

Synthesis and structural characterisation of Group I and II metal complexes involving the ligand tris(2-pyridylmethyl)amine

Alan Hazell,^a John McGinley^{*b} and Hans Toftlund^b

^a Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark

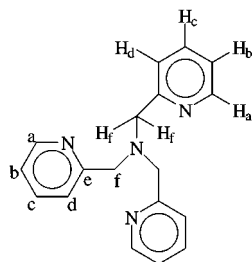
^b Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark.
E-mail: jgm@chem.ou.dk

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The first successful crystallisation and structure characterisation of protonated tris(2-pyridylmethyl)amine (TPA), $[H_3TPA][SO_4][NO_3]$, has been achieved. The reaction of the ligand with Group I and II metal salts led to the formation of either 1:1 or 1:2 metal to ligand complexes. One such 1:2 complex, $[Ca(TPA)_2][ClO_4]_2$ **2**, has been structurally characterised. The ionic radius of the metal can be used in predicting the solid state structure of the complexes resulting from reactions involving metal salts and this ligand. If the ionic radius of the metal ion is greater than 0.9 Å, then the preferentially formed complex will have a metal to ligand ratio of 1:2.

Introduction

Tripodal ligands have been applied extensively to the synthesis of metal complexes for several reasons, including their ease of preparation, the predictable changes in their physical properties with modification in ligand and the wealth of spectroscopic and X-ray crystallographic data obtainable. Transition metal complexes containing polypyridyl ligands have received and continue to receive considerable attention because of their potential applications to the fields of photoinitiated energy transfer, redox catalysis and bioinorganic chemistry. Consequently, the spectroscopic, photochemical and electrochemical properties of a large number of polypyridyl complexes have been studied in detail.^{1–16} Tris(2-pyridylmethyl)amine (TPA) is a versatile, potentially tetradentate ligand containing pyridyl groups and has been used to investigate the co-ordination chemistry of a wide variety of transition metal ions, since it was first reported in 1967 by Anderegg and Wenk.¹⁷ Because it has many potential co-ordination modes, TPA can confer certain geometries on metal complexes containing it, generally favouring symmetrical structures. Two types of co-ordination geometry have been generally observed: one in which the ligand is part of a co-ordination configuration that has a C_3 symmetry axis, exemplified by trigonal bipyramidal metal ion complexes of TPA,⁹ and one in which the ligand spans a meridional plane of the co-ordination sphere, as observed in octahedral metal ion complexes of TPA.^{1,2}



In the case of the alkali metals, tris(2-pyridylalkyl)amines have been shown to react with sodium, lithium and potassium ions. Toftlund and Ishiguro¹⁸ prepared a sodium complex of TPA and found it to be a 1:2 metal:TPA complex. They also showed that an acetonitrile solution of the 1:2 complex

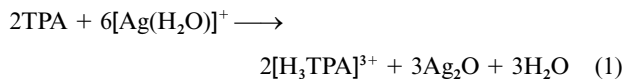
contained an equilibrium between the $Na(TPA)_2^+$ ion, the 1:1 $Na(TPA)^+$ ion and free TPA. Although they were unable structurally to characterise the 1:2 complex, they suggested that the sodium would achieve eight-co-ordination with a rhombohedral geometry and that a twisting of all six pyridyl rings would place H_d directly above the pyridine planes of the opposing ligand. A recent publication by Bebout *et al.*¹⁶ describes a mercury perchlorate complex of TPA, where two TPA units are bound to each mercury atom, giving a structure similar to that suggested previously for the sodium case.¹⁸ The structure of the lithium iodide complex¹⁹ with TPA has a trigonal bipyramidal geometry with the three pyridyl nitrogen donor atoms forming the equatorial plane about the lithium atom, and the amine nitrogen and iodine placed on the axis. The ethyl derivative of the ligand, tris(2-pyridylethyl)amine, shows a greater selectivity for lithium than for sodium.²⁰ This significant selectivity for lithium over sodium is not very common²¹ and has resulted in these complexes being tested as neutral carriers in the preparation of lithium selective electrodes or molecular sensors.

Despite the considerable interest in these compounds, work has concentrated on the complexes formed with only a few elements of Group I and II. We now report the synthesis and characterisation of the remaining important Group I and II metal complexes with TPA and also the conclusions which we have drawn regarding the prediction of the structure of the complex formed based on the ionic radius of the metal.

