 = NH_2$) and two (IX-XI, $R = R^1 = NH_2$) amino groups were obtained.

The reduced derivatives were subjected to acylation with the aid of acetic anhydride in the presence of catalytic amounts of pyridine or triethylamine (VIII, $R = NO_2$, $R^1 = NHAc$, and XII, $R = R^1 = NHAc$).

In the mass spectra of compounds (IV-VI), the ratio of the intensities of the isotopic peaks of the molecular ions of compounds of compounds (IV-VI) showed the presence of a metal atom; the high intensity of the peaks of the molecular ions and the occurrence of fragmentations connected only with the splitting out of the substituents indicated the presence of stable macrocyclic systems. The results of the mass spectrometry of compounds (IV-VI) indicated the presence of two nitro groups in each of them — the fragmentation characteristic for the splitting out of nitro groups was observed. For example, the palladium complex (IV) fragmented in accordance with the following scheme:

 $m/z \ 632(18) \frac{-C_3H_6}{-42} = M^+ \ 674(100) \frac{-N0}{-30} = m/z \ 644(54) \frac{-N0}{-30} = m/z \ 614(18) = -42 \left| -C_3H_6 \right| =$

The fragmentation of the reduced compounds was analogous to that of the macrocyclic complexes without peripheral functional groups ($R = R^1 = H$) obtained previously [16]; in this case, the fragmentation characteristic for compounds with nitro groups was absent:

$$M^{+}568(100)(X) \xrightarrow{-C_3H_6} m/z 526 \xrightarrow{-C_3H_6} m/z 484$$

At the same time, the fragmentation of compounds with one reduced nitro group (VII) took place in the following way:

$$m/z$$
 556 (12) $-\frac{C_3H_6}{-42}$ M^+ 598 (100) (VII) $\frac{-NO}{-30}$ m/z 568 (48)

A compound with one reduced nitro group that had then been acylated (VIII) showed the following scheme of fragmentation:

$$m/z$$
 610 (56) $\frac{-NO}{-30}$ M^{+} 640 (100) (VIII) $\frac{-COCH_2}{-42}$ m/z 598 (26) $\frac{-NO}{-30}$ m/z 568 (12)

The reduced and then acylated compound (XII) fragmented with the successive splitting out of two acyl groups in the form of ketene, which took place on cleavage at the carbonyl groups with a fairly high probability. The splitting out of the propyl substituents apparently took place in a second stage.

All the compounds (V, VII, X, and XII) were fairly stable thermally. Melting could be observed only in the case of compounds (X) (350° C) and (XII) (312° C), although in these cases, as well, it was observed against a background of the decomposition of the complexes. The most thermally stable compounds proved to be (V) and (XII). These complexes decomposed in two steps, beginning at 350°C. In the case of compounds (VII) and (X), each containing an NH₂

TABLE 1. Thermal Stability of the Ni Complexes (V, VII, X, and XII)

Com- pound	mp,	Decomposition										
	°C	t, °C	mass, %	<i>t</i> , °C	mass, %	<i>t</i> , °C	mass, %					
V VII X XII	 350 312	120—410 150—370 —	5,8; 7,0 6,0	350-430 410-510 370-490 420-520	39,5 12,3 15,0 25,9	430—900 510—900 490—900 520—900	40,0 21,9 31,0 37,6					

TABLE 2. PMR Spectra of the Ni Complexes (V, VII, VIII, X, and XII) and the Pd Complexes (IV and IX)

	1			Ç	hemical	shift, ppm						
Com-	Solvent		phe	nyl		pyrazolyl						
pound		6-H 7-R		8-H	9-H	3,13-CH ₃	α-CH₂	β-CH ₂	CH3			
IV ^a	CDCl₃+	8,48 d		8,05 d. d	7,10d	2,60s	4,05 t	1,74 m	0,79 t			
Va	CDCl ₃ +	8,44d		8,00 d.d	7,06 d	2,58 s	3,98 t	1,70 m	0,80 t			
VIIb	CDCl ₃	6,73 d	3,55 s	6,17 d.d	6,62 d	2,26 s	3,63 t	1,56 m	0,70 t			
VIIIC IXa X ^a XIIa	CDCl₃ ДMCO-D₅ CDCl₃ CDCl₃+ +CF₃COOH	7,53 d 6,63d 6,78 d 7,89 d	2,13 s 5,18 s 3,50 s 2,18 s 8,88 s	7,08 d.d 6,12 d.d 6,11d.d 6,7	6,75d 6,60 d 6,64 d 2 m	2,20 s 2,31 s 2,14s 2,22 s 2,31 s	3,72 t 3,86 t 3,68 t 3,64 t	1,62 m 1,57 m 1,58 m 1,44 m	0,60 t 0,72 t 0,68 t 0,71 t 0,66 t			

