Oxidative-addition Reaction of Platinum Acetylacetonate with Iodine in Solid State and Solution. Crystal Structure and Equilibrium Studies of *trans*-bis(acetylacetonato)di-iodoplatinum(IV)

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$Pt(acac)_2$ (acac = acetylacetonate) undergoes an oxidative-addition reaction with molecular iodine both in solution and in the solid state to yield *trans*-$Pt(acac)_2I_2$. In solution the reaction is readily reversible, and data for the equilibrium were determined spectrophotometrically. Mass spectral data of volatilized $Pt(acac)_2I_2$ indicate that the same equilibrium also occurs in the gas phase. A three-dimensional *X*-ray diffraction study from diffractometer data has established the stereochemistry of $Pt(acac)_2I_2$. Crystals are triclinic, space group $P\bar{1}$, with $Z = 1$ in a unit cell of dimensions $a = 7{\cdot}802$, $b = 8{\cdot}703$, $c = 7{\cdot}646$, $\alpha = 95{\cdot}866°$, $\beta = 116{\cdot}321°$, $\gamma = 114{\cdot}844°$. The structure was solved by Patterson and Fourier methods and refined by least squares to R 4·0% for 654 independent observations. The molecule lies on a crystallographic centre of symmetry. Each Pt^{IV} is octahedrally co-ordinated by two oxygen-chelated acetylacetonate ligands and by two iodine atoms in a *trans*-configuration which deviates only slightly from D_{2h} symmetry. The molecules are identically oriented in layers such that each iodine ligand has one unusually close intermolecular $I \cdots I$ contact of 3·559(2) Å. This short distance is indicative of weak intermolecular bonds leading to infinite chains of weakly linked molecules. The readily occurring solid-state reaction of crystalline $Pt(acac)_2$ with solid I_2 may involve diffusion by molecular iodine into the crystalline lattice of $Pt(acac)_2$ followed by electron transfer from the Pt^{II} to the I_2 molecule with concomitant cleavage of the molecular iodine bond to give Pt^{IV}–I formation.

RECENTLY much work has been devoted to oxidative-addition reactions of co-ordinatively unsaturated transition-metal complexes with various covalent molecules.[1,2] Of special interest to us is the class of reactions in

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which a square-planar d^8 metal complex reacts with small molecules to cause covalent bond fission with concomitant formation of a d^6 octahedral product: $M(d^8)L_4 + XY \longrightarrow M(d^6)L_4XY$. In general, these reactions are highly stereospecific, and it is of importance to determine the kinetic, thermodynamic, and other factors which control the formation of *cis*- or *trans*-addition products.

Our investigations of the kinetics and mechanism of oxidative-addition and other reactions of neutral bisbidentate d^8 metal complexes in non-(donor–acceptor) hydrocarbon and halogenocarbon solvents have included a series of reactions involving platinum acetylacetonate, $Pt(acac)_2$, which oxidatively adds molecular halogens [3] and alkyl halides [4] to yield octahedral-like products. $Pt(acac)_2$ also reacts with covalent molecules to give products in which the addendum molecule remains intact, *e.g.* with tetracyanoethylene [4] and nitric oxide.[3]

We report here the preparation of $Pt(acac)_2I_2$ by the solid-state reaction of $Pt(acac)_2$ and I_2, as well as by their reaction in non-aqueous solution. In addition to the results of spectrophotometric measurements on the dissociation equilibrium of $Pt(acac)_2I_2$ in solution and of mass spectral data of volatilized $Pt(acac)_2I_2$, we report a detailed stereochemical analysis of $Pt(acac)_2I_2$ by single-crystal *X*-ray diffraction study.

EXPERIMENTAL

$Pt(acac)_2$ and ultrapure iodine (Ventron Corporation, Alpha Products) were used for all equilibrium measurements; reagent-grade iodine was used for the synthetic reactions. The $Pt(acac)_2$ was purified by recrystallization from benzene. G.C.-Spectrophotometric grade CCl_4 (Baker) was dried (Linde 3A molecular sieves) before use as solvent for the equilibrium measurements.

Preparation of trans-*bis*(*acetylacetonato*)*di-iodoplatinum*(IV).—*Method* (*A*). Saturated CCl_4 solutions of $Pt(acac)_2$ (0·438 g, 0·0011 mol) and I_2 (0·283 g, 0·0011 mol) were mixed at room temperature. The $Pt(acac)_2I_2$ rapidly precipitated from solution as a finely divided black solid (93%).

Method (*B*). A mixture of $Pt(acac)_2$ (0·200 g, 0·005 mol) crystals and solid I_2 (0·129 g, 0·005 mol) was either finely ground for a few seconds or set aside for *ca.* 5 min. In either case a finely divided black solid was obtained; these were shown to be identical from comparison of i.r. spectra (KBr disc) with each other and with the product given by method (A).

The products of these procedures were recrystallized from benzene as dark amber-brown diamond-shaped, plate-like crystals.

