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Reaction of Molecular Iodine with *cis*-Dihalo(2,2′-bipyridyl)platinum(II) and *cis*-Dihalo(1,10-phenanthroline)platinum(II). Oxidative Addition and Inclusion Compounds

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The oxidation products obtained by the reaction of dihalo(2,2′-bipyridyl)platinum(II) and dihalo(1,10-phenanthroline)platinum(II) with molecular iodine were investigated. The former compounds yield only complexes of the stoichiometry $Pt(bpy)X_2I_2$ (bpy = 2,2′-bipyridyl; X = Cl, I). In the latter case compounds of the stoichiometry $Pt(phen)X_2I_4$ (phen = 1,10-phenanthroline; X = Cl, I), $Pt(phen)I_5$, and $Pt(phen)Cl_2I_5\cdot S$ (S = solvent molecule CH_2Cl_2 or $CHCl_3$) were obtained. The crystal structures of the compounds $Pt(phen)I_6$ (I) and $Pt(phen)I_5$ (II) were determined from diffractometer data. I crystallizes in the space group *Pbca*, $Z = 8$, with the cell parameters $a = 20.075$ (7) Å, $b = 14.523$ (3) Å, and $c = 13.852$ (2) Å. II crystallizes in the space group $P2_1/c$, $Z = 8$ (or 4 $Pt_2(phen)_2I_{10}$), with the cell parameters $a = 18.009$ (3) Å, $b = 14.673$ (2) Å, $c = 14.244$ (2) Å, and $\beta = 93.16$ (1)°. The structures were refined by least-squares methods to $R = 0.069$ for I and $R = 0.047$ for II. Both structures contain $Pt(phen)I_4$ octahedra linked by molecular iodine. None of the compounds contains I_3^- ions as postulated earlier.

Introduction

There has been much recent interest in the oxidation of planar four-coordinate platinum(II) compounds.[1,2] Besides many investigations concerned with the reaction mechanism only[3] two main aspects have been considered: (i) oxidative addition type reactions;[4-6] (ii) oxidations leading to mixed-valence linear-chain systems.[7-10] A few papers touch both of these fields simultaneously, e.g., recent investigations of Hodges et al.,[11] who reported the oxidation of *cis*-dihalo(1,10-phenanthroline)platinum(II) complexes using molecular iodine. The existence of triiodide ions in some of these solid reaction products was proposed. These findings are remarkable especially in light of an earlier suggestion that most of the compounds of stoichiometry *cis*-PtL_2X_2 (with X = halide or pseudohalide with L_2 = two monodentate or one bidentate neutral ligand) could be oxidized by iodine to mixed-valence solids some of them containing linear chains of triiodide ions.[10] Very recently we reacted *cis*-dihalo(1,10-phenanthroline)platinum(II) and *cis*-dihalo(2,2′-bipyridyl)platinum(II) compounds with molecular iodine in an attempt to obtain new linear-chain mixed-valence transition metal solids with additional triiodide chains.

Though none of the reaction products contains chains of directly interacting metal ions, the results are reported in the following because some of our conclusions differ considerably from earlier suggestions.[11]

Experimental Section

Chemicals. *cis*-Dichloro(1,10-phenanthroline)platinum(II) [$Pt(phen)Cl_2$], *cis*-diiodo(1,10-phenanthroline)platinum(II) [$Pt(phen)I_2$], *cis*-dichloro(2,2′-bipyridyl)platinum(II), [$Pt(bpy)Cl_2$], and *cis*-diiodo(2,2′-bipyridyl)platinum(II), [$Pt(bpy)I_2$] were prepared as described earlier.[11,12] The solvents were reagent grade purchased from Merck, Darmstadt. Analyses were carried out by Dr. Pascher Laboratorium, Bonn, GFR.

Analysis, properties, and stoichiometry of the products obtained by the oxidation of $Pt(phen)Cl_2$ and $Pt(phen)I_2$ with iodine differ partly from the earlier findings.[11] A solid of stoichiometry $Pt(phen)Cl_2I_6$ was obtained by Hodges by reacting a $CHCl_3$ slurry of $Pt(phen)Cl_2$ with iodine at 75 °C for 24 h. We found that a compound prepared in this manner loses iodine on washing with $CHCl_3$ very rapidly. The yellow starting material can be regained after several washing processes. Anal. Calcd for $Pt(phen)Cl_2$: C, 32.0; H, 1.8; N, 6.2; Pt, 43.0. Found for the end product after washing: C, 31.16; H, 1.79; N, 5.9; Pt, 43.31.

Therefore we modified the described procedures in order to isolate and identify the different compounds resulting by the reaction of $Pt(phen)Cl_2$ with iodine.

