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FULL PAPER

Theoretical and experimental studies of the protonated terpyridine cation. *Ab initio* quantum mechanics calculations, and crystal structures of two different ion pairs formed between protonated terpyridine cations and nitratolanthanate(III) anions †

Michael G. B. Drew,*[a] Michael J. Hudson,[a] Peter B. Iveson,[a] Mark L. Russell,[a] Jan-Olov Liljenzin,[b] Mats Skålberg,[b] Lena Spjuth[b] and Charles Madic[c]

[a] *Department of Chemistry, University of Reading, PO Box 224, Whiteknights, Reading, UK RG6 6AD. E-Mail: m.g.b.drew@reading.ac.uk*
[b] *Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Goteborg, Sweden*
[c] *Commissariat à l'Energie Atomique, Direction du Cycle du Combustible, B.P. 171, 30207 Bagnols-sur-Cèze, Cedex, France*

Ab initio quantum mechanics calculations have been carried out on all possible conformations of the terpyridine ligand and its mono- and di-protonated forms. Results show that the lowest energy form of the ligand is when the N–C–C–N torsion angles are *trans* but that in the protonated forms, the *cis* arrangement is prevalent being stabilised by intramolecular N–H · · · N hydrogen bonds. Results are consistent with the experimental crystal structure data found in the literature and also with two crystal structures reported here in which two different ion pairs formed between protonated terpyridine cations and lanthanate(III) nitrate anions have been prepared and analysed structurally. Compound **1** consists of discrete diprotonated terpyridine cations and hexanitratolanthanate anions, namely $3[H_2terpy]^{2+}2[La(NO_3)_6]^{3-}\cdot 3H_2O$. Water molecules are present as hydrogen bond acceptors in the diprotonated terpyridyl cavities. Each lanthanum atom is 12-co-ordinate and the La–O bond lengths vary between 2.609(11) and 2.765(10) Å. Compound **2** consists of a diprotonated $[H_2terpy]^{2+}$ cation together with a $[Sm(terpy)(NO_3)_4]^-$ anion, and a NO_3^- anion which is present as a hydrogen bond acceptor in the diprotonated terpyridyl cavity. The samarium atom is 11-co-ordinate, the Sm–O bond lengths vary between 2.494(5) and 2.742(5) Å while the Sm–N bond lengths vary between 2.626(4) and 2.650(5) Å.

Introduction

There is much current interest in the separation of lanthanide(III) and actinide(III) complexes by solvent extraction routes.[1] Various oligoamines have been shown to co-extract lanthanides and actinides from nitric acid solutions into an organic phase. Among these are the oligoamine ligands 2,4,6-tris(4-*tert*-butyl-2-pyridyl)-1,3,5-triazine[2] ligand L^1 and 2,2′ : 6′,2″-terpyridine L^2. It is thought that the species extracted at low levels of acidity are simple metal co-ordination complexes, for which there is plenty of structural evidence.[3] It is clear that the lanthanides (and by implication the similarly sized actinides) can fit into the tridentate cavity of the terpyridyl moiety. Thus we have previously reported the structure of $Ce(NO_3)_4L^1$ (ref. 2) and in addition complexes of L^2 with lanthanides are well known [*e.g.* $LnCl_3(L^2)\cdot xH_2O$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or Y)].[4] For Ln = La–Nd, $x = 5$, for Ln = Tb–Lu, $x = 4$ and for Ln = Sm or Gd there are between four and five water molecules in the co-ordination sphere. Also isolated was a dimeric species in which the Sm is co-ordinated to three N atoms from L^2, two bridging and two terminal chloride anions and one water molecule.

Although direct co-ordination of the metal ions to the polyamine ligands is thought to be necessary for the selective extraction of actinides over the lanthanides, the need still remains to establish the nature of the species which may be formed at higher acid concentrations, especially those in which the lanthanide or actinide ion exists as an anion such as $[Ln(NO_3)_6]^{3-}$ or the $[LnL(NO_3)_4]^-$ ion-pair. It has been demonstrated that terpyridine-type ligands in synergistic combination with 2-bromodecanoic acid show some selectivity for An(III) over Ln(III) ions.[5] The species involved in these extractions are not known with any certainty.

