Platinblau

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Abstract: Platinblau, the anomalously blue platinum amide complex previously thought to have the composition $Pt^{II}(CH_3CONH)_2 \cdot H_2O$, has been shown by crystallographic, analytical, infrared, and nmr studies to be $Pt^{IV}(CH_3CONH)_2(OH)_2$, the corresponding blue dichloride also having been prepared. A related divalent platinum complex, $Pt^{II}[(CH_3)_3CCONH_2]_2Cl_2$ (I), contains trimethylacetamide in its iminol form, RC(OH)═NH, with coordination of the square-planar Pt by the ═NH group. In a second compound of the formula $Pt^{IV}[(CH_3)_3CCONH]_2Cl_2$ (II), one of the amide ligands is present as an amide anion, $-C(=O)NH^-$, and the other as an iminol anion, $-C(OH)=N^-$. Yellow II is readily converted into its blue tautomer (III), which is the trimethylacetamide analog of the original Platinblau, and contains both amide groups as amide anions. The crystallographic study was performed on a crystal of I doped with 20% of II and 10% of III.

The complexes of platinum having first-row atoms as ligands exhibit a certain uniformity of color, being only infrequently red, and quite often yellow or even colorless. Such would seem to be the case almost without exception, for both the divalent and tetravalent oxidation states. In view of this, it is highly anomalous that the simple complex generally agreed to have the composition $Pt^{II}(CH_3CONH)_2 \cdot H_2O$ has a deep blue color. Called Platinblau by the early German workers,[1] this anomalous material was first prepared in 1909 by shaking Ag_2SO_4 with the yellow complex $Pt^{II}Cl_2(CH_3CN)_2$. The blue reaction product has a monomeric molecular weight in water and was concluded to be a divalent platinum complex, since on treatment with concentrated HCl, 90% of the platinum was recovered as $Pt^{II}Cl_4^{2-}$. Actually, other blue-violet platinum complexes are known,[2] but they are in all cases *polymeric* materials having strong metal–metal interactions.

As can be seen from Figure 1, Platinblau has been assigned a variety of structures, all of which have the common feature that the platinum is divalent. The structure most generally accepted involves square-planar platinum and chelating acetamido groups (A),[3,4] whereas other postulated structures involve six-coordinate dimers (B),[5] polymeric chains with bridging acetamido groups (C),[6] and one novel suggestion involving diazocyclobutadiene as a ligand (D).[7] Structures B and C are contradicted, of course, by the molecular weight first reported by Hofmann and Bugge.[1]

It was our original intention to study the electronic structure and electronic spectrum of this material after first having satisfied ourselves as to its molecular structure. This first step has now been completed, and we report the results of this study here. Inasmuch as unambiguous conclusions came rather slowly, we have had to use a variety of techniques to finally solve the structural aspects of the problem, including single-crystal X-ray structure analysis, nmr (60, 100, 220 MHz), infrared, and ultraviolet spectroscopic analysis. In fact, our evidence for the nature of Platinblau itself is somewhat indirect, since a large part of our work was actually done on alkylated analogs of the parent compound.

We found first that Platinblau, prepared by the method of Hofmann and Bugge, was badly contaminated by Ag_2SO_4, as determined by X-ray fluorescence analysis, and that repeated preparation consistently gave material which was amorphous to both X-rays and electrons. In order to circumvent this latter problem, we turned to the preparation of Platinblaus made with other amide ligands and found that a large number of deep blue or green platinum amide complexes could be prepared by a variety of methods. In fact, blues made with a large number of other amides and imides have already been reported.[4,8] Although we have been unable to prepare such a compound with any N-substituted amide, almost every unsubstituted amide tried yielded a blue or green complex, either by simply heating the solid or molten amide and dichlorobis(acetonitrile)platinum(II), or by the reaction of the amide and an aqueous solution of K_2PtCl_4. Only one of these complexes that formed by 2,2-dimethylpropanamide (trimethylacetamide, TMA) could be obtained in a crystalline form.

Experimental Section

Preparation of Compounds. The preparation of the crystalline platinum TMA complex has been described previously.[9] Dichlorobis(benzamido)platinum(IV) was prepared by gently heating an excess of benzamide with $PtCl_2(CH_3CN)_2$. Most of the unreacted benzamide was removed by ether extraction, and the remainder was sublimed away at ~90°. The remaining blue-green solid was washed several times with methanol and was then dissolved in dimethyl sulfoxide. Addition of water gave a deep green precipitate, which was dried under vacuum at room temperature. *Anal.* Calcd for $PtCl_2(C_6H_5CONH)_2$: Pt, 38.54; C, 33.21; O, 6.32; H, 2.39; mol wt, 506. Found: Pt, 38.60; C, 32.72; O, 6.50; H, 2.63; mol wt, 405 (in dimethylformamide). All microanalyses

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[1] K. A. Hofmann and G. Bugge, *Ber.*, **41**, 312 (1908).

[2] See, for example, K. Krogmann and H.-D. Hausen, *Z. Anorg. Allgem. Chem.*, **358**, 67 (1968).

[3] I. I. Chernyaev and L. A. Nazarova, *Izv. Sektora Platiny i Drug. Blagorodn. Metal., Inst. Obshch. i Neorg. Khim., Akad. Nauk SSSR*, **26**, 101 (1951).

[4] V. F. Barkovskii and L. M. Kul'berg, *ibid.*, **28**, 235 (1954).

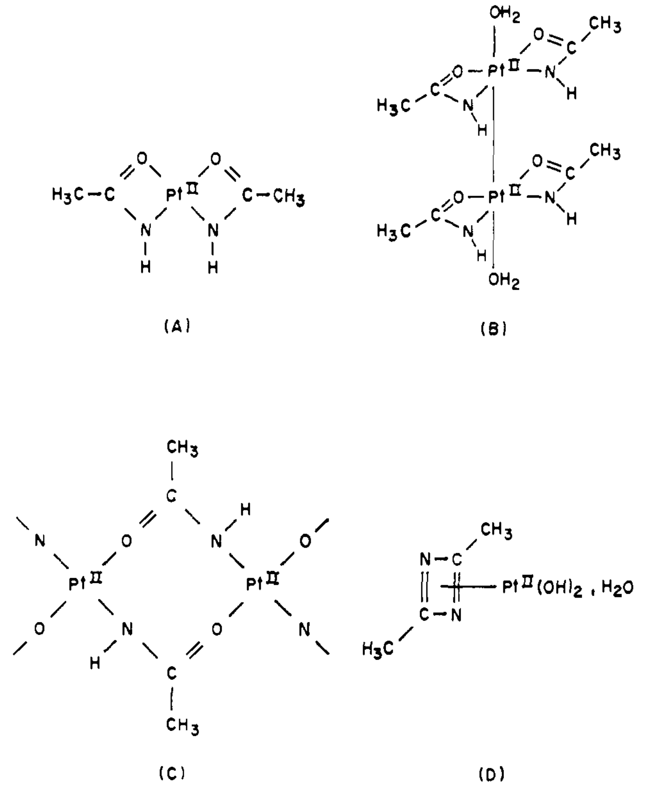
[5] I. I. Chernyaev, E. V. Shenderetskaya, L. A. Nazarova, and A. S. Antsyshkina, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm, 1962, p 260.