Preparation of "$Pt(phen)Cl_2I_6$". At room temperature 1.4 g of iodine was added to a solution of $Pt(phen)Cl_2$ (0.20 g) in 2 L of CH_2Cl_2. The reaction mixture was stirred over a period of 2 h and then filtered and cooled for 3 weeks at a temperature of −10 °C to obtain suitable crystals. Black crystals were obtained: yield 120 mg (23%). The solid contains 1 mol of CH_2Cl_2. Anal. Calcd for $Pt(phen)Cl_2I_6\cdot CH_2Cl_2$: C, 12.05; H, 0.85; N, 2.16; Pt, 15.05; I, 58.7; Cl, 10.95. Calcd for $Pt(phen)Cl_2I_{5.3}\cdot CH_2Cl_2$: C, 12.97; H, 0.84; N, 2.33; Pt, 16.22; I, 55.87; Cl, 11.78. Found: C, 13.20; H, 0.94; N, 2.40; Pt, 16.20; I, 55.50; Cl, 11.91.

The analytical data agree with a stoichiometry $Pt(phen)Cl_2I_{5.3}\cdot CH_2Cl_2$. A solution of 2.2 g of iodine in 80 mL of $CHCl_3$ was added to a fine slurry of $Pt(phen)Cl_2$ (0.30 g) in 40 mL of boiling $CHCl_3$. After reaction periods of 1, 2, and 14 h the mixture was filtered while hot. Three different products were gained and dried under vacuum.

The x-ray powder patterns of these compounds show that the first product is still $Pt(phen)Cl_2$, the second "$Pt(phen)Cl_2I_6$", and the third a new compound of stoichiometry $Pt(phen)I_6$.

Preparation of $Pt(phen)I_6$. Eight grams of iodine was added to a hot solution (170 °C) of 0.30 g of $Pt(phen)Cl_2$ in 1300 mL of 1,2-dichlorobenzene and the mixture was stirred for several days. Now the reaction mixture was cooled slowly and reached room temperature after a period of 2 months. The resulting black greenish crystals were filtered, washed thoroughly with 1,2-dichlorobenzene, and dried under vacuum. Anal. Calcd for $Pt(phen)I_6$: C, 12.65; H, 0.79; N, 2.46; Pt, 17.15; I, 67; Cl, 0. Calcd for $Pt(phen)I_{5.5}Cl_{0.5}$: C, 13.21; H, 0.74; N, 2.56; Pt, 17.89; I, 63.97; Cl, 1.62. Found: C, 13.13; H, 0.75; N, 2.73; Pt, 18.24; I, 63.78; Cl, 1.83.

Analytical data prove the replacement of Cl by I is not complete. The stoichiometry actually is closer to that for $Pt(phen)I_{5.5}Cl_{0.5}$. Guinier powder patterns show that reaction under the same conditions with $Pt(phen)I_2$ as the starting material gives pure $Pt(phen)I_6$ as the reaction product!

Preparation of $Pt(phen)I_5$. Three grams of iodine was added to a clear solution of 260 mg of $Pt(phen)Cl_2$ in 1100 mL of 1,2-dichlorobenzene (130 °C). After being stirred for 1 day the reaction mixture was slowly cooled to room temperature. The product consisted of long black needles ($Pt(phen)I_6$) and black plates, which had the stoichiometry $Pt(phen)I_5$. Anal. Calcd for $Pt(phen)I_5$: C, 14.2; H, 0.79; N, 2.77; I, 63; Pt, 19.3. Found: C, 14.2; H, 0.89; N, 2.77; I, 63.61; Pt, 18.48 (AAS).

Reaction of Molecular Iodine with $Pt(bpy)Cl_2$. (i) Diiododichloro(2,2′-bipyridyl)platinum(IV). A 500-mg sample of $Pt(bpy)Cl_2$ was dissolved in 630 mL of 1,2-dichlorobenzene at 140 °C. A 3.5-g amount of solid iodine was added under stirring to the clear yellow solution and the reaction mixture was slowly cooled down to room temperature. After filtration the green lustrous crystals were washed with 1,2-dichlorobenzene and dried under vacuum. Anal. Calcd for $Pt(bpy)Cl_2I_2$: C, 17.76; H, 1.18; N, 4.14; Pt, 28.9. Found: (a) C, 17.79; H, 1.20; N, 3.17; Pt, 29.28; (b) C, 17.49; H, 1.11; N, 3.40; Pt, 29.49.

(ii) Tetraiodo(2,2′-bipyridyl)platinum(IV) from $Pt(bpy)I_2$. Reacting 160 mg of $Pt(bpy)I_2$ in 650 mL of 1,2-dichlorobenzene with 8 g of iodine in the manner described above yielded dark needles. They were washed with acetone and dried under vacuum. Anal. Calcd for

Table I. Crystal Data for Pt(phen)I_6 and Pt(phen)I_5

	$Pt(C_{12}H_8N_2)$-$I_{6-0.5}Cl_{0.5}$	$Pt_2(C_{12}H_8N_2)_2I_{10}$
Mol wt	1090.85	2019.62
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a, Å	20.075 (7)	18.009 (3)
b, Å	14.523 (3)	14.673 (2)
c, Å	13.852 (2)	14.244 (2)
β, deg		93.16 (1)
Cell vol, $Å^3$	4038.5	3758.2
Density (calcd), g cm^{-3}	3.588	3.569
Z (no. of formula units per cell)	8	4
Linear absorption factor (Mo Kα), cm^{-1}	157.2	156.7
Size of crystal, mm^3	0.066 × 0.144 × 0.38	0.092 × 0.20 × 0.25
Rotation axis	*c*	*b*
$2\theta_{max}$, deg	50	40
Measd layers	*hk*0–*hk*14	*h*0*l*–*h*13*l*
No. of measd reflections	2673	3325
No. of unobsd reflections	395	271

Pt(bpy)I_4: C, 14.0; H, 0.93; N, 3.28; Pt, 22.7; I, 59.2. Found: C, 13.78; H, 1.10; N, 3.22; Pt, 23.26.

