data are available as supplementary material. All computations used the SHELXTL (Version 5.1) program library (Nicolet Corp., Madison, WI).

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-85-0228. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1990).

Registry No. $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2; $(THF)_3LiGe(SiMe_3)_3$, 116232-31-6; Cp_2ZrCl_2, 1291-32-3; Cp^*ZrCl_3, 75181-07-6; Cp^*HfCl_3, 75181-08-7; $Cp^*Cl_2ZrSi(SiMe_3)_3$, 116232-26-9; $Cp^*Cl_2HfSi(SiMe_3)_3$, 115677-43-5; $Cp^*Cl_2HfSi(SiMe_3)_3(py)$, 116232-27-0; $Cp_2Zr[Ge(SiMe_3)_3]Cl$, 116232-28-1; $Cp^*Cl_2ZrGe(SiMe_3)_3$, 116232-29-2; $Cp^*Cl_2HfGe(SiMe_3)_3$, 116232-30-5.

Supplementary Material Available: Tables of complete crystal and data collection parameters (Table 1S), bond distances (Tables 2S and 7S), bond angles (Tables 3S and 8S), anisotropic thermal parameters (Tables 4S and 9S), and hydrogen atom coordinates and their isotropic thermal parameters (Tables 5S and 10S) (10 pages); listings of calculated and observed structure factors (Tables 1S and 6S) (61 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of Potassium Aquatetrakis(nitrito)nitrosylplatinate(IV), a Blue, Mononuclear Platinum Complex with a Bent Nitrosyl Group, and of Potassium Trichlorobis(nitrito)nitrosylplatinate(IV)

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Received March 24, 1988

The compounds $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$ (**1**) and $K_2[Pt(NO_2)_2(NO)Cl_3]$ (**2**) have been synthesized and the structures determined by X-ray crystallography. Compound **1** is unusual because it is a mononuclear, blue platinum complex. It was isolated from the reaction that leads to binuclear platinum(III) sulfate and has been suggested to be an intermediate on the route to the sulfate. Both complexes feature a bent nitrosyl ligand and are best formulated as complexes of Pt(IV). They are the first mononuclear platinum nitrosyl complexes whose structures have been determined by X-ray crystallography. Crystallographic data are as follows: **1**, $P\bar{1}$, $a = 6.685$ (2) Å, $b = 8.712$ (2) Å, $c = 9.829$ (3) Å, $\alpha = 91.04$ (2)°, $\beta = 100.36$ (2)°, $\gamma = 92.11$ (2)°, $V = 562.6$ (3) Å^3, $Z = 2$ ($R = 0.065$, $R_w = 0.068$); **2**, $P2_1/c$, $a = 6.227$ (3) Å, $b = 11.690$ (2) Å, $c = 14.525$ (5) Å, $\alpha = 90°$, $\beta = 99.31$ (3)°, $\gamma = 90°$, $V = 1043.4$ (6) Å^3, $Z = 4$ ($R = 0.051$, $R_w = 0.050$).

Introduction

Although blue compounds are uncommon among the third-row transition metals, platinum seems to have three classes of them. Best known are the tetrameric, mixed-valence complexes.[1] A second class is less well characterized but is mononuclear and probably has a charge-transfer band in the long-wavelength part of the visible spectrum.[2,3] The third class has a single well-characterized example, a mononuclear platinum(III) species with rather bulky ligands, which may serve to prevent dimerization.[4]

Recently, it has been shown that certain simple platinum(II) complexes react with phosphoric[5] or sulfuric acid[6] to give dimeric platinum(III) complexes with platinum–platinum bonds.[7-12] The reaction conditions appear simple. All that is required is heating the platinum(II) complex with the appropriate acid. During the reaction, four color changes can be observed. The reaction mixture begins as a colorless solution. It becomes sequentially blue, green, yellow, and then red. The product is red-orange.

Several studies have been reported on the blue solutions that form when platinum(II) nitrites react with phosphoric or sulfuric acid.[13-15] The blue solutions owe their color to an absorption band near 630 nm. It has been asserted that the blue complexes are platinum nitrosyl complexes, but structural information has been unavailable owing to difficulties in handling them.[13,16] We are interested in elucidating the process by which platinum–platinum bonds form. We report the structure of the mononuclear blue platinum(IV) complex $K[Pt(NO_2)_4(NO)(H_2O)]$ (**1**), which forms in the early part of the reaction in phosphoric acid. We also report the structure of the mononuclear green platinum(IV) complex $K_2[Pt(NO_2)_2(NO)Cl_3]$ (**2**), which forms when chloride ion is added to the blue solution containing **1**.

