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Hydroxo-Bridged Platinum(II) Complexes. 3.[1]
Bis[*cyclo*-tri-μ-hydroxo-tris(*cis*-diammineplatinum(II))] Trisulfate Hexahydrate. Crystallographic Characterization and Vibrational Spectra

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Received October 28, 1977

The reaction of *cis*-Pt(NH₃)₂Cl₂ with silver sulfate in water yields the compound bis[*cyclo*-tri-μ-hydroxo-tris(*cis*-diammineplatinum(II))] trisulfate hexahydrate, [{(NH₃)₂Pt(OH)}₃]₂(SO₄)₃·6H₂O. The crystal structure has been determined by X-ray diffraction. The monoclinic space group $P2_1/n$ has cell dimensions $a = 14.505$ (6) Å, $b = 10.335$ (3) Å, $c = 13.539$ (4) Å, and $\beta = 118.69$ (2)° and has two formula units in the unit cell. Data were collected using Mo Kα radiation and a Syntex $P2_1$ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0546$ and $R_2 = 0.0627$ based on 3083 independent reflections. The cation is a hydroxide-bridge trimer with rough C_{3v} symmetry. The ligands about each platinum are roughly square planar so the oxygen atoms lie about 0.95 Å on one side of the three-platinum plane. The Pt–N and Pt–O distances are normal (ranges 2.01 (2)–2.06 (2) and 2.01 (2)–2.04 (2) Å, respectively). The vibrational spectrum is discussed.

Our interest in the hydrolyzed species of *cis*-dichlorodiammineplatinum(II), *cis*-Pt(NH₃)₂Cl₂, is twofold: It is the starting material of a new class of potent antitumor agents, the so-called "platinum pyrimidine blues" whose structure is still unclear at this moment,[3] and it is possibly also the species to which *cis*-dichlorodiammineplatinum(II) is transformed before its cancerostatic activity.[4] In previous papers we presented evidence that with nitrate as anion the aquated species of *cis*-Pt(NH₃)₂Cl₂ formed stable di- and trimeric, hydroxo-bridged platinum complexes.[1,5] We have now found that with sulfate as counterion dimeric and trimeric hydroxo-bridged complexes are also formed, but in contrast to the nitrates the cyclic trimer is formed preferably. Further, the steric arrangement of the trimeric cation in the sulfate salt is different in the solid state from that of the trimer nitrate. The dimer sulfate is the exact analogue of the dimer nitrate and is not considered here. We report here the molecular and crystal structure of the trimer, bis[*cyclo*-tri-μ-hydroxo-tris(*cis*-diammineplatinum(II))] trisulfate hexahydrate, [Pt₃(NH₃)₆(OH)₃]₂(SO₄)₃·6H₂O, and also briefly discuss its vibrational spectra.

Experimental Section

Preparation. The title compound was prepared in the following way: One gram of *cis*-dichlorodiammineplatinum(II) (Englehard Industries) was stirred with 1.03 g of Ag₂SO₄ in 15 mL of water in a stoppered flask (wrapped in aluminum foil) at room temperature for 20 h. The precipitated silver chloride was filtered and washed with 5 mL of water. The pale yellow filtrate (pH 2.4) was titrated with somewhat less than 1 equiv of 1 N NaOH to pH 6.65. The solution turned cloudy within 5 min. It was then concentrated to a 5-mL volume in a desiccator over concentrated sulfuric acid and then kept in air overnight. The resulting precipitate was filtered, washed four times with 5 mL of water and finally with some ethanol and ether, and dried under a rotary pump vacuum. The yield of the first crop of yellow crystals of [(NH₃)₆Pt₃(OH)₃]₂(SO₄)₃·6H₂O was 350 mg. The pH of the filtrate (4.0) was brought back to 6.65 by means of 1 N NaOH, and then the filtrate was put in a water bath at 40 °C. When the solution was concentrated to a 5-mL volume, it was taken from the bath and a second crop of very nicely shaped yellow crystals of the title compound was filtered off and washed as described; yield 50 mg. The crystals for the X-ray determinations were from this crop.

When exactly 1 equiv of NaOH was taken to titrate the diaquo species (pH 7.35), the first crop consisted of a mixture of the yellow crystals of the title compound (95%) and white opaque crystals of a second species whose IR spectrum clearly showed that it was the exact analogue of the di-μ-hydroxo-bis[diammineplatinum(II)] nitrate.[5] The identification of the compound as [(NH₃)₂Pt(OH)₂Pt(NH₃)₂]SO₄·xH₂O is based on the vibrational spectra, in particular upon the prominent Pt–N and Pt–O skeletal stretching vibrations. When more than 1 equiv of NaOH was used (e.g., 1.5 equiv), the solution turned dark very quickly and, in the course of several weeks

at 0 °C, a brown-black unidentified compound precipitated besides the trimer sulfate (which was no longer yellow but olive to brown) and a small amount of a deep yellow compound whose IR spectrum unambiguously identified it as [(NH₃)₂Pt(OH)₂Pt(NH₃)₂]SO₄ with an unknown amount of water of crystallization. In the preparations described we could not detect any formation of a dimeric, sulfato-bridged complex such as *cis*-sulfatodihydroxotetraamminediplatinum(II), which was claimed to be formed in a similar procedure.[6]

Anal. Calcd for [(NH₃)₆Pt₃(OH)₃]₂(SO₄)₃·3H₂O: H, 2.66; N, 9.24; O, 18.47; Pt, 64.34; S, 5.29. Found (Galbraith Laboratories): H, 2.30; N, 9.16; O, 18.42; Pt, 64.69; S, 5.25. Decomposition occurred above 220 °C. Solubility in water at room temperature was 220 mg/100 mL.

