unequal contributions of the metal $5d_{xz}$ and $5d_{yz}$ orbitals to skeletal bonding, which lead to "violations" of Wade's rules.[27] However, such arguments seem inapplicable to cobaltacarboranes, which rarely exhibit distortion in $(2n + 2)$-electron polyhedra.

Aside from the long C(2′)–B(3′) bond, the CoC_2B_7 framework in V is comparable to those of other 10-vertex closo borane systems that have been characterized by X-ray diffraction, including the $[(1,6\text{-}C_2B_7H_9)_2\text{-}2\text{-}Co]^-$ ion,[28] $2,6,1,10\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_6H_8$[29] (in which the skeletal carbon atoms occupy the 1,6- and 1,10-vertices, respectively), $2,3,10\text{-}(\eta^5\text{-}C_5H_5)_2NiCoCB_7H_8$,[30] $1,6\text{-}(CH_3)_2C_2B_8H_8$,[31] and the $B_{10}H_{10}^{2-}$ ion.[32] All of these are 22-electron $(2n + 2)$ systems that adopt regular bicapped-square-antiprism geometry as expected.

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Registry No. II, 80583-52-4; III, 80583-55-7; V, 80612-07-3.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, and selected least-squares planes (46 pages). Ordering information is given on any current masthead page.

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[27] Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602.

[28] St. Clair, D.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1972**, *11*, 377.

[29] Hoel, E. L.; Strouse, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 1388.

[30] Hardy, G. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* **1978**, *17*, 1662.

[31] Koetzle, T. F.; Lipscomb, W. N. *Inorg. Chem.* **1970**, *9*, 2279.

[32] Dobrott, R. D.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 1779.

Contribution from the Institute for Materials Research, McMaster University, Ontario L8S 4M1, Canada, and the Institute for Inorganic Chemistry of the Technical University of Munich, 8046 Garching, Federal Republic of Germany

Platinum(II) Complexes with Terminal Hydroxo and Aquo Groups: Crystal Structures of Hydroxo-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate Dihydrate, $[Pt(OH)(NH_3)_2(C_5H_7N_3O)]NO_3\cdot 2H_2O$, and *cis*-Diammineaquo(1-methylcytosine-N^3)platinum(II) Dinitrate Hydrate, $[Pt(NH_3)_2(H_2O)(C_5H_7N_3O)](NO_3)_2\cdot H_2O$

J. F. BRITTEN,[1a] B. LIPPERT,[1b] C. J. L. LOCK,*[1a] and P. PILON[1a]

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The preparation of *cis*-diammine(1-methylcytosine-N^3)platinum(II) complexes containing terminal H_2O, OH, and NO_3 groups, respectively, as fourth ligands, is reported: *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2\cdot H_2O$ (I), *cis*-$[Pt(NH_3)_2C(NO_3)]NO_3$ (Ib), *cis*-$[Pt(NH_3)_2C(OH)]NO_3\cdot 2H_2O$ (II), and *cis*-$[Pt(NH_3)_2C(OH)]NO_3$ (IIa) (C = 1-methylcytosine). The X-ray structures of I and II have been determined. I crystallizes in the triclinic form: $P\bar{1}$, $a = 12.380$ (6) Å, $b = 6.580$ (3) Å, $c = 10.895$ (3) Å, $\alpha = 90.39$ (3)°, $\beta = 110.26$ (3)°, $\gamma = 114.68$ (3)°, and $Z = 2$. II was obtained as monoclinic crystals, $P2_1/c$, $a = 12.207$ (4) Å, $b = 6.203$ (1) Å, $c = 18.853$ (5) Å, and $\beta = 109.64$ (2)°. Data for both crystals were collected with Mo Kα radiation and a Syntex $P2_1$ (II) or $P3$ (I) diffractometer. The crystal structures were determined by standard methods; that of I was refined to $R_1 = 0.0575$ and $R_2 = 0.0610$ on the basis of 3442 independent reflections and that of II to $R_1 = 0.0657$ and $R_2 = 0.0688$ on the basis of 3100 independent reflections. The structures of the two cations are very similar with the pyrimidine plane at roughly right angles to the ligand square plane. Bond lengths (Pt–N = 2.02 (1)–2.036 (8) Å; Pt–O = 2.027 (9), 2.052 (8) Å) are normal. To our knowledge, I and II represent the first examples of Pt(II) complexes containing terminal H_2O and OH ligands, respectively, that have been characterized with X-ray techniques. Their formation has been made possible by the specific hydrogen-bonding properties of H_2O and OH ligands in these complexes and by the poor donor strength of O(2) of the 1-methylcytosine toward platinum in aqueous solution. When warmed, II is readily transferred into compounds containing the N(4)-deprotonated C ligand as a bridge. Brief IR and Raman spectroscopic data are presented which enabled us to make predictions on the structures of I and II before verification by X-ray analysis.

Introduction

Platinum(II) complexes with terminal aquo and/or hydroxo groups are generally assumed to occur in aqueous solution.[2] Though the existence of hydroxo complexes in the solid state in some cases has been deduced by spectroscopic means, there have also been doubts as to whether other complexes claimed to contain OH ligands indeed were formulated correctly.[3] In recent years, we and others have reported the crystal structures of a series of di- and trimeric complexes of Pt(II) with hydroxo bridges,[4-7] thus proving that Pt(II) in this respect behaves very much like other transition metals, for which hydroxo-bridged complexes are quite common.[8] The large majority of the published structures on $(\mu\text{-OH})Pt^{II}$ complexes contained the *cis*-$Pt(NH_3)_2^{2+}$ moiety, which was of particular interest because of the remarkable antitumor activity of many of its derivatives.[9] As has been demonstrated by ^{195}Pt NMR, hy-

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[1] (a) McMaster University. (b) Technical University of Munich.

[2] See, e.g.: (a) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973; p 169 and references. (b) Elding, L. I. *Inorg. Chim. Acta* **1978**, *28*, 255. (c) Lim, M. C.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1911.

[3] Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1968**, 2745.

