

The complexing properties of the phenylsquarate ligand with Ru(II), Pt(II), Gd(III) and Tb(III) ions

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Abstract

Reaction of 3-phenyl-4-hydroxycyclobut-3-ene-1,2-dione (phenylsquarate) with $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ in acetonitrile afforded crystals of the monomeric species $\text{Ru}(\text{dmsO})_3\text{Cl}(\text{H}_2\text{O})(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)\cdot\text{H}_2\text{O}$ (**1**) in which the ruthenium is in a slightly distorted octahedral geometry with three *fac* S-bonded dmsO ligands. No complexation occurs when $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is reacted with the same ligand in aqueous solution; instead, the hydrogen-bonded salt $[\text{Pt}(\text{NH}_3)_4][\text{C}_6\text{H}_5\text{C}_4\text{O}_3]_2\cdot\text{H}_2\text{O}$ (**2**) is produced. The isomorphous complexes $\{[\text{M}(\mu\text{-C}_6\text{H}_5\text{C}_4\text{O}_3)(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ [$\text{M} = \text{Tb}$ (**3**), Gd (**4**)] formed by the reaction of the phenylsquarate ligand with the respective metal nitrate contain eight-coordinate metal centres surrounded by two μ -1,3-bridged and two pendant phenylsquarate ligands and four aqua ligands. In the solid state, **3** and **4** form interleaved π -stacked and hydrogen-bonded sheets with pronounced hydrophobic and hydrophilic surfaces. In compounds **1–4**, the phenylsquarate ligands participate in π - π interactions and exhibit multiple bond localisation, the pattern of bonding being the same in each structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phenylsquarate; Crystal structures; Transition metal and lanthanide complexes; Polymeric complexes

1. Introduction

After our successful synthesis and structural characterisation of several complexes of first-row transition and lanthanide metals with monosubstituted squarate ligands [1,2], we decided to focus our attention on the complexing properties of these ligands with second- and third-row transition metals. We were further prompted by the knowledge that, in spite of the enormous amount of research conducted on first-row transition and lanthanide metal complexes of the unsubstituted squarate ion, only a few second- and third-row complexes have been reported [3–7]. A possible reason for this paucity of complexes could be the low solubility of squaric acid and its complexes in non-polar organic solvents, a problem that we believed could be overcome by the use of monosubstituted squarate ligands.

Ruthenium was selected because of the potential for any polymeric ruthenium(II) complex to undergo partial oxidation to produce an Ru(II)/Ru(III) species [8–10], which should, in turn, have an enhanced potential for exhibiting conductivity. In view of its ease of synthesis and stability, we selected $\text{RuCl}_2(\text{dmsO})_4$ as a starting material; it also has the additional advantage that the resulting product(s) should also contain ruthenium–sulfoxide and ruthenium–halogen bonds, a characteristic of several antitumour agents [11–15]. Similarly, it is well documented that platinum(II) invariably adopts a square planar geometry, which, if present in a polymeric complex containing appropriately bridged monosubstituted squarate ligands, should facilitate extended delocalisation along the polymer chain and confer an enhanced potential for conductivity. Additionally, partially oxidised platinum(II) compounds also have the potential for exhibiting one-dimensional conductivity [16]. We also wanted to compare the coordination modes observed for the phenylsquarate ligand with first-row transition metals

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and lanthanides [1g,2] with, for example, representative second- (Ru) and third-row (Pt) transition metals.

2. Experimental

2.1. Preparation of the ligand

The 3-phenyl-4-hydroxycyclobut-3-ene-1,2-dione was prepared according to the method of Liebeskind et al. [17].

2.2. Preparation of $Ru(dmsO)_4Cl_2$ and $[Pt(NH_3)_4]Cl_2$

$Ru(dmsO)_4Cl_2$ was prepared according to the method of Evans et al. [18], and $[Pt(NH_3)_4]Cl_2$ was prepared according to the method of Keller [19].

2.3. Preparation of the metal complexes

2.3.1. $Ru(dmsO)_3Cl(H_2O)(C_6H_5C_4O_3) \cdot H_2O$ (**1**)

60 ml of a solution of $Ru(dmsO)_4Cl_2$ (0.28 g, 5.8×10^{-4} mol) in acetonitrile was added to 30 ml of a solution of phenylsquarate (0.10 g, 5.8×10^{-4} mol) in the same solvent. The mixture was then filtered and left to evaporate slowly at approximately 28°C until crystallisation was complete.

Yellow plates. Yield, 0.029 g (8.82%). *Anal.* Found: C, 32.2; H, 4.7; Cl, 7.3; Ru, 18.4; S, 16.3. Calc. for $C_{16}H_{27}ClO_8RuS_3$: C, 33.1; H, 4.7; Cl, 6.1; Ru, 17.4; S, 16.6%.

2.3.2. $[Pt(NH_3)_4][C_6H_5C_4O_3]_2 \cdot H_2O$ (**2**)

40 ml of a solution of $[Pt(NH_3)_4]Cl_2$ (0.19 g, 5.8×10^{-4} mol) in acetonitrile was mixed with a similar volume of a solution of phenylsquarate (0.10 g, 5.8×10^{-4} mol) in the same solvent. The filtered mixture was allowed to stand at approximately 28°C until crystallisation was complete.

Orange blocks. Yield, 0.028 g (7.82%). *Anal.* Found: C, 38.0; H, 3.8; N, 8.8; Pt, 31.0. Calc. for $C_{20}H_{24}N_4O_7Pt$: C, 38.3; H, 3.9; N, 8.9; Pt, 31.1%.