Results

Synthesis

The reaction of TPA with metal salts leads, in general, to the formation of metal-TPA complexes. Thus, the reaction of silver nitrate with TPA in acetonitrile was unusual in that, instead of the expected silver complex, the protonated ligand was isolated as crystals with the composition $[H_3TPA][SO_4][NO_3]$ **1** (the structure will be discussed in more detail later). While the presence of the nitrate anion can easily be rationalised, the presence of the sulfate anion is not so easily accounted for. As can be seen in the Experimental section, silver oxide precipitated when the acetonitrile solution was allowed to stand for several hours, indicating that hydrolysis had occurred, eqn. (1). This then



would leave a surplus of nitrate ions. The presence of the sulfate ion was explained by the realisation that sodium sulfate was used as a drying reagent during the preparation of the initial TPA ligand. Evidently, some of the drying agent formed a complex with the TPA ligand and got transferred to this reaction. Repeating the ligand synthesis using magnesium sulfate as drying agent also resulted in the complexation of the metal salt. Compound **1** could be synthesized directly by the reaction of TPA with nitric and sulfuric acids in water. Furthermore, repeating the reaction between TPA and silver nitrate in a water–acetonitrile solvent system yielded the expected silver–TPA complex.²²

In a previous paper on the reaction of TPA with sodium we have shown that there exists in solution an equilibrium between the free TPA and the $\text{Na}(\text{TPA})^+$ and $\text{Na}(\text{TPA})_2^+$ ions, with the precipitated solid containing the $\text{Na}(\text{TPA})_2^+$ ion only.¹⁸ The reaction of Group I and II metal salts with TPA, in a 1:2 molar ratio, resulted in all cases in solids precipitating, except in the case of magnesium perchlorate, which gave an oil. The electrospray mass spectrum of all the solids showed signals corresponding to either a 1:1 or a 1:2 metal:TPA or both complexes. It was always the 1:2 complexes that gave rise to signals for both species. In the case of the 1:1 complexes, signals were observed for both the “free” and complexed ligand. The observation of several signals for each metal complex was assumed to be due to breakdown of the complex under the electrospray conditions. The electrospray mass spectrum of the oil, obtained with magnesium perchlorate, showed the presence of free TPA as well as the anticipated 1:1 complex. Since magnesium, as lithium, favours five-co-ordination, the oily nature of the metal complex may result from the occupancy of the vacant co-ordination site by a water molecule from the solvent or the perchlorate anion. To overcome this problem it was decided to replace the perchlorate anion by a better co-ordinating anion, like thiocyanate. Redissolving the oil in water and adding one equivalent of ammonium thiocyanate in water resulted in a white solid precipitating. The electrospray mass spectrum of the solid showed the presence of both $\text{Mg}(\text{TPA})(\text{NCS})^+$ and $\text{Mg}(\text{TPA})(\text{ClO}_4)^+$ cations while the infrared spectrum showed the presence of a single sharp peak at 2083 cm^{-1} , indicative of an N-co-ordinated thiocyanate group. Microanalysis confirmed that the solid was the complex $[\text{Mg}(\text{TPA})(\text{NCS})][\text{ClO}_4]$.

Crystallography

The structures of $[\text{H}_3\text{TPA}][\text{SO}_4][\text{NO}_3]$ **1** and $[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$ **2** are reported herein. Selected bond distances and bond angles are given in Table 1. Thermal ellipsoid plots, with labelling, are shown in Figs. 1, 2 and 3.

Crystal structure of $[\text{H}_3\text{TPA}][\text{SO}_4][\text{NO}_3]$. The salt **1** crystallises in the cubic space group $P2_13$ with four formula units per cell so that the cation and both of the anions must lie on three-fold axes (Fig. 1). Although there are many examples of crystal structures of complexes containing the TPA ligand in the literature, this is the first structural characterisation of the protonated TPA ligand. The bond lengths and angles in the protonated ligand are very similar to those found in the previously reported metal complexes.^{1,5–8,11–13,16,19,23–29} However, the $\text{C}-\text{N}_{\text{py}}-\text{C}$ bond angle in the pyridine ring is about 5° larger than that found in most reported metal complexes. This is probably due to the lack of geometrical constraint, such as either octahedral or trigonal bipyramidal geometry, as a result of the absence of a metal centre. Indeed, in the case of $[\text{Fe}(\text{TPA})_2][\text{SO}_3\text{CF}_3]_2$,⁶ where one pyridyl arm of each TPA is not co-

