

Packing Effects on Molecular Geometries of Platinum Complexes. Synthesis and Crystal Structures of Di- μ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] Tetrafluoroborate and Di- μ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] Trifluoromethanesulfonate Dihydrate

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The crystal structures of di- μ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] tetrafluoroborate and di- μ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] trifluoromethanesulfonate dihydrate have been determined from X-ray intensity data, collected at room temperature with a CAD 4 diffractometer. Crystal data at room temperature (MoK α , $\lambda = 0.7107$ Å) are: [Pt₂(OH)₂(DMSO)₄](BF₄)₂, (DMSO = (CH₃)₂SO), triclinic, *P1*, *Z* = 1, *a* = 7.193(1), *b* = 8.681(3), *c* = 10.937(2) Å, $\alpha = 106.02(2)$, $\beta = 104.08(1)$, $\gamma = 103.30(2)^\circ$ and *V* = 603.5(2) Å³. The refinement converged to *R* = 0.064 for 1972 reflexions with *I* > 3 σ (*I*). [Pt₂(OH)₂(DMSO)₄](CF₃SO₃)₂·2H₂O, orthorhombic, *Pbca*, *Z* = 4, *a* = 11.188(1), *b* = 17.106(4), *c* = 16.226(3) Å and *V* = 3105.4(6) Å³. The refinement converged to *R* = 0.045 for 2030 reflexions with *I* > 3 σ (*I*).

Both compounds contain a centrosymmetric dinuclear complex, [(DMSO)₂Pt(OH)₂Pt(DMSO)₂]²⁺, in which the platinum atoms are bridged by hydroxo ligands. Each Pt atom has a square-planar coordination with the DMSO molecules bonded to Pt through their S atoms. Both structures are stabilized by hydrogen bonds. Half-normal probability plot analyses of the geometry of the cation indicate that torsion and bond angles are significantly different in the two compounds. A similar comparison of the cation in the tetrafluoroborate compound and in the isostructural perchlorate compound (literature data) revealed that only the torsion angles are affected in this case.

A bond distance M–X in a metal complex [MXL_{*n*}] is affected by intra- and intermolecular forces. The variation of the M–X distance in different complexes is often discussed in terms of intramolecular forces alone, thus neglecting packing effects.¹ This paper is an attempt to show how accurate this approximation is for a Pt(II) complex.

The influence of environment on molecular shape and dimensions can be investigated by studying a particular molecule or moiety in different crystallographic environments. Rochon *et al.* have previously made a careful structure determination of [Pt₂(OH)₂(DMSO)₄](ClO₄)₂, (DMSO = (CH₃)₂SO).² In order to elucidate the distortion susceptibility of the dinuclear complex [Pt₂(OH)₂(DMSO)₄]²⁺, we have synthesised and determined the crystal structures of two compounds containing this dinuclear metal complex with BF₄[–] and CF₃SO₃[–], respectively, as counter-ions. The perchlorate and tetrafluoroborate ions are similar in size,

shape and Lewis basicity, so the perchlorate and tetrafluoroborate structures can be anticipated to be closely isostructural. If so, the perturbation of the geometry of the dinuclear complex caused by the environment should be very similar. The trifluoromethanesulfonate ion, on the other hand, is expected to impose a drastically different packing arrangement. A comparison of the geometric parameters for the dinuclear platinum complexes in these three structures should give information about the rigidity of distortion of the complex in the different environments. Such comparisons can be made by half-normal probability plots.³

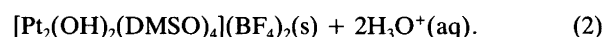
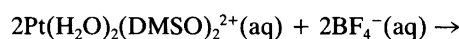
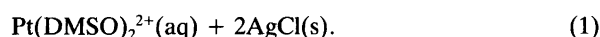
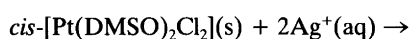
Experimental

Preparation of crystals. [Pt₂(OH)₂(DMSO)₄](BF₄)₂ was synthesised from 0.33 g solid *cis*-Pt(DMSO)₂Cl₂ and aqueous AgBF₄, prepared from 0.18 g Ag₂O, 0.28 ml HBF₄ and 10 ml water, according to reaction (1). The silver chloride was

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Table 1. Crystal data, collection and reduction of intensity data and least-squares refinement.

