Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Crystal and Molecular Structure of Bis(ethylenediamine)platinum(II) (*R*)-Tartrate. Causes for Its Slow Mutarotation in Aqueous Solution

WADE A. FREEMAN

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Bis(ethylenediamine)platinum(II) (*R*)-tartrate, $[Pt(C_2H_8N_2)_2]C_4H_6O_4$, crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ [C_2^2; No 4] with $a = 7.8371$ (15) Å, $b = 10.9885$ (14) Å, $c = 8.2164$ (21) Å, and $\beta = 112.17$ (2)°. Its crystal and molecular structure has been determined from three-dimensional single-crystal x-ray data collected by counter methods. The structure was refined by full-matrix least-squares methods to a R_F of 2.96% for 2267 independent data. The observed density of 2.35 (2) g cm^{-3} is consistent with the value of 2.348 g cm^{-3} calculated for $V = 655.24$ Å^3, mol wt 463.36, and $Z = 2$. No crystallographic symmetry is imposed on either ion. $[Pt(en)_2]^{2+}$ is slightly distorted from the usual planar geometry. (*R*)-Tartrate anion is also slightly distorted from the usual conformation found in other tartrates. An explanation, based on the nature of these distortions and on an ion-pairing model, is suggested for the slow mutarotation of freshly prepared aqueous solutions of this compound.

Introduction

In 1972, Eidson[1] reported that freshly prepared aqueous solutions of the title compound mutarotate rather slowly (half-life of about 110 min) from less positive to final molar rotations characteristic of the (*R*)-(+)$_{589}$-tartrate ion. The mutarotation experiment was repeatable in cycles by recrystallization and redissolution of an original sample. No changes in the conductances of these solutions or in their proton magnetic resonance spectra were observed during the course of the mutarotation. These observations and other evidence, including ORD and uv–visible spectra, led Eidson to conclude that (*R*)-tartrate in the crystalline state induces by some means temporary dissymmetry in the bis(ethylenediamine)platinum(II) ion. Since variations from the four-coordinate planar geometry usually found for platinum(II) do occur in the solid state, in particular the formation of Pt–Pt chains,[2-5] an x-ray crystallographic study was undertaken to determine the nature of the supposed dissymmetric influence in this crystal.

Collection of the X-Ray Diffraction Data

Colorless crystals of bis(ethylenediamine)platinum(II) (*R*)-(+)-tartrate, $[Pt(en)_2]$(*R*-tart), were prepared by metathetical reaction of $[Pt(en)_2]Cl_2$ with silver (*R*)-tartrate.[6] The crystal selected for the x-ray diffraction study was an irregular tetrahedral fragment with three of its four faces slightly curved. It was bounded approximately by the $(\bar{2}12)$, (210), and $(\bar{2}1\bar{2})$ planes and exactly by the $(0\bar{1}0)$ plane. It was mounted with a thin glass fiber affixed to the $0\bar{1}0$ face. Approximate areas of the four faces were, respectively, 0.075, 0.109, 0.087, and 0.138 mm^2.

Preliminary photographic data on several crystals had included precession and cone axis photographs. These indicated Laue symmetry $2/m$ and revealed the systematic absence $0k0$ for $k = 2n + 1$. The monoclinic space group $P2_1$ was thus indicated.

Data collection was carried out using a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal was accurately centered and was aligned with $[\bar{3}1\bar{4}]$ coincident with the ϕ axis of the diffractometer. Accurate cell dimensions were determined by least-squares procedures based on the angular position of 12 high 2θ ($2\theta = 42$–$54°$) reflections widely separated in reciprocal space. This and other aspects of the data collection and processing were as described elsewhere.[7] Details specific to the present analysis are summarized in Table I.

The conventional monoclinic axes, with *b* unique, were temporarily relabeled during data collection: *a* was relabeled *b*; *b* was relabeled *c*; and *c* was relabeled *a*. This change was made to cause the data collection routines to collect the members of each $h\bar{k}l$, hkl pair in close succession. The conventional labels were reapplied during the reduction of the data.