[6] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).

[7] L. E. Orgel, International Conference on Coordination Chemistry, Special Publication 13, The Chemical Society, London, 1959, p 96.

[8] N. Kurnakow, *J. Prakt. Chem.*, **51**, 234 (1895). Though Hofmann and Bugge[1] are generally given credit for the initial discovery of Platinblau, Kurnakow briefly described this type of compound almost 15 years earlier.

[9] D. B. Brown, M. B. Robin, and R. D. Burbank, *J. Amer. Chem. Soc.*, **90**, 5621 (1968).



(A) (B)

(C) (D)

Figure 1. Proposed structures for Platinblau.

and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Dichlorobis(acetamido)platinum(IV) was similarly prepared by heating acetamide and $PtCl_2(CH_3CN)_2$ in an open dish until the molten acetamide dissolved the platinum complex and became deep blue. Upon cooling, the solid mass was dissolved in methanol, and the deep blue complex was precipitated with ether. *Anal.* Calcd for $PtCl_2(CH_3CONH)_2$: Pt, 51.06; C, 12.57; N, 7.33; O, 8.37; H, 2.11. Found: Pt, 50.67; C, 12.66; N, 7.30; O, 8.07; H, 2.38.

Platinblau itself, formulated previously as $Pt(CH_3CONH)_2 \cdot H_2O$, was prepared as originally reported by Hofmann and Bugge.[1] X-Ray fluorescence analysis showed this material to be strongly contaminated by Ag_2SO_4 and, unless prepared using an excess of silver salt, by chloride as well. Ag_2SO_4 was removed by dissolving the sample in methanol and chromatographing on alumina, the Platinblau being recovered from the eluent by evaporation. The dried material was free of Cl, Ag, and S and had the analysis: Pt, 56.33; C, 13.75, N, 7.95; O, 18.36; and H, 2.81. While this analysis differs significantly from those reported for Platinblau in the past,[1,6,10] the disagreement can be explained. One of our samples of Platinblau, prepared using an excess of $PtCl_2(CH_3CN)_2$ in an attempt to minimize the silver impurities, had the analysis: no significant Ag impurity; Pt, 58.73; C, 14.22; N, 7.38; and H, 2.68, these being the elements for which analyses have generally been obtained. Since $Pt(CH_3CONH)_2 \cdot H_2O$ requires 59.26% Pt, 14.59% C, 8.51% N, and 3.06% H, the agreement between these two sets of figures is not bad, and it would be reasonable to conclude that the formulation is correct. However, since this same sample also contained 5.02% Cl, there clearly can be a significant disagreement with the earlier formulation when more complete analyses are obtained. The correct formulation of Platinblau will be discussed in the final section of this paper.

Blue complexes of trifluoroacetamide, fluoroacetamide, and chloroacetamide were also prepared by heating the appropriate solid amide and $PtCl_2(CH_3CN)_2$ in an open dish, while a deep blue complex with formamide was prepared by suspending $PtCl_2(CH_3CN)_2$ in the neat liquid for 3 days at room temperature. None of these complexes was isolated or characterized.

Conductivities of several of the compounds were measured on at least three solutions in the concentration range 10^{-3}–10^{-4} *M* using either CH_3CN or H_2O as solvent, with a Serfass conductivity bridge, Model RCM 15 Bl, and a standard conductivity cell.

Nmr spectra were measured at 60, 100, and 220 MHz, using Varian Associates A-60, HA-100, and HR-220 spectrometers. All spectra reproduced in this paper were obtained at 100 MHz, using either $CDCl_3$ or $(CD_3)_2SO$ as solvents, with tetramethylsilane as an internal standard.

Infrared spectra of our compounds in the range 200–5000 cm^{-1} were run as Nujol mulls, KBr pellets, and concentrated solutions in CCl_4, $CDCl_3$, or $(CD_3)_2SO$. A Cary Model 14 spectrophotometer was used to determine the optical spectra (8000–52,000 cm^{-1}) of certain of the blue compounds in CH_3CN, CH_3OH, or H_2O solutions, and as thin films on quartz plates.

Crystal Structure Analysis. The trimethylacetamide complex of nominal composition $PtCl_2[(CH_3)_3CCONH_2]_2$ was obtained as needle-like dichroic crystals of prismatic cross section by evaporation of an ether solution. Precession camera data showed that the crystals were orthorhombic, with extinctions corresponding to space group Pbcn = D_{2h}^{14}. The intensity distribution indicated that there were eight Pt atoms in x, y, z at approximately $^3/_8$, $^1/_8$, $^1/_4$, and four Pt atoms in 0, y, $^1/_4$ with y approximately $^1/_8$.

The crystal selected for X-ray study had dimensions 0.39 × 0.12 × 0.09 mm along the *a*, *b*, and *c* axes, respectively, with *a* along the needle axis and {021} prism faces. Mounting the crystal with the *a* axis parallel to the φ axis of a manually operated quarter-circle Eulerian cradle goniostat, cell constants and intensities were then measured using a copper X-ray tube operated at 50 kV and 15 mA (Cu $K\alpha_1$, λ 1.5405 Å). The unit cell dimensions were obtained from careful measurements of the $h00$, $0k0$, and $00l$ reflections.

Intensities were measured using a stationary-crystal–stationary-counter technique, together with Ni–Co balanced filters and 20-sec counting intervals. A total of 2990 independent intensities were measured out to a 2θ angle of 100°, with 943 intensities considered to be zero.

The unit cell of $PtCl_2[(CH_3)_3CCONH_2]_2$ at 24° has the dimensions $a = 11.526 \pm 0.004$, $b = 22.152 \pm 0.008$, and $c = 18.544 \pm 0.006$ Å, the error limits being estimates. The X-ray density for this composition is 1.820 g/cc (measured ~1.92), and the linear absorption coefficient is 198 cm^{-1}. The raw intensities were corrected for absorption and Lorentz polarization effects with a program written by Prewitt,[11] which can treat a crystal of arbitrary shape. The transmission varied by a factor of 2.57 between the extreme cases.

Using the Sly, Shoemaker, Van den Hende ERFR 2 program,[12] the Patterson function was computed in order to locate the Pt atoms more precisely. Pt coordinates were then refined through three cycles of isotropic least squares to $R = 0.254$. An electron density based on Pt phases showed a pair of strong secondary peaks associated with each Pt atom, which proved to be the Cl atoms. In the subsequent analyses with the Busing, Martin, Levy least-squares program,[13] minimizing the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$, the atomic scattering factors were taken from Table 3.3.1B of the International Tables,[14] together with the Cromer[15] corrections to the real and imaginary components of the anomalous dispersion for the Pt and Cl atoms. All of the nonzero reflections were given equal weight, and zero observed intensities were given zero weight.

