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Large Metal Ion-Centered Template Reactions. A Uranyl Complex of Cyclopentakis(2-iminoisoindoline)[1]

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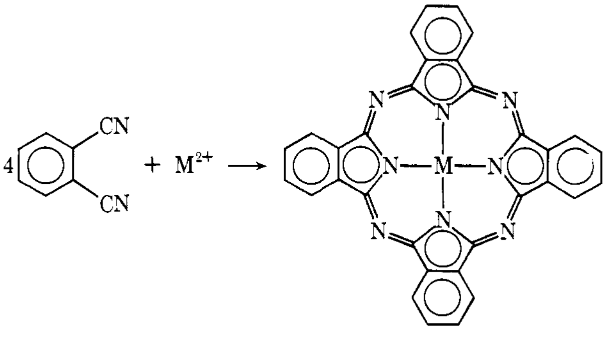
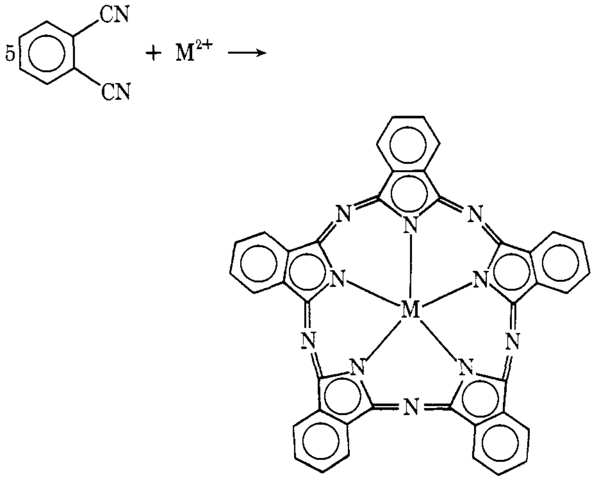
Abstract: The reaction of *o*-dicyanobenzene with anhydrous uranyl chloride *does not* yield a cyclic, four-subunit phthalocyanine complex. Rather, it yields an expanded, cyclic five-subunit pentakis(2-iminoisoindoline) complex—a "superphthalocyanine". Dioxocyclopentakis(2-iminoisoindoline)uranium(VI), $UO_2(N_2C_8H_4)_5$, crystallizes in the monoclinic space group, $P2_{1/c}$, with a = 8.210 (3) Å, b = 21.667 (7) Å, c = 18.462 (5) Å, β = 103.16 (2)°, and Z = 4 (ρ_{calcd} = 1.891, ρ_{obsd} = 1.882 g/cm^3). Intensity measurements were made for 9564 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 60.4°$ at 20 ± 1° with Nb-filtered Mo K$\bar{\alpha}$ radiation on a Syntex P$\bar{1}$ autodiffractometer. The structure was solved using the heavy atom technique. Cycles of anisotropic full-matrix least-squares refinement have given a final value of 0.054 for the conventional unweighted residual, R, for 4709 independent reflections having $I > 3\sigma(I)$. The coordination geometry of the uranium atom approximates an idealized compressed pentagonal bipyramid. The two axial ligands are oxygen atoms with an average U-O bond length of 1.744 (8) Å. The equatorial coordination is by five nitrogen atoms (the average U-N bond length is 2.524 (9) Å) of the 20-atom "inner" ring of the 50-atom (excluding hydrogens) macrocycle. The cyclopentakis(2-iminoisoindoline) ligand is severely and irregularly distorted from planarity, presumably as a consequence of appreciable steric strain within the macrocycle.

Considerable recent interest in coordination chemistry has centered around the role of metal ions as templates in the cyclization and condensation reactions which produce complexes of macrocyclic ligands.[5] A fascinating question related to such reactions is whether increasing the ionic radius of the template will yield an expanded macrocyclic ligand by allowing a greater number of subunits to coordinatively cyclize. In this contribution we present a portion of our work[6] in this area, related to the synthesis of phthalocyanine complexes,[5,7] eq 1, but with the modification that M be a far larger[8] actinide ion. For M = UO_2^{2+}, the reaction has been reported and was assumed[9] to yield a normal, tetradentate phthalocyanine complex even though satisfactory analytical data were not obtained. Mass spectral data[10] suggested that five dicyanobenzene subunits might be coordinated to the uranyl ion, and among the various conceivable structural formulations[10,11] is that arising from the reaction given by eq 2. As part of our studies of actinide-centered template reactions, we present here our chemical, spectroscopic, and structural investigations regarding the so-called uranyl phthalocyanine. It is seen that the coordinative preferences of the uranyl ion can dramatically alter the normal course of the cyclization reaction.



(1)



(2)

Experimental Section

Dioxocyclopentakis(2-iminoisoindolinato)uranium(VI). This compound (formal name, 5,35:14,19-diimino - 7,12:21,26:28,33 - trinitrilopentabenzo [*c*,*h*,*m*,*r*,*w*][1,6,11,16,21] pentaazacyclopentacosinatodioxouranium(VI)) was prepared by the literature procedure.[9b] Crystals suitable for diffraction studies were grown by slow evaporation of 1,2,4-trichlorobenzene solutions on a hot plate.

Anal. Calcd for $(N_2C_8H_4)_5UO_2$: C, 52.72; H, 2.22; N, 15.37. Found: C, 52.54; H, 2.16; N, 15.21. Calcd for $(N_2C_8H_4)_4UO_2$: C, 49.11; H, 2.06; N, 14.32.

Infrared spectrum (Nujol mull, cm^{-1}): 1505 ms, 1495 ms, 1460 m, 1410 m, 1370 w, 1330 s, 1280 m, 1180 vw, 1165 w, 1110 m, 1070 s, 1025 s, 1013 s, 940 w, 925 s, 897 w, 865 m, 765 m, 715 s, 700 s, 660 w, 625 w.

Crystallographic. Weissenberg and precession photographs used to determine the probable space group and a preliminary set of lattice constants indicated monoclinic, $2/m$, symmetry. The systematically absent reflections were those uniquely required by the centrosymmetric space group, $P2_{1/c}$-$C_{2h}{}^5$.[12] This choice was fully supported by the results of sensitive tests for piezoelectricity[13] and by all stages of the subsequent structure determination.

A nearly cube shaped specimen, 0.45 mm on an edge, was cut from a large single crystal, ground to a sphere having a diameter of 0.38 mm, and was glued to the end of a thin glass fiber having a tip diameter of 0.10 mm. This crystal was then accurately centered optically on a computer-controlled four-circle Syntex P$\bar{1}$ autodiffractometer and a total of 15 high-angle ($2\theta_{\mathrm{Mo}\,K\bar{\alpha}} > 25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1° with Nb-filtered Mo $K\bar{\alpha}$ radiation (λ 0.71069 Å) gave the lattice constants $a = 8.210 \pm 0.003$ Å, $b = 21.667 \pm 0.007$ Å, $c = 18.462 \pm 0.005$ Å, and $\beta = 103.16 \pm 0.02°$. A unit cell content of four $UO_2(N_2C_8H_4)_5$ molecules gives a calculated density of 1.891 g/cm^3, in good agreement with the observed density of 1.882 g/cm^3, measured by flotation in a bromoform–chloroform mixture.

Intensity measurements utilized Nb-filtered Mo $K\bar{\alpha}$ radiation and the θ–2θ scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. For those reflections having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 43°$, a scanning rate of 3°/min was employed for the scan between 2θ settings 1.0° above and below the calculated $K\alpha$ doublet values ($\lambda_{K\alpha_1}$ 0.70926 and $\lambda_{K\alpha_2}$ 0.71354 Å). A scanning rate of 2°/min was used for the remaining reflections. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range. A total of 9564 independent reflections having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 60.4°$ (1.3 times the number of data in the limiting Cu $K\bar{\alpha}$ sphere) were measured in concentric shells of increasing 2θ containing approximately 3700 reflections each. The six standard reflections, measured every 300 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either.