We have adopted a theoretical and experimental approach to the identification of these species. We are using quantum mechanical methods to investigate the conformational preferences of the ligand and also the likely structures of the protonated forms. In addition we are trying to prepare solid complexes in order to provide evidence for the kind of species which is involved in this type of extraction.

In this paper we report the results from our quantum mechanical calculations and also the crystal structures of two different ion pairs of diprotonated terpyridine and anionic lanthanide nitrates (**1** and **2**) both of which contain free diprotonated terpyridine moieties unco-ordinated to a metal ion. The asymmetric unit of **1** contains three diprotonated terpyridyl cations, two hexanitratolanthanate(III) anions and three water molecules, $3[H_2L^2]^{2+}2[La(NO_3)_6]^{3-}\cdot 3H_2O$ while the asymmetric unit of **2** contains an $[(H_2L^2)(NO_3)]^+$ cation together with a $[SmL^2(NO_3)_4]^-$ anion.

Experimental

The compounds $Ln(NO_3)_3\cdot 6H_2O$ (99.99%), $Sm(NO_3)_3\cdot 6H_2O$ (99.99%) and 2,2′ : 6′,2″-terpyridine (L^2) (98%) were used as received from Aldrich. 2-Bromodecanoic acid (98%) was purchased from Fluka and used without further purification.

Preparation of complex 1

This compound was prepared from $[H_2L^2][NO_3]_2$ which was initially prepared as a solid: L^2 (0.25 g, 0.001 mol) was dissolved

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† *Non-SI unit employed*: cal = 4.184 J.

Table 1 Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Formula	$3[H_2L^2]^{2+}2[La(NO_3)_6]^{3-}\cdot 3H_2O$	$[(H_2L^2)(NO_3)]^+[Sm(L^2)(NO_3)_4]^-$
Empirical formula	$C_{45}H_{45}La_2N_{21}O_{39}$	$C_{30}H_{24}SmN_{11}O_{15}$
M	1781.84	928.95
T/K	293(2)	293(2)
λ/Å	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
a/Å	10.826(9)	17.29(2)
b/Å	30.00(2)	10.230(9)
c/Å	11.140(9)	20.31(2)
β/°	104.76(1)	106.53(1)
U/Å^3	3498(5)	3445(6)
Z, D_c/g cm^{-3}	2, 1.692	4, 1.791
μ/mm^{-1}	1.316	1.796
F(000)	1776	1852
Size/mm	0.2 × 0.2 × 0.5	0.25 × 0.25 × 0.20
θ Range/°	2.82 to 25.07	1.83 to 25.94
hkl Range	$0 \leqslant h \leqslant 11, -35 \leqslant k \leqslant 35, -13 \leqslant l \leqslant 12$	$0 \leqslant h \leqslant 21, -12 \leqslant k \leqslant 12, -24 \leqslant l \leqslant 23$
Reflections observed, R_{int}	8750, 0.0508	9872, 0.0289
Unique reflections	8570	5838
Weighting scheme a, b*	0.144, 35.48	0.181, 25.94
Reflections, parameters	8570, 965	5838, 515
Final indices [$I > 2\sigma(I)$] $R1$, $wR2$	0.0582, 0.1779	0.0352, 0.0971
All data $R1$, $wR2$	0.0657, 0.1901	0.0514, 0.1080
Largest difference peak, hole/e Å^{-3}	0.928, −1.615	1.116, −0.984

* Weighting scheme $w = 1/[2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

in methanol (1 ml). The addition of 69% AnalaR nitric acid (0.14 ml, 0.0022 mol) to a stirred solution of the ligand resulted in the formation of a precipitate (yield 82%).[6]