The $PtCl_2$ portion of the structure was refined through two anisotropic least-squares cycles to $R = 0.164$. A difference synthesis then revealed reasonable locations for the C, N, and O atoms of the two trimethylacetamide groups coordinated to each Pt(2) atom in x, y, z. However, no light atoms could be identified with the $PtCl_2$ group centered in 0, y, $^1/_4$. The identifiable portion of the structure was refined through three cycles of isotropic least squares to $R = 0.143$, and then, through five cycles of anisotropic least squares to $R = 0.107$, $wR = 0.119$. These values do not include the unobservable reflections. Tables of the calculated and observed structure factors are available from the authors. Since the N and O atoms could not be distinguished from each other, the scattering factor for O was used for both atoms. The maximum final parameter shifts were 0.05σ for Pt, 0.08σ for Cl, and as large as 0.5σ for atom O(1). The position and thermal parameters so derived

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(10) W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **18**, 549 (1962).

(11) C. T. Prewitt, E. I. duPont de Nemours & Co., Wilmington, Del.

(12) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, Esso Research and Engineering Co., Report CBRL-22M-62, 1963.

(13) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report TM-305, 1962.

(14) "International Tables for X-ray Crystallography," The Kynoch Press, Birmingham, England, 1962.

(15) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

Table I. Positional Parameters in $PtCl_2[(CH_3)_3CCONH_2]_2$[a]

Atom	x	y	z
Pt(1)	0	0.1383 (01)	0.2500 (00)
Cl(1)	0.0376 (12)	0.1376 (06)	0.1271 (06)
Pt(2)	0.3117 (01)	0.1298 (01)	0.2702 (01)
Cl(2)	0.2861 (12)	0.2206 (06)	0.3271 (06)
Cl(3)	0.3404 (13)	0.0379 (05)	0.2177 (07)
N(1)	0.3647 (40)	0.1700 (22)	0.1720 (17)
O(1)	0.3008 (77)	0.2590 (25)	0.1856 (48)
C(1)	0.3523 (55)	0.2178 (39)	0.1429 (35)
C(2)	0.3915 (51)	0.2287 (28)	0.0641 (21)
C(3)	0.2716 (60)	0.2326 (38)	0.0230 (26)
C(4)	0.4750 (52)	0.1783 (41)	0.0381 (27)
C(5)	0.4622 (56)	0.2886 (26)	0.0592 (34)
N(2)	0.2533 (33)	0.0883 (18)	0.3623 (16)
O(2)	0.4161 (35)	0.0288 (18)	0.3837 (18)
C(6)	0.3058 (49)	0.0503 (24)	0.4013 (23)
C(7)	0.2629 (60)	0.0268 (28)	0.4739 (27)
C(8)	0.1397 (56)	0.0510 (37)	0.4879 (32)
C(9)	0.3478 (72)	0.0562 (44)	0.5345 (31)
C(10)	0.2864 (84)	−0.0418 (40)	0.4757 (41)

[a] Estimated standard deviations in parentheses refer to the last two figures reported.

are summarized in Tables I and II, while the bond distances and angles for the complex with Pt at x, y, z [Pt(2)], are given in Figure 2 and Tables III and IV. Two of these Pt(2) complexes are associated with a $PtCl_2$ group at 0, y, $^1/_4$ [Pt(1)], to form a triplet as shown in Figure 3.

Discussion

Since the Pt atom at 0, y, $^1/_4$ lies on a twofold rotation axis, with the linear $PtCl_2$ group normal to the axis, the coordinating organic ligands must either possess twofold rotational symmetry (impossible for trimethylacetamide) or be subject to some sort of disorder which satisfies the symmetry on a statistical basis. A difference synthesis was prepared which contained several concentrations of electron density along the twofold axis, but attempts at interpretation were not successful and required inordinate amounts of computer time because of the many reflections and parameters involved. It was at this point that we terminated the structure analysis and turned to a study of the other physical properties of $PtCl_2[(CH_3)_3CCONH_2]_2$, in order to determine the proton configurations within the amide groups in the x, y, z positions, and the character of the complex in the 0, y, $^1/_4$ position.

Table II. Thermal Parameters in $PtCl_2[(CH_3)_3CCONH_2]_2$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Δr, Å[b]
Pt(1)	0.0132 (03)	0.0035 (01)	0.0037 (01)	0.0000 (00)	−0.0005 (01)	0.0000 (00)	0.490 (03)
Cl(1)	0.0186 (16)	0.0051 (04)	0.0042 (04)	−0.0015 (07)	0.0003 (06)	0.0001 (04)	0.570 (11)
Pt(2)	0.0129 (02)	0.0038 (01)	0.0031 (01)	0.0004 (01)	−0.0002 (01)	0.0002 (01)	0.485 (02)
Cl(2)	0.0180 (16)	0.0044 (04)	0.0046 (04)	0.0009 (07)	−0.0008 (07)	−0.0004 (03)	0.557 (11)
Cl(3)	0.0227 (18)	0.0033 (03)	0.0060 (05)	0.0008 (06)	0.0001 (08)	−0.0002 (03)	0.583 (11)
N(1)	0.0278 (63)	0.0087 (18)	0.0029 (11)	−0.0020 (29)	−0.0012 (22)	−0.0001 (12)	0.674 (36)
O(1)	0.0622 (173)	0.0058 (18)	0.0344 (74)	0.0102 (46)	0.0131 (90)	−0.0025 (28)	1.078 (78)
C(1)	0.0164 (69)	0.0112 (34)	0.0080 (32)	−0.0007 (40)	−0.0007 (37)	0.0084 (29)	0.727 (72)
C(2)	0.0194 (71)	0.0069 (21)	0.0020 (13)	0.0047 (35)	−0.0002 (26)	0.0006 (14)	0.581 (50)
C(3)	0.0231 (90)	0.0127 (38)	0.0038 (20)	−0.0007 (49)	−0.0018 (36)	0.0013 (23)	0.733 (64)
C(4)	0.0159 (74)	0.0178 (47)	0.0039 (20)	0.0013 (49)	0.0028 (30)	−0.0041 (26)	0.786 (73)
C(5)	0.0239 (97)	0.0042 (17)	0.0100 (34)	−0.0029 (33)	−0.0025 (44)	−0.0006 (20)	0.663 (56)
N(2)	0.0194 (45)	0.0068 (14)	0.0039 (11)	0.0006 (22)	0.0002 (19)	0.0011 (10)	0.606 (31)
O(2)	0.0189 (46)	0.0073 (15)	0.0059 (15)	0.0033 (22)	0.0029 (22)	0.0031 (12)	0.642 (34)
C(6)	0.0145 (61)	0.0047 (16)	0.0035 (16)	0.0005 (27)	0.0011 (26)	0.0006 (13)	0.525 (41)
C(7)	0.0237 (88)	0.0048 (18)	0.0050 (21)	−0.0013 (33)	0.0055 (35)	0.0000 (16)	0.605 (50)
C(8)	0.0172 (74)	0.0124 (37)	0.0067 (27)	−0.0010 (45)	0.0052 (38)	0.0027 (26)	0.735 (63)
C(9)	0.0340 (123)	0.0150 (49)	0.0048 (23)	−0.0104 (65)	−0.0057 (45)	0.0023 (28)	0.828 (80)
C(10)	0.0427 (164)	0.0083 (33)	0.0107 (41)	0.0040 (63)	0.0100 (69)	0.0052 (31)	0.825 (79)