The following IR and Raman bands (in cm⁻¹) were observed. Infrared (KBr): 3670–3420 (s),[7a] 3400 (s), 3300–3080 (vs), 2900 (sh), 2620 (vw), 2400 (vw), 2230 (w), 2140 (vw), 2070 (vw), 1700–1640 (s), 1550 (s), 1450 (vw), 1380 (vw), 1335 (sh), 1325 (s), 1310 (s), 1160 (sh), 1110 (vs), 1015 (m), 980 (w), 870 (m), 840 (m), 785 (s), 735 (s), 625 (sh), 613 (s), 600 (m), 570 (m), 523 (s), 463 (m), 420 (w), 285 (w). Raman (solid):[7b] 1122 (0), 982 (5), 975 (3), 895 (1), 610 (1), 571 (1), 533 (10), 474 (4), 439 (2), 243 (2).

The compound readily decomposed in the laser beam and was therefore rotated every 50–100 wavenumbers. The deuterated analogue was prepared by recrystallizing the compound twice from D₂O.

Apparatus. pH measurements were performed with a Corning Model 7 pH meter and a combination electrode after calibration. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer from 4000 to 250 cm⁻¹ as KBr pellets and from 4000 to 400 cm⁻¹ as Nujol mulls and were calibrated against polystyrene. Raman spectra were obtained from powder samples at room temperature from 1200 to 200 cm⁻¹ on a Spex Model 1401 spectrometer with a Coherent Radiation Model 52 argon laser and calibrated against CCl₄.

Crystallography. The title compound crystallized as parallelepipeds. A crystal, chosen for its homogeneity when viewed with polarized light, was ground to a cylinder of 0.075-mm radius and 0.30-mm length and was used for X-ray studies. It was mounted roughly along the *a* axis, and preliminary precession photographs showed the systematic absences 0*k*0, $k = 2n + 1$, and *h*0*l*, $h + l = 2n + 1$, indicating uniquely the space group $P2_1/n$, an unconventional setting of $P2_1/c$ (No. 14).[8] The crystal was transferred to a Syntex $P2_1$ automatic diffractometer and unit cell parameters were obtained from a least-squares fit of χ, φ, and 2θ for 15 medium-angle (20° < 2θ < 35°) reflections: $a = 14.505$ (6) Å, $b = 10.335$ (3) Å, $c = 13.539$ (4) Å, $\beta = 118.69$ (2)° (λ 0.710 69 Å for Mo Kα radiation at 21 °C). With $Z = 4$ (for a trimer) ρ_{calcd} was 3.49 g cm⁻³ and ρ_{obsd}, determined by displacement in light paraffin oil, was 3.56 (5) g cm⁻³. The linear absorption coefficient was 249.7 cm⁻¹, and using the above crystal dimensions, the variation in the transmission coefficient was 11.60–16.22.

Intensity data were recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation for the hemidemisphere defined by $+h,+k,\pm l$, up to 2θ = 55°. Data were collected by using a coupled θ(crystal)–2θ(counter) scan 1° on either side of the peak,
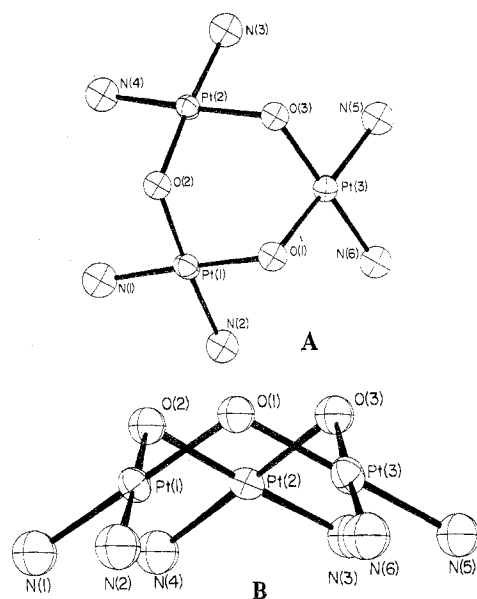
Figure 1. The molecular cation (A) viewed down to pseudo-C_{3v} axis, with all platinum atoms in the plane of the paper and (B) viewed down the vector Pt(2)–midpoint (Pt(1)–Pt(3)).

scan rates varying from 2.02 to 29.3° min^{-1} and being selected by the program supplied with the instrument.[9] The stability of the system was monitored by measuring a standard reflection, –3,0,–3, after every 15 reflections. The counting esd of the standard peak was 2.20%, and an analysis of the standard counts showed an overall variation of 5.0% with no systematic variation with time. The intensity of a reflection, I, its esd, $\sigma(I)$, and the derived unscaled structure factor amplitudes, F, and the standard deviations, $\sigma(F)$, were calculated as reported previously.[10] A total of 3083 independent reflections were recorded, of which 2323 had $I > 3\sigma(I)$ and were considered significant; 760 had $3\sigma(I) > I > \sigma(I)$ and were used in refinement only when $F_c > F_o$.

