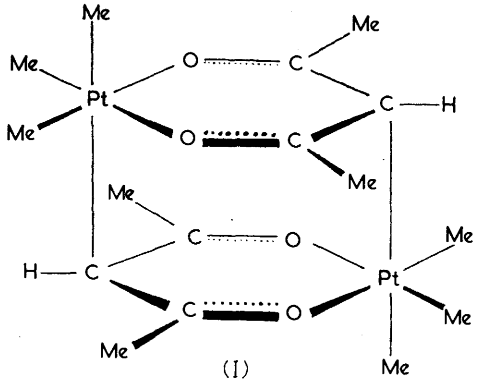
102. *The Stereochemistry of β-Diketo-complexes with Trimethylplatinum*(IV). *Part IV.* The Crystal Structure of μ-Ethylenediamine-bis[trimethyl(acetylacetonato)platinum*(IV)].

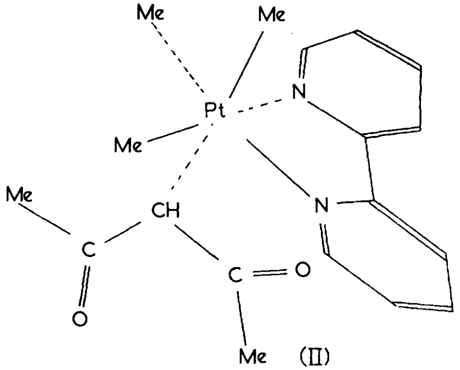
By Alan Robson and Mary R. Truter.

A partial three-dimensional crystal structure analysis of the complex named in the title has unequivocally established its stereochemistry. There are four molecules of the binuclear complex in a monoclinic unit cell having $a = 23{\cdot}19$, $b = 6{\cdot}46$, $c = 16{\cdot}42$ Å, $\beta = 103°$ and space group $I2/a$. Each molecule is arranged so that the centre of the carbon–carbon bond in the ethylenediamine group lies on a centre of symmetry in the crystal, and the two nitrogen atoms are co-ordinated to different platinum atoms so that the ethylenediamine group forms a bridge between the two halves of the binuclear complex. Each platinum atom is octahedrally co-ordinated by one nitrogen atom, by the two oxygen atoms of a chelate acetylacetone and three methyl groups in the usual *cis* configuration for a trimethylplatinum derivative. The acetylacetone group is planar and there are no other atoms close to the γ-carbon atom; in particular, there is no bond between this atom and platinum.

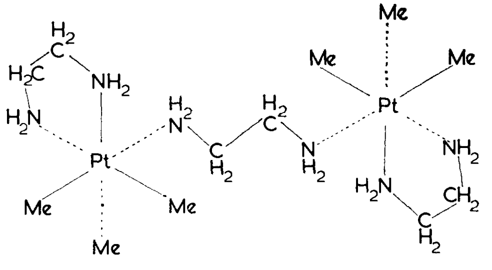
When a solution of trimethyl(acetylacetonato)platinum dimer $(Me_3Pt\ acac)_2$ (I) is treated with a solution of bipyridyl the yellow complex which results is trimethyl(diacetylmethyl)-bipyridylplatinum, Me_3 acac bipy Pt (II). Although the crystal structure of (I) itself has not been determined, the information available[1] strongly suggests that the dimeric molecule is structurally analogous to the dimeric trimethylplatinum complexes of 4,6-dioxononane[1]



(I)



(II)



(III)

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* Part III, Swallow and Truter, *Proc. Roy. Soc.*, 1962, *A*, **266**, 527.

[1] Swallow and Truter, *Proc. Roy. Soc.*, 1960, *A*, **254**, 205.

and ethyl acetoacetate[2] which contain a tridentate β-dicarbonyl compound. Determination of the crystal structure of (II) revealed[3] that the acetylacetone acts as a monodentate ligand.

In a study of the reactions between nitrogen-containing ligands and dimeric trimethyl-(β-diketo)platinum compounds,[4] one of the products was $(Me_3\,acac\,Pt)_2en$ (en = ethylenediamine). The infrared spectral data for this compound suggested that it contained a chelate acetylacetone ligand. Although it seems to be analogous to the known [5] cation in $[(Me_3\,en\,Pt)_2\,en]^{2+}2I^-$, (III), it could not be prepared from the latter by standard methods. An account of the preparation and properties of these compounds will be given separately.[4] We undertook a crystal structure analysis of $(Me_3\,acac\,Pt)_2en$ to establish its stereochemistry; for this purpose three-dimensional data about one axis sufficed.