2.3.3. $\{[Tb(\mu-C_6H_5C_4O_3)(C_6H_5C_4O_3)_2(H_2O)_4] \cdot H_2O\}_n$ (**3**)

20 ml of an aqueous solution of $Tb(NO_3)_3 \cdot 5H_2O$ (0.26 g, 5.8×10^{-4} mol) was added to an equal volume of an aqueous solution of phenylsquarate (0.10 g, 5.8×10^{-4} mol). The filtered mixture was allowed to stand at approximately 28°C until crystallisation was complete.

Yellow plates. Yield, 0.19 g (40%). *Anal.* Found: C, 47.2; H, 3.3; Tb, 20.1. Calc. for $C_{30}H_{25}O_{14}Tb$: C, 46.9; H, 3.3; Tb, 20.7%.

2.3.4. $\{[Gd(\mu-C_6H_5C_4O_3)(C_6H_5C_4O_3)_2(H_2O)_4] \cdot H_2O\}_n$ (**4**)

The procedure is identical to that for the preparation of **3** except that $Gd(NO_3)_3 \cdot 5H_2O$ (0.25 g, 5.8×10^{-4} mol) was used.

Yellow plates. Yield, 0.18 g (40%). *Anal.* Found: C, 47.2; H, 3.3; Gd, 19.2. Calc. for $C_{30}H_{25}GdO_{14}$: C, 47.0; H, 3.3; Gd, 20.5%.

2.4. Elemental analyses

C, H, N, S and metal analyses were done by MEDAC Limited, Brunel Science Centre, Egham, Surrey, UK.

2.5. Crystallographic analyses

2.5.1. Crystal data for **1**

$C_{16}H_{25}O_7S_3ClRu \cdot H_2O$, $M = 580.1$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.833(1)$, $b = 13.747(1)$, $c = 15.866(1)$ Å, $\beta = 109.19(1)^\circ$, $V = 2231.3(2)$ Å³, $Z = 4$, $D_c = 1.727$ g cm⁻³, $\mu(Mo K\alpha) = 11.4$ cm⁻¹, $F(000) = 1184$, $T = 105$ K; yellow needles, $0.25 \times 0.10 \times 0.10$ mm³, Nonius CAD-4 diffractometer, ω -scans, 6479 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.036$, $wR_2 = 0.081$ for 5464 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 60^\circ$] and 266 parameters. CCDC 156538.

2.5.2. Crystal data for **2**

$C_{20}H_{24}N_4O_7Pt$, $M = 627.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.099(1)$, $b = 8.708(1)$, $c = 17.660(2)$ Å, $\alpha = 90.47(1)$, $\beta = 93.18(1)$, $\gamma = 90.20(1)^\circ$, $V = 1090.1(2)$ Å³, $Z = 2$, $D_c = 1.912$ g cm⁻³, $\mu(Mo K\alpha) = 64.9$ cm⁻¹, $F(000) = 612$, $T = 293$ K; yellow prisms, $0.27 \times 0.23 \times 0.10$ mm³, Siemens P4/PC diffractometer, ω -scans, 3861 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.032$, $wR_2 = 0.072$ for 3475 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50^\circ$] and 306 parameters. CCDC 156539.

2.5.3. Crystal data for **3**

$C_{30}H_{23}O_{13}Tb \cdot H_2O$, $M = 768.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.228(1)$, $b = 9.861(1)$, $c = 19.282(2)$ Å, $\alpha = 94.38(1)$, $\beta = 92.92(1)$, $\gamma = 104.84(1)^\circ$, $V = 1503.8(3)$ Å³, $Z = 2$, $D_c = 1.697$ g cm⁻³, $\mu(Cu K\alpha) = 121.9$ cm⁻¹, $F(000) = 764$, $T = 293$ K; yellow scythes, $0.27 \times 0.27 \times 0.05$ mm³, Siemens P4/RA diffractometer, ω -scans, 4734 independent reflections. The structure was solved by the heavy atom method and the non-hy-

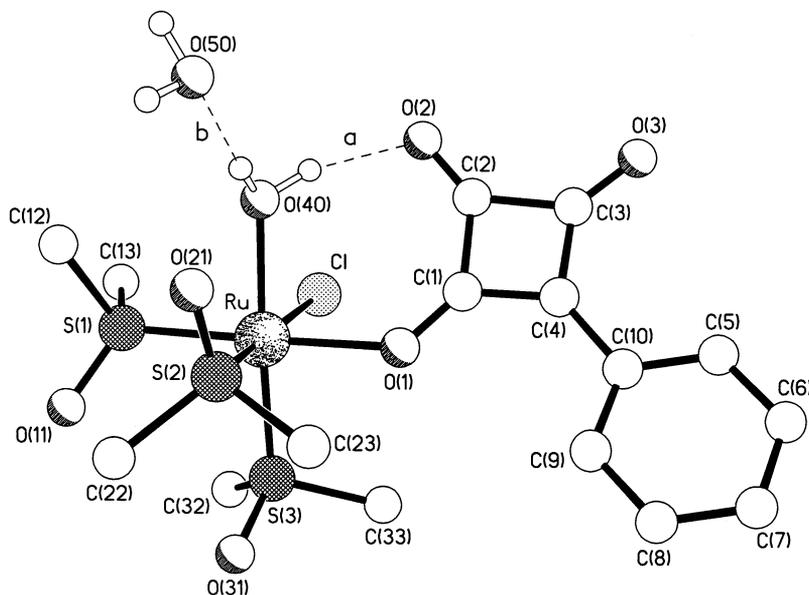


Fig. 1. The molecular structure of $[\text{Ru}(\text{dmsO})_3\text{Cl}(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**1**). The hydrogen bonding geometries are, $\text{O}\cdots\text{O}$, $\text{H}\cdots\text{O}$ (Å), $\text{O}-\text{H}\cdots\text{O}$ (°): (a) 2.71, 1.83, 164; (b) 2.70, 1.81, 167.

drogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.040$, $wR_2 = 0.098$ for 4298 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 124^\circ$] and 437 parameters. CCDC 156540.

