2708 *Inorg. Chem.* **1983**, *22*, 2708-2713

Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

Mononuclear Complexes of *cis*-Diammineplatinum(II) and -(IV) with α-Pyridone. Structures of *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$, *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$, and *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$

L. STEVEN HOLLIS and STEPHEN J. LIPPARD*

Received December 3, 1982

Two mononuclear platinum(II) complexes and one mononuclear platinum(IV) complex of α-pyridone have been synthesized and studied by X-ray diffraction. These complexes are the mono(2-hydroxypyridine) complex *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (**3**), the bis(2-hydroxypyridine) complex *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ (**1**), and *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (**2**). The 2-hydroxypyridine ligands in **1** are oriented in the anti rotational conformation, and the resulting atropisomer has crystallographically required C_2 symmetry. The isolation and characterization of these mononuclear complexes contribute significantly to the analysis of the reaction chemistry of *cis*-diammineplatinum(II) with α-pyridone that leads to the formation of the *cis*-diammineplatinum α-pyridone blue. Crystallographic data are as follows: compound **1**, monoclinic, $a = 9.072$ (2) Å, $b = 22.875$ (3) Å, $c = 8.003$ (1) Å, $\beta = 109.24$ (1)°, $V = 1568$ Å^3, $Z = 4$, space group $C2/c$; compound **2**, monoclinic, $a = 7.490$ (2) Å, $b = 9.309$ (2) Å, $c = 15.294$ (3) Å, $\beta = 100.09$ (3)°, $V = 1050$ Å^3, $Z = 4$, space group $P2_1/c$; compound **3**, triclinic, $a = 10.706$ (3) Å, $b = 12.552$ (4) Å, $c = 4.151$ (1) Å, $\alpha = 95.57$ (1)°, $\beta = 92.32$ (3)°, $\gamma = 99.05$ (3)°, $V = 547.4$ Å^3, $Z = 2$, space group $P\bar{1}$.

Introduction

Recent studies of the reactions of α-pyridone with *cis*-diammineplatinum(II) complexes have proven useful in elucidating the chemistry of platinum blues.[1-3] The interaction of *cis*-$Pt(NH_3)_2Cl_2$ or the aquated form of the complex, *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, with α-pyridone produces a variety of mononuclear and binuclear platinum complexes similar to the products obtained in the analogous reactions of free and substituted pyrimidine bases such as uracil, thymine, and cytosine.[4-6] The relationship between these two systems has provided a foundation for understanding the more complex chemistry of platinum–pyrimidine interactions[1,4] and has established a close correspondence between α-pyridone and the pyrimidines in their reactions with *cis*-diammineplatinum complexes.

X-ray crystallographic and ^{195}Pt NMR spectroscopic studies[1-3] have been used to characterize the products obtained from the reaction of α-pyridone with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$. These studies have focused primarily on the binuclear α-pyridonate-bridged products since these complexes are ultimately responsible for the formation of the blue platinum species. *cis*-Diammineplatinum α-pyridone blue, the subject of extensive structural, chemical, and spectroscopic investigations,[3,7] is a mixed-valent, tetranuclear complex, $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_5{\cdot}H_2O$, comprised of two α-pyridonate-bridged, metal–metal bonded binuclear units. The reactions that accompany the formation of *cis*-diammineplatinum α-pyridone blue have been shown from ^{195}Pt NMR studies[1b] to involve a variety of mononuclear platinum complexes, the structures of which, however, have not been examined in detail. In this report, we present the results of X-ray structural studies of two such mononuclear platinum–α-pyridone complexes, *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ (**1**) and *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (**3**), which are related to the mononuclear species discussed above. The geometry of **1** was previously described in preliminary form.[1a] We also examine the structure of a Pt(IV) complex, *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (**2**), obtained by oxidation of the corresponding mono(α-pyridone)platinum(II) complex (**3**).

Experimental Section

Preparation of Compounds. *cis*-Diamminebis(2-hydroxypyridine)platinum(II) Chloride (1), *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$. This complex can be obtained from the reaction of α-pyridone (Aldrich, recrystallized) with *cis*-$[Pt(NH_3)_2Cl_2]$ as follows. A suspension of 6.67 mmol of *cis*-$[Pt(NH_3)_2Cl_2]$ was stirred with 15 mmol of α-pyridone in 180 mL of water for 24 h at 65 °C. The resulting amber solution (pH 3.5) was reduced in volume to 15 mL with a rotoevaporator at 50 °C, cooled to ice temperature, and filtered to remove unreacted starting material (1.67 mmol of *cis*-$[Pt(NH_3)_2Cl_2]$). Continued evaporation (to dryness) followed by the addition of chloroform yielded a light beige product, which was filtered and air-dried (1.7 g). Recrystallization of this material from water gave white crystals of *cis*-chloro(2-hydroxypyridine)diammineplatinum(II) chloride, *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]Cl$ (30% yield).[1] The filtrate from the recrystallization was evaporated, and the residue was recrystallized from water–acetonitrile. Small quantities (30–50 mg) of amber crystals of compound **1** were obtained from air evaporation of this solution and characterized by X-ray crystallography (vide infra).

Compound **1** was also obtained as the nitrate salt from the reaction of α-pyridone with *cis*-$[Pt(NH_3)_2(C_5H_4NOH)(H_2O)]^{2+}$.[1] A solution of 0.653 mmol of *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]Cl$ in 8 mL of water was allowed to react with 1.306 mmol of $AgNO_3$ for 2.5 h at 50 °C. After the mixture was cooled on ice for 1.5 h, the resulting AgCl precipitate was removed by filtration and 0.66 mmol of α-pyridone was added to the filtrate. The pH of the solution was adjusted to 5 with 1 N NaOH, and after 24 h at 45 °C the solution was cooled to ice temperature for 8 h. Large crystals of the head-to-tail α-pyridonate-bridged dimer,[1] $[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2{\cdot}2H_2O$, were separated from the solution by filtration, and air evaporation of the filtrate provided 35 mg of *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2](NO_3)_2$. The identity of this product was confirmed by using ^{195}Pt NMR spectroscopy.[1]

***mer*-Diamminetrichloro(2-pyridonato-*N*)platinum(IV) (2), *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$.** This complex was obtained as a minor component from the reaction used to prepare *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (**3**). The procedure for synthesizing compound **3** has been described previously.[1] The yellow crystals of **2** were isolated when impure samples of the nitrate salt (**3**) were recrystallized from

---

*To whom correspondence should be addressed as the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

(1) (a) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230. (b) Hollis, L. S.; Lippard, S. J. *Ibid.* **1983**, *105*, 3494.

