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Registry No. Ia, 55683-80-2; Ib, 76108-95-7; IIa, 76108-97-9; IIb, 76108-99-1; IIc, 76109-01-8; III, 76081-91-9; IV, 76081-93-1; Λ-β-*S*,*S*-[$CoCO_3$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4, 76109-03-0; *trans*-*R*,*S*,-*R*,*R*-[$CoCl_2$(1,2*S*,10*S*,11-Me_4-2,3,2-tet)]ClO_4, 76095-36-8; 1,5*R*,7*R*,11-2,3,2-tet, 76108-93-5; *N*,*N'*-bis(carbobenzoxyglycyl)-(*R*,*R*)-2,4-pentanediamine, 76081-85-1; carbobenzoxyglycine, 1138-80-3; (*R*,*R*)-2,4-pentanediamine, 34998-98-6.

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Unique Octaiodide Configuration in Congested Macrocyclic Ligand Complexes

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The crystal and molecular structures of the iodine reaction products of complexes of palladium(II) and platinum(II) with the tetraaza macrocyclic ligand tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine have been determined. The complexes analyze for 8 I/macrocycle, exhibit thermal stability up to 180 °C, and are isomorphous, crystallizing in the space group $P2_1/n$. Unit cell dimensions for the palladium complex are $a = 7.756$ (7) Å, $b = 29.86$ (3) Å, $c = 17.64$ (3) Å, and $\beta = 112.9$ (1)°, and those for the platinum analogue are $a = 7.771$ (7) Å, $b = 29.95$ (7) Å, $c = 17.67$ (5) Å, and $\beta = 113.2$ (2)° with $Z = 4$. Within the macrocyclic cation the immediate coordination sphere of the metal is nearly planar; however, the overall geometry of the macrocyclic complex conforms to a hyperbolic paraboloid with cavities of 2.68 Å about the axial metal sites. The anion consists of discrete Z-shaped nonplanar chains of I_8^{2-}, each I_8^{2-} composed of two I_3^- units weakly associated with an elongated I_2.

Introduction

Novel and exciting chemistry has developed from the search for anisotropically behaving systems, particularly in the area of electrical conductivity. One approach to the design of highly conducting systems involves the synthesis of mixed-valent compounds.[1-5] Here electron transport is facilitated via partially occupied valence shells. With application of this rationale, considerable attention has been directed toward the utilization of the electron-acceptor properties of I_2 to remove electron density from a selected donor molecule.[6-20] The choice of iodine is judicious considering its propensity for forming stable catenated species capable of packing favorably in the crystal lattice by occupying channels in the one-dimensional network. The stoichiometry of the polyiodide acceptor product, the result of the interaction of the proposed electron-donor molecules with I_2, varies. A case in point involves the partially oxidized metal bis(dioximates). Bis(benzoquinone dioximato), $(bqd)_2$, complexes of nickel(II) and palladium(II) can be oxidized by I_2 to form $[M(bdq)_2][I]_{0.5}$.[16] Chains of I_3^- reside in channels in the crystal lattice in these complexes as determined by resonance Raman and ^{129}I Mössbauer techniques.[9] The analogous reaction of the bis(diphenylglyoximato), $(dpg)_2$,[13,17-20] systems with I_2 results in $[M(dpg)_2][I]$ in which I_5^- chains reside in channels formed by the ligand phenyl groups.[6,7] Higher polyiodides, I_7^-, I_8^{2-}, I_9^-, and I_{16}^{4-}, can also occur although structural characterizations by X-ray crystallographic techniques have been minimal.[21-26] In general, however, even the higher polyiodides

Table I. Crystallographic Data

compd	$[Pd(TAAB)][I_8]$	$[Pt(TAAB)][I_8]$
fw	1534.13	1662.82
a, Å	7.756 (7)	7.771 (7)
b, Å	29.86 (3)	29.95 (7)
c, Å	17.64 (3)	17.67 (5)
β, deg	112.9 (1)	113.2 (2)
V, Å^3	3764 (8)	3786 (16)
d(calcd), g cm^{-3}	2.708	2.847
d(obsd) (flotation), g cm^{-3}	2.71 (1)	2.84 (1)
Z	4	4
space group	$P2_1/n$	$P2_1/n$
abs coeff, cm^{-1}	71.46	105.2
transmission coeff limits	0.2434-0.4591	0.3512-0.4586
no. of independent reflections	6657	6703
no. with $I > 3\sigma(I)$	4883	4581
final R_1	0.036	0.056
final R_2	0.042	0.059

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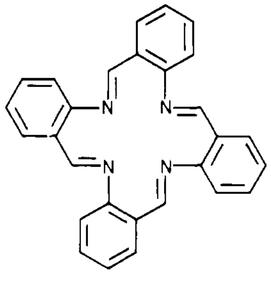
can be formulated in terms of I_3^-, I_2, and I^- linked via interactions of varying strengths. Some polyiodides occur in discrete units, while others such as I_7^- in $[(C_2H_5)_4N][I_7]$[21] form infinite chain networks, making the assignment of a particular unit somewhat arbitrary.

Recently, in an attempt to isolate donor–acceptor compounds with palladium(II) and platinum(II) complexes of a synthetic macrocyclic ligand (tetrabenzo[*b,f,j,n*][1,5,9,13]-tetraazacyclohexadecine (TAAB)) (I) and I_2, dark red crystals



I

with a highly metallic luster were isolated.[27,28] Elemental analysis reproducibly supported the assignment of eight iodine atoms per metal. Far-IR and resonance Raman experiments indicated the presence of I_3^-, leading to a formulation of $[M(TAAB)][I_3]_{2.7}$, reminiscent of the partially oxidized tetracyanoplatinates such as $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$.[29] The stoichiometry of the anion has now been ascertained unambiguously by X-ray crystallographic techniques, and the unanticipated result is reported herein.

