Monomers, Chains and Layers of $[Pt_2(SO_4)_4]$ Units in the Crystal Structures of the Platinum(III) Sulfates $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$, $K_4[Pt_2(SO_4)_5]$ and $Cs[Pt_2(SO_4)_3(HSO_4)]$

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The reaction of $Pt(NO_3)_2$ with concentrated sulfuric acid in sealed glass ampoules at 400 °C causes reduction of the nitrate ion to NH_4^+ and leads to single crystals of $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ [triclinic, $P\bar{1}$, Z = 1, a = 749.96(9), b = 754.2(1), c = 765.4(1) pm, α = 102.15 (1)°, β = 110.23(1)°, γ = 100.87(1)°, R_{all} = 0.0677]. In the crystal structure, Pt_2 dumbbells are coordinated by four bidentate-bridging sulfate ions and two axial H_2O molecules. The replacement of the axial H_2O molecules with SO_4^{2-}, which can be observed in the crystal structure of $K_4[Pt_2(SO_4)_5]$ [triclinic, $P\bar{1}$, Z = 2, a = 975.6(1), b = 1331.8(1), c = 1491.0(1) pm, α = 101.156(8)°, β = 96.278(8)°, γ = 102.849(8)°, R_{all} = 0.0459], causes a connection of the dumbbells into chains of the composition $^1_\infty[Pt_2(SO_4)_{4/1}(SO_4)_{2/2}]^{4-}$. $K_4[Pt_2(SO_4)_5]$ has been obtained from the reaction of $K_2[PtCl_4]$ and concentrated H_2SO_4 at 400 °C in sealed glass tubes. The same reaction with $Cs_2[PtCl_4]$ instead of $K_2[PtCl_4]$ leads to $Cs[Pt_2(SO_4)_3(HSO_4)]$ [monoclinic, $P2_1/c$, Z = 4, a = 1724.8(2), b = 881.28(9), c = 935.1(1) pm, β = 100.397(8)°, R_{all} = 0.0458]. In the crystal structure, part of the bidentate-bridging sulfate ions of the $[Pt_2(SO_4)_4]$ core act as monodentate ligands to further Pt_2 dumbbells leading to anionic layers of the composition $^2_\infty[Pt_2(SO_4)_{4/2}(SO_4)_{2/1}]^{2-}$ and neutral units with the formula $^2_\infty[Pt_2(SO_4)_{4/2}(HSO_4)_{2/1}]$. The two types of layers are stacked alternatingly with the ten coordinate Cs^+ ions.

Introduction

The dumbbell shaped Pt_2^{6+} ion was reported for the first time by Muraveiskaya et al. in the complex salt $K_2[Pt_2(SO_4)_4(H_2O)_2]$.[1,2] In the crystal structure of the latter, Pt_2^{6+} is coordinated by four bidentate-bridging sulfate groups and two monodentate water molecules which are located in the axial positions of the dumbbell. This motif has been extensively varied by Cotton and co-workers and other groups[3−10] by introducing other bridging ligands, for example HPO_4^{2-}. Furthermore the H_2O molecules in the axial positions can be replaced by other ligands, for example DMSO or pyridine but also by anions such as Cl^- and OH^-.[11] In all of the compounds which have been structurally characterised so far, the complexes remain monomeric, i.e. they are binuclear anions such as $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ or $[Pt_2(SO_4)_4Cl_2]^{4-}$. Recently we have shown that a linkage of the $[Pt_2(SO_4)_4]$ entities is possible if the axial positions of the Pt_2 dumbbell are occupied by further sulfate ions. For example, in $Pt_2(HSO_4)_2(SO_4)_2$, the SO_4^{2-} ions act as bidentate-bridging ligands to one platinum dumbbell and as monodentate ligands to the next Pt_2^{6+} ion so that layers of formula $^2_\infty[Pt_2(SO_4)_{4/2}(HSO_4)_{2/1}]$ are formed.[12] Another linkage may be found in the unique structure of $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ which shows six Pt_2^{6+} ions linked by sulfate groups and oxide ions into the cluster anions $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ with a distorted icosahedral Pt_{12} core.[13] As an extension of our work we present, in this paper, the first example of the linkage of $[Pt_2(SO_4)_4]$ units into chains as observed in the crystal structure of $K_4[Pt_2(SO_4)_5]$. Furthermore, we were able to characterise a second example with $[Pt_2(SO_4)_4]$ groups connected into sheets, namely the new sulfate $Cs[Pt_2(SO_4)_3(HSO_4)]$. Finally we report the crystallographic data for $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ as a representative of the monomeric species.