METHODS AND RESULTS

Crystal Data.—$C_{18}H_{40}N_2O_4Pt_2$, $M = 738{\cdot}7$, m. p. 196—198° (decomp.). Monoclinic, $a = 23{\cdot}19 \pm 0{\cdot}03$, $b = 6{\cdot}46 \pm 0{\cdot}01$, $c = 16{\cdot}42 \pm 0{\cdot}02$ Å, $\beta = 103{\cdot}0 \pm 0{\cdot}3°$. $U = 2397$ Å^3, $D_m = 2{\cdot}05$ (by flotation), $Z = 4$, $D_c = 2{\cdot}05$, $F(000) = 1400$. Space group $I2/a$ (C_{2h}^6, No. 15) determined by structure analysis. Cu-K_α radiation single-crystal oscillation and Weissenberg photographs, absorption coefficient, $\mu = 221$ cm.$^{-1}$, no absorption correction applied.

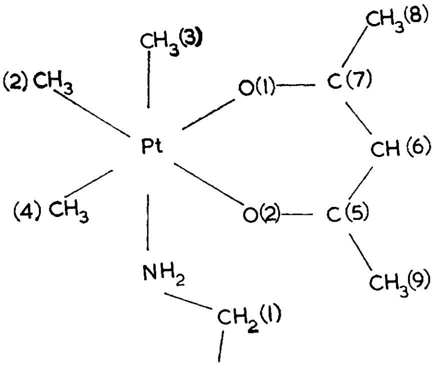

FIG. 1. The numbering of the atoms in the asymmetric unit.

Two-dimensional Structure Determination.—The systematic absences were consistent with two space groups, *Ia* and *I*2/*a* (this orientation has been chosen because the unit cell for *C*2/*c*, has an inconvenient β angle, 150°). The calculated molecular weight with four molecules per unit cell was 740, in agreement with the formula obtained by chemical analysis; if the space group were *Ia*, no molecular symmetry would be required, but in *I*2/*a* the one ethylenediamine group in the molecule must be situated with the centre of the carbon–carbon bond either on a centre of symmetry or on a 2-fold axis and the two platinum atoms would be related by this symmetry element.

We first located the platinum atoms by Patterson projections down [010] and [100]. In the [010] projection there was one large peak, identified as a Pt–Pt vector; this gave the x and z co-ordinates. The [100] projection was diagnostic for the space group; there were three large peaks of which one was on the line $v = 0$ at $w = 2z$ indicating that there were platinum atoms related by a 2-fold axis, the other two peaks were at $2y,0$ and $2y$, $2z$. From the two projections a consistent set of fractional co-ordinates was obtained for platinum, $x/a = 0{\cdot}10$, $y/b = 0{\cdot}88$, $z/c = -0{\cdot}075$. Refinement by least squares gave $R_{(h0l)} = 0{\cdot}211$ and $R_{(0kl)} = 0{\cdot}169$ for platinum only.

We had to locate one carbon atom, C(1) and one nitrogen atom, N, of the ethylenediamine, three methyl groups C(2), C(3), and C(4) and the five carbon and two oxygen atoms

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[2] Hazell and Truter, *Proc. Roy. Soc.*, 1960, *A*, **254**, 218.

[3] Swallow and Truter, *Proc. Roy. Soc.*, 1962, *A*, **266**, 527.

[4] Kite and Truter, Part V, in the press.

[5] Truter and Cox, *J.*, 1956, 948.

of acetylacetone; hydrogen atoms were ignored. The numbering of the atoms is shown in Fig. 1.

Three-dimensional Structure Determination.—Attempts to locate the light atoms in projection were unsuccessful so the three-dimensional observations were used for subsequent work. Refinement of the co-ordinates of the platinum brought $R_{(hkl)}$ to 0·217; the thermal motion of the platinum was assumed to be isotropic and the scale factor for each layer line about the b axis was adjusted to make $\Sigma|F_o| = \Sigma|F_c|$ for that layer line. A difference Fourier synthesis was then computed to give a map of the electron density from which the platinum contribution had been removed. An octahedral arrangement of atoms about platinum could be distinguished; the two with the highest electron density were adjacent and were taken to be the oxygen atoms.

At first we assumed that the centre of the ethylenediamine group lay on a 2-fold axis, as in the $[(\mathrm{Me_3\ en\ Pt})_2\mathrm{en}]^{2+}$ cation, so we also identified a small peak near this axis as C(1) and its neighbour in the octahedron as N; the three carbon atoms of the methyl groups were then in the *cis*-configuration, as found in all other trimethylplatinum derivatives. Two cycles of refinement with the platinum atom, and seven light atoms reduced R to 0·194. Study of the temperature factors showed that one oxygen with a high value of U (the mean square amplitude of vibration), 0·07 Å², should be interchanged with a carbon atom for which the value of U was apparently negative; the *cis*-configuration was preserved.

