

Notons la coordinence particulière du sélénium (+IV); la paire non liée $4s^2$ joue un rôle stéréochimique important. Elle complète 'l'environnement' du sélénium (+IV) celui-ci se trouvant en fait à l'intérieur d'un tétraèdre dont la base est formée par les trois atomes d'oxygène le doublet occupant l'apex.

La détermination précise de la structure originale de $ZnSe_2O_5$ apporte des éléments nouveaux et importants dans le domaine de la cristallographie du sélénium

(+IV), notamment sur la liaison Se-O et la disposition des motifs $(Se_2O_5)^{2-}$.

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The Crystal and Molecular Structure of a Germanium-Hemiporphyrzine

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Hemiporphyrzine-germanium-diethylene glycol monoethyl ether crystallizes in space group *Pbca* with lattice constants $a=23.067$, $b=17.360$ and $c=7.831$ Å with four molecules in the unit cell. The phase problem was solved by the heavy-atom method. Diffractometer data were refined to a final residual $R=3.7\%$. The hemiporphyrzine system is completely planar. The results of the structure analysis lead to the assumption of a superposition of three resonance forms of the molecule.

Introduction

The title compound was synthesized by Meyer & Wöhrle (1972) as a part of extensive chemical investigations on macrocycles. Recently the structure of the hemiporphyrzine system has been discussed on the basis of n.m.r. work (Esposito, Sutton & Kenney, 1967); X-ray data of this system are scarcely known. The paper of Speakman (1953) reports a structure determination of a nickel complex with hemiporphyrzine.

The planarity and aromaticity of this system is of special interest in comparison with the analogous system of the phthalocyanines. To obtain this and further information we found it useful to carry out a three-dimensional X-ray structure analysis of the germanium derivative of the hemiporphyrzine.

Experimental and structure determination

The compound crystallizes from ethylene glycol monoethyl ether as small, dark-blue needles. The space group was determined by oscillation- and Weissenberg photographs. From the orthorhombic symmetry and the systematically absent reflexions $hk0$ for $h=2n+1$, $0kl$ for $k=2n+1$ and $h0l$ for $l=2n+1$, it was assumed to be *Pbca*.

X-ray measurements were carried out with an automatic single-crystal diffractometer (Siemens AED) and Ni-filtered Cu $K\alpha$ radiation ($\lambda=1.5405$ Å). For the determination of precise lattice constants the scattering

angles of high-order axial reflexions were measured using a step-scan method with preset time per step. The intensities of reflexions with $4.5^\circ \leq \theta \leq 71^\circ$ were collected by the 'five-value' method (*Siemens AED-Handbuch*, 1966).

Because of the geometry of the diffractometer, a large number of reflexions with high θ and χ had an insufficient signal-to-noise ratio caused by back-scattering of the primary beam. We decided, therefore, to include of the 3123 reflexions measured only the 2571 reflexions with $l \leq 6$ in the data set. 916 had an intensity less than twice the statistical error and were coded as unobserved. The most important crystallographic data are given in Table 1.

Table 1. *Crystallographic data*

Hemiporphyrzine-germanium-diethylene glycol monoethyl ether

	(Ge-hp)
Chemical formula	$C_{34}H_{32}N_8O_4Ge$
Molecular weight	688.6
Cell parameters	$a=23.067$ (5) Å $b=17.360$ (5) $c=7.831$ (4)
Cell volume	$V=3136$ Å ³
Density	$\rho_{exp}=1.46$ (1) g cm ⁻³ $\rho_{X-ray}=1.458$ (1) g cm ⁻³
Space group: orthorhombic, <i>Pbca</i>	
Four molecules per unit cell	
Linear absorption factor $\mu=20.7$ cm ⁻¹ (Cu $K\alpha$)	
Crystal dimensions: 0.08 × 0.05 × 0.5 mm	