Solution of the Structure. The coordinates of the three platinum atoms were found from a three-dimensional Patterson synthesis, and three-dimensional electron density and difference maps revealed the nitrogen and oxygen atoms bound to the platinum atoms and also the sulfur atoms. Least-squares refinement[11] of the atom positions followed by further three-dimensional electron density synthesis and difference calculations revealed all the remaining nonhydrogen atoms. Anisotropic temperature factors were used for the platinum atoms and S(2) in these last cycles of refinement. A Cruickshank weighting scheme with weights equal to $(108.94 - 1.0127|F_o| + 0.004345F_o^2)^{-1}$ was used and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Refinement was terminated at $R_1 = 0.0546$ and $R_2 = 0.0627$.[12] In the last cycle of refinement no parameter shifted by more than 0.008 of its esd. Corrections were made for secondary extinction; g was 3.417×10^{-8}.

The final difference map showed little variation, the largest peaks being 0.96 e/Å^3 at 0.48, 0.00, 0.03 (in the region of O(H2)) and 0.70, 0.42, 0.83 (near Pt(2)). The deepest valleys were –1.12 e/Å^3 at 0.95, 0.00, 0.48 (near S(1)) and –0.96 e/Å^3 at 0.78, 0.42, 0.90 (between Pt(2) and O(3)). Throughout the refinement, the scattering curves used were taken from ref 13, and anomalous dispersion corrections from ref 14 were applied to the curves for platinum and sulfur. The positional and thermal parameters for the nonhydrogen atoms are listed in Table I.

Results and Discussion

The molecular cation is illustrated in Figure 1 and selected interatomic distances and angles are given in Table II. The cation is a hydroxo-bridged trimer of rough C_{3v} symmetry (see Figure 1A); thus all the bridging hydroxide groups lie on the same side of the three-platinum plane (see Figure 1B) in contrast to the trimer cation structure we have reported previously.[1] The ligand atoms bonded to each platinum atom and the platinum atom itself are planar within the errors,[15] and the angles these planes make with the three-platinum plane are 42.2° for the Pt(1) plane, 40.9° for the Pt(2) plane, and

Table I

Final Atomic Positions and Thermal Parameters ($\times 10^3$)

Atom	x	y	z	U, Å^2
Pt(1)	204.56 (6)	429.88 (7)	327.83 (6)	
Pt(2)	220.27 (6)	112.04 (7)	332.02 (6)	
Pt(3)	322.71 (6)	275.28 (8)	568.96 (6)	
O(1)	341 (1)	413 (1)	472 (1)	35 (3)
O(2)	247 (1)	277 (1)	267 (1)	35 (3)
O(3)	354 (1)	143 (1)	480 (1)	38 (3)
N(1)	70 (2)	435 (2)	180 (2)	50 (5)
N(2)	157 (2)	585 (2)	383 (2)	51 (5)
N(3)	199 (2)	–53 (2)	400 (2)	45 (5)
N(4)	85 (2)	84 (2)	182 (2)	47 (5)
N(5)	303 (2)	127 (2)	659 (2)	47 (5)
N(6)	294 (2)	406 (2)	665 (2)	55 (5)
S(1)^b	0	0	500	79 (3)
O(11)	23 (2)	–65 (2)	604 (2)	172 (22)
O(12)	64 (2)	116 (2)	525 (2)	165 (3)
O(13)	24 (2)	–86 (2)	431 (2)	195 (40)
O(14)	–110 (2)	35 (2)	440 (2)	106 (17)
S(2)	555.5 (4)	250.9 (4)	393.9 (4)	
O(21)	545 (2)	213 (2)	491 (2)	88 (7)
O(22)	599 (1)	147 (2)	356 (2)	63 (5)
O(23)	618 (2)	364 (2)	410 (2)	89 (7)
O(24)	452 (2)	283 (2)	300 (2)	64 (5)
O(H1)	309 (2)	214 (3)	882 (3)	117 (9)
O(H2)	592 (3)	175 (3)	148 (3)	133 (11)
O(H3)	18 (3)	294 (4)	366 (3)	150 (13)