Compound	[Pt ₂ (OH) ₂ (DMSO) ₄](BF ₄) ₂	[Pt ₂ (OH) ₂ (DMSO) ₄](CF ₃ SO ₃) ₂ · 2H ₂ O
Mol. wt.	455.17	535.44
Space group	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> /Å	7.193(1)	11.188(1)
<i>b</i> /Å	8.681(3)	17.106(4)
<i>c</i> /Å	10.937(2)	16.226(3)
α /°	106.02(2)	90.0
β /°	104.08(1)	90.0
γ /°	103.30(2)	90.0
<i>V</i> /Å ³	603.5(2)	3105.4(6)
<i>Z</i>	1	4
<i>D_x</i> /g cm ⁻³	2.505	2.290
Crystal size/mm	0.138 × 0.15 × 0.04	0.38 × 0.25 × 0.14
λ /Å	0.7107	0.7107
μ /mm ⁻¹	12.04	9.57
θ -interval	3.00–25.00	3.00–27.00
ω -2 θ scan width, $\Delta\omega$ /°	1.20 + 0.50 tan θ	0.8 + 0.5 tan θ
$\sigma(I)$ /I requested in a scan	0.028	0.028
Maximum recording time/s	120	120
No. of measured reflexions	2221	3337
No. of reflexions used in the refinements, <i>m</i>	1972	2030
No. of parameters refined, <i>n</i>	136	172
<i>hkl</i> range	-8 ≤ <i>h</i> ≤ 8, -10 ≤ <i>k</i> ≤ 10, -13 ≤ <i>l</i> ≤ 0	-14 ≤ <i>h</i> ≤ 0, -0 ≤ <i>k</i> ≤ 21, -20 ≤ <i>l</i> ≤ 0
<i>R</i> = $\Sigma(F_o - F_c)/\Sigma F_o $	0.064	0.045
<i>R_w</i> = $[\Sigma w(F_o - F_c)^2/\Sigma F_o ^{2w}]^{1/2}$	0.085	0.064
<i>S</i> = $[\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$	1.05	1.01
<i>C</i> ₁ (weighting scheme)	0.065	0.035
<i>C</i> ₂ (weighting scheme)	3.0	0.5
<i>Q</i> _{max} / <i>Q</i> _{min} /e Å ⁻³	4.79/-4.35	1.54/-3.23
δR slope	1.01	1.15
δR intercept	-0.06	-0.10



filtered off. After a few days at room temperature pale yellow single crystals of the desired compound were formed [reaction (2)].

[Pt₂(OH)₂(DMSO)₄](CF₃SO₃)₂ · 2H₂O was prepared as described above but with 0.10 g *cis*-Pt(DMSO)₂Cl₂ and the AgBF₄ solution exchanged for 0.12 g AgCF₃SO₃. Pale yellow crystals precipitated from the solution.

Table 2. Atomic coordinates and *U*_{eq} with e.s.d.s for [Pt₂(OH)₂(DMSO)₄](BF₄)₂.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} /Å ² ^a
Pt	0.18978(8)	0.05148(7)	0.12819(6)	0.0237(3)
S1	0.45080(58)	-0.04251(50)	0.17349(39)	0.0246(14)
S2	0.30614(66)	0.26781(55)	0.31716(42)	0.0317(15)
O10	-0.059(2)	0.123(2)	0.064(1)	0.046(5)
O11	0.637(2)	0.064(2)	0.167(1)	0.043(6)
O21	0.489(2)	0.285(2)	0.420(1)	0.057(6)
C11	0.381(3)	-0.252(3)	0.056(2)	0.044(8)
C12	0.506(3)	-0.072(3)	0.331(2)	0.046(8)
C21	0.113(4)	0.278(4)	0.394(2)	0.078(12)
C22	0.345(4)	0.449(3)	0.269(3)	0.069(11)
B	0.915(6)	0.680(5)	0.241(5)	0.079(19)
F1	0.750(4)	0.624(6)	0.245(4)	0.208(29)
F2	0.002(7)	0.652(5)	0.161(4)	0.265(32)
F3	0.947(8)	0.827(5)	0.298(7)	0.315(52)
F4	0.971(12)	0.609(13)	0.317(6)	0.445(89)

^a*U*_{eq} has been calculated from the average of the anisotropic temperature factors.