Experimental Section

Collection and Reduction of X-ray Intensity Data. The complexes $[M(TAAB)][I_8]$ where M is palladium or platinum were synthesized as reported previously.[27,28] Crystals of both compounds were obtained by slow evaporation of an acetonitrile–methylene chloride (5:4) solution of the TAAB complex with excess I_2. Small crystals (0.18 × 0.10 × 0.08 mm and 0.34 × 0.21 × 0.13 mm for the platinum and palladium complexes, respectively) were chosen and mounted approximately along the needle axis on a Syntex $P2_1$ diffractometer. Preliminary measurements indicated that the crystals were isomorphous and of monoclinic symmetry. The systematic absences $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$, unequivocally indicated the space group $P2_1/n$, a nonstandard setting of $P2_1/c$. Unit cell dimensions were determined from a least-squares fit of χ, Φ, and 2θ for 15 reflections well distributed in reciprocal space. Density measurements were obtained by flotation in CH_2I_2–CCl_4. A fully automated Syntex $P2_1$ diffractometer equipped with a pulse-height analyzer and scintillation counter was used for data collection with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Information related to data collection is tabulated in Table I. Intensity data were collected ($2\theta_{max} = 50°$) and treated as previously described.[30] Decomposition was virtually nonexistent as monitored by the standard reflections, which showed a random variation of 2.3% for the palladium and 1.7% for the platinum complexes. The data were corrected for Lorentz–polarization effects and absorption.[31] The platinum structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques during which the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights of $1/\sigma_{F^2} = 4LpI/(\sigma_I)^2$. The position of the platinum was readily located from the Patterson map along with the coordinates of three of the iodides. The remainder of the iodides as well as the atoms in the macrocycle were located from subsequent Fourier maps. The scattering factor tables were obtained from Cromer and Waber,[32] and anomalous dispersion corrections for palladium, platinum, and iodine were obtained from Ibers.[33] Several cycles of refinement resulted in isotropic convergence. The temperature factors for the iodine atoms ranged from 3.6 to 6.0 Å^2 with the exception of two which displayed somewhat larger temperature factors, I(6) and I(7) at 7.2 and 6.9 Å^2, respectively. X-ray diffuse scattering showed some streaking, evidence of thermal or disorder diffuse scattering. No suitable model for the disorder could be pinpointed from a difference Fourier map, however. At this point the thermal parameters of the nonhydrogen atoms were allowed to vary anisotropically. After further refinement convergence was reached at $R_1 = 0.061$ and $R_2 = 0.072$ where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The reflection data were examined for large differences in F_o and F_c. Twenty four reflections showed evidence of overlap with a neighboring strong reflection (a complication of the long *b* axis) and were deleted. At this point hydrogen atom positions were calculated at a distance of 1.0 Å from their atom of attachment and were included as fixed atoms in the final cycles of refinement. Convergence

Table II. Final Positional Parameters for $[Pd(TAAB)][I_8]$[a]

atom	*x*	*y*	*z*
Pd	−0.00660 (8)	0.13185 (2)	0.24708 (3)
I(1)	0.16108 (8)	0.33762 (2)	0.12173 (4)
I(2)	−0.00469 (8)	0.26105 (2)	0.01316 (3)
I(3)	−0.17749 (11)	0.18546 (2)	−0.09997 (4)
I(4)	0.18303 (13)	0.13768 (3)	−0.15934 (4)
I(5)	0.40379 (10)	0.09367 (3)	−0.22932 (4)
I(6)	0.64700 (12)	0.03054 (3)	−0.32504 (6)
I(7)	0.67014 (8)	−0.04890 (2)	−0.21397 (4)
I(8)	0.73471 (10)	−0.12382 (3)	−0.10423 (4)
N(1)	−0.0647 (10)	0.0721 (2)	0.2878 (4)
C(1)	−0.0428 (11)	0.0683 (3)	0.3740 (5)
C(2)	−0.1674 (12)	0.0454 (3)	0.3980 (5)
C(3)	−0.1464 (13)	0.0447 (3)	0.4801 (6)
C(4)	0.0051 (14)	0.0686 (4)	0.5398 (5)
C(5)	0.1288 (14)	0.0898 (3)	0.5159 (6)
C(6)	0.1081 (12)	0.0924 (3)	0.4331 (5)
C(7)	0.2516 (13)	0.1196 (3)	0.4180 (6)
N(2)	0.2283 (9)	0.1386 (2)	0.3495 (4)
C(8)	0.3875 (11)	0.1608 (3)	0.3416 (5)
C(9)	0.5704 (13)	0.1456 (3)	0.3843 (5)
C(10)	0.7211 (12)	0.1705 (4)	0.3813 (5)
C(11)	0.6901 (14)	0.2086 (3)	0.3351 (6)
C(12)	0.5100 (13)	0.2223 (3)	0.2904 (5)
C(13)	0.3571 (11)	0.1987 (3)	0.2918 (5)
C(14)	0.1713 (12)	0.2180 (3)	0.2409 (5)
N(3)	0.0169 (10)	0.1964 (2)	0.2164 (4)
C(15)	−0.1535 (11)	0.2214 (3)	0.1718 (5)
C(16)	−0.1709 (11)	0.2667 (3)	0.1885 (5)
C(17)	−0.3309 (12)	0.2908 (3)	0.1397 (5)
C(18)	−0.4724 (12)	0.2690 (3)	0.0755 (6)
C(19)	−0.4580 (11)	0.2245 (3)	0.0613 (5)
C(20)	−0.3035 (11)	0.1991 (3)	0.1099 (5)
C(21)	−0.3084 (11)	0.1514 (3)	0.0873 (5)
N(4)	−0.2065 (9)	0.1202 (2)	0.1333 (4)
C(22)	−0.2170 (11)	0.0759 (3)	0.0987 (5)
C(23)	−0.2507 (13)	0.0704 (3)	0.0152 (5)
C(24)	−0.2552 (16)	0.0269 (4)	−0.0159 (6)
C(25)	−0.2309 (15)	−0.0094 (3)	0.0338 (7)
C(26)	−0.1930 (13)	−0.0041 (3)	0.1175 (6)
C(27)	−0.1837 (11)	0.0386 (3)	0.1510 (5)
C(28)	−0.1361 (12)	0.0398 (3)	0.2395 (6)

[a] In this table and those subsequent estimated standard deviations in the least significant figure are given in parentheses.