^a The chemical shifts of the 6- and 16-H, the 8- and 18-H, the 9- and 19-H and the 7- and 17-R protons coincided. ^b Chemical shifts, ppm: 8.14 (d, 16-H); 7.58 (d.d, 18-H); 6.68 (d, 9-H). ^c Chemical shifts, ppm: 8.21 (d, 16-H); 7.68 (d.d, 18-H); 6.75 (d, 19-H).

group, decomposition began at considerably lower temperatures and was apparently complicated by the splitting out of the substituents. The loss in mass up to 300°C in the case of compound (X) corresponded to the splitting out of two amino groups, and in the case of compound (VII) to the splitting out of an amino and a nitro group. Common for all the compounds was the fairly strong exothermic effect in the 400°C region accompanied by a marked loss in mass. Although the intensity of this effect and the size of the loss in mass corresponding to it were different according to the combination of substituents, it may be assumed that at this stage the cleavage of the pyrazole rings took place. The nature of the thermal decomposition in the 500-900°C region was, on the whole, similar for all the compounds and was apparently due to the pyrolysis of the macrocycle (see Table 1).

The PMR and ¹³C NMR spectra (Tables 2 and 3) of the complexes of ligands with the same substituents in positions 7 and 17 show the magnetic chemical equivalence of the nuclei of the carbon and hydrogen atoms of the benzene and pyrazole rings in these compounds. As has been reported previously [17], such equivalence is a consequence of the trans position of the azo bonds in the hexaazatetradecine skeleton and the D_{2h} symmetry of these compounds. When one of these substituents was replaced, the benzene rings lost their equivalence. At the same time, in the ring with the unreplaced substituent the chemical shift remained practically constant: for the protons to within ±0.1 ppm (Table 2, compare (VII) and (X), and (VII) and (VII), and for the ¹³C nuclei in the range of ±0.5 ppm (only for C($_{13}$) on passing from (X) to (VII) did the change amount to 1.8 ppm). A slight nonequivalence of the H and C nuclei, on the whole decreasing with increasing remoteness from the chelate ring, was also observed under these conditions for the pyrazole rings.

A comparison of the ¹³C chemical shifts for the benzene rings in compounds (VII) and (X) with the chemical shifts in (XIII) ($R = R^1 = H$) revealed increments close to the usual ones for benzene derivatives [18], namely, for an NO₂ substituent (ppm): s + 26.2, ortho- 5.3 ± 0.4 ,

TABLE 3. ¹³C NMR Spectra of the Ni(II) Complexes of the Unsubstituted (XIV) and the Substituted (VII and X) Ligands (CDCl₃, 30° C).

Accientent	VIIIO	v	VIIb				
Assignment	AIVa	X	7-NH _e	17-NO2			
	Руг	azole ring					
3,13-CH ₃ 1,11- α -CH ₂ β -CH ₂ CH ₃ 3,13-C 3a,13a-C 10a,20a-C	12,37 149,97 136,29 138,84	$\begin{array}{c} 12,20\\ 52,36\\ 21,86\\ 11,15\\ 149,29\\ 136,53\\ 139,06 \end{array}$	12,28 52,49 21,83 11,09 149,47 135,69 137,69	$12,08 \\ 53,57 \\ 22,04 \\ 11,09 \\ 149,47 \\ 137,74 \\ 138,83$			
	Ber	nzene ring					
5a,15a—C 9a,19a-C 6,16-C 7,17-C 8,18-C 9,19-C	148,65 142,76 115,74 117,51 125,57 122,97	150,34 135,04 102,00 142,99 112,34 118,76	149,81 135,45 102,06 142,60 114,13 119,21	148,74 146,98 110,81 143,69 119,90 116,08			

a From [17]. ^b The assignments of the pyrazole rings and their substituents may be reversed.