After the addition of methanol (2 ml), the solid was filtered off and dried under vacuum over calcium chloride. Then $[H_2L^2][NO_3]_2$ (0.05 g) was stirred for 10 min in acetonitrile (20 ml), heated to reflux and another solution containing $La(NO_3)_3\cdot 6H_2O$ (0.0498 g, 0.0001 mol) dissolved in acetonitrile (15 ml) at *ca.* 40 °C was added dropwise to the stirred ligand solution. After the addition, the solution was stirred for 10 min and then allowed to stand at ambient temperature. Crystals suitable for X-ray analysis were deposited overnight at room temperature, $3[H_2L^2]^{2+}2[La(NO_3)_6]^{3-}\cdot 3H_2O$ (Found: C, 30.1; H, 2.7; N, 16.2. Calc. for $C_{45}H_{45}La_2N_{21}O_{39}$: C, 30.3; H, 2.5; N, 16.5%).

Preparation of complex 2

A solution of $Sm(NO_3)_3\cdot 6H_2O$ (0.077 g, 0.0002 mol) in acetonitrile (5 ml) was heated to around 40 °C and then added dropwise to a stirred solution of L^2 (0.051 g, 0.0002 mol) and 2-bromodecanoic acid (0.087 g, 0.000 35 mol) in acetonitrile (5 ml), also at around 40 °C. A small amount of precipitate appeared on mixing and a further four quantities of acetonitrile (5 ml) were added to dissolve the solid. After a few minutes of heating the solution was allowed to cool down slowly in an oil bath and crystals were formed on standing overnight, $[(H_2L^2)(NO_3)]^+[Sm(L^2)(NO_3)_4]^-$ (Found: C, 38.5; H, 2.55; N, 16.3. $C_{30}H_{24}N_{11}O_{15}Sm$ requires C, 38.8; H, 2.6; N, 16.6%).

Crystallography

Crystal data for complexes **1** and **2** are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-Kα radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm for **1** and 70 mm for **2** from the Image Plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[7] The structures were solved using direct methods with the SHELXS program.[8] In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The locations of the nitrogen atoms in the rings were selected *via* thermal parameters and confirmed from the structure refinement by comparison with other assignments which gave higher R values and unreasonable thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was made for both structures using the DIFABS program.[9] In **2**, the two extra protons in the cation were readily observed in a Fourier-difference map bonded to N(11) and N(31) and successfully included in the refinement with no constraints. By contrast in **1** these hydrogen atoms bonded to nitrogen (and also those bonded to the water oxygen atoms) could not be located definitively although positive areas of electron density were located in appropriate positions. In order to establish whether the data were of sufficient quality so that the hydrogen atoms bonded to nitrogen should be locatable (and that therefore we should draw the conclusion from their absence that they were not positioned on the nitrogen atom) we looked at the Fourier-difference map for the hydrogen atoms bonded to carbon in these cations. In the first 200 peaks, only 12 of the 33 hydrogen atoms could be located, *i.e.* peaks were within 0.5 Å of calculated positions. We conclude that the data are not of sufficient quality so that we would necessarily expect to find definitive positions for the hydrogen atoms bonded to nitrogen and we therefore conclude that their likely positions are equivalent to those in **2** [bonded to atoms N(11) and N(31)], which is consistent with the formation of hydrogen bonds to the water molecule. Therefore the hydrogens in the cations A, B and C were included in calculated positions bonded to these outer nitrogen atoms. The assignment of absolute structure in **1** was carried out by comparisons of two structures with opposite signs for y coordinates. The structure with the lowest R value was chosen. Both structures were refined on F^2 till convergence using SHELXL.[10] All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Relevant bond lengths in each structure are shown in Table 2. The hydrogen bonds are shown in Table 3.

CCDC reference number 186/1074.

See http://www.rsc.org/suppdata/dt/1998/2973/ for crystallographic files in .cif format.

