molecular interaction forcing the ring system down toward Cl(2) and Cl(2)′ rather than one in which it settles into a position of minimum repulsion after the geometry of the coordination sphere is determined. An inspection of molecular packing in the unit cell (Figure 3) and appropriate distances indicates that the interaction is probably an electrostatic attraction of the quaternized nitrogen atom for oxygen atoms (3.91 Å) and possibly Cl(2) atoms (4.43 Å) on neighboring molecules. This interaction appears to be at least partly responsible for the nonlinearity of the O–Ni–N(1) bond angle. No bond lengths in the ring structure are observed to be affected by these interactions; all C–N bonds agree with the average value of 1.493 Å within 1.5σ while the two independent C–C bonds agree closely with their average value of 1.515 Å.

Even though hydrogen atoms could be located with relative ease, the refinement of their positional parameters did not offer additional information concerning interactions of the ring system. The terminal methyl protons appear to be in well-defined potential minima as hydrogen peaks were located in a staggered configuration with respect to the ring. The over-all average C–H bond distance is 0.94 (11) Å and the average error in H–C–H bond angles is 6.1°. A peak corresponding to the hydrogen atom of the water molecule was also located and refined. It was found to be 2.42 Å from Cl(2) of a neighboring molecule and 0.854 (77) Å from the oxygen atom. The over-all Cl(2)–O distance of 3.189 (4) Å and the O–H···Cl(2) angle of 145° are in reasonable agreement with the wide variety of distances and angles reported for hydrogen bonds.[18,19] The coordinates determined for the hydrogen atom (and its mirror image) are consistent with a water molecule of tetrahedral geometry with one pair of electrons coordinated to the metal in a σ-type bond.

Electrostatic interactions appear to be the major forces leading to the stability of this complex. The hydrogen bonding mentioned previously provides rows of staggered interacting molecules (as shown for the shaded molecule in Figure 3) while the interactions of the quaternized nitrogen atoms cross-link these chains into sheets running diagonally through the unit cell.

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(18) G. Pimentel and A. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(19) W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin Inc., New York, N. Y., 1968.

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The Crystal Structure of Bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) Chloride Monohydrate

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The crystal structure of bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) chloride monohydrate, $C_{10}H_{23}N_4O_2PtCl \cdot H_2O$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 12.83 \pm 0.02$ Å, $b = 11.03 \pm 0.02$ Å, $c = 12.62 \pm 0.02$ Å, and $\beta = 93.0 \pm 0.2°$. The space group is $P2_1/c$. The density by flotation is 1.94 g/cm^3; four formula units in the unit cell give a calculated density of 1.95 g/cm^3. The structure is isomorphous with that of the corresponding nickel complex. Refinement by full-matrix least squares led to a conventional R factor of 8.9% using 1324 visually estimated reflections. The complex has approximate symmetry (C_s) with the four nitrogen atoms in square-planar coordination about platinum with average bond distances: Pt–N(oxime), 1.98 (3) Å; Pt–N(amine), 2.03 (3) Å. The intermolecular O---O hydrogen-bond distance is 2.48 (4) Å. Intermolecular hydrogen bonding involving the chloride ion, the water molecule, and the amine nitrogens of the cation plays a major role in stabilizing the crystal structure.

Introduction

Several metal–glyoxime complexes with short intramolecular hydrogen bonds have been studied by X-ray diffraction.[1–5] The shortest intramolecular O- - -O distance was observed for bis(dimethylglyoximato)nickel(II)[1] (2.40 (4) Å) while the longest was found for bis(dimethylglyoximato)platinum(II)[5] (3.03 (6) Å), suggesting a large difference in hydrogen-bond strength.

The crystal structure of bis(2-amino-2-methyl-3-butanoneoximato)nickel(II) chloride monohydrate was reported recently.[6] In that complex there is one intramolecular O- - -O hydrogen bond (2.38 (2) Å) rather than the two found in the glyoxime complexes. With only one intramolecular hydrogen bond, a short, possibly symmetrical O- - -O hydrogen bond might be found even with the larger platinum cation. For that reason the structure of bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) has been determined.

Experimental Section

Crystal Preparation.—The compound was kindly provided by Murmann.[7] The crystals used for this study were obtained by crystallization from dichloromethane–heptane solution.

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(1) (a) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953); (b) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

(2) M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, **22**, 468 (1967); R. K. Murmann and E. O. Schlemper, *ibid.*, **23**, 667 (1967).

(3) C. Panattoni, E. Frasson, and R. Zannetti, *Gazz. Chim. Ital.*, **89**, 2132 (1959).

(4) E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, **12**, 201 (1959).

(5) E. Frasson, C. Panattoni, and R. Zannetti, *ibid.*, **12**, 1027 (1959).