[a] The expression for the temperature factor exponent is $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. Estimated standard deviations in parentheses refer to the last two (or three) figures reported. [b] Apparent rms radial displacement of the atoms. See text and Table VI for interpretation.

Table III. Bond Distances in the Ordered Units of $PtCl_2[(CH_3)_3CCONH_2]_2$

Atom pair	Distance, A[a]
Pt(2)–Cl(2)	2.29 (0.01)
Pt(2)–Cl(3)	2.28 (0.01)
Pt(2)–N(1)	2.12 (0.04)
Pt(2)–N(2)	2.05 (0.03)
C(1)–N(1)	1.20 (0.07)
C(1)–O(1)	1.35 (0.09)
C(1)–C(2)	1.55 (0.07)
C(2)–C(3)	1.58 (0.07)
C(2)–C(4)	1.55 (0.08)
C(2)–C(5)	1.56 (0.07)
C(6)–N(2)	1.26 (0.05)
C(6)–O(2)	1.40 (0.05)
C(6)–C(7)	1.53 (0.06)
C(7)–C(8)	1.54 (0.08)
C(7)–C(9)	1.63 (0.08)
C(7)–C(10)	1.54 (0.08)

[a] Estimated standard deviations are in parentheses.

Much to our surprise, chromatography of the blue-green needles of $PtCl_2[(CH_3)_3CCONH_2]_2$ on a silica gel column yielded *three* distinct components, I, II, and III. Compound I, eluted with $CHCl_3$, was obtained in about 70% yield as yellow needles (*Anal.* Pt, 41.44; O, 6.58; N, 5.88; C, 25.77; H, 4.59), mp 173–176° dec; molecular weight in $CHCl_3$, 440 (calcd for $PtCl_2[(CH_3)_3CCONH_2]_2$, 468). Continued elution with $CHCl_3$ led to the collection of a second yellow material (II) in 20% yield, and finally, elution with ether led to the recovery of a deep blue, amorphous powder, III. Compounds II and III had analyses identical with those of I and the original blue-green needles, and moreover, the yellow needles I and II appear to be isostructural with the blue-green needles, as demonstrated with X-

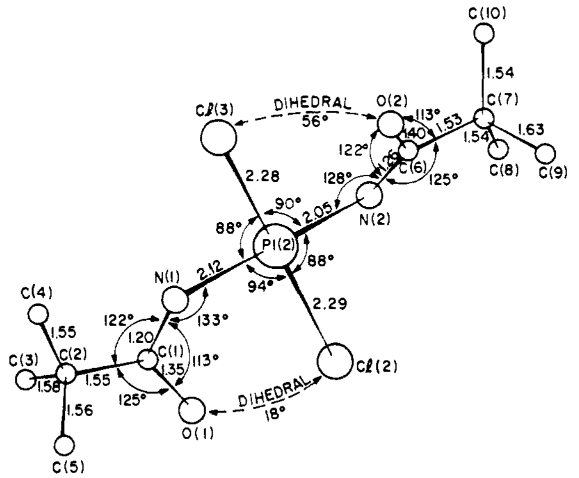


Figure 2. Bond distances and bond angles in the $PtCl_2[(CH_3)_3CCONH_2]_2$ complexes with Pt at *x*, *y*, *z*, in projection along the *a* axis.

ray powder patterns. All three fractions, as well as the blue-green needles, are monomeric in chloroform. Thus was it learned that the apparently homogeneous blue-green needles used in the X-ray study are really mixed crystals of the three components, I, II, and III.

Table IV. Bond Angles in the Ordered Units of $PtCl_2[(CH_3)_3CCONH_2]_2$

Atom pairs	Angle, deg[a]
Cl(2)–Pt(2)–Cl(3)	177.7 (0.4)
N(1)–Pt(2)–N(2)	176.8 (1.5)
N(1)–Pt(2)–Cl(2)	93.7 (1.3)
N(1)–Pt(2)–Cl(3)	88.1 (1.3)
N(2)–Pt(2)–Cl(2)	88.2 (1.1)
N(2)–Pt(2)–Cl(3)	90.2 (1.1)
C(1)–N(1)–Pt(2)	133.4 (4.9)
N(1)–C(1)–O(1)	112.8 (6.2)
N(1)–C(1)–C(2)	121.9 (7.6)
O(1)–C(1)–C(2)	125.3 (6.5)
C(1)–C(2)–C(3)	102.0 (4.6)
C(1)–C(2)–C(4)	111.2 (5.0)
C(1)–C(2)–C(5)	109.9 (5.4)
C(3)–C(2)–C(4)	115.6 (5.0)
C(4)–C(2)–C(5)	105.7 (5.1)
C(5)–C(2)–C(3)	112.5 (4.9)
C(6)–N(2)–Pt(2)	128.2 (4.9)
N(2)–C(6)–O(2)	122.0 (4.1)
N(2)–C(6)–C(7)	125.2 (5.2)
O(2)–C(6)–C(7)	112.6 (4.7)
C(6)–C(7)–C(8)	109.2 (5.4)
C(6)–C(7)–C(9)	106.1 (4.7)
C(6)–C(7)–C(10)	107.3 (4.7)
C(8)–C(7)–C(9)	107.4 (5.5)
C(9)–C(7)–C(10)	105.9 (6.9)
C(10)–C(7)–C(8)	120.1 (6.2)

[a] Estimated standard deviations are in parentheses.

The above observations can be correlated with the crystal structure analysis in the following manner. Considering the triplets of platinum found in the structure of the blue-green needles (Figure 3), the two outer members of a triplet, Pt(2) and Pt(2′), for which all heavy atoms were resolved, must yield compound I on chromatography, whereas the apparent disorder about the central platinum atom Pt(1) arises from the random occupation of this site by molecules of either II or III. Thus the crystal structure analysis has not given us the structure of the dark blue platinum complex, but does suggest that it must be very close to that of compound I.