Table I. Experimental Data for the X-Ray Diffraction Study

(A) Crystal Parameters (at 21 °C)[a]

$a = 7.8371$ (15) Å	Space group $P2_1$ [C_2^2; No. 4]
$b = 10.9885$ (14) Å	$Z = 2$
$c = 8.2164$ (21) Å	Mol wt 463.36
$\cos\beta = -0.3774$ (2)	ρ(calcd) = 2.348 g cm^{-3}
$\beta = 112.17$ (2)°	ρ(obsd) = 2.35 (2) g cm^{-3} [b]
$V = 655.24$ Å^3	$F(000) = 444$ e

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: Cu foil, inserted if $I > 10^4$ counts/s
Takeoff angle: 3.0°
Detector aperture: 5 mm × 5 mm
Crystal-detector distance: 330 mm
Crystal orientation: mounted on $[\bar{3}1\bar{4}]$
Reflections measd: $+h$, $\pm k$, $\pm l$
Maximum 2θ: 50°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 2.0°/min
Scan length: $\Delta(2\theta) = (1.20 + 0.692 \tan\theta)°$, starting 0.60° below the Mo Kα_1 peak
Background measurement: stationary crystal, stationary counter; 10 s each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an isotopic linear decay correction)[c] were 1.20% for 200, 0.76% for 060, and 0.93% for $00\bar{2}$
Reflections collected: 2311 independent measurements, 342 duplicate or equivalent measurements (averaged into primary data set), and 14 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 7, using an "ignorance factor" of $p = 0.030$
Absorption coefft: $\mu = 112.7$ cm^{-1}; maximum and minimum transmission factors were 0.278 and 0.135, respectively[d]

(D) Details of Refinement

Unique data used: 2267 (*none* rejected as "not significantly different from zero")
Final no. of variables: 182 independent, 62 dependent (for "riding" H's)
Final error in observation of unit wt: 1.22
Final R_F: 2.96%
Final R_{wF}: 3.90%

[a] Based on λ(Mo Kα_1) 0.709 300 Å: J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967). [b] By neutral bouyancy in CCl_4–CBr_4. [c] Data reduction (including averaging, linear decay correction, etc.) was performed using the Fortran IV program RDUS, by B. G. DeBoer. [d] Absorption corrections were carried out using the Fortran IV program DRABZ, by B. G. DeBoer.

To ascertain the severity of the absorption problem, the $\bar{3}1\bar{4}$ reflection was measured (by repeated θ–2θ scans) at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The variation in intensity as a function of ϕ [defined as (maximum – minimum)/average] was 44.6%. This indicated the necessity of an absorption correction. When these ϕ-scan data were later corrected (along with the primary data set) for the effects of absorption, the variation in intensity was reduced to 27.3%. Further correction for absorption was not possible owing to the great difficulty in modeling the curved faces of the crystal

Table II. Final Parameters for Nonhydrogen Atoms in $[Pt(en)_2](R\text{-tart})^{a,b}$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	−0.008 137 (27)	$^1/_4$	0.266 415 (28)	1.631 (15)	1.628 (15)	1.808 (15)	−0.046 (21)	1.063 (9)	−0.206 (38)
N1	−0.242 9 (10)	0.2316 (11)	0.315 3 (11)	2.0 (3)	2.1 (6)	3.3 (3)	−0.5 (2)	1.4 (2)	−1.0 (3)
N2	0.068 0 (10)	0.0960 (6)	0.418 2 (11)	2.3 (3)	1.9 (3)	3.0 (4)	0.2 (2)	1.2 (3)	0.1 (3)
C1	−0.220 6 (14)	0.1348 (10)	0.449 0 (15)	2.7 (4)	3.9 (4)	3.4 (5)	−0.8 (3)	1.9 (3)	0.0 (4)
C2	−0.100 8 (14)	0.0378 (8)	0.414 9 (14)	3.5 (4)	2.4 (3)	2.7 (4)	−0.8 (3)	1.6 (3)	0.1 (3)
N3	−0.088 5 (11)	0.3992 (7)	0.108 0 (11)	3.5 (4)	1.7 (3)	2.9 (4)	−0.1 (2)	1.5 (3)	−0.2 (3)
N4	0.220 5 (10)	0.2593 (18)	0.203 8 (11)	2.4 (3)	3.3 (5)	4.1 (3)	−0.1 (4)	2.5 (3)	−0.0 (5)
C3	0.071 0 (17)	0.4436 (10)	0.072 2 (17)	4.8 (5)	3.3 (5)	4.6 (6)	−0.7 (4)	2.8 (5)	1.5 (4)
C4	0.180 7 (17)	0.3376 (11)	0.052 4 (16)	5.1 (6)	5.4 (6)	3.2 (5)	−0.2 (5)	3.0 (4)	0.2 (5)
C5	0.421 7 (17)	0.1339 (10)	0.857 2 (18)	3.7 (6)	1.8 (4)	2.6 (5)	−0.6 (4)	1.5 (4)	0.1 (3)
C6	0.519 0 (14)	0.1976 (15)	0.747 6 (14)	3.0 (5)	1.5 (5)	2.0 (4)	−0.0 (3)	1.3 (4)	−0.2 (3)
C7	0.464 6 (18)	0.3307 (13)	0.719 6 (19)	3.1 (5)	1.7 (5)	3.9 (6)	0.3 (4)	2.7 (4)	0.3 (4)
C8	0.576 1 (14)	0.3976 (8)	0.627 7 (14)	2.8 (4)	2.3 (4)	3.3 (4)	−0.2 (3)	2.3 (3)	−0.1 (3)
O1	0.253 3 (9)	0.1145 (7)	0.783 1 (9)	4.3 (4)	3.5 (3)	2.9 (3)	−1.2 (3)	1.8 (3)	0.5 (2)
O2	0.519 2 (11)	0.1080 (7)	1.010 8 (11)	5.5 (4)	3.3 (3)	2.7 (3)	−1.9 (3)	0.4 (3)	0.9 (3)
O3	0.713 7 (10)	0.1874 (6)	0.832 1 (11)	2.9 (3)	3.0 (3)	4.4 (4)	0.7 (2)	1.7 (3)	−0.1 (3)
O4	0.498 7 (15)	0.3777 (9)	0.889 0 (15)	6.1 (6)	2.9 (3)	4.4 (6)	−0.8 (4)	4.4 (5)	−1.0 (3)
O5	0.686 8 (10)	0.4766 (6)	0.712 8 (10)	4.9 (4)	3.3 (3)	4.2 (4)	−1.9 (3)	3.1 (3)	−0.8 (3)
O6	0.539 5 (10)	0.3696 (7)	0.469 7 (10)	3.5 (3)	3.3 (3)	3.4 (3)	−0.6 (2)	2.4 (3)	−0.2 (2)