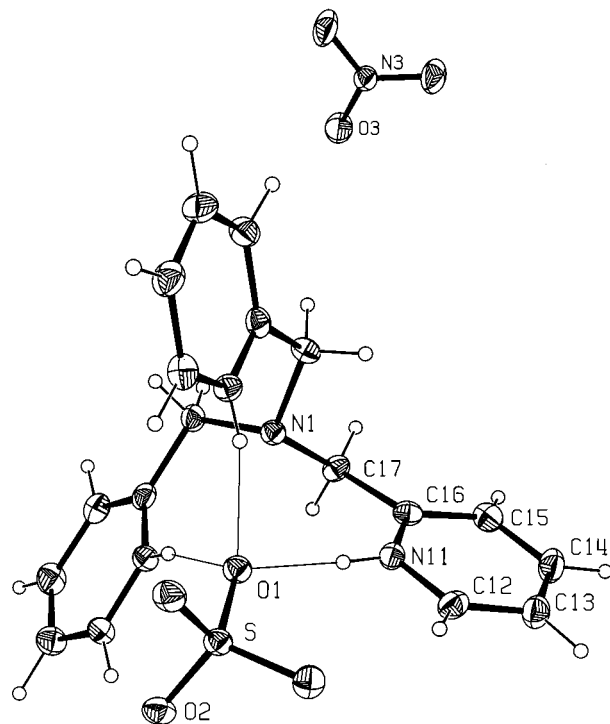


Fig. 1 Perspective drawing of $[\text{H}_3\text{TPA}][\text{SO}_4][\text{NO}_3]$ **1** showing the atomic numbering. Thermal ellipsoids are drawn at 50% probability level, hydrogen atoms are represented by open circles of arbitrary size.

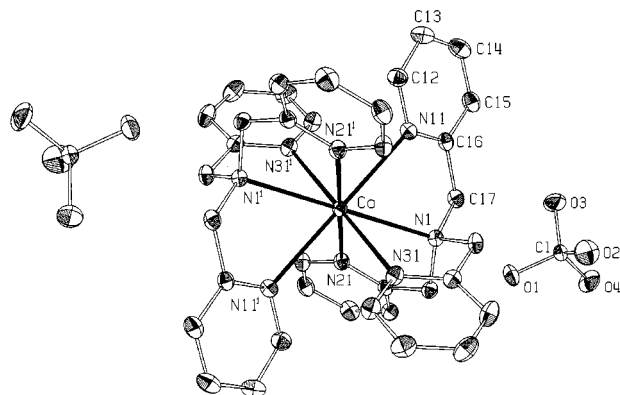


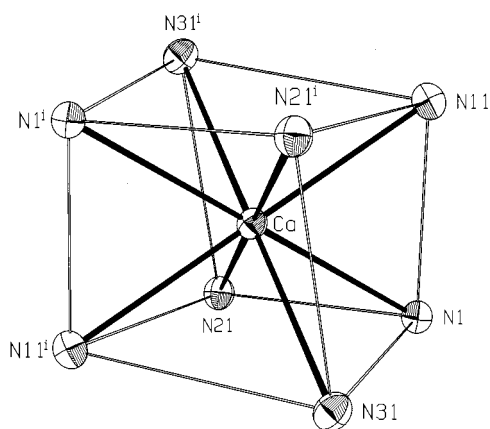
Fig. 2 Perspective drawing of $[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$ **2** showing the atomic numbering. Thermal ellipsoids are drawn at 50% probability level. Symmetry code: $i - x, -y, 1 - z$.

ordinated and where a difference in the $\text{C}-\text{N}_{\text{py}}-\text{C}$ bond angle between the bound and free pyridyl rings may be observed, this difference is quite small ($<1^\circ$). The pyridine nitrogen atoms are all hydrogen bonded to one oxygen atom of the sulfate anion [$\text{N}-\text{H}$ 0.81(3), $\text{O}\cdots\text{H}$ 1.91(3) Å, $\text{N}-\text{H}\cdots\text{O}$ 166(3) $^\circ$]. The $\text{S}-\text{O}$ bond distance for this oxygen atom [1.524(1) Å] is significantly longer than that [1.471(1) Å] of the other $\text{S}-\text{O}$ distances.

Crystal structure of $[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$. The salt **2** crystallises in the monoclinic space group $P2_1/n$ with two formula units in the cell so that the cation possesses an exact centre of symmetry (Fig. 2). The structure of the dication $[\text{Ca}(\text{TPA})_2]^{2+}$ shows an eight-co-ordinated calcium ion at the centre of a distorted cube (Fig. 3), in which the eight ligating nitrogen atoms of two different ligand molecules occupy the corner positions with interligand $\text{N}\cdots\text{N}$ distances of 3.192(2)–3.244(3) Å and intra-ligand $\text{N}\cdots\text{N}$ distances of 2.746(2)–2.788(2) Å and $\text{N}-\text{N}-\text{N}$ angles of 77.87(4)–94.49(4) $^\circ$. The stereochemistry of the six pyridyl nitrogens can also be described as forming the corners of a distorted octahedron (flattened by 12.9 $^\circ$) such that the

Table 1 Selected bond distances (Å) and bond angles (°) in $[\text{H}_3\text{TPA}][\text{SO}_4][\text{NO}_3]$ and $[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$