[4] (a) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *J. Am. Chem. Soc.* **1977**, *99*, 777. (b) *Inorg. Chem.* **1977**, *16*, 1192. (c) *Ibid.* **1978**, *17*, 1941. (d) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Ibid.* **1978**, *17*, 2971.

[5] Stanko, J. A.; Hollis, L. S.; Schreifels, J. A.; Hoeschele, J. D. *J. Clin. Hematol. Oncol.* **1977**, *7*, 138.

[6] Bushnell, G. W. *Can. J. Chem.* **1978**, *56*, 1773.

[7] Bhaduri, S.; Raithby, P. R.; Zuccaro, C. I.; Hursthouse, M. B.; Casella, L.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1978**, 991.

[8] See, e.g.: Tytko, K. H. *Chem. Unserer Zeit* **1979**, *6*, 184 and references therein.

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Table I. Crystal Data

	I	II
compd	$[Pt(NH_3)_2(OH_2)(C_5H_7N_3O)](NO_3)_2 \cdot H_2O$, $C_5H_{17}N_7O_9Pt$	$[Pt(NH_3)_2(OH)(C_5H_7N_3O)]NO_3 \cdot 2H_2O$, $C_5H_{18}N_6O_7Pt$
formula wt	514.32	469.33
crystal size, mm	sphere, $r = 0.10$	cylinder, $r = 0.10$, $l = 0.37$
systematic absences	none	$h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$
space group	$P\bar{1}$	$P2_1/c$
unit cell parameters	$a = 12.380$ (6) Å, $b = 6.580$ (3) Å, $c = 10.895$ (3) Å, $\alpha = 90.39$ (3)°, $\beta = 110.26$ (3)°, $\gamma = 114.68$ (3)	$a = 12.207$ (4) Å, $b = 6.203$ (1) Å, $c = 18.853$ (5) Å, $\beta = 109.64$ (2)°
V, Å^3	744.5 (5)	1344.5 (6)
Z	2	4
temp, °C	22	−65
ρ_{calcd}, g cm^{-3}	2.294	2.32
ρ_{obsd}, g cm^{-3}	2.31 (1)	2.29 (1)
linear abs coeff, cm^{-1}	91.0	110.2
abs corr factor, A^*, limits	3.447–3.658	5.26–5.90
max 2θ deg, reflctns	55, $h,\pm k,\pm l$	55, $h,k,\pm l$
std reflctn (esd, %)	211 (1.36), 111 (1.30)	127 (1.30), 504 (1.38)
no. of independent reflctns	3442	3100
no. with $I > 0$	3317	2844
$I < 0$, rejected	125	256
final R,[a] R_2[a]	0.0575, 0.0610	0.0657, 0.0688
final shift/error max of nonhydrogen atoms (hydrogen)	0.312 (4.8)	0.157
g (secondary extinction)	3.9×10^{-4}	2.6×10^{-4}
final difference map		
highest peak, e Å^{-3}; location	4.2; 0.00, 0.12, 0.25	2.5; 0.14, +0.01; 0.42
deepest valley, e Å^{-3}; location	2.8; 0.00, 0.02, 0.14	−2.2; 0.22, 0.12, 0.44
weighting	$w = (\sigma^2 + 0.0012F_o^2)^{-1}$	$w = (\sigma^2 + 0.0016F_o^2)^{-1}$
unit weight	1.117	1.315

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_2 = \Sigma w(|F_o| - |F_c|)^2/\Sigma(1)F_o^2)^{1/2}$.

droxo-bridged di- and trimers of *cis*-$Pt(NH_3)_2^{2+}$ also represent the major species in solution.[10] Surprisingly, all attempts to isolate crystalline Pt(II) complexes with terminal H_2O or OH groups have failed so far. For example, with the weakly coordinating NO_3^-, no *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$ could be isolated but only *cis*-$Pt(NH_3)_2(NO_3)_2$,[11] and diethylenetriammineplatinum(II) also crystallized with coordinated NO_3^- rather than coordinated H_2O.[12] In contrast to Pt(II), Pt(IV) is known to readily form stable Pt–OH bonds (bridging and terminal), and there are crystal structures of such complexes available.[13,14] In the course of our systematic studies on complexes of *cis*-$Pt(NH_3)_2^{2+}$ with model nucleobases, we now have obtained crystalline 1:1 complexes with 1-methylcytosine (C) of the composition *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2 \cdot H_2O$ (I) and *cis*-$[Pt(NH_3)_2C(OH)]NO_3 \cdot 2H_2O$ (II). The fact that these complexes were not isolated as the exclusive products from the respective solutions clearly shows that there must be a delicate balance of conditions leading to the crystallization of these complexes (cf. Experimental Section). There are, in our opinion, two main reasons for the formation of the above complexes: first, the specific hydrogen-bonding properties that stabilize OH and H_2O ligands in the two complexes, and which have been predicted by us previously,[12,15] and second, the poor nucleophilicity of O(2) of 1-methylcytosine toward Pt(II) in aqueous solution. With Ag, for example, N(3),O(2) bridging occurs rather than aquo complex formation,[16] and bidentate (N(3),O(2)) binding is also observed in complexes of Cd(II),[17] Hg(II),[18] and Cu(II).[18] Many more examples of varying degrees of O(2) involvement in metal binding are known.[19]

Experimental Section

Preparation of the Compounds: *cis*-$Pt(NH_3)_2Cl_2$ and C were reacted in 1:1 ratio in H_2O to give *cis*-$[Pt(NH_3)_2CCl]Cl \cdot H_2O$.[20] A 1-mmol sample of *cis*-$[Pt(NH_3)_2CCl]Cl \cdot H_2O$ was reacted with 2 mmol of $AgNO_3$ (15 mL of H_2O, 24 h, 22 °C) and the solution concentrated to a 1.5-mL volume (pH 1.8). Upon cooling, 230 mg of *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2 \cdot H_2O$ (I) were obtained. Further concentration of the filtrate and cooling gave a mixture of I (150 mg) and *cis*-$[Pt(NH_3)_2(OH)_2Pt(NH_3)_2](NO_3)_2$ (Ia) (10 mg).[21] Warming during the concentration process had to be avoided in order to prevent darkening of the solution and formation of a brown, glassy material. Anal. Calcd for I: C, 11.67; H, 3.34; N, 19.07. Found: C, 11.82; H, 3.47; N, 18.94. Recrystallization of I from H_2O at 22 °C gave a mixture of I (90%) and another crystalline species, *cis*-$[Pt(NH_3)_2C(NO_3)]NO_3$ (Ib). Anal. Calcd for Ib: C, 12.55; H, 2.74; N, 20.50. Found: C, 12.51; H, 2.89; N, 20.34. Titration of freshly prepared *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2$ with 1 equiv of NaOH under N_2 (1 mmol, 15-mL volume), subsequent concentration at low tem-