para- 4.2; and for NH₂: s +25.3 ± 0.2, ortho- 13.0 ± 0.8, para- 7.5 ± 0.2. The fact that the shifts of the C(9) and C(19) signals on passing from compound (XIII) to (VII) and (X) were substantially greater than was expected on the basis of the meta influence of the substituents (from -3.8 to -6.9 ppm) was apparently due to the replacement of the N-i- C_3H_7 substituent in (XIII) by n- C_3H_7 in (VII) and (X) and to the elimination of the steric interaction of the 9-H and 19-H protons with the iso-alkyl substituent.

According to IR spectra (see Table 4), no cis isomeric complexes are formed in the template self-cyclization of compound (III), in contrast to the corresponding azo compound containing no NO₂ substituent (R = R¹ = H) [17], which may be connected with the electron-accepting effect of the substituent. The IR spectra of all the complexes studied except (VIII) showed the band of the stretching vibrations of the C=C bonds of the benzene rings at about 1600 cm⁻¹, its position being practically independent of the metal, and absorption at about 1545 cm⁻¹ characteristic for an azopyrazole fragment. All the compounds having NH₂ groups (and also compound (V)) were characterized by absorption at 1495, 1440, and ~1415 cm⁻¹; one of the strongest bands in the spectrum was that of the vibrations of the pyrazole rings at ∿1315 cm⁻¹. For the Cu derivatives, the frequencies of the last-mentioned band were appreciably lower than for the corresponding Ni and Pd complexes. The assignment of the nonplanar deformation vibrations of a 1,2,4-trisubstituted benzene ring in the 800-850 cm⁻¹ region made in Table 4 is based on the expected high-frequency shift of this vibration on passing from the dinitro derivatives [19]. The frequencies of the stretching vibrations of the NO2 and NH2 substituents given in Table 4 showed the same dependence on the metal: Ni > Pd > Cu. However, for compounds (X) and (XI), for which it was possible to carry out measurements in CHCl3 solution the v_{as} and v_s frequencies characterizing free NH₂ groups practically coincided (3476 and 3395 cm⁻¹, respectively).

Some similarity of the electronic absorption spectra of the metalloporphyrins and complexes of the 16π -macrocyclic ligand 5,14-dihydrobenzo[b,i][1,4,8,11]tetraazacyclotetradecine (XIV) with transition metals has been reported previously [20]: an increased intensity of the two long-wave transitions corresponding to the Q (0,0) and Q (1,0) bands of the metalloporphyrins and a strong B-band at about 410 nm corresponding to the Soret band. However, the similarity of these systems must be more profound. The results that we have obtained permit the expectation that in accordance with the D_{2h} symmetry of the complexes of ligand (XIV) they should apparently have the D_{2h} type of spectrum of the porphyrins. In a four-band spectrum of a porphyrin of the D_{2h} type there is an additional — as compared with the two-band spectrum of the D_{4h} type — splitting of the Q (0,0) band into Q_x (0,0) and Q_y (0,0) bands, each of which is accompanied by a band of vibrational origin [21]. As can be seen from Table 5, for the Ni(II), Pd(II), and Cu(II) complexes, which possess D_{2h} symmetry, from two to four bands are TABLE 4. IR Absorption Spectra of Compounds (III-XII)