Table 2 Bond lengths (Å) for compounds **1** and **2**

Compound **1**			
La(1)–O(13)	2.609(11)	La(2)–O(45)	2.635(11)
La(1)–O(32)	2.649(11)	La(2)–O(56)	2.653(12)
La(1)–O(22)	2.663(11)	La(2)–O(52)	2.666(10)
La(1)–O(14)	2.665(13)	La(2)–O(58)	2.669(11)
La(1)–O(37)	2.672(12)	La(2)–O(66)	2.692(11)
La(1)–O(33)	2.674(10)	La(2)–O(41)	2.702(10)
La(1)–O(26)	2.683(11)	La(2)–O(47)	2.706(11)
La(1)–O(27)	2.702(13)	La(2)–O(53)	2.702(9)
La(1)–O(18)	2.726(11)	La(2)–O(43)	2.733(12)
La(1)–O(24)	2.734(12)	La(2)–O(63)	2.725(11)
La(1)–O(36)	2.741(12)	La(2)–O(68)	2.762(12)
La(1)–O(16)	2.758(14)	La(2)–O(64)	2.765(10)
Compound **2**			
Sm(1)–O(72)	2.494(5)	Sm(1)–O(82)	2.627(5)
Sm(1)–O(62)	2.537(5)	Sm(1)–N(11B)	2.635(5)
Sm(1)–O(51)	2.535(4)	Sm(1)–N(31B)	2.650(5)
Sm(1)–O(53)	2.554(4)	Sm(1)–O(74)	2.690(5)
Sm(1)–O(83)	2.559(4)	Sm(1)–O(63)	2.742(5)
Sm(1)–N(21B)	2.626(4)		

Table 3 Hydrogen bond distances (Å) in compounds **1** and **2**

Compound **1**			
O(1A)···O(63)	2.812(18)	O(1A)···O(16^{I})	3.005(19)
O(1A)···N(31A^{III})	2.814(19)	N(11A)···N(21A)	2.691(17)
O(1A)···N(11A^{III})	2.823(20)	N(21A)···N(31A)	2.691(19)
O(1B)···O(66^{II})	2.800(18)	O(1B)···O(17^{I})	2.965(22)
O(1B)···N(11B)	2.861(16)	O(1B)···O(67)	3.213(20)
O(1B)···N(31B)	2.800(16)	N(11B)···N(21B)	2.702(18)
O(1B)···O(16^{II})	3.018(19)	N(21B)···N(31B)	2.712(18)
O(1C)···O(38^{II})	2.799(18)	O(1C)···O(36^{II})	3.210(18)
O(1C)···N(31C^{IV})	2.827(18)	O(1C)···O(41)	3.255(19)
O(1C)···N(11C^{IV})	2.860(21)	N(11C)···N(21C)	2.660(21)
O(1C)···O(58)	3.035(19)	N(21C)···N(31C)	2.651(20)
O(1C)···O(47)	3.142(18)		
Compound **2**			
N(11A)···O(303)	2.750(14)	N(31A)···O(303)	2.767(14)
N(11A)···O(302)	3.095(16)	N(21A)···N(11A)	2.677(13)
N(21A)···O(303)	3.101(14)	N(21A)···N(31A)	2.648(13)

Symmetry elements: I 1 + *x*, *y*, *z*; II 1 − *x*, 0.5 + *y*, −*z*; III *x*, *y*, 1 + *z*; IV *x* − 1, *y*, *z* − 1.