The linear absorption coefficient of the crystal[14] for Mo $K\bar{\alpha}$ radiation is 6.43 mm^{-1}, yielding a μR of 1.21 for the spherical crystal used in data collection. The intensities of all reflections were corrected for absorption as a strict function of scattering angle[15] before reducing them to a set of relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 9564 reflections examined, 4855 were eventually rejected as objectively unobserved by applying the rejection criterion, $I < 3.0\sigma(I)$ where $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = (C_t + k^2B)$$

C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, $k = 1$), and B the total background count. The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares were used with the remaining 4709 observed intensities in the determination and refinement of the structure.

The atomic coordinates of the uranium atom were readily derived from the Patterson synthesis calculated with 3066 independent data having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 43°$ and $I > \sigma(I)$. Two cycles of least-squares refinement of the structural parameters for the uranium atom resulted in a conventional unweighted residual

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

of 0.259 and a set of phases which were sufficiently accurate to allow the location of all remaining atoms (except hydrogens) of the totally general-position asymmetric unit from a single difference Fourier synthesis. Unit-weighted full-matrix least-squares refinement of the fractional atomic coordinates and isotropic thermal parameters of the 53 crystallographically independent atoms resulted in $R = 0.097$ and a conventional weighted residual

$$r = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$$

of 0.098. These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[16] and an anomalous dispersion correction to the scattering factor of the uranium atom.[17] Utilization of anisotropic thermal parameters for all atoms in further cycles of least-squares refinement gave $R = 0.053$ and $r = 0.063$ for 3066 independent reflections having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} < 43°$ and $I > \sigma(I)$.

Additional cycles of unit-weighted full-matrix anisotropic least-squares minimization of the function $\sum w(|F_o| - K|F_c|)^2$ (where K is the scale factor and w is the weight assigned each reflection) using the complete data set with various values of the $I/\sigma(I)$ rejection criterion converged to: $R = 0.089$ for 6663 reflections having $I > \sigma(I)$; $R = 0.068$ for 5528 reflections having $I > 2\sigma(I)$; and $R = 0.056$ for 4709 reflections having $I > 3\sigma(I)$. Differences in the structural parameters resulting from these various refinements were insignificant.

Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n = 7.24 - 0.943 \times 10^{-1}F_o + 0.620 \times 10^{-3}F_o{}^2 - 0.599 \times 10^{-6}F_o{}^3$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

where the F_c values were calculated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion. The final cycles of totally anisotropic full-matrix least-squares refinement utilized these weights to give final values of 0.054 and 0.064 for R and r, respectively, for 4709 independent reflections. During the final cycle of refinement, no parameter shifted by more than $0.33\sigma_p$ with the average shift being $0.02\sigma_p$, where σ_p is the estimated standard deviation of the parameter. Since a careful examination of the final F_o and F_c values indicated the absence of extinction effects, extinction corrections were not made.

The following programs were used on an IBM 360/65 computer for this work: MAGTAPE, SCALEUP, and SCTFT2, data reduction programs written by Day; FORDAP, Fourier and Patterson synthesis program; ORFLSE, full-matrix least-squares structure refinement program, a highly modified version of Busing, Martin and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by Johnson; and MPLANE, least-squares mean plane calculation program from Dahl's group.

Results and Discussion

The reaction of anhydrous uranyl chloride with o-dicyanobenzene in dry dimethylformamide yields, after extractive work-up, a blue-black crystalline material, which analyzes for (dicyanobenzene)$_5$UO$_2$. The vibrational spectrum (see Experimental Section) gives no evidence for C≡N (2200–2300 cm^{-1}) which is commonly observed in phthalocyanine complexes of stoichiometry (phthalocyaninato)M·(o-dicyanobenzene).[11] In these cases, the extra nitrile is apparently coordinated as an independent, displaceable ligand.[11] The infrared spectrum of the present compound does exhibit a strong band at 925 cm^{-1} assignable to the antisymmetric O═U═O stretch of a uranyl moiety.[18] The extremely poor solubility of this complex has prevented the observation of a proton NMR spectrum even at high temperatures with extensive CW time averaging. Although the chemical, spectroscopic, and analytical data for this compound were consistent with the formation of a macrocycle containing five isoindoline subunits rather than four, attempts to build scaled models of the (idealized) ligand indicated the presence of severe steric constraints within the macrocycle. A three-dimensional crystal structure analysis was therefore performed to resolve this ambiguity. The results indicate that eq 2 does occur, and that *five* o-dicyanobenzene units have cyclized in the presence of the uranyl ion, to yield a "superphthalocyanine", SPc, complex.

Table I. Atomic Coordinates in Crystalline $UO_2(N_2C_8H_4)_5$[a]

Atom type[b]	Fractional coordinates		
	10^4x	10^4y	10^4z
O_1	264 (11)	2205 (4)	957 (5)
O_2	4462 (9)	2036 (4)	909 (5)
N_{a1}	1146 (13)	2531 (4)	−374 (4)
N_{a2}	1888 (14)	1688 (4)	−1166 (5)
N_{b1}	1985 (13)	1209 (4)	29 (5)
N_{b2}	1855 (15)	310 (5)	804 (5)
N_{c1}	2260 (14)	1151 (4)	1692 (5)
N_{c2}	2756 (13)	1539 (4)	2960 (5)
N_{d1}	3504 (12)	2402 (4)	2283 (5)
N_{d2}	4801 (13)	3408 (4)	2152 (5)
N_{e1}	2702 (11)	3257 (4)	986 (5)
N_{e2}	721 (13)	3589 (4)	−172 (5)
C_{a1}	492 (14)	3074 (5)	−540 (5)
C_{a2}	−539 (15)	3053 (5)	−1286 (5)
C_{a3}	−52 (15)	2524 (5)	−1616 (6)
C_{a4}	1170 (14)	2209 (5)	−1024 (5)
C_{a5}	−1729 (15)	3456 (5)	−1675 (6)
C_{a6}	−2429 (19)	3307 (7)	−2430 (7)
C_{a7}	−1888 (16)	2778 (5)	−2760 (6)
C_{a8}	−680 (17)	2391 (6)	−2367 (6)
C_{b1}	2353 (16)	1249 (5)	−667 (6)
C_{b2}	2992 (16)	658 (6)	−879 (7)
C_{b3}	2796 (17)	246 (5)	−347 (6)
C_{b4}	2205 (17)	598 (5)	224 (6)
C_{b5}	3572 (18)	480 (6)	−1487 (6)
C_{b6}	3951 (20)	−149 (6)	−1547 (8)
C_{b7}	3692 (18)	−581 (6)	−1000 (7)
C_{b8}	3115 (21)	−382 (6)	−383 (7)
C_{c1}	1736 (16)	572 (5)	1433 (5)
C_{c2}	1151 (16)	216 (6)	1984 (6)
C_{c3}	1313 (16)	592 (5)	2612 (6)
C_{c4}	2098 (17)	1150 (5)	2427 (6)
C_{c5}	578 (18)	−401 (6)	1992 (7)
C_{c6}	136 (18)	−599 (7)	2624 (8)
C_{c7}	252 (21)	−218 (7)	3247 (8)
C_{c8}	889 (17)	393 (6)	3264 (7)
C_{d1}	3558 (14)	2055 (5)	2886 (5)
C_{d2}	4716 (16)	2302 (6)	3532 (6)
C_{d3}	5387 (13)	2835 (5)	3295 (5)
C_{d4}	4559 (14)	2905 (6)	2505 (6)
C_{d5}	5221 (16)	2105 (7)	4265 (6)
C_{d6}	6443 (19)	2451 (7)	4751 (7)
C_{d7}	7051 (18)	2995 (6)	4498 (7)
C_{d8}	6587 (17)	3205 (6)	3767 (7)
C_{e1}	3901 (16)	3583 (5)	1490 (6)
C_{e2}	3949 (16)	4226 (5)	1254 (6)
C_{e3}	2654 (15)	4288 (5)	609 (6)
C_{e4}	1947 (16)	3679 (5)	462 (6)
C_{e5}	4987 (18)	4716 (6)	1539 (8)
C_{e6}	4632 (20)	5286 (5)	1169 (7)
C_{e7}	3304 (20)	5351 (6)	534 (8)
C_{e8}	2332 (18)	4858 (6)	251 (7)
	10^5x	10^5y	10^5z
U	23,620 (6)	21,148 (2)	9325 (2)

[a] Figures in parentheses are the estimated standard deviations.
[b] Each symbol for an atom of the cyclopentakis(2-iminoisoindolinato) macrocycle carries a literal subscript to identify its particular subunit (a, b, c, d, or e) and a numerical subscript that follows the numbering scheme used in Figures 1–6 to distinguish atoms of the same element within the same subunit. Numerical subscripts are used to distinguish between the two uranyl oxygen atoms.