Table 3. Atomic coordinates and U_{eq} with e.s.d.s for $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$.^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}/\text{Å}^2$ ^b
Pt	0.11982(4)	0.01802(2)	0.04675(2)	0.0209(2)
S1	0.3091(3)	-0.0055(2)	0.0198(2)	0.028(1)
S2	0.1678(3)	0.0747(2)	0.1645(2)	0.025(1)
O10	-0.0613(8)	0.0401(6)	0.0571(5)	0.032(3)
O11	0.3987(9)	0.0531(8)	0.0498(6)	0.049(4)
C11	0.3487(17)	-0.1003(10)	0.0585(12)	0.061(6)
C12	0.3222(16)	-0.0155(13)	-0.0906(8)	0.059(7)
O21	0.2508(12)	0.0305(6)	0.2164(5)	0.050(4)
C21	0.2235(13)	0.1700(9)	0.1467(9)	0.040(5)
C22	0.0326(13)	0.0930(9)	0.2214(7)	0.034(4)
S	0.1093(5)	0.2274(2)	-0.1121(2)	0.053(2)
O1	0.0011(19)	0.2661(13)	-0.0803(10)	0.130(9)
O2	0.1634(21)	0.1722(11)	-0.0606(9)	0.125(9)
O3	0.1900(16)	0.2819(8)	-0.1505(8)	0.089(6)
C	0.0483(29)	0.1725(10)	-0.1959(15)	0.091(11)
F1	0.0099(15)	0.2120(8)	-0.2542(7)	0.123(7)
F2	0.1166(24)	0.1240(16)	-0.2270(12)	0.226(17)
F3	-0.0275(28)	0.1233(13)	-0.1715(10)	0.214(14)
OW	-0.0962(15)	0.1909(9)	0.0583(8)	0.080(6)

^aS, O1, O2, O3, C, F1, F2, F3 represent the trifluoromethanesulfonate molecule and OW represents the hydrate water. ^b U_{eq} has been calculated from the average of the anisotropic temperature factors.

Structure determination. The intensity data sets were collected at room temperature on a CAD 4 diffractometer employing graphite-monochromated MoK α radiation and using the ω -2 θ scan technique. The scan interval was extended 25% at both ends for the background measurement. Three standard reflexions were measured at regular intervals. During the data collections the intensities decreased totally by ca. 15% for $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{BF}_4)_2$ and 26% for $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$. Both data sets were corrected for the changes in the intensity

Table 4. Angles (in °) and distances (in Å) for $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{BF}_4)_2$, with e.s.d.s.^a

Pt-O10	2.052(14)	S2-O21	1.46(2)
Pt-O10'	2.054(13)	S2-C21	1.79(2)
Pt-S1	2.216(4)	S2-C22	1.77(2)
Pt-S2	2.189(4)	B-F1	1.19(5)
Pt-Pt'	3.144(1)	B-F2	1.20(6)
S1-O11	1.47(1)	B-F3	1.19(6)
S1-C11	1.78(2)	B-F4	1.21(9)
S1-C12	1.77(2)	O10...O21	2.71(2)
S1-Pt-S2	95.0(2)	Pt-S2-O21	119.2(6)
S1-Pt-O10'	173.5(4)	Pt-S2-C21	110.2(9)
S1-Pt-O10'	93.7(4)	Pt-S2-C22	105.1(8)
S2-Pt-O10'	169.6(4)	O21-S2-C21	108(1)
S2-Pt-O10	91.1(4)	O21-S2-C22	109(1)
O10-Pt-O10'	80.0(6)	C21-S2-C22	104(1)
Pt-O10-Pt'	100.0(6)		
Pt-S1-O11	113.6(6)	F1-B-F2	136(5)
Pt-S1-C11	107.7(7)	F1-B-F3	100(4)
Pt-S1-C12	113.7(7)	F1-B-F4	86(5)
O11-S11-C11	110.1(9)	F2-B-F3	114(5)
O11-S1-C12	108.5(9)	F2-B-F4	104(5)
C11-S1-C12	103(1)	F3-B-F4	112(6)

^aThe prime (') indicates -*x*, -*y*, -*z*.