A substantial number of mononuclear platinum nitrosyl complexes have been synthesized.[15-17] None of the compounds that were characterized were blue. Of the three platinum nitrosyl complexes for which molecular structures have been reported, two are dinuclear[18,19] and the third is tetranuclear.[20]

Experimental Section

Preparation of $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$. $K_2Pt(NO_2)_4$ was prepared as described elsewhere.[21] A 3:1 solution of H_3PO_4 in H_2O was

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Table I. Summary of Crystal and Intensity Data and Structure Refinement

	$K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$	$K_2[Pt(NO_2)_2(NO)Cl_3]$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	6.685 (2)	6.227 (3)
b, Å	8.712 (2)	11.690 (2)
c, Å	9.829 (3)	14.525 (5)
α, deg	91.04 (2)	90
β, deg	100.36 (2)	99.31 (3)
γ, deg	92.11 (2)	90
V, Å^3	562.6 (3)	1043.4 (6)
Z	2	4
temp, °C	24	−120
d_{obsd}, g cm^{-3}	2.85	
d_{calcd}, g cm^{-3}	2.85	3.19
μ(Mo Kα), cm^{-1}	135.0	156.9
$F(000)$	448	912
radiation	Mo Kα	Mo Kα
scan mode	ω	ω
total no. of unique rflns	4069	3032
no. of obsd rflns, $I > 3\sigma(I)$	3148	1783
no. of params	167	148
data range (hkl)	±11,±14,+15	±8,+16,+20
transmission factors	0.009–0.119	0.261–0.568
R	0.065	0.051
R_w	0.068	0.050
goodness of fit	1.08	1.01

Table II. $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$: Atom Coordinates and Equivalent Isotropic Temperature Factors (Å^2) with Standard Deviations in Parentheses

	x/a	y/b	z/c	U_{eq}[a]
Pt	0.07549 (6)	0.25724 (4)	0.26640 (4)	0.0277 (1)
K[b]	0.4129 (4)	0.8425 (4)	0.2563 (3)	0.043 (1)
N(1)	0.287 (2)	0.232 (1)	0.444 (1)	0.040 (2)
N(2)	0.216 (2)	0.465 (1)	0.247 (1)	0.046 (2)
N(3)	−0.129 (2)	0.278 (1)	0.087 (1)	0.048 (2)
N(4)	−0.066 (2)	0.047 (1)	0.287 (1)	0.047 (2)
N(5)	−0.116 (2)	0.376 (2)	0.374 (2)	0.078 (2)
O(11)	0.273 (2)	0.310 (2)	0.545 (1)	0.079 (2)
O(12)	0.415 (2)	0.136 (2)	0.441 (1)	0.074 (2)
O(21)	0.112 (2)	0.585 (1)	0.265 (2)	0.088 (2)
O(22)	0.385 (2)	0.478 (1)	0.231 (2)	0.075 (2)
O(31)	−0.256 (3)	0.376 (2)	0.078 (2)	0.105 (3)
O(32)	−0.130 (2)	0.185 (2)	−0.006 (2)	0.083 (2)
O(41)	−0.249 (2)	0.042 (1)	0.280 (2)	0.071 (2)
O(42)	0.035 (2)	−0.066 (1	0.296 (2)	0.071 (2)
O(5a)[c]	−0.176 (4)	0.318 (3)	0.469 (2)	0.080 (4)
O(5b)	−0.262 (3)	0.328 (3)	0.416 (3)	0.080 (4)
O(5c)	−0.296 (2)	0.355 (4)	0.361 (4)	0.080 (4)
O(6)	0.305 (2)	0.148 (1)	0.137 (1)	0.055 (2)
O(7)	0.295 (2)	0.283 (1)	0.885 (1)	0.065 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] The potassium ion, two of the disordered O(5) positions, and the water of crystallization, O(7), are not shown in Figure 1 (top). [c] The site occupancy factors of the three O(5) positions used to model the nirosyl disorder are 0.413 (4), 0.346 (4), and 0.202 (4) for a, b, anc c, respectively.

prepared by volume, degassed, and stored under argon. To 0.50 mL of this solution was added 0.015 g $K_2Pt(NO_2)_4$ under argon in a 5-mL round-bottom flask. The resulting solution was heated in an oil bath at 80–85 °C until deep blue. This required from 60 to 75 s. Additional heating must be avoided because it results in evolution of NO_2 and the formation of a blue-green solution from which the product could not be obtained. The deep blue solution was cooled to −20 °C. Deep blue crystals of the monohydrate potassium salt **1** formed within 2–5 days. Approximately 0.005 g of product was obtained by filtration under argon. Complete removal of the mother liquor could not be accomplished without decomposition of the product; thus, an analytically pure sample for elemental analysis was not obtained despite repeated attempts.