Results and Discussion

Structure of $3[H_2L^2]^{2+}2[La(NO_3)_6]^{3-}\cdot 3H_2O$ 1

The asymmetric unit of **1** contains three diprotonated terpyridyl cations $[H_2L^2]^{2+}$, two $[La(NO_3)_6]^{3-}$ anions and three water molecules. Thus the protonated terpyridine ligand is not co-ordinated to the lanthanate(III) nitrate anion. Instead the two terminal pyridine nitrogen atoms are protonated. Each protonated terpyridyl cation encapsulates a water molecule with which it forms two strong hydrogen bonds. Two parts of the structure are shown in Figs. 1 and 2. Fig. 1 shows the environment of one protonated terpyridyl cation and Fig. 2 of one lanthanate(III) anion. It is noteworthy that the environments of the other cations and anions are almost identical such that there are three cations in the asymmetric unit together with just three water molecules each of which is similarly encapsulated. There are no additional water molecules in the unit cell, indicating that the role of the water molecules in the structure is to stabilise the cations by forming hydrogen bonds and also to stabilise the packing by additional hydrogen bonds to the anions. While it is not impossible to imagine a structure in which the lanthanate nitrate anions are hydrogen bonded directly to the diprotonated cation, clearly the present arrangement in which the interaction between cation and anion is mediated by the water molecules is more favoured.

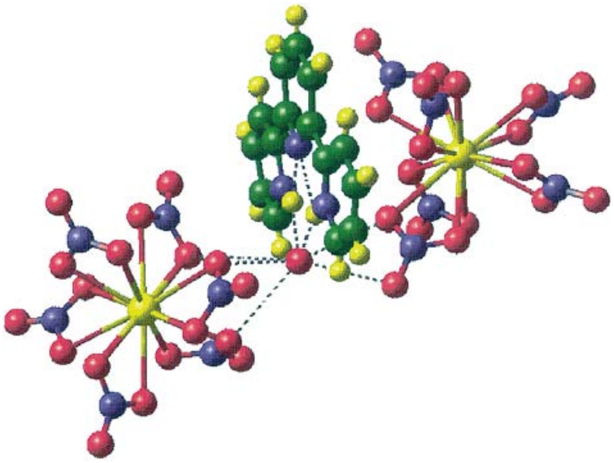


Fig. 1 The structure of compound **1** showing the environment of one $[H_2L^2]^{2+}$ cation with a water encapsulated within the cavity and forming N–H···O hydrogen bonds. In addition, the water molecule forms hydrogen bonds with oxygen atoms from the nitrates in the $[La(NO_3)_6]^{3-}$ anions. All hydrogen bonds are shown as dotted lines. The environments of the other two $[H_2L^2]^{2+}$ cations in the asymmetric unit are similar. Lanthanum yellow, oxygen red, carbon green, hydrogen yellow, nitrogen purple.

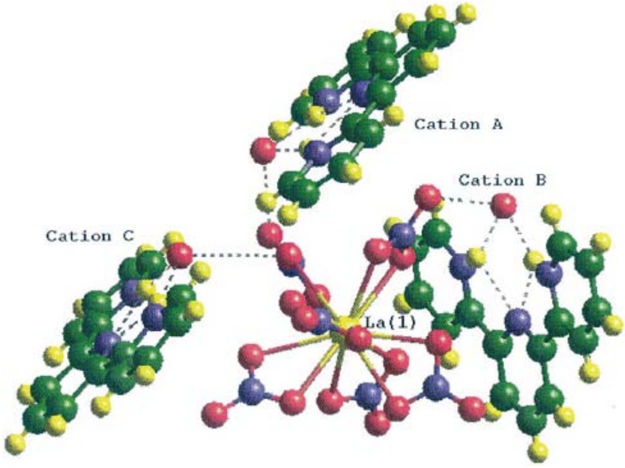


Fig. 2 The structure of compound **1** showing the environment of one $[La(NO_3)_6]^{3-}$ anion forming hydrogen bonds to the three water molecules which are each encapsulated within $[H_2L^2]^{2+}$ cations. All hydrogen bonds are shown as dotted lines. The environment of the second $[La(NO_3)_6]^{3-}$ anion in the unit cell is similar. Lanthanum yellow, oxygen red, carbon green, hydrogen yellow, nitrogen purple.