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(9) For a review of this subject see, e.g.: "Cisplatin—current status and new developments"; Prestayko, A. W., Crooke, S. T., Carter, S. K., Eds.; Academic Press: New York, 1980; pp 1–527.

(10) Chikuma, M.; Pollock, R. J.; Ott, K. C.; Gansow, O. A.; Rosenberg, B., submitted for publication in *J. Am. Chem. Soc.*

(11) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525.

(12) Britten, J.; Lock, C. J. L. *Acta Crystallogr.*, in press.

(13) (a) Spiro, T. G.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1968**, *7*, 2165. (b) Preston, H. S.; Mills, J. C.; Kennard, C. H. L. *J. Organomet. Chem.* **1968**, *14*, 447.

(14) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Rosenberg, B. *Can. J. Chem.*, in press.

(15) Lock, C. J. L. In "Inorganic Chemistry in Biology and Medicine"; Martell, E. D., Ed.; American Chemical Society: Washington, D.C., 1980; ACS Symp. Ser. No. 140, pp 209–224.

(16) Kistenmacher, T. J.; Rossi, M.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 240.

(17) Gagnon, C.; Beauchamp, A. L.; Tranqui, D. *Can. J. Chem.* **1979**, *57*, 1372.

(18) (a) Authier-Martin, M.; Beauchamp, A. L. *Can. J. Chem.* **1977**, *55*, 1213. (b) Marzilli, L. J.; Wilkowski, K.; Chiang, C. C.; Kistenmacher, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7504.

(19) For reviews see, e.g.: (a) Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 57. (b) Gellert, R.; Bau, R. *Ibid.* **1979**, *8*, 1. (c) Marzilli, L. G.; Kistenmacher, T. J.; Eichhorn, G. L. In "Nucleic Acid–Metal Ion Interactions"; Spiro, T. G., Ed.; Wiley: New York, 1980; p 181.

(20) The X-ray structure of this compound has been determined and will be published.

(21) Faggiani, R.; Lippert, B.; Lock, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

Table II. Atomic Positional Coordinates ($\times 10^3$)

atom	x	y	z
Pt	53.63 (3)	114.44 (6)	217.16 (3)
O(3)	122.0 (8)	448 (1)	288.6 (8)
N(5)	−11.3 (9)	−213 (2)	137 (1)
N(6)	−130.9 (9)	68 (2)	161.7 (9)
N(1)	431.7 (8)	299 (1)	241.3 (8)
C(2)	302.3 (9)	238 (2)	195.2 (9)
N(3)	240.4 (7)	169 (1)	283.3 (8)
C(4)	302.8 (9)	145 (2)	406 (1)
C(5)	437 (1)	205 (2)	451 (1)
C(6)	496 (1)	280 (2)	369 (1)
C(1)	499 (1)	385 (3)	154 (1)
O(2)	245.5 (7)	251 (1)	80.5 (7)
N(4)	237 (1)	73 (2)	483 (1)
N(7)	133 (1)	441 (2)	606 (1)
O(71)	197.1 (8)	566 (2)	545.1 (9)
O(72)	173 (1)	515 (2)	728.7 (9)
O(73)	41 (1)	262 (2)	547 (1)
N(8)	706.7 (9)	263 (2)	875.7 (9)
O(81)	670.2 (8)	285 (1)	754.9 (8)
O(82)	822.2 (8)	320 (2)	939.8 (9)
O(83)	626.5 (9)	184 (2)	926.5 (9)
O(7)	358.2 (9)	13 (2)	749.6 (9)

Table III. Atomic Positional Coordinates ($\times 10^3$)

atom	x	y	z
Pt	148.80 (4)	98.68 (7)	452.35 (2)
O(3)	207.7 (7)	−53 (1)	376.9 (5)
N(5)	86.9 (8)	239 (2)	528.0 (5)
N(6)	19.5 (8)	231 (2)	364.6 (5)
N(3)	283.1 (8)	−35 (2)	536.3 (5)
C(2)	263.2 (9)	−225 (2)	571.1 (6)
O(2)	164.3 (7)	−293 (2)	556.2 (5)
N(1)	356.8 (8)	−319 (2)	623.9 (5)
C(1)	332 (1)	−503 (2)	665.9 (8)
C(6)	465.0 (9)	−240 (2)	643.2 (6)
C(5)	487 (1)	−57 (2)	610.7 (7)
C(4)	392 (1)	50 (2)	555.7 (6)
N(4)	509.7 (9)	232 (2)	525.1 (6)
O(7)	355.8 (8)	612 (1)	427.4 (5)
O(8)	36.9 (9)	−344 (2)	303.7 (5)
N(7)	250 (1)	417 (2)	244.8 (6)
O(71)	259.3 (8)	315 (2)	302.4 (5)
O(72)	320 (1)	549 (2)	241.4 (9)
O(73)	157.8 (9)	382 (2)	186.7 (6)

perature to about a 0.7-mL volume, and cooling at 3 °C (2 days) gave 220 mg of thin, colorless columns of composition $[Pt(NH_3)_2C(OH)]NO_3$ (IIa). Anal. Calcd for IIa: C, 13.86; H, 3.26; N, 19.40. Found: C, 14.12; H, 3.37; N, 19.48. Further cooling of the filtrate (2 days) gave 90 mg of *cis*-$[Pt(NH_3)_2C(OH)]NO_3 \cdot 2H_2O$ (II) as tiny colorless cubes. Anal. Calcd for II: C, 12.80; H, 3.87; N, 17.91. Found: C, 12.72; H, 3.91; N, 17.72. Occasionally, but not reproducibly, a third crystalline compound, IIb, was isolated in low yield which analyzed as follows: C, 12.47; H, 2.94; N, 16.14; O, 11.92; Pt, 56.35. From the IR spectrum it is suspected that this compound contains bridging (N^3,N^4)-1-methylcytosinato ligands similar to the recently described C–H dimer.[21]