$[\text{H}_3\text{TPA}][\text{SO}_4][\text{NO}_3]$		$[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$					
N1–C17	1.477(2)	N–C(a) _{av}	1.347(2)	N1–Ca–N11	64.03(3)	N21–Ca–N31	102.29(4)
N11–C12	1.344(3)	N–C(e) _{av}	1.347(2)	N1–Ca–N21	64.80(3)	N11–Ca–N21 ⁱ	76.99(3)
N11–C16	1.343(3)	N–C(f) _{av}	1.474(2)	N1–Ca–N31	64.88(3)	N11–Ca–N31 ⁱ	76.59(3)
N11–HN11	0.81(3)	Ca–N1	2.603(1)	N1–Ca–N11 ⁱ	115.97(3)	N21–Ca–N31 ⁱ	77.71(4)
C(a) _{av} –N–C(e) _{av}	123.9(2)	Ca–N11	2.576(1)	N1–Ca–N21 ⁱ	115.20(3)	Ca–N–C(f) _{av}	109.23(7)
N–H···O	166.4(26)	Ca–N21	2.595(1)	N1–Ca–N31 ⁱ	115.12(3)	Ca–N–C(a) _{av}	123.57(8)
		Ca–N31	2.577(1)	N11–Ca–N21	103.01(3)	Ca–N–C(e) _{av}	117.87(8)
				N11–Ca–N31	103.41(3)	C(a) _{av} –N–C(e) _{av}	117.5(1)

**Fig. 3** The co-ordination polyhedron round the calcium atom in $[\text{Ca}(\text{TPA})_2][\text{ClO}_4]_2$.

N–Ca–N angles made by the pyridyl nitrogens on the same TPA molecule average 102.9° while those made by the *cis* pyridyl nitrogens on different TPA molecules average 77.1° . The amines then cap opposite faces of this distorted octahedron. These values correspond quite favourably with those reported for the manganese, mercury and iron complexes, $[\text{Mn}(\text{TPA})_2][\text{ClO}_4]_2$,⁷ $[\text{Hg}(\text{TPA})_2][\text{ClO}_4]_2$,¹⁶ and $[\text{Fe}(\text{TPA})_2][\text{BPh}_4]_2$.⁶ In fact, the calcium complex is isostructural with these three complexes, despite the iron complex having a different counter anion. The Ca–N_{amine} bond distance is slightly longer than the average Ca–N_{pyridyl} bond distance, the difference being 0.02 Å. The calcium–nitrogen bond distances of 2.576(1), 2.577(1), 2.595(1) and 2.603(1) Å are within the range (2.530–2.608 Å) reported for the two other eight-co-ordinate CaN_8 complexes in the literature, tetrakis(ethylenediamine)calcium(II) dibromide³⁰ and tetrakis(1,10-phenanthroline)calcium(II) diiodide.³¹ In both of those cases, the calcium ion is surrounded by four bidentate nitrogen donor ligands, either ethylenediamine or 1,10-phenanthroline, rather than the tetradentate ligands as used here. The average Ca–N distance for all three compounds is 2.58 Å which is, as expected, considerably longer than the value of 2.44 Å found for octahedrally co-ordinated CaN_6 complexes (average of the values of eight complexes found in the Cambridge Structural Database).³² Since the calcium ion is positioned in the centre of symmetry, all the N–Ca–N *trans* bond angles are 180° .

NMR Spectroscopy

The ^1H and ^{13}C NMR spectra were recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature for each of the complexes. The proton spectrum of the TPA ligand itself shows resonance signals similar to those observed for the calcium complex, for which the structure in the solid state was determined, and also to those of other metal complexes. When the shifts for TPA in $(\text{CD}_3)_2\text{SO}$ are compared to those in either CD_3CN or CD_2Cl_2 ,^{16,23} it becomes quite clear that the shifts are not in similar positions, despite possible differences due to different solvent systems. These shifts can only be due to a bound metal since the shift

positions for metal complexes in all three solvents are very similar. Repeating the synthesis of the ligand using magnesium sulfate as drying agent gave similar NMR results to those obtained when using sodium sulfate. The ^1H NMR spectrum of the protonated TPA ligand **1** is quite different from that of the non-protonated ligand. The signals are all shifted downfield as a consequence of the presence of the extra protons, which show up at δ 9.23. This signal is in a similar position as that observed for the complex $[\text{H}_3\text{TPA}][\text{ClO}_4]_3$.² All the acidic protons reside on the pyridyl nitrogens, even though it might be expected that at least one should be located on the amine nitrogen, since the pyridyl nitrogens are usually less basic than the amine nitrogen. The $\text{p}K_a$ values for the pyridyl nitrogens, as determined by Anderegg *et al.*,³³ are 6.17, 4.35 and 2.55 while that of the amine nitrogen has not been determined. The fact that they all reside on the pyridyl nitrogens substantiates the claim of Anderegg *et al.* which was solely based on kinetic results. It should be mentioned that the cationic $\text{H}_4\text{TPA}^{4+}$, where all the nitrogens are protonated, has never been observed, even under strongly acidic conditions.