Preparation of $K_2[Pt(NO_2)_2(NO)Cl_3]$. The deep blue solution containing **1** was prepared as described above. Three equivalents of KCl (0.023 g) was added to this solution, and the resulting green solution was cooled to −20 °C. Dark green crystals of the potassium salt **2** formed in 3–5 days. Approximately 0.010 g of product was obtained by filtration under argon. As was the case with **1**, the mother liquor could not be completely removed without decomposition of the product, so elemental analysis was not attempted.

Structure Determinations and Refinements. $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$. A blue crystal fragment (approximately 0.2 × 0.5 × 0.8 mm) was sealed in a glass capillary in the mother liquor to prevent decomposition or reaction with air. Unit cell dimensions were obtained by least-squares refinement using 25 centered reflections for which $26° < 2\theta < 34°$ (graphite-monochromatized Mo Kα radiation). Intensity data were taken on a Nicolet R3mE four-circle diffractometer. Three check reflections, monitored every 100 reflections, showed no significant loss of intensity over the course of data collection. Crystal data and information on data collection and structure refinement are given in Table I.

Data reduction,[22] including corrections for Lorentz and polarization effects, gave 4069 independent reflections in the range $3° < 2\theta < 65°$, of which 3148 with $I > 3\sigma(I)$ were used for structure refinement. The volume of the triclinic unit cell was appropriate for two formula units, so the centrosymmetric space group was assumed and later confirmed by successful structure solution and refinement. A Patterson synthesis yielded the platinum position, and the remaining non-hydrogen atoms were located by difference syntheses. These positions were refined with anisotropic thermal parameters by block-cascade least squares, minimizing $\sum w\Delta^2$ with 101 parameters refined in each full-matrix block. Absorption corrections were calculated by Gaussian integration using indexed planes to approximate the crystal shape with measured crystal dimensions. Atomic scattering factors, including terms for anomalous scattering, were taken from Cromer and Waber.[23] The weighting scheme used was $w = k(\sigma^2(F_o) + 0.0045F_o^2)^{-1}$. Two reflections showing significant extinction were excluded from the data set. Structure refinement led to an unreasonably short (0.91 Å) N–O distance for the nitrosyl ligand, suggestive of rotational disorder of the oxygen position, a common feature in structures with bent NO groups.[24] The equivalent isotropic thermal parameter for the nitrosyl oxygen was very large (U = 0.16 Å^2), and difference electron density maps showed a broad peak spread across an arc of about 90°.

The apparent disorder was modeled by using three positions for the nitrosyl oxygen with a common isotropic thermal parameter. The model was refined with the N–O distance constrained to 1.19 Å, the nitrosyl bond length in the structure of **2**. The site occupancy parameters for the three oxygen disorder positions were allowed to vary. Refinement of the disordered model gave a reasonable nitrosyl oxygen thermal parameter (U = 0.08 Å^2), and the refined occupancy parameters for the disordered oxygen positions summed to 0.96, indicating that the model accounts for most of the electron density for the nitrosyl oxygen. Atom coordinates are given in Table II. The final difference map was featureless except for the usual ripple near the platinum position. Hydrogen atom positions could not be identified with any certainty and were not included in the structure refinement.

$K_2[Pt(NO_2)_2(NO)Cl_3]$. A green plate-shaped crystal (approximately 0.04 × 0.12 × 0.12 mm) was transferred under argon to a 3:1 mixture of Paratone-N and mineral oil. It was then removed on the end of a glass fiber and immediately placed into a stream of nitrogen gas at approximately −120 °C. Thus, isolated from air, the crystal remained stable as long as the low-temperature environment was maintained. All crystallographic procedures were conducted at −120 °C. Unit cell dimensions were obtained from 24 reflections where $19° < 2\theta < 32°$. Crystal data and intensity measurement and structure refinement parameters are given in Table I. Data reduction gave 3032 independent reflections in the range $3° < 2\theta < 60°$, of which 1783 with $I > 3\sigma(I)$ were used for structure refinement. Absorption corrections were made as above; the data showed no significant extinction. Procedures were otherwise as described above.