Final coordinates and anisotropic thermal parameters for all atoms except hydrogen atoms are listed in Tables I and II, respectively.[19] The numbering scheme used to designate atoms of the $UO_2(N_2C_8H_4)_5$ molecule is as follows. Each symbol for an atom of the cyclopentakis(2-iminoisoindolinato) macrocycle carries a literal subscript to identify the particular 2-iminoisoindoline subunit (a, b, c, d, or e) and a numerical subscript to distinguish between atoms of the same element within the subunit. Numerical subscripts for atoms are assigned in the same way for each subunit. Numerical subscripts are also used to distinguish between the two uranyl oxygen atoms.

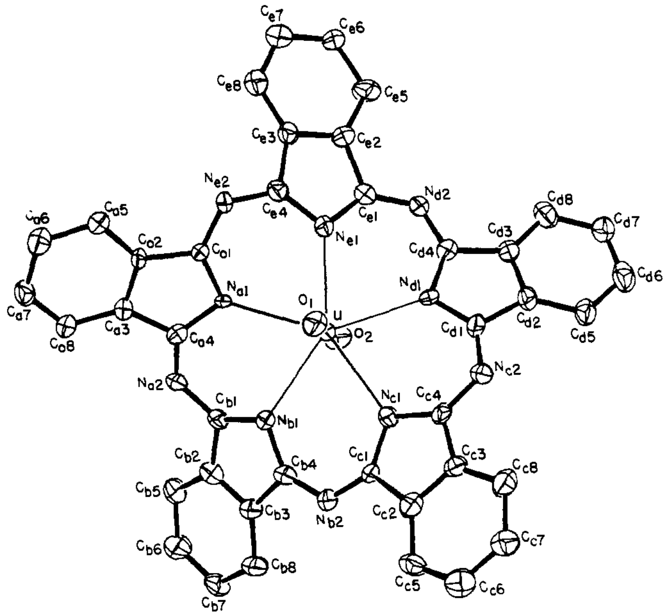


Figure 1. Model in perspective of the $UO_2(N_2C_8H_4)_5$ molecule. The view is essentially perpendicular to the mean plane of the macrocycle.

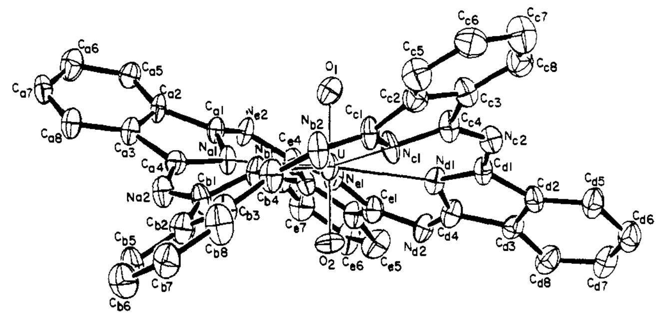


Figure 2. Model in perspective of the $UO_2(N_2C_8H_4)_5$ molecule. The view is 90° away from that of Figure 1 and is essentially normal to the axis of the uranyl group.

Models seen in perspective, representing different views of the contents of the asymmetric unit specified by the atomic coordinates of Table I, are illustrated in Figures 1 and 2; each atom is labeled in conformity with Tables I–VII and is represented by an ellipsoid having the shape, orientation, and relative size consistent with the thermal parameters listed in Table II. The view of the molecule in Figure 1 is nearly parallel to the C_∞ axis of the uranyl group and perpendicular to the mean plane of the macrocycle, while the view of Figure 2 is 90° away and nearly perpendicular to the C_∞ axis of the uranyl group.

The anticipated formation of a five-subunit macrocyclic analog of phthalocyanine (Pc) when UO_2^{2+} is used as the template is obvious from Figure 1. The formation of such a macrocycle is consistent with what is presently known about uranyl and phthalocyanine stereochemistry. Whereas a considerable number of seven-[20] and eight-coordinate[21] uranyl complexes are known whose coordination polyhedra approximate axially compressed pentagonal or hexagonal bipyramids, few examples are known of six-coordinate uranyl complexes.[22] In the seven- and eight-coordinate complexes, the uranyl group is essentially collinear with the idealized five- or sixfold axis of the coordination polyhedron. The coordinated atoms of the other ligands form a quasi-planar

Table II. Anisotropic Thermal Parameters in $UO_2(N_2C_8H_4)_5$[a]