Compound ^a	XI		1600 m	1555 sh	1530 s	1500	1435 m, s	1413 m, s	1465 m , s	1380 i 1365m	1304 s	824 W			3410 W	3300 W	1615 m
	x		1605 ^s	1566 s	15561	1501 m	1436 s	1420 i	1474 s	1369 m	1328 \$	815 w, m			3425 W	3318 ^w	1620 sh
	IX		1600 m	1560 ѕ, т	1540 m	1490 m	1432 i	1417 s	I464 m, s	1375 m	1325 m	810 w.m			3425 w	3307 w	1632 w, m
	XII		1595 m	1567 s	1537 s,m		1442 s,m	1413s	1470 s	1369 m, s	1312 s	830 W			3260m, w		1658 s
	VIII			1564 m	1545		1440 m, s	1417 m	1465 m	1370 w.m	1316 s	835 w, m	1545 s, m	1332 sh	3260 w		1637 .s, m
	VII		1608 m	1568 s,m		1500 m,s	1435 s	1425 s	1470 s	1378 w, m 1365 w, m	1310 s	827 w. m	1545 s, m	1310 s	3455 w	3375 w	1618 m
	Ν		1590 m		1541s		1441 s, m	1415s	1465 s,m	1388 m 1370 m	1311 s	838 w	1515 s , m	1335 i			
	Λ	1622 т	1592 m		1548 s	1490 s, m	1447 s	1422 s	1470 s	1388 m 1367 m	1320 s	840 W	1521 s.m	1336 î			
1	IV	1637 w	1592 m		1540 s		1437 s., m	1411 s	1460 m	1370 m	1320 s	838 w	1518 s,m	13301			
	III	1624 s,m		1560 w	1533 s, m	1494 W			1470 w	1380 w 1364 m s	1350 s	841 w	1518 m	1332 s			
	SUO	}			~							e)					
	VIDIAU			vC=C	vC=N	v=Nv			ôCH3, CH2, as	ôCH3, CH2, s	vpvrazole	γCH (benzen	vNO_2 , as	vNO _{2, S}	$vNH(NH_2)$	vNH ₂ , s	vCO (6NH2)

a s - Strong; m - medium; w - weak; i - inflection; sh - shoulder.

TABLE 5. Electronic Absorption Spectra of the Ni Complexes (V, VII, VIII, X, and XII), the Pd Complexes (IV and IX), and the Cu Complexes (VI and IX) in Solutions in CHCl₃ [λ_{max} , nm (log ε)]

والمستخلف والمراقب والمستحد	spu	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
	B-Bai	$ \begin{array}{c} 381 \ (4,37) \\ 388 \ i \ (4,45) \\ 388 \ (4,43) \\ 385 \ (4,43) \\ 386 \ (4,27) \\ 390 \ (4,27) \\ 390 \ (4,27) \\ 370 \ i \ (3,92) \\ 381 \ (4,15) \\ 381 \ (4,15) \\ 383 \ (4,22) \end{array} $
		407 (4,41) 427 (4,30)
		445 i (4,51) 446 (4,49) 438 i (4,30)
		466 (4,69) 479 î (4,56) 483 (4,49) 483 (4,48) 486 (4,43) 453 (4,43) 476 (4,46) 472 (4,27)
		498 (4,67) 505 (4,60) 505 (4,50) 518 i (3,96) 497 (4,15) 504 (4,19) 504 (4,19) 482 i (4,25)
	Qy (1, 0)	$\begin{array}{c} 541 & (3.96) \\ 601 i & (3.74) \\ 601 i & (3.75) \\ 628 i & (3.75) \\ 602 i & (3.61) \\ 576 & (3.64) \\ 610 i & (3.57) \\ 610 i & (3.64) \\ \end{array}$
	$Q_{y}(0, 0)$	583 (4,07) 595 th (3,56) 595 th (3,56) 642 (3,79) 643 (3,79) 617 (3,60) 659 (3,70) 616 1 (3,36) 651 (3,35) 651 (3,82)
	Q _x (1, 0)	653 i (3,06)
	Q _x (0, 0)	714 i (2,87) 736 i (2,86) 760 i (2,70) 760 i (2,78) 742 i (2,65)
ļ	Com- pound	V-Y-W-W-W-W-W-W-W-W-W-W-W-W-W-W-W-W-W-W-