Table 2. Fractional atomic coordinates and thermal parameters ($U \times 10^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	0.0	1.0	0.0	3.87 (2)	3.84 (2)	3.83 (6)	-0.31 (3)	-0.10 (3)	-0.11 (3)
N(1)	0.0346 (1)	0.9202 (2)	0.1882 (4)	4.4 (2)	4.1 (1)	4.0 (2)	0.1 (1)	-0.5 (1)	0.1 (1)
N(2)	-0.0449 (1)	0.9386 (2)	0.3901 (4)	6.0 (2)	5.7 (2)	4.4 (2)	0.2 (2)	0.5 (2)	0.9 (2)
N(3)	-0.0662 (1)	1.0191 (1)	0.1455 (4)	4.0 (1)	4.3 (2)	4.1 (2)	-0.1 (1)	0.2 (1)	0.1 (1)
N(4)	0.1195 (1)	0.8866 (2)	0.0176 (4)	5.3 (2)	6.4 (2)	4.1 (2)	1.2 (1)	-0.6 (2)	0.1 (2)
C(1)	0.0850 (2)	0.8804 (2)	0.1611 (5)	5.2 (2)	4.3 (2)	4.1 (3)	0.1 (2)	-0.8 (2)	-0.2 (2)
C(2)	0.1064 (2)	0.8282 (2)	0.2799 (6)	6.6 (3)	5.1 (2)	5.4 (3)	1.3 (2)	-1.3 (2)	-0.2 (2)
C(3)	0.0785 (2)	0.8150 (2)	0.4291 (6)	8.1 (3)	6.1 (3)	5.6 (3)	0.7 (2)	-1.4 (2)	1.7 (2)
C(4)	0.0291 (2)	0.8545 (2)	0.4606 (5)	7.3 (3)	6.2 (2)	5.1 (3)	-0.2 (2)	0.1 (2)	1.5 (2)
C(5)	0.0068 (2)	0.9061 (2)	0.3396 (5)	5.9 (2)	4.8 (2)	3.9 (2)	-0.5 (2)	-0.5 (2)	0.6 (2)
C(6)	-0.0749 (1)	0.9868 (2)	0.3052 (5)	5.1 (2)	4.7 (2)	4.4 (3)	-0.8 (2)	0.5 (2)	-0.2 (2)
C(7)	-0.1305 (2)	1.0173 (2)	0.3734 (5)	5.6 (2)	5.3 (2)	4.7 (3)	-0.6 (2)	1.1 (2)	-1.0 (2)
C(8)	-0.1514 (1)	1.0686 (2)	0.2560 (5)	4.3 (2)	6.0 (2)	5.2 (3)	-0.3 (2)	0.4 (2)	-0.9 (2)
C(9)	-0.1109 (1)	1.0705 (2)	0.1119 (5)	4.1 (2)	5.1 (2)	4.9 (3)	-0.2 (2)	-0.2 (2)	-0.6 (2)
C(10)	-0.1594 (2)	1.0019 (3)	0.5251 (6)	8.1 (2)	6.5 (2)	6.2 (3)	-0.1 (3)	2.1 (2)	0.2 (2)
C(11)	-0.2102 (2)	1.0405 (3)	0.5541 (7)	8.3 (3)	7.4 (3)	8.1 (4)	-0.9 (3)	4.1 (3)	-1.7 (3)
C(12)	-0.2311 (2)	1.0927 (3)	0.4368 (7)	5.7 (3)	9.0 (4)	9.2 (4)	0.1 (3)	1.8 (3)	-2.6 (3)
C(13)	-0.2026 (2)	1.1082 (3)	0.2860 (6)	5.2 (2)	8.9 (3)	6.2 (3)	1.2 (2)	0.0 (2)	-1.0 (2)
O(1)	0.0301 (9)	1.0797 (1)	0.1114 (3)	5.0 (1)	4.7 (1)	4.2 (2)	-1.1 (1)	0.2 (1)	-0.5 (1)
C(14)	0.0863 (2)	1.1111 (3)	0.0724 (8)	6.0 (3)	6.5 (3)	7.8 (4)	-1.9 (2)	1.1 (3)	-1.7 (2)
C(15)	0.0948 (2)	1.1859 (3)	0.1630 (8)	5.9 (3)	5.7 (3)	8.0 (4)	-1.2 (2)	1.2 (3)	-1.5 (2)
O(2)	0.1508 (1)	1.2124 (2)	0.1272 (4)	6.0 (2)	6.2 (2)	10.1 (1)	-2.5 (1)	2.2 (2)	-2.7 (2)
C(16)	0.1608 (2)	1.2899 (3)	0.1670 (9)	7.9 (3)	5.4 (3)	9.0 (4)	-1.9 (2)	-0.3 (3)	-1.0 (3)
C(17)	0.2204 (3)	1.3108 (5)	0.1253 (1)	10.1 (5)	8.8 (5)	14.5 (8)	-5.9 (4)	2.2 (5)	-2.5 (5)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(21)	0.140 (1)	0.807 (2)	0.246 (4)	6 (1)
H(31)	0.092 (2)	0.785 (2)	0.511 (6)	10 (1)
H(41)	0.109 (2)	0.854 (2)	0.557 (4)	9 (1)
H(101)	-0.143 (2)	0.967 (2)	0.611 (5)	9 (1)
H(111)	-0.232 (2)	1.029 (2)	0.652 (5)	9 (1)
H(121)	-0.268 (2)	1.117 (3)	0.458 (5)	10 (1)
H(131)	-0.215 (1)	1.140 (2)	0.194 (5)	7 (1)
H(141)	0.120 (2)	1.077 (3)	0.087 (6)	12 (2)
H(142)	0.091 (2)	1.119 (3)	-0.055 (7)	11 (2)
H(151)	0.062 (2)	1.225 (2)	0.147 (6)	8 (1)
H(152)	0.088 (2)	1.174 (3)	0.293 (8)	11 (2)
H(161)	0.125 (3)	1.321 (3)	0.099 (7)	13 (2)
H(162)	0.157 (3)	1.300 (4)	0.278 (9)	16 (3)
H(171)	0.221 (5)	1.303 (6)	0.02 (2)	30 (7)
H(172)	0.253 (4)	1.275 (5)	0.16 (1)	22 (4)
H(173)	0.227 (3)	1.356 (4)	0.141 (8)	13 (2)