Apparatus. IR spectra were recorded on a Perkin-Elmer 580 (Nujol mulls, CsI windows) and Raman spectra on a Coderg PH 1 with krypton laser (647.1-nm excitation). Slit widths were 2–6 cm^{-1}. pH measurements were performed with a combination electrode on a Knick potentiometer. The pK_a of the H_2O ligand in I was determined according to the method of Albert and Serjeant[22] in aqueous solution without another electrolyte added.

Collection of X-ray Data. Crystals of the two compounds were selected after examination under a polarizing microscope. A triclinic cell was obtained from precession photographs of I, and Delaunay reduction revealed the cell given here and showed no hidden symmetry. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $27.8° < 2\theta < 35°$ recorded on a Syntex P3 diffractometer. At room temperature II was unstable in the X-ray beam so the crystal was transferred to a Syntex P2$_1$ diffractometer and unit cell parameters were obtained at low temperature. The crystal was monoclinic, and the 15 reflections used to obtain unit cell parameters were in the range $20° < 2\theta < 27°$. Mo Kα_1 (λ 0.709 26 Å) radiation was used. Intensities for I were recorded on the Syntex P3 at room temperature while intensities for II were recorded on the Syntex P2$_1$ at −65 °C. Both diffractometers were operated in the coupled θ(crystal)–2θ(counter) scan mode. The methods of selection of scan rates and initial data treatment have been described.[11,23] Corrections were made for Lorentz–polarization effects and absorption.

Solution of the Structures. For both structures the coordinates of the platinum atom were found from a three-dimensional Patterson synthesis, and a series of full-matrix least-squares refinements followed by three-dimensional electron density differences syntheses revealed all the nonhydrogen atoms. At this point the temperature factors of the platinum atoms, and certain oxygen and nitrogen atoms, were made anisotropic. Tests were made at each stage to show the use of increased parameters was significant.[24] Further refinement with full-matrix least squares and with minimization of $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was about 0.1. At this point a search was made for hydrogen atoms.

In the case of I, all hydrogen atoms were found in a difference map. In further refinements each hydrogen atom was given a temperature factor 1.5 times that of the atom to which it was attached, and the positional parameters of the hydrogen atoms, but not the temperature factors, were varied. Refinement was terminated where the largest shift/error for nonhydrogen atoms, except N(6),[25] was 0.3 and that for hydrogen atoms 4.8.

For II it was not possible to find all hydrogen atoms and attempts to vary the positions were unjustified. Thus, the hydrogen atoms detected were found by refining all the nonhydrogen atoms until the shift/error was 0.16 and then generating a difference map with a weighting scheme[26] giving increased weight to the low-angle reflections. Eight peaks in chemically acceptable positions for hydrogen atoms were detected, in particular those around the coordinated hydroxide group. Corrections were made for secondary extinction with the method listed in SHELX.[27] Throughout the refinement the scattering curves were taken from ref 28, and anomalous dispersion corrections from ref 29 were applied to the curve for platinum. The atom parameters for nonhydrogen atoms are listed in Tables II and III.

Results and Discussion

Formation, Solution Behavior, and Spectroscopic Differentiation. A solution of *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2 \cdot H_2O$ (I) was titrated with 1 equiv of base to give *cis*-$[Pt(NH_3)_2C(OH)]NO_3$ (II). The pK_a for the deprotonation of the coordinated aquo ligand was determined as 5.9 and agreed well with data on similar Pt(II) complexes.[30] When I was treated

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(22) Albert, A.; Serjeant, E. P. "Ionization Constants of Acids and Bases"; Methuen: London, 1962; pp 1–42.

(23) Hughes, R. P.; Krishnamachari, N.; Lock, C. J. L.; Powell, J.; Turner, G. *Inorg. Chem.* **1977**, *16*, 314.

(24) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(25) The shift/error for N(6) was 1.3 for U_{33}. This portion of the temperature factor cycled back and forth in final refinement and was correlated with the maximum shift/error of 4.67 for z of H(62).

(26) The weighting scheme is described under FMAP in SHELX. The value of s chosen was 0.3.

(27) All calculations were carried out on a CYBER 170/730 computer. The programs DATCO5, ABSORB, and DATRDN from the XRAY76 program (Stewart, J. M. "The XRAY of 76 system", Technical Report TR-466, University of Maryland, College Park, MD, 1976) were used for preliminary data treatment. The structure was solved with SHELX (Sheldrick, G. M. "SHELX Program for crystal structure solution and refinement", University of Cambridge, Cambridge, England, 1976). Plane and dihedral angle calculations were made with NRC-22 (Pippy, M. E.; Ahmed, F. R. "Mean plane and torsional angles", Report NRC-22, National Research Council of Canada, Ottawa, Canada, 1978). Diagrams were prepared with the program ORTEP-II (Johnson, C. K. "ORTEP-II", U.S. Atomic Energy Commission Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976).

(28) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, p 72ff.

(29) Cromer, D. T. Reference 28; Table 2.3.1, pp 149–150.

(30) See, e.g.: (a) Reference 2c. (b) Jensen, K. A. *Z. Anorg. Allg. Chem.* **1939**, *242*, 87. (c) Perumareddi, J. R.; Adamson, A. W. *J. Phys. Chem.* **1968**, *72*, 414.