(6) E. O. Schlemper, *Inorg. Chem.*, **7**, 1130 (1968).

(7) R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 521 (1957).

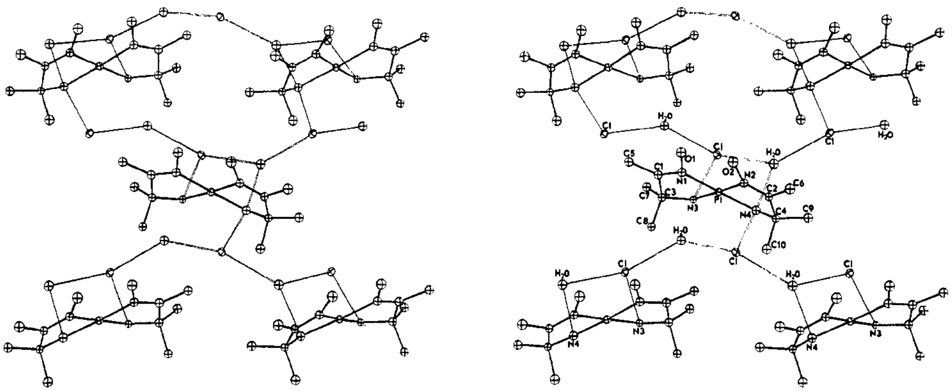
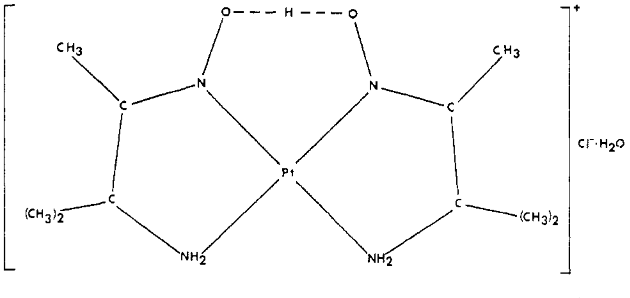


Figure 1.—View of one layer of cations, anions, and water molecules looking parallel to the *a* axis of the unit cell. Intermolecular hydrogen bonds are shown.

X-Ray Data.—Bis(2-amino-2-methyl-3-butanoneoximato)-platinum(II) chloride monohydrate crystallizes in the monoclinic crystal system with four molecules in a unit cell of dimensions $a = 12.83 \pm 0.02$ Å, $b = 11.03 \pm 0.02$ Å, $c = 11.62 \pm 0.02$ Å, and $\beta = 93.0 \pm 0.2°$. The reported errors represent the average deviations in the observed cell constants as measured from Mo Kα precession photographs from a camera calibrated with NaCl ($a = 5.638$ Å). A crude flotation measurement of the density in carbon tetrachloride–carbon tetrabromide solution gave 1.94 ± 0.01 g/cm^3. A calculated density of 1.950 ± 0.007 g/cm^3 is obtained, assuming four formula units per unit cell. The systematic extinctions *h*0*l* with *l* odd and 0*k*0 with *k* odd indicate that the space group is $P2_1/c$. The structure is isomorphous with that of the corresponding nickel complex.[6]



Two crystals approximately $0.10 \times 0.10 \times 0.08$ mm, mounted with a long dimension as the rotation axis, were used for intensity measurements, one for the Weissenberg data and the other for the precession data. Using a Zr filter and brass interleaving sheets, multiple-film Mo Kα Weissenberg photographs were taken of the 0*kl* through 9*kl* zones. Multiple exposures were taken of the *h*0*l*, *h*1*l*, *hk*0, *hk*1, and *hk*2 zones by the precession method. The relative intensities were estimated by visual comparison with a series of timed exposures of a selected reflection. There were 1324 independent reflections of measurable intensity. The usual Lorentz and polarization corrections were made. Absorption corrections were not made ($\mu = 91.9$ cm^{-1}). A rough estimate of the absorption factors for a given Weissenberg layer indicated a range of less than 15% in *I*. The data were placed on a common scale using the interlayer scaling program of W. C. Hamilton, J. S. Rollett, and R. A. Sparks.

Determination of the Structure.—The calculations were made on the IBM 7040 computer of the Computer Research Center of the University of Missouri. The programs used in this work were local versions of A. Zalkin's FORDAP program, W. R. Busing and H. A. Levy's ORFLS least-squares and ORFFE error-function programs, C. K. Johnson's ORTEP ellipsoid plot program, and data-handling programs of W. C. Hamilton and J. A. Ibers.