Relative structure factors were calculated from the intensity data with the usual corrections for Lorentz and polarization effects. An absorption correction was not applied.

The dimensions of the unit cell and the experimentally measured density indicated four molecules per unit cell. Because of the eightfold symmetry in this space group the molecule was assumed to be centrosymmetric with the germanium atom as symmetry centre.

On this assumption a Fourier synthesis was calculated with positive signs for all structure factors. This synthesis showed all nitrogen atoms of the system. After parameter refinements and Fourier synthesis calculations the complete molecule (except for hydrogen positions) was determined.

After isotropic and anisotropic refinements with the least-squares program *ORFLS* of the X-RAY 70 system the *R* value was 7.2%.

The hydrogen atoms were located from difference

syntheses and included in further refinements with isotropic temperature factors. After introduction of anomalous dispersion factors $\Delta f' = -1.3$ and $\Delta f'' = 1.0$ for the Ge atom (*International Tables for X-ray Crystallography*, 1962) and refinement of all parameters the *R* value was 3.8%. At this point a power-series type weighting scheme, $w = A + BF_{\text{obs}} + CF_{\text{obs}}^2 + DF_{\text{obs}}^3$, was applied for all reflexions, with $A = 5.45$, $B = -0.292$, $C = 6.1 \times 10^{-3}$, $D = -3.5 \times 10^{-5}$.

Analysis of several weighting schemes showed this power-series type scheme to be the most suitable for the distribution of $\bar{w}(\Delta F)^2$ versus F_{obs} .

