Notes

Contribution from the Department of Chemistry,
University of Kansas, Lawrence, Kansas 66045

Stabilization of Polyiodide Chains: Structural Influences in the Cation As Provided by the Metal Ion and Its Ligand

Alan J. Jircitano and Kristin Bowman Mertes*

Recently, a stable octaiodide dianion (I_8^{2-}) was isolated and structurally characterized in this laboratory as counterion to a sterically crowded, bulky macrocyclic ligand complex,[1] a textbook example of stabilization of a large anion by a large cation. The polyiodide chain was readily synthesized for the palladium(II) and platinum(II) complexes of the macrocycle tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine (TAAB); however, the long-chain halide was not easily obtained for the corresponding nickel(II) complex. This observation was initially surprising, since it was assumed that the role of the metal ion would be negligible and the large bulk of the macrocyclic ligand would be predominantly responsible for the stabilization of the polyiodide. All attempts to obtain the analogous nickel(II) octaiodide complex using acetonitrile as solvent (as in the palladium(II) and platinum(II) syntheses) failed. Instead, the six-coordinate nickel complex [Ni(TAAB)-(CH$_3$CN)$_2$][I$_3$]$_2$ was isolated. Thus, not only the macrocyclic bulk but also the coordination geometry of the metal ion apparently were influencing the polyiodide stabilization. The nickel octaiodide analogue was finally obtained with use of the reluctantly coordinating solvent ethanol. The structure of the nickel triiodide complex was solved by X-ray crystallographic techniques in order to better understand the influence of axial coordination in prohibiting the formation of the longer polyiodide chain.

Experimental Section

Synthesis of [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$. All chemicals were reagent grade. The starting complex [Ni(TAAB)][BF$_4$]$_2$ was synthesized by a previously reported method.[2] To a solution of the BF$_4^-$ salt (0.32 g, 0.50 mmol) in 100 mL of acetonitrile was added a solution of I$_2$ (0.56 g, 2.2 mmol) dissolved in 80 mL of dichloromethane. The solution was stirred for 5 min at room temperature. Slow evaporation over a period of 1 month yielded, almost quantitatively, dark red crystals suitable for X-ray analysis. Anal. Calcd for NiI$_6$C$_{32}$H$_{26}$N$_6$: C, 29.24; H, 1.99; N, 6.39; I, 57.91. Found: C, 29.05; H, 1.93; N, 6.25; I, 58.61.[3]

Synthesis of [Ni(TAAB)][I$_8$]. To a solution of [Ni(TAAB)][BF$_4$]$_2$ (0.32 g, 0.50 mmol) in 100 mL of ethanol was added [N(CH$_3$)$_4$][I$_5$][4] (1.0 g, 1.4 mmol) as a solid. This mixture was stirred at room temperature until all solid had dissolved. Slow evaporation over 3 weeks gave dark red crystals, similar in appearance to [M(TAAB)][I$_8$] (M = Pd, Pt). The crystals were suitable for X-ray analysis and were filtered and rinsed with dichloromethane. Anal. Calcd for NiI$_8$C$_{28}$H$_{20}$N$_4$: C, 22.63; H, 1.36; N, 3.77. Found: C, 23.00; H, 1.50; N, 3.80.

X-ray Data. Crystal data information for both iodide complexes is contained in Table I. Preliminary data for [Ni(TAAB)][I$_8$] showed it to have space group and unit cell parameters identical with those of both the palladium and platinum analogues.[1] A data set was not collected, therefore, due to the fact that the three structures are undoubtedly isomorphous. Preliminary measurements for the I$_3^-$

(1) Jircitano, A. J.; Colton, M. C.; Mertes, K. B. *Inorg. Chem.* **1981**, *20*, 890–6.
(2) Melson, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 4834–7.
(3) C, H, N, and I analyses were performed by Micro-Tech Laboratories, Skokie, IL.
(4) Hack, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321–4.