Spectroscopic and Equilibrium Measurements.—Equilibrium measurements were carried out on CCl_4 solutions contained in 1 cm pathlength cells which were thermostatted in the cell compartment of a Cary 14M spectrophotometer. Some solutions were prepared in an anhydrous nitrogen atmosphere with rigorous exclusion of oxygen, but since the results were identical with those data obtained for solutions prepared in air, most of the solutions were prepared in air under anhydrous conditions.

Perkin-Elmer 421 and 457 grating i.r. spectrometers were used to record solid-state spectra (4000—250 cm^{-1}). Mass spectra were run on an AEI MS 902 spectrometer over a temperature range of 110—240° by direct insertion of the samples into the ion source. ^1H n.m.r. spectra were recorded on Varian A 60A and T 60 spectrometers, and chemical shifts were measured with respect to tetramethylsilane as internal standard.

X-*Ray Crystallographic Analysis*

Large, well-formed crystals of $Pt(acac)_2I_2$ were obtained by the slow cooling and evaporation of a saturated benzene solution prepared by Soxhlet extraction of the product. A diamond-shaped crystal (0·20 × 0·04 × 0·28 mm along the [100], [010], and [001] directions) was used for data collection and was mounted inside a thin-walled glass capillary along the $[\bar{1}02]$ direction.

Crystal Data.—$C_{10}H_{14}I_2O_4Pt$, $M = 647$, Triclinic, $a = 7{\cdot}802 \pm 0{\cdot}001$, $b = 8{\cdot}703 \pm 0{\cdot}001$, $c = 7{\cdot}646 \pm 0{\cdot}001$ Å, $\alpha = 95{\cdot}866 \pm 0{\cdot}007°$, $\beta = 116{\cdot}321 \pm 0{\cdot}006°$, $\gamma = 114{\cdot}844 \pm 0{\cdot}004°$, $U = 396$ Å^3, $D_c = 2{\cdot}72$, $Z = 1$, $D_m = 2{\cdot}74$ (by flotation), $F(000) = 290$. Space group, $P\bar{1}$ (C_i^1), Mo-K_α radiation (Zr filter), $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 133·0 cm^{-1}.

Preliminary oscillation, Weissenberg, and precession photographs revealed triclinic Laue symmetry C_i-$\bar{1}$, but observed systematic absences of $\{hkl\}$ for $k + l$ odd indicated a crystal mounting which resulted in an *A*-centred cell. This cell was transformed to the conventional reduced primitive cell [5] for indexing purposes. With $Z = 1$, compliance to the centrosymmetric space group $P\bar{1}(C_i^1)$ [rather than the alternative $P1(C_1^1)$] requires that the monomer possess a crystallographic centre of symmetry. The choice of this centrosymmetric space group was verified by the successful refinement of the crystal structure.

Intensity data to 2θ 40° for all independent reflections of four octants (hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}l$) were collected on a full-circle, Datex-controlled General Electric diffractometer with Zr-filtered Mo-K_α radiation. A θ—2θ scan technique was used with a (stationary-crystal)–(stationary-counter) background measurement for 15 s on each side of the peak and a scan speed of 2° min^{-1} for a scan-width of 1·3°. Lattice constants were calculated and least-squares refined [6] from 2θ, χ, and ϕ values of 18 independently centred reflections. The intensities of four standard reflections, measured after each 100 reflections, showed no significant crystal decay or change in alignment during the entire data collection. A Lorentz-polarization correction was applied and a $|F_o|$ calculated for each reflection. Reflections having $I < 2\sigma(I)$ were considered unobserved and omitted from further consideration. The irregular dimensions of the crystal together with the high value of μ resulted in transmission factors varying from 0·105 to 0·601, and hence an absorption correction was applied.[7] No corrections for extinction were made. All data in the range $10° < 2\theta < 40°$ were merged into one asymmetric unit containing 654 independent observed reflections.

Structural Determination.—Initial co-ordinates for the

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TABLE 1

Final atomic positional and anisotropic temperature factors (10^4) [b,c] with estimated standard deviations in parentheses

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pt [a]	0	0	0	139(4)	68(2)	116(3)	31(2)	65(2)	6(2)
I	0·0281(2)	0·3091(1)	−0·0404(2)	291(5)	101(3)	248(4)	92(3)	147(4)	60(3)
O(1)	0·3121(16)	0·0981(13)	0·0672(15)	163(34)	126(22)	187(34)	59(23)	17(30)	5(22)
O(2)	0·0877(16)	0·0934(12)	0·2942(14)	214(37)	75(21)	126(29)	7(23)	83(27)	−18(21)
C(4)	0·7041(27)	0·2523(25)	0·2726(26)	253(59)	229(47)	238(52)	61(43)	114(46)	19(40)
C(1)	0·4827(24)	0·1902(21)	0·2531(24)	140(52)	135(38)	208(54)	50(37)	64(48)	43(38)
C(3)	0·4775(25)	0·2332(22)	0·4302(23)	185(54)	169(42)	162(48)	29(38)	70(40)	17(35)
C(2)	0·2908(27)	0·1865(20)	0·4423(22)	252(61)	94(34)	124(46)	38(38)	81(48)	−3(33)
C(5)	0·3225(28)	0·2468(25)	0·6529(25)	317(63)	206(46)	167(47)	1(43)	137(45)	−2(39)
H(31) [d]	0·6266	0·3066	0·5648						
H(41)	0·7212	0·3298	0·1862						
H(42)	0·8289	0·3243	0·4220						
H(43)	0·7093	0·1448	0·2224						
H(51)	0·2297	0·1395	0·6752						
H(52)	0·4842	0·3043	0·7652						
H(53)	0·2747	0·3365	0·6573						