After three cycles of refinement including all atom parameters convergence was obtained [maximum shift/error: 1.6, maximum shift 0.008 Å for the *y* coordinate of H(101)]. The final conventional *R* value was 3.7% for the observed reflexions, the final weighted *R* value was 3.2%. The expression used for calculation of *R* values was $\sum w||F_c| - |F_o|| / \sum w|F_o|$. The final Fourier difference synthesis showed no peaks higher than $0.2 \text{ e } \text{Å}^{-3}$ except small regions with $0.3 \text{ e } \text{Å}^{-3}$ in the neighbourhood of the Ge atoms. Scattering factors for all atom types were taken from *International Tables for X-ray Crystallography* (1962). In the final refinement the programs of the X-RAY system (1972) were used. Table 2 gives the final atom parameters, and in Table 3 calculated and observed structure factors are listed.

Discussion

In Fig. 1 a stereoscopic pair of drawings of the complete molecule is given and Fig. 2 shows the hemiporphyrzine skeleton including bond lengths and angles of the heavy atoms (standard deviations in parentheses). The mean C-H distances are 0.95 with mean standard deviations of 0.06 Å.

Table 3. Observed and calculated structure factors

The columns are: H, 10|F_o|, 10F_c.

Table with multiple columns containing numerical data for structure factors. The columns are labeled with H, 10|F_o|, and 10F_c. The rows represent different data points or reflections, with some rows grouped by a common label on the left (e.g., H=10, H=11, H=12, etc.). The data values are arranged in a grid-like format, with some cells containing multiple values or symbols.

Table 3 (cont.)