control reflexions, according to a linear least-squares fit. Information on the collection and reduction of the data is given in Table 1. The values of *I* and $\sigma(I)$ were corrected for Lorenz and polarization effects. Absorption corrections

Table 5. Angles (in °) and distances (in Å) for $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2(\text{H}_2\text{O})$, with e.s.d.s.^a

Pt-O10	2.063(9)	S2-O21	1.46(1)
Pt-O10'	2.068(9)	S2-C21	1.77(2)
Pt-S1	2.199(4)	S2-C22	1.80(1)
Pt-S2	2.209(3)	C1-F1	1.24(3)
Pt-Pt	3.1417(9)	C-F2	1.24(4)
Pt-OW	3.82(2)	C-F3	1.26(4)
Pt-OW'	3.97(2)	S-O1	1.47(2)
S1-O11	1.50(1)	S-O2	1.40(2)
S1-C11	1.79(2)	S-O3	1.44(2)
S1-C12	1.80(1)	S-C	1.78(2)
		OW...O10	2.61(2)
		OW...O1	2.81(2)
		OW...O3	2.86(2)
S1-Pt-S2	91.0(2)	O21-S2-C21	110.3(7)
S1-Pt-O10'	173.2(2)	O21-S2-C22	109.1(6)
S1-Pt-O10'	93.2(4)	C21-S2-C22	102.6(7)
S2-Pt-O10'	174.3(3)		
S2-Pt-O10	95.0(3)	O1-S-O2	117(1)
O10-Pt-O10'	81.0(4)	O1-S-O3	112(1)
Pt-O10-Pt'	99.0(4)	O2-S-O3	115(1)
Pt-S1-O11	117.2(5)	F1-C-F2	106(2)
Pt-S1-C11	109.5(6)	F1-C-F3	112(3)
Pt-S1-C12	107.0(6)	F2-C-F3	95(2)
O11-S1-C11	109.0(8)	S-C-F1	115(1)
O11-S1-C12	109.3(8)	C-S-O1	101(1)
C11-S1-C12	104.0(9)		
Pt-S2-O21	115.2(4)	O10...OW...O1	112.9(7)
Pt-S2-C21	110.4(5)	O10...OW...O3	106.8(6)
Pt-S2-C22	108.4(4)	O1...OW...O3	131.9(8)

^aThe prime (') indicates -*x*, -*y*, -*z*.

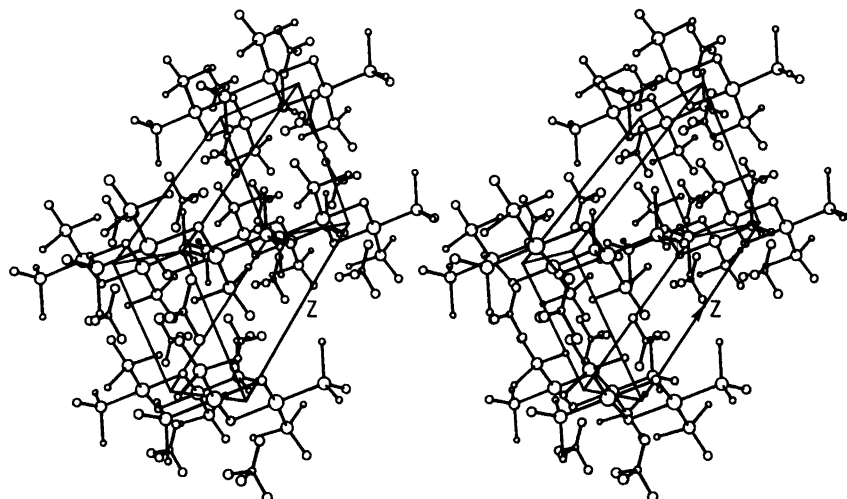


Fig. 1. Stereoscopic view of the crystal packing of $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{BF}_4)_2$.