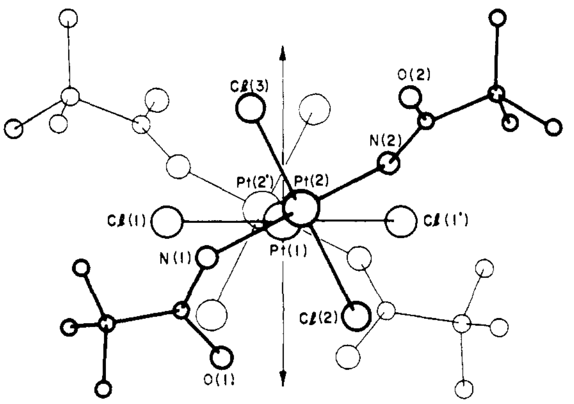
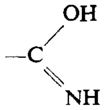


Figure 3. The association of two complexes of the iminol form with a substitutionally disordered complex of unspecified structure, projected down the *a* axis. The unit cell contains four such three-layered groups, each of which is centered on a twofold rotation axis perpendicular to *a*.

Nmr Spectra. The nmr spectrum of I (Figure 4) illustrates a curious arrangement of atoms. Looking first at the uncomplexed TMA (Figure 4), one sees a sharp band at τ 8.78 and a broad one at τ 4.16, with relative intensities 9:2, as expected for the methyl and amide protons of this molecule. The exaggerated width of the τ 4.16 resonance is due to the relaxation of the proton spins by the quadrupole moment of the nitrogen nucleus, and is generally taken as a characteristic of protons bonded to nitrogen. The proton nmr of compound I shows not only the sharp band at τ 8.78 and a broad one at τ 3.25, but a third sharp band at τ −0.44, the relative intensities being 9:1:1. Since the protons on the nitrogen atom of amides invariably appear as broad bands in the region τ 3–5, the sharp, low-field signal at τ −0.44 can only be interpreted as showing that one of the protons of the amide group ligand in complex I has been transferred to the oxygen atom. Because such an iminol structure



is analogous to a carboxylic acid, the hydroxyl proton would be expected to exhibit a low-field shift, as observed in the isoelectronic pivalic acid (τ −2.08)[16] and in protonated amides.[17] In addition, both the τ −0.44 and 3.25 resonances disappear in solutions of I in D_2O–acetone mixtures, as expected for the readily exchangeable protons of the –OH and =NH groups.

Several claims for amide tautomerism have been made in the past, based on solvent effects on the ORD spectra of optically active N-substituted benzamides,[18] the ultraviolet spectra of amides of trichloroacetic and benzoic acids,[19] and the infrared spectrum of

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(16) F. A. Bovey, "NMR Data Tables for Organic Compounds," Interscience Publishers, New York, N. Y., 1967, p 105.

(17) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

(18) V. M. Potapov and A. P. Terent'ev, *Zh. Obshch. Khim.*, **31**, 1720 (1961); *Chem. Abstr.*, **55**, 27195*i* (1961); *Dokl. Akad. Nauk SSSR*, **132**, 626 (1960).

(19) A. Hantzsch, *Ber.*, **64**, 661 (1931).

urea.[20] The evidence which has been presented is far from conclusive, and the nmr studies of Skulski, Palmer, and Calvin[21] have shown that in at least the first case, the results are better explained in terms other than amide–iminol equilibrium. Our claim for the iminol configuration in compound I is based essentially upon the nmr data quoted above, but also receives firm support from the infrared study to be discussed below.

Referring to Figure 2, the crystal structure analysis shows that the atom bonded to Pt(2) is that which is double-bonded to the carbon atom of the ligand, *i.e.*, the nitrogen atom of the iminol group. This is rather interesting, since in other transition metal amides, where the ligand is the normal amide configuration, it is known that metal–ligand coordination is through the oxygen.[22–25] However, one other feature of possible importance here is the well-known reluctance of oxygen to bond to divalent platinum.

The nmr spectrum of compound II shows it to have an even more surprising structure than that of compound I. In this compound, we find two sharp methyl peaks (τ 8.55, 8.78), a broad amide peak (τ $\sim$3.05), and a sharp low-field peak (τ -1.10), with intensity ratios 9:9:1:1 (Figure 4). These ratios are important, for they demonstrate that two protons are missing in compound II, thus implying the presence of amido anions and tetravalent platinum. The two nonmethyl protons can be assigned by placing one on a nitrogen in one ligand, giving the expected amido anion, and placing the remaining proton on the oxygen of the second ligand, giving the unexpected iminol anion. The different proton configurations in the two ligands then serve to make the methyl groups of the two ligands inequivalent, as observed. As with compound I, the infrared spectrum of II (*vide infra*) is in agreement with the configuration derived from the nmr experiments. While the amido anion is known from the heavy metal compounds $AgCH_3CONH$ and $Hg(CH_3CONH)_2$,[3,10] the iminol anion in II is a new species.

Unlike divalent platinum, tetravalent platinum prefers sixfold coordination and does not hestitate to bond to oxygen. On this basis, we are tempted to assign the amido and iminol anion ligands as bidentate in complex II. Such a ligand configuration would act to place ligand atoms between the Pt(1) and Pt(2) atoms in the blue-green needles, and would thereby explain their anomalously large separation (3.617 Å). If this is the case, then Pt–Pt bonding is ruled out altogether in all of these systems. On the other hand, the nmr spectrum of II in $CDCl_3$ does not show any sign of Pt–H coupling, as might reasonably be expected if the –OH group of the iminol were bonded to the platinum. Exchange of the –OH protons among themselves or with traces of water which are undoubtedly present would serve to eliminate the coupling, but we have not been able to prove this and thus we are forced to conclude that the iminol –OH group in compound II is probably not coordinated to the Pt atom in chloroform solution.