Table I. Crystal Data

	[Ni(TAAB)][I$_8$]	[Ni(TAAB)-(CH$_3$CN)$_2$][I$_3$]$_2$
formula	NiI$_8$C$_{28}$H$_{20}$N$_4$	NiI$_6$C$_{32}$H$_{26}$N$_6$
fw	1486.44	1314.74
cell parameters		
a, Å	7.810 (4)	10.34 (1)^a
b, Å	29.71 (2)	27.85 (5)
c, Å	17.54 (2)	15.33 (2)
β, deg	113.46 (5)	109.5 (1)
V, Å^3	3733 (5)	4162 (10)
Z	4	4
ρ_{calcd}, g/cm^3	2.645	2.098
ρ_{obsd} (flotation, CH$_2$I$_2$–CCl$_4$), g/cm^3	2.61 (1)	2.3 (1)
space group	$P2_1/n$	$P2_1/c$
cryst dimens, mm	0.25 × 0.25 × 0.17	0.20 × 0.20 × 0.20
temp, °C	25	25
radiatn	Mo Kα	Mo Kα
diffractometer	Syntex P2$_1$	Syntex P2$_1$
μ, cm^{-1}	62.35	49.96
check reflcns		$20\bar{2}$; $0\bar{5}2$; $\bar{2}\bar{1}2$
2θ range, deg		0.0–40.0
no. of indep. reflcns		3908
no. with $I > 3\sigma_I$		2237
final R_1		0.085
final R_2		0.087

^{a} Somewhat larger than desirable standard deviations in the lattice constants are the result of poor crystal quality. Repeated recrystallization attempts did not afford better crystals.

complex indicated monoclinic symmetry with systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, indicative of space group $P2_1/c$. Unit cell parameters were obtained from a least-squares fit of 15 reflections well distributed in reciprocal space. Intensity data were collected in concentric shells of 2θ out to 40°. At this point it was noted by an examination of the standard reflections that the crystal was beginning to deteriorate quite rapidly. Thus data collection was halted. The data were collected and treated as previously described.[5] The three standard reflections showed a decay of approximately 5%, which was fit to a linear-decay correction. An absorption correction was not applied due to the irregular shape of the crystal. The data were corrected for background, and Lorentz and polarization factors were applied to obtain structure factors.[6] Wilson's method was used to scale the F^2 values. The σ_I^2 values were scaled by increasing σ_I^2 obtained from counting statistics by $p\sigma_I^2$, where p was chosen as 0.01, the rms deviation of the standard reflections after the decay correction.[7]

Solution and Refinement of Structure. The structure was solved by using the direct-methods program for centrosymmetric structures, MAGIC.[6] The positions of the iodine atoms and the nickel ion were clearly revealed on an E map based on the phase solution of lowest discrepancy index of 168 reflections with $|E| > 2.0$. Subsequent Fourier maps revealed the coordinates of the remaining non-hydrogen atoms. Refinement was performed by using full-matrix least-squares techniques during which the function $\sum w(|F_o| - |F_c|)^2$ was minimized.

(5) Mertes, K. B. *Inorg. Chem.* **1978**, *17*, 49–52.
(6) Programs for structure determination and refinement were local modifications of R. B. K. Dewar and A. L. Stone's MAGIC, A. Zalkin's FORDAP for the Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares and function and error calculations, and C. K. Johnson's ORTEP-II for the molecular structure drawing. Computations were performed on the Honeywell 66/60 computer at the University of Kansas. Scattering factors were obtained from: Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A, 2.2B. Anomalous dispersion corrections for nickel and iodine atoms were obtained from: Ibers, J. A. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. II, Table 3.3.2C.
(7) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.
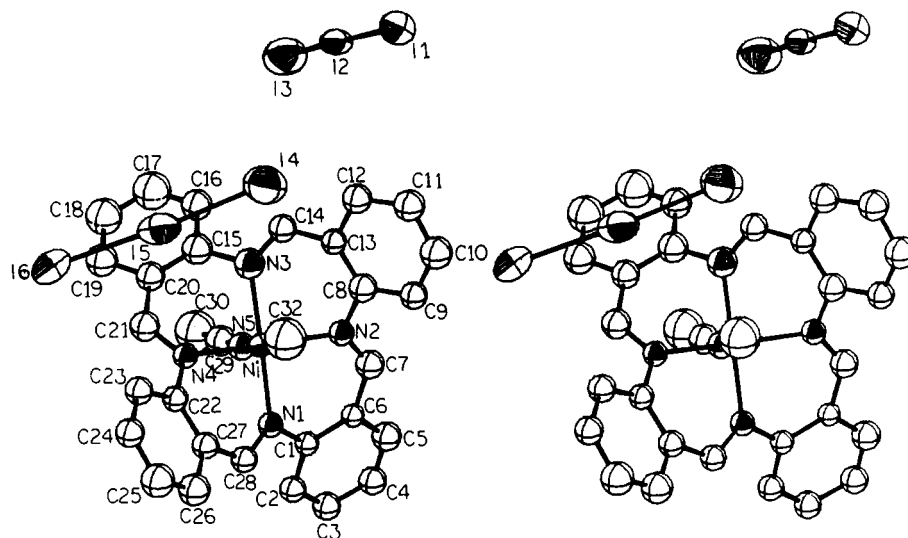
Figure 1. Overhead stereoview of [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$ showing macrocyclic numbering scheme. Thermal ellipsoids in this and the subsequent figure are 50% probability.