3. Results and discussion

3.1. $\text{Ru}(\text{dmsO})_3\text{Cl}(\text{H}_2\text{O})(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)\cdot\text{H}_2\text{O}$ (**1**)

The product of the reaction between $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ and phenylsquaresate was shown by single-crystal X-ray analysis to be $\text{Ru}(\text{dmsO})_3\text{Cl}(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)(\text{H}_2\text{O})\cdot\text{H}_2\text{O}$ (**1**) (Fig. 1). The coordination at ruthenium is slightly distorted octahedral with three *fac* S-bonded dmsO ligands. The Ru–S distances are in the range 2.246(1) to 2.265(1) Å, the longest bond being that trans to Cl; the two Ru–O distances are essentially the same (Table 1). The Ru–S distances are comparable to those in, for example, *cis, fac*- $\text{RuCl}_2(\text{dmsO})_3(\text{NH}_3)$ [12] and *cis, cis, cis*- $\text{RuCl}_2(\text{dmsO})_2(\text{py})(\text{Me}_3\text{Bzm})$ [py = pyridine; Me_3Bzm = 1,5,6-trimethylbenzimidazole] [14]. The pattern of bonding in the C_4 -ring of the phenylsquaresate ligand shows the usual pattern [1,2] of two short and two long C–C bonds [$\Delta(\text{C}-\text{C}) \approx 0.08$ Å], the short bonds being those adjacent to the phenyl substituent. The C_4 -cycle and the phenyl ring are nearly coplanar, the torsional twist about the C(4)–C(10) bond being approximately 11° , a geometry that enhances conjugation between the two ring systems, as evidenced by the shortening of the C(4)–C(10) bond [1.461(3) Å cf. a mean value of approximately 1.49 Å in, for example, biphenyls].

The conformation of the complex is stabilised by an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond between one of the hydrogen atoms on the aqua ligand and the ketonic oxygen O(2). The other aqua hydrogen atom links to the included solvent water molecule [O(50)], which in turn forms hydrogen bonds to the other ketonic oxygen atom O(3) and the Cl ligand of symmetry-related monomers to form extended two-dimensional sheets [$\text{O}\cdots\text{O}$, $\text{H}\cdots\text{O}$; 2.85, 2.00 Å, $\text{O}-\text{H}\cdots\text{O}$ 157° ; $\text{O}\cdots\text{Cl}$, $\text{H}\cdots\text{Cl}$ 3.37, 2.51 Å, $\text{O}-\text{H}\cdots\text{Cl}$ 160°]. Within these sheets, C_7 -related phenylsquaresate ligands are arranged in face-to-face, head-to-tail pairs (Fig. 2) with a mean interplanar separation of 3.64 Å. This geometry is the same as that observed between the pendant ligands in the polymeric europium(III) phenylsquaresate complex [1g]. Adjacent

Table 1
Selected bond lengths (Å) and angles (°) for $\text{Ru}(\text{dmsO})_3\text{Cl}(\text{H}_2\text{O})\cdot(\text{C}_6\text{H}_5\text{C}_4\text{O}_3)\cdot\text{H}_2\text{O}$ (**1**)

Ru–Cl	2.422(1)	Ru–S(1)	2.247(1)
Ru–S(2)	2.265(1)	Ru–S(3)	2.246(1)
Ru–O(1)	2.141(2)	Ru–O(40)	2.135(2)
O(1)–C(1)	1.254(3)	O(2)–C(2)	1.216(3)
O(3)–C(3)	1.219(3)	C(4)–C(10)	1.461(3)
C(1)–C(2)	1.507(4)	C(2)–C(3)	1.527(4)
C(3)–C(4)	1.448(4)	C(1)–C(4)	1.432(3)
O(40)–Ru–O(1)	90.07(7)	O(40)–Ru–S(3)	174.54(6)
O(1)–Ru–S(3)	88.66(5)	O(40)–Ru–S(1)	88.38(5)
O(1)–Ru–S(1)	177.86(5)	S(3)–Ru–S(1)	93.02(2)
O(40)–Ru–S(2)	91.05(6)	O(1)–Ru–S(2)	86.93(5)
S(3)–Ru–S(2)	94.18(2)	S(1)–Ru–S(2)	91.63(2)
O(40)–Ru–Cl	84.39(6)	O(1)–Ru–Cl	86.99(5)
S(3)–Ru–Cl	90.24(2)	S(1)–Ru–Cl	94.32(2)
S(2)–Ru–Cl	172.39(2)	C(1)–O(1)–Ru	131.1(2)