Atom type[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
U	3.00 (1)	1.60 (1)	1.44 (1)	−0.04 (2)	0.25 (1)	−0.15 (2)	1.9
O_1	3.1 (4)	2.8 (4)	2.8 (3)	0.1 (3)	0.1 (3)	0.3 (3)	3.0
O_2	1.8 (3)	2.6 (4)	3.8 (3)	0.4 (3)	0.7 (2)	0.1 (3)	2.6
N_{a1}	3.5 (4)	0.7 (3)	1.3 (3)	−0.0 (3)	0.2 (3)	−0.1 (2)	1.5
N_{a2}	4.2 (5)	1.6 (3)	2.0 (3)	−0.5 (3)	0.5 (3)	−0.4 (3)	2.3
N_{b1}	3.8 (5)	1.8 (3)	1.7 (3)	0.5 (3)	0.0 (3)	−0.0 (3)	2.3
N_{b2}	5.4 (6)	2.0 (4)	1.6 (3)	0.1 (4)	0.6 (3)	0.0 (3)	2.6
N_{c1}	4.6 (5)	2.0 (4)	1.5 (3)	0.2 (4)	1.2 (3)	−0.4 (3)	2.2
N_{c2}	3.2 (4)	1.8 (4)	2.2 (4)	−0.1 (3)	0.8 (3)	−0.1 (3)	2.3
N_{d1}	3.1 (4)	1.1 (3)	1.9 (3)	0.7 (3)	0.0 (3)	0.0 (2)	1.8
N_{d2}	3.4 (5)	1.9 (4)	2.0 (3)	−0.2 (3)	−0.3 (3)	−0.2 (3)	2.4
N_{e1}	2.8 (5)	2.2 (3)	1.7 (3)	−0.4 (3)	−0.1 (3)	−0.0 (3)	2.2
N_{e2}	3.3 (4)	2.1 (4)	1.4 (3)	0.4 (3)	−0.5 (3)	−0.2 (3)	2.1
C_{a1}	3.0 (5)	1.4 (3)	1.4 (3)	−0.2 (3)	0.1 (3)	0.1 (3)	1.8
C_{a2}	3.7 (5)	2.1 (4)	1.0 (3)	−0.5 (4)	−0.1 (3)	0.2 (3)	2.0
C_{a3}	3.3 (5)	2.3 (4)	1.6 (4)	−0.0 (4)	0.0 (3)	0.1 (3)	2.3
C_{a4}	2.6 (4)	1.9 (4)	2.0 (3)	−0.1 (3)	0.4 (3)	0.2 (3)	2.2
C_{a5}	2.9 (5)	2.2 (4)	2.2 (4)	0.3 (4)	0.2 (4)	0.2 (3)	2.5
C_{a6}	4.4 (7)	3.4 (6)	2.5 (5)	−0.3 (5)	0.0 (4)	0.6 (4)	3.4
C_{a7}	3.9 (5)	3.0 (6)	1.5 (3)	−0.8 (4)	0.6 (3)	0.0 (3)	2.5
C_{a8}	4.1 (6)	2.4 (5)	1.9 (4)	−0.1 (4)	0.2 (4)	0.2 (3)	2.6
C_{b1}	4.0 (6)	1.8 (4)	1.6 (3)	0.0 (4)	0.9 (4)	−0.5 (3)	2.2
C_{b2}	3.8 (7)	2.4 (4)	2.6 (4)	−0.1 (4)	0.5 (5)	−0.6 (4)	2.9
C_{b3}	3.9 (6)	1.9 (4)	2.4 (4)	0.2 (4)	0.6 (4)	−0.1 (3)	2.6
C_{b4}	4.4 (6)	1.7 (4)	2.3 (4)	−0.4 (4)	0.4 (4)	−0.4 (3)	2.6
C_{b5}	4.3 (6)	3.1 (5)	2.1 (4)	0.4 (5)	1.0 (4)	−0.6 (4)	2.9
C_{b6}	4.9 (7)	2.9 (5)	3.4 (6)	0.6 (5)	1.2 (5)	−0.7 (4)	3.5
C_{b7}	4.6 (7)	2.3 (5)	2.9 (5)	0.8 (4)	0.6 (4)	1.1 (4)	2.8
C_{b8}	6.3 (8)	1.7 (4)	3.0 (5)	0.0 (5)	1.1 (5)	−0.4 (4)	3.2
C_{c1}	4.3 (6)	1.5 (4)	1.4 (3)	0.2 (4)	0.3 (4)	0.2 (3)	2.1
C_{c2}	2.9 (5)	2.7 (5)	2.5 (4)	0.2 (4)	0.6 (4)	0.4 (4)	2.7
C_{c3}	3.6 (5)	1.8 (4)	2.3 (4)	0.3 (4)	1.0 (4)	0.2 (3)	2.4
C_{c4}	4.3 (6)	1.8 (4)	1.7 (4)	1.5 (4)	0.5 (4)	0.2 (3)	2.1
C_{c5}	4.2 (7)	2.2 (5)	3.3 (5)	−1.2 (4)	0.8 (5)	−0.7 (4)	2.9
C_{c6}	3.5 (6)	3.6 (6)	4.1 (6)	−1.3 (5)	1.1 (5)	0.4 (5)	3.4
C_{c7}	5.5 (8)	2.8 (5)	3.4 (6)	−0.7 (5)	1.2 (5)	−0.0 (4)	3.7
C_{c8}	3.7 (6)	3.2 (5)	2.8 (5)	0.2 (5)	0.7 (4)	0.7 (4)	3.2
C_{d1}	3.4 (5)	2.4 (4)	1.5 (3)	0.5 (4)	0.4 (3)	0.2 (3)	2.3
C_{d2}	3.2 (5)	2.6 (4)	1.6 (4)	0.4 (4)	0.7 (3)	−0.2 (3)	2.3
C_{d3}	2.3 (4)	2.3 (4)	2.1 (3)	1.0 (4)	0.1 (3)	−0.3 (4)	2.1
C_{d4}	3.3 (5)	2.1 (4)	2.2 (3)	0.2 (5)	−0.1 (3)	−0.0 (4)	2.5
C_{d5}	3.9 (5)	3.3 (5)	2.0 (4)	1.7 (5)	0.3 (3)	−0.2 (4)	2.7
C_{d6}	4.3 (7)	4.4 (7)	2.1 (4)	1.6 (5)	0.5 (4)	−0.6 (4)	3.2
C_{d7}	4.3 (6)	3.0 (6)	2.5 (4)	0.7 (5)	−0.3 (4)	−0.2 (4)	3.2
C_{d8}	3.5 (6)	3.5 (6)	2.7 (5)	0.9 (5)	−0.0 (4)	1.0 (4)	3.1
C_{e1}	3.3 (5)	2.1 (4)	2.2 (4)	−0.0 (4)	0.4 (4)	−0.3 (3)	2.5
C_{e2}	3.6 (5)	1.9 (4)	2.4 (4)	−0.3 (4)	0.5 (4)	0.3 (3)	2.6
C_{e3}	3.4 (5)	2.3 (4)	1.7 (4)	−0.5 (4)	0.8 (3)	−0.1 (3)	2.3
C_{e4}	3.6 (6)	2.2 (4)	1.9 (4)	−0.5 (4)	0.8 (4)	−0.3 (3)	2.4
C_{e5}	3.8 (6)	2.0 (4)	4.1 (6)	−1.2 (4)	0.2 (5)	−0.1 (4)	3.0
C_{e6}	5.7 (8)	1.7 (4)	2.5 (5)	−0.4 (5)	−0.0 (5)	0.2 (3)	2.9
C_{e7}	5.0 (7)	2.4 (5)	3.3 (5)	0.4 (5)	0.6 (5)	−0.4 (4)	3.4
C_{e8}	4.2 (6)	2.9 (5)	2.4 (4)	−0.2 (5)	0.7 (4)	−0.1 (4)	3.0

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [b] Each symbol for an atom of the cyclopentakis(2-iminoisoindolinato) macrocycle carries a literal subscript to identify its particular subunit (a, b, c, d, or e) and a numerical subscript that follows the numbering scheme used in Figures 1–6 to distinguish atoms of the same element within the same subunit. Numerical subscripts are used to distinguish between the two uranyl oxygen atoms. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

pentagonal or hexagonal girdle around the uranium atom which is essentially perpendicular to this axis. The extremely strong bonds of the uranyl group result in very short (~1.75 Å) U–O distances and necessitate an axial compression of the coordination polyhedra in these pentagonal and hexagonal bipyramidal uranyl complexes.

By analogy with porphyrins, the "radius of the central hole"[23a] of a phthalocyanine ligand may be defined as the distance from the isoindoline nitrogen atom to the center of the molecule. Whereas phthalocyanine and porphyrin ligands can easily accommodate smaller metal ions, such as Cu^{2+},[24] Ni^{2+},[25] Pt^{2+},[26] etc. in their "central holes" while maintaining an essentially coplanar configuration for the metal and macrocycle, Hoard[23] has shown that the radial strain in the core of a metalloporphyrin is minimized when the metal-to-coordinated-nitrogen distance is ~2.01 Å. Replacement of the bridging methine carbon atoms of a porphyrin macrocycle with the bridging nitrogen atoms of the phthalocyanine ligand reduces the size of the "central hole" by ~0.22 Å, from 4.02 to ~3.80 Å. Although an analysis by Hoard[23b] of the structural parameters for $SnCl_2Pc$[27] has indicated that "hole" shrinkage may not be responsible for the dramatic differences in molecular configuration observed between $SnCl_2Pc$[27] and α,β,γ,δ-tetraphenylporphinatodichlorotin(IV), $SnCl_2TPP$,[23c] the 1.11 Å displacement of the Sn^{2+} atom from the Pc mean plane in SnPc[28] clearly illustrates the inability of the four-subunit Pc macrocycle to accommodate larger cations. Whereas the metal and radial-

Table III. Bond Distances and Polyhedral Edge Lengths in the Coordination Group of $UO_2(N_2C_8H_4)_5$[a]