(2) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761.

(3) (a) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434. (b) Barton, J. K.; Caravana, C.; Lippard, S. J. *Ibid.* **1978**, *101*, 7269.

(4) (a) Davidson, J. P.; Faber, P. J.; Fischer, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; Van Camp, L. *Cancer Chemother. Rep., Part 1* **1975**, *59*, 287. (b) Lippert, B. *J. Clin. Hematol. Oncol.* **1977**, *7*, 26.

(5) (a) Lippert, B.; Pfab, R.; Neugebauer, D. *Inorg. Chim. Acta* **1979**, *37*, L495. (b) Lippert, B. *Ibid.* **1981**, *55*, 5.

(6) Lippert, B. *Inorg. Chem.* **1981**, *20*, 4326.

(7) (a) Barton, J. K.; Best, S. A.; Lippard, S. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 3785. (b) Fanwick, P. E.; Hollis, L. S.; Lippard, S. J., to be submitted for publication.

0020-1669/83/1322-2708$01.50/0 © 1983 American Chemical Society

Table I. Experimental Details of the X-ray Diffraction Studies of *cis*-[Pt$(NH_3)_2(C_5H_4NOH)_2$]Cl_2 (1), *mer*-[Pt$(NH_3)_2(C_5H_4NO)Cl_3$] (2), and *cis*-[Pt$(NH_3)_2(C_5H_4NOH)$Cl](NO_3) (3)

(A) Crystal Parameters[a] at 23 °C

	1	2	3		1	2	3
a, Å	9.072 (2)	7.490 (2)	10.706 (3)	*V*, Å^3	1568.0	1049.9	547.4
b, Å	22.875 (3)	9.309 (2)	12.552 (4)	space group	*C*2/*c*	*P*2$_1$/*c*	*P*$\bar{1}$
c, Å	8.003 (1)	15.294 (3)	4.151 (1)	*Z*	4	4	2
α, deg	90.00	90.00	95.57 (1)	ρ(calcd), g cm^{-3}	2.076	2.718	2.558
β, deg	109.24 (1)	100.09 (3)	92.32 (3)	ρ(obsd), g cm^{-3}	2.08 (2)[b]	2.70 (2)[b]	2.54 (2)[b]
γ, deg	90.00	90.00	99.05 (3)	mol wt	490.3	429.6	421.7

(B) Measurement of Intensity Data[c]

	1	2	3
instrument	Enraf-Nonius CAD-4F κ-geometry diffractometer		
radiation	Mo Kα ($\lambda_{\overline{\alpha}}$ = 0.710 73 Å) graphite monochromatized		
takeoff angle, deg	2.0	2.0	2.0
stds, measd every 1 h of X-ray exposure time	(022)[d] $(\bar{3}\bar{9}1)$ $(\bar{5}\bar{3}2)$	$(1\bar{6}3)$[d] $(1\bar{5}6)$ $(\bar{4}47)$	(511)[e] $(\bar{4}\bar{3}\bar{1})$ (350)
no. of reflcns collcd	2286 [$3 \leqslant 2\theta \leqslant 55°$ ($\pm h, +k, +l$)]	2580 [$3 \leqslant 2\theta \leqslant 55°$ ($+h, +k, \pm l$)]	2011 [$3 \leqslant 2\theta \leqslant 50°$ ($+h, \pm k, \pm l$)]

(C) Treatment of Intensity Data[f]

	1	2	3
μ, cm^{-1}	93.8	142.4	131.9
transmission factor range[h]	*g*	0.211–0.360	0.017–0.319
averaging, R_{av}[c]	0.032	0.019	0.136
no. of reflcns after averaging	1802	2402	1902
no. of obsd unique data [$F_o > n\sigma(F_o)$]	1546 (*n* = 5)	2047 (*n* = 4)	1560 (*n* = 4)

[a] From the least-squares fit of the setting angles of 25 reflections with 2θ > 30°. [b] By suspension in a mixture of $CHBr_3$ and $CHCl_3$. [c] See ref 11 for additional details. [d] Showed no decay. [e] Used to scale the data for isotropic decay (28%). [f] F_o and $\sigma(F_o)$ were obtained after corrections for background, attenuator, and Lorentz-polarization of X radiation as described in ref 11. [g] Since the crystal was small and nearly spherical in shape, an absorption correction was not performed. [h] Absorption corrections were performed with the Wehe–Busing–Levy ORABS program.

1 N HCl. The identity of compound **2** was determined crystallographically.

***cis*-Diamminechloro(2-hydroxypyridine)platinum(II) Nitrate (3), *cis*-[Pt$(NH_3)_2(C_5H_4NOH)$Cl](NO_3).** Compound **3** was obtained from the reaction of α-pyridone with *cis*-[Pt$(NH_3)_2$Cl(H_2O)]$^{2+}$ as previously described[1b] and recrystallized from 0.1 N HNO_3 as white needles.

Collection and Reduction of X-ray Data. *cis*-[Pt$(NH_3)_2(C_5H_4NOH)_2$]Cl_2 (1). The amber crystal used in the diffraction study was equidimensional (0.1 mm × 0.1 mm × 0.1 mm) and nearly spherical. The quality of the crystal was examined by taking open counter ω-scans of several strong low-angle reflections and was found to be acceptable for data collection ($\Delta\bar{\omega}_{1/2} \sim 0.08°$). The unit-cell parameters and intensity data were measured with a single-crystal diffractometer as described in Table I. The space group was determined to be either *C*2/*c* (C_{2h}^6, No. 15) or *Cc* (C_s^4, No. 9)[8] from the systematic absences, and the former choice was confirmed by the successful solution and refinement of the structure. Further details of the data collection are presented in Table I.