Approximate positions for the platinum and chlorine atoms were found in keeping with the isomorphism with the corresponding nickel complex by analysis of the Patterson function.[6] After two cycles of least-squares refinement of the positions of these atoms, a three-dimensional Fourier synthesis was prepared in which all carbon, nitrogen, and oxygen atoms were located

The above model was then refined by the full-matrix least-squares technique, minimizing the function $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma^2(F^2)$, and in the final stages of refinement, $\sigma = -0.01337(kF_o)^4 + (kF_o)^2$ for $(kF_o)^2 \leq 43.2$; $\sigma = -0.00104(kF_o)^4 + 0.38(kF_o)^3$ for $43.2 \leq (kF_o)^2 \leq 201.6$; $\sigma = -0.000269(kF_o)^4 + 0.235(kF_o)^2$ for $201.6 \leq (kF_o)^2 \leq 518.4$; and $\sigma = 0.0000394 \cdot (kF_o)^4 + 0.080(kF_o)^2$ for $(kF_o)^2 > 518.4$ with $k = 0.234$. This weighting scheme[6] was chosen to make the value of $\Delta|F^2|/\sigma(F^2)$ nearly independent of F_o^2 where $\Delta|F^2| = |F_o^2| - |F_c^2|$. In all calculations of structure factors, scattering factors[8a] for neutral atoms were used. Using the tabulated values[8b] of f' and f'' for Pt the effects of anomalous dispersion were included in F_c.[9] After several cycles of isotropic refinement, $R(F^2) = \Sigma(|F_o|^2 - |kF_c|^2)/\Sigma|F_o|^2 = 0.171$ and $R(wF^2) = [\Sigma w(|F_o|^2 - |kF_c|^2)^2/(\Sigma w|F_o|^2)^2]^{1/2} = 0.214$. Two cycles of refinement with the platinum and chlorine atoms given anisotropic thermal expression converged with $R(F^2) = 0.163$ and $R(wF^2) = 0.200$. The standard deviation of an observation of unit weight was 1.19. The maximum shift in any positional parameter at this stage was less than one-tenth the estimated standard deviation of that parameter. The conventional R $(= \Sigma(|F_o| - |kF_c|)/\Sigma|F_o|)$ was 0.089.

A Fourier synthesis using the observed structure magnitudes and phases from the last set of calculated structure factors showed the weakest carbon atoms to have peak densities of 4.5 e$^-$/Å^3. The largest peaks on the corresponding difference Fourier map were within 1 Å of the platinum atom and had densities as high as ± 4.8 e$^-$/Å^3. All other residuals were under 1.5 e$^-$/Å^3. No attempt was made to include the hydrogen atoms.

The observed and calculated structure factors (×10) from the last cycle of least squares are included in Table I. Unobserved reflections were not included in the calculations or Table I. The positional and thermal parameters are given in Table II.

Discussion

Nature of the Structure.—The structure is isomorphous with that of the corresponding nickel complex.[6] The platinum atom is coordinated in a square-planar geometry to four nitrogen atoms. The closest approach of an atom outside the complex to the platinum involves a water molecule at 3.66 Å. The platinum and four nitrogens define a weighted ($w = 1/\sigma^2$) least-squares plane which in the monoclinic coordinate system has the equation: $5.54x - 3.09y - 10.2z + 1.76 = 0$. The maximum deviation of any nitrogen from the plane

[8] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 216.