Type[b]	Length, Å	Type[b]	Length, Å
$U-O_1$	1.745 (9)	O_2-N_{a1}	3.197 (12)
$U-O_2$	1.743 (7)	O_2-N_{b1}	2.912 (13)
		O_2-N_{c1}	3,197 (13)
$U-N_{a1}$	2.523 (8)	O_2-N_{d1}	2.930 (12)
$U-N_{b1}$	2.548 (9)	O_2-N_{e1}	3.034 (12)
$U-N_{c1}$	2.526 (9)		
$U-N_{d1}$	2.533 (9)	$N_{a1}-N_{b1}$	2,967 (12)
$U-N_{e1}$	2.490 (9)	$N_{a1}-N_{e1}$	2.942 (12)
		$N_{b1}-N_{c1}$	3.030 (12)
O_1-N_{a1}	2.926 (12)	$N_{c1}-N_{d1}$	3.011 (13)
O_1-N_{b1}	3.270 (13)	$N_{d1}-N_{e1}$	2.980 (12)
O_1-N_{c1}	2.955 (13)		
O_1-N_{d1}	3.207 (12)		
O_1-N_{e1}	3.025 (13)		

[a] Figures in parentheses are the estimated standard deviations.
[b] Each symbol for an atom of the cyclopentakis(2-iminoisoindolinato) macrocycle carries a literal subscript to identify its particular 2-iminoisoindoline subunit (a, b, c, d, or e) and a numerical subscript that follows the numbering scheme used in Figures 1–6 to distinguish atoms of the same element within the same subunit. Numerical subscripts are used to distinguish between the two uranyl oxygen atoms.

ly expanded porphinato core (Sn–N distance of 2.098 (2) Å) are essentially coplanar in $SnCl_2TPP$, the tin atom and Pc macrocycle are decidedly nonplanar in $SnCl_2Pc$. The large equatorial radius of uranium in uranyl complexes and the ~2.55 Å U–N distance observed in other seven-coordinate uranyl complexes[20f,h,i] seems to preclude the formation of a uranyl Pc and favors the formation of a larger macrocycle.

Complexing bond lengths and polyhedral edge lengths are given with their estimated standard deviations in Table III and rounded-off values of polyhedral edge lengths are carried in Figure 3 which shows the coordination polyhedron of $UO_2(N_2C_8H_4)_5$. The angles subtended at the uranium(VI) atom are given with their estimated standard deviations in Table IV. The average uranyl U–O bond length of 1.744 (8, 1, 1) Å[29] and the O–U–O bond angle of 179 (1)° are in good agreement with the values reported for other uranyl complexes.[20,21]

The average U–N bond length of 2.524 (9, 14, 34) Å[29] is in good agreement with those of other seven-coordinate uranyl compounds containing nitrogen ligands. The precision obtained in this study is generally greater, by at least a factor of two, than that of other X-ray structural studies of uranyl complexes.

Although the maximum (0.30 Å) and average (0.20 Å) displacements of the five coordinated nitrogen atoms from their unit-weighted least-squares mean plane are statistically significant, being 33 and 22 times the average positional estimated standard deviation for these atoms, respectively, the coordination polyhedron can still best be described as an axially compressed pentagonal bipyramid with the five isoindoline nitrogen atoms forming the pentagonal girdle. The uranium atom is displaced by only 0.02 Å from this mean plane toward O_1. The averaged values of 72.5 (3, 6, 9)°, 90.4 (4, 47, 71)°, and 89.6 (4, 46, 64)° for the five acute N_iUN_i, five O_IUN_i, and five O_2UN_i bond angles in $UO_2(N_2C_8H_4)_5$ do not differ significantly from the corresponding values of 72.0, 90.0, and 90.0° for an idealized axially compressed pentagonal bipyramid. The least-squares mean plane for the pentagonal girdle of coordinated nitrogen atoms is virtually coplanar with that of the entire 50-atom (excluding hydrogen atoms) macrocycle, making an angle of only 2.4° with it. The equation of the least-squares mean plane for the macrocycle is given by $0.001X$ –

Table IV. Bond Angles Subtended at the U(VI) Atom in the Coordination Group of $UO_2(N_2C_8H_4)_5$[a]

Type[b]	Angle, deg	Type[b]	Angle, deg
O_1UO_2	179.2 (13)	$N_{a1}UN_{b1}$	71.6 (3)
O_1UN_{a1}	84.5 (4)	$N_{a1}UN_{e1}$	71.9 (3)
O_1UN_{b1}	97.5 (4)	$N_{b1}UN_{c1}$	73.3 (3)
O_1UN_{c1}	85.5 (4)	$N_{c1}UN_{d1}$	73.0 (3)
O_1UN_{d1}	95.3 (4)	$N_{d1}UN_{e1}$	72.8 (3)
O_1UN_{e1}	89.4 (4)	$N_{a1}UN_{c1}$	141.8 (3)
O_2UN_{a1}	95.3 (4)	$N_{a1}UN_{d1}$	144.6 (3)
O_2UN_{b1}	83.2 (4)	$N_{b1}UN_{d1}$	142.8 (3)
O_2UN_{c1}	95.2 (4)	$N_{b1}UN_{e1}$	141.9 (3)
O_2UN_{d1}	84.4 (4)	$N_{c1}UN_{e1}$	144.8 (3)
O_2UN_{e1}	89.8 (4)		

[a] Figures in parentheses are the estimated standard deviations.
[b] Each symbol for an atom of the cyclopentakis(2-iminoisoindolinato) macrocycle carries a literal subscript to identify its particular 2-iminoisoindoline subunit (a, b, c, d, or e) and a numerical subscript that follows the numbering scheme used in Figures 1–6 to distinguish atoms of the same element within the same subunit. Numerical subscripts are used to distinguish between the two uranyl oxygen atoms.

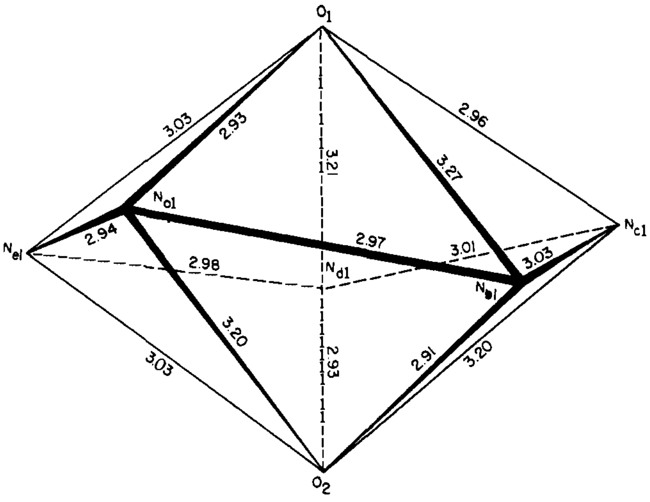


Figure 3. Perspective view (adapted from an ORTEP drawing) of the axially compressed pentagonal bipyramidal coordination polyhedron as observed in the $UO_2(N_2C_8H_4)_5$ molecule.

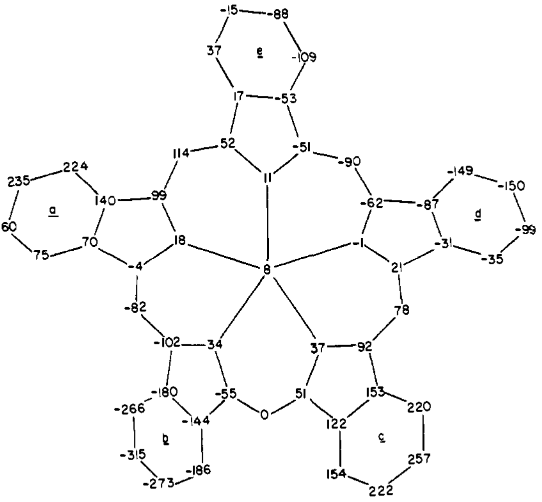


Figure 4. Diagram derived from Figure 1 to illustrate the nonplanarity of the cyclopentakis(2-iminoisoindolinato) macrocycle in $UO_2(N_2C_8H_4)_5$. The perpendicular displacement of the atoms from the 50-atom macrocycle mean plane, in units of 0.01 Å, replaces the symbols of the atoms given in Figure 1.