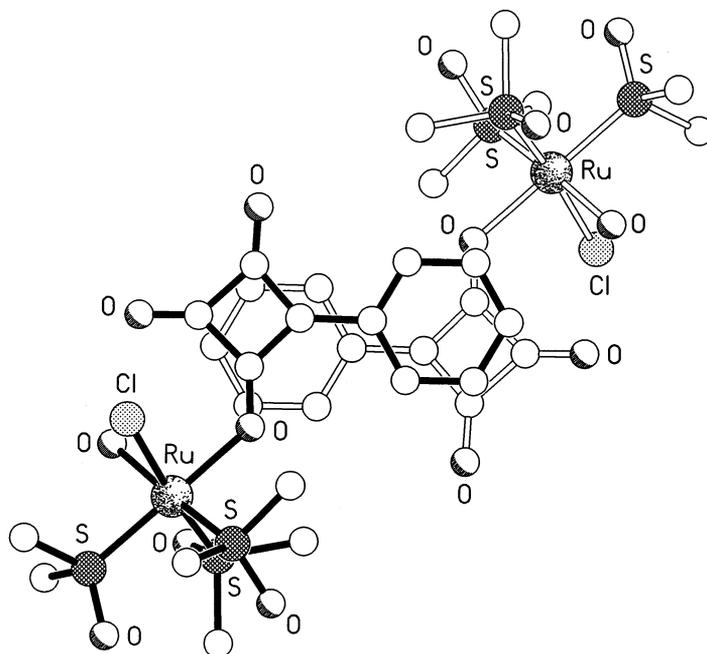


Fig. 2. The face-to-face, head-to-tail stacking of C_7 -related pairs of coordinated phenylsulfonate ligands in the structure of **1**. The mean interplanar separation between the ring systems is 3.64 Å, the phenyl and C_4 -ring systems being inclined by approximately 11° to each other.

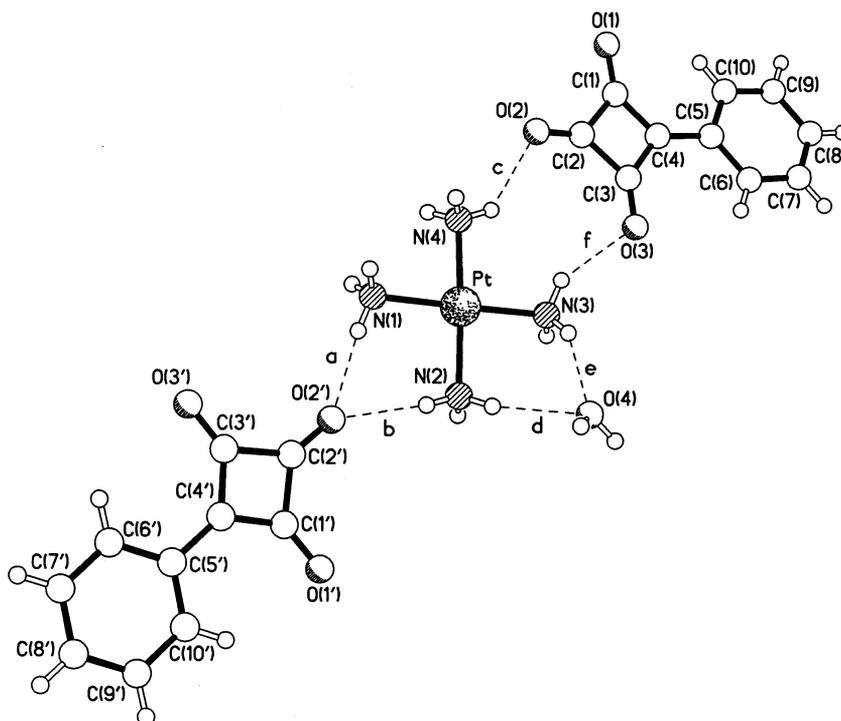


Fig. 3. The molecular structure of the hydrogen-bonded salt **2**. The hydrogen-bonding geometries are, $N\cdots O$, $H\cdots O$ (Å), $N-H\cdots O$ ($^\circ$): (a) 2.97, 2.08, 173; (b) 3.01, 2.15, 159; (c) 2.89, 2.17, 137; (d) 3.02, 2.18, 156. (e) 3.01, 2.19, 150; (f) 3.19, 2.40, 147.

hydrogen-bonded sheets are cross-linked weakly by $C-H\cdots O$ hydrogen bonds between one of the methyl hydrogen atoms attached to C(13) in one layer and the sulfoxide oxygen O(31) in the next [$C\cdots O$, $H\cdots O$; 3.23, 2.35 Å, $C-H\cdots O$ 151°].

3.2. $[Pt(NH_3)_4][C_6H_5C_4O_3]_2 \cdot H_2O$ (**2**)

Instead of the desired platinum phenylsulfonate complex being formed when a solution of $[Pt(NH_3)_4]Cl_2$ in acetonitrile was mixed with phenylsulfonate in the same

Table 2
Selected bond lengths (Å) and angles (°) for [Pt(NH₃)₄]-[C₆H₅C₄O₃]₂·H₂O (2)

Pt–N(1)	2.063(5)	Pt–N(2)	2.055(5)
Pt–N(3)	2.064(5)	Pt–N(4)	2.047(5)
O(1)–C(1)	1.247(8)	C(2)–O(2)	1.215(8)
C(3)–O(3)	1.222(7)	C(4)–C(5)	1.461(8)
C(1)–C(2)	1.514(8)	C(2)–C(3)	1.511(8)
C(3)–C(4)	1.461(8)	C(1)–C(4)	1.427(8)
O(1')–C(1')	1.250(8)	C(2')–O(2')	1.210(9)
C(3')–O(3')	1.236(8)	C(4')–C(5')	1.442(8)
C(1')–C(2')	1.513(8)	C(2')–C(3')	1.529(9)
C(3')–C(4')	1.428(8)	C(1')–C(4')	1.433(8)
N(1)–Pt–N(2)	91.6(2)	N(1)–Pt–N(3)	179.0(2)
N(1)–Pt–N(4)	85.8(2)	N(2)–Pt–N(3)	89.2(2)
N(2)–Pt–N(4)	177.4(2)	N(3)–Pt–N(4)	93.3(2)