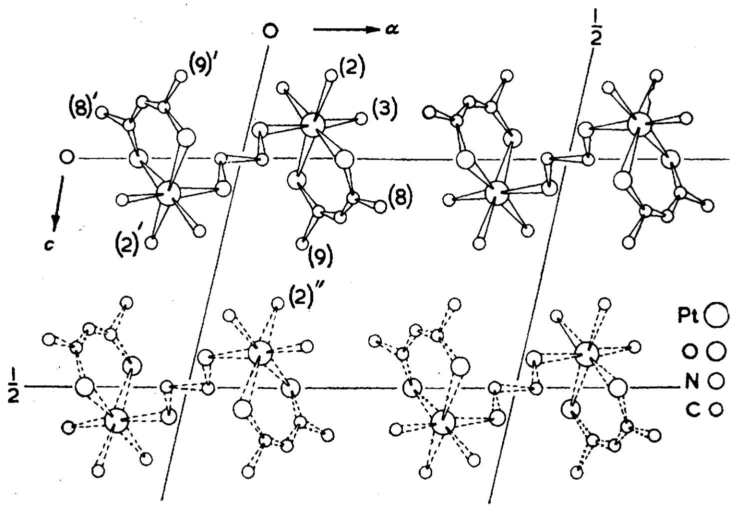

FIG. 2. Projection of the structure along [010]. The molecules shown by full lines lie on the centres of symmetry at (0,½,0) and (½,½,0) molecules shown by broken lines lie on the centres of symmetry at (0,0,½) and (½,0,½).

With the new allocation of oxygen atoms it was possible to find the remaining atoms of the acetylacetone group in the difference map; these were added and the R value for the platinum and all the light atoms was 0·182. However, the temperature factor for C(1) was large, 0·19 Å², and increased in every cycle indicating that this atom had been misplaced, further the value of U for nitrogen was 0·08 Å² while that for C(3) was 0·04 Å². Interchange of N and C(3) would preserve the *cis*-configuration and require C(1) to be near the centre of symmetry at 0,½,0. A suitable peak was visible on the difference map so C(1) was put in at the new position, N and C(3) were interchanged and a new set of structure factors was calculated; R fell to 0·138 and no atoms showed abnormalities of temperature factor. The structure is shown in projection in Fig. 2.

Four cycles of refinement, all the atoms being assumed to vibrate isotropically, reduced R to 0·09 and gave no more shifts in parameters as large as their corresponding standard deviations. As a final check on the correctness of the structure, a three-dimensional

TABLE 1.

Final atomic parameters.

				Å						Å	
	x/a	y/b	z/c	X'	Y	Z	$\sigma(X)$	$\sigma(Y)$	$\sigma(Z)$	$\bar{U}_{\text{iso}}$	$\sigma(\bar{U})$
Pt......	0·0969	0·0916	−0·0745	2·522	0·592	−1·193	0·003	0·004	0·003	0·0303	0·0006
O(1) ...	0·158	0·310	−0·001	3·67	2·00	−0·02	0·04	0·04	0·04	0·05	0·01
O(2) ...	0·093	−0·047	0·045	1·99	−0·31	0·73	0·03	0·04	0·03	0·03	0·01
N	0·017	0·295	−0·064	0·63	1·90	−1·02	0·05	0·06	0·05	0·05	0·02
C(1) ...	0·032	0·431	0·002	0·73	2·79	0·03	0·07	0·08	0·08	0·07	0·02
C(2) ...	0·107	0·260	−0·185	3·16	1·68	−2·96	0·07	0·10	0·07	0·07	0·02
C(3) ...	0·167	−0·083	−0·090	4·20	−0·54	−1·44	0·06	0·09	0·07	0·05	0·02
C(4) ...	0·036	−0·094	−0·159	1·42	−0·61	−2·54	0·06	0·08	0·06	0·05	0·02
C(5) ...	0·136	−0·025	0·114	2·74	−0·16	1·82	0·06	0·07	0·06	0·04	0·02
C(6) ...	0·173	0·103	0·128	3·54	0·67	2·05	0·05	0·08	0·06	0·04	0·02
C(7) ...	0·184	0·297	0·077	3·98	1·92	1·23	0·06	0·08	0·07	0·05	0·02
C(8) ...	0·232	0·434	0·103	5·00	2·80	1·66	0·07	0·09	0·07	0·06	0·02
C(9) ...	0·123	−0·163	0·185	2·16	−1·05	2·97	0·07	0·09	0·08	0·07	0·03