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and were derived from the inverse of the final least-squares matrix. [b] Anisotropic thermal parameters are in units of Å^2 and enter the structure factor equation in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

fragment under study. Maximum and minimum transmission coefficients were 0.277 and 0.135, respectively.

Solution and Refinement of the Structure

Computer programs used during the structural analysis include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and least-squares refinements, by B. G. DeBoer), STAN1 (distances and angles, with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). All calculations were performed on an IBM 370/158 computer.

Scattering factors for neutral platinum, oxygen, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[8] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[9] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[10]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^2(|F_o|)$. Discrepancy indices used below are as defined previously.[11]

The structure was solved by the heavy-atom technique. Analysis was begun using a set of 1147 data obtained by averaging hkl and $h\bar{k}l$ values in the original 2311 independent measurements. A three-dimensional Patterson map led to the location of the Pt atom at (0.0, $^1/_4$, 0.25), where the y coordinate was a matter of arbitrary choice in this polar space group. In addition to the usual ambiguity found in $P2_1$ when the "observed" Fourier synthesis is phased by a single heavy atom—the appearance of false mirror planes at the heavy-atom y coordinates[12]—the accidental location of the Pt atom near $z = {}^1/_4$ led in this case to false C centering in the "observed" Fourier synthesis. Thus the "observed" Fourier map, as phased by the single Pt atom, had apparent symmetry $C2_1/m$.

The true structure was separated from its three rivals in stages starting with two cycles of full-matrix least-squares refinement of a trial structure comprised of the single platinum atom with anisotropic thermal parameters. The "platinum-atom-only" R factors were $R_F = 22.1\%$, $R_{wF} = 28.7\%$. Examination of the difference-Fourier synthesis computed on this model allowed the location of three ethylenediamine nitrogen atoms which, on the basis of their slightly larger peak intensities and stereochemical considerations, were taken to belong to the same image. Insertion of these atoms reduced R_F to 11.25% and R_{wF} to 16.0%. The location of the remaining nonhydrogen atoms and assignment of their chemical identities then proceeded without difficulty. After all 19 of the nonhydrogen atoms were located, the discrepancy indices were 6.30% and 7.62%, respectively. This model was noted at this point fortuitously to correspond to the known absolute configuration of the (R)-tartrate ion.[13]

The refinement of the structure was continued in the following steps: (1) the use of the full unaveraged data set (2311 data); (2) the application of the absorption correction; (3) the conversion to anisotropic thermal parameters for all 19 nonhydrogen atoms; (4) the insertion of 18 of the 20 hydrogen atoms in idealized position based on d(C–H) = 0.95 Å and d(N–H) = 0.87 Å[14] (with shifts set equal to the shifts of their attached atoms and with an overall isotropic thermal parameter for hydrogens attached to a given atom). Each of these steps led to reductions in the discrepancy indices. Correction for the effects of anomalous dispersion was included at all times. Values after these steps were $R_F = 3.12\%$, $R_{wF} = 4.17\%$.