[a] The platinum atom lies on the crystallographic centre of symmetry and the positional parameters have been so constrained. [b] The anisotropic thermal parameters are of the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. [c] Hydrogen atom isotropic temperature factors were arbitrarily fixed at B 2·5 Å^2. [d] Hydrogen atoms are numbered according to the carbon atom to which they are bonded.

crystallographically independent iodine atom were obtained from a three-dimensional Patterson map. With the platinum atom positioned on the centre of symmetry at the origin, a Fourier map phased on the platinum and iodine atoms failed to indicate the positions of the acetylacetonate carbon and oxygen atoms. Hence, a preliminary least-squares refinement (with anisotropic thermal parameters for the platinum and iodine atoms) followed by a Fourier difference map was carried out to locate the two independent oxygen and five independent carbon atoms, for which R was 14·9%. Anisotropic full-matrix least-squares refinement of the platinum, iodine, oxygen, and carbon atoms converged at R 4·4% and R' 5·4% $\{R' = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{\frac{1}{2}} \times 100$. A Fourier difference map revealed positive peaks indicative of the approximate locations of the acetylacetonate hydrogen atoms. Idealized methyl hydrogen positions were calculated [8] by: (i) a choice of the best-defined hydrogen peak about each methyl carbon, (ii) taking the (ring carbon)–(methyl carbon)–hydrogen bond angle as 109·5° and C–H 1·00 Å, and (iii) a rotation of the idealized hydrogen position twice by 120·0° around the vector formed by the methyl carbon atom and attached ring carbon atom. The idealized position of the seventh hydrogen atom, attached to the central-ring carbon C(3), was calculated assuming C–H 1·00 Å from C(3) on the bisector of the angle formed by the three acetylacetonate ring carbon atoms. The positional and thermal parameters of the seven hydrogen atoms were not varied in the course of the final refinement; an isotropic temperature factor of 2·5 Å^2 was arbitrarily assigned to each hydrogen atom, and idealized hydrogen positions were recalculated after each least-squares cycle. The last least-squares cycle converged at R 4·0% and R' 5·2% with no parameter changing by $>0.5\ \sigma$. A Fourier difference map phased on the input of the last cycle showed the absence of any residual electron density >0.6 eÅ^{-3} except for three peaks of 1·8, 1·2, and 1·2 eÅ^{-3} all peaks being <1.5 Å from either a platinum or iodine position and hence being attributed to 'noise' effects from the heavy atoms. All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors were taken from ref. 9 except those for hydrogen which were from ref. 10. Real and imaginary corrections for the anomalous dispersion of the platinum

TABLE 2

Distances (Å) and bond angles (deg.) with means based on an idealized D_{2h} geometry; estimated standard deviations are in parentheses

(*a*) Intramolecular bonding distances

Pt–I	2·667(1)	C(1)–C(4)	1·506(22)
		C(2)–C(5)	1·515(21)
Pt–O(1)	1·994(9)	Mean	1·511
Pt–O(2)	1·996(8)		
Mean	1·995	C(1)–C(3)	1·390(20)
		C(2)–C(3)	1·388(20)
O(1)–C(1)	1·276(16)	Mean	1·389
O(2)–C(2)	1·262(17)		
Mean	1·269		

(*b*) Selected nonbonding distances

I · · · I$^{\rm I}$	3·559(2)	I · · · O(1)	3·327(9)
O(1) · · · O(2)	2·954(12)	I · · · O(2)	3·308(9)
O(1) · · · O(2′)	2·681(13)	I · · · O(1′)	3·333(10)
		I · · · O(2′)	3·354(9)
		Mean	3·330

(*c*) Bond angles

O(1)–Pt–O(2)	95·4(4)	O(1)–C(1)–C(3)	125·6(12)
O(1)–Pt–O(2′)	84·4(4)	O(2)–C(2)–C(3)	127·2(12)
I–Pt–I′ *	180·0(–)	Mean	126·4
Pt–I–I$^{\rm I}$	155·8(1)		
		O(1)–C(1)–C(4)	114·4(13)
I–Pt–O(1)	89·9(3)	O(2)–C(2)–C(5)	113·3(13)
I–Pt–O(2)	89·1(3)	Mean	113·8
I–Pt–O(1′)	90·1(3)		
I–Pt–O(2′)	90·9(3)	C(3)–C(1)–C(4)	119·9(13)
Mean	90·0	C(3)–C(2)–C(5)	119·4(13)
		Mean	119·7
Pt–O(1)–C(1)	122·3(9)		
Pt–O(2)–C(2)	121·4(8)	C(1)–C(3)–C(2)	127·8(12)
Mean	121·9		

I$^{\rm I}$ is the intermolecular iodine atom related to I by $-x$, $1 - y$, $-z$.