(iii) Tetraiodo(2,2′-bipyridyl)platinum(IV). The same compound can be obtained if diiododichloro(2,2′-bipyridyl)platinum(IV) is recrystallized in an excess of iodine from 1,2-dichlorobenzene. On slow cooling, dark needles of stoichiometry Pt(bpy)I_4 are obtained. They were shown to be identical with the above-mentioned compound (ii) by their Guinier powder patterns and analysis. Anal. Found: C, 14.11; H, 0.82; N, 3.23; Pt, 21.31; I, 59.1. Crystals of all of these compounds were obtained by slowly cooling saturated solutions in $CHCl_3$ or 1,2-dichlorobenzene.

Crystal Data and Intensity Measurements of Pt(phen)I_5 and Pt(phen)I_6

The cell constants were obtained from precession photographs and refined with the indexed reflections of Guinier films. The crystal material that was used for x-ray measurements of Pt(phen)I_6 had the stoichiometry $C_{12}H_8Cl_{0.5}I_{5.5}N_2Pt$. Intensity data were collected on a STOE Weissenberg diffractometer with Mo Kα radiation (graphite monochromator) using the ω-scan technique. The scan rate was 1.2° min^{-1}. The background counts were measured on both sides of the reflections for 20 s. The scan range was varied because of the elongation of the reflections at low θ angles on higher levels. *Lp* and absorption corrections were applied to the intensities (range of absorption corrections: for Pt(phen)I_5, 0.25–0.50; for Pt(phen)I_6, 0.35–0.60). Reflections with standard deviations σ_I greater than the intensity *I* were considered unobserved and not included in the refinement [$\sigma_I = (Z + (U_1 + U_2)^2q^2 + (0.04I)^2)^{1/2}$, where *Z* is the scan count, U_1 and U_2 the background counts, and *q* is the ratio of the scan time for the reflection to the time for both background measurements]. Crystal data and details of the intensity measurements are given in Table I.

The x-ray powder diffraction films were made with Guinier-Hägg XDC 700 camera (Cu $K\alpha_1$ radiation, quartz monochromator, internal standard $Pb(NO_3)_2$).

Structure Solution and Refinement

The structures were solved by the heavy-atom method and refined by the least-squares method minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weight *w* was set equal to $1/\sigma_F^2$, where $\sigma_F = 0.5\sigma_I((Lp)I)^{-1/2}$. Atomic scattering factors were taken from the article of Cromer and Mann.[13] The anomalous dispersion corrections for Pt and I were included.[14]

(a) Pt(phen)I_6. The refinement of Pt(phen)I_6 with all nonhydrogen atoms (anisotropic temperature factors for Pt and I) converged to $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.069$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.067$. In spite of the formula based on the analysis the structure was first refined with six iodine atoms. For one of the iodine atoms [I(3)] attached to platinum the temperature factor was larger and the distance somewhat shorter than for the other iodine atoms. The attempt to replace this atom by a chlorine and an iodine atom with the multiplicity 0.5 in the calculated positions from platinum (Pt–Cl = 2.30 Å, Pt–I = 2.62 Å) gave slightly better *R* values (R_1 = 0.064 and R_2 = 0.057), but the temperature factor for chlorine became non positive definite. A refinement of the multiplicity factors did not improve the result. As this is not reasonable, we give here the results of the refinement without consideration of the chlorine. The atomic parameters of this refinement are listed in Table II; the resulting interatomic distances and angles are summarized in Table IV.

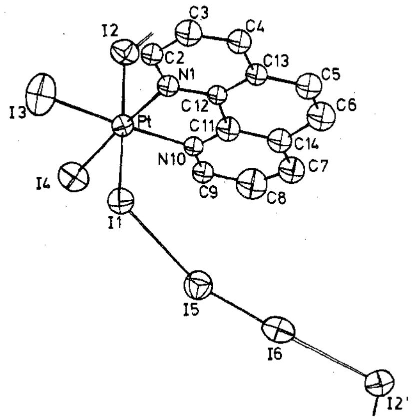

Figure 1. Molecular structure and labeling in Pt(phen)I_6.

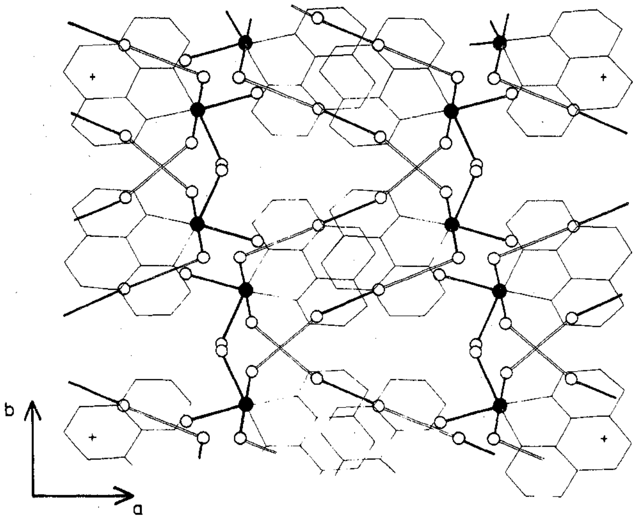

Figure 2. Projection of Pt(phen)I_6 on the *ab* plane.