Results and Discussion

As described recently, the reaction of $Pt(NO_3)_2$ with concentrated sulfuric acid in sealed glass ampoules at 400 °C leads to deep red single crystals of $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$.[13] As a side product of this reaction, yellow single crystals were also observed. According to an X-ray investigation, this side product is $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$. This compound has been reported previously, however, but without accompanying crystallographic data.[2,5] It is worth-

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while mentioning that the NH_4^+ ion originates from the reduction of the initial nitrate, clearly by Pt^{2+}.

$(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ crystallizes in the form of yellow plates and can be easily separated from the deep red single crystals of $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$. $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ is isotypic with $K_2[Pt_2(SO_4)_4(H_2O)_2]$ as can be expected from the comparable radii of K^+ and NH_4^+. The compound contains the typical lantern shaped $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ anion as can be seen in Figure 1. The Pt−Pt distance within the ion was found to be 246.3(1) pm which is not significantly different from the values reported previously for similar compounds.[1−11] The four sulfate groups act as bidentate-bridging ligands with the Pt-O distances being uniformly around 200 pm (Table 2). The S−O distances within the SO_4^{2-} ions differ remarkably. Those to the oxygen atoms which are attached to platinum atoms lie between 151.2(11) and 154.7(13) pm, the noncoordinated oxygen atoms can be found at distances from 142.1(15) up to 144.3(12) pm. The significant differences in the bond lengths also affect the energies of the IR bands (Table 5). For an ideal SO_4^{2-} tetrahedron (T_d symmetry), four vibrations can be theoretically predicted but only the two of symmetry species F_2 can be observed in the IR spectrum at around 1100 [ν_{as}(S−O)] and 610 cm^{-1} [$\delta_{as}(SO_4)$], respectively. In the present case, the SO_4^{2-} ions exhibits only C_1 symmetry and a factor group splitting must also be assumed. Thus, many more bands may be found covering quite a wide range from 1284 down to 850 cm^{-1} [ν(S−O)] and from 651 to 453 cm^{-1} [$\delta(SO_4)$]. In particular, the symmetric stretching vibrations are shifted remarkably to lower wavenumbers compared with the values usually found for sulfates. This can be expected owing to the very long S−O distances of up to almost 155 pm. Such distances are more typical of hydrogensulfates (S−OH) and, for the latter, stretching vibrations around 870 cm^{-1} are not unusual.[14,15]

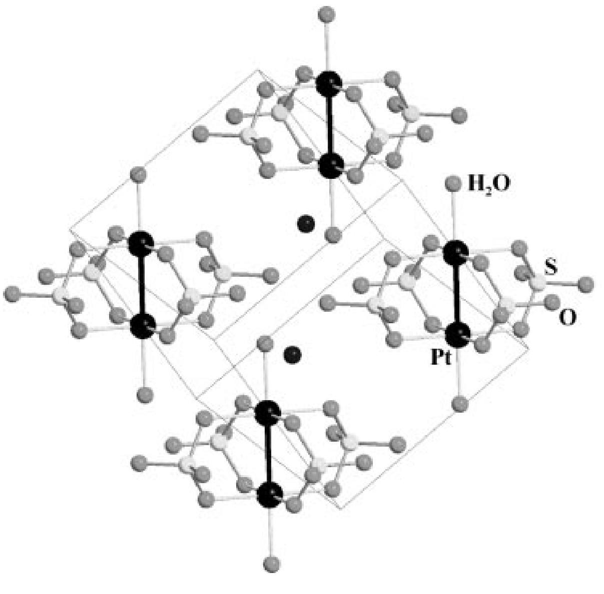

Figure 1. Crystal structure of $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$. The Pt−Pt distance within the lantern shaped complex anion is 246.3(1) pm.

The oxygen stoms of the water molecules (O1) in the axial positions of the Pt_2 dumbbell are at a distance of 209.9(11) pm from the platinum centres and the angle Pt−Pt′−O(1) is 179.3(4)°. According to the space group symmetry of the compound, the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ anion should belong to the point group C_i with the inversion centre in the mid-point of the Pt−Pt bond but in fact it has nearly C_{4h} symmetry. The NH_4^+ ions which act as charge compensators are in ninefold coordination environments of oxygen atoms with the NH_4−O distances ranging from 282(2) up to 333(4) pm (Table 2). Besides the findings from the X-ray investigation, the presence of NH_4^+ is also clear from the IR spectra which display typical bands at 3245 cm^{-1} [ν(N−H)] and 1431 cm^{-1} [$\delta(NH_4)$].