[9] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

K	L	FO	FC
H= 0			
0	2	3015	2875
0	4	855	851
0	8	1217	1251
0	10	855	875
0	12	687	617
0	14	292	200
1	2	804	770
1	3	1050	1086
1	5	705	728
1	6	414	467
1	7	732	841
1	9	809	893
1	11	732	736
1	13	432	394
2	0	1781	1712
2	1	385	445
2	2	1377	1191
2	4	960	935
2	5	440	522
2	6	275	325
2	7	284	322
2	8	842	946
2	10	781	765
2	12	466	542
3	1	2381	2067
3	2	656	579
3	3	1161	1174
3	4	219	358
3	6	669	818
3	7	868	909
3	8	255	265
3	9	765	879
3	11	617	643
3	13	240	305
4	0	1923	1885
4	2	1342	1374
4	3	214	367
4	4	588	551
4	5	804	880
4	6	232	307
4	7	522	556
4	8	667	747
4	10	673	688
4	12	483	480
5	1	1664	1526
5	2	340	226
5	3	600	607
5	4	635	701
5	5	405	356
5	6	627	742
5	7	307	395
5	9	633	731
5	11	557	529
5	13	305	280
6	0	1492	1475
6	1	431	498
6	2	1040	1029
6	3	547	700
6	4	472	459
6	5	887	936
6	7	486	517
6	8	523	497
6	10	426	465
6	12	262	326
7	1	875	968
7	2	593	667
7	3	726	727
7	4	563	650
7	6	716	801
7	9	267	296
7	11	292	287
8	0	738	656
8	1	463	538
8	2	668	785
8	3	501	584
8	4	279	318
8	5	583	642
8	7	554	540
9	1	490	426
9	2	644	657
9	3	495	490
9	4	672	732
9	6	660	703
9	8	294	316
9	9	255	264
10	0	236	197
10	2	361	325
10	3	484	543
10	5	663	682
10	7	412	449
11	4	357	439
11	6	409	423
11	8	249	243
12	3	333	349
12	5	358	341
12	7	311	251
13	4	341	267
H= 1			
0	2	2760	2463
0	4	1713	1589
0	6	1647	1487
0	8	1027	915
0	14	356	341
1	1	1331	1214
1	3	2587	2314
1	4	386	365
1	5	1805	1688
1	7	1375	1329
1	9	332	321
1	13	419	308
2	1	301	310
2	2	1942	1670
2	3	488	427
2	4	2063	1859
2	6	1803	1731
2	8	914	884
2	9	246	114
3	0	703	659
3	1	552	457
3	2	981	935
3	3	2054	1846
3	5	1687	1544
3	7	1374	1436
3	8	396	437
3	9	339	334
3	10	360	367
4	1	2222	1938
4	2	1800	1508
4	3	586	569
4	4	2134	1755
4	6	1387	1219
4	8	884	767
4	9	468	559
5	0	966	901
5	1	756	679
5	2	1508	1346
5	3	1443	1341
5	5	1343	1192
5	7	1025	874
5	8	447	484
5	9	390	338
5	10	302	395
6	1	919	932
6	2	561	521
6	3	318	361
6	4	1170	1040
6	6	1035	932
6	8	537	482
6	9	512	531
7	0	949	947
7	1	344	322
7	2	874	859
7	3	745	607
7	5	1008	838
7	7	438	454
7	8	484	452
7	10	364	365
8	1	1299	1173
8	2	402	360
8	3	340	400
8	4	629	544
8	6	416	409
8	9	435	405
9	0	937	913
9	2	696	717
9	3	405	340
9	5	453	434
9	7	262	199
9	8	402	333
10	1	706	659
10	3	352	375
10	4	440	346
10	6	316	245
10	9	221	327
11	0	610	554
11	2	515	439
11	5	324	247
12	1	497	439
13	0	481	387
13	2	320	286
0	-2	1777	1741
0	-4	2509	2288
0	-6	1747	1660
0	-8	1195	1065
0	-10	461	421
0	-12	289	210
0	-14	292	261
1	-2	191	163
1	-3	2301	2067
1	-4	859	684
1	-5	2601	2451
1	-6	347	327
1	-7	1310	1209
1	-9	722	672
1	-13	394	324
2	-2	1041	948
2	-3	449	461
2	-4	2576	2390
2	-6	1724	1611
2	-8	799	778
2	-12	337	351
3	-1	591	554
3	-3	1149	1235
3	-4	672	642
3	-5	1935	1826
3	-7	955	1003
3	-9	589	568
4	-1	281	299
4	-2	442	441
4	-3	742	800
4	-4	1663	1515
4	-6	1469	1373
4	-7	359	378
4	-8	726	736
4	-10	292	294
5	-1	331	382
5	-2	816	718
5	-3	861	878
5	-4	792	833
5	-5	1062	1070
5	-7	675	818
5	-9	417	377
5	-10	340	403
6	-1	488	530
6	-2	727	690
6	-3	793	836
6	-4	870	858
6	-6	796	794
6	-8	467	461
6	-11	388	386
7	-1	324	295
7	-2	793	809
7	-3	868	835
7	-4	388	446
7	-5	780	798
7	-7	679	656
7	-10	401	395
8	-1	1081	1014
8	-2	522	524
8	-3	627	634
8	-4	518	527
8	-6	573	578
8	-7	272	264
8	-9	380	394
9	-2	670	649
9	-4	185	367
9	-5	395	354
9	-7	296	356
10	-1	646	597
10	-3	472	517
10	-6	394	287
11	-2	547	486
11	-4	317	231
12	-1	562	439
12	-3	414	271
13	-2	345	314
H= 2			
0	2	2579	2515
0	4	512	531
0	6	760	677
0	8	707	694