(b) Pt(phen)I_5. The refinement of the structure of Pt(phen)I_5 with all nonhydrogen atoms (anisotropic temperature factors for Pt and I) converged to R_1 = 0.047 and R_2 = 0.050. The atomic parameters are given in Table III; the interatomic distances and angles, in Table IV.

Structure Description

(a) Pt(phen)I_6. The structure of Pt(phen)I_6 consists of Pt(phen)I_4 and I_2 molecules. The platinum is octahedrally coordinated by the phenanthroline molecule and four iodine atoms. The distance from platinum to the iodine atom I(3) is shorter than the other Pt–I distances. This atom is probably partially chlorine, and the position is hereby affected. The I_2 molecule connects the Pt(phen)I_4 octahedra via the axial iodine atoms thus forming zigzag chains in the direction of the *b* axis (Figures 1 and 2). The I_2 molecule and the two adjacent iodine atoms form a slightly bent unit, which is also found in other structures.

(b) Pt(phen)I_5. The structure of Pt(phen)I_5 is built up by two different Pt(phen)I_4 octahedra and one I_2 molecule. The Pt(phen)I_4 molecules of the first type are connected by the I_2 molecules in the same manner as in Pt(phen)I_6 (Figure 3). They form chains in the direction of the *b* axis (Figure 4). The

Table II

Atom Parameters of Pt(phen)I_6[a]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
Pt	0.297 25 (5)	0.091 75 (6)	0.180 05 (5)		C(4)	0.418 5 (14)	−0.162 5 (17)	0.030 9 (16)	3.4 (5)
I(1)	0.308 43 (9)	0.181 44 (12)	0.012 01 (10)		C(5)	0.522 3 (14)	−0.084 1 (17)	0.092 3 (16)	3.5 (5)
I(2)	0.285 17 (10)	−0.000 47 (13)	0.345 22 (11)		C(6)	0.552 6 (16)	−0.014 8 (19)	0.137 9 (19)	4.6 (6)
I(3)	0.179 43 (13)	0.045 73 (20)	0.131 65 (18)		C(7)	0.537 4 (15)	0.133 0 (19)	0.231 9 (18)	4.2 (6)
I(4)	0.249 41 (12)	0.240 35 (14)	0.260 63 (11)		C(8)	0.491 1 (17)	0.190 3 (20)	0.274 9 (20)	5.2 (7)
I(5)	0.437 48 (11)	0.334 82 (14)	0.060 22 (13)		C(9)	0.422 1 (12)	0.182 8 (15)	0.266 4 (15)	2.6 (4)
I(6)	0.058 83 (12)	0.411 79 (13)	0.395 52 (13)		C(11)	0.436 9 (13)	0.055 4 (16)	0.172 5 (16)	3.0 (5)
N(1)	0.342 1 (10)	−0.023 2 (12)	0.115 1 (12)	2.7 (4)	C(12)	0.408 6 (12)	−0.021 8 (14)	0.123 3 (14)	2.4 (4)
N(10)	0.397 5 (9)	0.118 2 (11)	0.210 8 (11)	2.2 (3)	C(13)	0.450 3 (12)	−0.090 2 (15)	0.080 6 (14)	2.3 (4)
C(2)	0.310 0 (12)	−0.093 7 (17)	0.065 7 (15)	3.1 (4)	C(14)	0.510 4 (13)	0.061 7 (16)	0.182 3 (16)	3.1 (5)
C(3)	0.350 0 (14)	−0.159 9 (17)	0.026 7 (17)	3.6 (5)					

Anisotropic Temperature Factors[b] of Pt(phen)I_6

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	2.56 (4)	2.72 (4)	1.96 (3)	0.26 (4)	0.08 (3)	−0.23 (3)
I(1)	3.38 (9)	4.29 (8)	2.56 (6)	0.61 (7)	0.02 (6)	0.37 (5)
I(2)	5.46 (11)	4.48 (9)	2.77 (6)	0.74 (8)	1.04 (7)	0.92 (5)
I(3)	4.77 (13)	10.03 (17)	6.84 (11)	−0.23 (12)	0.74 (11)	−2.05 (11)
I(4)	6.25 (12)	4.77 (9)	3.42 (7)	1.56 (9)	0.16 (8)	−0.94 (6)
I(5)	4.91 (12)	4.85 (10)	4.73 (8)	0.87 (9)	0.93 (8)	0.25 (7)
I(6)	6.75 (13)	3.90 (9)	4.54 (8)	−0.82 (10)	−1.08 (9)	0.92 (7)

[a] Here, and in other tables, estimated standard deviations are given in parentheses. [b] The form of the anisotropic temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III