The replacement of the axial water molecules in the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ anion by monodentate SO_4^{2-} ions can be observed in the crystal structure of $K_4[Pt_2(SO_4)_5]$. This species can be obtained as orange prismatic single crystals from the reaction of $K_2[PtCl_4]$ with concentrated H_2SO_4. Like $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$, $K_4[Pt_2(SO_4)_5]$ is quite stable towards moisture but in contrast to the former, only slightly soluble in water. The four crystallographically different $[Pt_2(SO_4)_4]$ cores of the compound remain nearly unchanged compared with those in $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$. The respective Pt−O distances lie in the same range from 200.6(6) up to 202.6(5) pm and the sulfate groups also show the same significant bond length differences for coordinating ($d_{av.}$ = 143.3 pm) and noncoordinating oxygen atoms ($d_{av.}$ = 152.9 pm), respectively. Accordingly, the findings of the IR spectroscopic measurements (Table 5) are almost the same as those discussed for $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$.

The Pt−O distances to the axial oxygen atoms range from 211.0(5) up to 213.2(5) pm. These distances are slightly longer than observed in $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$. Furthermore, in contrast to the related angles mentioned previously, the Pt−Pt′−O angles in this species involving the axial oxygen atoms show slight but significant deviations from linearity with values between 171.9(1) and 173.7(1)°. The axial oxygen atoms belong to the sulfate groups $S(8)O_4^{2-}$ and $S(10)O_4^{2-}$. These anions link the $[Pt_2(SO_4)_4]$ units into two crystallographically different infinite chains according to the formula $^1_\infty[Pt_2(SO_4)_{4/1}(SO_4)_{2/2}]^{4-}$ (Figure 2) which are oriented in the [110] direction (Figure 3). The linking sulfate groups show the same characteristics as observed for the bidentate-bridging sulfate groups. Thus, the S−O distances to the oxygen atoms which are coordinated to the platinum atoms are about 10 pm longer than the respective values for the noncoordinating oxygen atoms. The charge compensation for the $^1_\infty[Pt_2(SO_4)_{4/1}(SO_4)_{2/2}]^{4-}$ chains is achieved by eight crystallographically different K^+ ions which show coordination numbers between 7 and 11 if distances up to 339.5(6) pm from these centres are taken into account (Table 3).

The linkage of $[Pt_2(SO_4)_4]$ units into layers can be seen in the crystal structure of $Cs[Pt_2(SO_4)_3(HSO_4)]$ which is formed from the reaction of $Cs_2[PtCl_4]$ and concentrated H_2SO_4. The plate-shaped red single crystals of

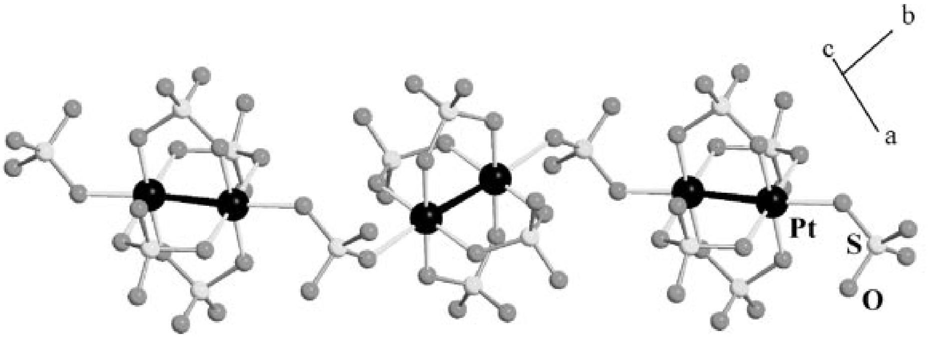

Figure 2. Connection of $[Pt_2(SO_4)_4]$ units via sulfate ions to anionic chains with the formula $^1_\infty[Pt_2(SO_4)_{4/1}(SO_4)_{2/2}]^{4-}$ in the crystal structure of $K_4[Pt_2(SO_4)_5]$. There are two crystallographically different chains which, however, do not differ significantly. The linking SO_4^{2-} ions act as bidentate bridging ligands and the O−S−O angles between their coordinated oxygen atoms and the sulfur atoms are 104.2(3)° and 108.4(3)°, respectively.