Anisotropic Temperature Factors ($\times 10^4$, Å^2)^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	267 (5)	292 (4)	253 (4)	14 (3)	88 (3)	–18 (3)
Pt(2)	248 (5)	280 (4)	316 (4)	1 (3)	125 (3)	–23 (3)
Pt(3)	304 (5)	363 (4)	260 (3)	25 (3)	95 (3)	–10 (3)
S(2)	314 (21)	286 (20)	357 (32)	–2 (10)	133 (12)	–8 (10)

^{a} Estimated standard deviations from the least-squares programs are given in parentheses. The temperature factor parameters U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$, where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ in the structure factor expression and b_i are the reciprocal lattice vectors. ^{b} S(1) sits at a center of symmetry and thus the SO$_4$ group is disordered with a 50:50 occupancy of the two arrangements related by the center of symmetry. Refinement was carried out using the local program GROUPLS and defining the oxygen atoms about S(1) as a rigid cube with an S–O bond length of 1.450 Å.

42.0° for the Pt(3) plane; the interplane angles are 69.0° for the Pt(1) plane–Pt(2) plane, 71.9° for the Pt(1) plane–Pt(3) plane, and 68.9° for the Pt(2) plane–Pt(3) plane. The Pt–N bond lengths (range 2.01 (2)–2.06 (2) Å) and Pt–O bond lengths (range 2.01 (2)–2.04 (2) Å) do not differ significantly and agree well with values found previously.[1,5,9] Comparable angles at the platinum atoms subtended by the bonded ligand atoms do differ significantly, but all are close to 90° and we suggest that the minor variations observed are to accommodate hydrogen bonding interactions. The Pt–O–Pt angles (range 107.8 (9)–109.2 (11) Å) are close to the tetrahedral angle and are not significantly different, but they differ quite substantially from corresponding angles in the C_2 trimer cation reported previously (111 (1), 118 (1), 123 (1)°).[1] Pt–Pt distances in the compound studied here (range 3.282 (2)–3.291 (2) Å) are therefore shorter than those observed previously (range 3.341 (2)–3.521 (2) Å).[1] We assume that in solution the cation is stereochemically nonrigid and undergoes the rearrangement shown in Figure 2. Thus, the cation studied here represents the stable end species, whereas the trimer reported previously represents the intermediate species. The intermediate should be strained and probably this is the cause of the larger Pt–O–Pt angles. There are two crystallographically distinct sulfate ions in the crystal. One has no symmetry restrictions and the S–O bond lengths (range 1.43

Table II. Selected Interatomic Distances (A) and Angles (deg)[k]

Selected Bonded Distances

Pt(1)–O(1)	2.02 (1)	Pt(2)–O(2)	2.03 (2)	Pt(3)–O(1)	2.04 (2)
Pt(1)–O(2)	2.01 (2)	Pt(2)–O(3)	2.04 (1)	Pt(3)–O(3)	2.02 (2)
Pt(1)–N(1)	2.01 (2)	Pt(2)–N(3)	2.04 (2)	Pt(3)–N(5)	2.06 (2)
Pt(1)–N(2)	2.02 (2)	Pt(2)–N(4)	2.06 (2)	Pt(3)–N(6)	2.05 (3)
S(2)–O(21)	1.45 (3)	S(2)–O(22)	1.46 (2)	S(2)–O(23)	1.43 (3)
S(2)–O(24)	1.47 (2)				

Nonbonded Distances (<3.4 A) (Possible Hydrogen Bonds)

O(1)–N(4)[a]	3.30 (2)	O(1)–N(4)[b]	3.28 (2)	O(1)–O(23)[c]	2.70 (2)
O(2)–N(3)[b]	3.26 (3)	O(2)–O(24)	2.79 (3)	O(3)–O(21)	2.80 (2)
O(3)–N(1)[a]	3.10 (3)	N(1)–O(22)[b]	3.15 (2)	N(1)–O(21)[d]	2.85 (3)
N(1)–O(H3)	3.30 (4)	N(2)–O(23)[c]	3.16 (3)	N(2)–O(24)[b]	3.01 (3)
N(2)–O(H1)[e]	3.26 (4)	N(3)–O(14)[f]	3.00 (4)	N(3)–O(22)[g]	3.33 (3)
N(3)–O(13)	2.78 (3)	N(3)–O(24)[h]	3.05 (3)	N(4)–O(21)[i]	3.17 (3)
N(4)–O(24)[h]	3.18 (3)	N(5)–O(12)	3.05 (2)	N(5)–O(14)[f]	2.97 (3)
N(5)–O(22)[g]	3.22 (3)	N(5)–O(H1)	3.11 (4)	N(5)–O(H3)[a]	3.14 (4)
N(6)–O(11)[b]	3.00 (3)	N(6)–O(14)[a]	3.36 (3)	N(6)–O(23)[c]	3.09 (3)
N(6)–O(H2)[j]	2.95 (5)	O(H1)–O(14)[a]	2.80 (3)	O(H1)–O(23)[j]	3.08 (5)
O(H1)–O(H3)[a]	3.15 (6)	O(H2)–O(13)[b]	2.88 (3)	O(H2)–O(12)[d]	2.64 (4)
O(H2)–O(22)	2.79 (5)	O(H3)–O(11)[f]	2.52 (4)	O(H3)–O(12)	2.66 (4)