were made according to the method suggested by Walker and Stuart.⁴ Reflexions with $I < 2\sigma(I)$ were considered insignificantly different from the background and were excluded from all subsequent calculations [$\sigma(I)$ is based on counting statistics]. Cell dimensions were obtained from least-squares fits of 50 and 25 θ -values for the tetrafluoroborate and trifluoromethanesulfonate compounds, respectively. The θ -values were determined on the diffractometer as $\theta_{hkl} = (\omega_{hkl} - \omega_{h\bar{k}l}^-)/2$ with $\omega_{h\bar{k}l}^-$ measured at negative θ angle. For $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{BF}_4)_2$ the Laue class $\bar{1}$ and the absence of systematic extinctions gave $P1$ and $P\bar{1}$ as possible space groups. For $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ the Laue class is mmm and systematic extinctions are $0kl : k \neq 2n$, $h0l : l \neq 2n$ and $hk0 : h \neq 2n$, which uniquely determine the space group as $Pbca$. Both structures were solved by Patterson and difference Fourier methods. They were refined by full-matrix least squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w^{-1} = [\sigma_c^2/4|F_o|^2 + (C_1|F_o|)^2 + C_2]$. C_1 and C_2 are given in Table 1.

Scattering factors with correction for anomalous dispersion were taken from Ref. 5. Non-H atoms were refined with anisotropic thermal parameters. The positions of the H atoms could not be located in difference Fourier maps, and these atoms were not included in the structure factor calculations. Details of the refinements are given in Table 1 and the final atomic parameters in Tables 2 and 3. Selected interatomic distances and angles are given in Tables 4 and 5. Computer programs used were those compiled and amended by Lundgren.⁶

Description of the structures

Our results show that di- μ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] tetrafluoroborate (Fig. 1) is isostructural with the analogous perchlorate compound studied by Rochon *et al.*² The salt is composed of hydroxo-bridged centrosymmetric dinuclear complexes, $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$ (Fig. 2) and tetrafluoroborate ions, with Pt(OH)(DMSO)₂(BF₄) in the asymmetric unit. The S₂PtO₂PtS₂ moiety is essentially planar. Pt shows the largest deviation from the least-squares plane through these atoms, $\pm 0.0613(6)$ Å.

Bond lengths and angles are given in Table 4. The angles around the Pt atom show considerable strain inside the four-membered ring. The O10–Pt–O10' angle is $80.0(6)^\circ$, while the Pt–O10–Pt' angle is $100.0(6)^\circ$. The Pt–O10 distances $2.05(1)$ Å are not significantly different from those found in the perchlorate analogue (2.03 – 2.06 Å)² or those found in the dinuclear complex $[\text{Pt}_2(\text{OH})_2(\text{NH}_3)_4]^{2+}$ (2.02 – 2.05 Å).⁷ The Pt–S bonds [$2.216(4)$ – $2.189(4)$ Å] agree with values found in other compounds with O in the *trans* position and O/S in the *cis* positions {*cis*-[Pt(DMSO)₂(NO₃)₂]⁸ and *cis*-[Pt(DMSO)₄](CF₃SO₃)₂}. Obviously, bond distances to Pt are not significantly affected by the formation of a bridged complex. The S atoms in the DMSO molecules and B atom in the tetrafluoroborate ion are, as expected, located in approximately tetrahedral environments. The

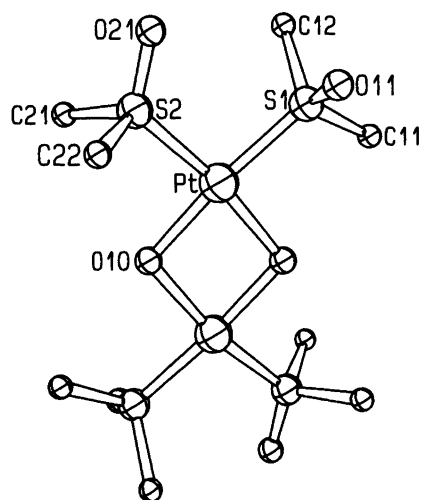


Fig. 2. Atomic numbering in the cation $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$.