Table II. Final Positional Parameters for [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$

atom	x	y	z
Ni	0.0256 (4)	0.1293 (2)	0.1970 (3)
I(1)	0.4670 (3)	0.0167 (1)	0.8551 (2)
I(2)	0.5178 (3)	0.0995 (1)	0.7440 (2)
I(3)	0.5822 (3)	0.1746 (1)	0.6316 (2)
I(4)	0.0641 (4)	0.0986 (2)	0.5950 (2)
I(5)	-0.1101 (3)	0.1822 (1)	0.5081 (2)
I(6)	-0.2748 (4)	0.2687 (1)	0.4299 (2)
N(1)	-0.096 (3)	0.1069 (9)	0.068 (2)
C(1)	-0.030 (3)	0.0874 (11)	0.007 (2)
C(2)	-0.086 (3)	0.0992 (11)	-0.090 (2)
C(3)	-0.020 (3)	0.0819 (12)	-0.149 (2)
C(4)	0.099 (3)	0.0550 (12)	-0.120 (2)
C(5)	0.151 (3)	0.0419 (12)	-0.025 (2)
C(6)	0.094 (3)	0.0606 (10)	0.040 (2)
C(7)	0.173 (3)	0.0497 (12)	0.138 (2)
N(2)	0.161 (2)	0.0710 (9)	0.206 (2)
C(8)	0.223 (3)	0.0526 (13)	0.302 (2)
C(9)	0.237 (3)	0.0017 (12)	0.311 (2)
C(10)	0.296 (4)	-0.0183 (13)	0.404 (2)
C(11)	0.341 (4)	0.0121 (14)	0.480 (2)
C(12)	0.326 (3)	0.0644 (13)	0.469 (2)
C(13)	0.261 (3)	0.0836 (11)	0.379 (2)
C(14)	0.252 (3)	0.1351 (12)	0.381 (2)
N(3)	0.170 (3)	0.1591 (10)	0.315 (2)
C(15)	0.172 (4)	0.2139 (13)	0.314 (2)
C(16)	0.305 (4)	0.2369 (14)	0.349 (2)
C(17)	0.314 (4)	0.2850 (17)	0.348 (3)
C(18)	0.192 (4)	0.3136 (15)	0.320 (3)
C(19)	0.057 (4)	0.2930 (14)	0.284 (2)
C(20)	0.053 (4)	0.2423 (13)	0.280 (2)
C(21)	-0.095 (3)	0.2236 (13)	0.235 (2)
N(4)	-0.121 (2)	0.1790 (9)	0.203 (2)
C(22)	-0.264 (3)	0.1650 (11)	0.169 (2)
C(23)	-0.352 (3)	0.1817 (12)	0.216 (2)
C(24)	-0.494 (3)	0.1663 (12)	0.185 (2)
C(25)	-0.537 (4)	0.1358 (14)	0.106 (2)
C(26)	-0.452 (4)	0.1185 (13)	0.057 (2)
C(27)	-0.307 (3)	0.1318 (12)	0.094 (2)
C(28)	-0.231 (3)	0.1109 (11)	0.040 (2)
N(5)	0.121 (2)	0.1744 (10)	0.122 (2)
C(29)	0.164 (4)	0.2067 (14)	0.096 (2)
C(30)	0.230 (4)	0.2484 (17)	0.063 (3)
N(6)	-0.068 (3)	0.0870 (10)	0.272 (2)
C(31)	-0.123 (4)	0.0677 (13)	0.314 (2)
C(32)	-0.207 (5)	0.0445 (17)	0.371 (3)

The data were weighted according to $1/\sigma_{F^2} = 4LpI/\sigma_I^2$. Residuals were calculated as $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Refinement of positional and isotropic thermal parameters resulted in convergence at $R_1 = 0.145$ and $R_2 = 0.140$.