Other Nonbonded Distances

Pt(1)–Pt(2)	3.291 (2)	Pt(1)–Pt(3)	3.283 (2)	Pt(2)–Pt(3)	3.282 (2)
Pt(1)–Pt(2)[b]	3.418 (2)				

Angles Involving Bonded Atoms

O(1)–Pt(1)–O(2)	88.7 (6)	O(2)–Pt(2)–O(3)	90.4 (6)	O(1)–Pt(3)–O(3)	87.4 (7)
O(1)–Pt(1)–N(1)	176.1 (8)	O(2)–Pt(2)–N(3)	178.2 (6)	O(1)–Pt(3)–N(5)	176.3 (8)
O(1)–Pt(1)–N(2)	93.5 (7)	O(2)–Pt(2)–N(4)	89.0 (7)	O(1)–Pt(3)–N(6)	94.4 (8)
O(2)–Pt(1)–N(1)	87.5 (8)	O(3)–Pt(2)–N(3)	88.0 (6)	O(3)–Pt(3)–N(5)	89.0 (8)
O(2)–Pt(1)–N(2)	177.8 (7)	O(3)–Pt(2)–N(4)	179.3 (8)	O(3)–Pt(3)–N(6)	177.7 (7)
N(1)–Pt(1)–N(2)	90.4 (8)	N(3)–Pt(2)–N(4)	92.7 (8)	N(5)–Pt(3)–N(6)	89.3 (10)
Pt(1)–O(1)–Pt(3)	107.8 (9)	Pt(1)–O(2)–Pt(2)	109.2 (11)	Pt(3)–O(3)–Pt(2)	107.9 (10)
O(21)–S(2)–O(22)	112 (1)	O(21)–S(2)–O(23)	115 (2)	O(21)–S(2)–O(24)	110 (2)
O(22)–S(2)–O(23)	108 (2)	O(22)–S(2)–O(24)	108 (1)	O(23)–S(2)–O(24)	105 (1)

Angles Involving Nonbonded Atoms (Possible Hydrogen Bonds)

Pt(1)–O(1)–N(4)[a]	169 (1)	Pt(3)–O(1)–N(4)[a]	83 (1)	Pt(2)–N(4)[a]–O(1)	165 (1)
Pt(1)–O(1)–N(4)[b]	79 (1)	Pt(3)–O(1)–N(4)[b]	166 (1)	Pt(2)–N(4)[b]–O(1)	105 (1)
Pt(1)–O(1)–O(23)[c]	109 (1)	Pt(3)–O(1)–O(23)[c]	106 (1)	Pt(1)–O(2)–N(3)[b]	95 (1)
Pt(2)–O(2)–N(3)[b]	156 (1)	Pt(2)–N(3)[b]–O(2)	90 (1)	Pt(1)–O(2)–O(24)	115 (1)
Pt(2)–O(2)–O(24)	111 (1)	Pt(2)–O(3)–O(21)	123 (1)	Pt(3)–O(3)–O(21)	107 (1)
Pt(2)–O(3)–N(1)[a]	155 (1)	Pt(3)–O(3)–N(1)[a]	95 (1)	Pt(1)–N(1)[a]–O(3)	161 (1)
Pt(1)–N(1)–O(22)[b]	119 (1)	Pt(1)–N(1)–O(21)[d]	122 (1)	Pt(1)–N(1)–O(H3)	72 (1)
Pt(1)–N(2)–O(23)[c]	94 (1)	Pt(1)–N(2)–O(24)[b]	112 (1)	Pt(1)–N(2)–O(H1)[e]	140 (1)
Pt(2)–N(3)–O(14)[f]	119 (1)	Pt(2)–N(3)–O(22)[g]	116 (1)	Pt(2)–N(3)–O(13)	121 (1)
Pt(2)–N(3)–O(24)[h]	105 (1)	Pt(2)–N(4)–O(21)[i]	115 (1)	Pt(2)–N(4)–O(24)[h]	100 (1)
Pt(3)–N(5)–O(12)	97 (2)	Pt(3)–N(5)–O(14)[f]	121 (2)	Pt(3)–N(5)–O(22)[g]	115 (1)
Pt(3)–N(5)–O(H1)	114 (2)	Pt(3)–N(5)–O(H3)[a]	89 (2)	Pt(3)–N(6)–O(11)[b]	112 (1)
Pt(3)–N(6)–O(14)[a]	136 (2)	Pt(3)–N(6)–O(23)[c]	93 (2)	Pt(3)–N(6)-O(H2)[j]	105 (1)

[a–j] Atoms with superscripts above are related to those listed in Table I by the operations: (a) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (b) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (c) $1 - x$, $1 - y$, $1 - z$; (d) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; (e) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $1.5 - z$; (f) $-x$, $-y$, $1 - z$; (g) $1 - x$, $-y$, $1 - z$; (h) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (i) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; (j) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $\frac{1}{2} + z$. [k] S(1)–O(1x) (x = 1–4) distances were constrained to be 1.450 A and the O(1x)–S(1)–O(1y) (y = 2–4) angles to 109.45°.