0	10	1007	1001
0	12	508	511
1	1	2004	1889
1	3	2064	1791
1	4	198	201
1	5	476	504
1	6	309	342
1	7	681	724
1	8	351	360
1	9	939	948
1	11	778	746
1	13	344	283
2	0	1722	1589
2	2	1941	1721
2	3	646	582
2	4	818	740
2	5	319	362
2	6	669	659
2	8	1128	990
2	10	958	878
2	12	459	414
3	1	1791	1774
3	2	279	325
3	3	1438	1328
3	4	842	884
3	6	291	341
3	7	803	758
3	8	309	308
3	9	869	880
3	11	494	561
4	0	1657	1555
4	1	331	246
4	2	1852	1672
4	3	1103	1010
4	4	311	279
4	5	746	812
4	6	532	561
4	7	335	436
4	8	693	683
4	10	768	697
4	12	413	393
5	1	1741	1577
5	2	648	647
5	3	966	885
5	4	1183	1073
5	6	525	489
5	7	659	617
5	8	343	368
5	9	907	802
5	11	645	570
6	0	1485	1386
6	1	427	394
6	2	907	946
6	3	942	878
6	4	328	317
6	5	826	741
6	6	323	326
6	7	451	519
6	8	608	561
6	9	254	223
6	10	630	560
6	12	293	303
7	1	926	871
7	2	481	462
7	3	350	352
7	4	597	892
7	6	451	478
7	7	296	300
7	8	425	394
8	0	894	888
8	1	384	366
8	2	583	474
8	3	725	755
8	5	675	634
8	7	343	313
8	8	304	303
9	1	650	585
9	2	482	487
9	3	257	248
9	4	773	765
9	6	461	479
9	7	287	249
9	8	251	254
10	0	446	400
10	3	576	518
10	5	642	608
10	7	342	349
11	2	388	325
11	4	459	469
11	6	450	424
12	3	384	374
12	5	397	377
13	4	303	299
0	-2	4222	3828
0	-4	804	765
0	-6	346	235
0	-8	831	825
0	-10	588	541
0	-12	564	537
0	-14	372	305
1	-1	2439	2913
1	-2	1579	1760
1	-3	2331	2542
1	-4	775	809
1	-5	256	213
1	-7	352	394
1	-8	292	313
1	-9	1113	997
1	-11	730	732
1	-13	466	474
2	-2	2879	2700
2	-3	923	1109
2	-4	904	901
2	-5	358	378
2	-8	649	665
2	-10	949	[illegible]
2	-12	510	513
3	-1	2794	2104
3	-2	270	[illegible]
3	-3	1497	1476
3	-4	329	405
3	-6	254	294
3	-7	319	386
3	-8	398	428
3	-9	874	824
3	-11	591	659
3	-13	311	307
4	-2	1592	1545
4	-3	332	462
4	-4	792	792
4	-5	343	485
4	-6	266	237
4	-7	375	464
4	-8	507	557
4	-10	616	627
4	-12	359	423
5	-1	1623	1455
5	-2	395	430
5	-3	949	954
5	-4	776	[illegible]
5	-5	277	279
5	-6	499	538
5	-8	431	454
5	-9	556	564
5	-11	427	449
6	-2	1179	1109
6	-3	834	909
6	-4	371	451
6	-5	521	620
6	-7	425	556
6	-8	379	369
6	-10	358	401
6	-12	314	290
7	-1	1282	1150
7	-2	358	346
7	-3	592	606
7	-4	690	760
7	-6	542	578
7	-8	396	470
7	-9	283	310
7	-11	286	326
8	-2	560	555
8	-3	746	752
8	-5	608	693
8	-7	492	576
8	-9	294	292
9	-1	407	384
9	-2	452	424
9	-3	349	339
9	-4	741	782
9	-6	484	579
9	-8	387	409
10	-3	424	454
10	-5	567	567
10	-7	424	422
11	-4	384	446
11	-6	366	419
11	-8	345	273
12	-3	306	319
12	-5	395	397
12	-7	278	257
H= 3			
0	0	1007	1053
0	2	248	317
0	4	1610	1433
0	6	1228	1172
0	8	387	373
0	12	397	386
0	14	350	359
1	0	546	591
1	1	1070	1109
1	2	697	605
1	3	1758	1590
1	5	2406	2029
1	7	677	754
1	9	401	315
1	13	551	429
2	0	814	738
2	1	392	396
2	2	2181	1856
2	3	505	525
2	4	2668	2150
2	6	1966	1678
2	8	545	582
3	0	635	674
3	1	1269	1202
3	2	315	309
3	3	2008	1576
3	4	643	581
3	5	2099	1819
3	7	1169	1070
3	8	389	391
4	0	318	313
4	1	758	756
4	2	1670	1432
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1	-7	492	462
1	-9	472	368
H=14			
0	0	500	472
0	6	434	400
1	5	424	337
1	7	475	428
1	9	367	257
2	0	478	413
4	0	399	321
6	0	317	185
7	0	363	195
0	-2	493	497
0	-4	413	467
0	-6	310	332
1	-1	576	502
1	-3	541	463
1	-5	480	427
2	-2	519	524
3	-1	456	466
4	-2	521	500
H=15			
0	0	480	411
0	2	536	584
0	4	354	370
1	1	545	515
1	3	495	475
1	5	382	279
2	0	393	346
2	2	470	510
3	1	416	415
4	0	314	273
6	0	361	273
0	-6	296	312
1	-1	389	255
1	-7	417	273
H=16			
1	5	371	292
1	7	392	259
0	-2	432	425
0	-4	395	383
1	-1	385	315
1	-3	535	449
H=17			
1	1	372	328
1	3	398	282
1	-1	374	267