Table III. Interatomic Distances (Å) for [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$

Ni-N(1)	2.05 (2)	C(16)-C(17)	1.34 (5)
Ni-N(2)	2.12 (2)	C(17)-C(18)	1.43 (5)
Ni-N(3)	2.09 (3)	C(18)-C(19)	1.44 (4)
Ni-N(4)	2.08 (2)	C(19)-C(20)	1.41 (4)
N(1)-C(1)	1.45 (3)	C(20)-C(21)	1.54 (4)
C(1)-C(2)	1.43 (4)	C(21)-N(4)	1.33 (4)
C(1)-C(6)	1.42 (4)	N(4)-C(22)	1.44 (3)
C(2)-C(3)	1.39 (4)	C(22)-C(27)	1.43 (4)
C(3)-C(4)	1.39 (4)	C(22)-C(23)	1.42 (4)
C(4)-C(5)	1.43 (4)	C(23)-C(24)	1.45 (4)
C(5)-C(6)	1.40 (4)	C(24)-C(25)	1.42 (4)
C(6)-C(7)	1.48 (4)	C(25)-C(26)	1.41 (4)
C(7)-N(2)	1.26 (3)	C(26)-C(27)	1.46 (4)
N(2)-C(8)	1.48 (4)	C(27)-C(28)	1.43 (4)
C(8)-C(13)	1.41 (4)	C(28)-N(1)	1.33 (3)
C(8)-C(9)	1.43 (4)	Ni-N(5)	2.15 (3)
C(9)-C(10)	1.46 (4)	Ni-N(6)	2.10 (3)
C(10)-C(11)	1.39 (4)	N(5)-C(29)	1.13 (4)
C(11)-C(12)	1.47 (4)	C(29)-C(30)	1.52 (5)
C(12)-C(13)	1.42 (4)	N(6)-C(31)	1.12 (4)
C(13)-C(14)	1.44 (4)	C(31)-C(32)	1.56 (5)
C(14)-N(3)	1.28 (3)	I(1)-I(2)	3.016 (5)
N(3)-C(15)	1.52 (4)	I(2)-I(3)	2.924 (6)
C(15)-C(20)	1.40 (4)	I(4)-I(5)	2.974 (6)
C(15)-C(16)	1.45 (4)	I(5)-I(6)	2.963 (6)

Further refinement in which the thermal parameters of the heavy atoms, Ni and I, were allowed to vary anisotropically resulted in convergence at $R_1 = 0.085$ and $R_2 = 0.087$. In the final cycle, no atom shifted by more than 0.20 of its esd. A final difference map showed only small amounts of residual electron density. Final positional parameters are given in Table II. Bond lengths and angles are found in Tables III and IV, respectively. Listings of observed and calculated structure factors and thermal parameters are available as supplementary material.