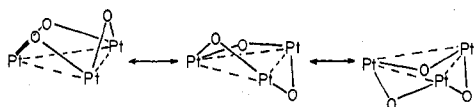**Figure 2.** The probable geometric rearrangement of the framework of the $[(NH_3)_2Pt(OH)]_3^{3+}$ cation in solution.

(3)–1.47 (2) Å) and angles (range 105 (1)–115 (2)°) are normal,[16] even though some of the angles differ significantly. The distortion from tetrahedral geometry is small, however, and is probably caused by hydrogen bonding. The sulfur atom of the other sulfate group sat on an inversion center and thus the sulfate ion had to be disordered.

The three water molecules found (O(H1), O(H2), O(H3)) present a problem since the analytical figures are clearly in good agreement with a formulation of the compound as $[(NH_3)_6Pt(OH)_3]_2(SO_4)_3\cdot3H_2O$ and in poor agreement with values calculated for the formula suggested by the X-ray determination, namely, $[(NH_3)_6Pt(OH)_3]_2(SO_4)_3\cdot6H_2O$ (H, 2.91; N, 8.97; O, 20.50; Pt, 62.49; S, 5.13). We examined the

possibility of partial occupancy of the water sites by conducting a series of refinements starting with half-occupancy of each water site in turn and then trying combinations. In every case the occupancy rose rapidly to about ~0.9. Further, in no case was the R factor lower than in the case where the occupancy was 1.0. Since from one to three extra variables were used, the refinements with partial occupancy are less satisfactory. Partial occupancy of some of the sites is not unreasonable. As we have noted, the S(1) sulfate is disordered. As a result, some of the O(H)–O(sulfate) distances are very short (O(H3)–O(11), 2.52 (4); O(H2)–O(12), 2.64 (4); O(H3)–O(12), 2.66 (4) Å). Such short bonds have been observed in $H_2SO_4\cdot H_2O$,[17] but in our compound all involve the disordered sulfate group and it is possible that where the sulfate group is in the orientation to give the short distance, the water site is empty. We cannot decide on the basis of present data. All X-ray results presented herein are based on full occupancy of the water sites. There is one other possibility and this is that the compound exists as various hydrates and that the hydrate sent for analysis is different from the hydrate used for the X-ray structural
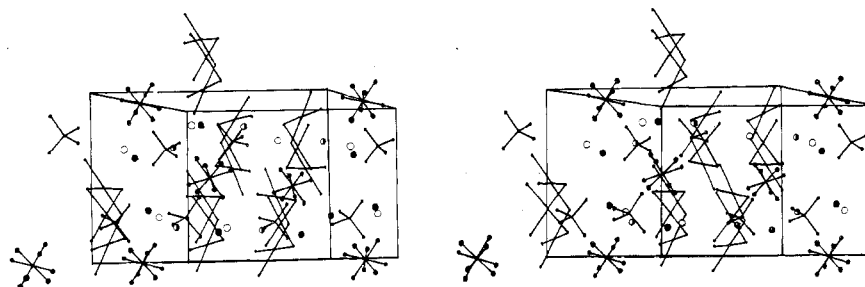
Figure 3. Stereogram (stereoscopic pair of perspective projections) of {[(NH$_3$)$_2$Pt(OH)]$_3$}$_2$(SO$_4$)$_3$·6H$_2$O. The contents of the unit cell plus extra ions and water molecules are shown in order to illustrate the packing. O(H1) is shown as ◐, O(H2) as ●, and O(H3) as ○. The a and b axes are parallel to the side and top of the page, respectively, and the view is along c.

examination. We have experienced this problem before with {[(NH$_3$)$_2$Pt(OH)$_2$Pt(NH$_3$)$_2$]$_2$}(CO$_3$)$_2$·4H$_2$O.[19] Nevertheless, the water molecules are involved in extensive hydrogen bonding and are clearly important in holding the structure together.

The packing of the molecules within the unit cell is shown in Figure 3. In the b direction the trimer molecules are arranged so that they form a double chain. Within the chain the molecules are arranged such that the plane about Pt(1) lies essentially parallel to the plane about Pt(2) in the molecule related by the twofold screw axis giving the relatively short Pt(1)–Pt(2) distance (3.418 (2) Å). These chains are separated in both the a and c directions by sulfate ions and the water molecules. Both the ordered and disordered SO$_4^{2-}$ ions lie close to the $x = 0$ and $x = \frac{1}{2}$ planes and near each other, and hydrogen bonding to the water molecules is obviously important in holding the two anions close to each other.