Atom Parameters of Pt(phen)I_5

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
Pt(A)	0.717 02 (6)	0.887 88 (6)	0.315 96 (6)		C(6A)	0.4533 (17)	0.0526 (18)	0.3685 (18)	4.7 (6)
Pt(B)	0.156 08 (6)	0.870 39 (5)	0.241 53 (6)		C(7A)	0.4443 (17)	0.8932 (18)	0.2772 (18)	4.8 (6)
I(1A)	0.710 66 (10)	0.816 40 (10)	0.487 60 (10)		C(8A)	0.4821 (17)	0.8265 (19)	0.2388 (18)	4.9 (6)
I(2A)	0.723 04 (11)	0.967 58 (12)	0.148 09 (10)		C(9A)	0.5592 (15)	0.8178 (16)	0.2455 (15)	3.6 (5)
I(3A)	0.861 78 (10)	0.903 06 (12)	0.342 78 (11)		C(11A)	0.5677 (15)	0.9574 (16)	0.3305 (15)	3.3 (5)
I(4A)	0.741 78 (11)	0.726 83 (11)	0.246 66 (12)		C(12A)	0.6138 (13)	0.0216 (14)	0.3769 (13)	2.2 (4)
I(5A)	0.564 23 (12)	0.667 38 (13)	0.443 16 (13)		C(13A)	0.5806 (16)	0.1042 (17)	0.4134 (17)	4.3 (6)
I(6A)	0.432 73 (12)	0.579 64 (11)	0.398 60 (12)		C(14A)	0.4908 (16)	0.9681 (17)	0.3257 (17)	4.4 (6)
I(1B)	0.077 02 (10)	0.853 03 (10)	0.393 49 (10)		C(2B)	0.0833 (16)	0.0527 (18)	0.1915 (17)	4.4 (6)
I(2B)	0.232 05 (11)	0.894 15 (12)	0.087 87 (12)		C(3B)	0.0196 (15)	0.1097 (16)	0.1510 (16)	3.7 (5)
I(3B)	0.236 79 (11)	0.990 91 (11)	0.334 53 (13)		C(4B)	−0.0444 (17)	0.0688 (18)	0.1089 (18)	4.8 (6)
I(4B)	0.248 79 (11)	0.742 35 (10)	0.299 64 (11)		C(5B)	−0.1001 (16)	0.9241 (18)	0.0567 (17)	4.4 (6)
N(1A)	0.688 3 (10)	0.012 6 (10)	0.375 0 (10)	1.7 (3)	C(6B)	−0.1057 (16)	0.8347 (17)	0.0483 (17)	4.2 (6)
N(10A)	0.603 4 (10)	0.881 8 (11)	0.293 3 (11)	2.6 (4)	C(7B)	−0.0388 (15)	0.6815 (15)	0.0897 (15)	3.3 (5)
N(1B)	0.076 5 (10)	0.963 6 (11)	0.186 4 (11)	2.2 (4)	C(8B)	0.0212 (16)	0.6422 (17)	0.1276 (17)	4.2 (6)
N(10B)	0.078 8 (11)	0.780 6 (12)	0.171 7 (11)	2.5 (4)	C(9B)	0.0836 (14)	0.6899 (15)	0.1689 (15)	2.8 (5)
C(2A)	0.734 4 (14)	0.075 7 (15)	0.418 1 (15)	3.2 (5)	C(11B)	0.0174 (14)	0.8251 (15)	0.1329 (15)	3.0 (5)
C(3A)	0.701 8 (14)	0.155 3 (15)	0.461 8 (15)	3.0 (5)	C(12B)	0.0180 (12)	0.9250 (14)	0.1418 (13)	1.9 (4)
C(4A)	0.632 9 (15)	0.168 2 (16)	0.459 1 (16)	3.7 (5)	C(13B)	−0.0426 (14)	0.9738 (15)	0.1031 (15)	3.1 (5)
C(5A)	0.501 8 (18)	0.107 1 (19)	0.411 5 (19)	5.4 (7)	C(14B)	−0.0442 (16)	0.7775 (17)	0.0886 (16)	3.9 (6)

Anisotropic Temperature Factors for Pt(phen)I_5

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt(A)	2.59 (5)	1.81 (4)	2.10 (4)	0.25 (4)	−0.01 (3)	−0.19 (3)
Pt(B)	3.03 (5)	1.42 (4)	2.18 (4)	0.15 (4)	0.17 (3)	0.11 (3)
I(1A)	3.61 (10)	2.16 (7)	2.51 (7)	−0.20 (7)	0.06 (6)	0.24 (6)
I(2A)	4.25 (10)	4.53 (8)	2.82 (7)	1.17 (8)	0.64 (7)	1.00 (7)
I(3A)	2.82 (9)	5.49 (9)	3.65 (8)	−0.17 (8)	−0.05 (6)	0.61 (7)
I(4A)	5.44 (12)	2.98 (7)	4.18 (8)	1.53 (8)	−0.10 (8)	−1.47 (7)
I(5A)	5.42 (12)	4.11 (9)	5.77 (10)	−1.35 (9)	0.05 (8)	0.41 (8)
I(6A)	5.37 (12)	3.19 (10)	4.65 (9)	−0.66 (8)	−0.04 (8)	−0.23 (7)
I(1B)	4.11 (10)	3.03 (7)	2.63 (7)	−0.71 (7)	0.82 (6)	−0.17 (6)
I(2B)	5.36 (12)	4.29 (8)	3.80 (8)	1.55 (9)	1.84 (8)	1.52 (7)
I(3B)	4.79 (11)	2.87 (7)	5.38 (9)	−0.90 (8)	−0.69 (8)	0.62 (7)
I(4B)	5.57 (12)	2.85 (7)	3.61 (8)	1.57 (8)	−0.30 (7)	0.43 (6)