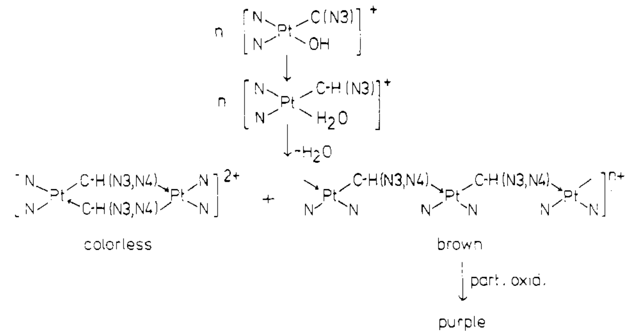

Figure 1. Conversion of *cis*-$[Pt(NH_3)_2C(OH)]^+$ into the μ-(CH)-bridged species. The intermediate with the terminal C–H ligand is given for formal reasons only and may not exist.

with 0.5 equiv of base of a pH corresponding to the pK_a, a compound of composition $[Pt_2(NH_3)_4C_2OH](NO_3)_3$ was isolated, which was a Pt dimer with a single hydroxo bridge.[31] Solution Raman spectra (H_2O) of I and II clearly indicate monodentate binding of C through N(3) in these compounds. Typical C bands are observed at 646, 794, 833, 1168, 1203, and 1540 cm^{-1} for I, and 645, 793, 831, 1166, 1205, 1539 cm^{-1} for II, respectively,[32] very similar to closely related complexes such as *cis*-$[Pt(NH_3)_2CCl]NO_3$,[33] *cis*-$[Pt(NH_3)_2C_2](NO_3)_2$,[34] or *cis*-$[Pt(NH_3)_2C(T-H)]ClO_4$[35] (with (T–H) being the thymine monoanion), which also contain C bonded at Pt through N(3). Although there was some condensation reaction upon ageing an aqueous solution of I, as concluded from ^1H NMR and potentiometric titration studies,[31] such products formed were not of a sufficient concentration to be detected by Raman spectroscopy.

Warming of an aqueous solution of *cis*-$[Pt(NH_3)_2C(OH)]NO_3 \cdot 2H_2O$ (I) (80–90 °C, 3–5 h, stoppered flask) lead to a rapid darkening (brownish black) of the originally colorless solution, and a simultaneous drop in pH from 11–12 to 7–8. From the concentrated solution a small amount of colorless crystals of *cis*-$[Pt(NH_3)_2(C-H)_2Pt(NH_3)_2](NO_3)_2$ (Ia)[21] were isolated together with a glassy, brown material as the major product. When this glassy material was treated with dilute HNO_3 (to pH –5) and kept in air, it turned dark purple, and from the solution small quantities of Ia were again isolated. From the IR spectrum of the purple material it was concluded that it also contained 1-methylcytosinato-N^3,N^4 bridges like Ia: while C–N(3) complexes always have two characteristic IR absorptions around 1545 (s, sh) and 1520 cm^{-1} (s), the (C–H)-N(3),N(4) dimer Ia and the purple material exhibited instead two bands at 1540 (vs, br) and 1500 cm^{-1} (s). These findings suggested a conversion of II as indicated in Figure 1. The observed rise in pH certainly was consistent with the proposed sequence, and the fact that only small quantities of the crystalline head-to-tail dimer Ia were formed, yet a large amount of a presumably oligomeric material is reasonable.[36] Partial oxidation of the latter may account for the intense coloration of this material.

The unexpected stability of the C–H-bridged complexes even in the acidic solution was further confirmed by the finding that the dimer Ia was formed even from an acidic solution (pH 1.8) of *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2$ (cf. Experimental Section). This is in contrast with the apparent instability of an N(3),O(2) bridge in aqueous solution, which was manifested by the inability to crystallize such a compound from H_2O.

A differentiation of the various isolated complexes was, apart from their differing crystal habits, achieved by combined infrared and Raman spectroscopy. *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2 \cdot H_2O$ (I) had all the characteristics of N(3)-platinated C as far as the Raman active C modes were concerned.[33-35] The spectra showed the typical absorptions of ionic NO_3^- (Ra 1047 vs. 708 w; IR 1380 vs, 823 m, 1760 vw) and intense H_2O bands at 3540 and 3430 cm^{-1} in the IR spectrum. On the other hand, *cis*-$[Pt(NH_3)_2C(NO_3)]NO_3$ (Ib) again showed the typical Raman bands of N(3)-platinated C, no H_2O absorptions in the IR, but absorptions of both coordinated (IR 1490 s, 1280 s, 985 s) and ionic nitrate (IR 1385 vs, 825 m, 1770 vw). *cis*-$[Pt(NH_3)_2(C-H)_2Pt(NH_3)_2](NO_3)_2$ (Ia) was unambiguously identified by its IR spectrum.[21] *cis*-$[Pt(NH_3)_2C(OH)]NO_3 \cdot 2H_2O$ (II) again exhibited the typical Raman bands of N(3)-platinated C, absorptions of ionic NO_3^- only, and strong IR bands at 3560 and 3475 cm^{-1} with an additional broad and intense IR band ranging from 3000 to 2200 cm^{-1}, indicating very strong hydrogen bonding. Although a differentiation of OH and H_2O absorptions in the IR stretching region was not possible, an alternative formulation as $[Pt(NH_3)_2C(H_2O)]OH \cdot NO_3 \cdot H_2O$ was ruled out on the basis of the Pt–NH_3 and Pt–O skeletal stretching vibrations, which then should have been very similar to those observed for I. This was, however, not the case.[37] For *cis*-$[Pt(NH_3)_2C(OH)]NO_3$ (IIa), C and NO_3^- modes favor this formulation. Two sharp absorptions of medium intensity at 3540 and 3525 cm^{-1} in the IR and a rather broad one between 2800 and 2100 cm^{-1} suggested the OH groups were strongly hydrogen bonded.

In all cases, but particularly with II and IIa, only Nujol spectra gave reproducible and reliable results, whereas with KBr disks spectra were obtained that varied considerably, in particular in the OH stretching region.

Structure. The molecular cations are illustrated in Figure 1 and selected interatomic distances and angles are given in Table IV. The cations are very similar. There are no significant differences in equivalent bond lengths and angles, and they agree well with values we have reported previously.[33,38] The principal difference is in the square plane–ring dihedral angle (Table V), which is 90.9 (5)° for the aquo complex but only 79.8 (5)° for the hydroxo complex, and we assume this difference is caused by the hydrogen-bonding requirements.