solvent, the hydrated hydrogen-bonded salt [Pt(NH₃)₄]-[C₆H₅C₄O₃]₂·H₂O was produced (Fig. 3). The two phenylsquarate moieties have essentially identical geometries, with both exhibiting delocalisation that extends from the deprotonated oxygen atom O(1) via C(4) to O(3) (Table 2). The bond linking the C₄⁻ and C₆-rings is the same as that observed in **1**. There is, however, a small difference in the torsional twist about this bond in the two independent molecules [approximately 8° about C(4)–C(5), cf. approximately 1° about C(4')–C(5')]. It is interesting to note that although there

is essentially maximum conjugation between the phenyl and C₄-rings, the delocalisation in the latter ring is incomplete (i.e. it does not extend to include all four C–C bonds). This pattern is in striking contrast to the bonding observed in the manganese(II) aminosquarate salt [1c], where all of the C–C bonds in the C₄ ring are the same. Despite the overlap between the π systems in the phenylsquarate ligand, the absence of mobile electron density in the substituent, which is present on the nitrogen atom in the case of the aminosquarate ion, is, we believe, responsible for the lack of complete delocalisation in the former.

The cations and anions are linked by N–H⋯O hydrogen bonds. However, the pattern of bonding to the two independent phenylsquarate units differs. In one case there is a pair of hydrogen bonds from two *cis* ammine groups to the carbonyl trans to the phenyl substituent (**a** and **b** in Fig. 3). The other pair of ammine groups form one hydrogen bond each (**c** and **f** in Fig. 3) to adjacent carbonyl groups on the other phenylsquarate anion. This hydrogen-bonded unit is then linked via the included solvent water molecule to its centrosymmetrically related neighbours by N–H⋯O and O–H⋯O hydrogen bonds to form tapes (Fig. 4). Adjacent tapes are linked both from above and below by further N–H⋯O and O–H⋯O hydrogen bonds, using all of the remaining non-utilised donors to form continuous cross-linked

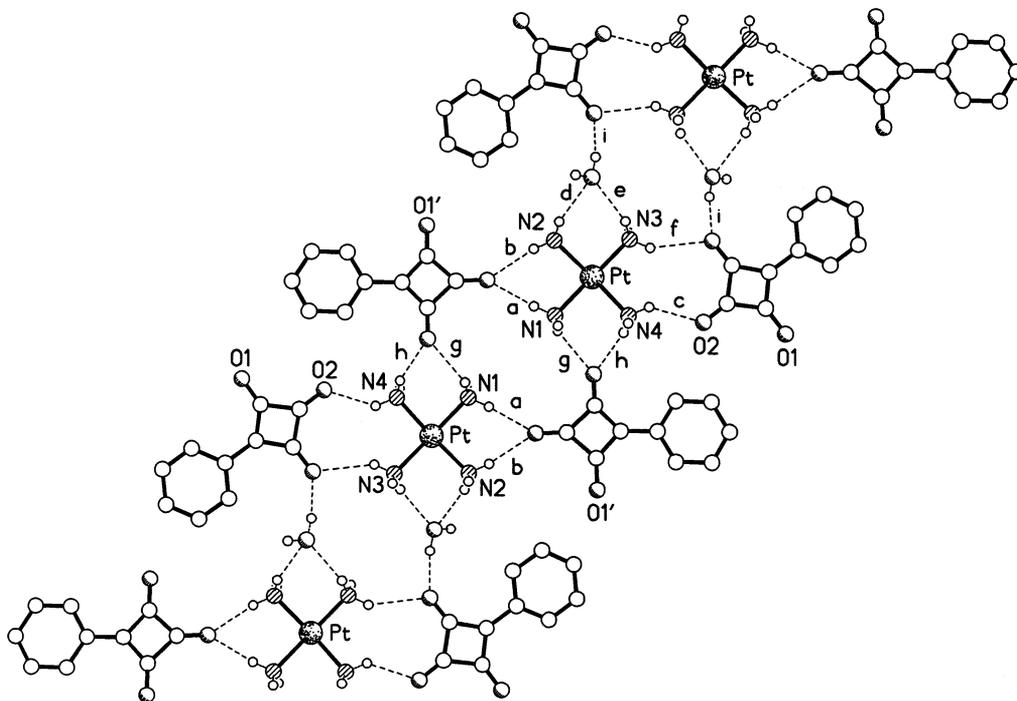


Fig. 4. One of the hydrogen-bonded tapes formed by the linking via the included water molecule of adjacent hydrogen-bonded salts in [Pt(NH₃)₄][C₆H₅C₄O₃]₂·H₂O (**2**). The hydrogen-bonding geometries are, X⋯O, H⋯O (Å), X–H⋯O (°): (**g**) 3.00, 2.26, 139; (**h**) 2.93, 2.09, 154; (**i**) 2.79, 1.90, 169. There are additional inter-tape hydrogen-bonding interactions that utilise the remaining ammine and water hydrogen atoms. That from N(1)–H is to O(1') [**j**], from N(2)–H is to O(2) [**k**], from N(3)–H is to O(1) [**l**], from N(4)–H is to O(1') [**m**] and that from the water molecule O(4)–H to O(1) [**n**]. The geometries are (**j**) 3.01, 2.22, 147 (**k**) 3.01, 2.23, 145 (**l**) 3.08, 2.20, 165 (**m**) 2.91, 2.17, 140 and (**n**) 2.93, 2.20, 138.

corrugated sheets. These interactions are supplemented by 'reverse' π stacking of the phenylsuarate ring systems analogous to that observed in the ruthenium complex **1**. The C(1)/C(10)-based phenylsuarate units overlay their centrosymmetrically related counterparts with a mean interplanar separation of 3.38 Å. These π -stacked pairs of phenylsuarate units pack in a stepped fashion with their lattice-translated neighbours. The C(1')/C(10') phenylsuarate units stack in a similar fashion, with a mean interplanar separation of 3.37 Å and with the lattice-translated counterpart also being in an overlapping geometry with an interplanar separation of 3.49 Å.