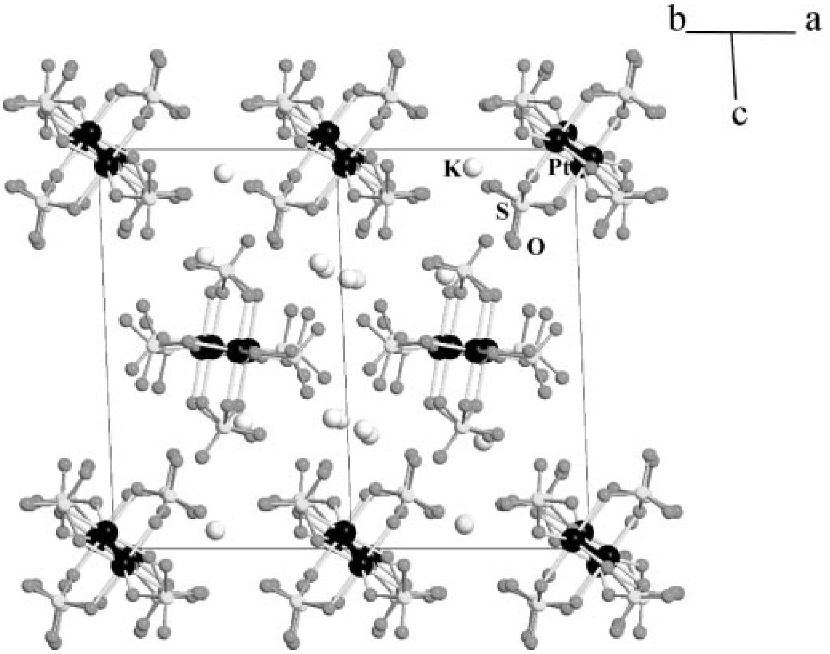

Figure 3. Arrangement of the $^1_\infty[Pt_2(SO_4)_{4/1}(SO_4)_{2/2}]^{4-}$ chains shown in Figure 2 along the [110] direction in the triclinic unit cell of $K_4[Pt_2(SO_4)_5]$. The K^+ ions take act as charge compensators and exhibit coordination numbers between 7 and 11.

$Cs[Pt_2(SO_4)_3(HSO_4)]$ are extremely moisture sensitive and turn immediately cloudy when exposed to air. As described for $K_4[Pt_2(SO_4)_5]$, the Pt_2^{6+} dumbbells in this compound are also coordinated by four bidentate-bridging and two monodentate tetrahedra. The Pt−O distances are comparable to those observed in $K_4[Pt_2(SO_4)_5]$ and lie between 199.2(4) and 202.0(4) pm for the bidentate-bridging ligands and at 212.2(4) and 215.6(4) pm for the monodentate ones (Table 4). In contrast to $K_4[Pt_2(SO_4)_5]$, the axial sulfate groups do not act as *monodentate* but as *bidentate-bridging* ligands towards further Pt_2^{6+} ions and, vice versa, two of the bidentate-bridging tetrahedra are monodentate towards neighbouring Pt_2 dumbbells. The remaining two bidentate-bridging tetrahedra are not bonded to further platinum atoms. The connection leads to layers as depicted in Figure 4. Two different layers can be distinguished crystallographically. One can be formulated as $^2_\infty[Pt_2(SO_4)_{4/2}(SO_4)_{2/1}]^{2-}$ while for the second, half of the tetrahedra can be clearly viewed as hydrogensulfate ions leading to neutral sheets with the composition $^2_\infty[Pt_2(SO_4)_{4/2}(HSO_4)_{2/1}]$. The identification of HSO_4^- ions can be carried out unambiguously with respect to the S−O distances which range from 140.7(4) up to 147.8(4) pm for the oxygen atoms which are not attached to platinum atoms and from 150.1(4) up to 152.7(4) pm for the Pt coordinated oxygen atoms. The only exception is O42 which shows a distance of 150.9(4) pm to the sulfur atom *without* being attached to a platinum atom itself. Furthermore, the hydrogen atom of the HSO_4^- ion can be found in the difference Fourier map. It is involved in a short hydrogen bond with O21 as the acceptor atom