A close examination of $|F_o|$ vs. $|F_c|$ for strong low-order reflections now suggested that a secondary extinction correction would be required. A parameter (C) for such a correction was therefore included in the model. It entered the equations for the corrected structure factor as described previously.[11]

Examination of $|F_o|$ vs. $|F_c|$ also revealed three small separate groups of reflections, distinct in orientation, in which somewhat high deviations ($||F_o| - |F_c||/\sigma > 3.0$) occurred. Each group consisted of reflections collected consecutively. In each group nearly all deviations had the same sign. The standard reflections on both sides of each group were unremarkable. On the assumption then of the existence of unassigned systematic error, 44 data were assigned zero weight in the least-squares refinement. Two final cycles of refinement led to $R_F = 2.96\%$, $R_{wF} = 3.90\%$ (not including the 44).

The largest shifts during the last cycle of refinement were 0.12 for a nonhydrogen parameter and 0.14σ for an isotropic (hydrogen) parameter. The "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 1.217, where m (the number of observations) was 2267, n (the number of variables) was 182, and $m{:}n$ = 12.46:1. The final value of the secondary extinction parameter was $C = 1.48\ (29) \times 10^{-5}$ mm^{-1} e^{-2}. The five highest peaks on a final difference Fourier map were all in the $y = {}^1/_4$ plane and within 1.3 Å of the Pt atom. (The largest was 3.73 e/Å^3 at (0.855, 0.25, 0.25), about 1.1 Å from the Pt atom.) The distribution of these peaks (all near the Pt atom) suggested that they were due to systematic error resulting from incompletely corrected absorption. The largest peak away from the Pt atom was 0.95 e/Å^3. Final positional and thermal parameters for all nonhydrogen and hydrogen atoms are given in Tables II and III. A last two cycles of refinement with enantiomeric coordinates led to significantly higher discrepancy indices ($R_F = 4.36$, $R_{wF} = 6.31$), confirming the correctness of handedness in the model (and consistent with the known absolute configuration of the (R)-tartrate).

Results and Discussion

The crystal structure consists of discrete bis(ethylenediamine)platinum(II) ions held by a network of hydrogen bonds to neighboring (R)-tartrate ions. (See Figure 1.) The closest Pt to Pt approach is 6.68 Å and the closest Pt to O approach is 3.48 Å. There is no question of Pt–Pt or Pt–O bonds.

Interestingly, this appears to be the first report of the crystal structure of any salt of the bis(ethylenediamine)platinum(II) ion. Cox and Preston[15] reported in 1933 that $[Pt(en)_2]Cl_2$ is isomorphous with $[Pd(en)_2]Cl_2$, crystallizing in the $P\bar{1}$ space

Table III. Final Parameters for "Riding" Hydrogen Atoms[a]

Atom	*x*	*y*	*z*	B[b]
C1H1	−0.1594 (14)	0.1670 (10)	0.5637 (15)	3.4 (17)
C1H2	−0.3367 (14)	0.1027 (10)	0.4389 (15)	
C2H1	−0.0735 (14)	−0.0246 (8)	0.5010 (14)	1.6 (12)
C2H2	−0.1644 (14)	0.0039 (8)	0.3017 (14)	
C3H1	0.1458 (17)	0.4925 (10)	0.1679 (17)	6.4 (26)
C3H2	0.0294 (17)	0.4908 (10)	−0.0324 (17)	
C4H1	0.2923 (17)	0.3657 (11)	0.0453 (16)	8.5 (34)
C4H2	0.1114 (17)	0.2944 (11)	−0.0518 (16)	
C6H	0.4841 (14)	0.1584 (15)	0.6368 (14)	2.4 (23)
C7H	0.3378 (18)	0.3410 (13)	0.6489 (19)	6.0 (36)
N1H1	−0.2680 (10)	0.3005 (11)	0.3537 (11)	2.9 (18)
N1H2	−0.3335 (10)	0.2115 (11)	0.2188 (11)	
N2H1	0.1357 (10)	0.1159 (6)	0.5257 (11)	2.8 (16)
N2H2	0.1296 (10)	0.0473 (6)	0.3771 (11)	
N3H1	−0.1280 (11)	0.4554 (7)	0.1597 (11)	6.7 (27)
N3H2	−0.1763 (11)	0.3789 (7)	0.0096 (11)	
N4H1	0.3217 (10)	0.2885 (18)	0.2923 (11)	7.5 (36)
N4H2	0.2485 (10)	0.1871 (18)	0.1781 (11)	

[a] Estimated standard deviations, shown in parentheses, of positional parameters are equal to those of the attached carbon or nitrogen atom. Also, see footnote *a*, Table II. [b] Isotropic thermal parameters, in units of Å^2. Parameters for hydrogen atoms attached to the same carbon or nitrogen were held equal.