The Pt–O distances are comparable to the Pt–N distances; in particular the Pt–OH_2 distance (2.052 (8) Å) is not unduly long. The Pt–OH distance (2.027 (9) Å) is comparable to the Pt–O distance for hydroxo-bridged complexes we have reported previously (range 1.99 (3)–2.07 (2) Å)[4] and is insignificantly longer than the Pt–O value (2.00 (1) Å) in $Pt(NH_3)_2Cl_2(OH)_2$.[14] Thus the distances give no indication of weakness of the Pt–O bond which has been suggested by the rapid rate of reaction of square-planar d^8 complexes. We suggest, therefore, that the rapid rate of reaction of OH and OH_2 groups on platinum is associated with a marked weakening of the Pt–O bond in the five-coordinate state. We have demonstrated such a weakening previously in Rh^I complexes when the Rh–O distances to an acetylacetonate ion increased from 2.025 (5) and 2.037 (5) Å in the square-planar complex[39] to 2.217 (9)

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(31) Lippert, B., to be submitted for publication.

(32) Only those C bands are listed that have been found to be most indicative of N(3)-platinum binding (cf. ref. 34).

(33) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 335.

(34) Faggiani, R.; Lippert, B.; Lock, C. J. L. submitted for publication in *Inorg. Chem.*

(35) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Pfab, R. *Inorg. Chem.* **1981**, *20*, 2381.

(36) The oligomeric (or polymeric) nature of this material is assumed on the basis of its ^1H NMR spectrum: H5, H6 resonances are ca. 0.8 ppm wide and occur at positions close to the corresponding sharp doublets of Ia.

(37) For example: ν(Pt–NH_3) at 561 s, 538 s in I, yet at 545 s, 523 w in II (Raman).

(38) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 808.

Table IV. Selected Interatomic Distances (Å) and Angles (Deg) for *cis*-Diammine(1-methylcytosine-N^3)aquoplatinum(II) Dinitrate Hydrate (I) and Hydroxo-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate Dihydrate (II)[a]

	I	II		I	II		I	II
Pt–N(3)	2.034 (9)	2.035 (8)	Pt–N(5)	2.02 (1)	2.02 (1)	Pt–N(6)	2.03 (1)	2.036 (8)
Pt–O(3)	2.052 (8)	2.027 (9)	N(1)–C(2)	1.37 (1)	1.37 (1)	C(2)–N(3)	1.39 (2)	1.41 (2)
N(3)–C(4)	1.34 (1)	1.36 (2)	C(4)–C(5)	1.43 (2)	1.44 (2)	C(5)–C(6)	1.31 (2)	1.36 (2)
C(6)–N(1)	1.38 (1)	1.34 (2)	N(1)–C(1)	1.45 (2)	1.48 (2)	C(2)–O(2)	1.23 (1)	1.22 (1)
C(4)–N(4)	1.33 (2)	1.32 (2)	N(7)–O(71)	1.26 (2)	1.23 (2)	N(7)–O(72)	1.26 (1)	1.21 (2)
N(7)–O(73)	1.21 (1)	1.30 (1)	N(8)–O(81)	1.27 (1)		N(8)–O(82)	1.24 (1)	
N(8)–O(83)	1.22							

Hydrogen Bond Distances

			I		
O(3)–O(81)^{i}	2.74 (1)	O(3)–H(32)	0.8 (2)	H(32)–O(81)^{i}	2.0 (2)
O(3)–O(71)	2.60 (1)	O(3)–H(31)	0.9 (2)	H(31)–O(71)	1.8 (1)
N(5)–O(72)^{ii}	2.98 (2)	N(5)–H(51)	0.9 (2)	H(51)–O(72)^{ii}	2.1 (2)
N(5)–O(2)^{iii}	2.95 (1)	N(5)–H(52)	1.1 (2)	H(52)–O(82)^{iv}	2.0 (2)
N(5)–O(82)^{iv}	3.07 (2)	N(5)–H(53)^{i}	0.9 (1)	H(53)–O(2)^{iii}	2.2 (1)
N(6)–O(2)^{iii}	2.87 (1)	N(6)–H(61)	1.0 (1)	H(61)–O(2)^{iii}	2.0 (2)
N(6)–O(7)^{ii}	3.13 (2)	N(6)–H(62)	0.9 (2)	H(62)–O(7)^{ii}	2.8 (2)
N(6)–O(82)^{v}	2.97 (2)	N(6)–H(63)	1.1 (2)	H(63)–O(82)^{v}	2.0 (2)
O(7)–O(72)	3.07 (1)	O(7)–H(72)	0.9 (2)	H(72)–O(72)	2.2 (1)
			II		
O(3)–O(71)	2.86 (1)	O(3)–H(31)	0.9 (1)	H(31)–O(71)	1.9 (1)
O(3)–O(7)^{vi}	2.71 (1)	O(3)–H(72)^{vi}	1.7 (1)	H(72)–O(7)	1.1 (1)
O(3)–O(8)	2.75 (1)	O(3)–H(81)	2.3 (1)	H(81)–O(8)	1.0 (1)
N(5)–O(2)^{ii}	2.96 (1)	N(5)–H(51)	0.7 (1)	H(51)–O(2)^{ii}	2.5 (1)
N(5)–O(73)^{vii}	2.92 (1)	N(5)–O(2)^{viii}	3.05 (1)	N(6)–O(73)^{ix}	2.98 (2)
N(6)–O(8)^{ix}	3.05 (1)	N(6)–H(61)	0.7 (1)	H(61)–O(8)^{ix}	2.3 (1)
N(6)–O(8)^{viii}	2.91 (1)	N(4)–O(7)	2.93 (1)	N(4)–O(7)^{i}	2.87 (1)
O(7)–O(71)	2.91 (1)	O(7)–H(71)	1.2 (1)	H(71)–O(71)	2.5 (1)
O(8)–O(73)^{x}	2.82 (2)	O(8)–H(82)	1.0 (1)	H(82)–O(73)^{x}	1.8 (1)