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Table III. Final Thermal Parameters for $[Pd(TAAB)][I_8]$[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.0310 (3)	0.0271 (4)	0.0276 (3)	−0.0010 (2)	0.0058 (2)	−0.0020 (2)
I(1)	0.0577 (4)	0.0506 (4)	0.0448 (3)	0.0002 (3)	0.0133 (3)	−0.0044 (2)
I(2)	0.0491 (3)	0.0474 (4)	0.0368 (3)	−0.0011 (2)	0.0173 (2)	0.0069 (2)
I(3)	0.0934 (5)	0.0542 (4)	0.0491 (4)	−0.0210 (4)	0.0213 (4)	−0.0030 (2)
I(4)	0.1316 (7)	0.0596 (4)	0.0547 (4)	−0.0107 (4)	0.0283 (5)	0.0030 (2)
I(5)	0.0774 (5)	0.0727 (4)	0.0522 (4)	−0.0163 (4)	0.0092 (4)	0.0135 (2)
I(6)	0.0869 (6)	0.0845 (4)	0.1046 (7)	0.0108 (4)	0.0480 (5)	0.0219 (5)
I(7)	0.0408 (3)	0.0664 (4)	0.0584 (4)	−0.0029 (3)	0.0191 (3)	−0.0241 (2)
I(8)	0.0693 (4)	0.0642 (4)	0.0728 (4)	−0.0079 (3)	0.0401 (4)	−0.0113 (2)
N(1)	0.045 (4)	0.036 (4)	0.051 (4)	0.002 (3)	0.015 (4)	0.000 (2)
C(1)	0.046 (5)	0.036 (4)	0.036 (4)	0.017 (4)	0.016 (4)	0.015 (5)
C(2)	0.044 (5)	0.045 (4)	0.043 (5)	0.006 (4)	0.009 (4)	0.000 (5)
C(3)	0.055 (6)	0.050 (4)	0.063 (7)	0.013 (4)	0.026 (5)	0.020 (5)
C(4)	0.066 (7)	0.068 (9)	0.035 (5)	0.014 (5)	0.019 (5)	0.010 (5)
C(5)	0.059 (6)	0.045 (4)	0.048 (5)	0.009 (4)	0.014 (5)	0.007 (5)
C(6)	0.043 (5)	0.045 (4)	0.043 (5)	0.011 (4)	0.015 (4)	0.010 (5)
C(7)	0.062 (6)	0.045 (4)	0.044 (5)	0.004 (4)	0.006 (5)	0.005 (5)
N(2)	0.041 (4)	0.041 (4)	0.044 (4)	0.009 (3)	0.007 (4)	0.000 (2)
C(8)	0.037 (5)	0.041 (4)	0.040 (5)	−0.010 (4)	0.014 (4)	−0.017 (5)
C(9)	0.058 (6)	0.041 (4)	0.046 (5)	0.011 (4)	0.024 (5)	0.002 (5)
C(10)	0.036 (5)	0.081 (9)	0.040 (5)	0.015 (5)	0.010 (4)	−0.020 (5)
C(11)	0.047 (5)	0.059 (4)	0.050 (5)	−0.006 (4)	−0.028 (5)	−0.015 (5)
C(12)	0.048 (6)	0.063 (4)	0.042 (5)	−0.002 (4)	0.019 (4)	−0.002 (5)
C(13)	0.040 (5)	0.059 (4)	0.029 (4)	0.000 (4)	0.006 (4)	−0.017 (5)
C(14)	0.053 (5)	0.041 (4)	0.032 (4)	−0.008 (4)	0.009 (4)	−0.007 (5)
N(3)	0.050 (4)	0.041 (4)	0.043 (4)	0.000 (3)	0.015 (4)	0.000 (2)
C(15)	0.037 (4)	0.041 (4)	0.035 (4)	0.013 (3)	0.018 (4)	0.017 (5)
C(16)	0.043 (5)	0.041 (4)	0.040 (5)	0.000 (4)	0.017 (4)	0.002 (5)
C(17)	0.056 (5)	0.041 (4)	0.040 (5)	0.008 (4)	0.019 (4)	0.000 (5)
C(18)	0.050 (5)	0.036 (4)	0.054 (5)	0.011 (4)	0.010 (5)	0.002 (5)
C(19)	0.035 (5)	0.054 (4)	0.052 (5)	−0.001 (4)	0.012 (4)	0.000 (5)
C(20)	0.049 (5)	0.027 (4)	0.050 (5)	0.002 (4)	0.025 (4)	0.000 (5)
C(21)	0.036 (5)	0.059 (4)	0.038 (5)	−0.005 (4)	0.009 (4)	0.007 (5)
N(4)	0.042 (4)	0.050 (4)	0.040 (4)	0.000 (3)	0.012 (4)	−0.002 (2)
C(22)	0.038 (5)	0.036 (4)	0.047 (5)	−0.012 (4)	0.016 (4)	−0.017 (5)
C(23)	0.062 (6)	0.045 (4)	0.046 (5)	−0.004 (4)	0.021 (5)	−0.012 (5)
C(24)	0.093 (8)	0.063 (9)	0.040 (5)	−0.005 (6)	0.023 (5)	−0.015 (5)
C(25)	0.085 (8)	0.041 (4)	0.074 (8)	−0.005 (5)	0.036 (6)	−0.017 (5)
C(26)	0.062 (6)	0.041 (4)	0.064 (7)	0.001 (4)	0.026 (5)	−0.002 (5)
C(27)	0.033 (4)	0.050 (4)	0.035 (4)	−0.003 (4)	0.009 (4)	−0.002 (5)
C(28)	0.036 (5)	0.059 (4)	0.058 (5)	−0.001 (4)	0.011 (4)	−0.010 (5)

[a] Anisotropic thermal parameters in this table and Table V are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

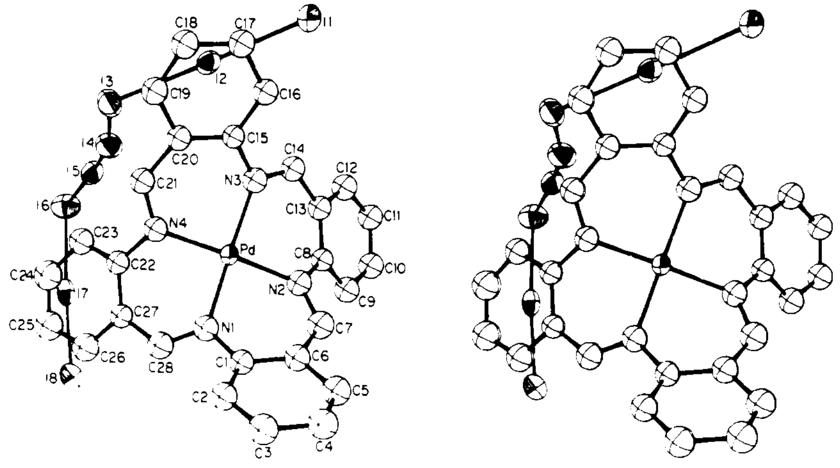

Figure 1. Stereoscopic view of $[Pd(TAAB)][I_8]$ showing ellipsoids of 50% probability.

was achieved at $R_1 = 0.056$ and $R_2 = 0.059$. The maximum shift/error in the final cycle was 0.17. The Patterson map for the palladium analogue was essentially the same as that for the platinum with the exception of the anticipated difference in peak intensity ratios for palladium compared to platinum. Consequently, the palladium and iodine atoms were assigned the same positional coordinates as in the platinum compound. The ensuing Fourier map indicated that the positional parameters for the atoms of the macrocyclic ligand were also nearly identical with those of the platinum complex. Refinement for the palladium analogue was performed in an analogous fashion to that of the platinum and resulted in anisotropic convergence at $R_1 = 0.036$ and $R_2 = 0.042$ with a maximum shift/error of 0.09. A final difference Fourier map for both complexes was virtually featureless.