After all atoms had been refined anisotropically and absorption corrections had been applied, a difference map showed a relatively large peak (2.9 e Å^{-3}) 1.3 Å from one of the chlorine positions, indicating possible disorder. The equivalent isotropic thermal parameter for the proximate chlorine, Cl(2) (see Figure 1 (bottom) for labeling scheme), was twice as large as for the other two chlorines in the complex. This suggested that for a relatively small fraction of sites (the R value at this point was 0.052), there is an alternative orientation of the complex where

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Table III. $K_2[Pt(NO_2)_2(NO)Cl_3]$: Atom Coordinates and Equivalent Isotropic Temperature Factors (Å^2) with Standard Deviations in Parentheses

	x/a	y/b	z/c	U_{eq}[a]
Pt	0.1145 (1)	0.27041 (5)	0.12613 (4)	0.0142 (1)
K(1)[b]	0.4432 (7)	0.8946 (3)	0.6538 (3)	0.032 (1)
K(2)	−0.1778 (7)	0.9513 (3)	0.0969 (3)	0.031 (1)
N(1)	−0.056 (2)	0.219 (1)	0.229 (1)	0.021 (3)
N(2)	0.273 (2)	0.328 (1)	0.023 (1)	0.019 (3)
N(3)	−0.009 (4)	0.434 (2)	0.123 (2)	0.040 (4)
O(11)	−0.074 (2)	0.284 (1)	0.294 (1)	0.029 (3)
O(12)	−0.137 (2)	0.121 (1)	0.226 (1)	0.028 (3)
O(21)	0.349 (2)	0.424 (1)	0.026 (1)	0.040 (3)
O(22)	0.292 (2)	0.266 (1)	−0.046 (1)	0.028 (3)
O(3)	−0.176 (2)	0.451 (1)	0.151 (1)	0.045 (4)
Cl(1)	0.393 (1)	0.3389 (6)	0.2361 (4)	0.018 (1)
Cl(2)	−0.172 (1)	0.2089 (4)	0.0149 (3)	0.028 (1)
Cl(3)	0.297 (1)	0.0741 (4)	0.1259 (4)	0.019 (1)
N(3′)	−0.124 (7)	0.240 (4)	0.013 (3)	0.040
O(3′)	−0.234 (6)	0.318 (5)	−0.021 (3)	0.045
Cl(1′)	0.291 (5)	0.097 (1)	0.137 (3)	0.018
Cl(2′)	−0.045 (5)	0.449 (1)	0.133 (3)	0.046 (5)
Cl(3′)	0.431 (4)	0.332 (3)	0.252 (2)	0.019

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] The potassium ions and the minor positions of disordered atoms, N(3′) to Cl(3′), are not shown in Figure 1 (bottom).

the positions of the nitrosyl and Cl(2) ligands are exchanged. In the minor orientation the nitrite ligands would also be exchanged, and Cl(1) and Cl(3) would replace each other. To model this apparent disorder, additional positions were introduced for Cl(2) and the nitrosyl ligand, with use of the peak from the difference map for the nitrosyl oxygen. Because of a significant difference in bond distances (see Results and Discussion), additional positions for Cl(1) and Cl(3) were also included in the disorder model. The nitrites are oriented such that their alternate positions would be superimposed.

The disordered model was refined with some constraints imposed on parameters for the minor orientation. Bond distances were constrained to corresponding values from the major orientation, as was the nitrosyl bond angle. Isotropic thermal parameters were assigned in like manner for all except Cl(2′), which was allowed to refine with anisotropic thermal parameters. Refinement of the disordered model led to smaller thermal parameters for Cl(2), a slightly shorter nitrosyl N–Pt distance (2.06 vs 2.12 Å), and a longer nitrosyl N–O distance (1.19 vs 1.09 Å) compared to values obtained without modeling disorder. These differences are consistent with the assumed disorder, and the nitrosyl distances are closer to expected values when the disorder is included in the refinement model. Other bond distances and angles were not significantly affected by including disorder in the model nor were the refinement statistics. The site occupancy ratio for the two orientations was refined as approximately 84% to 16% and was fixed in the final least-squares cycles to facilitate convergence. Atom coordinates are given in Table III, including minor orientation positions. The final difference map was featureless except for ripples near platinum and chlorine positions. Corrections for extinction were not needed.

Other Measurements. Magnetic moments were measured by the Evans method[25] using tris(ethylenediamine)chromium(III) chloride as a calibrant. Solutions containing $Pt[(NO_2)_4(NO)(H_2O)]^-$ were shown to be diamagnetic in this way. Infrared spectra were recorded on a Nicolet MX-1 Fourier transform infrared spectrometer in IR-tran cells. Spectra of the platinum complexes were recorded in the difference mode by subtracting the spectrum of the phosphoric acid–water solution from identical solutions containing the platinum complexes. Visible absorption spectra were measured with a Cary 14 instrument. ESCA data were recorded on a L-H EA II (Leybold Heraeus) spectrometer. Monochromatic Mg Kα radiation (1253.6 eV) was used as the X-ray excitation source. The powdered sample was dispersed on an indium metal surface. Under these conditions the carbon 1s binding energy was found to be 284.6 eV, and this binding energy was used regularly for calibration of the instrument. During the time when the spectra of the platinum complexes were recorded, this C_{1s} peak had a full width at half-maximum (fwhm) of 1.0 (±0.2) eV. The chemical shift of the C_{1s} peak remained the same with variation of the pass energy ($\Delta E/E$) and with variation in the current supplied to the X-ray source, suggesting minimal surface charging effects.