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observed in the 760-540 nm region which, by analogy with the porphyrins, may be considered as the Q_x (0,0), Q_x (1,0), Q_y (0,0), and Q_y (1,0) transitions. The distances between the ground and vibrational transitions amount to 990-1520 cm⁻¹, and between Q_y and Q_x to 2000-3150 cm⁻¹, i.e., close to those observed for free porphyrin and its analogs [21]. The strongest Q_y (0,0) transition is observed in all the compounds studied, but its intensity for the Cu complexes is 2-3 times lower than for the Ni and Pd complexes. The Q_y (1,0) transition, which is usually weaker in the Ni and Pd complexes, is not observed in the Cu complexes. The Q_x (0,0) and Q_x (1,0) bands are five and more times weaker than the corresponding Q_y transitions and in a number of cases are not observed at all because of their low intensity. The Q_y (0,0) bands for the Ni(II) complexes are shifted appreciably (by 40 nm) into the long-wave region as compared with the corresponding Cu(II) and Pd(II) complexes. The magnitude of the long-wave shift of the Q bands observed on passing from the dinitro to the diamino compounds also depends on the metal.

In the complexes studied, apparently as the result of the lifting of the degeneracy from the transitions corresponding to the B band in the complexes (XIV), from 1 to 3 strong transitions are observed in the 520-420 nm region, and one or two strong bands at 390-370 nm (407 and 385 nm for compound (VI)). The additional strong absorption band at 345-330 nm observed in the dinitro derivatives is obviously caused by a $n-\pi^*$ transition connected with the NO₂ substituent.

We also measured the reflection spectra of a number of complexes. The shifts of the longwave transitions, as compared with the absorption spectra in solutions, did not exceed 10 nm, which permits us to conclude that the nature of the coordination is retained on passing from the solid phase into solution.

EXPERIMENTAL

The PMR and ¹³C NMR spectra were obtained on a Varian XL-100-12 spectrometer at frequencies of 100 and 25.16 MHz, respectively, relative to TMS. In view of the difficulty of dissolving individual derivatives, CDCl3, DMSO-d6, and a 0.5-1.0 M solution of CF3COOH in CDCl3 with a constant ratio (10:1) of CF_3COOH to substrate were used as solvents. The assignment of the ¹³C NMR signals was performed on the basis of a comparison of the spectra with complete and with nonselective suppression of spin-spin coupling with protons and without the suppression of this coupling, and also on the basis of a comparison of the spectra in two solvents CDC13 and DMSO-d6. IR absorption spectra were recorded on a Specord IR-75 spectrophotometer in KBr tablets or, in individual cases, in solutions in CCl4 and CHCl3. Electronic absorption spectra were measured on a Specord UV-VIS spectrophotometer in CHCl₃ solutions at concentrations of 1.10⁻⁵-1.10⁻⁶ M. Reflection spectra were measured on a Shimadzu MPS-50L spectrophotometer. Mass spectra were obtained on MS-702 and Varian MAT-311 mass spectrometers with the direct introduction of the sample into the source. The molecular masses of compounds containing metal or halogen atoms are given for the isotopes with the lowest mass or, in the case of palladium complexes, for the ¹⁰⁴Pd isotope. The thermal decomposition of the nickel compound was studied on an OD-102 derivatograph in an atmosphere of nitrogen. The weights of the samples amounted to 20-40 mg and the rate of rise in the temperature to 10°C/min. The purity of the compounds was checked by TLC on Silufol UV-254.

5-Amino-4-(2-bromo-5-nitrophenylazo)-3-methyl-1-propyl-pyrazole (III). With stirring and cooling to 0°C, a solution of 7.0 g (0.1 mole) of sodium nitrite in 21 ml of water was added to a solution of 21.8 g (0.1 mole) of 2-bromo-5-nitroaniline [22] in 100 ml of concentrated H₂SO₄. The mixture was stirred at 0°C for another 30 min. The resulting solution was added to a solution of 13.9 g (0.1 mole) of 5-amino-3-methyl-1-propylpyrazole [23] in 220 ml of ace-tic acid cooled to 10°C. The mixture was kept for 3 h and was neutralized with 20% sodium carbonate solution. The precipitate that deposited was filtered off, washed with water, and dried in the air. This gave 28.7 g (78%) of yellow-orange plates (from ethanol), mp 291-292°C. The substance was soluble in methanol, ethanol, and DMFA, sparingly soluble in chloroform and benzene, and almost insoluble in water, hexane, and ether. Found: C 42.5; H 4.1; Br 21.6; N 22.6%; M⁺ 366. C₁₃H₁₅BrN₆O₂. Calculated: C 42.3; H 4.1; Br 21.7; N 22.8%. Mol. wt. 366.