	I	II		I	II		I	II
N(3)–Pt–N(5)	92.2 (4)	91.2 (4)	N(3)–Pt–N(6)	176.7 (4)	177.0 (5)	N(3)–Pt–O(3)	90.3 (4)	88.5 (4)
N(5)–Pt–N(6)	90.1 (5)	91.7 (4)	N(5)–Pt–O(3)	176.6 (4)	177.7 (4)	N(6)–Pt–O(3)	87.6 (4)	88.7 (4)
Pt–N(3)–C(2)	116.6 (6)	118.9 (7)	Pt–N(3)–C(4)	122.6 (8)	120.6 (8)	C(6)–N(1)–C(2)	120 (1)	123 (1)
N(1)–C(2)–N(3)	118.0 (8)	117.6 (9)	C(2)–N(3)–C(4)	120.8 (9)	120.4 (8)	N(3)–C(4)–C(5)	120 (1)	120 (1)
C(4)–C(5)–C(6)	118 (1)	118 (1)	C(5)–C(6)–N(1)	122 (1)	121 (1)	C(6)–N(1)–C(1)	121 (1)	119.9 (9)
C(1)–N(1)–C(2)	118.5 (9)	117 (1)	N(1)–C(2)–O(2)	120 (1)	123 (1)	O(2)–C(2)–N(3)	122 (1)	119.8 (9)
N(3)–C(4)–N(4)	118 (1)	120.3 (9)	N(4)–C(4)–C(5)	122 (1)	120 (1)	O(71)–N(7)–O(72)	115.6 (8)	122 (1)
O(71)–N(7)–O(73)	119 (1)	118 (1)	O(72)–N(7)–O(73)	122 (1)	120 (1)	O(81)–N(8)–O(82)	119 (1)	
O(81)–N(8)–O(83)	119.3 (9)		O(82)–N(7)–O(83)	122 (1)				

[a] Atoms are related to those in Tables II and III by the following transformations: (i) $1-x, 1-y, 1-z$; (ii) $-x, -y, 1-z$; (iii) $-x, -y, -z$; (iv) $1-x, -y, 1-z$; (v) $x-1, y, z-1$; (vi) $x, y-1, z$; (vii) $x, {}^1/_2-y, {}^1/_2+z$; (viii) $x, 1+y, z$; (ix) $-x, {}^1/_2+y, {}^1/_2-z$; (x) $-x, y-{}^1/_2, {}^1/_2-z$.

and 2.235 (8) Å in the five-coordinate complex.[23]

We have postulated previously[15] that in order to form aquo and terminal hydroxo complexes of Pt^{II} certain hydrogen-bonding requirements would have to be fulfilled. In particular, for I the coordinated water molecule would have to form two strong hydrogen bonds, where it donates the protons, and in II the hydroxide group would have to form strong hydrogen bonds where it accepts protons from other groups. Clearly both requirements are fulfilled; for I O(3)–O(81) is 2.74 (1) Å and O(3)–O(71) is 2.60 (1) Å, whereas for II O(3)–O(7) is 2.71 (1) Å and O(3)–O(8) is 2.75 (1) Å, and the hydrogen atoms are in the correct positions.

The packing of I is shown in Figure 2. It is characterized by a series of parallel layers, formed by the cytosine ring, the N(7) nitrate ion and the water molecule, lying roughly parallel to the *ac* face. Surprisingly there is no hydrogen bonding within these layers. In particular, the amino group $N(4)H_2$ is not involved in hydrogen bonds. The layers are arranged such that the cytosine ring of a molecule related to another by the *c* translation is in the next layer. The platinum atoms lie close to the $y = 0$ plane and here there is extensive hydrogen bonding. Two cations related by the 0,0,0 inversion center lie with the square planes separated by roughly 3.4 Å, a feature we have seen extensively before for cis-amine complexes.[40] This cation pair is hydrogen bonded together through N(5)···O(2)^{iii}, N(6)···O(2)^{iii}. Hydrogen bonding in the **c** direction is through N(5)···O(72), O(3)···O(71) and in both the **a** and

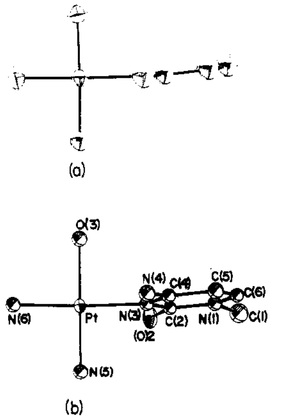

Figure 2. (a) The cation $[Pt(NH_3)_2(OH_2)(C_5H_7N_3O)]^{2+}$, the orientation of the ring, and numbering as in (b). (b) The cation $[Pt(NH_3)_2(OH)(C_5H_7N_3O)]^+$, showing the atom numbering. Both diagrams are drawn to put the ligand square plane in the plane of the paper.

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(39) Allen, D.; Lock, C. J. L.; Turner, G.; Powell, J. *Can. J. Chem.* **1975**, *53*, 2707.

(40) Lock, C. J. L.; Speranzini, R. A.; Zvagulis, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1789.

Inorg. Chem. **1982**, *21*, 1941–1946

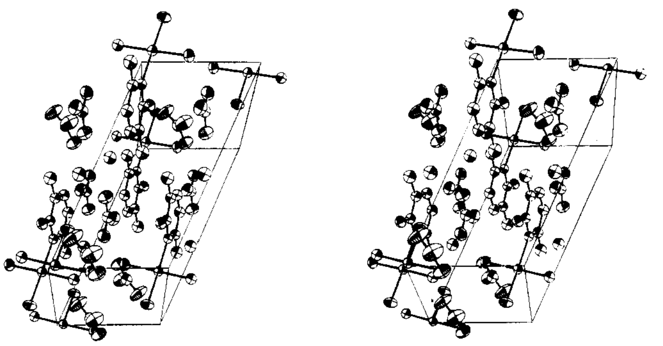

Figure 3. Packing in the unit cell of $[Pt(NH_3)_2(OH_2)(C_5H_7N_3O)](NO_3)_2 \cdot H_2O$. **b** and **b** × **c*** are parallel to the bottom and side of the page, respectively, and the view is down **c***.