* Required by a crystallographic centre of symmetry to be exactly 180·0°.

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and iodine atoms were applied in the final least-squares cycles and were taken from ref. 11.

The positional and thermal parameters with their estimated standard deviations from the output of the final cycle of refinement are listed in Table 1.* Interatomic distances and bond angles with their estimated standard deviations computed from the full variance-covariance matrix are presented in Table 2.

Computer Programs.—All Patterson and Fourier calculations were carried out with the Blount program,[12] while least-squares refinements were carried out with a local modification of the Busing–Martin–Levy OR FLS program.[13] Other programs used in the structural determination include CABRCELL, a local modification of TRACER,[5] for transformation to a reduced triclinic cell, ANGSET[6] for refinement of lattice parameters and generation of crystal angles for diffraction maxima, DEAR (Blount) for absorption correction based on the Busing–Levy method,[7] DREDGE[14] for data reduction, SORTMERGE[8] for the sorting and merging of data, BLANDA for the calculation of distances and bond angles, MIRAGE[8] for calculations of idealized positions based on given distances and bond angles, PLANES[15] for least-squares planes along with perpendicular displacements of atoms from these planes, ORFFE[16] for calculation of distances and bond angles with e.s.d.s, and ORTEP[17] for drawings.

RESULTS AND DISCUSSION

The mechanism of this surprising and unusual solid-state reaction of molecular iodine with $Pt(acac)_2I_2$ presumably involves rapid diffusion of iodine molecules into the crystalline lattice of $Pt(acac)_2$ molecules followed by electron transfer from Pt^{II} to iodine molecules to give Pt^{IV}–I bonds with concomitant cleavage of the molecular iodine bond. Although the structure of $Pt(acac)_2$ is unknown, the crystal structure of $Pt(acac)_2I_2$ provides evidence in support of this hypothesis.

Description of the Structure.—The crystal structure of $Pt(acac)_2I_2$ consists of discrete monomeric molecules with the two iodine ligands octahedrally co-ordinated to the planar $Pt(acac)_2$ moiety to give a resulting *trans* configuration (Figure 1). The one molecule in the unit cell is crystallographically constrained to C_i-$\bar{1}$ site-symmetry with the platinum atom lying on the centre of symmetry.

The acetylacetonate ligand is experimentally planar, deviations of the atoms being $\pm 0{\cdot}004$ Å, and with the platinum atom only $-0{\cdot}017$ Å out of this plane. The additional equivalence of the corresponding bond lengths and angles of the acetylacetonate ligand results in it possessing the expected localized C_{2v} symmetry. The identical orientations of the two crystallographically equivalent Pt–I bonds within 2° of the normal of the mean $Pt(acac)_2$ plane show that the $Pt(acac)_2I_2$ molecule closely conforms to D_{2h} symmetry. Another corresponding bis(acetonacetonato)dihalogenometal(IV) complex whose structure has been elucidated by *X*-ray crystallography is $Re(acac)_2Cl_2$, which was shown by Lock and Wan[18] to possess two co-planar oxygen-chelated acetylacetonate ligands with the two *trans*-chlorine atoms completing an octahedral-like environment about the central Re^{IV}; the molecule of crystallographic site-symmetry C_i $\bar{1}$ also has an idealized D_{2h} geometry. *trans*-Bis(acetylacetonato)dihalogenometal(IV) complexes are uncommon relative to the known *cis*-isomers, at least in solution[19-29] (*vide infra*).

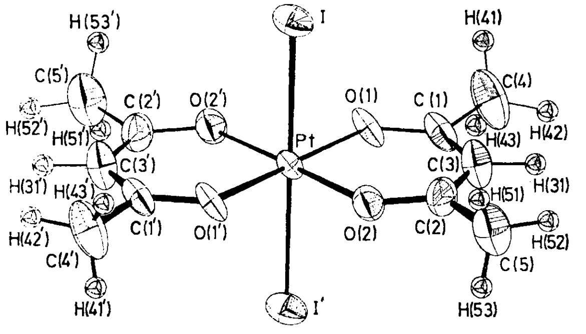

FIGURE 1 Molecular configuration of *trans*-$Pt(acac)_2I_2$. The molecule of idealized D_{2h} geometry has crystallographic site-symmetry C_i-$\bar{1}$. The non-hydrogen atoms are shown as 50% probability thermal ellipsoids