For the ^1H NMR spectra of the metal complexes, the general trend is for a downfield shift of the resonances when compared to those of the “free” ligand. This phenomenon is most pronounced for the methylene protons (H_f) and those occupying the 6 position (H_a) of the pyridine rings. The remaining protons appear to behave similarly, although the chemical shift differences are not as large. The changes in chemical shift observed for the methylene and pyridine- H_a protons result, presumably, from their proximity to the nitrogen donor atoms; these protons would be expected to experience the strongest σ -donation effects. The number of pyridine and methylene peaks observed shows that the TPA ligand effectively maintains the threefold symmetry in solution, suggesting that all the pyridyl rings remain bound to the metal. If one of the rings were no longer bound, extra resonances would be expected in the ^1H NMR spectrum. There are no significant shifts in the resonances in the ^{13}C spectra compared to that of the ligand itself in the same deuterated solvent.

Structure prediction

On the basis of all available data for TPA complexes, summarised in Table 2, we suggest that the ionic radius of any metal can be used to predict the solid state product of the reaction between TPA and that metal. Since the ionic radius is either known for most oxidation states or can be calculated,³⁴ this could obviously be a very useful tool for predicting the geometry and structure of the products. The possibility of the formation of metal complexes with different stoichiometries in solution has to be considered, but no attempt to predict the nature of these solution structures was undertaken. We are here only concerned with the solid state structure of the complex. The data in Table 2 show the metal ions which have been used in either the recent structural determinations or earlier preparations involving the ligand TPA. We suggest that any metal which has an ionic radius greater than approximately 0.9 Å will be able to form a complex with a metal to ligand ratio of 1:2 with TPA. Some first row transition metals in oxidation

Table 2 Ionic radius *versus* the metal to ligand ratio

Metal ion	Ionic radius ^a /Å	Metal to ligand ratio	Ref.
V ⁴⁺	0.60	1:1	1
Fe ³⁺	0.69 ^{b,c}	1:1	5
Cu ²⁺	0.71	1:1	40
Mg ²⁺	0.71	1:1	This work
Li ⁺	0.73	1:1	19
Zn ²⁺	0.74	1:1	13
Cu ⁺	0.74	1:1	23
Fe ²⁺	0.75 ^{b,c}	1:1/1:2	6
Co ³⁺	0.75 ^{b,c}	1:1	2
Ga ³⁺	0.76 ^b	1:1	Unpublished results
Re ⁴⁺	0.77 ^b	1:1	28
Fe ³⁺	0.79 ^{b,d}	1:1	5
Rh ³⁺	0.81 ^b	1:1	27
Ni ²⁺	0.83 ^b	1:1	8
Co ²⁺	0.89 ^{b,c}	1:1	33
Fe ²⁺	0.92 ^{b,d}	1:1/1:2	6
Cd ²⁺	0.92	1:1	26
Mn ²⁺	0.97 ^{b,d}	1:2	7
Ca ²⁺	1.26	1:2	This work
Hg ²⁺	1.28	1:2	16
Na ⁺	1.32	1:2	18
Sr ²⁺	1.40	1:2	This work
Pb ²⁺	1.43	1:2	Unpublished results
Ba ²⁺	1.56	1:2	This work
K ⁺	1.65	1:2	This work
Tl ⁺	1.73	1:2	Unpublished results
Rb ⁺	1.75	1:2	This work
Cs ⁺	1.88	1:2	This work

^a Values taken from ref. 35. ^b Value quoted is for a co-ordination number of 6. Otherwise, value is for four- (1:1) or eight-co-ordinate (1:2) complex. ^c Value for low-spin complex. ^d Value for high-spin complex.

state II (iron and cobalt) can form both high- and low-spin states. This results in a difference in ionic radius of the metal ion with the radius changing from 0.92 Å in the high-spin state to 0.75 Å in the low-spin state for iron(II) and changing from 0.97 Å in the high-spin case to 0.81 Å in the case of manganese(II). The low spin manganese should predictably be 1:1, if this complex could be prepared. It should be noted that these values are only for six-co-ordinate metal ions whereas the complexes would make both metal ions eight-co-ordinate. It is also known that the ionic radius of a metal increases with increased co-ordination number. It is interesting that iron(III) follows the rule, despite the fact that it too can have either high- or low-spin states. Since it has ionic radii of 0.69 and 0.79 Å for the low- and high-spin states with a co-ordination number of six in each case, the iron(III) ion should always give a metal to ligand ratio of 1:1, even allowing for the increase in ionic size due to the expected increase in co-ordination number to eight. The 1:1 nature of the iron(III) complexes has been proven by several structure determinations.^{5,24,25}