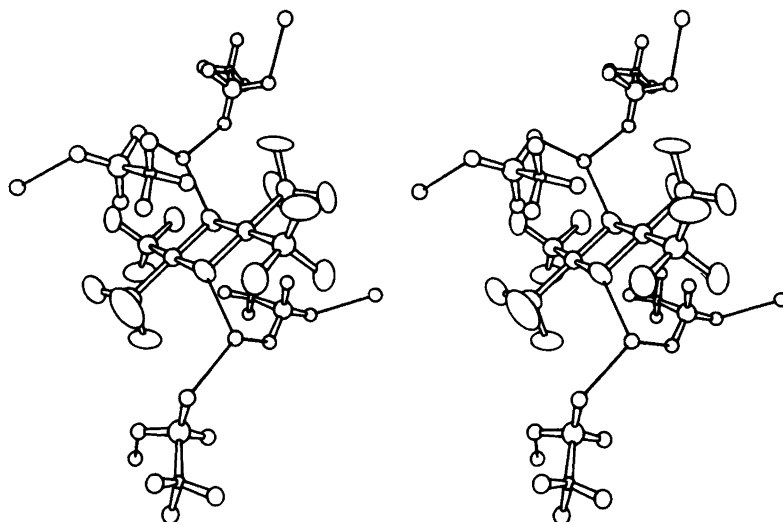


Fig. 3. Stereoscopic view of the coordination in $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ with hydrogen bonds as thin lines.

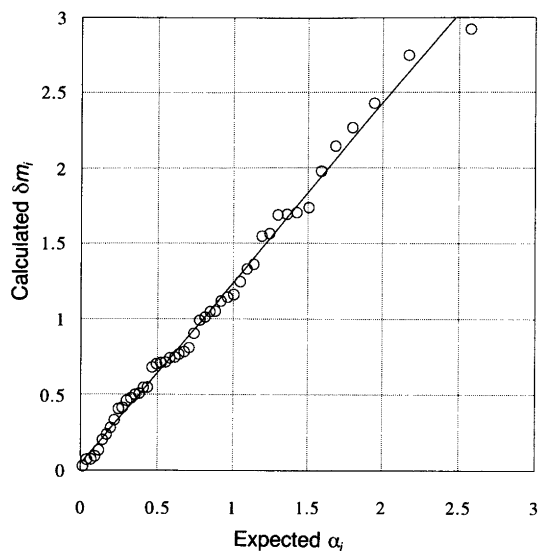
dinuclear complexes, $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$, are linked by hydrogen bonds between the bridging hydroxyl oxygen and O21 in DMSO, $\text{O10} \cdots \text{O21} = 2.71(2) \text{ \AA}$, forming a hydrogen-bond network running in the *a*-direction, i.e. each cation donates two hydrogen bonds and accepts two. The tetrafluoroborate ions are located between these hydrogen-bonded columns of cations, the closest $\text{F} \cdots \text{CH}_3$ contacts being in the range 3.1–3.8 \AA , which are normal van der Waals contacts.

Di- μ -hydroxo-bis[bis(dimethylsulfoxide)platinum(II)] trifluoromethanesulfonate dihydrate, with $\text{Pt}(\text{OH})(\text{DMSO})_2(\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})$ in the asymmetric unit, also contains a hydroxo-bridged centrosymmetric complex, $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$, as the major building block. The largest deviation from the least-squares plane through $\text{S}_2\text{PtO}_2\text{PtS}_2$ is shown by O10, $\pm 0.088(9) \text{ \AA}$. In contrast to the situation in the tetrafluoroborate and perchlorate analogues, the metal complexes are not directly linked by hydrogen bonds. Instead, the hydroxo bridging oxygen atom donates a hydrogen bond to the water molecule, which in turn donates two hydrogen bonds to two oxygen atoms in two different trifluoromethanesulfonate ions (Table 5). Each bridged complex is bonded to four neighbouring ones, through the sequence $>\text{O}-\text{H} \cdots \text{O}^-\text{W}-\text{H} \cdots \text{O1}-\text{S}-\text{O}_3 \cdots \text{H}-\text{O}^-\text{W} \cdots \text{H}-\text{O10}<$, forming a three-dimensional network (Fig. 3). The two trifluoromethanesulfonate ions are located on each side of the complex cation in such a way that a pseudo-octahedral geometry around platinum is achieved. In this description platinum also coordinates O2 and F3, with the distances $\text{Pt}-\text{O2} = 3.20(2) \text{ \AA}$ and $\text{Pt}-\text{F3} = 3.32(2) \text{ \AA}$ and the angles $\text{O2}-\text{Pt}-\text{F3} = 168.7(6)^\circ$, $\text{O10}-\text{Pt}-\text{O2} = 90.1(4)^\circ$ and $\text{O10}-\text{Pt}-\text{F3} = 92.7(4)^\circ$. The geometry of the complex cation is very similar to those observed in the tetrafluoroborate and perchlorate analogues (*vide infra*), and the geometry of the trifluoromethanesulfonate ion is not different from those observed in other compounds containing this anion.^{9–11}