The final positional parameters are listed in Table II and anisotropic thermal parameters in Table III for the palladium complex. The corresponding tables are Tables IV and V for the platinum complex. Tables X and XI, the calculated hydrogen atom positional and thermal parameters, and Tables XII and XIII, the observed and calculated structure factors, for the palladium and platinum complexes, respectively, are available as supplementary material.

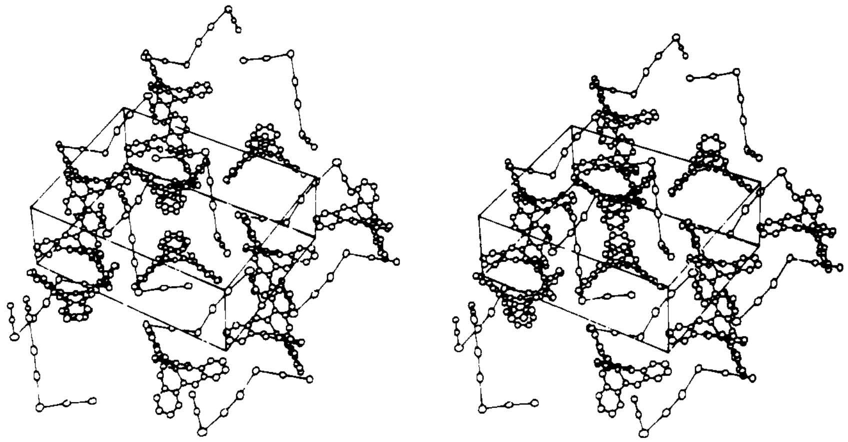

Figure 2. Packing diagram for $[Pd(TAAB)][I_8]$ as viewed down the z axis (slightly rotated) with x vertical.

Results and Discussion

Bond lengths and angles are given in Tables VI and VII, respectively, for the palladium and platinum complexes. The atom numbering scheme is shown in the overhead stereoview in Figure 1. The structures of both complexes were performed to determine whether differences observed in the conductivities were due to structural or crystal packing effects. The resulting structures were virtually identical. Due to the apparently better quality of the palladium data the structural aspects of $[Pd(TAAB)][I_8]$ will be discussed in the subsequent paragraphs with the exception of a few references to the platinum bonding.

The Cation. As found for previously reported TAAB structures, the geometry of the cation shows a distinctly saddle-shaped S_4 symmetry, mathematically described as a hyperbolic paraboloid and evident in the packing diagram in Figure 2. The cavities formed by the four benzo groups about the axial metal sites (i.e., the distance from the farthest carbon in each benzo group to the PdN_4 plane) average 2.68 Å and are comparable to that found for $[Pd(TAAB)][BF_4]_2$ (2.70 Å).[28] The palladium is located at the center of a saddle-shaped surface formed by the four coordinated nitrogens as shown in the mean plane calculations in Table VIII. The average Pd–N bond length is 2.030 (8) Å, slightly longer than that found for the BF_4^- salt (2.004 (8) Å). In the platinum analogue an average Pt–N of 2.016 (15) Å is obtained, agreeing well with the average 1.98 Å observed in the α and γ polymorphs of (phthalocyaninato)platinum(II).[35] The absence of disorder in the cation allows a more accurate determination of positional parameters in the ligand than in previously reported structures of TAAB. In all of the latter, disorder, represented by two orthogonal pseudo mirror planes oriented perpendicular to the MN_4 plane and bisecting opposing benzo groups, clouded certain of the ligand atom coordinates. The bond lengths agree well with other TAAB structures (Table IX) and lie within ranges observed for their appropriate bond orders. The bond angles within the benzo groups average 120.0 (9)° as expected. The inner ring angles are comparable to those found in the nickel complex of the macrocyclic trimeric condensate $Ni(TRI)(H_2O)_2(NO_3)_2$,[36] indicating minimal if any strain is introduced in the tetrameric over the trimeric condensate. Artifacts of the disorder in previously determined TAAB structures apparently result in distortions of some of the inner ring angles in these compounds.[37]

The characterization of the rarely occurring polyiodide I_8^{2-} is undoubtedly the most interesing aspect of the structure.

Table IV. Final Positional and Isotropic Thermal Parameters for $[Pt(TAAB)][I_8]$

atom	x	y	z
Pt	−0.00825 (8)	0.13202 (2)	0.24775 (4)
I(1)	0.16013 (17)	0.33726 (4)	0.12145 (7)
I(2)	−0.00539 (16)	0.26062 (4)	0.01310 (7)
I(3)	−0.17725 (23)	0.18489 (5)	−0.09983 (8)
I(4)	0.18373 (28)	0.13720 (5)	−0.15980 (9)
I(5)	0.40366 (22)	0.09318 (5)	−0.22993 (8)
I(6)	0.64661 (24)	0.03056 (6)	−0.32574 (11)
I(7)	0.66924 (16)	−0.04862 (4)	−0.21403 (8)
I(8)	0.73352 (20)	−0.12315 (5)	−0.10364 (9)
N(1)	−0.0675 (21)	0.0720 (5)	0.2856 (11)
C(1)	−0.0469 (27)	0.0686 (6)	0.3741 (10)
C(2)	−0.1676 (25)	0.0448 (6)	0.3983 (10)
C(3)	−0.1498 (26)	0.0461 (6)	0.4779 (13)
C(4)	0.0029 (34)	0.0666 (7)	0.5395 (12)
C(5)	0.1294 (29)	0.0908 (7)	0.5136 (12)
C(6)	0.1086 (25)	0.0912 (6)	0.4319 (11)
C(7)	0.2434 (31)	0.1195 (7)	0.4179 (13)
N(2)	0.2262 (19)	0.1382 (5)	0.3488 (9)
C(8)	0.3909 (25)	0.1598 (6)	0.3427 (11)
C(9)	0.5694 (28)	0.1462 (6)	0.3866 (11)
C(10)	0.7199 (26)	0.1705 (8)	0.3817 (12)
C(11)	0.6890 (26)	0.2087 (7)	0.3352 (11)
C(12)	0.5037 (26)	0.2230 (7)	0.2887 (10)
C(13)	0.3546 (23)	0.1983 (7)	0.2933 (10)
C(14)	0.1691 (23)	0.2179 (6)	0.2405 (9)
N(3)	0.0183 (20)	0.1961 (5)	0.2182 (8)
C(15)	−0.1562 (24)	0.2222 (7)	0.1728 (10)
C(16)	−0.1715 (23)	0.2696 (6)	0.1882 (10)
C(17)	−0.3311 (27)	0.2922 (6)	0.1393 (11)
C(18)	−0.4735 (23)	0.2688 (6)	0.0745 (10)
C(19)	−0.4564 (26)	0.2242 (7)	0.0631 (13)
C(20)	−0.3014 (24)	0.2004 (6)	0.1112 (11)
C(21)	−0.3090 (25)	0.1507 (6)	0.0878 (10)
N(4)	−0.2088 (20)	0.1214 (5)	0.1352 (9)
C(22)	−0.2191 (22)	0.0763 (6)	0.0987 (11)
C(23)	−0.2549 (28)	0.0713 (7)	0.0164 (11)
C(24)	−0.2625 (32)	0.0279 (8)	−0.0153 (12)
C(25)	−0.2280 (33)	−0.0098 (8)	0.0366 (15)
C(26)	−0.1918 (28)	−0.0038 (7)	0.1178 (14)
C(27)	−0.1838 (23)	0.0388 (7)	0.1507 (10)
C(28)	−0.1336 (25)	0.0395 (6)	0.2456 (12)