***mer*-[Pt$(NH_3)_2(C_5H_4NO)Cl_3$] (2).** The yellow crystal chosen for the diffraction study was tabular in shape with dimensions of 0.2 mm × 0.1 mm × 0.1 mm and was bounded by the faces (011), $(0\bar{1}\bar{1})$, $(0\bar{1}1)$, $(01\bar{1})$, $(10\bar{2})$, and $(\bar{1}02)$. Inspection of several strong low-angle ω-scans indicated the crystal to be acceptable for data collection ($\Delta\bar{\omega}_{1/2} \sim 0.1°$). The space group was determined to be *P*2$_1$/*c* (C_{2h}^5, No. 14)[9] from the systematic absences. Further details of the data collection are given in Table I.

***cis*-[Pt$(NH_3)_2(C_5H_4NOH)$Cl](NO_3) (3).** The colorless crystal used for data collection was a needle with dimensions of 0.55 mm × 0.05 mm × 0.05 mm, bounded by the faces (001), $(00\bar{1})$, (010), $(0\bar{1}0)$, (100), and $(\bar{1}00)$. Inspection of several low-angle ω-scans indicated that the crystal was acceptable for data collection ($\Delta\bar{\omega}_{1/2} \sim 0.10°$). The space group was determined to be either *P*$\bar{1}$ (C_i^1, No. 2) or *P*1 (C_1^1, No. 1),[10] and the former choice was confirmed by the successful solution and refinement of the structure. Further details of the data collection are given in Table I. As indicated by the large value (0.13) for R_{av}, which was based on 208 equivalent reflections, the data set obtained on compound **3** was of poor quality. The large dimension (~0.6 mm) of the needle length, coupled with instrumental alignment problems, was partially responsible for the observed disagreement between equivalent reflections. The quality of the data set also was reduced by problems with crystal decomposition; the intensity of standards decreased by 28% during the data collection.

Structure Solution and Refinement. *cis*-[Pt$(NH_3)_2(C_5NOH)_2$]Cl_2 (1). The structure was solved by standard Patterson and Fourier methods and refined with anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were obtained from ref 13; hydrogen atom scattering factors were taken from ref 14. The positions of all hydrogen atoms were refined with constraints using isotropic thermal parameters. The hydrogen atoms attached to the carbon atoms of the α-pyridone ring were placed at calculated positions [*d*(C–H) = 0.95 Å] and constrained to "ride" on the carbon atoms to which they are attached.[12] The hydrogen atoms of the ammine ligands were refined as a rigid group by fixing[12] the following interatomic distances: N–H = 0.87 (1) Å, H–H = 1.42 (1) Å, and Pt–H = 2.47 (1) Å, for each hydrogen in the group. The hydrogen atoms of the pyridone ring were given an independent set of common thermal parameters in the refinement, and the hydrogen atoms of the ammine ligands were refined with fixed thermal parameters (U_{iso} = 0.06 Å^2). The hydrogen atom attached to the exocyclic oxygen atom of the 2-hydroxypyridine ligand, which was located from a difference Fourier map during the latter stages of refinement, was included in the final refinement by using a fixed position and thermal parameter (U_{iso} = 0.06 Å^2).

---

(8) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1973; Vol. I, pp 101, 89.

(9) Reference 8, p 99.

(10) Reference 8, pp 74–75.

(11) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

(12) All calculations were performed on a DEC VAX-11/780 computer using SHELX-76: Sheldrick, G. M. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C. Eds.; Delft University Press: Delft, 1978; pp 34–42.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Final Positional Parameters for *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ (**1**)[a]

ATOM	X	Y	Z
Pt	0.0000	0.21566(2)	0.2500
Cℓ1	0.5000	0.22575(13)	0.2500
Cℓ2	0.5000	0.07317(13)	0.7500
N1	0.1266(7)	0.1521(3)	0.1823(8)
N2	0.1321(8)	0.2774(3)	0.1848(10)
O2	0.2432(7)	0.1315(3)	0.4721(7)
C2	0.2260(9)	0.1181(3)	0.3038(10)
C3	0.3009(10)	0.0716(4)	0.2545(11)
H3	0.3712(10)	0.0476(4)	0.3419(11)
C4	0.2725(12)	0.0610(4)	0.0798(12)
H4	0.3199(12)	0.0283(4)	0.0444(12)
C5	0.1760(11)	0.0965(4)	-0.0448(12)
H5	0.1592(11)	0.0900(4)	-0.1669(12)
C6	0.1038(9)	0.1418(3)	0.0081(10)
H6	0.0362(9)	0.1667(3)	-0.0788(10)
H1N2	0.134(6)	0.3089(10)	0.247(6)
H2N2	0.092(4)	0.2855(20)	0.073(2)
H3N2	0.227(2)	0.2644(12)	0.208(8)
H1O2	0.3388	0.1041	0.5593

[a] Estimated standard deviations in the last significant digit(s) are given in parentheses. The atom-labeling scheme is given in Figure 1.