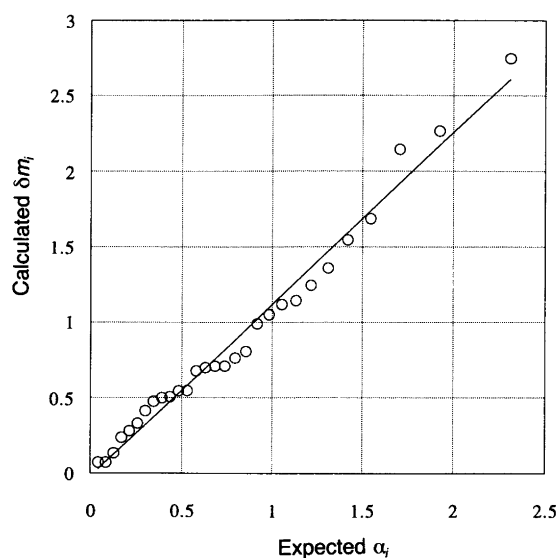
Discussion

A major objective of this investigation was to study the importance of intermolecular forces on the geometry of a Pt(II) complex. The geometry of the complex cation $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$ in the following compounds: $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{BF}_4)_2$, $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{ClO}_4)_2$ and $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$, can be compared by the method of half-normal probability plots.³ This method is convenient in detecting minor differences in the molecular species compared.

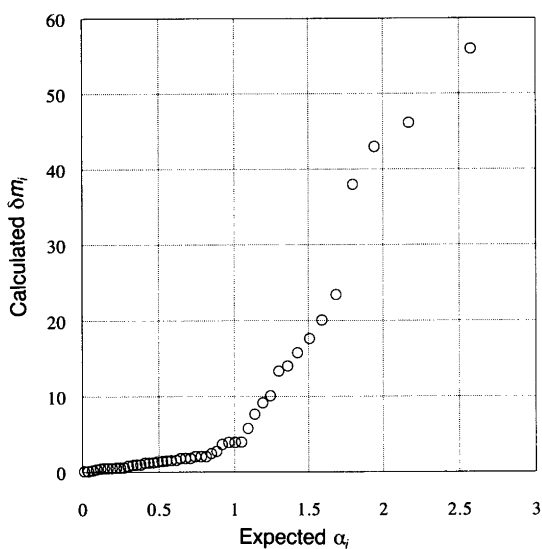
Interatomic distances are used as chemical coordinates. Observed ranked values of $\delta m_i = |d(1)_i - d(2)_i| / [\sigma^2 d(1)_i + \sigma^2 d(2)_i]^{1/2}$ are plotted versus the values α_i expected for a half-normal distribution of errors. The values of α_i are calculated according to Ref. 5. The quantities $d(1)_i$ and $d(2)_i$ are the corresponding intramolecular distances, with estimated standard deviations $\sigma d(1)_i$ and $\sigma d(2)_i$, in the structures 1 and 2, respectively. In calculating the interatomic distances a non-linear transformation is applied to the atomic coordinates. Even if the latter quantities are normally distributed, the non-linearity of the transformation might cause the error distribution in the derived quantities to be non-normal, which might introduce errors into the plot, especially at higher values of α_i . However, Albertsson and Schultheiss¹² have shown that differences in atomic distances are close to a normal distribution, and half-normal probability plots may be used to detect systematic geometrical differences in two molecular species. A linear plot with a slope of unity and a zero intercept indicates a correct match between measured and assumed distributions with correctly estimated standard deviations. A linear plot with a non-zero intercept indicates systematic differences,¹³ which may be caused by one or more of the following factors: (i) errors in the measurement procedure, (ii) physical differences in the specimens used, such as mosaic structure,^{9–11} and (iii) geometrical differences. How-