Bearing this value of 0.9 Å in mind, we would expect that reactions between the TPA ligand and the Group I and II metal ions would give a 1:1 metal to ligand complex in the case of magnesium (0.71 Å), and a 1:2 metal to ligand complex in the cases of potassium (1.65 Å), rubidium (1.75 Å), caesium (1.88 Å), calcium (1.26 Å), strontium (1.40 Å) and barium (1.56 Å). The values in parentheses are the ionic radii for each metal ion for a co-ordination number of either four or eight. We found, from the analyses of the complexes obtained, that we do indeed get a 1:1 complex with the magnesium ion and 1:2 complexes in all other cases. This is conclusively proven in the case of the calcium ion where the X-ray structural study was undertaken. Furthermore, the charge of the metal ion appears to be less important than the actual size of the metal ion. We would expect the main group metals will also follow this behaviour and this is currently being investigated, as well as replacing one

or more pyridine rings on the TPA ligand by alkylamines and observing how this effects the co-ordination chemistry.²²

Experimental

Methods and materials

All starting materials were of commercially available reagent quality and used without further purification. All of the perchlorate salts included in this work were stable for routine synthesis and purification techniques. However, **CAUTION** should be exercised because perchlorate salts of metal complexes with organic ligands are potentially explosive. The IR spectra as solids in KBr discs were measured using a Hitachi 270–30 spectrometer, NMR spectra on a Bruker AC 250 FT spectrometer. Electrospray (ES) mass spectra were obtained using a Finnigan TSQ 710 instrument with a combined electrospray and atmospheric pressure chemical ionisation source, fast atom bombardment (FAB) mass spectra on a KRATOS MS50TC. Elemental analyses were performed at the micro-analytical laboratory of the H. C. Ørsted Institute, Copenhagen.

Syntheses

Tris(2-pyridylmethyl)amine (TPA). The ligand TPA was prepared using a variation of the procedure described by Toftlund and Ishiguro.¹⁸

[H₃TPA][SO₄][NO₃]. To a stirred solution of TPA (500 mg, 1.72 mmol) in 10 cm³ acetonitrile was added nitric acid (4 M, 1.72 mmol) in 5 cm³ deionised water and sulfuric acid (2 M, 1.72 mmol) in 5 cm³ deionised water. Stirring was continued for 30 min. The solution was then left to stand. Over several days the product was deposited as a white, microcrystalline solid. It was collected and dried in the air (90% yield) (Found: C, 47.91; H, 4.55; N, 15.64. Calc. for C₁₈H₂₁N₅O₇S: C, 47.89; H, 4.69; N, 15.51%). ESMS: *m/z* 290.9 (TPA⁺, 100%). ¹H NMR (d₆-DMSO): δ 9.21 (br, 3 H), 8.78 (d, 3 H, *J* = 4, H_a), 8.29 (t, 3 H, *J* = 8, H_c), 7.90 (d, 3 H, *J* = 8, H_d), 7.76 (t, 3 H, *J* = 6 Hz, H_b) and 4.28 (s, 6 H, H_f). ¹³C NMR (d₆-DMSO): δ 153.79 (C_e), 144.30 (C_a), 143.98 (C_c), 126.31 (C_d), 125.37 (C_b) and 56.56 (C_f). This salt was also obtained from Na₂SO₄-contaminated TPA (100 mg, 0.34 mmol) in 10 cm³ acetonitrile by addition to a stirred solution of AgNO₃ (115 mg, 0.68 mmol) in 20 cm³ acetonitrile. A clear solution resulted immediately. Stirring was continued for 30 min. The solution was then left to stand. On standing a black material precipitated. This material was removed by filtration and the filtrate allowed to stand for several days. A colourless, microcrystalline material crystallised from the solution. The crystals were collected and dried in the air (35% yield). The X-ray crystallographic study revealed that the compound was the protonated TPA ligand with sulfate and nitrate as counter anions (Found: C, 48.01; H, 4.65; N, 15.84%). ESMS: *m/z* 290.9 (TPA⁺, 100%). ¹H NMR (d₆-DMSO): δ 9.23 (br, 3 H), 8.81 (d, 3 H, *J* = 4, H_a), 8.31 (t, 3 H, *J* = 8, H_c), 7.92 (d, 3 H, *J* = 8, H_d), 7.78 (t, 3 H, *J* = 6 Hz, H_b) and 4.30 (s, 6 H, H_f). ¹³C NMR (d₆-DMSO): δ 153.75 (C_e), 144.34 (C_a), 143.93 (C_c), 126.36 (C_d), 125.32 (C_b) and 56.60 (C_f).