Table III. Final Positional Parameters for *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (**2**)[a]

ATOM	X	Y	Z
Pt	0.76930(3)	-0.06119(2)	0.667970(10)
Cℓ1	1.0800(2)	-0.05588(18)	0.66888(12)
Cℓ2	0.7141(2)	-0.15753(19)	0.52653(10)
Cℓ3	0.8197(3)	0.0231(2)	0.81229(10)
O2	0.5152(7)	0.2066(5)	0.6993(3)
N1	0.7361(7)	0.1433(5)	0.6170(3)
N2	0.8087(9)	-0.2646(6)	0.7193(4)
N3	0.4990(7)	-0.0811(7)	0.6686(4)
C2	0.6155(9)	0.2413(7)	0.6441(4)
C3	0.6146(10)	0.3821(8)	0.6083(5)
H3	0.5386(10)	0.4534(8)	0.6271(5)
C4	0.7209(11)	0.4172(8)	0.5475(5)
H4	0.7171(11)	0.5119(8)	0.5242(5)
C5	0.8349(10)	0.3154(8)	0.5191(5)
H5	0.9090(10)	0.3386(8)	0.4766(5)
C6	0.8357(10)	0.1808(7)	0.5551(4)
H6	0.9104(10)	0.1096(7)	0.5354(4)
H1N2	0.741(5)	-0.280(2)	0.760(3)
H2N2	0.781(7)	-0.3289(10)	0.6773(11)
H3N2	0.923(2)	-0.278(2)	0.743(3)
H1N3	0.454(2)	-0.157(3)	0.638(3)
H2N3	0.4762(19)	-0.091(6)	0.7227(9)
H3N3	0.4378(17)	-0.006(3)	0.644(3)

[a] Estimated standard deviations in the last significant digit(s) are given in parentheses. Atom labels are defined in Figure 2.

Table IV. Final Positional Parameters for *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (**3**)[a]

ATOM	X	Y	Z
Pt	0.12063(9)	0.31895(8)	0.0985(2)
Cℓ	0.1905(6)	0.4881(5)	0.3677(16)
N2	-0.061(2)	0.3494(19)	0.116(7)
N3	0.055(2)	0.1665(18)	-0.136(6)
N1	0.2995(20)	0.2873(17)	0.070(5)
O2	0.2540(17)	0.1408(14)	0.344(4)
C2	0.340(2)	0.2014(18)	0.190(5)
C3	0.458(2)	0.175(2)	0.132(7)
H3	0.482(2)	0.111(2)	0.204(7)
C4	0.543(3)	0.247(3)	-0.036(6)
H4	0.624(3)	0.230(3)	-0.082(6)
C5	0.507(2)	0.335(2)	-0.120(6)
H5	0.564(2)	0.385(2)	-0.220(6)
C6	0.387(2)	0.356(2)	-0.074(5)
H6	0.363(2)	0.420(2)	-0.143(5)
N4	-0.225(2)	0.0993(18)	0.427(5)
O41	-0.210(2)	0.1972(16)	0.483(5)
O42	-0.146(2)	0.055(2)	0.272(6)
O43	-0.3216(19)	0.0423(18)	0.517(8)

[a] Estimated standard deviations in the last significant digit(s) are given in parentheses. Figure 3 depicts the atom-labeling scheme.

Table V. Interatomic Distances (Å) and Angles (deg) for *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ (**1**)[a]

	Coordination Sphere		
Pt-N1	2.035(6)	Pt-N2	2.029(6)
N1-Pt-N2	89.8(3)	N1-Pt-N2'	178.2(2)
N1-Pt-N1'	88.7(3)	N2-Pt-N2'	91.7(4)
	Ligand Geometry		
N1-C2	1.335(9)	C2-C3	1.386(11)
N1-C6	1.361(9)	C3-C4	1.358(12)
C2-O2	1.340(9)	C4-C5	1.358(13)
N1-O2	2.259(8)	C5-C6	1.366(11)
Pt-N1-C2	121.8(5)	N1-C2-C3	121.0(7)
Pt-N1-C6	119.2(5)	C2-C3-C4	119.1(8)
C2-N1-C2	118.9(6)	C3-C4-C5	120.4(8)
O2-C2-N1	115.2(7)	C4-C5-C6	119.0(8)
O2-C2-C3	123.7(7)	C5-C6-N1	121.4(7)
	Possible Hydrogen Bonds		
Cℓ2-H1O2	1.870(1)	Cℓ2-H1O2-O2	164.8(3)
Cℓ1-H2N2	2.45(2)	Cℓ1-H2N2-N2	161(4)
Cℓ1-H3N2'	2.55(2)	Cℓ-H3N2'-N2'	162(4)

[a] For atom-labeling scheme, see Figure 1. Distances have not been corrected for thermal motion.

Full-matrix least-squares refinement of the structure using 99 parameters converged at $R_1 = 0.037$ and $R_2 = 0.047$.[15] The function minimized during the refinement was $\sum w(|F_o| - |F_c|^2)$, where $w = 1.000/[\sigma^2(F_o) + 0.000625F_o^2]$. The maximum parameter shift in the final cycle of refinement was 0.06σ, and the only residual peaks of significant height (<2.5 e Å^{-3}) in the final difference Fourier map were located within 1.0 Å from the platinum atom. The average $w\Delta^2$ values for groups of data sectioned according to parity group, $(\sin\theta)/\lambda$, $|F_o|$, $|h|$, $|k|$, or $|l|$ showed good consistency, and the weighting function was found to be acceptable.

The final atomic positional parameters together with their estimated standard deviations are reported in Table II. The interatomic distances and angles with estimated standard deviations are presented in Table V. A complete listing of atomic positional and thermal parameters for compound **1** (Table S1) and a listing of final observed and calculated structure factors (Table S2) are available as supplementary material.

***mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (2).** The position of the Pt atom was determined from a Patterson map. Phasing of the data using this refined position provided the location of all non-hydrogen atoms in the difference Fourier map. As described above, all non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were refined with constraints using isotropic thermal parameters. The hydrogen atoms of the α-pyridonate ring were given an independent set of common thermal parameters, and the thermal parameters of the hydrogen atoms of the ammine ligands were fixed with U_{iso} set to 0.06 Å^2.

Full-matrix least-squares refinement of the structure converged at $R_1 = 0.027$ and $R_2 = 0.036$,[15] using 138 parameters. The weighting function used in the refinement was $w = 1.000/[\sigma^2(F_o) + 0.000625F_o^2]$, and the maximum parameter shift in the final cycle of refinement was 0.4σ (H1N2 position). The only peaks of significant height (1.3 e Å^{-3}) that were observed in the final difference Fourier map were located within 1.0 Å from the Pt atom. The $w\Delta^2$ values for groups of data sectioned as above showed good consistency, and the weighting function was considered acceptable.