2 315	-312	17	130	117	0	52*	1	2	52*	-332	H12+5	H1+4	5	48*	-15	16	326	337	8	32*	330	10	86*	81	5	53*	-9	2	197	18*	3	53*	-79	8	101	109				
2 315	-312	17	130	117	0	52*	1	2	52*	-332	H12+5	H1+4	5	48*	-15	16	326	337	8	32*	330	10	86*	81	5	53*	-9	2	197	18*	3	53*	-79	8	101	109				
3 616	604	19	40*	-52	11	52*	-17	5	21*	-21*	1	76	62	1	52*	56	9	48*	53	19	88	-128	11	56*	108	13	56*	-111	8	97	10*	5	107	-112	6	152	-164	11	45*	17
4 45*	-43	20	47*	12	32	53*	16	1	106*	106*	0	52*	36	10	43*	-12	22	55*	158	12	37*	302	12	55*	-32	9	245*	-103	6	159	-124	7	53*	-23	12	48*	-1			
5 651	639	21	46*	37	13	101	-99	7	305	-308	3	186*	200	3	52*	59	11	42*	39	22	52*	-57	13	57*	-42	15	131	-176	10	56*	17	7	53*	-53	6	83	13	43*	16	
6 230	-230	22	44*	27	14	86	101	8	53*	-60	10	195	-207	4	76	-96	5	103	57	5	111	105	14	411	406	16	54*	-58	10	100	-114	9	56*	27	7	138	127			
7 40*	41*	23	45*	17	15*	86	101	8	53*	-60	10	195	-207	4	76	-96	5	103	57	5	111	105	14	411	406	16	54*	-58	10	100	-114	9	56*	27	7	138	127			
8 51*	-57	17	15*	86	101	8	53*	-60	10	195	-207	4	76	-96	5	103	57	5	111	105	14	411	406	16	54*	-58	10	100	-114	9	56*	27	7	138	127					
9 6*	65*	17	15*	86	101	8	53*	-60	10	195	-207	4	76	-96	5	103	57	5	111	105	14	411	406	16	54*	-58	10	100	-114	9	56*	27	7	138	127					
10 52*	11	458	455	18	48*	23	12	118	-122	8	53*	-58	8	86	-70	2	45*	-26	1	127	12*	1	188	185	20	49*	-23	15	51*	-21	12	101	-108	13	47*	60	1	40*	13	
11 48*	472	2	285	-285	19	58*	13	52*	-26	9	52*	-26	7	148*	135	1	233	228	2	51*	-49	2	348	352	12	42*	29	16	50*	-13	4	52*	-28	4	48*	19	2	169	169	
12 179	193	3	250	248	20	48*	-17	14	128	125	10	98	-112	10	49*	-61	4	45*	5	3	50*	-70	3	145	-143	17	40*	23	14	96	80	15	45*	55	4	252	252			
13 225	227	4	82	-86	21	81	78	15	50*	-16	11	51*	-11	14*	116	11	51*	-11	14*	116	11	51*	-11	14*	116	11	51*	-11	14*	116	11	51*	-11	14*	116	11	51*	-11		
14 52*	-75	5	38*	38*	16	76	78	12	50*	15	12	47*	-11	6	44*	22	5	112	102	5	203	-362	H9+6	H9+6	531	20	42*	36	17	102	106	H12+6	4	108	106	7	138	127		
15 362	364	6	52*	-45	H9+5	17	48*	5	13	49*	-13	13	45*	-7	1	160	170	6	113	93	6	347	346	0	64*	531	20	42*	36	17	102	106	H12+6	4	108	106	7	138	127	
16 85	-124	7	64*	65*	H9+5	18	72	67	14	78	57	14	44*	36	8	42*	-2	7	52*	-67	7	55*	-70	1	42*	215	17	52*	-34	17	52*	-34	17	52*	-34	17	52*	-34		
17 188	193	8	240	-243	1	299	295	19	91	93	15	47*	-30	15	43*	11	H18+5	H18+5	6	53*	61	8	193	213	2	39*	326	H18+6	H18+6	6	103	103	8	114	102	10	100	100		
18 51*	-59	9	688	609	2	52*	-37	20	42*	26	18	48*	64	14	44*	54	H18+5	H18+5	6	53*	61	8	193	213	2	39*	326	H18+6	H18+6	6	103	103	8	114	102	10	100	100		
19 247	243	10	62	59	3	370	358	20	42*	26	17	44*	54	H18+5	H18+5	6	53*	61	8	193	213	2	39*	326	H18+6	H18+6	6	103	103	8	114	102	10	100	100	10	100	100		
20 48*	-28	11	336	331	4	52*	-45	H9+5	17	48*	5	13	49*	-13	13	45*	-7	1	160	170	6	113	93	6	347	346	0	64*	531	20	42*	36	17	102	106	H12+6	4	108	106	
21 217	218	12	67	107	124	118	11	29*	276	H13+5	H13+5	1	261	259	1	63	46	11	86	-137	11	57*	104	5	176	-202	1	107	-83	0	526	522	3	77	59	11	43*	-6		
22 44*	10	13	277	279	6	146	138	1	29*	276	H13+5	H13+5	1	261	259	1	63	46	11	86	-137	11	57*	104	5	176	-202	1	107	-83	0	526	522	3	77	59	11	43*	-6	
23 177	177	14	91	-86	7	462	476	16	76	78	12	50*	15	12	47*	-11	6	44*	22	5	112	102	5	203	-362	H9+6	H9+6	531	20	42*	36	17	102	106	H12+6	4	108	106		

The bond Ge-O(1) is almost normal to the plane of the molecule and the angle O(1)-Ge-N(1) is 90.3° and O(1)-Ge-N(3) is 85.2° (1).

The hemiporphyrzine system is completely planar, with mean deviations from the least-squares plane of 0.02 Å. The maximum deviation is 0.03 Å of atom C(4). This result does not agree with previous studies of this system (Speakman, 1953; Esposito, Sutton & Kenney, 1967).