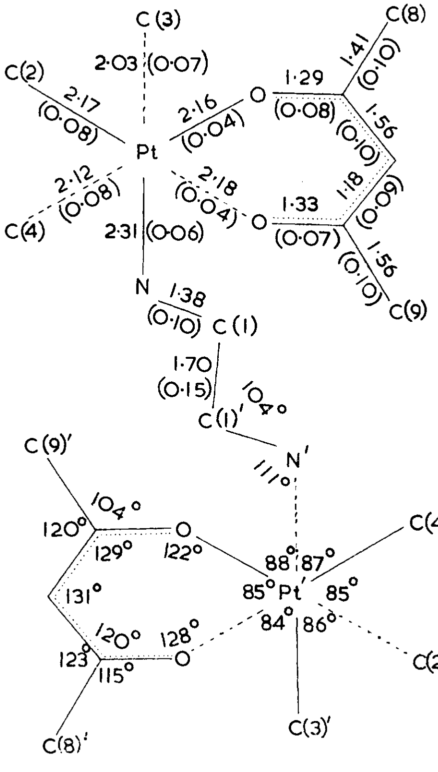

FIG. 3. Diagram of one molecule showing the bond lengths, in Å, with their standard deviations in parentheses, and most of the bond angles. The standard deviations in the bond angles are 6° for ∠C–C–C, ∠O–C–C, and ∠N–C(1)–C and 4° for ∠C–O–Pt, and ∠C(1)–N–Pt. All the bond angles round the platinum atom and their standard deviations are given in Table 3.

For clarity only some atoms have been designated, the designations of the others can be deduced by comparison with Fig. 1.

difference Fourier synthesis was computed; the resulting electron density map did not show any significant peaks or troughs.

Results.—The final atomic parameters are shown in Table 1 as fractional co-ordinates, and as co-ordinates (X', Y, and Z') in Å with respect to orthogonal axes parallel to the crystallographic a, b, and c^* axis, respectively. The standard deviations in Å with respect to the crystallographic axes, and the mean square amplitudes of vibration, U_{iso} and their standard deviations are also included.

Observed and calculated structure factors are given in Table 2. The bond lengths, their standard deviations and most of the bond angles are displayed in Fig. 3; the bond angles round the platinum atom and their standard deviations are shown in Table 3.

The plane through the 7 atoms of the acetylacetone group was calculated, its equation

TABLE 2.