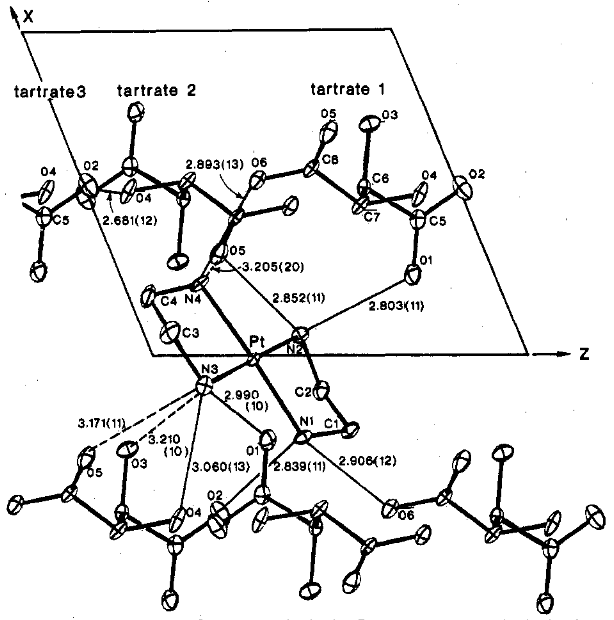

Figure 1. Orthogonal projection of structure of [Pt(en)$_2$]-(C$_4$H$_4$O$_6$) onto (010), showing hydrogen bonding and the unit cell. All atoms in the unique anion and cation are labeled. The second [Pt(en)$_2$]$^{2+}$ ion in the unit cell (related by 2$_1$ to the one shown) is omitted. All hydrogen atoms are omitted. Probable hydrogen bonds are indicated by thin solid lines. Other N· · ·O approaches are indicated by dotted lines. Tartrates 1, 3, 4, and 6 are translationally equivalent to each other as are tartrates 2 and 5. Note that tartrate 2 is below tartrates 1 and 3 whereas tartrate 5 is above tartrates 4 and 6.

group. Watt and Klett[16] also reported in 1963 the space group and cell dimensions of [Pt(en)$_2$]Cl$_2$. Neither completed a solution of the structure. The crystal structure of the [Pd(en)$_2$]Cl$_2$ has however since been studied.[17] It has δλ gauche chelate rings with the Pd lying at a crystallographic center of symmetry.

In approximate terms, the structure of the [Pt(en)$_2$]$^{2+}$ ion in this crystal is just as might be expected by comparison to the above result. (Bond distances and angles are given in Figure 2.) The complex ion is "square planar". The ethylenediamine chelate rings are gauche. The first ring (Pt-N1-N2) has the δ and the second (Pt-N3-N4) the compensating λ conformation. But effects of crystal packing and hydrogen bonding cause important distortions from the above general picture and lead to the absence of any element of symmetry in the complex ion.

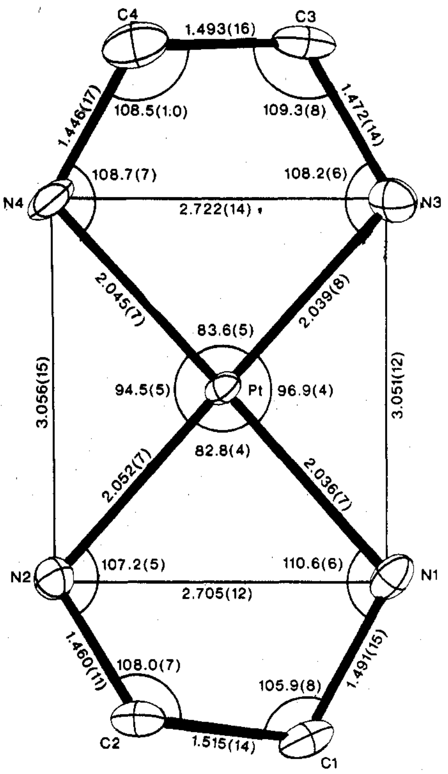

Figure 2. View perpendicular to the plane of the bis(ethylenediamine)platinum(II) ion. Interatomic distances and angles with esd's are shown (see footnotes to Table II). Hydrogens are omitted.