Table V. Bond Lengths in the Cyclopentakis(2-iminoisoindolinato) Macrocycle[a]

Type[b]	Subunit a	Subunit b	Subunit c	Subunit d	Subunit e	Average[c]
N_1–C_1	1.408 (13)	1.387 (14)	1.377 (14)	1.336 (13)	1.384 (14)	1.379 (14, 14, 43)
N_1–C_4	1.363 (13)	1.374 (14)	1.393 (13)	1.394 (15)	1.372 (14)	
N_2–C_4	1.327 (14)	1.326 (15)	1.315 (14)	1.310 (16)	1.372 (14)	1.323 (14, 12, 49)
N_2–C_{x1}[d]	1.319 (14)	1.316 (13)	1.320 (15)	1.330 (14)	1.298 (13)	
C_1–C_2	1.443 (13)	1.471 (16)	1.443 (15)	1.449 (15)	1.463 (16)	1.454 (15, 12, 19)
C_3–C_4	1.473 (14)	1.469 (16)	1.447 (17)	1.469 (14)	1.442 (15)	
C_2–C_3	1.397 (16)	1.363 (17)	1.397 (16)	1.392 (17)	1.411 (16)	1.397 (17, 13, 34)
C_2–C_5	1.383 (15)	1.372 (16)	1.419 (16)	1.389 (15)	1.386 (16)	
C_3–C_8	1.395 (15)	1.391 (16)	1.396 (16)	1.408 (16)	1.398 (17)	
C_5–C_6	1.418 (17)	1.408 (18)	1.368 (18)	1.402 (19)	1.411 (17)	
C_6–C_7	1.418 (19)	1.428 (20)	1.401 (20)	1.399 (20)	1.414 (19)	
C_7–C_8	1.373 (17)	1.397 (17)	1.421 (19)	1.394 (18)	1.364 (19)	

[a] The figure in parentheses following each individual distance is the estimated standard deviation in the last significant digit. [b] Atoms labeled in agreement with Figures 1–6 and Tables I and II. [c] The figures in parentheses following each averaged value are the root mean square value of the estimated standard deviation for an individual datum, the mean deviation, and the maximum deviation. [d] A subscripted x refers to an atom in the adjacent (in a counterclockwise sense) subunit of the macrocycle in Figures 1, 4, and 5.

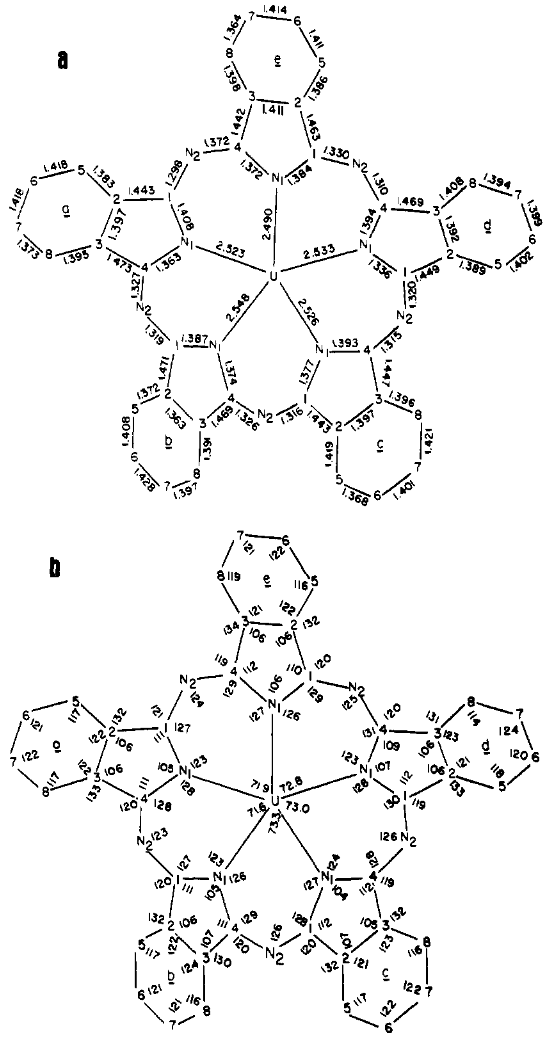


Figure 5. Diagrams derived from Figure 1 of the cyclopentakis(2-iminoisoindolinato) skeleton showing bond lengths (a) and bond angles (b) in the ligand. Symbols for carbon atoms are replaced by the numerical subscripts used to identify these atoms in the tables. The literal subscript used to identify the subunit for each atom is at the center of the six-membered ring of each isoindoline group.

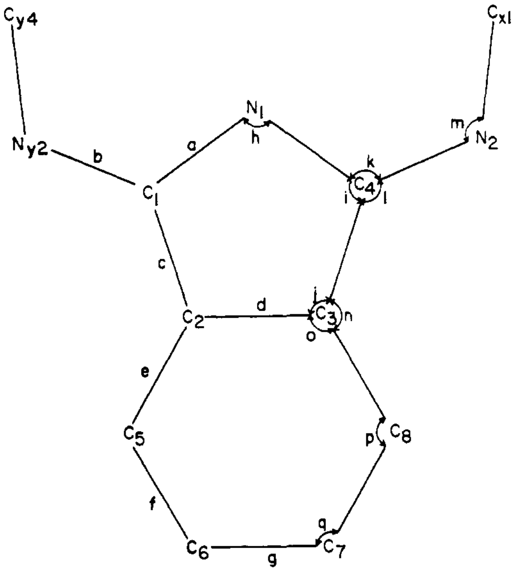


Figure 6. Diagram showing the basis for the bond length and angle comparisons given in Table VII for isoindoline groups in the cyclopentakis(2-iminoisoindoline) and various phthalocyanine macrocycles. The group is assumed to have a mirror plane (with respect to all bond lengths and angles) which contains atom N_1 and the midpoints of the C_2–C_3 and C_6–C_7 bonds. A subscripted x refers to an atom in the adjacent (in a counterclockwise sense) subunit of the macrocycle in Figures 1, 4, and 5. A subscripted y refers to an atom in the adjacent subunit in a clockwise sense.

$0.109Y - 0.084Z = 0.978$ where X, Y, and Z are orthogonal coordinates measured in ångströms along a, b, and c^*, respectively, of the crystallographic coordinate system; the individual atomic displacements from this plane are shown in Figure 4. Unlike the four-subunit phthalocyanine macrocycle which is essentially planar as the free acid[30,31] and even in many of its metal complexes,[24-26] the five-subunit cyclopentakis(2-iminoisoindolinato) macrocycle is decidedly nonplanar in $UO_2(N_2C_8H_4)_5$, a fact that is dramatically illustrated in Figures 2 and 4.

Bond lengths and angles within the macrocycle are given with their estimated standard deviations in Tables V and VI, respectively, and are compared with corresponding bond lengths and angles of several phthalocyanine ligands in Table VII. Rounded-off values of bond lengths and angles within the macrocycle of $UO_2(N_2C_8H_4)_5$ are given in Figure 5. The particular bond lengths and angles being compared in Table VII are shown in the isoindoline subunit of Figure 6. It can be seen from Table VII that no significant differences in bond lengths within the isoindoline subunit are observed between the superphthalocyanine, SPc, and Pc macrocycles, and that only a few differences in bond angles are observed—all involving atoms of the 20-atom "inner" ring of the macrocycle (N_1, N_2, C_1, and C_4 for each subunit). The averaged values of 1.379 (14, 14, 34) Å,

Table VI. Bond Angles in the Cyclopentakis(2-iminoisoindolinato) Macrocycle[a]