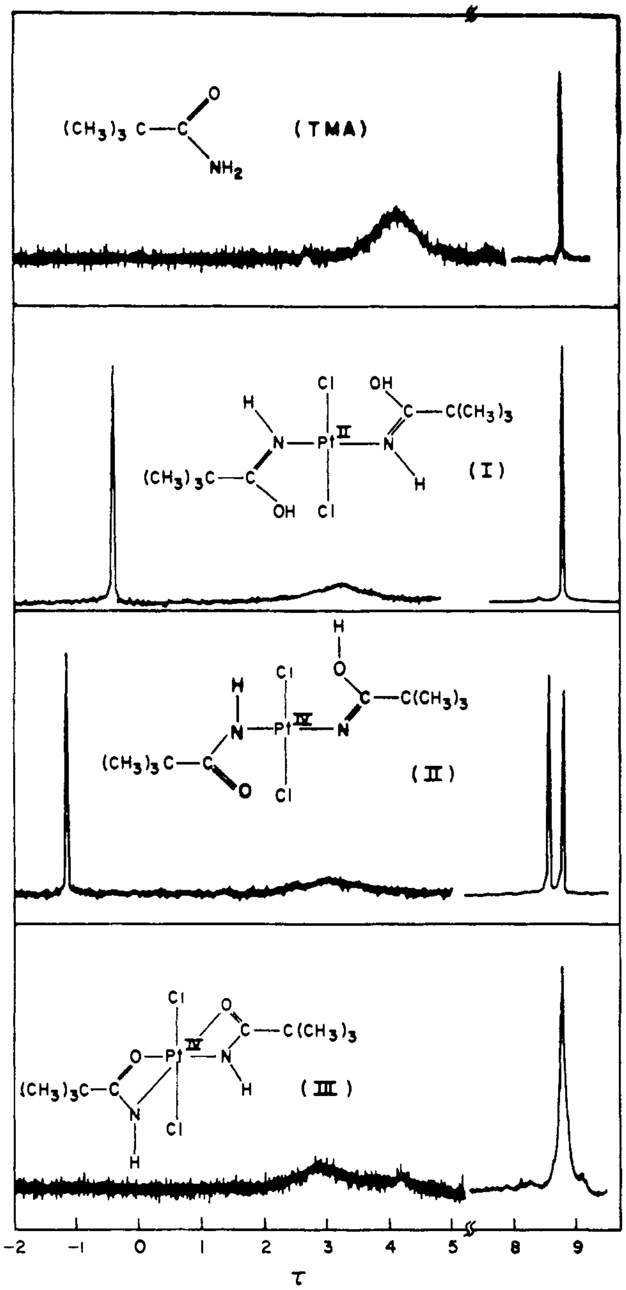

Figure 4. The 100-MHz proton nmr spectra of TMA and components I, II, and III in $CDCl_3$ solution.

The final component of the chromatography, constituting about 10% of the original needles, is a deep blue, amorphous powder, and, of course, it is the object of our initial interest in these materials. The nmr of compound III (Figure 4) shows no low-field resonance to indicate iminol formation, but as in the case of compound II, exhibits a 9:1 ratio of methyl to amide protons, again indicating amido anions and tetravalent platinum. Unlike the situation with compound II, the nmr spectrum of compound III does not rule out the possibility that the amido anion ligands are bidentate, for the great width of the N–H proton resonance precludes finding any Pt–H coupling. The unusually large separation between Pt(1) and Pt(2) in the blue-green needles is more than enough to accommodate the placing of the fifth and sixth ligands about the Pt(1) atom if it were octahedrally coordinated.

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[20] Z. Piasek and T. Urbanski, *Tetrahedron Letters*, 723 (1962); *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **10**, 113 (1962).

[21] L. Skulski, G. C. Palmer, and M. Calvin, *Tetrahedron Letters*, 1773 (1963); *Roczniki Chem.*, **38**, 789 (1964).

[22] R. A. Mackay and E. J. Poziomek, *Inorg. Chem.*, **7**, 1454 (1968).

[23] C. S. Kraihanzel and S. C. Grenda, *ibid.*, **4**, 1037 (1965).

[24] W. E. Bull, S. K. Madan, and J. E. Willis, *ibid.*, **2**, 303 (1963).

[25] C. L. Rollinson and R. C. White, *ibid.*, **1**, 281 (1962).

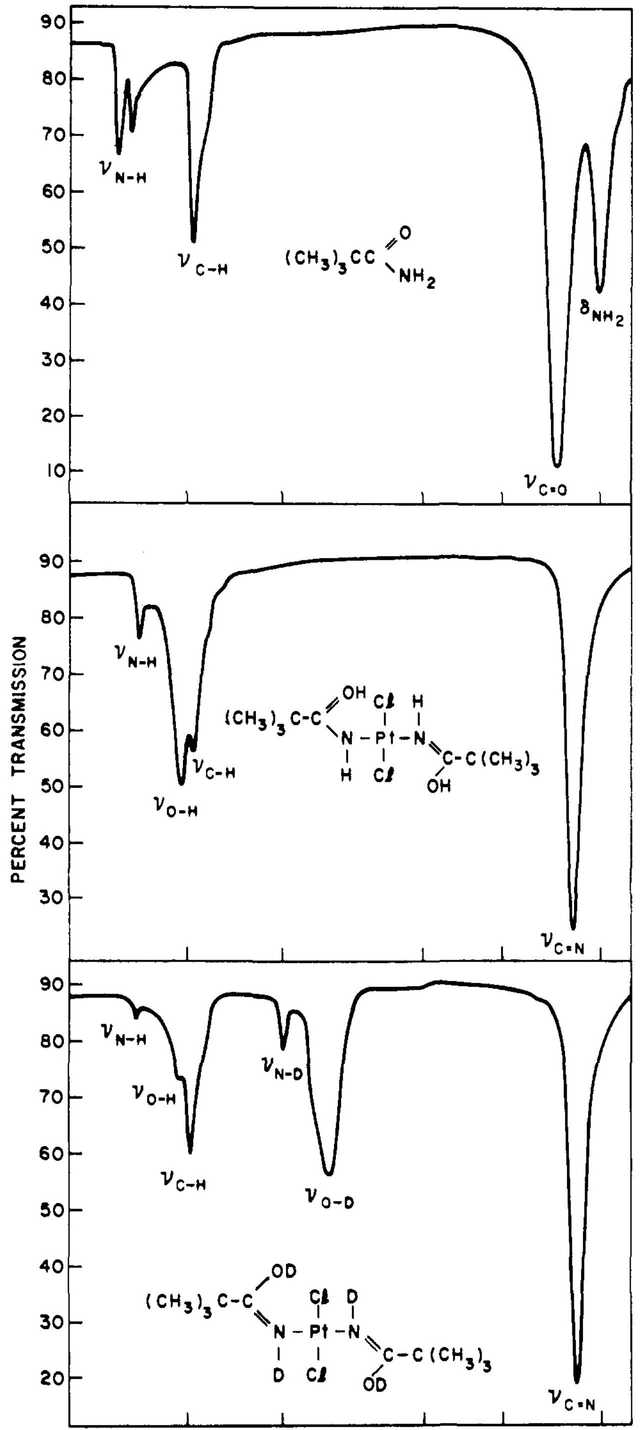

Figure 5. The infrared spectra of TMA in CDCl$_3$ (upper); compound I in CCl$_4$ (middle); and deuterated compound I in CCl$_4$ solution (lower). Solvent absorptions have been repressed in these spectra.