While there are literally hundreds of examples of L^2 complexed to metals recorded in the Cambridge Crystallographic Database (CCDS), there is only one previously reported example of the $[H_2L^2]^{2+}$ cation, namely in the salt $2[H_2L^2]^{2+}$-$[Tb(OH_2)_8]\cdot 7Cl^-$.[11] The nitrogen atoms in the outer pyridine rings are protonated and a chloride anion was located in the diprotonated cavity. This structure containing $[H_2L^2]^{2+}$ together with those established in the four structures presented in our previous work[2] for $[H_nL^1]^{n+}$ suggest that the diprotonated terpyridyl species always attracts hydrogen bonding species into the tridentate cavity.

In **1** in addition to the above three $[H_2L^2]^{2+}\cdot H_2O$ moieties the asymmetric unit contains two $[Ln(NO_3)_6]^{3-}$ anions. The Ln–O distances in this structure vary between 2.609(11) and 2.765(10) Å. Although there are numerous structures in the CCDS with Ln–O (nitrate) bonds, there are only three previously reported structures with $[Ln(NO_3)_6]^{3-}$ anions. For these anions and the two in the present work, the average Ln–O distance is 2.67 Å [$n = 60$, $\sigma(n-1) = 0.044$ Å]. It has been suggested previously that an analysis of the metal co-ordination sphere for this type of structure can be simplified by considering a bidentate ligand of small 'bite' such as nitrate to occupy only one site of a co-ordination polyhedron rather than two. The new metal co-ordination sphere would have a lower co-ordination number which is easier to analyse.[12] Thus, for $[Ln(NO_3)_6]^{3-}$ the arrangement of nitrogen atoms around Ln should be close to an octahedral geometry. This is indeed the case for the environment around Ln(2) in which the N–Ln–N angles only vary between 82(1) and 97(1)° and indeed there are six O–Ln(2)–O angles within 8° of 180°. There are larger deviations, however, around Ln(1), the N–Ln–N angles varying between 71(1) and 117(1)° and while there are three O–Ln–O angles within 5° of 180°, the other potentially *trans* angles are *ca.* 160°. It is not clear why there should be such big geometrical differences between the two anions though it seems likely that the geometry could well be affected by the significant numbers of hydrogen bonds found in the unit cell. Non-bonded nitrate oxygen atoms and bonded nitrate oxygen atoms in both anions are involved to approximately the same extent in hydrogen bonding with the water molecules in the terpyridyl cavity. This has the effect of weakening the corresponding Ln–O bonds, for example, there are 10 bonds longer than 2.7 Å in the anions; however it is not clear why the geometry of one anion should be so different from that of the other.

The hydrogen bond dimensions are shown in Table 3. The distances between each water atom and the two protonated nitrogen atoms with which hydrogen bonds are formed are all between 2.80 and 2.87 Å. In addition, each water molecule forms several hydrogen bonds to the nitrate oxygen atoms, one strong at a distance of *ca.* 2.80 Å and several weaker (at distances of 3.0–3.3 Å). In Fig. 1 we show the arrangement of one water molecule which forms hydrogen bonds to two different anions. The cations are approximately planar with N–C–C–N torsion angles of −0.1(2), 3.4(2)° in ligand A, 1.7(1), −0.9(1)° in ligand B and −0.5(2), −6.4(2)° in ligand C, respectively. It is difficult to establish the exact hydrogen bond pattern around each oxygen as there are so many short contacts [four for O(1A), six for O(1B), seven for O(1C)] less than 3.26 Å. It seems likely that the positions of the hydrogen atoms are fluxional and that weak interactions can occur to any of the close nitrate oxygen atoms.

In Fig. 2 the environment around one anion which forms hydrogen bonds to all three $[H_2L^2]^{2+}\cdot H_2O$ moieties is shown. It is interesting that one of the nitrate oxygen atoms forms hydrogen bonds to two different water molecules. The distances between the protonated N(11) and N(31) atoms and the central unprotonated N(21) atom vary between 2.65(2) and 2.71(2) Å while the corresponding N–H···N angles are all between 106 and 108°. These angles are similar to those found in the structure of 2,2′:6′,2″-terpyridinium trifluoromethanesulfonate (Fig. 7) which contains a monoprotonated terpyridyl cation with an N–N distance of 2.65 Å and an N–H···N angle of 103°, dimensions which are considered to be indicative of weak intramolecular hydrogen bonds.[13] The corresponding N–N distances in the salt $2[H_2L^2]^{2+}[Tb(OH_2)_8]^{3+}\cdot 7Cl^-$ are also very similar, varying between 2.61 and 2.67 Å.[11]