is 0.03 ± 0.03 Å, indicating no significant deviation from planarity. The distances of the cation atoms from this plane are given in Table III. The ligands are puckered in almost exactly the same way as in the nickel complex,[6] lowering the cation symmetry from C_{2v} to essentially $C_s(m)$. The most pronounced differences are found for C(5) and C(6) which are closer to the plane in the platinum complex.

A view of one layer of cations, anions, and water molecules, looking parallel to the *a* axis, is shown in Figure 1. The hydrogen bonds between water molecules, chloride ions, and amine nitrogen atoms are shown as open lines. The shorter intermolecular contacts are given in Table IV. The first six distances are those of the intermolecular hydrogen bonds which play a large role in stabilizing the crystal structure. The hydrogen bonding involving amine N(4) is obviously stronger than that involving N(3). No other unusually short intermolecular distances are observed.

The root-mean-square components of thermal motion along the principal axes are given for the platinum and chlorine atoms in Table V. Neither atom deviates a great deal from isotropic motion. The shapes and orientations of the ellipsoids can be seen in Figure 1.

Bond Distances and Angles.—The bond distances and angles are shown in Figure 2.

None of the observed differences in distances or angles expected to be chemically equivalent can be considered significant. Within experimental error, the symmetry of the cation is $C_s(m)$. The average plati-

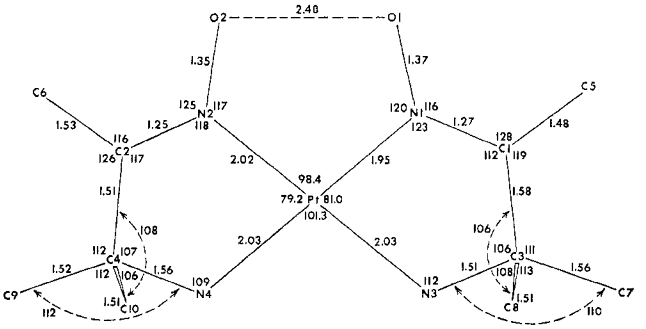

Figure 2.—Bond angles and distances for the complex cation. The standard deviations in distances are: Pt–N, 0.03 Å; N–O, N–C, and O–O, 0.04 Å; and C–C, 0.05 Å. The standard deviations in the angles are: N–Pt–N, 1°; Pt–N–O and Pt–N–C, 2°; and all others, 3°.

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS[a]

Atoms	x	y	z	B, Å^2
Pt	−0.2403 (1)	−0.0181 (1)	0.0473 (1)	...
Cl	0.4742 (7)	−0.0430 (9)	0.2053 (8)	...
O(1)	−0.099 (2)	−0.158 (2)	0.198 (2)	6.3 (6)
O(2)	−0.042 (2)	0.052 (2)	0.159 (2)	6.8 (6)
N(1)	−0.186 (2)	−0.164 (3)	0.123 (3)	5.0 (6)
N(2)	−0.116 (2)	0.091 (3)	0.081 (2)	4.4 (6)
N(3)	−0.361 (2)	−0.134 (2)	0.016 (2)	3.5 (5)
N(4)	−0.297 (2)	0.136 (3)	−0.027 (3)	5.4 (7)
C(1)	−0.230 (3)	−0.267 (3)	0.114 (3)	5.3 (8)
C(2)	−0.114 (3)	0.191 (3)	0.029 (3)	4.2 (7)
C(3)	−0.327 (3)	−0.265 (3)	0.024 (3)	4.8 (7)
C(4)	−0.204 (3)	0.219 (3)	−0.056 (3)	3.8 (6)
C(5)	−0.195 (3)	−0.384 (3)	0.165 (3)	5.2 (8)
C(6)	−0.019 (3)	0.272 (4)	0.057 (4)	6.2 (9)
C(7)	−0.418 (3)	−0.344 (3)	0.068 (3)	5.8 (8)
C(8)	−0.292 (3)	−0.304 (3)	−0.092 (3)	4.6 (7)
C(9)	−0.234 (3)	0.352 (3)	−0.054 (3)	5.5 (8)
C(10)	−0.171 (3)	0.180 (4)	−0.173 (4)	6.1 (9)
H_2O	−0.412 (2)	0.212 (3)	0.163 (3)	7.2 (7)

	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00516 (8)	0.0086 (1)	0.0071 (1)	0.0010 (1)	0.00005 (6)	−0.0002 (1)
Cl	0.0072 (6)	0.0113 (9)	0.0103 (8)	−0.0011 (6)	0.0010 (6)	−0.0016 (1)