The final atomic positional parameters with estimated standard deviations are presented in Table III. The interatomic distances and angles along with estimated standard deviations are listed in Table VI. A complete listing of atomic positional and thermal parameters for compound **2** (Table S3) and a listing of observed and calculated structure factors (Table S4) are available as supplementary material.

***cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (3).** The platinum atom was located by using a Patterson map, and a difference Fourier map, phased on this atom, was used to locate all non-hydrogen atoms. The structure was refined as above, by using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms attached to the carbon atoms of the α-pyridone rings were given an independent set of common isotropic thermal parameters during refinement. No attempt was made to refine the positions of hydrogen atoms of the ammine ligands. The hydrogen atom attached to the oxygen atom (O2) of the α-pyridone ligand was not located.

Full-matrix least-squares refinement of the structure using 137 parameters converged at $R_1 = 0.068$ and $R_2 = 0.088$.[15] The weighting function used in the refinement was $w = 0.407/[\sigma^2(F_o) + 0.000625F_o^2]$,

---

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

Table VI. Interatomic Distances (Å) and Angles (deg) for *mer*-$Pt(NH_3)_2(C_5H_4NO)Cl_3$ (**2**)[a]

	Coordination Sphere		
Pt-N1	2.056(5)	Pt-Cℓ1	2.326(2)
Pt-N2	2.052(5)	Pt-Cℓ2	2.311(2)
Pt-N3	2.034(5)	Pt-Cℓ3	2.310(2)
N1-Pt-N2	178.7(2)	N2-Pt-Cℓ3	87.6(2)
N1-Pt-N3	91.8(2)	N3-Pt-Cℓ1	176.0(2)
N1-Pt-Cℓ1	92.1(2)	N3-Pt-Cℓ2	87.4(2)
N1-Pt-Cℓ2	90.8(1)	N3-Pt-Cℓ3	91.3(2)
N1-Pt-Cℓ3	92.1(1)	Cℓ1-Pt-Cℓ2	91.6(1)
N2-Pt-N3	89.5(2)	Cℓ1-Pt-Cℓ3	89.5(1)
N2-Pt-Cℓ1	86.6(2)	Cℓ2-Pt-Cℓ3	176.8(1)
N2-Pt-Cℓ2	89.5(2)		
	Ligand Geometry		
N1-C2	1.397(8)	C2-C3	1.420(9)
N1-C6	1.349(8)	C3-C4	1.366(11)
C2-O2	1.266(8)	C4-C5	1.394(11)
N1-O2	2.323(8)	C5-C6	1.369(9)
Pt-N1-C2	122.3(4)	N1-C2-C3	116.6(6)
Pt-N1-C6	117.4(4)	C2-C3-C4	121.3(7)
C2-N1-C6	120.4(6)	C3-C4-C5	120.8(7)
O2-C2-N1	121.4(6)	C4-C5-C6	117.2(6)
O2-C2-C3	122.0(6)	C5-C6-N1	123.7(6)
	Possible Hydrogen Bonds		
O2-H1N2'	2.13(4)	O2-H1N2'-N2'	152(3)
O2-H2N3'	2.23(5)	O2-H2N3'-N3'	127(4)
O2-H3N3	2.19(3)	O2-H3N3-N3	118(3)

[a] For atom-labeling scheme, see Figure 2. Distances have not been corrected for thermal motion.

Table VII. Interatomic Distances (Å) and Angles (deg) for *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (**3**)[a]

	Coordination Sphere		
Pt-N1	2.02(2)	Pt-N3	2.06(2)
Pt-N2	2.04(2)	Pt-Cℓ	2.300(7)
N1-Pt-N2	178.7(9)	N2-Pt-N3	90.2(9)
N1-Pt-N3	88.9(8)	N2-Pt-Cℓ	89.1(7)
N1-Pt-Cℓ	91.8(6)	N3-Pt-Cℓ	178.8(7)
	Ligand Geometry		
N1-C2	1.35(3)	C2-C3	1.39(3)
N1-C6	1.37(3)	C3-C4	1.43(4)
C2-O2	1.33(3)	C4-C5	1.30(4)
N1-O2	2.25(3)	C5-C6	1.36(3)
Pt-N1-C2	124(1)	N1-C2-C3	122(2)
Pt-N1-C6	120(2)	C2-C3-C4	118(2)
C2-N1-C6	117(2)	C3-C4-C5	119(2)
O2-C2-N1	115(2)	C4-C5-C6	122(2)
O2-C2-C3	123(2)	C5-C6-N1	123(3)
	Anion Geometry		
N4-O41	1.21(3)	O41-N4-O42	120(2)
N4-O42	1.25(3)	O41-N4-O43	120(2)
N4-O43	1.25(3)	O42-N4-O43	120(2)
	Possible Hydrogen Bonds		
N2-O41	2.88(3)	N3-O42	3.05(3)
N3-O2	2.93(3)	O2-O43	2.62(3)

[a] For atom-labeling scheme, see Figure 3. Distances are not corrected for thermal motion.

and the largest parameter shift per esd in the final cycle of refinement was 0.03. Two large peaks (~5.7 e Å^{-3}) were observed in the final difference map at positions less than 1 Å from the Pt atom. A number of smaller peaks (1–2 e Å^{-3}) were also found near the Pt atom (≤1.5 Å), and the largest peak (1.4 e Å^{-3}) away from the Pt atom was in the vicinity (1.2 Å) of the chlorine atom. Since the quality of the data was substandard (vide supra), the errors in the final structural parameters are larger than normal.

The final atomic positional parameters for compound **3** are given in Table IV. A listing of interatomic bond distances and angles with estimated standard deviations is presented in Table VII. Complete listings of atomic positional and thermal parameters (Table S5) as well as observed and calculated structure factors (Table S6) are available as supplementary material.