[Cs(TPA)₂]⁺II. The compound TPA (500 mg, 1.72 mmol) in 10 cm³ acetonitrile was added to a stirred solution of CsI (223 mg, 0.85 mmol) in 30 cm³ deionised water. Stirring was continued for 30 min. The solution was then left to stand. Over several hours the product was deposited as a pale yellow-white, microcrystalline solid. It was collected and dried in the air (84% yield) (Found: C, 51.80; H, 4.86; N, 13.94. Calc. for C₃₆H₃₆CsIN₈: C, 51.44; H, 4.32; N, 13.33%). ESMS: *m/z* 291.1 (TPA⁺, 100), 422.9 [Cs(TPA)⁺, 40] and 713.3 [Cs(TPA)₂⁺, 15%]. ¹H NMR (d₆-DMSO): δ 8.48 (d, 6 H, *J* = 4, H_a), 7.75 (t, 6 H, *J* = 8, H_c), 7.58 (d, 6 H, *J* = 8, H_d), 7.23 (t, 6 H, *J* = 6 Hz, H_b) and 3.76 (s, 12 H, H_f). ¹³C NMR (d₆-DMSO): δ 159.16 (C_e), 149.07 (C_a), 136.84 (C_c), 122.74 (C_d), 122.38 (C_b) and 59.42 (C_f).

[Ca(TPA)₂][ClO₄]₂. The compound TPA (500 mg, 1.72 mmol) in 10 cm³ acetonitrile was added to a stirred solution of Ca(ClO₄)₂·4H₂O (267 mg, 0.86 mmol) in 30 cm³ deionised water. Stirring was continued for 30 min. The solution was then left to stand. Over several hours the product was deposited as white prismatic crystals. The crystals were collected and dried in the air (88% yield) (Found: C, 52.74; H, 4.28; N, 13.58. Calc. for C₃₆H₃₆CaCl₂N₈O₈: C, 52.74; H, 4.39; N, 13.67%). ESMS: *m/z* 310.6 [Ca(TPA)₂²⁺, 100] and 719.3 [Ca(TPA)₂(ClO₄)⁺, 50%]. ¹H NMR (d₆-DMSO): δ 8.49 (d, 6 H, *J* = 4, H_a), 7.77 (t, 6 H, *J* = 8, H_c), 7.59 (d, 6 H, *J* = 8, H_d), 7.25 (t, 6 H, *J* = 6 Hz, H_b) and 3.78 (s, 12 H, H_f). ¹³C NMR (d₆-DMSO): δ 159.64 (C_e), 149.63 (C_a), 137.42 (C_c), 123.31 (C_d), 122.92 (C_b) and 59.93 (C_f).

The following complexes were synthesized using a similar procedure to that above.

[Rb(TPA)₂]⁺ClO₄⁻. White solid (85% yield) (Found: C, 54.87; H, 4.86; N, 14.63. Calc. for C₃₆H₃₆IN₈Rb: C, 54.52; H, 4.58; N, 14.13%). ESMS: *m/z* 291.1 (TPA⁺, 15), 375.0 [Rb(TPA)⁺, 100] and 665.2 [Rb(TPA)₂²⁺, 20%]. ¹H NMR (d₆-DMSO): δ 8.49 (d, 6 H, *J* = 4, H_a), 7.76 (t, 6 H, *J* = 8, H_c), 7.58 (d, 6 H, *J* = 8, H_d), 7.24 (t, 6 H, *J* = 6 Hz, H_b) and 3.77 (s, 12 H, H_f). ¹³C NMR (d₆-DMSO): δ 159.12 (C_e), 149.00 (C_a), 136.73 (C_c), 122.66 (C_d), 122.28 (C_b) and 59.37 (C_f).

[Sr(TPA)₂][ClO₄]₂. White solid (85% yield) (Found: C, 49.86; H, 4.02; N, 12.88. Calc. for C₃₆H₃₆Cl₂N₈O₈Sr: C, 49.86; H, 4.18; N, 12.92%). ESMS: *m/z* 334.1 [Sr(TPA)₂²⁺, 100] and 767.3 [Sr(TPA)₂(ClO₄)⁺, 20%]. ¹H NMR (d₆-DMSO): δ 8.48 (d, 6 H, *J* = 4, H_a), 7.76 (t, 6 H, *J* = 8, H_c), 7.56 (d, 6 H, *J* = 8, H_d), 7.24 (t, 6 H, *J* = 6 Hz, H_b) and 3.78 (s, 12 H, H_f). ¹³C NMR (d₆-DMSO): δ 158.97 (C_e), 149.00 (C_a), 136.78 (C_c), 122.69 (C_d), 122.28 (C_b) and 59.46 (C_f).