{3,13-Dimethyl-7,17-dinitro-1,11-dipropyl-1,10,11,20-tetrahydrodibenzo[c,j]dipyrazolo[3, 4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecinato(2-)}palladium (IV). A mixture of 3.7 g (0.1 mole) of the pyrazole (III), 0.9 g (0.05 mole) of palladium(II) chloride, 5.5 g (0.4 mole) of potassium carbonate, and 200 ml of DMFA was boiled for 7 h. After cooling to 50°C, the reaction mixture was filtered, and the filtrate was left to cool. The precipitate that deposited was filtered off, washed with hot water, and dried, giving 1.8 g (53%) of black-brown needles with mp above 350°C which were soluble in DMFA, pyridine, and dioxane, sparingly soluble in chloroform, and almost insoluble in water and hexane. Found: C 46.0; H 3.9; N 24.8; Pd 15.7%; M^+ 674. $C_{26}H_{26}N_{12}O_4Pd$. Calculated: C 46.1; H 3.9; N 24.8; Pd 15.7%; mol. wt. 674.

Compound (V) was obtained similarly: nickel acetate tetrahydrate was used as the metal salt; yield 58% of a dark-green microcrystalline substance soluble in DMFA, pyridine, and dioxane, sparingly in chloroform, and almost insoluble in water, benzene, and acetone. Found: C 49.4; H 4.3; N 26.6; Ni 9.4%; M⁺ 628. $C_{26}H_{26}N_{12}NiO_4$. Calculated: C 49.6; H 4.2; N 26.7; Ni 9.3%; mol. wt. 628.

Compound (VI) was obtained in a similar manner to compounds (IV) and (V). The metal salt used was $CuCl_2$ and the reaction time was 4 h; yield 59% of a brownish microcrystalline substance with mp above 350°C, soluble in DMFA, pyridine, and dioxane, sparingly soluble in acetone and chloroform, and almost insoluble in water, hexane, and ether. Found: C 49.0; H 4.3; Cu 10.1; N 26.4%; M⁺ 633. C₂₆H₂₆CuN₁₂O₄. Calculated: C 49.2; H 4.1; Cu 10.0; N 26.5%; mol. wt. 633.

 $\frac{\{7-\text{Amino}-3,13-\text{dimethyl}-17-\text{nitro}-1,11-\text{dipropyl}-1,10,11,20-\text{tetrahydrodibenzo}[c,j]\text{dipyrazo-lo[3,4-f:3',4'-m][1,2,5,8,9,12]} hexaazacyclotetradecinato(2-)}nickel (VII). A 15% aqueous so-lution of sodium sulfide [86.6 ml of water and 11.0 g (5.0 mmole) of sodium sulfide; chromato-graphic check] was added over 2 h to a solution of 3.0 g (3 mmole) of compound (V) in 500 ml of dioxane at 95-100°C. After the end of reduction, the solvent was distilled off to dryness and the residue was recrystallized from 80 ml of CCl₄. This gave 2.0 g (66%) of a dark-green microcrystalline substance. It dissolved in the majority of solvents and sparingly in hexane. Found: C 52.3; H 4.4; N 28.0; Ni 9.6%; M⁺ 598. C₂₆H₂₈N₁₂NiO₂. Calculated: C 52.1; H 4.6; N 28.1; Ni 9.8%; mol. wt. 598.$