In the plane of the four neighbouring nitrogen atoms the octahedral coordination of the central Ge atom is distorted to a rectangular arrangement, with bonding distances of 2.175 (3) and 1.934 (3) Å between the germanium atom and the pyridine-nitrogen and the isoindole-nitrogen atoms respectively. For comparison of these bond lengths only data of the homologous macrocyclic complexes of tin were available. A comparison of several Sn^{IV}-macrocycles (Cullen & Meyer, 1973) shows Sn-N bond distances in the range 2.051 (2) to 2.35 (2) Å with a normal Sn-N bond length of about 2.18 Å. Since the covalent radius of germanium is about 0.2 Å smaller than the radius of tin (tin: 1.40 Å, Ge: 1.22 Å; Cotton & Wilkinson, 1968)

we assume that germanium-nitrogen bond distances in analogous macrocyclic complexes are in the range 1.85 to 2.15 Å. The bond distance of 2.175 (3) Å therefore indicates weak bonding between germanium and N(1).

Fig. 3(a)-(c) shows the three possible formulations of the hemiporphyrzine system without charge separation. In (b) and (c) the system is conjugated.

The differences in the Ge-N bond and the non-equal bond lengths of the bridging nitrogen atoms to the pyridine and isoindole system favour formula (a). However, the shortening of the C(9)-N(3) [1.389 (4) Å] bond in the isoindole system (C-N single bond 1.44 Å, C-N partial double bond 1.35-1.33 Å; *International Tables for X-ray Crystallography*) cannot be explained by formula (a). On the other hand a value near to that of a partial double bond can be derived from formulae (b) and (c). (Mean bond lengths are shown in Table 4.)

A comparison with the analogous phthalocyanine system (Fischer, Templeton, Zalkin & Calvin, 1971) shows some difference in the pyrrole and benzene moieties and indicates less conjugation in the hp-system. A superposition of formulae (a)-(c) with four

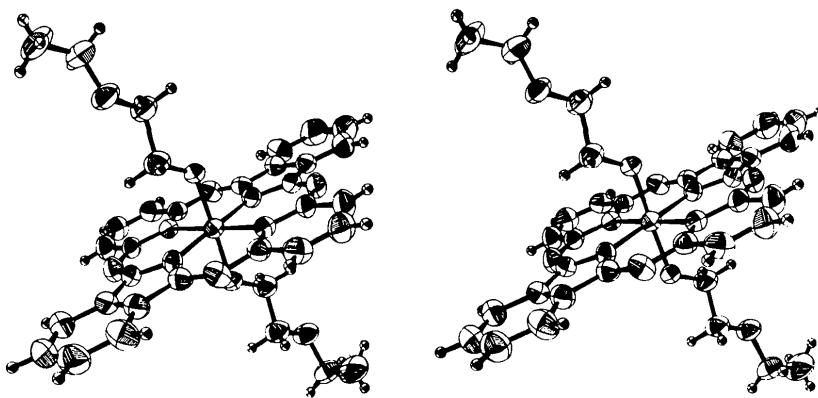


Fig. 1. A stereoscopic view of the molecular structure (Johnson, 1965). The ellipsoids enclose 50% probability of thermal motion, hydrogen positions are represented by spheres of constant weight.

resonance forms of type (a) and one of type (b) and (c) leads to a bond order of 1.2 for the C(5)–N(2) bond and for the C–N bonds in the isoindole system and of

1.8 for the C(6)–N(2) bond. These bond orders are in accordance with the bond lengths observed. A small ring current should therefore occur in the hp-system