Far-IR and Raman techniques indicated the presence of I_3^-. A weak ESR signal for the palladium analogue at $g = 2.1$ along with the absence of a signal in the reactant BF_4^- salts and I_2 suggested the possibility of partial oxidation. Hence, the complex was initially formulated as $[Pd(TAAB)][I_3]_{2.7}$.[27] With the isolation of the platinum analogue ambiguity as to the metal ion oxidation state was introduced in the form of a very weak ESR signal centered at $g = 2.1$ in the starting $[Pt(TAAB)][BF_4]_2$ complex.[28] In addition X-ray photoelectron spectroscopic data indicated the presence of only divalent palladium and platinum. Due to the crystallographic findings,

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(36) Fleischer, E. B.; Klem, E. *Inorg. Chem.* **1965**, *4*, 637–642.
(37) Hawkinson, S. W.; Fleischer, E. B. *Inorg. Chem.* **1969**, *11*, 2402–2410.

Table V. Final Thermal Parameters for [Pt(TAAB)][I_8]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.0261 (3)	0.0259 (4)	0.0286 (3)	−0.0003 (3)	0.0092 (2)	−0.0022 (2)
I(1)	0.0554 (8)	0.0504 (9)	0.0478 (7)	0.0005 (6)	0.0175 (6)	−0.0030 (5)
I(2)	0.0485 (7)	0.0486 (9)	0.0394 (7)	−0.0026 (6)	0.0208 (5)	−0.0069 (5)
I(3)	0.0980 (11)	0.0568 (9)	0.0541 (8)	−0.0247 (9)	0.0274 (8)	0.0022 (7)
I(4)	0.1345 (15)	0.0600 (9)	0.0639 (9)	−0.0112 (10)	0.0356 (10)	0.0037 (7)
I(5)	0.0764 (10)	0.0772 (9)	0.0580 (8)	−0.0165 (9)	0.0126 (8)	0.0158 (7)
I(6)	0.0855 (12)	0.0863 (14)	0.1106 (13)	0.0095 (10)	0.0521 (11)	0.0244 (10)
I(7)	0.0374 (7)	0.0645 (9)	0.0607 (8)	−0.0016 (6)	0.0218 (6)	−0.0224 (7)
I(8)	0.0714 (9)	0.0632 (9)	0.0760 (9)	−0.0087 (8)	0.0469 (8)	−0.0101 (7)
N(1)	0.054 (10)	0.014 (9)	0.119 (15)	0.003 (8)	0.051 (11)	−0.005 (10)
C(1)	0.063 (13)	0.055 (14)	0.029 (9)	0.025 (11)	0.028 (10)	0.015 (10)
C(2)	0.050 (11)	0.036 (9)	0.041 (11)	0.014 (9)	0.015 (9)	0.000 (7)
C(3)	0.047 (12)	0.027 (9)	0.083 (15)	0.009 (9)	0.031 (11)	0.012 (10)
C(4)	0.095 (17)	0.064 (14)	0.056 (13)	0.010 (13)	0.050 (14)	0.007 (12)
C(5)	0.064 (14)	0.059 (14)	0.053 (12)	0.016 (11)	0.019 (11)	−0.002 (10)
C(6)	0.041 (11)	0.036 (9)	0.053 (12)	0.008 (9)	0.021 (9)	0.000 (10)
C(7)	0.083 (16)	0.045 (14)	0.063 (13)	0.033 (12)	0.027 (12)	0.020 (10)
N(2)	0.038 (8)	0.068 (14)	0.041 (8)	0.003 (8)	0.011 (7)	−0.007 (7)
C(8)	0.049 (11)	0.041 (9)	0.052 (12)	−0.012 (10)	0.033 (10)	−0.017 (10)
C(9)	0.059 (13)	0.036 (9)	0.051 (12)	0.015 (10)	0.026 (11)	−0.010 (10)
C(10)	0.041 (11)	0.082 (18)	0.053 (12)	0.003 (12)	0.018 (10)	−0.039 (12)
C(11)	0.051 (12)	0.055 (14)	0.044 (11)	−0.008 (10)	0.027 (10)	−0.010 (10)
C(12)	0.045 (12)	0.077 (14)	0.028 (9)	0.001 (11)	0.011 (8)	−0.022 (10)
C(13)	0.027 (10)	0.064 (14)	0.047 (11)	0.004 (9)	0.014 (8)	−0.022 (10)
C(14)	0.031 (10)	0.045 (9)	0.033 (9)	−0.009 (9)	0.004 (8)	−0.007 (7)
N(3)	0.046 (10)	0.064 (9)	0.045 (8)	0.012 (9)	0.028 (8)	0.010 (7)
C(15)	0.037 (10)	0.068 (14)	0.044 (11)	0.039 (10)	0.029 (9)	0.044 (10)
C(16)	0.037 (10)	0.041 (9)	0.040 (9)	0.000 (9)	0.021 (8)	0.005 (7)
C(17)	0.058 (12)	0.055 (14)	0.044 (11)	−0.009 (11)	0.028 (10)	−0.010 (10)
C(18)	0.039 (10)	0.036 (9)	0.044 (11)	0.006 (9)	0.009 (8)	0.005 (10)
C(19)	0.037 (11)	0.059 (14)	0.082 (15)	−0.009 (10)	0.025 (11)	−0.005 (12)
C(20)	0.039 (11)	0.045 (14)	0.049 (11)	−0.018 (9)	0.022 (9)	−0.010 (10)
C(21)	0.053 (12)	0.041 (9)	0.031 (9)	−0.013 (10)	0.002 (9)	0.005 (10)
N(4)	0.044 (9)	0.054 (9)	0.045 (9)	0.006 (8)	0.021 (8)	0.007 (7)
C(22)	0.027 (9)	0.059 (14)	0.060 (12)	−0.013 (9)	0.021 (9)	−0.034 (10)
C(23)	0.065 (13)	0.055 (14)	0.039 (11)	0.008 (11)	0.018 (10)	−0.007 (10)
C(24)	0.084 (17)	0.091 (18)	0.041 (12)	−0.016 (14)	0.029 (12)	−0.022 (12)
C(25)	0.086 (17)	0.059 (18)	0.078 (16)	−0.012 (13)	0.034 (14)	−0.017 (12)
C(26)	0.059 (13)	0.050 (14)	0.091 (17)	0.009 (11)	0.042 (13)	−0.012 (12)
C(27)	0.031 (10)	0.064 (14)	0.041 (11)	0.004 (9)	0.018 (8)	0.007 (10)
C(28)	0.045 (11)	0.018 (9)	0.078 (13)	−0.002 (9)	0.012 (10)	0.005 (10)