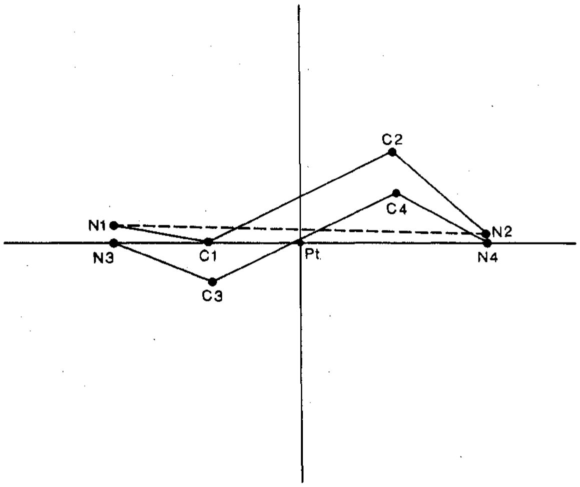

Figure 3. Projection of atomic positions in [Pt(en)$_2$]$^{2+}$ upon a plane perpendicular to the plane Pt-N3-N4. Distortions from nominal C_{2h} symmetry, in which ethylenediamine chelate rings would exactly eclipse each other, are apparent.

First, the PtN$_4$ chromophore finds itself distorted from planarity. The Pt-N1-N2 plane is at an angle of 4.3 (8)° to the Pt-N3-N4 plane. This distortion includes both of its possible components. Figure 3, which represents a projection of atomic positions in the complex ion onto a plane perpendicular to the Pt-N3-N4 plane, clearly shows the distortion of the [Pt(en)$_2$]$^{2+}$ ion from the nominal C_{2h} symmetry.

Also, the two chelate rings are not mirror images. In ring 1, C1 and C2 deviate from the Pt-N1-N2 plane by +0.208

(6), and −0.308 (6) Å, respectively. In ring 2, C3 and C4 deviate from the Pt–N3–N4 plane by +0.291 (7) and −0.373 (7) Å. These deviations are significantly different for each "mirror-related" pair of carbon atoms. Ring 1 is more puckered than ring 2. It is also interesting to compute the dihedral angles defined between the two N–C–C planes in each ring. This dihedral angle is 54.6 (8)° in ring 1 and 52.1 (5)° in ring 2. These values are close to those reported for the two Pt–en rings in *cis*-$[Pt(en)_2Cl_2]^{2+}$ (53.55°)[18] but less than the same measure of puckering in $[Pt(en)Cl_2]$ (68°)[19].

It seems clear that hydrogen bonds are responsible for the communication of this asymmetry from the optically active tartrate ions to the complex ions. The two ethylenediamine rings in the complex ion are quite distinctly different with respect to their hydrogen-bonding possibilities. Both nitrogens of the first ring (N1 and N2, Figure 1) have two hydrogen bonds to neighboring tartrate oxygens. The four N to O distances in these hydrogen bonds range from 2.803 (11) to 2.906 (12) Å. Such distances are considerably shorter than the average amine nitrogen to oxygen hydrogen-bond distance (3.04 Å)[20] and even somewhat shorter than the average amide nitrogen to oxygen hydrogen-bond distance (2.93 Å)[20] to which they are more properly comparable. With the second ethylenediamine chelate ring the hydrogen-bonding situation is less clear-cut. N3 has two probable hydrogen bonds. But both of these distances (N3–O1 = 2.990 (10) Å; N3–O4 = 3.060 (13) Å) exceed significantly any of the distances involving the nitrogens of the first ring. In addition N3 has two subsidiary approaches that are somewhat close: N3–O5 = 3.171 (11) Å; N3–O3 = 3.210 (11) Å (see Figure 1). N4 has one quite probable hydrogen bond (N4–O6 = 2.893 (13) Å). The only other N4 to oxygen approach at all close is N4–O5 (3.205 (20) Å). Hydrogens were not located in this study. Therefore it cannot be absolutely stated, particularly in the case of the longer nitrogen to oxygen distances, whether a hydrogen bond is or is not present. For example, hydrogens could be disordered among the several N to O approaches involving the atom N3. There is however no doubt about the difference between the two chelate rings' hydrogen-bonding interactions.

Another way to visualize the hydrogen bonding is to consider tartrate 1 (in Figure 1) to "belong" to the $[Pt(en)_2]^{2+}$, being held to it by two hydrogen bonds through carboxyl oxygens to N2 and N4. Then the N2, N4 side of the complex ion is plainly much different from the N1, N3 side where tartrate 6 (a translation of tartrate 1) hydrogen bonds through a carboxyl and a hydroxyl oxygen, not through two carboxyl oxygens.