The most prominent crystallographic feature is found from an examination of the crystal arrangement of the $Pt(acac)_2I_2$ molecules shown in Figures 2 and 3. The molecules are identically aligned in layers with the *trans*-Pt–I bonds directed nearly along the *b* axis such that each iodine ligand has one abnormally close intermolecular contact of 3·559(2) Å with an iodine ligand in another molecule related to the first by one lattice translation along the *b* axis. No other intermolecular contacts $<4{\cdot}0$ Å exist in $Pt(acac)_2I_2$ except for H · · · H distances which are all $>2{\cdot}8$ Å, appreciably

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20574 (2 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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longer than the normal van der Waals separation[30] of 2·4 Å for such contacts. The I · · · I separation, which is 0·74 Å shorter than twice the van der Waals radius of iodine (*viz.*, 4·30 Å),[30] is similar to the closest intermolecular contacts[31] of 3·56 Å for crystalline iodine; also, the planar I_8^{2-} anion (of crystallographic site-symmetry C_i $\bar{1}$ and of idealized C_{2h} $2/m$ geometry) found[32] in the crystal structure of CsI_4 has a distance of 3·42 ± 0·015 Å ascribed to a weak bond. On a basis of large differences in nuclear quadrupole effects between crystalline and gaseous iodine together with the crystallographic information, Townes and Dailey[33] suggested that crystalline iodine contains two weak intermolecular covalent bonds per iodine atom. Bersohn[34] later presented a more explicit quantum mechanical treatment of the intermolecular bonding in crystalline I_2 in terms of a band structure and justified his model by its simple description of the iodine nuclear quadrupole coupling constant, the anisotropy of the electrical conductivity, and the optical absorption.* Similarly, the short I · · · I distances in crystalline $Pt(acac)_2I_2$ indicate stronger than van der Waals interactions which lead to the formation of infinite chains of $Pt(acac)_2I_2$ molecules with weak intermolecular linkages. The resulting crystal structure of $Pt(acac)_2I_2$ is in harmony with the suggested mechanism of the solid-state reaction between crystalline $Pt(acac)_2$ and crystalline iodine (*vide supra*).

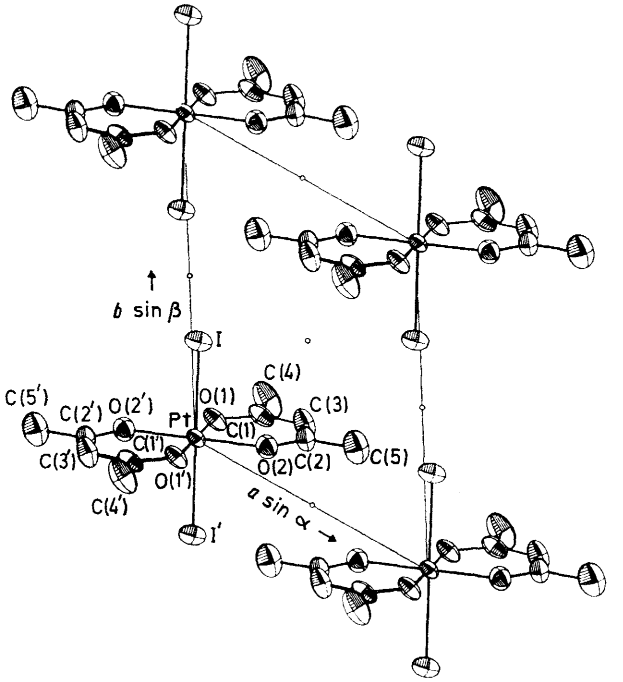

FIGURE 2 [001] Projection of the triclinic unit cell, showing the weak intermolecular I · · · I interactions approximately along the *b* axis

The mean bond lengths for the acetylacetonate ligand in $Pt(acac)_2I_2$ are in excellent agreement with the normally invariant mean values (given in parentheses) reported[37] in a survey of crystallographic data for a considerable number of metal chelates of acetylacetone: C–O 1·269 (1·274), C–C 1·389 (1·390 Å), and $C-CH_3$ 1·511 (1·524 Å).

The mean $Pt^{IV}-O$ bond distance (1·995 Å) in $Pt(acac)_2I_2$ is much shorter than those in trimethyl-4,6-(dioxonyl)platinum(IV) dimer[38] (2·15) and in μ-ethylenediamine-bis[trimethyl(acetylacetonato)platinum-(IV)][39] (2·17 Å) because of the very strong *trans*-influence exerted by the methyl groups opposite the Pt–O bonds in these two trimethyl–metal complexes.[40] In $Pt(acac)_2I_2$ the mean $Pt^{IV}-O$ bond distance, which does not deviate greatly from the Pt–O distance of 1·97 Å predicted from the sum of covalent radii,[30] is closer to the $Pt^{II}-O$ bond distances in $K[Pt(acac)_2Cl]$ for which the mean of the two asymmetric Pt–O bonds