Table VI. Interatomic Distances (Å) for [M(TAAB)][I_8]

atoms	M = Pd	M = Pt	atoms	M = Pd	M = Pt
M–N(1)	2.039 (8)	2.034 (15)	C(15)–C(16)	1.402 (12)	1.460 (25)
M–N(2)	2.016 (7)	1.997 (15)	C(16)–C(17)	1.403 (12)	1.379 (24)
M–N(3)	2.031 (8)	2.020 (16)	C(17)–C(18)	1.395 (12)	1.426 (24)
M–N(4)	2.033 (8)	2.014 (15)	C(18)–C(19)	1.364 (12)	1.365 (25)
N(1)–C(1)	1.467 (11)	1.514 (23)	C(19)–C(20)	1.396 (12)	1.370 (25)
C(1)–C(2)	1.378 (12)	1.375 (25)	C(20)–C(21)	1.478 (12)	1.541 (25)
C(1)–C(6)	1.424 (12)	1.410 (24)	C(21)–N(4)	1.285 (11)	1.251 (21)
C(2)–C(3)	1.394 (13)	1.360 (25)	N(4)–C(22)	1.446 (11)	1.485 (15)
C(3)–C(4)	1.428 (14)	1.398 (27)	C(22)–C(27)	1.405 (12)	1.409 (25)
C(4)–C(5)	1.345 (14)	1.436 (28)	C(22)–C(23)	1.402 (12)	1.379 (24)
C(5)–C(6)	1.408 (13)	1.389 (25)	C(23)–C(24)	1.405 (13)	1.407 (28)
C(6)–C(7)	1.483 (13)	1.444 (27)	C(24)–C(25)	1.362 (14)	1.415 (29)
C(7)–N(2)	1.282 (11)	1.303 (23)	C(25)–C(26)	1.398 (14)	1.363 (28)
N(2)–C(8)	1.455 (18)	1.475 (15)	C(26)–C(27)	1.394 (12)	1.394 (27)
C(8)–C(13)	1.397 (12)	1.406 (25)	C(27)–C(28)	1.457 (12)	1.568 (26)
C(8)–C(9)	1.398 (12)	1.358 (24)	C(28)–N(1)	1.263 (11)	1.194 (21)
C(9)–C(10)	1.404 (13)	1.410 (27)	I(1)–I(2)	2.939 (3)	2.942 (6)
C(10)–C(11)	1.365 (14)	1.372 (28)	I(2)–I(3)	2.966 (3)	2.970 (6)
C(11)–C(12)	1.373 (12)	1.415 (24)	I(3)–I(4)	3.637 (3)	3.658 (5)
C(12)–C(13)	1.388 (12)	1.404 (25)	I(4)–I(5)	2.797 (3)	2.805 (5)
C(13)–C(14)	1.486 (12)	1.496 (23)	I(5)–I(6)	3.527 (3)	3.532 (6)
C(14)–N(3)	1.277 (10)	1.262 (20)	I(6)–I(7)	3.037 (3)	3.048 (6)
N(3)–C(15)	1.453 (10)	1.500 (20)	I(7)–I(8)	2.872 (3)	2.878 (6)
C(15)–C(20)	1.414 (11)	1.383 (24)			

the fact that the I_2 band (from $I_3^-\cdots I_2\cdots I_3^-$ of the I_8^{2-}) at 180 cm^{-1} was not observed in the Raman must be attributed to decomposition of the compound in the laser beam, a distinct problem during the measurements.[28,29] As observed for other I_8^{2-} moieties, two I_3^- units with I–I bonds within the range normally found for I_3^- are separated by weak interactions with an I_2 which exhibits an elongated I–I compared to solid I_2. Two major differences are noted between this structure and other I_8^{2-} anions: weaker $I_3^-\cdots I_2$ interactions and considerable deviation from planarity. The former is reflected in the $I_3^-\cdots I_2$