Results and Discussion

In [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$, as is found in other TAAB structures, the cation retains its distinct, saddle-shaped, S_4 symmetry. The cavity distance, from the farthest carbon in each benzo group to the NiN$_4$ plane, averages 2.72 Å, virtually identical with that of [Pd(TAAB)][I$_8$].[1] The axial coordination of acetonitrile molecules gives an overall six-coordinate octahedral complex with the metal located at the center of the saddle-shaped surface formed by coordination of the four in-plane macrocyclic ligand nitrogens. The average in-plane Ni-N bond length is 2.09 (2) Å, and the corresponding axial length is 2.12 (3) Å. The average Ni-N bond in square-planar [Ni(TAAB)][BF$_4$]$_2$ is 1.90 (2) Å,[8] while in six-coordinate
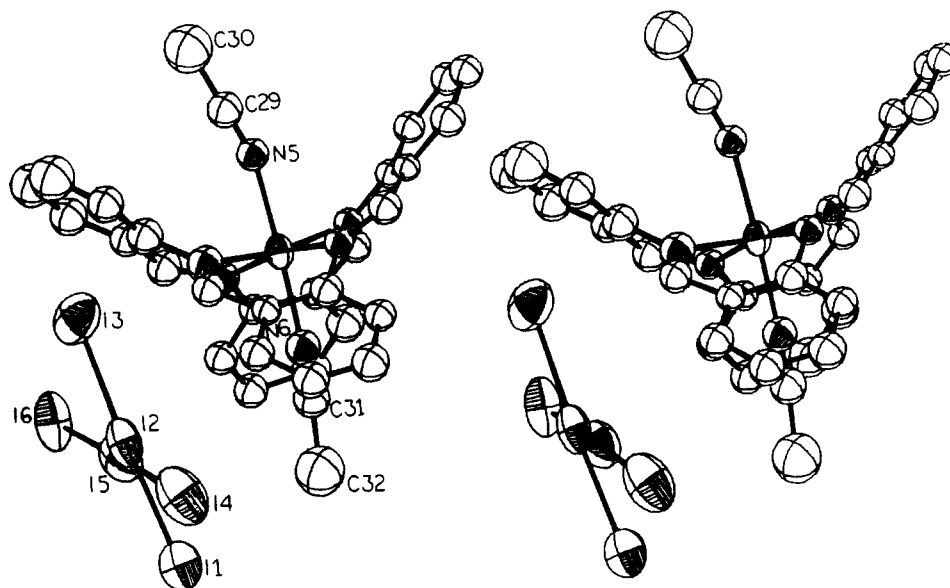
Figure 2. Side stereoview of [Ni(TAAB)(CH₃CN)₂][I₃]₂ showing acetonitrile and triiodide numbering.

Table IV. Bond Angles (deg) for [Ni(TAAB)(CH₃CN)₂][I₃]₂

N(1)-Ni-N(2)	91 (1)	C(13)-C(14)-N(3)	122 (3)
N(2)-Ni-N(3)	89 (1)	C(14)-N(3)-Ni	125 (3)
N(3)-Ni-N(4)	91 (1)	C(14)-N(3)-C(15)	122 (3)
N(4)-Ni-N(1)	91 (1)	Ni-N(3)-C(15)	113 (2)
N(1)-Ni-N(5)	85 (1)	N(3)-C(15)-C(20)	124 (3)
N(1)-Ni-N(6)	96 (1)	N(3)-C(15)-C(16)	117 (3)
N(2)-Ni-N(5)	94 (1)	C(20)-C(15)-C(16)	119 (3)
N(2)-Ni-N(6)	87 (1)	C(15)-C(16)-C(17)	120 (4)
N(3)-Ni-N(5)	85 (1)	C(16)-C(17)-C(18)	120 (4)
N(3)-Ni-N(6)	94 (1)	C(17)-C(18)-C(19)	123 (4)
N(4)-Ni-N(5)	96 (1)	C(18)-C(19)-C(20)	115 (3)
N(4)-Ni-N(6)	83 (1)	C(19)-C(20)-C(15)	123 (3)
Ni-N(1)-C(1)	118 (2)	C(19)-C(20)-C(21)	111 (3)
N(1)-C(1)-C(6)	122 (2)	C(20)-C(21)-N(4)	122 (3)
N(1)-C(1)-C(2)	118 (3)	C(21)-N(4)-Ni	125 (2)
C(6)-C(1)-C(2)	120 (3)	C(21)-N(4)-C(22)	116 (3)
C(1)-C(2)-C(3)	118 (3)	Ni-N(4)-C(22)	118 (2)
C(2)-C(3)-C(4)	124 (3)	N(4)-C(22)-C(23)	119 (3)
C(3)-C(4)-C(5)	117 (3)	N(4)-C(22)-C(27)	118 (3)
C(4)-C(5)-C(6)	122 (3)	C(27)-C(22)-C(23)	123 (3)
C(5)-C(6)-C(1)	119 (3)	C(22)-C(23)-C(24)	119 (3)
C(5)-C(6)-C(7)	115 (3)	C(23)-C(24)-C(25)	117 (3)
C(1)-C(6)-C(7)	126 (3)	C(24)-C(25)-C(26)	125 (4)
C(6)-C(7)-N(2)	125 (3)	C(25)-C(26)-C(27)	117 (3)
C(7)-N(2)-Ni	124 (2)	C(26)-C(27)-C(22)	118 (3)
C(7)-N(2)-C(8)	122 (3)	C(26)-C(27)-C(28)	111 (3)
Ni-N(2)-C(8)	113 (2)	C(22)-C(27)-C(28)	130 (3)
N(2)-C(8)-C(13)	122 (3)	C(27)-C(28)-N(1)	124 (3)
N(2)-C(8)-C(9)	116 (3)	C(28)-N(1)-C(1)	120 (2)
C(13)-C(8)-C(9)	122 (3)	C(28)-N(1)-Ni	122 (2)
C(8)-C(9)-C(10)	118 (3)	Ni-N(5)-C(29)	163 (3)
C(9)-C(10)-C(11)	120 (3)	N(5)-C(29)-C(30)	176 (4)
C(10)-C(11)-C(12)	121 (3)	Ni-N(6)-C(31)	174 (3)
C(11)-C(12)-C(13)	119 (3)	N(6)-C(31)-C(32)	175 (4)
C(12)-C(13)-C(8)	119 (3)	I(1)-I(2)-I(3)	175.3 (1)
C(12)-C(13)-C(14)	111 (3)	I(4)-I(5)-I(6)	176.9 (1)
C(8)-C(13)-C(14)	129 (3)		