3.3. $\{[M(\mu-C_6H_5C_4O_3)(C_6H_5C_4O_3)_2(H_2O)_4]\cdot H_2O\}_n$
 $[M = Tb$ (**3**); $M = Gd$ (**4**)]

The terbium and gadolinium complexes are isomorphous. The terbium complex is seen from the X-ray structure to be polymeric, with each terbium centre being coordinated to two pendant and two μ -1,3-bridging phenylsuarate ligands, the remaining coordination sites being occupied by four aqua ligands. In each case the phenylsuarate ligands coordinate via oxygen atoms *cis* to the phenyl substituent. The geometry at terbium can be considered as either distorted bicapped trigonal prismatic with O(31) and O(33) as the capping

atoms, or as distorted square antiprismatic with the 'upper' and 'lower' faces comprised of O(31) to O(34) and O(1), O(11), O(21), O(3A) respectively (Fig. 5). In this latter interpretation it is interesting to note that all of the phenylsuarate ligands lie on one square face of the antiprism, a feature also observed in the related europium phenylsuarate analogue, though in the europium structure the opposite face was populated by two aqua and two methanol ligands [19]. The Tb–O(suarate) distances are in the range 2.326(4)–2.376(4) Å, whereas those to the aqua ligands are in a much wider range [2.347(4)–2.449(4) Å]; the angles at the coordinated ketonic oxygen atoms range between 136.4(3)° at O(1) and 146.0(4)° at O(21) (Table 3). There is no difference in the patterns of bonding in the three independent phenylsuarate ligands. They all exhibit delocalisation that extends from the coordinated oxygen via the carbon atom linked to the phenyl substituent to the trans ketonic oxygen atom regardless of their coordination mode. The C–C bonds to the carbonyl carbon trans to the phenyl substituent are, in all cases, single in nature [1.505(7)–1.530(7) Å]. As in structures **1** and **2**, the bond linking the C₄- and C₆-rings [range 1.442(8)–1.447(8) Å] is, in each case, shorter than a conventional single bond, reflecting conjugation between the two ring systems (the torsional twists about this bond range between only 2 and 4°).

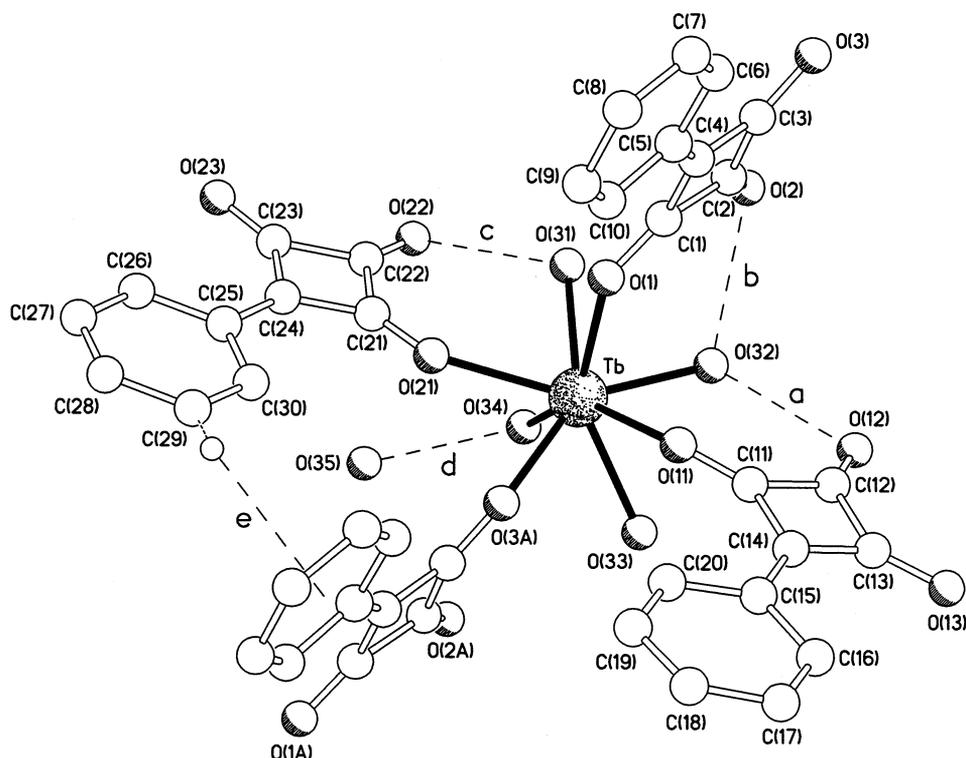


Fig. 5. The coordination environment of the terbium atom in $\{[Tb(\mu-C_6H_5C_4O_3)(C_6H_5C_4O_3)_2(H_2O)_4]\cdot H_2O\}_n$ (**3**), also showing the intramolecular hydrogen bonds and the linking to the included water molecule [O(35)]. The phenylsuarate ligand coordinated through O(3A) is related by symmetry to that coordinated through O(1). The hydrogen bonding geometries are O \cdots O, H \cdots O (Å), O–H \cdots O (°): (a) 2.71, 1.89, 151; (b) 2.84, 2.03, 150; (c) 2.75, 1.93, 151; (d) 2.72, 1.86, 159. The C–H \cdots π interaction (e) has H \cdots π , 2.81 Å, C–H \cdots π , 152°.