Table VII. Bond Angles (Deg) for $[M(TAAB)][I_8]$

atoms	M = Pd	M = Pt	atoms	M = Pd	M = Pt
N(1)–M–N(2)	91.0 (3)	91.8 (7)	N(3)–C(15)–C(20)	118.8 (7)	117.6 (16)
N(2)–M–N(3)	90.0 (3)	89.6 (6)	N(3)–C(15)–C(16)	121.4 (7)	122.1 (15)
N(3)–M–N(4)	90.8 (3)	90.7 (6)	C(20)–C(15)–C(16)	119.8 (7)	120.2 (15)
N(4)–M–N(1)	90.6 (3)	89.9 (7)	C(15)–C(16)–C(17)	120.1 (7)	118.7 (16)
M–N(1)–C(1)	118.7 (6)	117.0 (12)	C(16)–C(17)–C(18)	119.2 (8)	118.9 (17)
N(1)–C(1)–C(6)	116.8 (7)	115.4 (15)	C(17)–C(18)–C(19)	120.6 (8)	120.7 (17)
N(1)–C(1)–C(2)	123.0 (7)	123.4 (15)	C(18)–C(19)–C(20)	121.9 (8)	122.0 (18)
C(6)–C(1)–C(2)	120.0 (8)	121.2 (16)	C(19)–C(20)–C(15)	118.2 (8)	119.3 (18)
C(1)–C(2)–C(3)	120.9 (8)	120.2 (17)	C(19)–C(20)–C(21)	115.7 (7)	113.9 (16)
C(2)–C(3)–C(4)	119.3 (9)	122.0 (18)	C(15)–C(20)–C(21)	126.0 (7)	126.8 (17)
C(3)–C(4)–C(5)	119.1 (9)	116.7 (17)	C(20)–C(21)–N(4)	125.8 (8)	123.4 (17)
C(4)–C(5)–C(6)	122.9 (9)	121.5 (19)	C(21)–N(4)–M	123.0 (6)	125.9 (14)
C(5)–C(6)–C(1)	117.5 (8)	117.8 (17)	C(21)–N(4)–C(22)	118.5 (6)	115.7 (14)
C(5)–C(6)–C(7)	115.2 (8)	112.8 (18)	M–N(4)–C(22)	118.0 (6)	117.5 (10)
C(1)–C(6)–C(7)	127.2 (8)	129.0 (18)	N(4)–C(22)–C(23)	120.4 (7)	120.8 (16)
C(6)–C(7)–N(2)	124.8 (7)	127.0 (18)	N(4)–C(22)–C(27)	118.8 (7)	118.5 (15)
C(7)–N(2)–M	123.2 (6)	121.3 (16)	C(27)–C(22)–C(23)	120.6 (7)	120.6 (17)
C(7)–N(2)–C(8)	118.5 (7)	119.1 (17)	C(22)–C(23)–C(24)	119.0 (8)	118.8 (18)
M–N(2)–C(8)	117.7 (6)	119.1 (11)	C(23)–C(24)–C(25)	120.6 (9)	120.8 (18)
N(2)–C(8)–C(13)	119.2 (7)	115.9 (16)	C(24)–C(25)–C(26)	120.6 (9)	119.0 (20)
N(2)–C(8)–C(9)	121.5 (7)	123.1 (16)	C(25)–C(26)–C(27)	120.5 (9)	121.3 (21)
C(13)–C(8)–C(9)	119.3 (8)	120.7 (17)	C(26)–C(27)–C(22)	118.6 (8)	119.4 (17)
C(8)–C(9)–C(10)	119.6 (8)	119.6 (18)	C(26)–C(27)–C(28)	115.4 (8)	114.3 (17)
C(9)–C(10)–C(11)	120.5 (8)	120.9 (18)	C(22)–C(27)–C(28)	126.0 (8)	126.3 (16)
C(10)–C(11)–C(12)	119.7 (9)	120.0 (18)	C(27)–C(28)–N(1)	127.3 (9)	120.8 (18)
C(11)–C(12)–C(13)	121.6 (9)	118.7 (18)	C(28)–N(1)–C(1)	119.0 (8)	113.8 (16)
C(12)–C(13)–C(8)	119.1 (8)	120.0 (16)	C(28)–N(1)–M	121.9 (6)	128.8 (13)
C(12)–C(13)–C(14)	115.3 (9)	111.7 (18)	I(1)–I(2)–I(3)	178.48 (2)	178.52 (6)
C(8)–C(13)–C(14)	125.5 (8)	128.2 (17)	I(2)–I(3)–I(4)	107.17 (8)	107.49 (13)
C(13)–C(14)–N(3)	124.8 (8)	122.6 (17)	I(3)–I(4)–I(5)	169.20 (4)	169.20 (8)
C(14)–N(3)–M	123.9 (6)	126.1 (13)	I(4)–I(5)–I(6)	174.47 (3)	174.71 (7)
C(14)–N(3)–C(15)	117.5 (8)	115.5 (16)	I(5)–I(6)–I(7)	90.99 (10)	90.40 (19)
M–N(3)–C(15)	118.2 (6)	118.2 (16)	I(6)–I(7)–I(8)	173.84 (3)	173.83 (6)

distances of 3.637 (3) and 3.527 (3) Å compared to previously determined structures of I_8^{2-} where ranges from 3.39 to 3.42 Å[22,26] have been observed. The distances observed in the TAAB complexes are actually the same as or greater than those found for $I_2\cdots I_2$ interactions in solid I_2 (3.56 Å at 20 °C[38] and 3.50 Å at −163 °C).[39] The question is thus introduced as to whether the unit should be considered as I_8^{2-}, $[I_3^-]_2\cdot I_2$, or $I_5^-\cdots I_3^-$. Considering the last formulation first, the I_5^- ion can be written as $I(I_2)_2^-$ and visualized as I^- symmetrically placed between two I_2 acceptor molecules.[40] Structural evidence has confirmed this picture as exemplified by $[(CH_3)_4N][I_5]$, which contains two elongated I_2 units (I–I = 2.82 Å) interacting with I^- at 3.17 Å. Both linear and bent I_5^- anions have been observed.[41,42] As a result of the absence of these structural characteristics in the TAAB complexes $I_5^-\cdots I_3^-$ can be ruled out as a fomulation. Although the assignment in the case of certain polyiodides is somewhat arbitrary, particularly in those with infinite interlinking chains, it is proposed that the polyiodide species in the TAAB complexes be referred to as I_8^{2-} rather than $[I_3^-]_2\cdot I_2$. The assignment is made on the basis of several observations. The asymmetry of the I_3^- units as well as the elongated I(4)–I(5) bond of 2.797 (3) Å indicates the presence of interactions (albeit weak) among the three moieties. The longer I–I bond in both of the I_3^- anions is associated with the terminal I of closest approach to I(4) or I(5). The more asymmetric I(6)–I(7)–I(8) with I–I bonds of 3.037 (3) and 2.872 (3) Å is, as anticipated, linked to the I(5) by a "stronger" interaction (3.527 (3) Å) than the more symmetric I(1)–I(2)–I(3) (I(1)–I(2) of 2.939 (3) Å and I(2)–I(3) of 2.966 (3) Å) association with I(4) at 3.637 (3) Å. It is recognized that these interactions are greater than that found for other polyiodides and are, quantitatively at least, analogous to intermolecular interactions in solid I_2. The $I_3^-\cdots I_2\cdots I_3^-$ moiety in the TAAB complexes occurs as a discrete unit, however, with nearest nonbonded iodine interactions at 4.074 (10) Å, on the order of van der Waals contacts.[43] Although bond lengths may be affected by subtle disorder in the iodine positions, a major argument for the formulation is the thermal stability of the complexes. Thermal gravimetric analysis for the palladium complex shows thermal stability up to 185 °C followed by a 40% weight loss up to 335 °C, corresponding to five iodides (41.4%). The integral nature of the I_8^{2-} as well as the high thermal stability of the palladium and platinum complexes argues for the formulation of the eight iodine atoms as one unit.