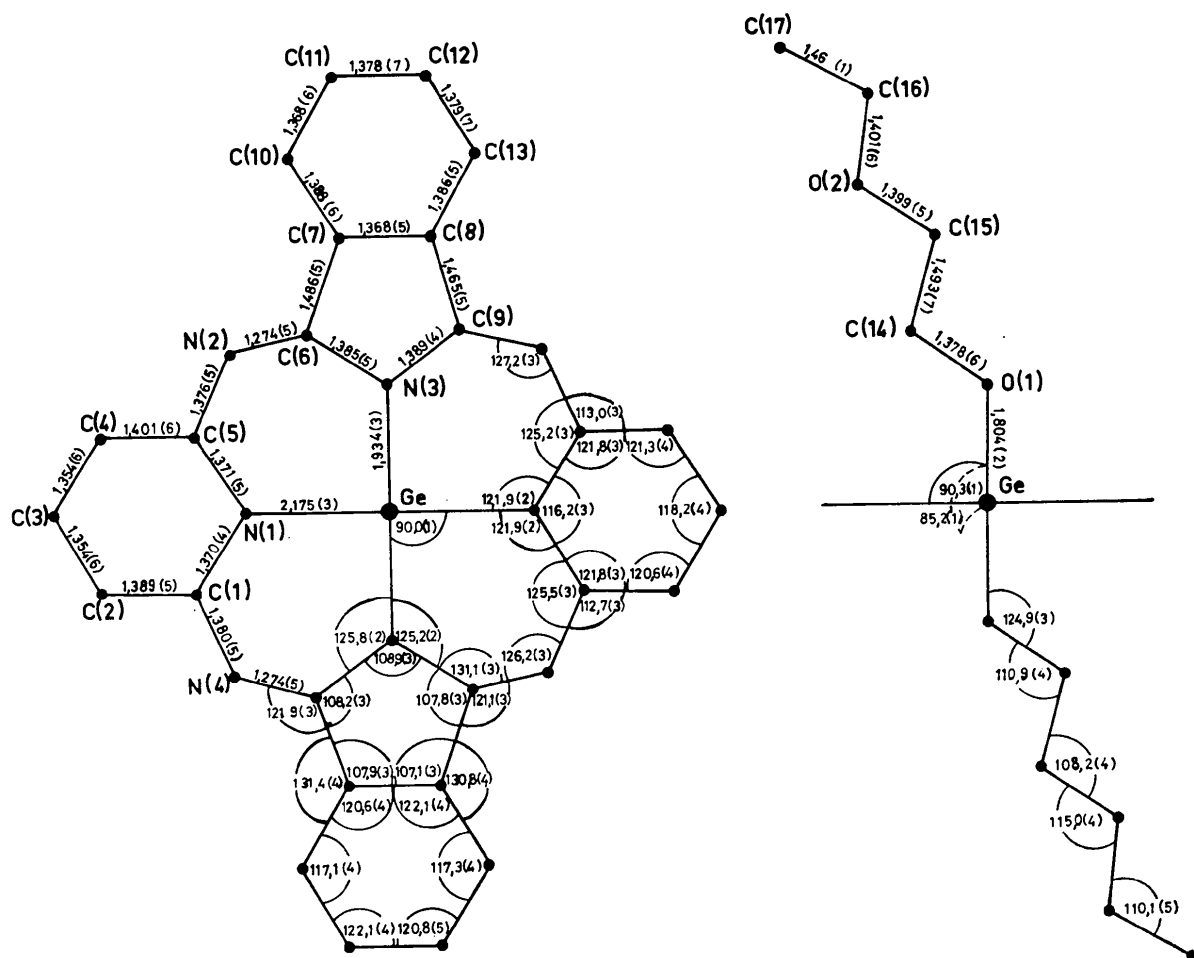


Fig. 2. Bond lengths and angles in the hemiporphyrzine system.