Table 3

Selected bond lengths (Å) and angles (°) for $\{[\text{Tb}(\mu\text{-C}_6\text{H}_5\text{C}_4\text{O}_3)(\text{C}_6\text{H}_5\text{-C}_4\text{O}_3)_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**3**)

Tb–O(1)	2.360(4)	Tb–O(3A)	2.326(4)
Tb–O(11)	2.376(4)	Tb–O(21)	2.351(4)
Tb–O(31)	2.449(4)	Tb–O(32)	2.347(4)
Tb–O(33)	2.422(4)	Tb–O(34)	2.389(4)
O(1)–C(1)	1.239(6)	C(2)–O(2)	1.206(7)
C(3)–O(3)	1.250(7)	C(4)–C(5)	1.447(8)
C(1)–C(2)	1.530(7)	C(2)–C(3)	1.505(7)
C(3)–C(4)	1.421(7)	C(1)–C(4)	1.425(7)
O(3A)–Tb–O(32)	143.66(14)	O(3A)–Tb–O(21)	70.82(14)
O(32)–Tb–O(21)	145.02(14)	O(3A)–Tb–O(1)	107.23(13)
O(32)–Tb–O(1)	87.0(2)	O(21)–Tb–O(1)	85.1(2)
O(3A)–Tb–O(11)	74.43(14)	O(32)–Tb–O(11)	79.35(14)
O(21)–Tb–O(11)	129.14(14)	O(1)–Tb–O(11)	71.00(14)
O(3A)–Tb–O(34)	99.2(2)	O(32)–Tb–O(34)	88.1(2)
O(21)–Tb–O(34)	77.3(2)	O(1)–Tb–O(34)	141.32(14)
O(11)–Tb–O(34)	145.00(14)	O(3A)–Tb–O(33)	74.69(14)
O(32)–Tb–O(33)	73.6(2)	O(21)–Tb–O(33)	129.5(2)
O(1)–Tb–O(33)	140.77(14)	O(11)–Tb–O(33)	72.1(2)
O(34)–Tb–O(33)	73.1(2)	O(3A)–Tb–O(31)	146.03(13)
O(32)–Tb–O(31)	69.74(13)	O(21)–Tb–O(31)	75.38(14)
O(1)–Tb–O(31)	72.64(14)	O(11)–Tb–O(31)	132.85(14)
O(34)–Tb–O(31)	69.7(2)	O(33)–Tb–O(31)	127.61(14)
C(1)–O(1)–Tb	136.4(3)	C(3)–O(3)–Tb'	140.6(3)
C(11)–O(11)–Tb	137.5(4)	C(21)–O(21)–Tb	146.0(4)

The complex and polymer chain conformations are, to some extent, controlled by intramolecular O–H···O and C–H··· π interactions (**a** to **e** in Fig. 5), though these are complemented by additional interchain O–H···O (**f** and **g** in Fig. 6) and π – π interactions resulting in the formation of sheets comprised of interleaved chains (Fig. 7). A feature of these sheets is that one of their surfaces is dominated by the phenyl rings of the phenylsquatrate ligands and is thus hydrophobic, whereas the other surface is populated entirely by either ketonic oxygen atoms or aqua ligands, making it hydrophilic. Adjacent centrosymmetrically related sheets are arranged back-to-back such that the two hydrophilic surfaces are adjacent and are cross-linked by additional O–H···O hydrogen bonds. The hydrophobic surfaces are only in van der Waals contact with their centrosymmetrically related counterparts. This sheet packing motif is distinctly different from that seen in the related europium structure [1g], where adjacent polymer chains alternate 'up' and 'down' (i.e. they do not have distinct hydrophobic and hydrophilic surfaces) and there are no inter-sheet hydrogen bonds. The included solvent water molecule [O(35)] in **3** adopts a dual role, forming both intra- and inter-sheet hydrogen bonds; the intra-sheet