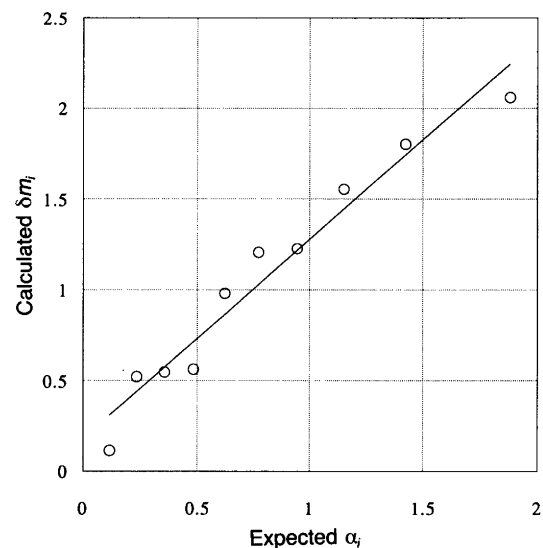
(a)



(b)



(c)



(d)

Fig. 4. Half-normal probability plot comparisons for the distances in the cation $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$ with different anions. The error limits denote a 95 % confidence interval. (a) Comparison of 49 distances less than 5.3 Å representing bond distances, bond angles and torsion angles in the cation with BF_4^- and ClO_4^- as anions. Slope 1.19 ± 0.03 , intercept 0.046 ± 0.029 , correlation coefficient 0.997. (b) Comparison of 29 distances less than 4.3 Å representing bond distances and bond angles in the cation with BF_4^- and ClO_4^- as anions. Slope 1.14 ± 0.06 , intercept -0.018 ± 0.059 , correlation coefficient 0.991. (c) Comparison of 49 distances less than 5.3 Å representing bond distances, bond angles and torsion angles in the cation with CF_3SO_3^- and BF_4^- as anions. (d) Comparison of 10 distances less than 2.22 Å representing bond distances in the cation with CF_3SO_3^- and BF_4^- as anions. Slope 1.09 ± 0.20 , intercept 0.184 ± 0.188 , correlation coefficient 0.977.

ever, the occurrence of non-linear plots is the best indication of systematic differences.

Fig. 4 shows some relevant half-normal probability plots of the cation $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$. A comparison of this unit in the tetrafluoroborate and perchlorate compounds that includes atomic distances less than 5.3 Å, representing bond distances, bond angles and torsion angles, shows a linear plot with slope 1.19 ± 0.03 , intercept 0.05 ± 0.03 and

correlation coefficient 0.997 (Fig. 4a). The error limits denote a 95 % confidence interval. Thus at the chosen level of confidence the intercept is significantly different from zero, which indicates systematic differences. However, a plot including distances less than 4.3 Å, representing bond distances and bond angles, results in a linear relationship with slope 1.14 ± 0.06 , intercept -0.02 ± 0.06 and correlation coefficient 0.991 (Fig. 4b). Thus, no systematic geo-

metrical differences can be claimed in this case. The slope indicates that the e.s.d.s for one or both structures appear to be slightly optimistic.

A similar comparison of the geometry between $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$ in the trifluoromethanesulfonate compound and that in the tetrafluoroborate compound (Fig. 4c) that includes atomic distances less than 5.3 Å, representing bond distances, bond angles and torsion angles, reveals large systematic differences. A plot (not shown here) including distances less than 4.3 Å, representing bond distances and bond angles, results in a linear relationship except for three outlines representing S1...S, S2...O10 and Pt...C12. If these are excluded the slope is 1.25 ± 0.07 , the intercept 0.12 ± 0.07 and the correlation coefficient 0.991. However, if only bond distances are included (Fig. 4d) the slope is 1.09 ± 0.20 , the intercept 0.18 ± 0.19 and the correlation coefficient 0.977. This may imply that torsion- and bond angles but not bond distances are significantly affected by differences in packing arrangement in this case. The e.s.d.s appear to be realistic for both structures.

In conclusion, there are systematic differences in torsion angles, but not in bond angles and bond distances, of the dinuclear complex $[\text{Pt}_2(\text{OH})_2(\text{DMSO})_4]^{2+}$ in the closely isostructural perchlorate and tetrafluoroborate compounds. If the packing arrangement is drastically different (as in the tetrafluoroborate compared to the trifluoromethanesulfonate compound) there are systematic differences in torsion angles as well as in bond angles, but not in bond distances. Thus it may be justified to discuss significant

variations of a Pt-X distance in different complexes as being due to intramolecular effects.

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