Table IV. Bond Lengths (Å) and Angles (deg) with Standard Deviations for $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$

Bond Lengths			
Pt–N(1)	2.06 (1)	Pt–N(2)	2.04 (1)
Pt–N(3)	2.04 (1)	Pt–N(4)	2.06 (1)
Pt–N(5)	2.10 (2)	Pt–O(6)	2.37 (1)
N(1)–O(11)	1.21 (2)	N(1)–O(12)	1.22 (2)
N(2)–O(21)	1.26 (2)	N(2)–O(22)	1.17 (2)
N(3)–O(31)	1.22 (2)	N(3)–O(32)	1.21 (2)
N(4)–O(41)	1.21 (2)	N(4)–O(42)	1.20 (2)
N(5)–O(5)[a]	1.19		
Bond Angles			
N(1)–Pt–N(2)	87.4 (4)	N(1)–Pt–N(3)	178.2 (5)
N(1)–Pt–N(4)	92.5 (5)	N(1)–Pt–N(5)	91.9 (5)
N(1)–Pt–O(6)	89.0 (4)	N(2)–Pt–N(3)	93.0 (5)
N(2)–Pt–N(4)	180.0 (6)	N(2)–Pt–N(5)	86.5 (6)
N(2)–Pt–O(6)	87.7 (5)	N(3)–Pt–N(4)	87.1 (5)
N(3)–Pt–N(5)	89.9 (6)	N(3)–Pt–O(6)	89.3 (5)
N(4)–Pt–N(5)	93.5 (6)	N(4)–Pt–O(6)	92.3 (5)
N(5)–Pt–O(6)	174.1 (5)	Pt–N(1)–O(11)	119 (1)
Pt–N(1)–O(12)	118 (1)	O(11)–N(1)–O(12)	124 (1)
Pt–N(2)–O(21)	118 (1)	Pt–N(2)–O(22)	122 (1)
O(21)–N(2)–O(22)	119 (1)	Pt–N(3)–O(31)	120 (1)
Pt–N(3)–O(32)	119 (1)	O(31)–N(3)–O(32)	121 (2)
Pt–N(4)–O(41)	118 (1)	Pt–N(4)–O(42)	119 (1)
O(41)–N(4)–O(42)	123 (1)	Pt–N(5)–O(5a)	120 (2)
Pt–N(5)–O(5b)	129 (2)	Pt–N(5)–O(5c)	126 (2)

[a] The nitrosyl disorder model was refined with an N–O distance constraint for all three O(5) positions.

Table V. Bond Lengths (Å) and Angles (deg) with Standard Deviations for $K_2[Pt(NO_2)_2(NO)Cl_3]$

Bond Lengths			
Pt–N(1)	2.06 (1)	Pt–N(2)	2.04 (1)
Pt–N(3)	2.06 (2)	Pt–Cl(1)	2.303 (5)
Pt–Cl(2)	2.320 (5)	Pt–Cl(3)	2.562 (5)
N(1)–O(11)	1.23 (2)	N(1)–O(12)	2.26 (2)
N(2)–O(21)	1.21 (2)	N(2)–O(22)	1.25 (2)
N(3)–O(3)	1.19 (3)		
Bond Angles			
N(1)–Pt–N(2)	177.1 (5)	N(1)–Pt–N(3)	93 (1)
N(1)–Pt–Cl(1)	91.0 (3)	N(1)–Pt–Cl(2)	89.2 (3)
N(1)–Pt–Cl(3)	91.3 (4)	N(2)–Pt–N(3)	84 (1)
N(2)–Pt–Cl(1)	89.7 (3)	N(2)–Pt–Cl(2)	90.0 (3)
N(2)–Pt–Cl(3)	91.5 (4)	N(3)–Pt–Cl(1)	86.0 (6)
N(3)–Pt–Cl (2)	91.7 (6)	N(3)–Pt–Cl(3)	175.1 (7)
C(1)–Pt–Cl(2)	177.6 (2)	Cl(1)–Pt–Cl(3)	91.6 (2)
Cl(2)–Pt–Cl(3)	90.8 (2)	Pt–N(1)–O(11)	120 (1)
Pt–N(1)–O(12)	120 (1)	O(11)–N(1)–O(12)	120 (1)
Pt–N(2)–O(21)	121 (1)	Pt–N(2)–O(22)	121 (1)
O(21)–N(2)–O(22)	118 (1)	Pt–N(3)–O(3)	119 (2)