Structure of $[H_2L^2]^{2+}[SmL^2(NO_3)_4]^-[NO_3]^-$ 2

The structure of **2** is shown in Fig. 3. The asymmetric unit contains a $[Sm(L^2)(NO_3)_4]^-$ anion and an $[H_2L^2]^{2+}$ cation with an encapsulated NO_3^- anion. The stoichiometry and indeed the structure of the $[Sm(L^2)(NO_3)_4]^-$ anion is similar to that recently observed in the structure of $[La(L^2)_2(NO_3)_2]^+[La(L^2)(NO_3)_4]$.[14] In both structures the metal atoms in the anion are 11-co-ordinate. There are nine other structures in the Cambridge Database containing Sm–O (nitrate) bonds. However, the Sm(III) ion is co-ordinated only to oxygen atoms in the surveyed structures but to both oxygen and nitrogen atoms in our structure. Six of these previously reported structures contain a 10-co-ordinate Sm(III) ion. Only one of the reported structures contains Sm(III) in both the anion and the cation and in both ions the metal is 11-co-ordinate.[15] The Sm–O bond lengths in our structure vary between 2.494(5) and 2.742(5) Å. The average Sm–O (nitrate) distance from all the surveyed structures is 2.56 Å [$n = 56$, $\sigma(n - 1) = 0.093$ Å]. It is difficult to explain why there is such a broad range in Sm–O distances in our structure. It is interesting to note that the oxygen atom involved in the longest Sm–O bond is *trans* to the shortest Sm–N bond which involves the nitrogen atom in the central pyridine ring. The three Sm–N bond lengths are all longer than those observed in the two previously published structures containing L² with Sm.[4] In the first of these structures the Sm(III) is either eight- or nine-co-ordinate depending on the cation. Thus, the formula can be described as $Sm(L^2)(Cl)(H_2O)_{4,5}$. In the second structure the Sm(III) is eight-co-ordinate, the metal being co-ordinated to three L² N atoms, four Cl atoms and one water molecule. The Sm–N bond lengths vary between 2.56 and 2.59 Å in both of these structures, while in **2** the Sm(III) ion is 11-co-ordinate and the bond lengths vary between 2.62 and 2.65 Å. The increased Sm–N distances in **2** are clearly a consequence of the higher co-ordination number compared to the other structures.

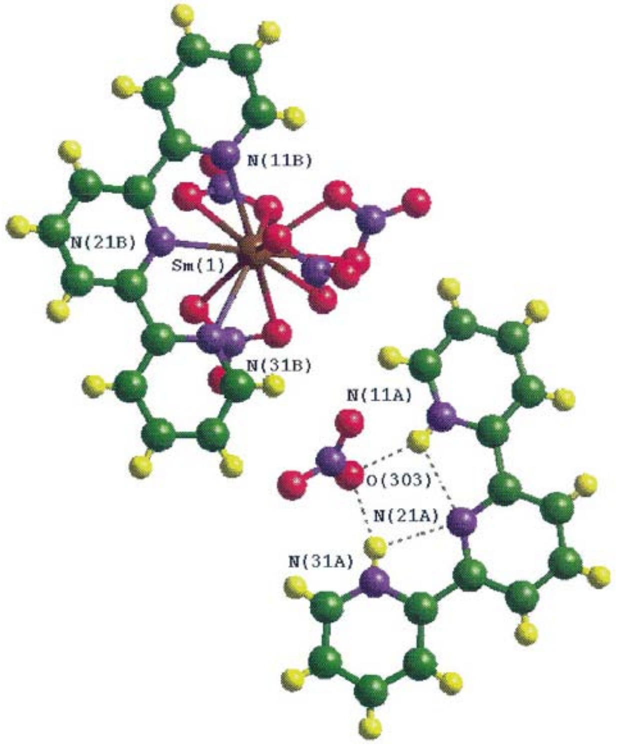


Fig. 3 The structure of compound **2** showing both the $[H_2L^2]^{2+}$ cation hydrogen bonded to a nitrate anion together with the $[Sm(NO_3)_4L^2]$ anion. Samarium brown, oxygen red, carbon green, hydrogen yellow, nitrogen purple.