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
0	2	0	210	206	8	0	-2	277	322	5	1	4	200	-165	9	1	-6	202	-214
0	4	0	230	-211	10	0	-2	265	279	7	1	4	212	-173	13	1	-6	164	167
0	6	0	306	-207	12	0	-2	115	-109	9	1	4	84	54	15	1	-6	125	99
0	0	2	452	507	14	0	-2	357	-352	11	1	4	207	189	17	1	-6	110	-52
0	0	4	230	-206	16	0	-2	142	-142	15	1	4	155	-133	4	1	-7	349	320
0	0	6	387	-403	18	0	-2	218	216	2	1	5	164	148	6	1	-7	286	273
0	0	8	346	-334	20	0	-2	160	170	4	1	5	357	331	8	1	-7	164	-152
0	0	12	211	229	2	0	-4	374	-381	8	1	5	238	-212	10	1	-7	288	-309
0	0	14	208	211	4	0	-4	162	-167	10	1	5	228	-213	12	1	-7	114	-111
2	0	0	199	215	6	0	-4	317	339	14	1	5	231	200	14	1	-7	201	211
4	0	0	411	-515	8	0	-4	300	315	1	1	6	270	231	16	1	-7	171	207
6	0	0	304	-325	12	0	-4	306	-332	3	1	6	205	164	20	1	-7	142	-177
8	0	0	103	106	14	0	-4	169	-170	7	1	6	192	-179	1	1	-8	188	164
10	0	0	386	399	16	0	-4	117	117	11	1	6	161	149	3	1	-8	196	167
12	0	0	235	232	18	0	-4	219	218	13	1	6	133	130	7	1	-8	205	-200
14	0	0	262	-264	2	0	-6	236	-233	2	1	7	197	-183	9	1	-8	88	-51
16	0	0	323	-320	4	0	-6	244	238	4	1	7	253	221	11	1	-8	178	171
20	0	0	207	185	6	0	-6	394	407	6	1	7	270	284	13	1	-8	123	126
0	1	1	428	463	10	0	-6	372	-397	10	1	7	241	-221	2	1	-9	237	204
0	1	5	293	-313	12	0	-6	267	-289	12	1	7	173	-153	4	1	-9	246	235
0	1	7	345	-351	14	0	-6	112	86	16	1	7	183	188	6	1	-9	87	35
0	1	9	187	-175	16	0	-6	226	256	3	1	8	173	152	8	1	-9	267	-265
0	1	13	171	169	20	0	-6	161	-166	5	1	8	159	144	10	1	-9	203	-205
0	1	15	112	107	4	0	-8	409	407	7	1	8	97	-94	12	1	-9	124	125
0	2	2	161	133	6	0	-8	177	192	9	1	8	180	-160	14	1	-9	253	266
0	2	4	87	-102	8	0	-8	280	-294	2	1	9	340	-323	16	1	-9	112	58
0	2	6	175	-177	10	0	-8	395	-439	6	1	9	256	239	18	1	-9	142	-155
0	2	8	101	-78	14	0	-8	298	320	8	1	9	183	186	1	1	-10	175	140
0	3	1	51	18	16	0	-8	126	148	12	1	9	182	-192	5	1	-10	188	-184
0	3	3	49	50	18	0	-8	131	-134	1	1	10	192	-168	7	1	-10	96	-66
0	4	2	112	-113	20	0	-8	161	-193	5	1	10	180	161	9	1	-10	141	134
0	4	4	95	73	2	0	-10	282	295	2	1	11	196	-188	11	1	-10	147	155
0	4	6	160	165	4	0	-10	200	212	4	1	11	200	-196	15	1	-10	112	-134
0	4	8	107	124	6	0	-10	133	-112	8	1	11	180	173	2	1	-11	290	266
0	5	1	269	-258	8	0	-10	255	-277	10	1	11	114	95	6	1	-11	201	-193
0	5	5	155	160	10	0	-10	116	-101	1	1	12	152	-144	8	1	-11	179	-170
0	5	7	158	205	12	0	-10	243	241	3	1	12	111	-106	12	1	-11	189	199
0	6	2	176	-110	14	0	-10	228	245	2	1	13	113	43	3	1	-12	130	-119
0	6	6	133	159	18	0	-10	209	-201	4	1	13	164	-139	9	1	-12	173	143
0	6	8	104	126	2	0	-12	227	234	6	1	13	142	-123	6	1	-13	207	-210
2	0	2	451	452	6	0	-12	211	-227	3	1	14	142	-120	10	1	-13	197	179
4	0	2	183	142	10	0	-12	173	184	2	1	15	141	150	16	1	-13	141	-143
6	0	2	305	-320	12	0	-12	205	205	6	1	15	133	-144	2	2	0	48	68
8	0	2	261	-280	16	0	-12	174	-189	4	1	-1	486	-551	4	2	0	104	-134
10	0	2	167	176	4	0	-14	160	-188	6	1	-1	274	-308	6	2	0	201	-210
12	0	2	395	435	10	0	-14	209	217	8	1	-1	189	198	10	2	0	146	131
14	0	2	136	89	14	0	-14	159	-171	10	1	-1	338	349	3	2	1	303	-385
16	0	2	243	-255	16	0	-14	125	-144	14	1	-1	267	-264	5	2	1	199	-252
18	0	2	223	-224	1	1	0	194	-266	16	1	-1	148	-163	7	2	1	215	246
2	0	4	390	403	3	1	0	246	-262	20	1	-1	183	186	9	2	1	409	409
4	0	4	321	357	7	1	0	183	156	1	1	-2	374	-382	13	2	1	202	-227
6	0	4	112	-112	9	1	0	180	158	3	1	-2	165	-161	15	2	1	119	-134
8	0	4	335	-337	11	1	0	114	-80	5	1	-2	307	307	19	2	1	156	178
10	0	4	154	-149	13	1	0	256	-234	7	1	-2	112	110	2	2	2	170	159
12	0	4	216	206	17	1	0	132	119	9	1	-2	183	-163	4	2	2	66	-48
14	0	4	289	268	2	1	1	315	289	11	1	-2	194	-197	6	2	2	196	-201
18	0	4	207	-188	4	1	1	312	-278	13	1	-2	125	-109	8	2	2	86	-69
4	0	6	281	311	6	1	1	348	-344	17	1	-2	170	147	12	2	2	131	120
6	0	6	243	268	8	1	1	144	-113	2	1	-3	412	-374	1	2	3	274	300
8	0	6	122	-121	10	1	1	317	292	4	1	-3	258	-272	3	2	3	147	-162
10	0	6	298	-318	12	1	1	284	266	8	1	-3	345	360	5	2	3	398	-431
12	0	6	117	-100	16	1	1	251	-247	10	1	-3	168	171	7	2	3	104	-106
14	0	6	199	203	20	1	1	142	117	12	1	-3	169	-183	9	2	3	259	271
16	0	6	160	156	22	1	1	136	154	14	1	-3	210	-221	11	2	3	196	213
2	0	8	350	-362	1	1	2	93	64	18	1	-3	207	201	15	2	3	194	-211
4	0	8	99	84	3	1	2	202	-167	1	1	-4	188	-180	2	2	4	184	168
6	0	8	389	390	5	1	2	317	-278	5	1	-4	242	239	4	2	4	136	121
8	0	8	139	132	9	1	2	252	232	9	1	-4	268	-240	8	2	4	165	-155
10	0	8	225	-217	11	1	2	105	97	11	1	-4	142	-137	1	2	5	395	405
12	0	8	200	-233	13	1	2	151	-124	15	1	-4	142	147	3	2	5	218	210
2	0	10	350	-369	15	1	2	148	-141	2	1	-5	402	-355	5	2	5	233	-241
4	0	10	230	-216	2	1	3	362	346	4	1	-5	162	154	7	2	5	280	-309
6	0	10	190	167	4	1	3	183	159	6	1	-5	321	295	11	2	5	240	268
8	0	10	234	250	6	1	3	294	-278	8	1	-5	198	193	13	2	5	148	149
12	0	10	161	-193	8	1	3	334	-318	10	1	-5	138	-131	15	2	5	127	-122
14	0	10	131	-152	12	1	3	280	264	12	1	-5	265	-278	17	2	5	178	-195
4	0	12	234	-238	14	1	3	178	175	16	1	-5	196	227	4	2	6	158	154
8	0	12	128	140	16	1	3	136	-119	18	1	-5	112	132	6	2	6	120	102
2	0	14	131	153	18	1	3	164	-174	3	1	-6	262	229	10	2	6	114	-95
2	0	-2	230	-213	1	1	4	257	240	5	1	-6	176	152	1	2	7	172	146
4	0	-2	520	-600	3	1	4	96	83	7	1	-6	173	-164	3	2	7	286	298