Results and Discussion

The structures of $[Pt(NO_2)_4(NO)(H_2O)]^-$ (anion of **1**) and $[Pt(NO_2)_2(NO)Cl_3]^{2-}$ (anion of **2**) are shown in Figure 1. Bond distances and angles are given in Table IV for **1** and in Table V for **2**. The reliability of distances and angles involving light atoms can be gauged by the ranges in these values for the nitrite groups in both complexes. For **1**, nitrite N–O distances range from 1.17 to 1.26 Å (average 1.21 Å) and angles around nitrite nitrogen atoms range from 118 to 124°. The corresponding ranges for **2** are 1.21–1.26 Å (average 1.24 Å) and 118–121°. This would indicate that the reported standard deviations in Tables IV and V are underestimated by a factor of 3 for the structure of **1** and a factor of 2 for the structure of **2**. For both structures the accuracy of the absorption correction is probably the limiting factor determining the quality of the crystallographic data. In both structures refined positional coordinates and derived values are undoubtedly affected to some degree by the models chosen to treat disorder effects, but both models exhibited well-behaved structure refinements under the limited constraints described above. Except for the constrained nitrosyl N–O distance in the structure of **1**, the distances and angles derived from the disordered models and reported in Tables IV and V did not differ greatly from values

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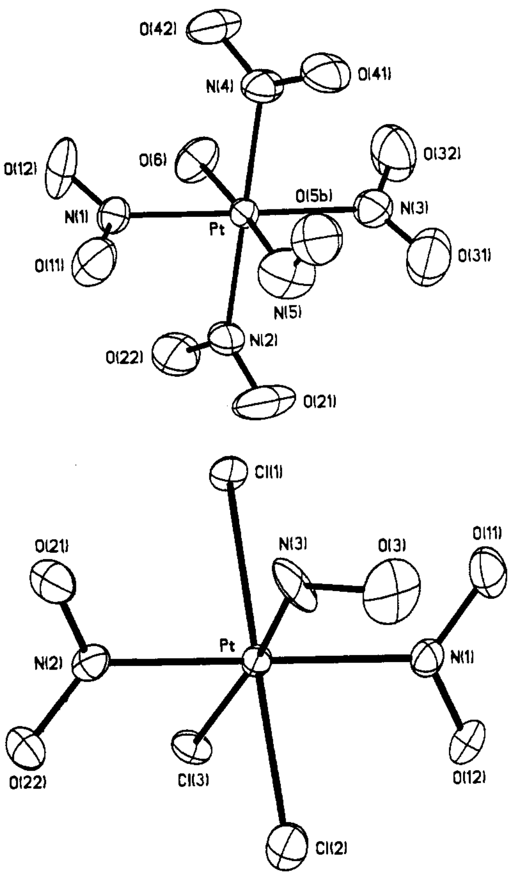

Figure 1. Thermal ellipsoid drawings (50% probability) of $[Pt(NO_2)_4(NO)(H_2O)]^-$ (anion of **1**, top) and $[Pt(NO_2)_2(NO)Cl_3]^{2-}$ (anion of **2**, bottom) and atom-labeling schemes.

obtained from refinements without including disorder in the models.

Both structures display features that are characteristic of complexes with strongly bent nitrosyl groups. In the terminology of Enemark and Feltham,[24] they fall into the class $\{MNO\}^8$ and are best represented as complexes of NO^-.[26,27] The N(3)–O(3) distance, 1.19 (3) Å, and Pt–N(3)–O(3) angle, 119 (2)°, for **2** are within the ranges reported for other $\{MNO\}^8$ complexes with bent NO groups, as are the Pt–N(5)–O(5) angles for the three disordered O(5) positions in the structure of **1**, the weighted average being 125°. The nitrosyl Pt–N distances for the two structures are slightly longer, but not significantly longer, than the nitrite Pt–N distances. Both structures illustrate the trans-bond-lengthening effect of the bent nitrosyl group.[28] In the structure of **1** the Pt–O distance for the water ligand is 2.37 (1) Å, about 0.3 Å longer than expected. The Pt–Cl distance for Cl(3) in the structure of **2** is 2.562 (5) Å, which is about 0.25 Å longer than the other Pt–Cl distances in the complex. We are aware of no other crystallographic structures for mononuclear platinum nitrosyl complexes.