Pt(phen)I_4 molecules of the other type are not bound to the I_2 molecules, but there exist some short contacts to the iodine atoms of the other Pt(phen)I_4 molecules (I(3B)–I(4A) = 3.677 (2) Å, I(3B)–I(1A) = 3.879 (2) Å). The group Pt(A)–I(4A)···I(3B) is almost linear and there may be a weak interaction which connects the two octahedra. A similar arrangement is found in *trans*-bis(acetonylacetonato)diiodoplatinum(IV) where the I–I distance is 3.56 Å.[15]

Comparison of the two Structures

The three independent Pt(phen)I_4 octahedra in both structures are very similar. The axial Pt–I distances (2.67 Å) are longer than those which lie in the plane of the phenanthroline ring (2.61 Å). The distances in the phenanthroline

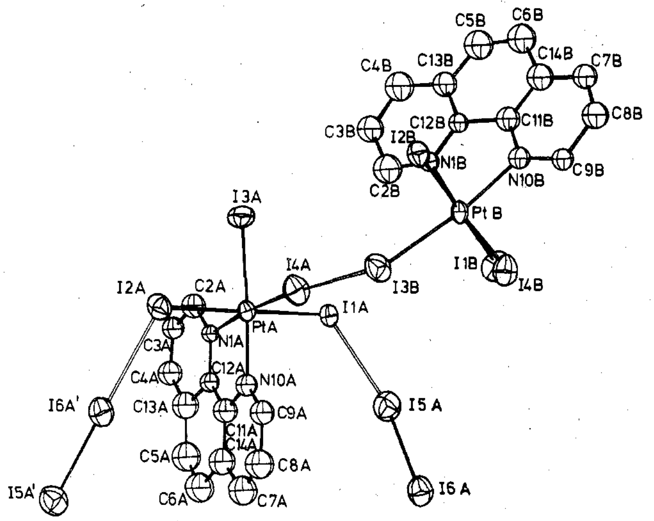

Figure 3. Molecular structure and labeling in Pt(phen)I_5.

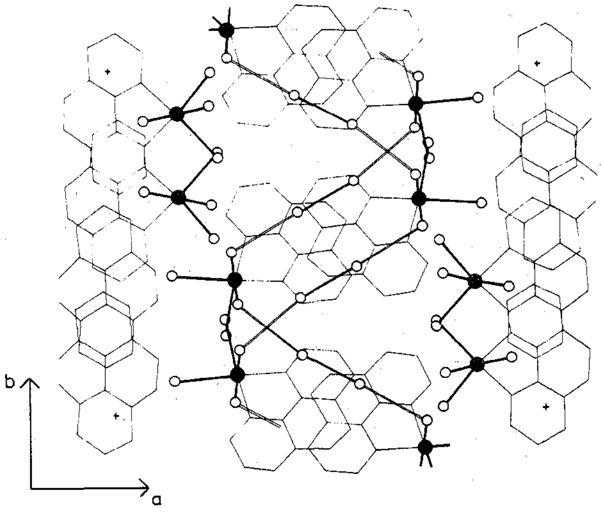

Figure 4. Projection of Pt(phen)I_5 on the *ab* plane.

rings are not very precise (esd 0.02–0.03 Å). They deviate by a maximum of 0.1 Å from the corresponding mean values of 16 different phenanthroline structures.[16] But the mean values of the three independent rings in Pt(phen)I_6 and Pt(phen)I_5 are in better agreement with those values (maximum deviation 0.03 Å).

The approximately linear group of four iodine atoms is found in some other structures and is described as an I_4^{2-} ion.[17–19] All these compounds show a similar arrangement. The ion is linear or only slightly bent. The distance between the inner iodine atoms (2.74–2.83 Å) is somewhat larger than in an isolated I_2 molecule. The outer distances lie in the range 3.30–3.45 Å and indicate relatively weak bonds. In most cases the outer iodine atoms are part of another molecule, a complex (e.g., $Cu(NH_3)_4I_4$[17,18]) or an I_3^- ion (e.g., Cs_2I_8).[19] The I_4 groups in Pt(phen)I_6 and Pt(phen)I_5 are more bent. The central distance is slightly shorter and the outer distances somewhat larger than in the other known I_4^{2-} structures, indicating a weaker interaction between the I_2 and the outer iodine atoms. Neither I_4^{2-} ion is symmetrical, especially the one in Pt(phen)I_5 where the two outer I–I distances are 3.29 and 3.46 Å.