Not unexpectedly, the differences in the vibrational spectra between the trimer nitrate and the trimer sulfate are, apart from the anion vibrations and the fact that the sulfate contains water of crystallization, not great but they nevertheless exist. The skeletal stretching vibrations provide a good example. The two most intense Raman bands occur at 533 and 474 cm^{-1} for the trimer sulfate but at 540 and 516 cm^{-1} for the trimer nitrate. The vibrations of the ammine groups are almost identical in both species and, therefore, will not be considered in detail. An interesting detail should be mentioned, however. The infrared spectrum of the deuterated trimer sulfate contains bands at 1015 (s) and 1070 (sh) cm^{-1} which can be attributed to δ_s(NH). Bands at 1310 and 1325 cm^{-1} in the spectrum of the nondeuterated species exhibit clearly asymmetric curve shapes with shoulders at higher energy. Similar effects were observed for the trimer nitrate and were interpreted as arising from differently hydrogen-bonded ammine groups.[1] Using the same interpretation, the higher energy shoulders represent the more tightly hydrogen-bound ammine groups. N(1)–O(21) (2.85 (3) Å) and N(3)–O(13) (2.78 (3) Å) are relatively short and would represent fairly strong hydrogen bonds. The other ammine nitrogen atoms have shortest N–O distances which are quite a bit longer. N(5)–O(14) is 2.97 (3) Å and N-(6)–O(H2) is 2.95 (6) Å while for N(2) and N(4) no distance is less than 3.00 Å. In contrast, the dimer sulfate, like the dimer nitrate, shows only two sharp, symmetric bands (1320, 1310 cm^{-1}) in this range, in agreement with the known equivalence of the ammine groups.[5]

The stretching vibrations of the hydroxo groups in the trimer sulfate suggest differences in the degree of hydrogen bonding ("free" OH groups at 3400 cm^{-1}, strongly hydrogen-bonded OH groups below 3300 cm^{-1}), in agreement with the observation that each OH group is distinct with respect to possible hydrogen bonds. O(1) has one short (<3.0 Å) distance (O(1)–O(23), 2.70 (6) Å), while O(2) has two (O(2)–O(24), 2.79 (3); O(2)–O(21), 2.80 (2) Å) and O(3) has none. The position of the Pt–OH bending vibration in the trimer sulfate (1015 cm^{-1}) is distinctly lower than in the dimer nitrate and somewhat lower than in the trimer nitrate and should probably

be attributed to the unrestrained bond angles at the bridging oxygens. The sulfate vibrations in infrared and Raman spectra reveal that the symmetry of one or both of the anions is lower than for the unperturbed sulfate ion of point group T_d. The infrared forbidden ν_1 vibration (980 cm^{-1}) is observed, and the infrared-active ν_3 vibration is extremely broad (1160–1100 cm^{-1}). In addition there are two Raman-active ν_1 vibrations (982, 975 cm^{-1}) and also two ν_4 vibrations in the IR spectrum (625, 613 cm^{-1}). Differences in the degree of hydrogen bonding to the sulfate oxygen atoms might, as in the case of the trimer nitrate, account for the appearance of a weak ν_1 band in the infrared spectrum but probably are not sufficient to cause a splitting of the ν_4 band because of lowered symmetry. Even slightly bound water of crystallization as in [Cu(H$_2$O)$_4$]SO$_4$·H$_2$O[18] seems not to perturb the T_d symmetry enough to cause splitting of the ν_4 modes; therefore, the bands mentioned are assigned to vibrations of the nonequivalent sulfate ions rather than to a single kind of sulfate ion whose symmetry is markedly lower than T_d. The Raman-active ν_2 vibration is assigned to the 439-cm^{-1} band. This band, as well as the Raman-active ν_3 (1122 cm^{-1}) and ν_4 (610 cm^{-1}) modes, is too low in intensity and not sufficiently well resolved to allow observation of two components which might be expected for the case of nonequivalent sulfate ions.

Registry No. *cis*-Pt(NH$_3$)$_2$Cl$_2$, 15663-27-1; [(NH$_3$)$_6$Pt$_3$(O-H)$_3$]$_2$(SO$_4$)$_3$·6H$_2$O, 66213-36-3.

Supplementary Material Available: A table of moduli of the observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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(8) The cell used here may be transformed to the more conventional $P2_1/c$ cell with $a = 13.539$ Å, $b = 10.335$ Å, $c = 14.323$ Å, and $\beta = 123.98°$ by the matrix 001/010/–1,0,–1.
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Existence of the Monomeric Cu(CN)₃²⁻ Anion in the Solid State. Molecular Structure and Disorder of Sodium Tricyanocuprate(I) Trihydrate