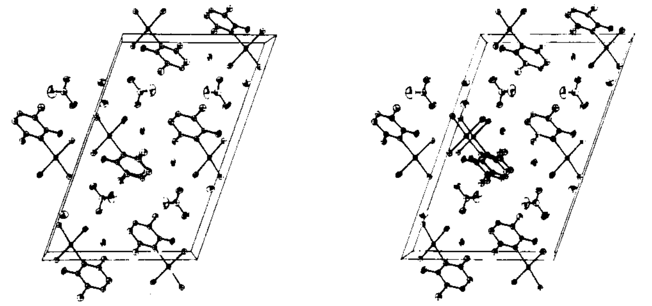

Figure 4. Packing in the unit cell of $[Pt(NH_3)_2(OH)(C_5H_7N_3O)](NO_3) \cdot 2H_2O$. **a** and **c*** are parallel to the bottom and side of the page, respectively, and the view is down **b**.

c direction through N(5)···O(82)$^{\mathrm{iv}}$, N(6)···O(82)$^{\mathrm{v}}$. Other hydrogen bonds stabilizing the structure and providing cation–anion links are O(3)···O(81)$^{\mathrm{i}}$ and N(6)···O(7)$^{\mathrm{ii}}$ and O(7)···O(72).

For II (Figure 3) the cations are arranged in layers centered in the planes $z = 0, {}^1/_2$. The anions lie in separating layers at $z = {}^1/_4, {}^3/_4$. Within a layer the cations are stacked up along the *b* direction and canted so there is some cytosine ring overlap; the rings are overlapped like tiles on a roof. This stack of cations is hydrogen bonded together through O(3)···O(7)$^{\mathrm{vi}}$, O(7)···N4), N(5)···O(2)$^{\mathrm{i2}}$, N(6)···O(8)$^{\mathrm{vii2}}$, and N(6)$^{\mathrm{vi}}$···O(8). At the $x = {}^1/_2$ plane, cations in adjacent stacks are hydrogen bonded through N(4)···O(7)$^{\mathrm{i}}$, N(4)$^{\mathrm{i}}$···O(7) giving a four centered system of two N(4) and two O(7) in a diamond shape. We have seen this type of hydrogen bonding involving cytosine before,[32] although the oxygen atoms were from nitrate groups. At $x = 0$ the hydrogen bonding between cation stacks is through N(5)···O(2)$^{\mathrm{ii}}$. Hydrogen bonding to the nitrate ion provides binding in the *c* direction, besides the ionic interactions, through O(3)···O(71), O(7)···O(71) and N(5)···O(73)$^{\mathrm{vi2}}$, N(6)···O(73),$^{\mathrm{2x}}$ and some binding in the *a* direction through the extra O(8)···O(73)$^{\mathrm{x}}$ hydrogen bonds. The large thermal motion of O(72) clearly arises because it is not involved in hydrogen bonding.

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Registry No. I, 80662-72-2; Ib, 80662-74-4; II, 80662-77-7; IIa, 80662-76-6.

Supplementary Material Available: Tables of temperature factors, best planes and dihedral angles, hydrogen atom parameters, and moduli of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

Contribution from the Institute for Materials Research,
McMaster University, Hamilton, Ontario, Canada, L8S 4M1

Preparation, Spectroscopic Properties, and Structure of 1-Oxo-2,3,6-(D-penicillaminato-*N*,*S*,*O*)-4,5-(D-penicillaminato-*N*,*S*)technetium(V)

KENNETH JAMES FRANKLIN, HELEN ELAINE HOWARD-LOCK, and COLIN JAMES LYNE LOCK*

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1-Oxo-2,3,6-(D-penicillaminato-*N*,*S*,*O*)-4,5-(D-penicillaminato-*N*,*S*)technetium(V), $TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)$, has been obtained as orthorhombic crystals: $P2_12_12_1$; $a = 21.878$ (5) Å, $b = 11.711$ (2) Å, $c = 5.924$ (1) Å; $Z = 4$. Data were collected with Mo Kα radiation and a Syntex P2$_1$ diffractometer. The crystal structure was solved by standard methods and refined to $R_1 = 0.0592$ and $R_2 = 0.0439$ on the basis of 3401 independent reflections. The technetium is six-coordinate, being bonded to oxygen (Tc–O = 1.657 (4) Å), the S, N, and O atoms of a D-penicillamine dianion deprotonated at S and O, and to the S and N atoms of a D-penicillamine anion deprotonated at S. The second Tc–O distance is longer (2.214 (4) Å), comparable to the Tc–N distances (2.185 (5), 2.209 (6) Å). Tc–S distances are normal (2.283 (2), 2.296 (2) Å). The molecules are strongly hydrogen bonded from carboxylic acid to carboxylate into a helical chain in the crystal. NMR, vibrational, and electronic spectra are reported.

Introduction

The nuclidic properties of technetium-99m (6-h half-life, 140-keV γ-ray, low radiation dosage) make this isotope an ideal radionuclide for the development of scanning agents in diagnostic medicine.[1] In fact, technetium-99m-labeled complexes have been a major contributing factor to the rapid growth of nuclear medicine.[2]

Relatively little is known, however, about the chemistry of technetium and its complexes,[3,4] and, thus far, serendipity has

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(1) McAfee, J. G. "Radiopharmaceuticals", Subramanian, G., Rhodes, B. A., Cooper, J. F., Sodd, V. J., Eds.; The Society of Nuclear Medicine: New York, 1975; p 3.

(2) Hayes, R. L. "The Chemistry of Radiopharmaceuticals", Heindel, N. D., Burns, H. D., Honda, T., Brady, L. W., Eds.; Masson et Cie, Paris, 1978; p 155.

(3) Spitsyn, V. I.; Kuzina, A. F.; Oblova, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 1030; *Usp. Khim.* **1977**, *46*, 1947.

0020-1669/82/1321-1941$01.25/0