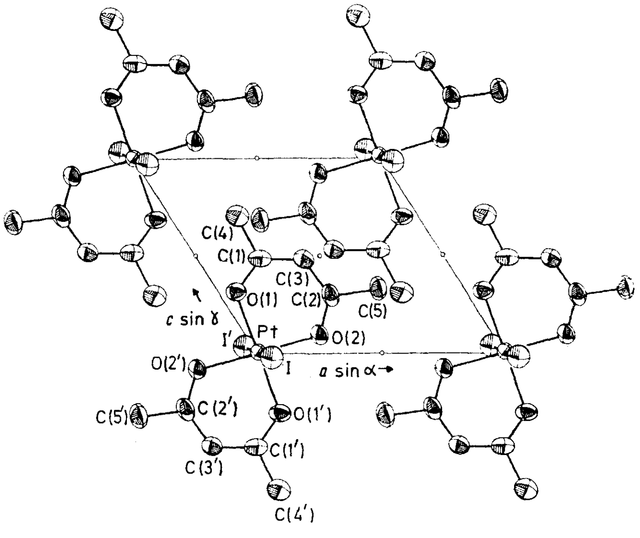

FIGURE 3 [010] Projection of the triclinic unit cell

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* The differences between the reported bond distance of I_2 in the crystalline state (2·68 ± 0·01 Å from *X*-ray crystallography[31]) and those in the gaseous state (2·662 Å from electron diffraction[35] and 2·667 Å calculated from precise spectroscopic measurement[36]) are not statistically significant owing to the relatively large error obtained from the *X*-ray diffraction study done in the pre-(least-squares refinement) time. Hence, there is no bond-length support for the argument[33] that these auxiliary intermolecular bonds are formed at the expense of the main molecular I_2 bond.

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of 1·968(14) and 2·072(14) Å in the one oxygen-chelated acetylacetonate ligand is 2·02 Å.[41] Similarly, it compares favourably with the shorter of the two mean Pt^{II}–O bond distances in bis(acetylacetonato-μ-allyl-platinum) dimer, $[Pt(C_3H_5)(acac)]_2$.[42] In this oxygen-chelated acetylacetonate molecule of pseudo-two-fold symmetry, the two Pt–O distances ***trans*** to the σ bonded bridging allyl ligands are both 2·07(2) Å, while those ***trans*** to the π bonded bridging allyl ligands are 1·98(2) and 1·99(2) Å.

The i.r. and n.m.r. measurements made for various metal acetylacetonate complexes and the resulting controversial interpretations concerning the extent of aromatic character of a metal–acac ring system have been comprehensively reviewed.[43] It was concluded that, while electron delocalization occurs within the six-membered heterocyclic ring for various transition metals and observably influences molecular properties (as reflected by their i.r., n.m.r., e.s.r., and electronic spectra, and by crystallographic data), the n.m.r. spectra provide little or no evidence for the existence of accompanying ring currents (*i.e.*, no magnetic anisotropy relative to that in benzene). A recent review [4] has discussed the structures and bonding of inorganic derivatives of β-diketones.

The O(1) ··· O(2) distance, or 'bite' of the actylacetonate ligand, which varies over a range of *ca.* 0·25 Å for known transition-metal acetylacetonate structures,[37,45] is 2·954 Å in $Pt(acac)_2I_2$. The corresponding values of 2·95 in μ-ethylenediamine-bis[trimethyl(acetylacetonato)platinum(IV)] [39] and 2·976 Å in potassium bis(acetylacetonato)chloroplatinate(II),[41] are both analogous to this, whereas in bis[acetylacetonato-μ-allyl-platinum(II)] the calculated bites (2·88 and 2·85 Å) are smaller. These data are in contradistinction to the trend noted by Lingafelter [45] that the O ··· O bite 'apparently decreases with increasing oxidation state of the metal.' The equality of these distances in the two Pt^{IV} molecules, which have a difference of 0·15 Å in Pt^{IV}–O bond distances, is made possible by the significant change in the O–Pt–O angle from 95·4(4)° in $Pt(acac)_2I_2$ to 85(1)° in $[PtMe_3(acac)]_2(en)$.[39]

The Pt^{IV}–I bond length [2·667(1) Å] is close to the mean value (2·62 Å) found for the terminal Pt^{IV}–I bonds in $[PtI_4]_\infty$ [46] and to the sum of covalent radii (2·64 Å).[30] This covalent Pt^{IV}–I bonding is contrasted to the Pt^{II}–I bonding in $Pt[C_6H_4(AsMe_2)_2]_2I_2$.[47] In this latter centrosymmetric complex, the square-planar Pt^{II} achieves a distorted octahedral co-ordination with elongated Pt^{II}–I distances of 3·50(1) Å which suggests a much more ionic interaction (in the extreme corresponding to a Pt^{II} dication and two I^- anions). From a MO view-point, this tremendous increase in the two Pt^{II}–I distances relative to the two normal bonding Pt^{IV}–I distances may be attributed to the extra electron pair in the Pt^{II} complex occupying a strongly anti-bonding σ-like orbital encompassing primarily the I–Pt–I′ atoms.