Infrared Spectra. The infrared spectra of the various compounds of interest are displayed in Figures 5 and 6 and support the conclusions of the nmr studies discussed above. TMA itself shows two strong bands at 1675 and 1595 cm^{-1}, the characteristic amide I [ν(C=O)] and amide II [δ(NH$_2$)] bands, respectively, and a pair of bands at 3490 and 3380 cm^{-1}, assignable to the in-phase and out-of-phase N–H stretching motions.[26] By contrast, compounds I, II, and III show only *one* band in the 1600-cm^{-1} region and only *one* band in the 3400-cm^{-1} region, as is characteristic of *secondary* amides having only one N–H bond. The most reasonable inference here is that the –NH$_2$ group of TMA has become an –NH group in the complexes. In addition, the iminol structures of I and II, if correct, should show O–H stretching vibrations as well as the lack of –NH$_2$ group motions. The OH stretching motions can be located at 3020 (I) and 2925 cm^{-1} (II), where they are badly overlapped by C–H absorptions. However, on partial deuteration (Figures 5 and 6), the O–D bands then appear unobstructed at 2280 (I) and 2230 cm^{-1} (II). One feature of the infrared spectrum of II is somewhat suspicious, however, and must be pointed out. Since the two ligands of compound II are demonstrably different, one would expect two bands in the C=O, C=N stretching region (1600–1700 cm^{-1}). Only one is found, and we must attribute this to either an accidental degeneracy of the C=X stretches in the two halves of the molecule, or a very low intensity in one of the transitions.

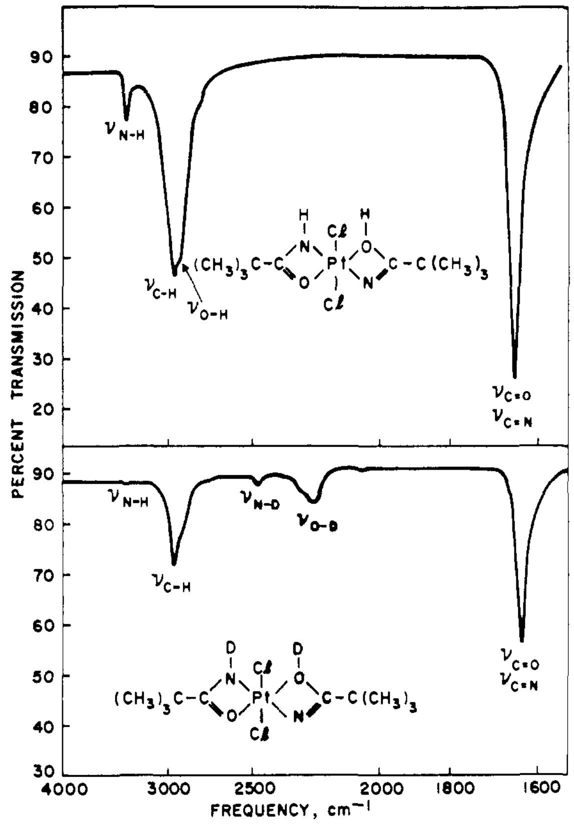

Figure 6. The infrared spectra of compound II in CCl$_4$ (upper), and deuterated compound II in CCl$_4$ (lower).

It might at first be thought that the tetravalency of the platinum in compound II could be confirmed by comparing its Pt–Cl distances and vibrational frequencies with those of other platinum chlorides known to be either divalent or tetravalent. Surprisingly, the differences are inconsequential. Thus, the Pt–Cl distances in both divalent and tetravalent platinum chlorides[27] are 2.32 ± 0.03 Å, just that found here for compounds I, II, and III. Also, comparing Pt^{IV}Cl$_6^{2-}$ with

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[26] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, pp 209–220.

[27] A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962.

$Pt^{II}Cl_4^{2-}$,[28] the totally symmetric stretching frequencies (ν_1) in the two ions are 344 and 335 cm^{-1}, and the two comparable bending motions ν_5 and ν_6 have frequencies of 162 and 164 cm^{-1}, respectively, in the two ions. Our complex I exhibits bands at 342 and 168 cm^{-1} which are not present in the uncomplexed amide, and which can reasonably be assigned to the Pt-Cl stretching and bending motions discussed above. Solutions of I, II, and III in acetonitrile were found to be nonconducting, indicating that the chloride remains bound to platinum in these complexes in solution as well.

The three platinum TMA complexes are obviously very closely related, with II and III being tautomers, and I a reduced form of III. If this is correct, then their interconversion should be possible, and this is found to be the case. Yellow solutions of I and II in methanol become blue upon standing in air, and even in the solid state II very slowly becomes blue. Similarly, a blue solution of III turns yellow on addition of reducing agents like stannous chloride, sodium bisulfite, or hydrazine. However, we have not identified any of the products of these reactions in a positive way.

Crystallographic Analysis. Having settled certain of the structural features by spectroscopic means, we turn again to the results of the crystal structure analysis. Knowing that the iminol form occurs in the ordered portion of the structure, it is possible to identify which atoms are N and which atoms are O in the lists of coordinate and thermal parameters given in Tables I and II. The iminol complex I is in a *trans* configuration which is nearly planar. The sum of the six bond angles at Pt(2) is 714.7 *vs.* 720° for a planar configuration. The sums of the three bond angles at C(1) and at C(6) are 360.0 and 359.8°, respectively, as required for planar configurations, while the sums of the six bond angles at C(2) and at C(7) are 656.9 and 656.0°, respectively, *vs.* 656.82° for a tetrahedral configuration.

The iminol complex I has many similarities with the structure reported for diamminebis(acetamidine)platinum(II) chloride monohydrate, $Pt(NH_3)_2[CH_3C(NH_2)NH]_2Cl_2 \cdot H_2O$.[29] In the acetamidine complex, there is a planar arrangement, with two *trans* NH_3 ligands, and two acetamidine ligands bonded to Pt through the $=NH$ group, rather than through the $-NH_2$ group. The C=NH—Pt and C—C=NH angles in the acetamidine complex are 130.2 and 122.3°, respectively, compared to the average values of 130.8 and 123.6° for these angles in component I of the blue-green needles. The acetamidine complex is also centrosymmetric, with a dihedral angle of 45.5° between the acetamidine plane and the Pt coordination plane. If the iminol complex could be placed in an environment similar to that of the acetamidine complex, it too would presumably be centrosymmetric with both iminol ligands forming identical dihedral angles between the -C(OH)NH planes and the Pt coordination plane. This is not the case, however, in our crystal, as indicated by the nonbonded distances and angles listed in Table V and illustrated in Figures 2 and 3. The Pt atoms in a triplet are separated by over 3.6 Å and form a not quite linear sequence making an angle of 174°, four such groups being contained in the unit cell. (The shortest distances between Pt atoms in different triplets are in excess of 4.3 Å.) Consequently the iminol complexes are in a very unsymmetrical environment. The iminol ligands N(2)-C(6)-O(2) which are oriented outward from the Pt-atom triplets encounter little steric hindrance and make a dihedral angle of 56° between the -C(OH)NH plane and the coordination plane. The iminol ligands which are oriented in the opposite sense toward the center of the Pt-atom triplets have to give way because of steric hindrance from the central disordered complex, and the dihedral angle is consequently reduced to 18°. This gives rise to the short distance of 2.76 Å between O(1) and Cl(2) as compared with 3.21 Å between O(2) and Cl(3). The distances C(1)-O(1) and O(1)-Cl(2) have the largest uncertainty of any in the structure, and this is presumably a consequence of the combined effects of the substitutional disorder with the "wrong" dihedral orientation of the O(1)-containing iminol ligand.[30]

Table V. Nonbonded Distances and Angles in $PtCl_3[(CH_3)_3CCONH_2]_2$

Atom pair	Distance, Å[a]
Pt(1)-Pt(2)	3.617 (0.002)
O(1)-Cl(2)	2.76 (0.09)
O(2)-Cl(3)	3.21 (0.04)
Atom pairs	**Angle, deg[a]**
Pt(2)-Pt(1)-Pt(2′)	174.0 (0.1)
O(1)C(1)N(1)-N(1)Pt(2)Cl(2)	18.4 (2.9), dihedral
O(2)C(6)N(2)-N(2)Pt(2)Cl(3)	56.1 (1.6), dihedral

[a] Estimated standard deviations are in parentheses.