[a] Standard deviations are in parentheses. [b] The anisotropic temperature factors for the Pt and Cl atoms are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III

DISTANCES OF CATION ATOMS FROM COORDINATION PLANE[a]

Atom	Dist, Å	Atom	Dist, Å
Pt	0.0001 (13)	C(3)	0.53 (3)
N(1)	−0.01 (3)	C(4)	0.52 (3)
N(2)	−0.01 (3)	C(5)	0.19 (3)
N(3)	−0.01 (3)	C(6)	0.23 (3)
N(4)	0.03 (3)	C(7)	−0.19 (3)
O(1)	−0.32 (3)	C(9)	−0.08 (3)
O(2)	−0.25 (3)	C(8)	2.02 (3)
C(1)	0.16 (3)	C(10)	2.01 (3)
C(2)	0.23 (3)		

[a] Standard deviations are in parentheses. Pt and N were used to define the least-squares plane.

num to oxime nitrogen distance (1.98 (3) Å) is probably significantly shorter than the platinum to amine nitrogen distance (2.03 (3) Å) since the difference is identical with that observed for the nickel complex.[6] In platinum dimethylglyoxime, the Pt–N distance is reported[5] to be 1.94 (4) Å. The average N–O distance (1.36 (3) Å) is in good agreement with that observed in a number of similar complexes. The average C–N (oxime) distance (1.26 (4) Å) appears to be shorter, but the significance of the difference is questionable (see Table VIII of ref 6). The C–C distances are normal. The average C–N(amine) distance is in good agreement with that found in the nickel complex.

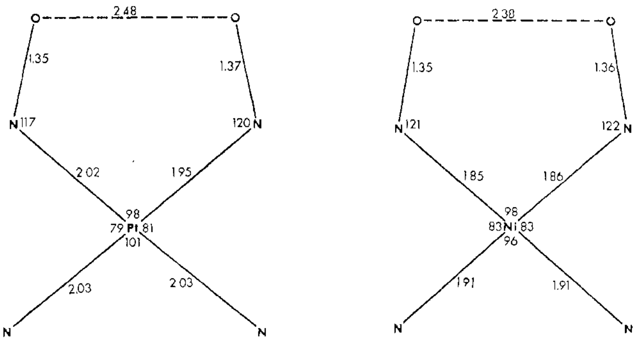

Figure 3.—A comparison of the coordination planes and intramolecular hydrogen bonds in the platinum and nickel complexes.

TABLE IV

INTERMOLECULAR DISTANCES[a]

Dist	Value, Å	Dist	Value, Å
N(4)–H_2O	2.84 (4)	O(1)–C(8)	3.59 (5)
Cl–H_2O	3.22 (3)	O(1)–C(10)	3.51 (5)
Cl–H_2O	3.22 (3)	O(1)–C(6)	3.62 (5)
Cl–N(4)	3.16 (3)	O(2)–C(5)	3.64 (5)
Cl–N(3)	3.29 (3)	N(1)–C(6)	3.65 (5)
Cl–N(3)	3.48 (3)	N(1)–C(8)	3.66 (5)
Cl–C(7)	3.53 (3)	N(3)–H_2O	3.60 (4)
Pt–H_2O	3.66 (3)	C(1)–C(8)	3.63 (5)
O(1)–C(6)	3.25 (5)	C(7)–H_2O	3.67 (5)

[a] Standard deviations are in parentheses.

TABLE V

ROOT-MEAN-SQUARE COMPONENTS OF THERMAL DISPLACEMENT (Å) IN THE DIRECTION OF THE PRINCIPAL AXES[a]

Atom	Axis 1	Axis 2	Axis 3
Pt	0.201 (2)	0.217 (2)	0.239 (2)
Cl	0.233 (12)	0.244 (12)	0.289 (11)

[a] Standard deviations are in parentheses.

The intermolecular O- - -O distance (2.48 (4) Å) appears to be significantly longer than the 2.38 (2) Å distance observed for the corresponding nickel complex and is definitely shorter than that reported[5] for platinum dimethylglyoxime (3.03 (6) Å). A large part of the difference relative to platinum dimethylglyoxime is due to the difference in the Pt–N(oxime)–O angle. This angle was found to be 135 (4)° in platinum dimethylglyoxime but only 119 (2)° in this complex. A comparison of bond angles in the coordination plane (Figure 3) with those found for the nickel complex indicates some twisting of the ligand coordination to allow for a shorter O- - -O distance than would be expected on the basis of the increase in metal–nitrogen distances from the platinum complex to the nickel complex.

Although some twisting of the square-planar coordination geometry to allow for a shorter hydrogen bond in this complex than that observed in platinum dimethylglyoxime was anticipated, a large difference in the Pt–N–O angle was not expected. In all other complexes of this type with known structure the Pt–N–O angle never deviates from 120° by more than 5°.