Solution Equilibria.—On dissolution in non-(donor–acceptor) solvents such as CCl_4 and cyclohexane, $Pt(acac)_2I_2$ partially dissociates into $Pt(acac)_2$ and molecular iodine. The equilibria involved in the reversible interaction of $Pt(acac)_2$ and I_2 were determined spectrophotometrically in CCl_4 at 24·8° in the region 240—700 nm; the equilibrium data are listed in Table 3.

TABLE 3

Spectrophotometric data from the equilibrium study at 24·8 ± 0·1° for CCl_4 solution

	Total analyt. concn. [a]		Absorbance			
			446 nm		296 nm	
Sol. no.	$10^5 \times [Pt]_T$ (*M*)	$10^5 \times [I]_T$ (*M*)	Obs.[b]	Calc.[c]	Obs.[b]	Calc.[c]
1	2·57	1·414	0·054	0·057	0·356	0·342
2	2·57	2·02	0·074	0·077	0·391	0·398
3	2·59	2·62	0·096	0·098	0·447	0·454
4	2·57	3·32	0·115	0·118	0·501	0·509
5	2·58	4·08	0·137	0·139	0·562	0·566
6	2·58	4·94	0·160	0·160	0·624	0·624
7	2·57	6·04	0·181	0·182	0·678	0·682
8	2·57	7·46	0·209	0·207	0·755	0·747
9	1·54	5·92	0·120	0·122	0·432	0·439
10	2·05	5·92	0·153	0·153	0·562	0·563
11	2·93	5·92	0·199	0·197	0·754	0·749
12	1·46	5·24	0·111	0·109	0·406	0·399
13	1·47	11·00	0·153	0·152	0·516	0·508
14	1·46	13·54	0·162	0·161	0·537	0·529
15	1·46	17·42	0·167	0·171	0·537	0·552

[a] Corrected for CCl_4 density change. [b] Measured in matched 1 cm pathlength cells with respect to a solvent blank. [c] Calc. on the basis of the least-squares value of (6·8 ± 1·1) $\times 10^4$ l. mol^{-1} for the formation constant and the determined molar absorptivities.

In normal room light, equilibrium was attained within the time of mixing of the reactants in all 15 solutions examined.

The rate of attainment of equilibrium was much slower in the dark, however. The kinetics and mechanism of both the thermal and the photochemical reaction are being investigated.[3] The product(s) of the reaction exhibited intense bands at 296 and 446 nm. The relationship between the absorbances of both these bands and the analytical concentrations of platinum and iodine were analysed by conventional nonlinear least-squares techniques [48] on absorbance and mass balance equations of feasible products. The data show that the only product or products formed in significant concentrations have the stoicheiometry $Pt(acac)_2I_2$: $Pt(acac)_2 + I_2 \rightleftharpoons Pt(acac)_2I_2$. The complex has a formation constant of (6·8 ± 1·1) $\times 10^4$ l mol^{-1} for $K = [Pt(acac)_2I_2]/[Pt(acac)_2][I_2]$ and molar absorptivities of 43,500 ± 1900 and 13,400 ± 590 at 296 and 446 nm.

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These values of the parameters were used to calculate the theoretical absorbances given in Table 3. The differences between observed and calculated absorbances are randomly distributed and show no smooth trends when the concentration of either of the reactants is varied with the concentration of the other held constant. The two intense bands of the electronic spectrum of the product(s) most likely result from the sole formation of the *trans*-isomer of the octahedral-like $Pt(acac)_2I_2$, as discussed later, and probably arise from charge-transfer transitions of electrons on the iodide ligands to the Pt^{IV}. The energies of the two bands are in qualitative agreement with the predicted values calculated (on the basis of assumed regular octahedral co-ordination) with Jørgensen's equation, $\tilde{\nu} = 30{,}000\ [X_{opt}(L) - X_{opt}(M)]$ (units in cm^{-1}), involving optical electronegativities.[49] Values of $X_{opt}\ (Pt^{IV}) = 1{\cdot}7$ and $X_{opt}(I^-) = 2{\cdot}5$ for a π and $3{\cdot}0$ for a σ electron[49] were used to calculate the band energies of 24,000 cm^{-1} for a $\pi(I)\rightarrow e_g(Pt^{IV})$ transition and 39,000 cm^{-1} for a $\sigma(I)\rightarrow e_g(Pt^{IV})$ transition which may be compared with the observed values of 22,500 and 33,000 cm^{-1}.