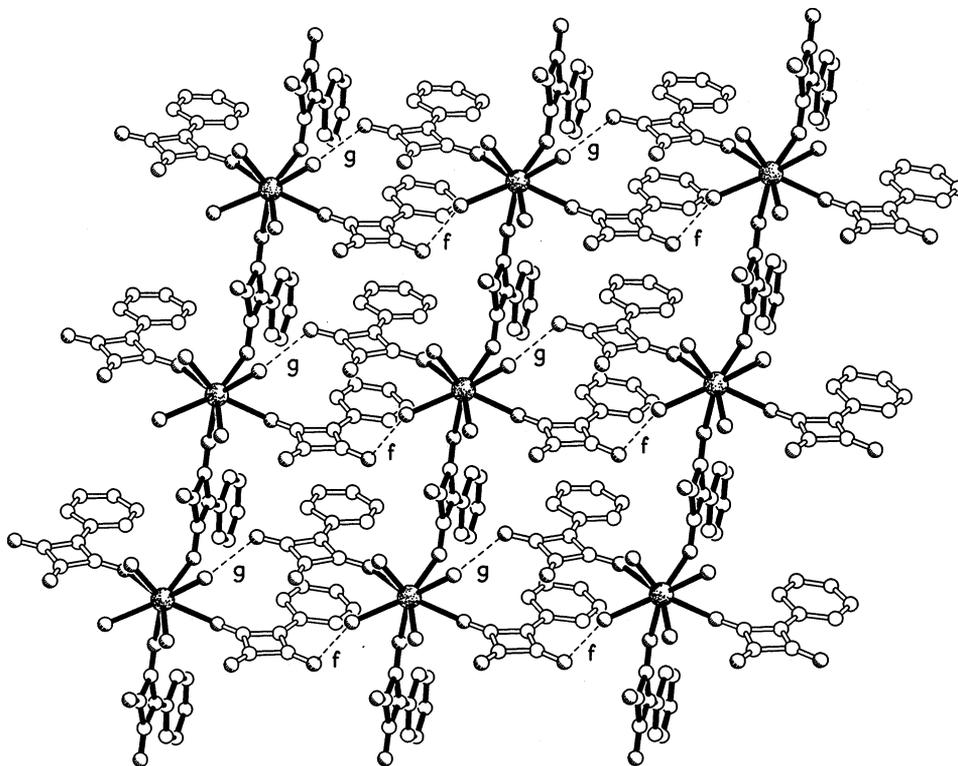


Fig. 6. Part of one of the sheets formed by the interleaving of adjacent lattice-translated polymer chains. The hydrogen-bonding geometries are O···O, H···O (Å), O–H···O (°): (**f**) 2.71, 1.83, 164; (**g**) 2.70, 1.81, 167. The mean interplanar separations between the π -stacked phenylsquatrate ring systems are 3.55 Å and 3.57 Å respectively.

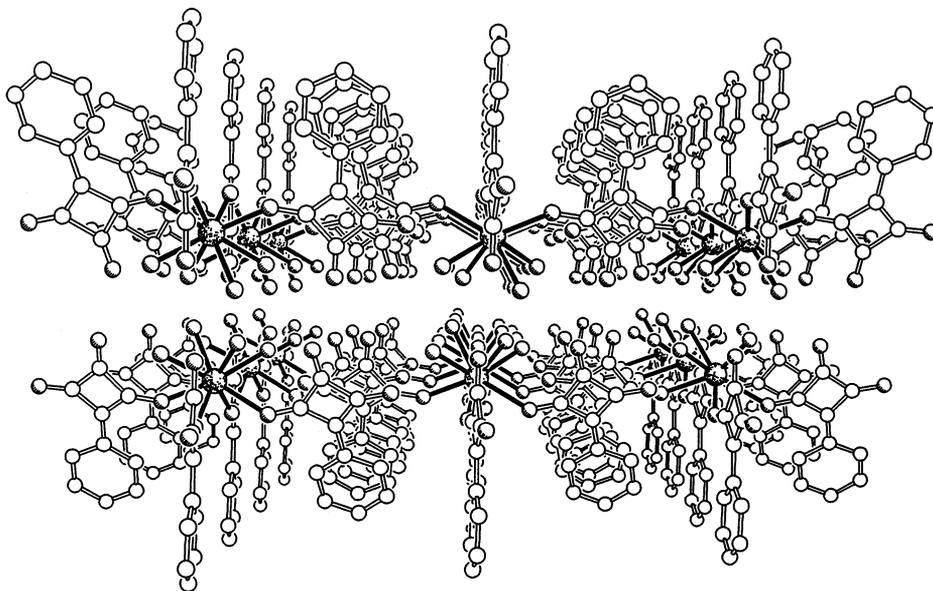


Fig. 7. The back-to-back packing of the interleaved and hydrogen-bonded sheets present in the structure of **3**. The sheets are cross-linked by O–H···O hydrogen bonds between O(33) in one sheet and O(35) in the next and between O(34) in one sheet and O(2) in the other [O···O, H···O (Å), O–H···O (°): 2.79, 1.93, 159 and 2.92, 2.14, 145 respectively] (see Fig. 5 for numbering scheme).

hydrogen bond is to the ketonic oxygen O(13) of an adjacent chain [O···O, H···O, 2.84, 1.95 Å; O–H···O 175°], whilst the inter-sheet linkage is to the ketonic oxygen O(22) of an adjacent sheet [O···O, H···O, 2.88, 2.06 Å; O–H···O 150°].

4. Conclusions

The unpredictability of the complexing behaviour of monosubstituted squarate ligands has again been demonstrated with the formation of a simple monomer with Ru(dmsO)₄Cl₂, and polymers with terbium and gadolinium, whereas with platinum only a hydrogen-bonded salt resulted. This study, however, has provided further insight into the factors that must be taken into consideration when attempting to engineer specific crystal architectures. The platinum compound described here shows that monosubstituted squarate ligands that exist as resonance-stabilised anions in polar solvents can react to form salts in the presence of stable cationic species. Additionally, because these ligands appear to have only medium field strengths, replacement of stronger ligands from reactants such as Ru(dmsO)₄Cl₂ will tend to be inhibited and polymerisation will be prevented.

However, in spite of the fact that no polymeric species were produced with ruthenium(II), the formation of a monomeric complex with ruthenium–halogen and ruthenium–sulfoxide linkages provides a useful prototype for the synthesis of monomers with other monosubstituted squarate ligands. This result now expands the range of compounds that can be synthesised

and explored for their potential as, for example, antitumour agents.

The formation of polymeric species with gadolinium and terbium suggests that, as observed previously with europium phenylsquarate [1g], the steric demand of the phenyl substituent, which is almost invariably coplanar with the C₄-ring, does not hinder polymer formation with the lanthanides.

5. Supplementary material

X-ray crystallographic files, in CIF format, containing data for the structures of **1–3** are available free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336; e-mail: deposit@ccdc.cam.ac.uk).

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