TABLE 2. (*Continued.*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
7	2	7	215	−226	6	2	−6	202	174	4	3	3	75	−51	13	3	−4	127	132
9	2	7	199	−192	1	2	−7	208	204	1	3	4	382	399	15	3	−4	272	261
13	2	7	178	194	3	2	−7	331	361	5	3	4	365	−360	19	3	−4	142	−140
2	2	8	99	−117	[illegible]	2	−7	312	−310	7	3	4	257	−254	21	3	−4	135	−157
6	2	8	110	137	9	2	−7	172	−150	9	3	4	121	117	8	3	−5	110	−76
1	2	9	148	−125	11	2	−7	167	117	11	3	4	250	258	12	3	−5	103	83
3	2	9	204	182	13	2	−7	240	238	15	3	4	183	−182	1	3	−6	103	80
5	2	9	214	219	17	2	−7	198	−202	17	3	4	140	−169	3	3	−6	354	360
9	2	9	174	−196	4	2	−8	180	154	21	3	4	150	154	5	3	−6	161	148
11	2	9	127	−134	8	2	−8	102	−78	2	3	5	98	−63	7	3	−6	247	−231
15	2	9	149	160	10	2	−8	152	−137	1	3	6	275	277	9	3	−6	317	−254
2	2	10	138	−133	14	2	−8	120	103	3	3	6	253	244	13	3	−6	242	228
1	2	11	206	−194	1	2	−9	308	299	7	3	6	318	−324	15	3	−6	196	161
5	2	11	150	169	5	2	−9	264	−247	9	3	6	131	−121	17	3	−6	114	−136
7	2	11	154	183	7	2	−9	249	−230	11	3	6	178	179	19	3	−6	163	−187
11	2	11	153	−192	11	2	−9	215	225	13	3	6	200	196	4	3	−7	111	−57
3	2	13	156	−177	15	2	−9	152	−145	17	3	6	156	−167	1	3	−8	253	252
7	2	13	153	192	17	2	−9	178	−172	3	3	8	249	234	3	3	−8	213	192
1	2	−1	235	−271	2	2	−10	154	132	5	3	8	166	149	5	3	−8	182	−151
3	2	−1	230	−247	1	2	−11	143	140	7	3	8	173	−140	7	3	−8	297	−283
5	2	−1	211	197	3	2	−11	200	−185	9	3	8	197	−212	9	3	−8	103	−58
7	2	−1	382	423	5	2	−11	270	−263	13	3	8	140	151	11	3	−8	242	187
9	2	−1	92	114	9	2	−11	254	227	1	3	10	203	−187	13	3	−8	158	130
11	2	−1	233	−230	11	2	−11	150	155	5	3	10	197	182	17	3	−8	183	−197
13	2	−1	224	−226	13	2	−11	126	−92	7	3	10	114	97	1	3	−10	229	201
17	2	−1	214	211	15	2	−11	156	−199	9	3	10	116	−132	3	3	−10	107	−82
4	2	−2	176	−185	2	2	−12	122	105	11	3	10	139	−180	5	3	−10	312	−285
6	2	−2	132	−131	3	2	−13	218	−211	1	3	10	200	−187	7	3	−10	133	−118
8	2	−2	127	137	7	2	−13	199	200	3	3	12	116	−121	9	3	−10	175	146
10	2	−2	168	180	9	2	−13	178	173	7	3	12	180	207	11	3	−10	242	203
14	2	−2	134	−114	13	2	−13	154	−169	11	3	12	126	−143	15	3	−10	247	−195
1	2	−3	304	−308	7	2	−15	154	167	13	3	12	93	−98	17	3	−10	113	−101
5	2	−3	357	389	11	2	−15	152	−149	3	3	14	186	−183	19	3	−10	133	92
7	2	−3	280	301	1	3	0	175	−186	7	3	14	93	119	3	3	−12	269	−226
9	2	−3	244	−253	3	3	0	266	−308	9	3	14	92	121	5	3	−12	200	−175
11	2	−3	288	−332	5	3	0	70	−67	5	3	16	107	−116	7	3	−12	140	114
15	2	−3	229	248	7	3	0	308	322	1	3	−2	405	−337	9	3	−12	232	220
17	2	−3	150	165	9	3	0	202	231	3	3	−2	145	−142	13	3	−12	164	−145
2	2	−4	118	−119	11	3	0	117	−107	5	3	−2	293	289	15	3	−12	179	−165
6	2	−4	109	90	13	3	0	209	−248	7	3	−2	339	328	19	3	−12	158	163
8	2	−4	146	126	17	3	0	165	166	9	3	−2	105	−78	1	3	−14	163	−131
10	2	−4	93	66	19	3	0	163	145	11	3	−2	311	−325	3	3	−14	200	−172
12	2	−4	144	−138	6	3	1	92	83	13	3	−2	147	−132	7	3	−14	200	184
1	2	−5	130	−90	1	3	2	118	114	15	3	−2	136	131	11	3	−14	160	−121
3	2	−5	358	383	3	3	2	307	−293	17	3	−2	200	228	13	3	−14	173	−153
5	2	−5	305	281	5	3	2	357	−387	21	3	−2	135	−166	17	3	−14	136	123
7	2	−5	81	−72	9	3	2	282	293	2	3	−3	103	84	19	3	−14	105	92
9	2	−5	346	−301	11	3	2	143	130	1	3	−4	239	−238	1	3	−16	157	−138
11	2	−5	157	−130	13	3	2	153	−151	3	3	−4	228	185	5	3	−16	127	126
13	2	−5	218	223	15	3	2	180	−174	5	3	−4	368	381	7	3	−16	130	98
15	2	−5	233	248	19	3	2	138	165	7	3	−4	82	48	11	3	−16	145	−132
19	2	−5	178	−196	21	3	2	126	118	9	3	−4	345	−315					
4	2	−6	211	197	2	3	3	127	−101	11	3	−4	290	−266					