[Ba(TPA)₂][ClO₄]₂. White solid (89% yield) (Found: C, 47.17; H, 4.09; N, 12.76. Calc. for C₃₆H₃₆BaCl₂N₈O₈: C, 47.16; H, 3.96; N, 12.22%). ESMS: *m/z* 291.1 (TPA⁺, 100), 359.0 [Ba(TPA)₂²⁺, 20%], 527.0 [Ba(TPA)(ClO₄)⁺, 40] and 817.1 [Ba(TPA)₂(ClO₄)⁺, 15%]. ¹H NMR (d₆-DMSO): δ 8.48 (d, 6 H, *J* = 4, H_a), 7.78 (t, 6 H, *J* = 8, H_c), 7.57 (d, 6 H, *J* = 8, H_d), 7.24 (t, 6 H, *J* = 6 Hz, H_b) and 3.78 (s, 12 H, H_f). ¹³C NMR (d₆-DMSO): δ 158.99 (C_e), 149.00 (C_a), 136.75 (C_c), 122.69 (C_d), 122.26 (C_b) and 59.42 (C_f).

[Mg(TPA)(NCS)]ClO₄. The compound TPA (500 mg, 1.72 mmol) in 10 cm³ acetonitrile was added to a stirred solution of Mg(ClO₄)₂·6H₂O (190 mg, 0.85 mmol) in 30 cm³ deionised water. Stirring was continued for 30 min. The solution was then left to stand. Over several days a pale yellow oil resulted. The oil was redissolved in water and an aqueous solution of NH₄SCN added. The resulting suspension was stirred for an hour. The white, microcrystalline solid was collected and dried in the air (89% yield) (Found: C, 48.69; H, 3.99; N, 14.61. Calc. for C₁₉H₁₈ClMgN₅O₄S: C, 48.33; H, 3.84; N, 14.83%). ESMS: *m/z* 291.0 (TPA⁺, 30), 371.9 [Mg(TPA)(NCS)⁺, 20] and 414.2 [Mg(TPA)(ClO₄)⁺, 20%]. ¹H NMR (d₆-DMSO): δ 8.49 (d, 3 H, *J* = 4, H_a), 7.75 (t, 3 H, *J* = 8, H_c), 7.58 (d, 3 H, *J* = 8, H_d), 7.24 (t, 3 H, *J* = 6 Hz, H_b) and 3.76 (s, 6 H, H_f). ¹³C NMR (d₆-DMSO): δ 159.22 (C_e), 149.11 (C_a), 136.91 (C_c), 122.81 (C_d), 122.45 (C_b) and 59.49 (C_f).

X-Ray crystallography

Colourless, plate-like crystals of salt **1** were grown by slow evaporation of the filtrate after removal of the black material. White, prismatic crystals of **2** were precipitated directly from the reaction mixture.

Crystal data for salt 1. C₁₈H₂₁N₅O₇S, *M* = 451.453, cubic, space group = *P*2₁3 (no. 198), *a* = 12.6301(4) Å, *U* = 2014.8(1)

Å³, *T* = 120 K, *Z* = 4, $\mu(\text{Mo-K}\alpha) = 0.214 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 11037 reflections measured, 1382 unique ($R_{\text{int}} = 0.037$), $R1 = 0.035$ and $wR(F^2) = 0.050$ for 1346 reflections with $I > 3\sigma(I)$ and 124 parameters. A crystal of approximate dimensions $0.42 \times 0.40 \times 0.14 \text{ mm}$ was used for data collection.

Crystal data for salt 2. C₃₆H₃₆CaCl₂N₈O₈, *M* = 819.715, monoclinic, space group = *P*2₁/*n* (no. 14), *a* = 9.7069(5), *b* = 10.8978(5), *c* = 18.3622(9) Å, $\beta = 103.411(1)^\circ$, *U* = 1889.5(1) Å³, *T* = 120 K, *Z* = 2, $\mu(\text{Mo-K}\alpha) = 0.370 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 12025 reflections measured, 4561 unique ($R_{\text{int}} = 0.026$), $R1 = 0.029$ and $wR(F^2) = 0.051$ for 3903 reflections with $I > 3\sigma(I)$ and 251 parameters. A crystal of approximate dimensions $0.36 \times 0.32 \times 0.26 \text{ mm}$ was used for data collection.

Crystals were mounted on a Siemens SMART CCD single crystal diffractometer and cooled to 120 K by a stream of cold dry nitrogen.³⁵ A hemisphere of data was collected using ω scans and graphite monochromatised radiation. Intensities were corrected for Lorentz-polarisation and absorption effects. The structures were solved by direct methods³⁶ and refined by the full-matrix least-squares method on *F*. All non-hydrogen atoms were refined anisotropically; for salt **1** hydrogen atoms were refined isotropically, for **2** hydrogen atoms were kept fixed in calculated positions (C–H 0.95 Å) with *U*_{iso} 20% larger than *U*_{eq} for the atom to which they were attached. Programs used were SMART, SAINT and XPREP³⁷ for data collection and processing, other programs were from the KRYSTAL³⁸ package. Atomic scattering factors and anomalous dispersion corrections were from ref. 39.

CCDC reference number 186/1352.

See <http://www.rsc.org/suppdata/dt/1999/1271/> for crystallographic files in .cif format.

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