Bond distances and angles in the tartrate ion are summarized in Table IV. The close agreement among the four carboxyl C–O bond distances confirms that the anion here is indeed tartrate and not hydrogen tartrate as in the possible formulation [Pt(en-H)(en)]Htart. In the crystal, each tartrate is hydrogen bonded to a twofold screw-axis-related neighbor (O2–O4 = 2.681 (12) Å; see Figure 1). In addition each tartrate is hydrogen bonded to five neighboring $[Pt(en)_2]^{2+}$ ions (just as each of these latter is hydrogen bonded to five tartrates). This hydrogen bonding is discussed above. The bond distances and angles are normal and in agreement with those found in other tartrates with the exception of the C6–C7–O4 bond angle. This value is significantly smaller than comparison values (105.4 (1.2)° vs. 113°,[21] for example) and smaller, too, than the comparable angle, C5–C6–O3, on "the other side" of this tartrate (105.4 (1.2)° vs. 109.8 (8)°). O4 is a hydroxide oxygen. It is involved in two hydrogen bonds, the one to the screw-axis-related tartrate and the other to N3 of the $[Pt(en)_2]^{2+}$ ion. O3, in contrast, is not involved in hydrogen bonds.

Table IV. Selected Interatomic Distances (Å) and Angles[a,b] with Esd's for (*R*)-Tartrate Ion in $[Pt(en)_2](C_4H_4O_6)$

	Distances		
C5–C6	1.549 (19)	C7–O4	1.413 (17)
C6–C7	1.516 (18)	C8–O5	1.239 (12)
C7–C8	1.540 (15)	C8–O6	1.258 (13)
C5–O1	1.245 (13)	O3–O4	2.833 (12)
C5–O2	1.237 (14)	O3–O2	2.632 (12)
C6–O3	1.422 (12)	O4–O5	2.657 (12)
	Angles		
O1–C5–O2	126.3 (13)	O6–C8–C7	116.0 (9)
O5–C8–O6	126.3 (9)	C5–C6–O3	110.7 (9)
O1–C5–C6	117.2 (10)	C8–C7–O4	112.1 (11)
O2–C5–C6	116.5 (10)	O3–C6–C7	109.8 (8)
O5–C8–C7	117.6 (10)	O4–C7–C6	105.4 (12)

[a] See Figure 1 for numbering of atoms. [b] Esd's, here and in Figure 2, are shown in parentheses and are right adjusted to the last digit of the preceding number. Their calculation includes the effects of all elements of the positional covariance matrix as well as the uncertainties in unit cell dimensions. No corrections have been applied for the effects of thermal motion.

The conformation of the tartrate ion is of the same general sort found in other tartrates but again differs in detail. The five nonhydrogen atoms of each $-CH(OH)COO^-$ half of the ion are approximately coplanar (largest deviation from one least-squares plane is 0.12 Å and from the other 0.05 Å). As a token of the packing effects in this crystal the angle between these two planes is distinctly less than the corresponding angle in other tartrates (45.7 (6)° vs. 65,[21] 63°[13]). Further, the dihedral angle between the planes defined by the central carbon–carbon bond with first one and then the other hydroxyl oxygen is 70.0 (6)° in this crystal (vs. 51[21] and 57°[13] in other tartrates).

As mentioned in the Introduction, it had been concluded that the slow mutarotation reflects the relaxation of some dissymmetric configuration of the $[Pt(en)_2]^{2+}$ back to C_{2h} symmetry. This x-ray study reveals just such a dissymmetric configuration. But, since distortions are found in both ions, the study by itself does not rule out the possibility that the course of mutarotation involves both ions or even the tartrate exclusively. It does rule out the possibility that mutarotation comes from conversion from the $\delta\delta$ (or $\lambda\lambda$) conformation of the chelate rings in the solid state to the inactive $\delta\lambda$ conformation in solution. It rules out as well various five-coordinate Pt(II) species that might be speculated as the source of the dissymmetry. The nature of the dissymmetry turns out, as seen above, to be more subtle than any of these suppositions.

The remarkable aspect of the situation is not that relatively small distortions should cause detectable changes in ORD spectra. Optical rotary power in d–d transitions for instance is in various theories a sensitive function of the location of the donor atoms.[22] What is remarkable rather is the observed slow rate of relaxation of the effect (half-life 110 min). Conceivably the slow mutarotation could, as suggested above, result from the independent relaxation of the distortions imposed by crystal formation upon either (or both) of the ions in this substance. But an explanation of the slowness would preferably involve the persistence of the stereospecific $[Pt(en)_2]^{2+}$ to (*R*)-tartrate interaction from crystal into solution; it is hard to imagine what other factors would keep the distorted $[Pt(en)_2]^{2+}$ ion, or the distorted (*R*)-tartrate ion, from readily finding a mechanism rapidly to relax to a nondistorted form. A likely possible means by which the stereospecific interaction could be preserved is outer-sphere coordination or ion pairing.