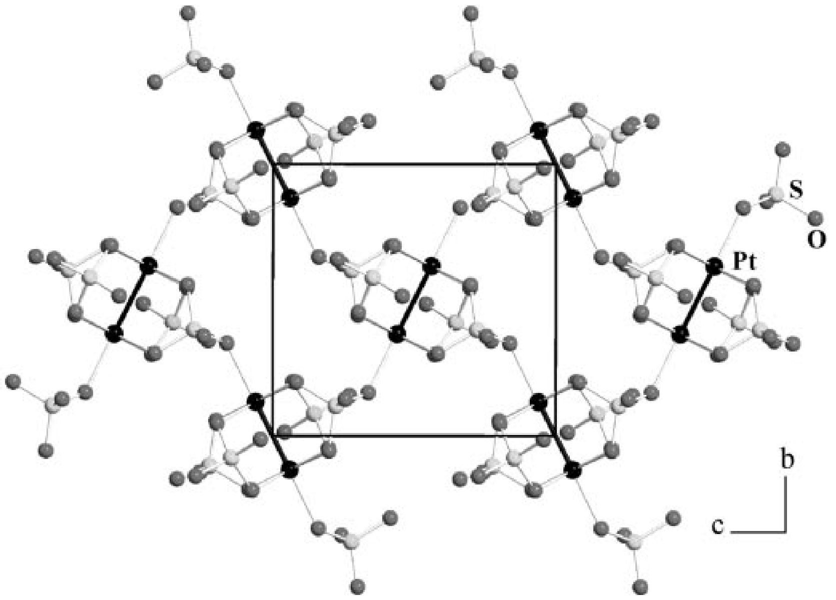

Figure 4. Connection of $[\mathrm{Pt_2(SO_4)_4}]$ units by sulfate ions to anionic layers of forumla to ${}^{2}_{\infty}[\mathrm{Pt_2(SO_4)_{4/2}(SO_4)_{2/1}}]^{2-}$ in the crystal structure of $\mathrm{Cs[Pt_2(SO_4)_3(HSO_4)]}$. One half of the sulfate ions acts as bidentate-bridging ligands, the other half of them are bidentate-bridging to one $\mathrm{Pt_2}$ dumbbell and monodentate to the next. In a second very similar layer, the two uniquely bidentate-bridging sulfate groups are replaced by $\mathrm{HSO_4}^-$ ions leading to neutral sheets with the composition ${}^{2}_{\infty}[\mathrm{Pt_2(SO_4)_{4/2}(HSO_4)_{2/1}}]$.

with a short distance of 246.7(6) pm from O42 and an angle O42−H−O21 of 167(2)°. With respect to the donor−acceptor distance, the hydrogen bond can be classified as strong.[16,17] It is worthwhile pointing out that the observed O−H−O angle is relatively small for a strong hydrogen bond which usually show values around 180°. However, similar observations of other compounds have been made and a fairly recent neutron diffraction study on $\mathrm{NaH_2PO_4}$ (donor−acceptor distance: 248.5 pm, angle O−H−O: 167.7°) may serve as an example.[17,18] Interestingly, the structural characteristics of the neutral ${}^{2}_{\infty}[\mathrm{Pt_2(SO_4)_{4/2}(HSO_4)_{2/1}}]$ sheets are identical to those recently reported for $\mathrm{Pt_2(SO_4)_2(HSO_4)_2}$.[12] Thus, the structure of $\mathrm{Cs[Pt_2(SO_4)_3(HSO_4)]}$ might be described as a composite of $\mathrm{Pt_2(SO_4)_2(HSO_4)_2}$ and the hitherto unknown sulfate $\mathrm{Cs_2[Pt_2(SO_4)_4]}$. The neutral and anionic layers are stacked in the [100] direction and alternate with the Cs^+ ions (Figure 5). The latter are in tenfold coordination environments of oxygen atoms with the Cs−O distances ranging from 295.2(4) up to 366.9(5) (Table 4).

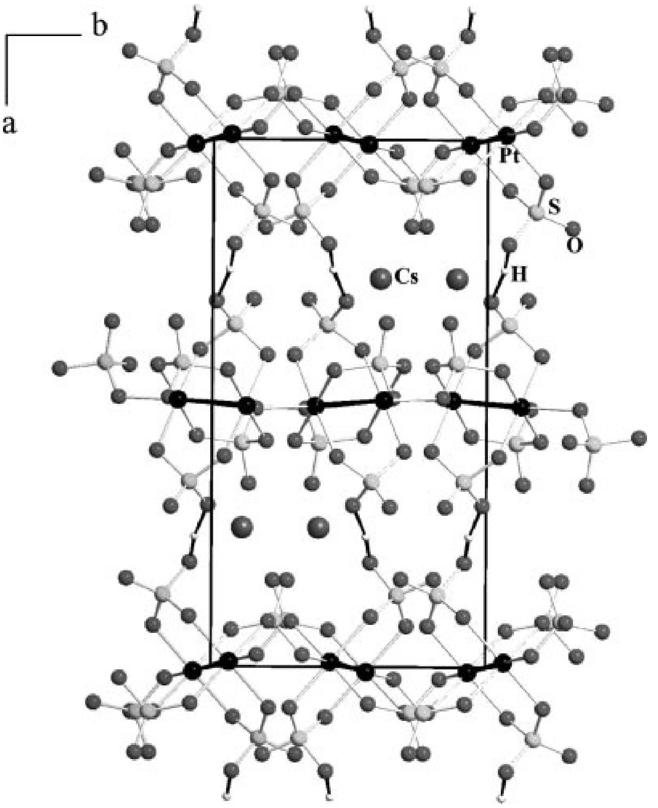

Figure 5. Stacking of the two different layers in the crystal structure of $\mathrm{Cs[Pt_2(SO_4)_3(HSO_4)]}$ along the [100] direction. The layers are connected by Cs^+ ions in tenfold coordination environments of oxygen atoms and short hydrogen bonds with a donor (O42) acceptor (O21) distance of 246.7(6) pm.