Results and Discussion

The treatment of the platinum compounds *cis*-dihalo(1,10-phenanthroline)platinum(II) and *cis*-dichloro(2,2′-bipyridyl)platinum(II) with molecular iodine yields a variety of

Table IV. Interatomic Distances (Å) and Angles (deg)

		Pt(phen)I_5	
	Pt(phen)I_6	Molecule A	Molecule B
Pt-N(1)	2.10 (2)	2.09 (2)	2.10 (2)
Pt-N(10)	2.09 (2)	2.06 (2)	2.12 (2)
Pt-I(1)	2.677 (2)	2.669 (2)	2.668 (2)
Pt-I(2)	2.662 (2)	2.669 (2)	2.667 (2)
Pt-I(3)	2.548 (3)	2.624 (2)	2.604 (2)
Pt-I(4)	2.613 (2)	2.609 (2)	2.617 (2)
N(1)-Pt-N(10)	79.7 (7)	80.5 (7)	79.2 (7)
N(1)-Pt-I(1)	88.7 (5)	87.2 (4)	88.9 (4)
N(1)-Pt-I(2)	90.4 (5)	90.0 (4)	88.8 (4)
N(1)-Pt-I(3)	94.4 (5)	97.7 (5)	95.6 (5)
N(1)-Pt-I(4)	176.0 (5)	175.0 (5)	174.4 (5)
N(10)-Pt-I(1)	90.4 (4)	92.0 (4)	87.5 (5)
N(10)-Pt-I(2)	90.3 (4)	88.1 (4)	92.8 (5)
N(10)-Pt-I(3)	174.0 (5)	177.5 (5)	173.0 (5)
N(10)-Pt-I(4)	96.6 (5)	95.2 (5)	95.3 (5)
I(1)-Pt-I(2)	178.82 (7)	177.16 (6)	177.61 (6)
I(1)-Pt-I(3)	88.66 (8)	89.57 (6)	87.71 (6)
I(1)-Pt-I(4)	90.02 (6)	90.43 (6)	91.98 (6)
I(2)-Pt-I(3)	90.55 (8)	90.24 (6)	91.80 (7)
I(2)-Pt-I(4)	90.85 (6)	92.39 (6)	90.36 (6)
I(3)-Pt-I(4)	89.30 (8)	86.72 (7)	89.89 (6)
I(1)-I(5)	3.481 (3)	3.457 (3)	
I(2)-I(6)	3.452 (3)	3.289 (3)	
I(5)-I(6)	2.750 (3)	2.739 (3)	
Pt-I(1)-I(5)	101.94 (6)	98.72 (6)	
Pt-I(2)-I(6)	106.05 (7)	108.90 (7)	
I(1)-I(5)-I(6)	164.21 (9)	168.73 (9)	
I(2)-I(6)-I(5)	177.26 (9)	177.52 (8)	
N(1)-C(2)	1.39 (3)	1.37 (3)	1.31 (3)
C(2)-C(3)	1.36 (3)	1.46 (3)	1.51 (3)
C(3)-C(4)	1.38 (4)	1.25 (3)	1.40 (4)
C(4)-C(13)	1.41 (3)	1.46 (3)	1.40 (3)
C(13)-C(5)	1.46 (3)	1.42 (4)	1.40 (3)
C(5)-C(6)	1.33 (3)	1.31 (4)	1.32 (3)
C(6)-C(14)	1.53 (4)	1.55 (4)	1.48 (3)
C(14)-C(7)	1.36 (3)	1.52 (4)	1.41 (3)
C(7)-C(8)	1.38 (4)	1.33 (3)	1.31 (3)
C(8)-C(9)	1.39 (4)	1.39 (4)	1.42 (3)
C(9)-N(10)	1.31 (3)	1.39 (3)	1.33 (3)
N(10)-C(11)	1.32 (3)	1.40 (3)	1.37 (3)
C(11)-C(12)	1.43 (3)	1.40 (3)	1.47 (3)
C(12)-C(13)	1.43 (3)	1.46 (3)	1.39 (3)
C(11)-C(14)	1.48 (3)	1.39 (3)	1.43 (3)
C(12)-N(1)	1.34 (3)	1.35 (3)	1.33 (3)
C(2)-N(1)-C(12)	121 (2)	120 (2)	121 (2)
C(3)-C(2)-N(1)	116 (2)	119 (2)	118 (7)
C(4)-C(3)-C(2)	126 (3)	121 (2)	121 (2)
C(13)-C(4)-C(3)	117 (2)	122 (3)	116 (3)
C(13)-C(5)-C(6)	123 (3)	129 (3)	128 (3)
C(5)-C(6)-C(14)	119 (3)	112 (3)	118 (3)
C(6)-C(7)-C(8)	114 (3)	116 (3)	120 (3)
C(7)-C(8)-C(9)	126 (3)	125 (3)	124 (2)
C(8)-C(9)-N(10)	119 (2)	121 (2)	117 (2)
C(9)-N(10)-C(11)	120 (2)	117 (2)	121 (2)
N(10)-C(11)-C(12)	120 (2)	116 (2)	116 (2)
N(10)-C(11)-C(14)	121 (2)	123 (2)	122 (2)
C(12)-C(11)-C(14)	119 (2)	121 (2)	122 (2)
N(1)-C(12)-C(11)	117 (2)	119 (2)	118 (2)
N(1)-C(12)-C(13)	123 (2)	121 (2)	124 (2)
C(11)-C(12)-C(13)	121 (2)	119 (2)	118 (2)
C(5)-C(13)-C(12)	120 (2)	117 (3)	122 (3)
C(4)-C(13)-C(5)	123 (2)	128 (3)	121 (3)
C(4)-C(13)-C(12)	117 (2)	115 (2)	118 (2)
C(6)-C(14)-C(7)	123 (3)	121 (3)	128 (3)
C(6)-C(14)-C(11)	118 (2)	122 (3)	116 (2)
C(7)-C(14)-C(11)	119 (2)	117 (3)	116 (3)
Pt-N(1)-C(2)	127 (2)	128 (2)	125 (2)
Pt-N(1)-C(12)	112 (2)	111 (2)	114 (2)
Pt-N(10)-C(9)	128 (2)	130 (2)	126 (2)
Pt-N(10)-C(11)	112 (2)	112 (2)	113 (2)