CHARLES KAPPENSTEIN and RENÉ P. HUGEL*

The crystal and molecular structure of sodium tricyanocuprate(I) trihydrate, Na₂Cu(CN)₃·3H₂O, has been determined by a three-dimensional X-ray crystallographic analysis. The crystal system is hexagonal with $a = 25.256$ (5) Å, $c = 7.188$ (3) Å, $d = 1.81$ g cm⁻³, and $Z = 18$, but an abnormal distribution of the intensities (very weak for $h - k \neq 3n$ or $l \neq 2n$) reveals a disorder along the z axis. Thus the structure was solved by Patterson and Fourier methods in a subcell which is considered to be ideally disordered over one part of the atomic positions ($a = 14.582$ Å, $c = 3.594$ Å, and $Z = 3$; space group $P6_3/m$). The least-squares refinements led to the final discrepancy factors $R = 0.044$ and $R_w = 0.052$ for 669 independent reflections ($I \geq 2\sigma(I)$) collected with a CAD 4 Nonius diffractometer. The main characteristic of this structure is the existence in the solid state of the simple mononuclear planar tricoordinated species Cu(CN)₃²⁻ (point group D_{3h}). One set (2/3) of these ions forms a three-dimensional ordered network (Cu–C = 1.929 (3) Å; C–N = 1.133 (5) Å) with the sodium cations in which channels appear parallel to the ternary axes; anions of the second type (1/3) occur in a disordered manner (Cu–C = 1.946 (13) Å; C–N = 1.160 (19) Å) in these channels. The nitrogen atoms of the ordered species are in contact with three sodium cations and these sodium cations are octahedrally surrounded by nitrogen and oxygen (water) atoms. The water molecules are also of two types, ordered and disordered, and exhibit a hydrogen bond (O⋯O = 2.732 (14) Å). Raman and infrared spectra show also the presence of two types of Cu(CN)₃²⁻ anion and are interpreted on the basis of these results.

Introduction

In a preceding paper[1] we have described the structure of sodium dicyanocuprate(I) dihydrate, NaCu(CN)₂·2H₂O, and the main characteristic of this compound was the absence of the Cu(CN)₂⁻ ion but the presence of a polymeric anionic chain with a planar three-coordinated copper(I). Thus it can be noted that up to now all cyanocuprates with ratios CN/Cu ≤ 2 are polymeric.

The species corresponding to a ratio CN/Cu = 3, viz., the complex ion Cu(CN)₃²⁻, displays a higher thermodynamic stability, in aqueous solution, than the two other known ions.[2]

$$Cu(CN)_2^- + Cu(CN)_4^{3-} \rightleftarrows 2Cu(CN)_3^{2-} \qquad \log K = 3.82$$
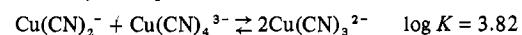
The structure of this ion may be planar (D_{3h})[3] or pyramidal (C_{3v}) with or without a coordinated water molecule.[4] As pointed out by Wicholas and Wolford,[5] the isolation of Cu(CN)₃²⁻ in the solid state would be of particular significance in that it would represent sterically the simplest example of three-coordinated copper(I). These authors have isolated a mixed-valence compound [Cu(en)₃][Cu(CN)₃] but did not yet report the structure. We have prepared the sodium salt Na₂Cu(CN)₃·3H₂O for which we describe the structure and discuss the vibrational spectra herein.

Experimental Section

Preparation. Copper cyanide (2.25 g, 25 mmol) was dissolved in 50 mL of water containing sodium cyanide (2.5 g, 50 mmol) and the solution was evaporated to 15 mL. After several days in a desiccator white shaggy needles appeared and were dried on filter paper. To obtain single crystals suitable for an X-ray study, the same solution was slowly evaporated at room temperature. Anal. Calcd for

Table I. Experimental Data for Na₂Cu(CN)₃·3H₂O

(A) Crystal Data

Laue symmetry group 6/m

$a = 25.256$ (5) A	$d_{exptl} = 1.81$ g cm⁻³
$c = 7.188$ (3) A	$d_{calcd} = 1.818$ g cm⁻³
$V = 3970.7$ A	$Z = 18$
Mol wt 241.62	$\mu(\lambda_{Mo}) = 26$ cm⁻¹

(B) Measurement of Intensity Data

Radiation: Mo Kα (λ 0.710 69 A)

Monochromator: graphite

Scan technique: θ–2θ

Scan length: 1 + 0.2 tan θ

Reflections measd: +h, +k, +l for 2θ < 66°

Takeoff angle: 3 + 0.5 tan θ

Max scanning time: 1 min

Prescan speed: 20°/min

Check reflections: three, remeasured after every 50 reflections (00$\bar{4}$, $\bar{1}$42, $\bar{6}$62) with a standard deviation less than 2% for the intensities

Na₂Cu(CN)₃·3H₂O: Cu, 26.30; Na, 19.03; H₂O, 22.4. Found: Cu, 25.9; Na, 18.6; H₂O, 23.3.

The thermogravimetric analysis showed the loss of two water molecules at 46 °C and a third at 91 °C.

Spectra. See ref 1.

Crystal Data and Collection of Intensities. Examination under a polarizing microscope revealed extinction in the direction of the spindle axis of the hexagonal prismatic needle. A preliminary study with the de Jong and Bouman method showed that the crystal belongs to the hexagonal system and revealed an abnormal distribution of the intensities with all tested crystals. Accurate unit cell parameters (Table IA) as well as reflection intensities (Table IB) were measured at room temperature with a Nonius CAD 4 automated diffractometer. The