Experimental Section

Synthesis: All reactions were carried out in sealed thick-walled (2 mm) glass ampoules (ϕ = 10 mm, l = 100 mm) which were placed in a resistance furnace at a temperature of 400 °C. In all cases 2 mL (37.31 mmol) of concentrated sulfuric acid were used. For the synthesis of $\mathrm{(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]}$ the platinum source was $\mathrm{Pt(NO_3)_2}$ (0.7 g, 5.59 mmol, ABCR, 99.99%) which was used as purchased. For the preparation of $\mathrm{K_4[Pt_2(SO_4)_5]}$ and $\mathrm{Cs[Pt_2(SO_4)_3(HSO_4)]}$ $\mathrm{K_2[PtCl_4]}$ (0.5 g, 1.20 mmol) and $\mathrm{Cs_2[PtCl_4]}$ (0.5 g, 0.83 mmol), respectively, were used in the reactions. $\mathrm{K_2[PtCl_4]}$ was synthesised from elemental platinum according to literature procedures.[19] $\mathrm{Cs_2[PtCl_4]}$ cannot be obtained in the same way due to the very low solubility of $\mathrm{Cs_2[PtCl_6]}$. Instead, it was precipitated from a solution of $\mathrm{H_2[PtCl_4]}$ which was obtained by reducing $\mathrm{H_2[PtCl_6]}$ with $\mathrm{(N_2H_6)Cl_2}$. The preparation of $\mathrm{H_2[PtCl_6]}$

Table 1. Crystal data and structure refinements

Compound	$(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$	$K_4[Pt_2(SO_4)_5]$	$Cs[Pt_2(SO_4)_3(HSO_4)]$
Lattice constants	a = 749.96 (9) pm	a = 975.6 (1) pm	a = 1724.8 (2) pm
	b = 754.2 (1) pm	b = 1331.8 (1) pm	b = 881.28 (9) pm
	c = 765.4 (1) pm	c = 1491.0 (1) pm	c = 935.1 (1) pm
	α = 102.15 (1)°	α = 101.156 (8)°	
	β = 110.23 (1)°	β = 96.278 (8)°	β = 100.397 (8)°
	γ = 100.87 (1)°	γ = 102.849 (8)°	
Cell volume	380.67(8) Å^3	1829.3(3) Å^3	1398.1(2) Å^3
No. of formula units	1	2	4
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (no.1)	$P\bar{1}$ (no.1)	$P2_1/c$ (no. 14)
Diffractometer	Stoe IPDS II	Stoe IPDS II	Stoe IPDS II
Radiation	Mo-K_α (graphite-monochromated, λ = 71.07 pm)		
Temperature	293K		
Theta range	5° < 2θ <56°	5° < 2θ < 56°	5° < 2θ <56°
Rotation range; ~ increment	0° < ω < 180°; 2°	0° < ω < 180°	0° < ω < 180°
φ-Positions	0°, 90°	0°, 90°, 135°	0°, 90°
Index range	$-9 \le h \le 9$	$-12 \le h \le 12$	$-22 \le h \le 22$
	$-8 \le k \le 8$	$-17 \le k \le 17$	$-11 \le k \le 11$
	$-9 \le l \le 10$	$-19 \le l \le 19$	$-12 \le l \le 12$
No. of images	180	270	180
Exposure time	5 min	1 min	3 min
Detector distance	80 mm	80 mm	80 mm
Absorption correction	numerical after crystal shape optimisation[9]		
μ	19.01 mm^{-1}	16.86 mm^{-1}	23.24 mm^{-1}
Measured reflections	3497	24347	13324
Unique reflections	1667	8830	3383
With $I_o > 2\sigma(I)$	1302	6882	2971
No. of parameters	119	560	213
$R_{int.}/R_\sigma$	0.0794/0.1084	0.0623/0.0544	0.0507/0.0327
Structure determinations	SHELXS-97 and SHELXL-97[10][11]		
Scattering factors	Intern. Tables, Vol. C		
Goodness of fit	0.962	0.933	1.039
Extinction coefficient	0.007(2)	0.00066(4)	0.00104(5)
$R1$; $wR2$ $[I_o > 2\sigma(I_o)]$	0.0481; 0.1095	0.0311; 0.0678	0.0232; 0.0299
$R1$; $wR2$ (all data)	0.0677; 0.1196	0.0459; 0.0719	0.0458; 0.0473
ICSD	414037	414039	414038

is well-known.[19] $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ crystallises in the form of yellow plates which can be easily separated from the deep red single crystals of $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ which are formed in the same reaction.[13] $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ is the minor product of the reaction and the yield is about 20% with respect to the initial nitrate. With respect to the X-ray powder patterns of the products, the other two compounds are the only phases to be formed in the reactions. They were obtained in a 50% yield with respect to the initial chlorides. The single crystals of $K_4[Pt_2(SO_4)_5]$ and $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ can be handled under ambient conditions while $Cs[Pt_2(SO_4)_3(HSO_4)]$ is extremely moisture sensitive.