The solution and solid-state electronic spectra of $Pt(acac)_2I_2$ are closely similar. The solid-state spectrum of a thin film of the compound sublimed on a quartz window has bands at 293 and 475 nm as compared with the CCl_4 solution bands at 296 and 446 nm. Thus, it is most likely that $Pt(acac)_2I_2$ retains its *trans*-configuration upon dissolution. A sharp singlet resonance of the methyl protons was observed for a saturated solution (*ca.* 8 g l^{-1}, $\sim 1 \times 10^{-3}M$) of $Pt(acac)_2I_2$ in CD_2Cl_2 at 30°. (Under these conditions *ca.* 5% of $Pt(acac)_2I_2$ is dissociated in solution.) The chemical shift of this peak, δ 1·52 p.p.m., is shifted upfield from the methyl resonance of the parent $Pt(acac)_2$ at δ 1·90 p.p.m. The rate of equilibrium interchange, $Pt(acac)_2 + I_2 \rightleftharpoons Pt(acac)_2I_2$, is slow on the n.m.r. time-scale in the dark at ambient temperatures.[3] With the reasonable assumption that the Pt–O bonds of $Pt(acac)_2I_2$ are nonlabile at ambient temperatures, then the observation of a single methyl resonance is also consistent with the *trans*-configuration. Unfortunately, variable-temperature ^1H n.m.r. experiments were difficult to perform because of the low solubility of $Pt(acac)_2I_2$ in a wide range of solvents, and thus we cannot definitely rule out the possibility that the observation of a single methyl resonance for $Pt(acac)_2I_2$ is due to a rapid exchange on the n.m.r. time-scale. The stereochemistry in solution of dihalogenobis(acetylacetonato)-complexes of the Group IV elements of Ti^{IV},[19-21] Zr^{IV},[21,22] Hf^{IV},[21,22] Ge^{IV},[23,24] and Sn^{IV} [21,23,25-27] has been extensively subjected to a large number of spectroscopic and dipole-moment studies, and with few exceptions the results overwhelmingly point to the existence of these monomeric complexes in solution as non-rigid *cis*-geometrical isomers. Apart from the suggestion that $Si(acac)_2Cl_2$ has a *trans*-configuration in solution,[28] it has been recently indicated[24] from n.m.r. data that *ca.* 15—20% of the $Ge(acac)_2Cl_2$ molecules adopt a *trans*-configuration in solution instead of the exclusively *cis*-configuration previously reported.[23] The $Ti(acac)_2I_2$ complex was recently prepared[29] and estimated from conductance, e.s.r., and low-temperature n.m.r. studies to exist in dichloromethane solution not only as *ca.* 50% *cis*- and *ca.* 40% *trans*-$Ti(acac)_2I_2$ but also as *ca.* 10% of an electrolytic dissociation product presumed to be $[Ti(acac)_2I]^+I^-$. The n.m.r. spectra exhibited the effects of rapid *cis–trans* isomerization.[29]

Other interesting comparisons with the $Pt(acac)_2$ oxidation are the oxidative addition reactions of square-planar platinum(II) complex ions with molecular halogens in aqueous solution in the presence of halide anions: $PtL_4 + X_3^- \rightleftharpoons PtL_4X_2 + X^-$ where L is a nitrogen base or CN^- and X is Cl, Br, or I.[50] These reactions, which invariably yield a *trans*-product,[51] have been widely used in the stereospecific synthesis of platinum(IV) compounds.[51] One notable exception to *trans*-addition is the oxidation of $Pt(PEt_3)_3Ph_2$ by iodine in which the addition gives the *cis*-product.[52]

Mass Spectral Measurements.—$Pt(acac)_2I_2$ readily sublimes and condenses unchanged on a cold finger. The gas-phase behaviour of the compound was investigated with mass spectroscopy. In the highest temperature range examined, 190—240°, the data indicate that almost complete dissociation of $Pt(acac)_2I_2$ into $Pt(acac)_2$ and I_2 occurs in the gas phase. At these temperatures and at several ionizing voltages in the range 14—70 eV, the mass spectrum of $Pt(acac)_2I_2$ is essentially a superposition of those of $Pt(acac)_2$[53] and I_2 [the ions $I_2^{\cdot+}$ (*m/e* 254) and I^+ (*m/e* 127) were observed]. At the lowest electron-beam energy (14 eV) and at 240°, the predominant ions in the spectrum are $Pt(acac)_2^{\cdot+}$ (*m/e* 393) and $I_2^{\cdot+}$ (*m/e* 254) with ion currents of 67 and 22% relative to the total ion current. However, in the temperature range 110—180° both the molecular ion, $Pt(acac)_2I_2^{\cdot+}$ (*m/e* 647) and the ion $Pt(acac)_2I^+$ (*m/e* 520) were detected with abundances relative to $Pt(acac)_2^{\cdot+}$ of 0·75 and 9·0%, respectively, at 110° and 70 eV. At any given ionizing voltage, the ratio of the $Pt(acac)_2I_2^{\cdot+}$ ion current to the ion current of either $Pt(acac)_2^{\cdot+}$ or $I_2^{\cdot+}$ decreases markedly with increasing temperature. The ion $Pt(acac)_2I^+$ exhibits behaviour similar to that of the molecular ion. These temperature dependencies are relatively independent of ionizing voltage. Hence, these data strongly indicate that the abundances of the molecular ion and of the $Pt(acac)_2I^+$ ion are largely under thermodynamic control.

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