Pt(phen)I_5			
I(3B)-I(4A)	3.677 (3)	Pt(B)-I(3B)-I(4A)	123.00 (7)
I(3B)-I(1A)	3.879 (3)	I(3B)-I(4A)-Pt(A)	174.22 (7)

reaction products depending on the special conditions.

(a) Dihalo(2,2′-bipyridyl)platinum(II) and Iodine. Generally the dihalo(2,2′-bipyridyl)platinum(II) species are more readily oxidized than the dihalo(1,10-phenanthroline)platinum(II) compounds.[11] The same can be said for the chloride–iodide exchange that occurs with an excess of iodine even on recrystallization of the $Pt(bpy)I_2Cl_2$ species resulting in the tetraiodo(2,2′-bipyridyl)platinum(IV) compounds. This difference in behavior with respect to molecular iodine explains the different products that can be obtained by using either $Pt(phen)Cl_2$ or $Pt(bpy)Cl_2$ as starting materials.

In the case of $Pt(bpy)Cl_2$ the normally expected products are actually obtained. Oxidation with a small excess of molecular iodine under moderate conditions (Experimental Section) gives the trans-addition product. By using a large excess of iodine in a high-boiling solvent an additional chloride–iodide exchange occurs and $Pt(bpy)I_4$ is obtained in good yield. This compound can be isolated after addition of iodine to *cis*-diiodo(2,2′-bipyridyl)platinum(II) as well (identical analytical data and coincidence of the lines of the Guinier powder patterns).

(b) Dihalo(1,10-phenanthroline)platinum(II) with Iodine. Starting with $Pt(phen)Cl_2$ a different spectrum of compounds is obtained as pointed out earlier.[11] The occurence of triiodide ions was proposed, but our results show that the additional iodine connects $Pt(phen)I_4$ octahedra forming I_4 units.

The earlier described reaction of iodine with $Pt(phen)Cl_2$ under comparably mild conditions (boiling $CHCl_3$ slurry) finally leads to a black solid with general stoichiometry $Pt(phen)I_6$. The compound "$Pt(phen)Cl_2I_6$"[11] is formed only as an intermediate as evidenced by x-ray powder data. By this reaction it cannot be isolated without by-products. It was obtained in crystalline form only as described above. It crystallizes with 1 mol of solvent/platinum atom. The formula is actually $Pt(phen)Cl_2I_5\cdot S$ ($S = CH_2Cl_2, CHCl_3$) as shown by the analysis and the x-ray structure, which will be published elsewhere. $Pt(phen)Cl_2I_5\cdot CH_2Cl_2$ is built up by $Pt(phen)Cl_2I_2$ octahedra, which are connected by I_2 molecules, with the CH_2Cl_2 molecules only weakly bound. In any case the reaction of $Pt(phen)Cl_2$ or $Pt(phen)I_2$ under moderate conditions (excess of iodine in 1,2-dichlorobenzene, and reaction temperatures up to 170 °C for several days) yields the compound of the stoichiometry $Pt(phen)I_6$, which seems to be the most stable product. Only minor amounts of $Pt(phen)I_5$ can be obtained by this procedure at lower temperatures.

The results show that none of the compounds contains triiodide ions which is in agreement with the spectral data of Hodges et al.[11] Furthermore the columnar stacks of the starting materials[20,21] are not preserved in the oxidation products.

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Registry No. $Pt(phen)I_6$, 53432-57-8; $Pt(phen)I_5$, 62059-01-2; "$Pt(phen)Cl_2I_6$", 53432-69-2; $Pt(bpy)Cl_2I_2$, 62059-02-3; $Pt(bpy)I_4$, 62059-03-4; I_2, 7553-56-2; $Pt(phen)Cl_2$, 18432-95-6; $Pt(bpy)Cl_2$, 13965-31-6; $Pt(bpy)I_2$, 16593-26-3.

Supplementary Material Available: Listings of the structure factors F_o and F_c for $Pt(phen)I_6$ and $Pt(phen)I_5$ (27 pages). Ordering information is given on any current masthead page.

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