Results and Discussion

Description of the Structures. *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ (**1**). The structure of the divalent cation

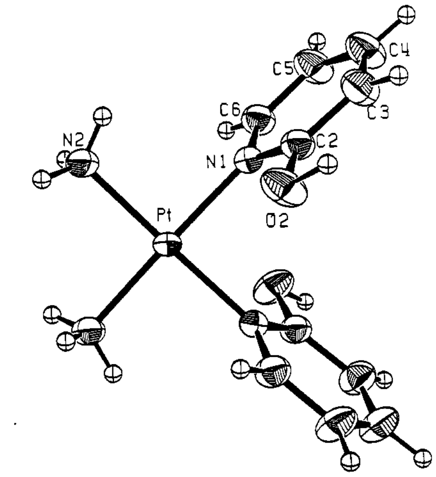


Figure 1. ORTEP illustration of the structure of the bis(2-hydroxypyridine)diammineplatinum(II) cation, *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]^{2+}$ (**1**), showing the 40% probability thermal ellipsoids. For clarity the hydrogen atoms are depicted as spheres with B set to 1 Å^2. The platinum atom lies on a crystallographic twofold symmetry axis.

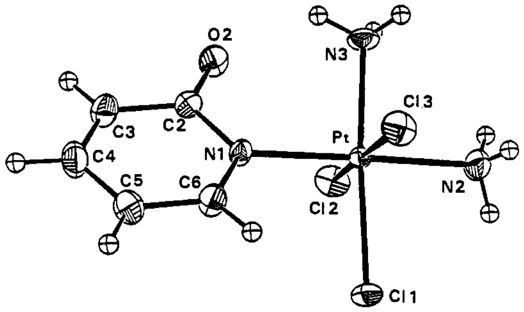


Figure 2. Structure of *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (**2**) showing the 40% probability thermal ellipsoids. For clarity the hydrogen atoms are shown as spheres with B set to 1 Å^2.

consists of a *cis*-diammineplatinum(II) unit attached to two 2-hydroxypyridine ligands through the heterocyclic nitrogen atoms (N1) (Figure 1). The platinum atom is situated on a crystallographic twofold symmetry axis that lies in the plane of the cation and bisects the N1–Pt–N1′ bond angle. As a consequence, the two exocyclic hydroxyl groups are anti to one another, a situation encountered in other platinum(II) complexes containing two purine or pyrimidine derivatives as ligands.[16,17] The syn atropisomer presumably can occur in solution since it is required to form the head-to-head dimer $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$ in the reaction of **1** with *cis*-diammineplatinum(II).[1] Interatomic distances and angles are given in Table V. The square-planar geometry of the ligands in the primary coordination sphere of the platinum atom is normal. The Pt–N bond distances and the N–Pt–N angles are within the range observed in a variety of related Pt(II) complexes.[1,5b,17-19] The four nitrogen ligands and the platinum atom define a plane with a rms deviation of 0.015 Å. The α-pyridone ligand is also planar (rms deviation of 0.010 Å), and the dihedral angle between this plane and the platinum coordination plane is 72.2°. The dihedral angle between the symmetry-related α-pyridone rings is 106.2°.

---

(16) de Castro, B.; Kistenmacher, T. J.; Marzilli, L. G. *Agents Actions Suppl.* **1981**, *AAS8*, 435.

(17) (a) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 335. (b) Marcelis, A. T. M.; Korte, H.-J.; Krebs, B.; Reedijk, J. *Ibid.* **1982**, *21*, 4059.

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

(19) Britten, J. F.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936.

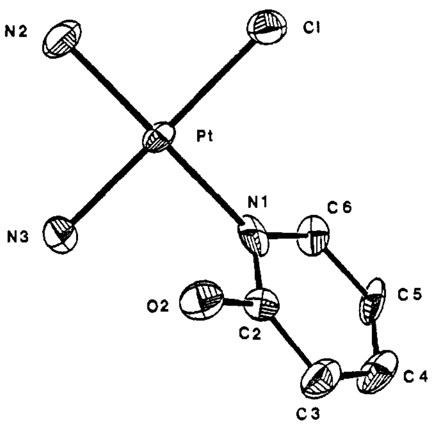


Figure 3. ORTEP illustration of the *cis*-chloro(2-hydroxypyridine)diammineplatinum(II) cation, *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]^+$ (3), showing the 40% probability thermal ellipsoids.

The geometry of the 2-hydroxypyridine ligand in compound **1** is different from that of the free ligand in a number of respects. α-Pyridone has been found, from X-ray structural studies,[20] to crystallize in the oxo tautomeric form. The hydroxyl tautomer is found in the structure of compound **1**. The coordination of platinum to N1 and the presence of the proton on the exocyclic oxygen atom (O2) produce several structural changes in the ring. The most significant differences occur in the bonds and angles at the atoms (N1, C2, and C6) adjacent to the platinum binding site. In the platinum complex, the C2–N1–C6 angle is 4.6° (6σ)[21] smaller and the adjacent N1–C2–C3 angle is 5.6° (8σ) larger than the corresponding angles in α-pyridone. Similar changes are observed in both the head-to-head and head-to-tail α-pyridonate-bridged dimers of *cis*-diammineplatinum(II).[1] Two additional angles, O2–C2–N1 and O2–C2–C3, are significantly smaller [3.6° (5σ) and 2.2° (3σ), respectively] in compound **1** than in the free ligand. These angles are also the ones that differ the most when compared to the ring angles in the α-pyridonate-bridged dimers. For example, the O2–C2–N1 angle in compound **1** is 8.5° (8σ) smaller and the neighboring O2–C2–C3 angle is 7.5° (7σ) larger than the corresponding angles in the head-to-tail α-pyridonate-bridged dimer, $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$.[1] An increase in the O2–C2–N1 angle in the amidate-bridged complexes has been noted in previous studies.[1,22] The bond lengths in the 2-hydroxypyridine ring of compound **1** that show the most significant changes, in comparison to α-pyridone, are between the N1, C2, and O2 atoms. The C2–O2 distance is 0.078 Å (8σ) longer and the N1–C2 distance is 0.038 Å (6σ) shorter in the platinum complex. These differences are similar to those found when the structures of the oxo and hydroxyl forms of related cyclic amides are compared.[20b]