[Ni(TAAB)(I)(H₂O)][I] the bond length of 2.09 (3) Å[8] is comparable to that of [Ni(TAAB)(CH₃CN)₂][I₃]₂. The longer in-plane distances are expected for a high-spin nickel(II) octahedral complex due to the presence of electrons in the antibonding e_g orbitals. The absence of disorder in macrocycle atom positions in [Ni(TAAB)(CH₃CN)₂][I₃]₂ allows for a more accurate determination of bond lengths and angles within the ligand than in the previous nickel structures.[8] Bond lengths and angles within the macrocyclic ligand are comparable to those found for [M(TAAB)][I₈] (M = Pd, Pt).[1] The bound

acetonitrile molecules in the axial positions are strongly coordinated to the nickel ion as indicated by nearly identical Ni–N bond lengths for axial and in-plane coordination. The C≡N bonds of 1.13 (4) and 1.12 (4) Å are approximately on the order of the corresponding bond in free acetonitrile, 1.157 Å.[9] Bond lengths and angles of the coordinated solvent are comparable to those found in the macrocyclic complex [Fe-(C₁₈H₁₈N₆)(CH₃CN)₂][ClO₄]₂.[10] The C≡N bond is nearly identical, at 1.136 (6) Å, in the iron complex. C(29)–C(30) and C(31)–C(32) distances of 1.52 (5) and 1.56 (5) Å are also similar to the analogous bond length in the iron macrocycle (1.489 (8) Å).[10] Bond angles Ni–N(6)–C(31) and N(6)–C-(31)–C(32) of 174 (3) and 175 (4)°, respectively, in [Ni-(TAAB)(CH₃CN)₂][I₃]₂ are matched by similar angles in the iron complex (174.1 (4) and 175.9 (6)°). The N(5)–C-(29)–C(30) angle of 176 (4)° and the Ni–N(5)–C(29) angle of 163 (3)° indicate that the coordinated solvent molecules are not colinear, however, although N(5)–Ni–N(6) is nearly linear at 178 (1)°. This tilting of the acetonitrile ligand may be a result of packing restrictions or weak interactions with adjacent triiodide anions. I(3) and I(5) are found at 3.87 (7) and 3.98 (7) Å, respectively, from C(30)′ (C(30)′ is related to C(30) via the 2₁ screw axis). C(32) of the other acetonitrile is associated with I(5) at 3.87 (7) Å. These interactions are indeed weak, being very close to the sum of the van der Waals radii.[11]

The propensity toward longer chain formation observed in the palladium(II) and platinum(II) analogues is most probably related to the preference of the two metals for square-planar coordination. All attempts to prepare the analogous nickel complex in solvents with coordinating ability resulted in isolation of the triiodide complex, and elemental analyses invariably indicated solvate molecules also were incorporated. The octaiodide analogue was finally prepared with [N(C-H₃)₄][I₅] as starting iodide and ethanol as reluctantly coordinating solvent. The resulting complex, [Ni(TAAB)][I₈], is apparently isomorphous to [M(TAAB)][I₈] (M = Pd, Pt) in view of the X-ray crystallographic data (Table I). Thus it was reasoned that the axial metal ion coordination must in some way disrupt stabilizing interactions of the I₈²⁻ chain with the macrocyclic ligand. The relationship between the two I₃⁻

(8) Hawkinson, S. W.; Fleischer, E. B. *Inorg. Chem.* **1969**, *8*, 2402–10.