It has been suggested, on the basis of infrared and Raman spectroscopy, that for the tetrakis(nitrito)platinate(II) ion in solution the nitrite groups are perpendicular to the plane of the square around the platinum.[29] In **1** and **2** and in the crystal structure of $K_2Pt(NO_2)_4$[30] the nitrite moieties are neither perpendicular to nor coplanar with the platinum coordination planes. For these compounds in the solid state π bonding must be minimal between platinum and the nitrite groups. Packing effects in the solids may outweigh any additional bonding that might be present in solution. The O(6)–O(7) distance (2.76 Å) in the structure of $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$, indicates hydrogen bonding between the water ligand and the lattice water molecule.

Although both compounds were too reactive to obtain satisfactory elemental analyses by conventional methods, the structure determination of $K_2[Pt(NO_2)_2(NO)Cl_3]$ allows an unambiguous identification of **2** as a six-coordinate Pt(IV) complex. However, since hydrogen atoms could not be located in the structure of the blue compound, the formulation $K[Pt(NO)_4(NO)(H_2O)]\cdot H_2O$ cannot be established unequivocally from X-ray data alone. In principle valences of +2, +3, or +4 could be assigned to the platinum and each could be logically defended by assuming an appropriate number of protons added to the water and nitrosyl ligands. One might also question whether the nitrosyl group has been correctly identified, given the rotational disorder we have described. The structure of **2** supports the identification of the nitrosyl ligand in **1**, as does the observation of an intense infrared band at 1655 cm^{-1} for solutions containing **1**. This band is assigned to NO stretching and is in the appropriate region for the stretching of bent NO groups.[31] A six-coordinate Pt(II) complex with small inorganic ligands seems highly unlikely, and solutions of the compound are diamagnetic. Therefore, the assignment of a +4 valence to the platinum in **1** is most reasonable. Although hydrogen atom positions could not be located, these considerations and the requirement of charge balance favor the formulation $K[Pt(NO_2)_4(NO)(H_2O)]\cdot H_2O$. An alternative formulation with a protonated nitrosyl group and either an OH^- ligand or an OH^- counterion seems unlikely in 10 M phosphoric acid. The blue color is likely to be the consequence of a charge-transfer band arising from the transfer of the lone electron pair on the nitrosyl group to the platinum ion.[2,3]

It has been suggested that nitrosyl complexes are responsible for the blue solutions formed when $K_2Pt(NO_2)_4$ dissolves in sulfuric, phosphoric, or nitric acid, but it has not been possible to determine any structure or structures responsible for the blue color until now. Wilkinson isolated a yellow compound by evaporation of a blue nitric acid solution but could not obtain a blue solid.[15] He reported several green nitrosyl complexes of six-coordinate platinum obtained from nitric oxide saturated acid solutions of four-coordinate compounds and from reactions of four-coordinate complexes with nitrosyl chloride in chloroform. Nazarova, Chernyaev, and Kolesnikova isolated a very unstable blue compound formulated as $K_2[Pt(NO_2)_4(NO)(NO_3)]$ from nitric acid solutions of $K_2Pt(NO_2)_4$, but the complex was too unstable for detailed structural work. The blue solutions we have studied containing **1** have a maximum at 607 nm in nitric, sulfuric, or phosphoric acid. We find that in water $NOBF_4$ reacts slowly with $K_2Pt(NO_2)_4$ to give a blue solution with a maximum at 625 nm. This maximum shifts promptly to 607 nm upon the addition of sulfuric acid. We interpret these observations as further support for the formulation of **1** as a nitrosyl complex.

Lastly, it is worth commenting that our interest in the structure of **1**, aside from its unusual color, stems from the fact that it is present in systems that eventually produce compounds with metal–metal bonds. We expect to report structures of other compounds from these solutions in the future. Since **1** contains five nitrogen atoms, simple stoichiometric considerations demand that there must be at least one other platinum complex with less than four nitrogen atoms also present in the reaction mixtures containing **1**. ESCA data obtained from the blue powder isolated by removing the solvent from the reaction mixture show the presence of two platinum species. The two sets of platinum $4f_{5/2,7/2}$ doublets in this sample have been assigned to the presence of two different platinum species, one in the platinum(II) oxidation state and the other in the platinum(IV) oxidation state. The $4f_{7/2}$ binding energies for the two species were found to be 72.9 and 75.2 eV. The signal intensities suggest approximately a 1:1 mixture of the two platinum species. A possible pathway for the initial step in platinum–platinum bond formation may require the

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presence of both platinum(IV) and platinum(II) in solution before the platinum(III)-platinum(III) bond can be formed.