Table 2. Selected distances (pm) and angles (°) in $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ (# symmetry transformation for equivalent atoms: $-x$, $-y$, $-z$)

Pt−O11	199.4(12)	S1−O13	142.5(11)
−O24	200.6(9)	−O14	143.7(13)
−O12	200.9(13)	−O12	151.5(15)
−O23	200.9(10)	−O11	154.7(11)
−O1	209.9(11)		
		S2−O22	142.1(15)
Pt−Pt#	246.3(1)	−O21	144.3(12)
		−O24	151.2(11)
N−O22	282(2)	−O23	154.7(13)
−O13	286(2)		
−O14	287(2)	Pt−Pt#−O1	179.3(4)
−O13	292(2)		
−O21	295(2)		
−O11	297(2)		
−O14	306(3)		
−O23	309(3)		
−O21	333(4)		

X-ray Diffraction: Several single crystals of each compound were selected under sodium dried paraffin and mounted in glass capillaries. Their quality was checked with the help of a precession camera equipped with an image plate system. For the best specimens, intensity data were collected with an image plate diffractometer (STOE IPDS II). A numerical absorption correction was applied to the data using the programs X-SHAPE and X-RED in each case.[20,21] The solutions of the crystal structures were successful using direct methods provided by the program SHELXS-97.[22] For the refinements of the structures the program SHELXL-97[23] was used, introducing anisotropic thermal parameters for all nonhydrogen atoms. The position of the H atom in $Cs[Pt_2(SO_4)_3(HSO_4)]$ was observed in the final difference Fourier map. It was refined isotropically without restrains. Further details of the data collection and relevant crystallographic data are summarised in Table 1−4. Furthermore, the data have been deposited with the Fach-

Table 3. Selected distances (pm) and angles (°) in $K_4[Pt_2(SO_4)_5]$ ($^{\#}$symmetry transformation for equivalent atoms: $-x$, $-y$, $-z$)

Pt1−O62	200.8(5)	Pt2−O21	200.6(6)
−O34	201.8(5)	−O91	201.4(6)
−O31	201.9(5)	−O22	201.4(5)
−O61	202.6(5)	−O92	202.2(6)
−O83	211.0(5)	−O102	213.2(5)
Pt1−Pt1$^{\#}$	247.60(6)	Pt2−Pt2$^{\#}$	248.02(6)
Pt1−Pt1$^{\#}$−O83	172.6(2)	Pt2−Pt2$^{\#}$−O102	171.9(1)
Pt3−O72	201.0(5)	Pt4−O42	201.5(5)
−O71	201.3(5)	−O13	201.7(5)
−O52	201.3(5)	−O41	202.0(5)
−O51	201.4(5)	−O11	202.0(5)
−O82	211.0(5)	−O101	212.7(4)
Pt3−Pt3$^{\#}$	247.62(6)	Pt4−Pt4$^{\#}$	248.96(6)
Pt3−Pt3$^{\#}$−O82	173.6(2)	Pt4−Pt4$^{\#}$−O101	173.7(1)
S1−O12	143.8(6)	S2−O24	142.5(7)
−O14	144.1(6)	−O23	144.1(7)
−O13	152.3(5)	−O21	151.9(6)
−O11	153.1(5)	−O22	152.4(6)
S3−O32	142.8(6)	S4−O44	142.9(6)
−O33	143.1(5)	−O43	143.3(6)
−O31	152.3(6)	−O41	153.0(5)
−O34	154.2(5)	−O42	153.2(5)
S5−O53	142.8(6)	S6−O64	142.9(7)
−O54	143.4(6)	−O63	143.7(6)
−O51	151.8(6)	−O61	152.2(6)
−O52	153.4(5)	−O62	154.3(6)
S7−O73	143.1(6)	S8−O81	139.6(8)
−O74	144.2(7)	−O84	143.7(6)
−O72	151.8(6)	−O82	149.4(6)
−O71	153.5(5)	−O83	150.4(5)
S9−O94	142.1(7)	S10−O103	144.0(6)
−O93	143.3(6)	−O104	144.8(5)
−O91	153.0(6)	−O102	150.5(5)
−O92	153.4(6)	−O101	151.2(5)
K1−O73	261.8(6)	K2−O24	260.1(7)
−O44	275.5(6)	−O53	271.4(6)
−O102	275.8(6)	−O32	274.6(6)
−O103	278.9(6)	−O33	286.7(6)
−O103	282.2(6)	−O34	291.5(6)
−O13	288.9(6)	−O93	292.9(8)
−O14	290.1(7)	−O62	304.1(6)
		−O83	329.7(6)
		−O92	333.3(7)
K3−O104	267.1(7)	K4−O93	283.3(8)
−O43	278.6(7)	−O23	294.3(7)
−O33	280.1(6)	−O72	301.3(5)
−O61	283.6(5)	−O14	305.2(6)
−O63	289.5(7)	−O31	309.1(6)
−O71	291.2(6)	−O94	315.6(8)
−O51	294.1(6)	−O62	322.1(6)
−O74	303.5(6)	−O83	325.2(7)
−O82	323.2(7)	−O82	327.2(8)
−O103	335.2(6)	−O84	329.3(10)
		−O64	332.2(7)
K5−O14	282.0(6)	K6−O73	276.4(7)
−O23	282.1(7)	−O12	277.4(7)
−O94	289.2(7)	−O53	279.1(7)
−O11	293.9(6)	−O84	282.0(7)
−O63	295.2(7)	−O24	283.5(7)
−O23	308.3(7)	−O43	297.2(7)
−O22	311.5(7)	−O71	300.9(6)
−O64	326.7(7)		
−O44	326.9(7)		
−O94	328.3(7)		
K7−O104	266.6(7)	K8−O81	256.0(8)
−O54	266.9(6)	−O12	268.6(6)
−O64	272.0(7)	−O84	275.5(7)
−O32	278.6(6)	−O54	282.2(6)
−O101	297.7(5)	−O74	286.6(7)
−O34	305.7(5)	−O13	327.5(6)
−O33	330.8(6)	−O43	336.1(7)
−O92	339.5(6)		