(9) Weiss, M. C.; Bursten, B.; Peng, S.-M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8021–31.

(10) Goedken, V. L.; Park, Y.; Peng, S.-M.; Norris, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 7693–7701.

(11) Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper & Row: New York, 1978; pp 232–3.

moieties in [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$, compared with interactions found in I$_8$$^{2-}$, were examined to shed some light on factors influencing polyiodide formation. I–I distances in I(4)–I(5)–I(6) of 2.974 (6) and 2.963 (5) Å indicate a symmetrical I$_3$$^-$; however, the corresponding distances in I(1)–I(2)–I(3) are slightly asymmetric at 3.016 (6) and 2.924 (5) Å, probably due to either intermolecular interactions or packing effects. The closest approaches of the triiodides with macrocycle and acetonitrile carbons range from 3.69 (7) to 3.98 (7) Å and are considerably longer than even the weak associations of I$_8$$^{2-}$ with macrocyclic benzo groups in [Pd-(TAAB)][I$_8$] (3.52 Å).[1] The triiodide asymmetry thus is more probably due to packing effects. The two I$_3$$^-$ units do not appear to be related in any discernible fashion, their closest approach being 4.216 (7) Å (I(6) to I(4)″; I(4)″ is related to I(4) by a unit cell translation along the *a* axis). Iodine–benzo group or iodine–acetonitrile interactions do not appear to be systematic or related to the interactions observed in [Pd-(TAAB)][I$_8$], therefore. The presence of axial coordination may thus be sufficient to disrupt the packing of the cations to the extent that required stabilizing influence of iodine–benzo group interactions necessary for higher chain polyiodide formation is prevented.

Registry No. [Ni(TAAB)(CH$_3$CN)$_2$][I$_3$]$_2$, 85479-99-8; [Ni-(TAAB)][I$_8$], 85480-00-8; [Ni(TAAB)][BF$_4$]$_2$, 14220-76-9.

Supplementary Material Available: Tables of observed and calculated structure factors and thermal parameters (15 pages). Ordering information is given on any current masthead page.

Contribution from the Centro Chimica Metallorganica del CNR, Istituto Chimica Industriale, University of Padua, 35100 Padova, Italy

Mechanism of Reductive Elimination of 1,1,1-Trifluoroethane from *cis*-Hydrido(2,2,2-trifluoroethyl)bis(triphenylphosphine)platinum(II)

Rino A. Michelin,* Sergio Faglia, and Paolo Uguagliati

The mechanism of 1,1 reductive elimination processes involving formation of hydrogen–hydrogen,[1] hydrogen–carbon,[2–4] and carbon–carbon[5,6] species from transition-metal complexes is a subject of current interest.

In particular, *cis*-hydridoalkylplatinum(II)–tertiary phosphine complexes are rather unstable toward alkane elimination[3,7a,8] unless the alkyl group bears electron-withdrawing stabilizing substituents.[9–11]

In our search for structure–reactivity correlations for or-

ganoplatinum derivatives with electronegative metal-bonded (sp^3) carbon groups, we were led to investigate the ability of fluoroalkyls to stabilize Pt(II) metal complexes containing the hydride ligand. We found that the complex *cis*-PtH-(CH$_2$CF$_3$)(PPh$_3$)$_2$ (**1**) is easily isolated from the reaction of the cationic Pt(CH$_2$CF$_3$)(PPh$_3$)$_2$(solvent)$^+$ with NaBH$_4$ in ethanol at 0 °C.

Since **1** appeared to undergo slow thermal reductive elimination of CH$_3$CF$_3$ at room or slightly above room temperature in contrast with the highly unstable hydrido–methyl analogue[3] (eq 1), we thought it worthwhile to undertake a kinetic in-

$$\textit{cis-}PtH(CH_2CF_3)(PPh_3)_2 \rightarrow \text{``}Pt(PPh_3)_2\text{''} + CH_3CF_3 \quad (1)$$

vestigation of this elimination reaction, the results of which will be reported in a sequel.