Acknowledgment. We wish to acknowledge Dr. Ed Mooberry, Department of Biochemistry, University of Wisconsin, Madison, WI, and Dr. Ed Waali, Department of Chemistry, University of Montana, Missoula, MT, for the use of their Fourier transform infrared spectroscopy facilities and Dr. Gerald Lapeyre and the CRISS facility staff for help with ESCA data acquisition and processing. This work was supported by NSF Grants CHE-8306254 and CHE-7826160.

Registry No. **1**·H_2O, 116053-26-0; **2**, 116053-27-1; $K_2Pt(NO_2)_4$, 13815-39-9.

Supplementary Material Available: Listings of thermal parameters, least-squares planes, and nonbonded distances and packing diagrams (4 pages); a listing of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Glasslike Structure in Crystalline Macrocyclic Complexes: Synthesis, X-ray Diffraction, and Laser-Spectroscopic Investigation of Neodymium(III) and Europium(III) Complexes with 4,13-Dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane[1]

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Received February 22, 1988

Nd and Eu nitrates react with the macrocyclic ligand 4,13-dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, abbreviated $Me_2(2,2)$, to yield crystalline complexes with a 4:3 metal:ligand ratio. Their crystal and molecular structures have been determined at 150 K (Nd) and 293 K (Eu) from single-crystal X-ray diffraction. The two complexes are isostructural, pseudocentric, and disordered and crystallize in the monoclinic space group $C2$ (ITC No. 5) with $Z = 2$. Lattice parameters are $a = 30.140$ (13) Å, $b = 11.031$ (2) Å, $c = 12.494$ (6) Å, $\beta = 112.21$ (4)° for Nd and $a = 31.340$ (9) Å, $b = 11.017$ (3) Å, $c = 12.533$ (2) Å, and $\beta = 116.04$ (2)° for Eu. The structures were solved by Patterson and Fourier techniques and refined by least squares, using soft constraints and unit weights, to final conventional R values of 0.069 (Nd) and 0.065 (Eu). The complexes are comprised of three $[Ln(NO_3)_2{\cdot}Me_2(2,2)]^+$ cations and one $[Ln(NO_3)_6]^{3-}$ anion. Two equivalent complex cations are in general positions while the other is in a special position with C_2 symmetry; the Ln(III) ions are 10-coordinate. The anion has C_2 symmetry, close to C_{2h}, and contains a 12-coordinate Ln(III) ion. The metal ion sites of the Eu complex have been probed by high-resolution excitation and emission spectra at variable temperature. At 77 K, the $[Eu(NO_3)_6]^{3-}$ anions give rise to a luminescence spectrum dominated by the $^5D_0 \rightarrow {}^7F_1$ transition; this points to anions with a local symmetry very close to C_{2h}. Analysis of the spectra generated by the $[Eu(NO_3)_2{\cdot}Me_2(2,2)]^+$ cations revealed a wide dispersion of the cationic sites. This is due to the complex cations being evenly distributed among different conformations. Such a situation is analogous to what is observed in the vitreous state. These conclusions are supported by the values of the lifetimes determined at 293 and 77 K.

Introduction

Lanthanide ions react with synthetic ionophores to form guest-host complexes[4] in which the metal ion is partly protected from solvent interaction. Investigation of these complexes is a logical extension[5,6] of the work on alkali-metal and alkaline-earth-metal complexes started in the late 1960s[7] and bears the following specific motivations: (i) systematic study of the coordination properties of rare-earth ions, (ii) design of efficient separation[8,9] and analytical processes,[10] (iii) stabilization of unusual oxidation states, (iv) use of lanthanide macrocyclic complexes as probes in the analysis of biological materials,[11] and (v) synthesis of relaxation agents for NMR-imaging experiments.[12] The subject has been recently reviewed[13] and is presently attracting considerable interest in its synthetic,[14] structural,[15] photophysical,[16,17] kinetic,[18] thermodynamic,[19] and applied[20] aspects.

On the other hand, lanthanide luminescent probes are being increasingly used to solve a variety of structural and analytical problems. In particular, owing to selective laser excitation, the Eu(III) ion probe[21] displays a high sensitivity, which contributes to the determination of the local structures in crystalline materials,[22] glasses,[23] and solutions.[24,25] It facilitates the study of the effects of chemical and thermal treatments on catalysts[26] and potential catalysts[27] and is also provided in the development of immunoassays having a sensitivity comparable to that of radioisotopic methods.[28] In our laboratory, special attention has been given to the relationship between the structure and the

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