Type[b]	Subunit a	Subunit b	Subunit c	Subunit d	Subunit e	Average[c]
UN_1C_1	122.5 (6)	122.6 (7)	127.4 (7)	128.0 (7)	126.1 (7)	125.5 (7, 18, 30)
UN_1C_4	127.7 (6)	125.6 (7)	124.4 (7)	123.2 (7)	127.2 (7)	
$C_1N_1C_4$	105.2 (8)	105.0 (9)	104.1 (9)	107.1 (9)	105.8 (9)	105.5 (9, 4, 16)
$N_1C_1C_2$	111.0 (9)	111.0 (10)	111.7 (9)	111.6 (10)	110.4 (10)	111.2 (10, 7, 20)
$N_1C_4C_3$	111.4 (9)	110.9 (10)	112.2 (10)	109.2 (10)	112.2 (10)	
$C_1C_2C_3$	106.2 (9)	105.7 (11)	106.8 (10)	106.3 (9)	105.9 (10)	105.9 (10, 5, 12)
$C_2C_3C_4$	105.7 (9)	106.8 (10)	104.7 (10)	105.7 (10)	105.5 (10)	
$N_1C_1N_{y2}$[d]	126.6 (9)	127.1 (11)	128.2 (10)	129.9 (10)	129.3 (11)	128.6 (10, 10, 26)
$N_1C_4N_2$	128.2 (10)	128.7 (11)	127.9 (12)	131.2 (9)	129.3 (10)	
$N_{y2}C_1C_2$[d]	120.7 (9)	120.3 (10)	119.7 (10)	118.5 (9)	119.8 (10)	119.7 (10, 6, 12)
$N_2C_4C_3$	120.4 (9)	120.2 (10)	119.2 (10)	119.5 (11)	118.5 (10)	
$C_4N_2C_{x1}$[d]	123.0 (10)	125.7 (10)	126.4 (10)	125.4 (10)	124.0 (10)	124.9 (10, 11, 19)
$C_1C_2C_5$	131.8 (10)	132.4 (12)	132.4 (11)	133.0 (12)	132.2 (11)	132.1 (11, 8, 25)
$C_4C_3C_8$	132.6 (11)	129.6 (11)	132.3 (11)	131.0 (12)	134.0 (11)	
$C_2C_3C_8$	121.7 (10)	123.6 (12)	122.7 (11)	123.3 (10)	120.5 (11)	121.9 (11, 8, 17)
$C_3C_2C_5$	122.0 (9)	121.7 (12)	120.7 (11)	120.7 (11)	121.9 (11)	
$C_2C_5C_6$	116.6 (11)	117.4 (12)	117.2 (12)	118.0 (13)	116.4 (12)	116.8 (12, 10, 25)
$C_3C_8C_7$	117.2 (11)	116.2 (12)	115.5 (12)	114.3 (13)	118.7 (12)	
$C_5C_6C_7$	120.7 (12)	120.6 (12)	122.2 (13)	119.6 (12)	121.6 (12)	121.3 (12, 8, 17)
$C_6C_7C_8$	121.7 (10)	120.5 (11)	121.6 (13)	124.0 (12)	120.8 (12)	

[a] The figure in parentheses following each individual angle is the estimated standard deviation in the last significant digit. [b] Atoms labeled in agreement with Figures 1–6 and Tables I and II. [c] The figures in parentheses following each averaged value are the root mean square value of the estimated standard deviation for an individual datum, the mean deviation, and the maximum deviation. [d] A subscripted x refers to an atom in the adjacent (in a counterclockwise sense) subunit of the macrocycle in Figures 1, 4, and 5. A subscripted y refers to an atom in the adjacent subunit in a clockwise sense.

Table VII. Comparison of Averaged Isoindoline Subunit Bond Lengths and Angles in the Cyclopentakis(2-iminoisoindoline) Macrocycle with Those in Various Phthalocyanine (Pc) Ligands

	Compound											
Bond parameter[a]	UO_2-$(N_2C_8H_4)_5$	Pc	β-CuPc	α-PtPc	γ-PtPc	O(Mn-PcPy)$_2$	$SnCl_2Pc$	MgPc·2Py·$2H_2O$	U(Pc)$_2$	Sn(Pc)$_2$	Sn(Pc)	ZnPc·*n*-hexylamine
						Bond Lengths, Å						
a	1.379	1.37	1.366	1.38	1.40	1.37	1.379	1.367	1.38	1.375	1.373	1.39
b	1.323	1.32	1.328	1.33	1.33	1.33	1.332	1.336	1.32	1.321	1.328	1.34
c	1.454	1.47	1.453	1.48	1.44	1.45	1.454	1.456	1.46	1.467	1.456	1.47
d,e,f,g[b]	1.397	1.40	1.391	1.40	1.42	1.41	1.388	1.387	1.40	1.407	1.392	1.42
						Bond Angles, deg						
h	105.5	109	107.3	110	108	108	111.5	108.3	107.9	108.1	108.2	109
i	111.2	109	110.4	107	110	109	106.8	109.5	109.4	109.2	109.2	109
j	105.9	106	106.0	107	106	107	107.5	106.4	106.6	106.6	106.6	106
k	128.6	128	127.6	129	127	127	127.6	127.5	127.6	128.7	128.1	128
l	119.7	123	122.1	123	123	124	125.5	123.1	123.0	121.8	122.7	123
m	124.9	124	122.2	120	124	124	126.3	123.7	123.9	121.3	122.4	123
n	132.1	132	133.0	130	134	130	131.5	132.5	131.8	130.5	132.0	132
o	121.9	122	121.1	123	120	123	121.1	121.1	121.6	122.7	121.3	121
p	116.8	118	118.0	115	118	115	117.3	117.5	116.8	115.3	117.3	116
q	121.3	121	121.0	122	122	122	121.6	121.4	121.5	121.8	121.3	122
Reference	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*

[a] The bond parameters are shown in the isoindoline subunit of Figure 6. [b] The value given in the table represents an average for all six (one d, two e, two f, and one g) phenyl ring C–C bonds. [c] This work. [d] See ref 31. [e] See ref 24. [f] See ref 26. [g] See ref 26. [h] L. H. Vogt, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 6, 1725 (1967). [i] See ref 27. [j] M. S. Fischer, D. H. Templeton, A. Zalkin, and M. Calvin, *J. Am. Chem. Soc.*, **93**, 2622 (1971). [k] A. Gieren and W. Hoppe, *Chem. Commun.*, 413 (1971). [l] W. E. Bennett, D. E. Broberg, and N. C. Baenziger, *Inorg. Chem.*, 12, 930 (1973). [m] See ref 28. [n] T. Kobayashi, T. Ashida, N. Uyeda, E. Suito, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, 44, 2095 (1971).

1.323 (14, 12, 49) Å, 1.454 (15, 12, 19) Å, and 1.397 (17, 13, 34) Å for the N_1–C_1, N_2–C_1, C_1–C_2, and phenyl C–C bond lengths, respectively, in the 2-iminoisoindoline subunits of the cyclopentakis(2-iminoisoindoline) macrocycle compare quite favorably with the values found for corresponding bond lengths in the 2-iminoisoindoline subunits of the phthalocyanine ligands listed in Table VII. The small differences in certain bond angles for the two macrocycles ($C_1N_1C_4$ and $C_3C_4N_2$ bond angles smaller and $C_3C_4N_1$ bond angle larger in the subunits of $UO_2(N_2C_8H_4)_5$) seem to be systematic and to manifest themselves in rather large displacements of the N_2 nitrogen atoms from the least-squares mean planes of the five-membered pyrrole rings which they bridge. While each of the five-membered pyrrole and six-membered phenyl rings are nearly planar (maximum displacement of any atom from its least-squares mean plane being 0.04 and 0.02 Å, respectively), the N_2 nitrogen atoms are displaced from the mean planes of the pyrrole rings they bridge by as much as 0.42 Å. The uranium atom is displaced by 0.97, 1.14, 0.91, 0.61, and 0.40 Å from the five-membered pyrrole ring mean planes of subunits a, b, c, d, and e, respectively.