TABLE 3.

Bond angles round the platinum atom and their standard deviations.

O(1)–Pt–O(2)	85°	± 1°	O(2)–Pt–N	88°	±2°	O(1)–Pt–C(3)	89°	±2°
C(4)–Pt–C(2)	85°	±3°	O(2)–Pt–C(3)	95		O(1)–Pt–C(2)	88	
C(3)–Pt–C(2)	86		O(2)–Pt–C(4)	101		C(4)–Pt–N	87	
N–Pt–C(2)	91		O(1)–Pt–N	92		C(4)–Pt–C(3)	92	

is: $0{\cdot}728\ X' - 0{\cdot}617\ Y - 0{\cdot}299\ Z' - 1{\cdot}448 = 0$. The largest deviation from this plane is 0·12 Å for C(6). In the other trimethylplatinum-β-diketo-complexes we have studied, the β-diketone ring is non-planar in a systematic way; we tested for the same kind of deviation from planarity by calculating the planes through O(2), C(5), C(6), and C(9) and through O(1), C(7), C(6), and C(8) and determining the angle between their normals. It was 9 ± 6°, not significantly different from zero, as required for a completely planar group, and in contrast to the value 27° found in the other trimethylplatinum complexes.

The platinum atom is 0·39 Å out of the plane of the acetylacetone, in harmony with the observation for other β-diketo-complexes, *e.g.*, in $[(\text{acac})_2\,2\text{H}_2\text{O Co}]^6$, so that the plane through C(2),C(4), O(2),O(1), and Pt for which the equation is: $0{\cdot}790\ X' - 0{\cdot}607\ Y - 0{\cdot}076\ Z' - 1{\cdot}727 = 0$, is not parallel to that of the acetylacetone but the planes are " hinged " about the O(1)–O(2) line, the angle between their normals being 13 ± 4°.

All the intermolecular distances of less than 3·9 Å were calculated, only 7 were found, of these the shortest was 3·44 Å between two methyl groups, C(9) and C(2)″ in the molecule related to the original asymmetric unit by a *c* glide at $y/b = \frac{1}{4}$. The absence of improbably short van der Waals separations is another indication that the structure is correct. In contrast to the other trimethylplatinum-β-diketo-complexes studied in this laboratory there are no short contacts to the " active " γ-carbon atom, C(6). The intramolecular platinum–platinum separation is 7·68 ± 0·007 Å, compared with 7·8 ± 0·1 Å in the $[(Me_3\ en\ Pt)_2\ en]^{2+}$ cation.[5]

DISCUSSION

In a platinum compound the value of the agreement index is insufficient criterion for the correctness of the location of the light atoms and we have accordingly taken care to apply other tests. A final electron-density map was featureless indicating that there were no additional atoms unlocated. Throughout the analysis the temperature factors of the individual atoms had been used to check the plausibility of their location, and they proved sensitive not merely to the incorrect location of one atom but even to the distinction between oxygen, carbon and nitrogen atoms.