There is then either something very unusual about platinum dimethylglyoxime or a large error in the reported angle. This can only be resolved by a more complete study of the structure of platinum dimethylglyoxime which has been studied[5] only in projections.

A nearly complete neutron diffraction study[10] of the nickel complex indicates a single equilibrium position for the hydrogen atom in the hydrogen bond. This would be less likely for the platinum complex with the longer O- - -O distance.

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[10] E. O. Schlemper, S. J. LaPlaca, and W. C. Hamilton, unpublished work.

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Crystal and Molecular Structure of Ferrocenedicarboxylic Acid

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Ferrocenedicarboxylic acid crystallizes as orange-red laths in the monoclinic space group $P2_1/c$ with $a = 8.403 \pm 0.010$ Å, $b = 8.910 \pm 0.010$ Å, $c = 14.192 \pm 0.018$ Å, $\beta = 90.41 \pm 0.08°$, and four molecules per unit cell. The structure was refined by least-square methods with anisotropic thermal parameters to a final R of 6.2% for the 1618 observed reflections measured using an automatic diffractometer with molybdenum radiation. Two molecules of ferrocenedicarboxylic acid form hydrogen-bonded dimers. The average C–C distance in the cyclopentadienide rings of 1.424 ± 0.013 Å is normal. The two cyclopentadienide rings are twisted by an average of 1° 38′, making the molecule one of the most nearly eclipsed ferrocene derivatives.

Introduction

Ferrocene and many of its derivatives are characterized by weak intermolecular forces in the crystalline state. Crystal structure studies carried out at room temperature frequently find high thermal motion which reduces the accuracy of the measured bond distances and angles. The hydrogen bonding of the two carboxyl groups in ferrocenedicarboxylic acid would give rise to strong intermolecular forces and might limit the thermal motion of the molecule. Thus, the possibility of obtaining precise distances for the ferrocene molecule was one reason for the crystal structure determination of ferrocenedicarboxylic acid.

The relative orientation of the two cyclopentadienide rings in ferrocene derivatives appears to be dependent on the substituents on the rings. Trotter and Macdonald,[1] Churchill and Mason,[2] and Churchill and Wormald[3] have discussed the relationship between orientation and intermolecular forces. The conformation of ferrocenedicarboxylic acid is important since strong intermolecular forces will be present because of the hydrogen bonding. The question of the effect of the hydrogen bonding on the orientation of the cyclopentadienides provided the second reason for the investigation of this compound.

Experimental Section

Ferrocenedicarboxylic acid was purchased from Alfa Inorganics. Crystals were grown by cooling slowly a solution of the acid in hot glacial acetic acid. The crystals were orange-red laths which were found to be elongated along b. Weissenberg photographs taken about [010] revealed only the systematic extinctions $h0l$ absent when l is odd.

One small, well-developed lath was cleaved with a razor blade to give a small crystal (0.11 × 0.18 × 0.05 mm parallel to a, b, and c, respectively) which was mounted on a glass fiber. The fiber and crystal were dipped into liquid nitrogen and then mounted on a General Electric single-crystal orienter. The long dimension of the crystal (the b axis) was parallel to the ϕ axis of the orienter. The unit cell dimensions were determined using a narrow beam of molybdenum radiation ($\lambda(\alpha_1)$ 0.70926 and $\lambda(\alpha_2)$ 0.71354). The average of these measurements were: $a = 8.403 \pm 0.010$ Å, $b = 8.910 \pm 0.010$ Å, $c = 14.192 \pm 0.018$ Å, $\beta = 90.41 \pm 0.08°$. The density calculated for four molecules per unit cell is 1.713 g/cm^3, while the density determined by flotation in a carbon tetrachloride–methylene iodide solution is 1.715 g/cm^3. A survey of the $0k0$ reflections with the diffractometer revealed the additional systematic absence, $0k0$ absent if k is odd. The most probable space group was therefore $P2_1/c(C_{2h}^5)$.

The intensity measurements were made with a scintillation counter using a wide beam of molybdenum radiation (takeoff angle of 3.7°). A linear amplifier–pulse height selector combination together with a zirconium filter was employed to eliminate the majority of the noncharacteristic radiation. The diffractometer was automated by the Datex Corp. and was controlled by a prepunched paper tape. The stationary counter–stationary crystal technique was employed in measuring 4348 reflections with $2\theta \leq 60.0°$. A 20-sec count was made for each reflection. Four standard reflections were counted periodically with 46 measurements of each standard being made during the course of the intensity measurements. The root-mean-square deviation for each of the four reflections was about 2% with no apparent trend, indicating good crystal and instrument stability. Reflections of the type $h0l$ with $l = 2n + 1$, required by the space group to be absent, were also measured. Those absent reflections which were not on a radiation streak were used to derive

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