Table 4. Selected distances (pm) and angles (°) in $Cs[Pt_2(SO_4)_3(HSO_4)]$ ($^{\#}$symmetry transformation for equivalent atoms: $-x$, $-y$, $-z$)

Pt1−O12	199.2(4)	Pt2−O44	200.0(4)
−O23	200.6(4)	−O43	200.7(4)
−O11	201.1(4)	−O34	201.1(4)
−O22	202.0(4)	−O33	201.4(4)
−O14	212.2(4)	−O31	215.6(4)
Pt1−Pt1$^{\#}$	246.84(4)	Pt2−Pt2$^{\#}$	247.66(4)
Pt1−Pt1$^{\#}$−O14	177.7(1)	Pt2−Pt2$^{\#}$−O31	176.6(1)
S1−O13	143.5(4)	S2−O24	143.0(4)
−O14	147.8(4)	−O21	146.8(5)
−O12	150.1(4)	−O22	152.3(4)
−O11	152.7(4)	−O23	152.4(4)
S3−O32	143.2(4)	S4−O41	140.7(4)
−O31	147.6(4)	−O43	150.9(4)
−O34	151.7(4)	−O42	150.9(4)
−O33	152.2(4)	−O44	151.8(4)
Cs−O13	295.2(4)	Hydrogen bonds	
−O24	309.9(4)	O42−H	101(15)
−O32	311.3(4)	O21−H	146(15)
−O41	313.6(4)	O42−O21	246.7(6)
−O32	318.2(4)	O42−H−O21	167(2)
−O11	327.7(4)		
−O22	335.5(3)		
−O13	338.7(4)		
−O33	345.9(4)		
−O21	366.9(5)		

Table 5. IR bands (cm^{-1}) and their assignments for $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ and $K_4[Pt_2(SO_4)_5]$

Assignment	$(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$	$K_4[Pt_2(SO_4)_5]$
ν(O−H)	3405 (s)	
ν(N−H)	3245 (s)	
$\delta(H_2O)$	1656 (ms)	
$\delta(NH_4)$	1431 (ms)	
ν_{as}(S−O)	1284 (s), 1232 (ms), 1170 (vs)	1291 (s), 1249 (ms), 1169 (vs)
ν_s(S−O)	1070 (s), 1006 (s), 855 (s), 850 (s)	1069 (s), 1005 (vs), 961 (w), 891 (s), 851 (ms)
$\delta_{as}(SO_4)$	651 (w), 613 (w) 576 (vs)	675 (w), 649 (w), 582 (s)
$\delta_s(SO_4)$	503 (w), 453 (ms)	499 (w), 454 (ms)

informationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (crysdata@FIZ-Karlsruhe.de) and are available on quoting the deposition numbers given in Table 1.

IR Spectroscopy: For the collection of IR data several single crystals of $(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2]$ and $K_4[Pt_2(SO_4)_5]$ were selected and prepared in KBr pellets. No IR data for $Cs[Pt_2(SO_4)_3(HSO_4)]$ could be gained due its extreme moisture sensitivity. Data collection was performed with a Bruker IFS66v/s IR spectrometer in the range from 400 to 4000 cm^{-1}. Data are summarised in Table 5.

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