The deviation from a linear array for the three Pt atoms in a group is presumably the result of a compromise among several competing steric factors. The "thermal" parameters of Table II are so large that they cannot possibly represent only thermal motions, since the crystals are stable at room temperature, and in fact they can be heated to 158° before they decompose. The "thermal" parameters in Table II can be expressed as rms radial displacements, Δr, and are equivalent to thermal B values ranging from 18 to 90 Å^2. It is obvious that the greater part of these displacements must be static displacements associated with the substitutional disorder. In the structure of the acetamidine complex, a single B value of 1.67 Å^2 was reported.[29] It would not be unreasonable to postulate the rms radial thermal displacement for the Pt atoms to be ~0.1 Å in the acetamidine complex and to assume that this value is about right for the Pt atoms in the iminol complex. An estimate can then be made of the static displacements caused by the substitutional disorder. In Table VI the rms radial displacements of Table II have been averaged for the Pt atoms, the Cl ligands, and the C, N, and O atoms of the iminol ligands with the exception of atom O(1). Subtracting the radial thermal displacement from the total displacement for the Pt atoms gives a radial static displacement of 0.388 Å, which should be appropriate for most of the atoms in the complex. The most notable exception is atom O(1) where unfavorable steric factors are maximized and an additional displacement of 0.391 Å is proposed. Then

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(28) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(29) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 801 (1962).

(30) The apparent "thermal ellipsoid" of vibration for O(1), calculated from the parameters of Table II, is oriented such that the largest component of displacement is roughly normal to both the O(1)-C(1) and O(1)-Cl(2) lines.

Table VI. Interpretation of "Thermal" Parameters in Terms of Static Displacements Arising from Substitutional Disorder

Atoms averaged	Apparent rms radial thermal displacement, Å	Postulated rms radial static displacement, Å	Resultant rms radial thermal displacement, Å	Equiv thermal B, Å^2
Pt(1), Pt(2)	0.488	0.388	0.100	0.79
Cl(1), Cl(2), Cl(3)	0.570	0.388	0.182	2.62
All C, N, O except O(1)	0.687	0.388	0.299	7.06
O(1)	1.078	0.388 + 0.391	0.299	7.06

the resultant rms radial thermal displacements run 0.1, 0.18, and ~0.3 Å for Pt atoms, Cl ligands, and iminol ligands, respectively, and the equivalent thermal B values are reasonable, as summarized in Table VI.

The Original Platinblau

In order to circumvent the problem of silver contamination, an attempt was made to prepare Platinblau by the solid reaction of $PtCl_2(CH_3CN)_2$ and acetamide, as described in the Experimental Section. Although the resulting deep blue powder appears, visually, to be very similar to Platinblau, it is clear from the analysis that it is in fact a chloride complex, $PtCl_2(CH_3CONH)_2$, analogous to the blue trimethylacetamide complex III described above. This similarity is confirmed by integration of the nmr spectrum, which indicates the presence of acetamido anions, and, consequently, the existence of a Pt^{IV} complex.

With this clue, we return to the analysis of the chloride-free Platinblau. Virtually perfect agreement for all elements can be obtained for the analysis of Platinblau if it is written as the tetravalent complex, $Pt^{IV}(CH_3CONH)_2(OH)_2$ [Calcd: Pt, 56.51; C, 13.92; N, 8.12; O, 18.54; and H, 2.92], and this is our new formulation for the complex. Consistent with this formulation, the mass spectrum of Platinblau shows mass peaks beyond those of the parent ion of $Pt(CH_3CONH)_2 \cdot H_2O$ (329), but none higher than that of the parent ion of $Pt(CH_3CONH)_2(OH)_2$ (345). Moreover, the divalent hydrate formulation of Platinblau would lead to a band in the 1600–1640-cm^{-1} region of the infrared spectrum due to the H_2O bending vibration, and, in fact, Kutzelnigg and Mecke[10] have assigned a band at 1658 cm^{-1} in Platinblau to this mode. However, contrary to this, we find that the material recovered from dissolution of Platinblau in D_2O, followed by evaporation of the solvent, has an infrared spectrum in the 1600–1700-cm^{-1} region which is identical with that of the material before deuteration.

By analogy to the other blue complexes, Platinblau must be a Pt^{IV} complex, containing two anionic ligands in addition to the two acetamido anions, and the analytical, mass spectral, and infrared evidence obtained here indicate that the correct formulation is as the tetravalent hydroxide complex.

The electronic spectra of the three blue materials studied here are, as expected, very similar. In each case the most prominent feature is an extremely broad absorption centered at 15,100 cm^{-1} in $PtCl_2[(CH_3)_3CCONH]_2$, at 16,700 cm^{-1} in $PtCl_2(CH_3CONH)_2$, and at 14,500 cm^{-1} in $Pt(OH)_2(CH_3CONH)_2$. Although the intensities of these bands are somewhat concentration dependent, most likely indicating some polymerization, the molar extinction coefficients of the visible band for all three compounds are approximately 4000. The most probable origin of the visible band in Platinblau is an amide-to-metal charge transfer, about which we hope to say more in the future.

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Chloroxyperfluoroalkanes

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Abstract: The preparation, identification, and characterization of the new class of compounds, the chloroxyperfluoroalkanes, are described. Chloroxytrifluoromethane, chloroxypentafluoroethane, and 2-chloroxyheptafluoropropane are discussed. Derivatives of chloroxytrifluoromethane, including CF_3OOCF_3, CF_3ONF_2, and CF_3OCClO, were prepared in high yield.

The preparation of fluoroxyperfluoroalkyl compounds has been the subject of several recent papers.[1-3] The best synthesis for compounds of this type is that of Lustig, Pitochelli, and Ruff[3] which involves an alkali metal fluoride catalyzed addition of fluorine across the

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[1] J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965).

[2] J. H. Prager, *J. Org. Chem.*, **31**, 392 (1966).

[3] M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Am. Chem. Soc.*, **89**, 2841 (1967).