Comparison to the two previous structural determinations of I_8^{2-} yields interesting differences. With respect to the configuration of the Z, the anion of the TAAB complex more closely approaches that of Cs_2I_8. I(2)–I(3)–I(4) and I(5)–I(6)–I(7) angles are 107.17 (8) and 90.99 (10)°, respectively, for the TAAB complex. The corresponding Cs_2I_8 angles are both 80°,[22] while in $[(CH_2)_6N_4CH_3]_2I_8$ an outstretched Z is observed with angles of 131.9°.[26] Furthermore, the anion in the TAAB complexes shows considerable deviations from planarity as evidenced by the dihedral angle between I(2)–I(3)–I(4) and I(5)–I(6)–I(7) of 73.7 (1).° Previously I_8^{2-} anions have been found to be essentially planar. In the two reported I_8^{2-} structures, $[(CH_2)_6N_4CH_3]_2I_8$ and Cs_2I_8, maximum deviations of 0.09[26] and 0.07 Å,[22] respectively, from the mean plane of the anion were observed. Even in the higher polyiodide I_{16}^{4-} (which can be written as $I_3\cdots I_2\cdots I_3\cdots I_3\cdots I_2\cdots I_3^{4-}$) the maximum deviation of any atom from the plane of the

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Table VIII. Selected Least-Squares Planes and Atom Displacements (Å) for [Pd(TAAB)][I_8]

atom	dist	atom	dist
A. Pd–N(1)–N(2)–N(3)–N(4)			
$0.839x - 0.377y - 0.392z = -4.518$			
Pd	−0.004	N(3)	−0.206
N(1)	−0.204	N(4)	0.206
N(2)	0.208		
B. C(1)–C(2)–C(3)–C(4)–C(5)–C(6)			
$-0.551x + 0.821y - 0.151z = 2.352$			
C(1)	−0.003	C(4)	0.020
C(2)	−0.006	C(5)	−0.025
C(3)	−0.002	C(6)	0.016
C. C(8)–C(9)–C(10)–C(11)–C(12)–C(13)			
$0.302x - 0.549y - 0.780z = -6.733$			
C(8)	−0.026	C(11)	−0.007
C(9)	0.020	C(12)	0.007
C(10)	−0.007	C(13)	0.013
D. C(15)–C(16)–C(17)–C(18)–C(19)–C(20)			
$0.738x + 0.231y - 0.634z = -2.020$			
C(15)	0.032	C(18)	0.014
C(16)	−0.011	C(19)	0.007
C(17)	−0.012	C(20)	−0.030
E. C(22)–C(23)–C(24)–C(25)–C(26)–C(27)			
$-0.977x - 0.044y - 0.207z = 1.861$			
C(22)	0.015	C(25)	0.015
C(23)	−0.001	C(26)	0.000
C(24)	−0.014	C(27)	−0.014
F. I(1)–I(2)–I(3)–I(4)–I(5)			
$0.008x + 0.617y - 0.787z = 4.660$			
I(1)	0.012	I(5)	0.037
I(2)	−0.016	I(6)[a]	0.118
I(3)	0.031	I(7)[a]	−2.771
I(4)	−0.064	I(8)[a]	−5.558
G. I(4)–I(5)–I(6)–I(7)–I(8)			
$-0.647x - 0.384y - 0.659z = -1.556$			
I(1)[a]	−3.893	I(5)	−0.105
I(2)[a]	−1.500	I(6)	0.001
I(3)[a]	0.944	I(7)	−0.105
I(4)	0.057	I(8)	−0.052

[a] Atoms not included in least-squares plane calculation.

central $I_3^-\cdots I_2$ units is only 0.56 Å.[25] Mean plane calculations using two separate $I_3^-\cdots I_2$ units for plane calculations are provided in Table VIII for the TAAB complex. Each of the $I_3^-\cdots I_2$ portions is relatively planar (maximum deviations of −0.105 and −0.064 Å), yet the I_3^- not included in the calculations shows displacements up to 5.558 Å. Also notable in this system is the absence of a center of symmetry, found to be present in all other I_8^{2-} moieties. In the TAAB complex the nonplanarity may be linked to interactions between the I_3^- units and the benzo group of the macrocycle. Both C(8) through C(13) and C(15) through C(20) are associated with I_3^-. Although the closest approach of a given iodide to a macrocyclic atom is on the order of van der Waals radii (I(8)–C(21)′ = 3.52 Å, C(21)′ related to C(21) by the inversion center), each of the I_3^- units is almost coplanar with two benzo groups. The overall picture is thus a linear stacking of alternating benzo and I_3^- units at distances slightly greater than van der Waals radii. The nonplanar configuration of the I_8^{2-} could be related to both electronic and packing effects. It is possible that the electronic interactions may be responsible for the semiconducting behavior of these complexes.[28]

Table IX. Interatomic Distances (Å) and Angles (Deg) for Selected TAAB Structures

	[Ni(TAAB)]-[BF_4]$_2$[a]	[Pd(TAAB)]-[BF_4]$_2$[b]	[Pd(TAAB)]-[I_8]
Distances			
M–N	1.90 (2)[c]	2.004 (8)	2.030 (8)
N–C_{Ph}	1.41 (2)	1.467 (10)	1.455 (11)
C_{Ph}–C_{Ph}	1.33 (4)	1.370 (11)	1.394 (12)
C–C_{Ph}	1.48 (2)	1.575 (13)	1.476 (12)
C=N	1.32 (4)	1.290 (14)	1.276 (11)
Angles			
M–N=C	123 (2)	124.2 (8)	123.0 (6)
N=C–C_{Ph}	119 (2)	115.1 (9)	125.7 (8)
C–C_{Ph}–C_{Ph}	130 (3)	141.7 (8)	126.2 (8)
C_{Ph}–C_{Ph}–N	113 (3)	103.1 (7)	118.4 (7)
C_{Ph}–N–M	121 (2)	125.3 (7)	118.1 (6)
C_{Ph}–C_{Ph}–C_{Ph}	120 (2)	120.0 (7)	120.0 (8)

[a] Reference 37. [b] Reference 29. [c] Esd's given are the mean of the esd's for parameters included in the average.

The [M(TAAB)][I_8] complexes provide a classic example of stabilization of large ions by large counterions. The thermal stability, undoubtedly imparted to the polyiodide by weak interactions with the macrocyclic system, again indicates the varied aspects of macrocyclic utility. Further investigations into the influence of electronic and steric effects of macrocyclic ligands on the formation of stable polyiodides are in progress.

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Registry No. [Pd(TAAB)][I_8], 76136-15-7; [Pt(TAAB)][I_8], 76136-17-9.

Supplementary Material Available: Tables X–XIII, giving H atom positional and isotropic thermal parameters and structure factor amplitudes (60 pages). Ordering information is given on any current masthead page.