This analysis has shown unequivocally that the product of the reaction between the trimethyl(acetylacetonato)platinum(IV) dimer and ethylenediamine is a centrosymmetrical binuclear complex, in which the ethylenediamine group forms a bridge between the two platinum atoms. Each platinum atom is octahedrally co-ordinated, to one nitrogen atom, to the two oxygen atoms of the acetylacetone group and to three carbon atoms in methyl groups. The methyl groups are, as usual in trimethylplatinum compounds, in the *cis*-configuration. This is the first complex of trimethylplatinum in which a β-diketone has been shown to have the chelate form, normal in complexes with other metals; the planarity of this group and its geometrical relation to the remaining atoms of the octahedron round the metal atom are just the same as in comparable complexes with other metals.[6]

The bond lengths we have found (see Fig. 3), within the limits of their necessarily large standard deviations, agree with those from comparable compounds; Pt–C = 2·05 ± 0·02 Å and Pt–N = 2·15 ± 0·01 Å in Me_3 | acac | bipyridyl Pt,[3] Pt–O = 2·15 ± 0·02 Å in $[Me_3\ (C_3H_9CO)_2CH\ Pt]_2$,[1] and similarly the light atom–light atom distances are not significantly different from the usual values. They are all reasonable enough to confirm the correctness of the structure but not accurate enough to permit a detailed discussion of the nature of the bonding. Only two of the bond angles round platinum (Table 3) differ from 90° by amounts which are significant statistically, O(1)–Pt–O(2) is smaller ($\Delta/\sigma = 3{\cdot}0$) and O(2)–Pt–C(4) is larger ($\Delta/\sigma = 5{\cdot}7$). There does not appear to be any chemical significance in these values, the environment of O(2) is similar to that of O(1) in other respects.

If the acac group and the en group are regarded just as chelate groups, the stereochemistry of $(Me_3\ acac\ Pt)_2en$ can be compared with that of $[Me_3\ en\ Pt)_2en]^{2+}$. Both approximate to $2/m$ symmetry so that the crystallographic requirement of a centre of symmetry in one case and a two-fold axis in the other does not represent a fundamental difference. There is, however, a difference in the orientation of the two halves of the molecule; this only requires rotation about the platinum-nitrogen bonds and probably depends on the packing in the crystal (compare III with Fig. 3).

EXPERIMENTAL

The preparation of the compound is described by Kite and Truter.[4] All *X*-ray photographs were taken with Cu-K_α radiation. Unit cell dimensions were measured from Weissenberg

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[6] Bullen, *Acta Cryst.*, 1959, **12**, 703.

photographs. Equi-inclination Weissenberg photographs were taken about the *b* axis of a crystal 0·3 mm. long and 0·02 × 0·01 mm. in cross-section for the zero to the third layer inclusive; the zero layer about the *a* axis was also measured. A multiple-film technique was used and the intensities of the spots were estimated visually with the aid of a calibration strip. For the non-zero layers the Phillips spot-shape correction factor [7] was applied; this and the application of Lorentz and polarisation factors were carried out on the Leeds University Ferranti Pegasus computer with a programme written by Mr. J. G. F. Smith. No absorption correction was applied. The scale factor for $F(h0l)$ was obtained by Wilson's method [8] in the first instance, then for both the $F(h0l)$ and $F(0kl)$ the scale was found from plots of $\log(F_c/F_o)$ against $\sin^2 \theta$ which also gave the value of $B = 2{\cdot}3$ Å^2 (equivalent to $U = 0{\cdot}0285$ Å^2). The other layers about the *b* axis were scaled approximately by comparison with the common reflections on the $(0kl)$ layer but there were so few suitable reflections that these scale factors had to be treated as parameters until all the atoms had been located and they were altered to make $\Sigma|F_o| = \Sigma|F_c|$ for each layer line.

The scattering factors were those of Thomas and Umeda [9] for platinum, corrected for the real part of the anomalous dispersion,[10] and of Berghuis *et al.*[11] for carbon, nitrogen, and oxygen. Refinement was carried out by the method of least squares on the Pegasus computer with programmes written by Cruickshank *et al.*; [12] the function minimised was $R' = \Sigma w(|F_o| - |F_c|)^2$, where w was taken as $1/|F_o|$. Three-dimensional Fourier syntheses and calculations of interatomic distances and angles were carried out on the computer with programmes which have been described; [12] the estimated standard deviations in the dimensions of the molecule were computed with a programme written by Mr. J. G. F. Smith.

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[7] Phillips, *Acta Cryst.*, 1954, **7**, 746.
[8] Wilson, *Nature*, 1942, **150**, 152.
[9] Thomas and Umeda *J. Chem. Phys.*, 1957, **26**, 293.
[10] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.
[11] Berghuis, Haanappel, Potter, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[12] Cruickshank, Pilling, Bujosa, Lovell, and Truter, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, London, 1961, p. 32.