A stereoview of the unit-cell packing diagram for *cis*-$[Pt(NH_3)_2(C_5H_4NOH)_2]Cl_2$ is given in ref 23. The cations pack in the crystal lattice with the platinum coordination planes lying roughly perpendicular to the crystallographic *c* axis. The chlorine anions are hydrogen bonded to the ammine ligands and to the 2-hydroxyl group of the cation. The chloride anion Cl1 forms two sets of symmetry-equivalent hydrogen bonds to the ammine groups of two adjacent cations [Cl1–H2N2 = 2.45 (2) Å and Cl1–H3N2′ = 2.55 Å; see Table V]. The chlorine anion Cl2 is tightly hydrogen bonded to the hydroxyl proton of the 2-hydroxypyridine ligand [Cl2–H1O2 = 1.87 Å, Cl2–H1O2–O2 = 165°]. The only other contact (less than 2.9 Å) to the chlorine anions is between Cl1 and H6 (2.783 (8) Å), and the closest intercation Pt–Pt distance is 5.49 Å.

***mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$ (2).** The structure of compound **2** (Figure 3, Table VI) is comprised of a *cis*-diammineplatinum(IV) unit bound to three meridional chlorine ligands and to a deprotonated α-pyridonate ligand coordinated through the heterocyclic nitrogen atom (N1). The geometry of the platinum coordination sphere is octahedral, and the bond lengths and angles to the platinum atom are normal for Pt(IV)–chloroammine complexes. The Pt–Cl and Pt–N distances in compound **2** compare favorably with the Pt–Cl (range 2.31–2.33 Å) and Pt–N (range 2.05–2.08 Å) distances in the Pt(IV) complex *fac*-$[Pt(dien)Cl_3]Cl\cdot 2H_2O$.[24] The bond angles between the adjacent donor ligands in the platinum coordination sphere are close to the normal value of 90°, with the largest deviation being −3.4° (N2–Pt–Cl1). Three sets of four adjacent ligands in the octahedral coordination sphere lie in a plane, with a rms deviation of 0.010 Å for the atoms N1, N2, N3, Cl1 (plane 1), 0.0222 Å for atoms N1, N2, Cl2, Cl 3 (plane 2), and 0.028 Å for atoms N3, Cl1, Cl2, Cl3 (plane 3). The largest displacement of the platinum atom from this set of planes is 0.067 Å (plane 3). The dihedral angles between the plane of the α-pyridonate ligand (rms deviation 0.017 Å) and the three coordination planes are 38.5° to plane 1, 53.1° to plane 2, and 92.4° to plane 3.

Differences between the geometry of free α-pyridone and the α-pyridonate ligand in **2** result from replacement of the N1 proton in α-pyridone with a Pt(IV) center in compound **2**. The major structural differences between the two rings are found in the bond angles to atoms N1 and C2. Both the C2–N1–C6 and O2–C2–C3 angles are smaller [3.1° (5σ) and 3.9° (6σ), respectively] in the platinum complex **2**. The removal of the proton from an annular nitrogen atom in a conjugated ring is generally accompanied by a decrease in the internal angle at the nitrogen and an increase in the adjacent internal ring angles.[22,25] This effect is observed in the geometry of the α-pyridonate ligand in compound **2**.

A comparison of the bond lengths and angles within the 2-hydroxypyridine ligand in compound **1** and the α-pyridonate ligand in compound **2** also reveals a number of significant differences. The C2–O2 bond distance in the Pt(IV) complex is 0.074 Å (6.2σ) shorter and the N1–C2 bond distance is 0.062 Å (5σ) larger in the Pt(IV) complex **2**. As mentioned above, these differences are typical of those found when structures of the oxo and hydroxy forms of cyclic amides are compared. Two bond angles are also found to differ significantly. The N1–C2–O2 angle in the Pt(IV) complex is 6.2° (6.7σ) larger and the N1–C2–C3 angle is 4.4° (4.8σ) smaller than the corresponding angles in compound **1**. These bond angles in compound **2** are closer to the values found in σ-pyridone (118.8° for N1–C2–O2 and 115.4° for N1–C2–C3) and are characteristic of the oxo tautomeric form of α-pyridone.[20]

The crystal-packing diagram for compound **2**[23] and a listing of hydrogen-bond contacts (H···acceptor) less than 2.5 Å (Table VI) reveal the principal intermolecular hydrogen bonds to occur between the exocyclic oxygen atom O2 of the α-pyridonate ligand and the hydrogen atoms of two ammine ligands of an adjacent molecule [O2–H1N2′ = 2.13 (4) Å and O2–H2N3 = 2.23 (5) Å]. The exocyclic oxygen O2 is also involved in a close intramolecular contact to the hydrogen atom of the N3 (ammine) ligand [O2–H3N3 = 2.19 (3) Å and O2···N3 = 2.717 (8) Å].

***cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ (3).** As shown in Figure 3 and Table VII, the *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]^+$

---

[20] (a) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591. (b) Almlöf, J.; Kvick, Å; Olovsson, I. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1201.

[21] The esd is calculated by using $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$ where σ_1 and σ_2 are the errors in the bond lengths or angles being compared.

[22] Lock, C. J. L.; Pilon, P.; Lippert, B. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2533.

[23] Hollis, L. S. Ph.D. Dissertation, Columbia University, 1982.

[24] Britten, J. F.; Lock, C. J. F. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2958.

[25] Singh, C. *Acta Crystallogr.* **1965**, *19*, 861.

Inorg. Chem. **1983**, *22*, 2713–2716 **2713**

cation has square-planar geometry typical for complexes of platinum(II). While the estimated standard deviations in the bond lengths and angles are large by comparison to those in compound **1**, the geometry of the platinum coordination sphere is normal. The Pt–N and Pt–Cl bond lengths and interbond angles are comparable to those found in compounds **1** and **2**. The four ligands attached to the platinum define a plane with a rms deviation of 0.017 Å, and the platinum atom lies in the plane (0.001 Å displacement). The platinum coordination plane makes a dihedral angle of 56.8° with the plane of the 2-hydroxypyridine ligand. This angle is ~15° smaller than the corresponding angle in compound **1**.