There is evidence for the existence of ion pairs in solutions of $[Pt(en)_2]$(*R*-tart). The equivalent conductance of a dilute solution at room temperature is 98 Ω^{-1} $cm^2/equiv$[23] (*c* 0.001 27 M). This is much less than the sum of the equivalent ionic conductances at infinite dilution of $[Pt(en)_2]^{2+}$ (139.5 Ω^{-1}

$cm^2/equiv^{24}$) and (*R*)-tartrate (59.6 Ω^{-1} $cm^2/equiv^{25}$). This reduction in the equivalent conductance of the 2:2 electrolyte indicates considerable association between the ions in solution. The equivalent conductance is reported not to change with time.[1]

The observation (slow mutarotation of fresh solutions with no change in conductance) could be explained by a rapid reaction upon dissolution to give equilibrium quantities of (hydrated) $[Pt(en)_2]^{2+}$ ions, $C_4H_4O_6^{2-}$ ions, and the ion pair $\{[Pt(en)_2]^{2+}, R\text{-}C_4H_4O_6^{2-}\}$. A fraction of the $\{[Pt(en)_2]^{2+}, R\text{-}C_4H_4O_6^{2-}\}$ ion pairs would be "originals" from the crystal, still persisting (at first) in the solution. The fraction could be quite small since there is no estimate of the magnitude of the "extra" rotatory power present in the stereospecifically linked ion pairs. Mutarotation then would follow the loss of this persisting fraction of "original" ion pairs in the dynamic association–dissociation process. Newly associated ion pairs, lacking the directing effect of packing in the crystal lattice would not, even if the same sort of distortions were imposed upon their component ions, have an excess of distortions of one configurational sense, as in the original case. In this explanation, the true source of the mutarotation effect is mutual, stemming from the ion pair. Still, the "extra" rotatory power might be predominantly the consequence of the distortions in one or two other of the ions.

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Registry No. $[Pt(en)_2](C_4H_4O_6)$, 59710-52-0.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Preparation and Structure of a Multiply Bonded Re_2^{5+} Species Bridged by Two Diphosphinomethane Ligands

F. ALBERT COTTON,* LARRY W. SHIVE, and B. RAY STULTS

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The compound $Re_2Cl_5[(Ph_2P)_2CH_2]_2 \cdot 2PhMe$ is prepared by refluxing a mixture of $(Bu_4N)_2Re_2Cl_8$ and bis(diphenylphosphino)methane in acetone for 24 h. Toluene was used to wash the solid reaction products; from this filtrate the substance was obtained as red-brown, air-stable crystals of diffraction quality. The crystals are monoclinic with cell dimensions $a = 14.274$ (3) Å, $b = 23.380$ (7) Å, $c = 18.577$ (3) Å, $\beta = 94.58$ (2)°, and $V = 6180$ (2) Å^3, having space group $P2_1/n$ with $Z = 4$. The structure was solved and refined to $R_1 = 0.061$ and $R_2 = 0.080$ using 4305 reflections with $I > 3\sigma(I)$ in the range $0° < 2\theta < 45°$ (Mo Kα). Two trans phosphine ligands bridge the strong metal–metal bond while chlorine atoms occupy the four remaining equatorial and one of the two coaxial positions on the metal atoms. The molecule has a virtual mirror plane containing the rhenium and chlorine atoms. Important distances in the molecule are Re–Re = 2.263 (1) Å, Re–P = 2.47 (3) Å, Re–Cl$_{equat}$ = 2.35 (4) Å, and Re–Cl$_{axial}$ = 2.575 (6) Å; an ESR spectrum of the complex suggests that there is one unpaired electron coupled to two metal nuclei, each with $I = {}^5/_2$.

Introduction

Soon after the existence of the quadruple bond was recognized[1-3] in the $Re_2Cl_8^{2-}$ ion, the preparation of derivatives in which neutral ligands replace some of the anionic ligands[4-9] was reported to produce species such as $Re_2Cl_6(PR_3)_2$ and $[ReCl_3(DTH)]_x$, where DTH = $CH_3SCH_2CH_2SCH_3$. It was recognized then that reactions with neutral ligands can involve more than simple replacement, namely, reduction; the first example was $Re_2Cl_5(DTH)_2$.[5-7] Since then, Walton and co-workers have explored other reductive reactions of $Re_2Cl_8^{2-}$ and Re_3Cl_9 with phosphines and shown that there is an extensive chemistry of this kind.[10,11]

We have examined the reaction of the diphosphine $Ph_2PCH_2PPh_2$, bis(diphenylphosphino)methane, commonly abbreviated dppm, with $(Bu_4N)_2Re_2Cl_8$. Since dppm is known[12] to be sterically capable of forming approximately parallel bonds to two adjacent metal atoms which are bonded to each other, it was our hope that one or both of the products,