Three major types of distortion are possible within each subunit which would preserve the planarity of the five-membered pyrrole ring and that of the six-membered phenyl ring while destroying the planarity of the macrocycle as a whole. The first of these would involve rotation about the unique twofold axis of an idealized planar isoindoline subunit (this axis contains N_1 and bisects the C_2–C_3 and C_6–C_7 bonds). The second involves rotation about the vector between C_1 and C_4 while the third involves a folding of the idealized isoindoline subunit about the C_2–C_3 bond. Distortions of the first and second types are primarily responsible for deviations from nonplanarity for the cyclopentakis(2-iminoisoindolinato) macrocycle in this compound, since the amount of folding along the C_2–C_3 bond is 3.5, 3.6, 2.9, 1.1, and 2.6° for subunits a, b, c, d, and e, respectively. Each of the nine-membered isoindoline subunits is therefore nearly planar, the maximum displacement of any atom from its least-squares mean plane being 0.08 Å. The normals to the isoindoline mean planes of subunits a, b, c, d, and e, make angles of 39.8, 38.7, 29.4, 28.2, and 31.2°, respectively, with the normal to the mean plane for the entire ligand given above.

The wave-like nature of the ligand in going from subunit a through subunit e is evident from Figure 2 and is probably required to minimize steric strains built into the "inner ring" of 20 atoms surrounding the "central hole" of the ligand and by incorporation of a fifth subunit into the macrocycle. Examination of the polyhedral edge lengths given in Table III reveals no O···N contacts which are smaller than the 2.90 Å sum of the van der Waal's radii for oxygen and nitrogen[32] and four N–N contacts which are only slightly less than the 3.00 Å van der Waal's diameter of nitrogen.[32] Average O···N and N···N distances in the coordination polyhedron are 3.065 and 2.986 Å, respectively. Since an idealized axially compressed D_{5h} pentagonal bipyramidal coordination polyhedron for this compound with U–O distances of 1.744 Å and U–N distances of 2.524 Å would have O···N and N–N contacts of 3.068 and 2.967 Å, respectively, van der Waal's contacts within the coordination polyhedron are probably not responsible for the observed nonplanarity of the macrocycle. Minimization of strain in the "inner ring" of the ligand is probably also responsible for the small systematic differences between the bond angles in this ligand and similar ones of the phthalocyanine macrocycles given in Table VII.

While there are eight pairs of "short" intermolecular contacts, all involving carbon atoms with separations which are less than the 3.40 Å van der Waal's thickness of an aromatic carbon atom,[32] only one of these, that involving atoms C_{b2} and C_{c5} separated by 3.22 (2) Å across the inversion center at the origin of the unit cell, is seriously short. The other "short" intermolecular C····C contacts range from 3.29 (2) to 3.39 (2) Å. Although packing forces within the crystal may contribute to the nonplanar nature of the cyclopentakis(2-iminoisoindolinato) macrocycle in $UO_2(N_2C_8H_4)_5$, minimization of steric effects within the ligand is probably the dominant factor.

The pronounced tendency of the uranyl ion to form seven-coordinate pentagonal bipyramidal complexes having U–N bond lengths of ~2.55 Å suggests that this group is ideally suited for constructing five-membered macrocyclic porphyrin analogs via template reactions. Similar studies of other template reaction systems are underway,[6] as are crystallographic studies of the "free" superphthalocyanine ligand. Substitution of the uranyl group by other metals may, in some cases,[6b] provide a series of interesting new compounds for chemical, spectroscopic, and crystallographic investigation. These studies are in progress. Studies employing metal atom clusters as templates have also begun.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4519.

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A Nuclear Magnetic Resonance Investigation of the Nature of the Boron–Carbon Bond in Some Vinylboranes

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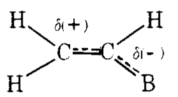
Abstract: The ^{13}C chemical shifts of the terminal vinyl carbons in trivinylborane, six vinylhaloboranes, and several Lewis acid-base adducts of the vinylboranes have been determined. Treatment of these compounds as monosubstituted ethylene derivatives indicates that in any of the tricoordinate boron species a vinyl group behaves as a mesomeric donor and in the vinylhaloboranes the ability of a vinyl substituent to supply π-electron density to boron is not very sensitive to the interchange of halogens (F, Cl, Br). Boron-11 NMR chemical shifts of the vinylboranes are also discussed. The preparation and properties of the new compound divinylbromoborane are presented. Some properties of several adducts of the vinylboranes are also presented.

Trivinylborane and the vinylhaloboranes are excellent examples of a chemically interesting group of compounds which contain an electron-deficient central atom that is directly bonded to electron-rich substituents. Since the boron atom possesses a low-lying vacant p_π orbital it could accept electron density by delocalization of the π systems of the vinyl groups, by p_π–p_π back-donation from the halogens to boron or by a combination of these two effects. Thus, mesomeric interactions could lead to contributions from the structure



which could play a substantial role in the ground state properties in vinylboranes. The question of the occurrence of a significant amount of π-character in these boron–carbon bonds has received considerable attention and evidence both for and against such bonding can be found in the literature.

The earliest evidence suggesting mesomeric interaction between boron and vinyl substituents was based on the chemical stability of various vinylboranes[2] and (perfluorovinyl)boranes.[3] Evidence from NMR spectroscopy[4,5] has also been rationalized in terms of delocalization of π-electron density from the vinyl group to boron.

The infrared and Raman spectra of some vinylboranes[5-9] as well as the microwave spectrum of vinyldifluoroborane[6] have been investigated. The structural study of vinyldifluoroborane[6] has found that molecule to be planar in both the fluid and solid states with a barrier to internal rotation about the B–C bond of 4.17 kcal/mol. It is believed, however, that this apparently high value simply reflects the fact that the internal rotation involves a twofold barrier and is not indicative of any significant double-bond character in the B–C bond. A complete structural determination of the molecule using isotopic substitution is currently in progress in our laboratories.[7] The photoelectron spectrum of trivinylborane[10] has been interpreted as suggesting that only a small amount of conjugation through the B–C bond can occur in this compound. The observation of absorption maxima in the ultraviolet spectra of several vinylborane species[5,11a] has also been interpreted to show that some electron delocalization occurs in these systems. The vinylboranes have also been the subject of several theoretical studies.[11a,12,13]

In order to obtain a better understanding of the nature of the B–C bond in vinylboranes as well as the effects of halogen substitution, an NMR investigation of trivinylborane, six vinylhaloboranes, and several adducts of the vinylboranes was undertaken. The results of this study are presented herein.

Experimental Section

All preparative work involved in the synthesis of trivinylborane and the vinylhaloboranes was carried out in a conventional high-vacuum system employing greaseless stopcocks. In general, the preparative routes followed were those of Brinckman and Stone.[14] Trivinylborane was obtained by two different synthetic methods, both of which have been previously described in detail.[9,15]

The preparation of $ClB(C_2H_3)_2$ and $Cl_2B(C_2H_3)$ involved the reaction of BCl_3 with $Sn(C_2H_3)_4$ in a 2:1 mole ratio. Boron trichloride was obtained commercially (Matheson) and was purified by trap-to-trap fractionation until the vapor pressure was 476 mmHg at 0°.[16] Tetravinyltin was also obtained commercially (Columbia Organic Chemicals, Inc.) and its purity was checked by ^1H NMR. The reaction of 27.9 mmol of $Sn(C_2H_3)_4$ with 56.4 mmol of BCl_3 in a sealed 1.0-l. bulb, at ambient temperature, for approximately 26 hr, yielded 16.6 mmol of $(ClB(C_2H_3)_2$ and 19.9 mmol of $Cl_2B(C_2H_3)$. These products were separated by distillation on a variable-temperature vacuum fractionation column.[17] Purity was determined by infrared[14] and ^{11}B NMR[11a] spectroscopy. A vapor pressure of 128 mmHg at 24.9° was found for $ClB(C_2H_3)_2$ (lit. value:[14] 126.7 mmHg at 24.9°). The vapor pressure of