The geometry of the 2-hydroxypyridine ligand in compound **3** is equivalent to that found in compound **1**. Although an accurate comparison is precluded by the large errors in **3**, the largest difference ($<2\sigma$) is found in the C3–C4 bond length. The small dihedral angle between the plane of the ring and platinum coordination plane may be a result of an intramolecular hydrogen bond between the exocyclic oxygen (O2) and the ammine ligand (N3). While hydrogen atoms were not located in the structure, the short N3–O2 distance, 2.93 (3) Å, is suggestive of a hydrogen bond between these two groups.

A stereoview of the unit-cell packing of compound **3** is given in ref 23. As suggested by the length of the crystallographic *c* axis, 4.151 (1) Å, the relatively flat cations stack in columns along the [001] direction. The shortest interaction Pt–Pt′ distance is 5.68 Å (between cations stacked along *c*). The planar nitrate anions also stack in channels along the crystallographic *c* axis. The plane of the nitrate anion makes a dihedral angle of 35.9° with the platinum coordination plane. The nitrate anion is involved in three possible hydrogen-bond contacts to neighboring cations. The oxygen atoms O41 and O42 lie close to the ammine nitrogen atoms N2 and N3 (Table VII), and consequently the nitrate anion appears to form a hydrogen-bonded bridge between adjacent ammines of the same cation. The remaining nitrate oxygen atom (O43) lies 2.62 (3) Å from the 2-hydroxyl group of a neighboring cation.

Conclusion

The structures of three mononuclear *cis*-diammineplatinum complexes of α-pyridone have been determined crystallographically. The mono- and bis(α-pyridone) complexes of *cis*-diammineplatinum(II) contain 2-hydroxypyridine ligands bound to platinum through the heterocyclic nitrogen atom. Recrystallization of the mono(2-hydroxypyridine) complex *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl](NO_3)$ from 1M HCl provides small quantities of the α-pyridonate complex of Pt(IV) *mer*-$[Pt(NH_3)_2(C_5H_4NO)Cl_3]$. Deprotonation of the α-pyridone ligand in this last complex is promoted by the high electrostatic Lewis acid strength of Pt(IV),[26] despite the acidic conditions of the medium. Knowledge of the structures of each of these mononuclear complexes is valuable in assessing the chemistry of *cis*-diammineplatinum(II) complexes with nucleic acid bases and their analogues.

Acknowledgment. This work was supported by National Institutes of Health Research Grant CA-15826. We thank Engelhard Industries for a loan of K_2PtCl_4 used to prepare all platinum complexes.

Registry No. **1**, 76761-67-6; **2**, 86471-90-1; **3**, 86471-92-3; *cis*-$[Pt(NH_3)_2Cl_2]$, 15663-27-1; *cis*-$[Pt(NH_3)_2(C_5H_4NOH)Cl]Cl$, 85336-86-3; $[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2$, 76775-76-3; *cis*-$[Pt(NH_3)_2Cl(H_2O)]^{2+}$, 53861-42-0.

Supplementary Material Available: Atomic positional and thermal parameters for compounds **1**–**3** (Tables S1–S3) as well as final observed and calculated structure factors (Tables S4–S6) (26 pages). Ordering information is given on any current masthead page.

---

[26] Zhang, Y. *Inorg. Chem.* **1982**, *21*, 3889 and references cited therein.

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843,
and East Tennessee State University, Johnson City, Tennessee 37614

Cobalt(III) Complexes of Amino Alcohols. Structural Consequences of Protonation

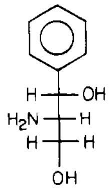
A. CLEARFIELD,*[†] PHIL RUDOLF,[†] and JEFF G. WARDESKA[‡]

Received December 3, 1982

The crystal structure of the diprotonated form of $cis\text{-}\alpha\text{-}\Delta\text{-}(-)_{589}\text{-}[Co\{(+)\text{-}PAHP\}_2en\text{-}\delta\delta\gamma]^+$ (PAHP = monoanion of 1-phenyl-2-amino-1,3-dihydroxypropane), $Co(C_9H_{12}NO_2H)_2(C_2N_2H_8)Cl_3\cdot 2H_2O$, has been determined by single-crystal X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 14.113$ (2) Å, $b = 18.782$ (5) Å, $c = 10.175$ (2) Å, and $Z = 4$. Full-matrix least-squares refinement gave an R index of 0.044 for 2060 observed reflections with intensities greater than 3σ. The absolute configuration was determined by refinement of both enantiomorphs. The protonation sites were inferred to be the alcohol oxygens bonded to cobalt from the very short Cl–O interatomic distances. As a consequence, the Co–O and C–O bonds are lengthened. The effect of protonation upon other structural features is described.

Introduction

As part of a study of complexes containing substituted 2-aminoethanol ligands, we have recently reported the characterization of several isomeric complexes of cobalt(III) containing ethylenediamine and either (1*S*,2*S*)- or (1*R*,2*R*)-1-phenyl-2-amino-1,3-dihydroxypropane (PAHPH) (structure I).[1] The complexes $[Co(PAHP)_2en]^+$ are strongly acidic (diprotic) and were isolated containing the chelated amino alcoholate ligand $PAHP^-$. As part of this characterization, the crystal structure of the complex shown to be $cis\text{-}\alpha\text{-}\Delta\text{-}(-)_{589}\text{-}[Co\{(+)\text{-}PAHP\}_2en\text{-}\delta\delta\gamma]^+$, the *cis*-α(Δ)$^+$ isomer, was reported.[1] This showed that the $PAHP^-$ chelates via the amine and the secondary alcoholate groups. In acid solution this complex and its isomers reversibly add two protons, the site of protonation presumably being the coordinated alcoholate



I

[†] Texas A&M University.

[‡] East Tennessee State University.

0020-1669/83/1322-2713$01.50/0 © 1983 American Chemical Society