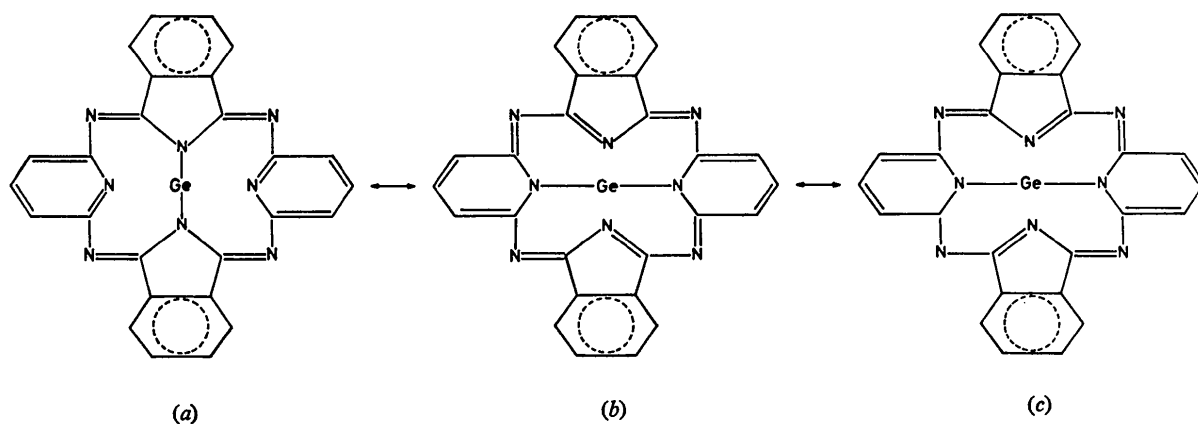


Fig. 3. Possible resonance forms of the hemiporphyrzine system.

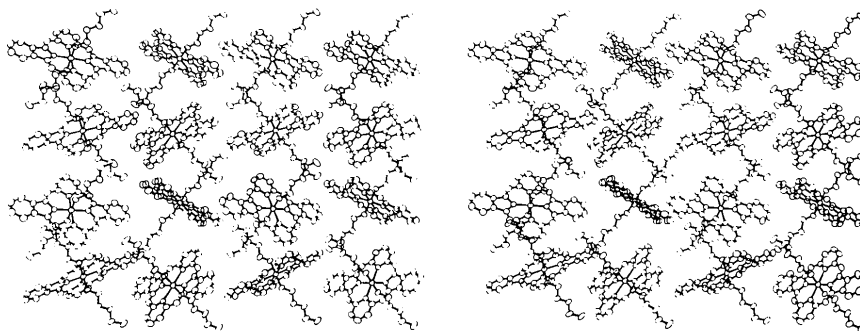


Fig. 4. A stereoscopic view of the molecular packing.

Table 4. Mean bond lengths in the isoindole system

	Ge-hp	Mg-phthalocyanine
N-C _α	1.387 (5)	1.367 (4)
C _α -C _β	1.476 (5)	1.456 (5)
C-C _{benz}	1.373 (6)	1.394 (5)
	1.387 (6)	1.391 (5)
	1.374 (7)	1.377 (5)

because of the participation of the conjugated forms (b) and (c).

All intermolecular distances are significantly greater than the van der Waals distances. Apart from aesthetic considerations there are no special features in the molecular packing (Fig. 4).

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Dinitratobis(antipyrine)zinc(II)

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Zn(C₁₁ON₂H₁₂)₂(NO₃)₂, tetragonal, *P*4₁, *a* = *b* = 9.94 ± 0.02, *c* = 25.50 ± 0.10 Å, *D*_c = 1.492 ± 0.012, *D*_m = 1.48 ± 0.02, μ = 15 cm⁻¹ (Cu Kα), *Z* = 4, |*F*(000)| = 1168, *M* = 566, *R* = 0.107 for 2179 unweighted reflexions. The structure, solved by the heavy-atom method, contains Zn(antipyrine)₂(NO₃)₂ in van der Waals contacts. The zinc atom is surrounded by two oxygen atoms from two similar antipyrine molecules and by four oxygen atoms belonging to one symmetric and one unsymmetric bidentate NO₃⁻.

Introduction

Les cristaux sont préparés selon la méthode décrite par Souchay (1940), en chauffant légèrement dans les

proportions stoechiométriques, de l'antipyrine et du nitrate de zinc. Des recristallisations dans l'alcool amylique fournissent des petits cristaux incolores, transparents, ayant la forme de petites pyramides à