Experimental Section

General Procedures, Apparatus, and Materials. All reactions were carried out under dry nitrogen or argon atmosphere. The solvents benzene, toluene, tetrahydrofuran, and diethyl ether were distilled under nitrogen from sodium and degassed before use by a series of freeze–pump–thaw cycles. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification.

IR spectra were recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 597 spectrophotometer calibrated against polystyrene film. ^{1}H NMR spectra were registered on Varian FT-80 A and Bruker WH-360 instruments in CD$_2$Cl$_2$ (99%); all the chemical shifts are reported from tetramethylsilane by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. ^{19}F NMR spectra (CD$_2$Cl$_2$) were run on a Varian FT-80 A spectrometer with CFCl$_3$ as internal reference. ^{31}P{^{1}H} NMR spectra (CD$_2$Cl$_2$) were recorded on the above instruments with H$_3$PO$_4$ (85%) or PEt$_3$ as external reference. In the case where PEt$_3$ was used as external reference, the chemical shifts are reported from H$_3$PO$_4$ (85%) with use of the conversion δ(H$_3$PO$_4$) = δ(PEt$_3$) – 19.7 ppm (at 30 °C). In all the spectra, negative chemical shifts are *upfield* from the reference used. The correctness of the NMR data analyses was checked by spectral simulation.

UV spectra were recorded with a Varian Cary 219 C spectrophotometer equipped with an F3-C Haake circulating-fluid cryothermostat.

Melting points were taken on a hot plate apparatus and are uncorrected. Elemental analyses were performed by the Institute of Organic Chemistry of the University of Padua. 2-Iodo-1,1,1-trifluoroethane and NaBD$_4$ were used as purchased from EGA-Chemie, Steinheim, FRG.

cis-PtI(CH$_2$CF$_3$)(PPh$_3$)$_2$ was prepared according to a literature procedure.[12]

Preparation of the Complexes. *cis*-PtH(CH$_2$CF$_3$)(PPh$_3$)$_2$ (1). A solution of *cis*-PtI(CH$_2$CF$_3$)(PPh$_3$)$_2$ (1.86 g, 2.0 mmol) in CH$_2$Cl$_2$ (100 mL) was treated with a solution of AgBF$_4$ (0.39 g, 2.0 mmol) in MeOH (3 mL) and stirred at room temperature for 2 h. AgI was filtered off and the volume of the filtrate reduced to ca. 20 mL. Dropwise addition of Et$_2$O gave a white precipitate of the cationic solvato complex, which was filtered and dried under vacuum. This was dissolved in absolute EtOH (150 mL) and cooled in an ice–water bath. A solution of NaBH$_4$ (0.08 g, 2.11 mmol) in EtOH (50 mL) was added dropwise in a period of 1 h. The pale cream solid that precipitated from the alcoholic solution was filtered. Recrystallization from CH$_2$Cl$_2$/MeOH by evaporation under reduced pressure gave **1** as a white product (1.0 g, 62% yield), mp 109–111 °C dec with effervescence. Anal. Calcd for C$_{38}$H$_{33}$F$_3$P$_2$Pt: C, 56.78; H, 4.14. Found: C, 56.66; H, 4.22.

^{1}H NMR: δ(H) = –4.79 (doublet of double quartets ($^1J_{PtH}$ = 1113, $^2J_{PH(trans)}$ = 194, $^2J_{PH(cis)}$ = 21.3, $^3J_{FH}$ = 4.5 Hz), δ(CH$_2$) = 1.66

(1) Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277 and references therein. Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138.
(2) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 295.
(3) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.
(4) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1676, 3396. Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Ibid.* **1981**, *103*, 3404.
(5) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892.
(6) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. Loar, M. K.; Stille, J. K. *Ibid.* **1981**, *103*, 4174. Moravskiy, A.; Stille, J. K. *Ibid.* **1981**, *103*, 4182. (b) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *Ibid.* **1974**, *96*, 6140. (c) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *Ibid.* **1976**, *98*, 7255.

(7) (a) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17. (b) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.
(8) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263.
(9) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1977**, *139*, 355; **1978**, *161*, 75; **1979**, *165*, 107.
(10) Ros, R.; Michelin, R. A.; Carturan, G.; Belluco, U. *J. Organomet. Chem.* **1977**, *133*, 213.
(11) Michelin, R. A.; Belluco, U.; Ros, R. *Inorg. Chim. Acta* **1977**, *24*, L33.
(12) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239.