 $\frac{\{7-\text{Acetylamino}-1,3-\text{dimethyl}-17-\text{nitro}-1,11-\text{dipropyl}-1,10,11,20-\text{tetrahydrodibenzo}[c,j]\text{dipyr}-azolo}{[3,4-f:3',4'-m][1,2,5,8,9,12]\text{hexaazacyclotetradecinato}(2-)}\text{nickel (VIII).} At the boil, a solution of 0.1 g (0.6 mmole) of the amine (VII) in 50 ml of chloroform was treated with 3 ml (3.2 mmole) of acetic anhydride and 0.1 ml of pyridine. After the end of acylation, the solvent was distilled off to dryness, and the residue was dissolved in 30 ml of chloroform and chromatographed on Silufol in the benzene-chloroform-acetone (7:2:1) system. Evaporation of the solvent yielded 0.06 g (60% of a dark-brown microcrystalline substance with mp above 350°C. The compound dissolved in the majority of solvents but was sparingly soluble in hexane and water. Found: C 52.4; H 4.8; N 26.2; Ni 9.1%; M⁺ 640. C₂₆H₃₀N₁₂NiO₃. Calculated: C 52.5; H 4.7; N 26.3; Ni 9.2%; mol. wt. 640.$

 $\{7,17-\text{Diamino}-3,13-\text{dimethyl}-1,11-\text{dipropyl}-1,10,11,25-\text{tetrahydrodibenzo}[c,j]dipyrazolo[3, 4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecinato(2-)}palladium (IX). A 15% aqueous solution of sodium sulfide (8.0 ml of water and 1.3 g (1.5 mmole) of sodium sulfide) was added over 6 h to a solution of 0.1 g (0.6 mmole) of compound (IV) in 300 ml of pyridine at 100-110°C. After the end of reduction, the solvent was distilled off to dryness. The residue was recrystallized from 100 ml of chloroform. This gave 0.06 g (60%) of a dark-green microcrystalline substance with mp above 350°C. The substance dissolved in DMFA, benzene, acetone, and alcohols and was sparingly soluble in hexane and CCl₄ and almost insoluble in water. Found: C 50.8; H 4.9; N 27.3; Pd 17.3%; M⁺ 616. C₂₆H₃₀N₁₂Pd. Calculated: C 50.7; H 4.8; N 27.3; Pd 17.3%; mol. wt. 616.$

 $\{7,17-\text{Diamino-3},13-\text{dimethyl-1},10-\text{dipropyl-1},10,11,20-\text{tetrahydrodibenzo[c,j]dipyrazolo[3,$ 4-f:3',4'-m][1,2,5,8,9,12]hexaazacyclotetradecinato(2-)]nickel (X). A 15% solution of sodiumsulfide [86.6 ml of water and 13.0 g (5.4 mmole) of sodium sulfide] was added over 4 hours toa solution of 2.0 g (3 mmole) of compound (V) in 500 ml of dioxane at 90-100°C. After the endof the reduction, the solvent was distilled off to dryness. The residue was dissolved in 100ml of CCl4 and the solution was left to crystallize. This gave 0.92 g (51%) of a dark-greenmicrocrystalline substance, which was soluble in DMFA, chloroform, dioxane, pyridine, ethanol,and acetone, sparingly soluble in hexane, and almost insoluble in water. Found: C 55.0; H5.4; N 29.7; Ni 10.2%; M⁺ 568. C₂₆H₃₀N₁₂Ni. Calculated: C 54.8; H 5.3; N 29.6; Ni 10.3%;mol. wt. 568.

Compound (XI) was obtained similarly, the residue being dissolved in 80 ml of chloroform and this solution being left to crystallize; yield 0.98 g (52%), brownish microcrystalline substance with mp above 350°C; soluble in DMFA, dioxane, pyridine, and chloroform, less well in benzene, acetone, and alcohols, and almost insoluble in hexane and water. Found: C 54.5; H 5.3; Cu 11.2; N 29.4%; M⁺ 573. C₂₆H₃₀CuN₁₂. Calculated: C 54.4; H 5.3; Cu 11.1; N 29.3%; mol. wt. 573.

Compound (XII) was obtained in a similar manner to compound (VIII): The residue was dissolved in 50 ml of chloroform and this solution was left to crystallize. Yield 0.08 g (80%), greenish microcrystalline substance soluble in DMFA, pyridine, dioxane and chloroform, sparingly soluble in benzene, acetone, and alcohols, almost insoluble in water, hexane, and pentane. Found: C 55.3; H 5.3; N 25.8; Ni 9.1%; M⁺ 652. $C_{30}H_{34}N_{12}NiO_2$. Calculated: C 55.2; H 5.2; N 25.8; Ni 9.0%; mol. wt. 652.

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