The terpyridine co-ordinated to the Sm(III) ion is almost planar, the N–C–C–N dihedral angles are 5.6(1) and 3.7(1)°. The terpyridyl cation shows more distortion from planarity with corresponding dihedral angles of −3.6(1) and 11.0(1)°. The nitrate ion in the terpyridyl cavity is hydrogen bonded to the N–H protons through one oxygen only. As with the diprotonated terpyridine in **1**, it is also possible to describe the N–H···N interactions as weak intramolecular hydrogen bonds.

Theoretical structural analysis of L², $[HL^2]^+$ and $[H_2L^2]^{2+}$

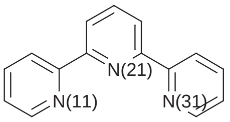
The terpyridyl ligand L². There are three possible conformations for L² which can be characterised by the N–C–C–N torsion angles as *tt* (*trans*,*trans*), *ct* (*cis*,*trans*) and *cc* (*cis*,*cis*).

Table 4 Results from quantum mechanics calculations on terpy, $[Hterpy]^+$ and $[H_2terpy]^{2+}$. Geometry optimisation was carried out using the 6-31G** basis set. Energies in au (= 627.509 kcal mol^{-1})

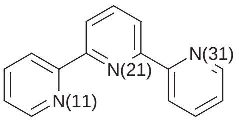
Compound	Protonated nitrogen	Conformation *cis*,*cis*	 *cis*,*trans*	 *trans*,*trans*
L^2		−737.798 (*cc*)	−737.807 (*ct*)	−737.818 (*tt*)
$[HL^2]^+$	N(11)	−738.202 (H-*cc*1)	−738.203 (H-*ct*1)	−738.195 (H-*tt*1)
	N(21)	−738.213 (H-*cc*2)	−738.206 (H-*ct*2)	−738.195 (H-*tt*2)
	N(31)	*a*	−738.189 (H-*ct*3)	*a*
$[H_2L^2]^{2+}$	N(11), N(21)	−738.457 (2H-*cc*1)	−738.443 (2H-*ct*1)[b]	−738.443 (2H-*tt*1)
	N(11), N(31)	−738.486 (2H-*cc*2)	−738.484 (2H-*ct*2)	−738.479 (2H-*tt*2)
	N(21), N(31)	*c*	−738.443 (2H-*ct*3)[b]	*c*

[a] Structures with N(31) protonated are equivalent to structures with N(11) protonated. [b] Structures unstable to geometry optimisation. The 2H-*tt*1 structure was obtained. [c] Structures with N(21) and N(31) protonated are equivalent to structures with N(21) and N(11) protonated.

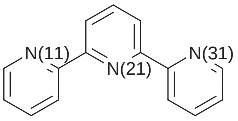
We have analysed these conformations for L^2, $[HL^2]^+$ and $[H_2L^2]^{2+}$ using the GAUSSIAN 94 program.[16] Starting models were built using the CERIUS2 software[17] and the three rings were made approximately coplanar but no symmetry was imposed. Structures were then optimised using the 6-31G* basis set.[18] Results are summarised in Table 4.



cis, cis



cis, trans



trans, trans

For the neutral ligand L^2, it was found that the order of energies was *tt* < *ct* < *cc* and this is consistent with the fact that the *tt* conformation is observed in the crystal structure of L^2[19] and also the 4′-phenyl,[20] 4-aniline[21] and 4′-NMe_2[22] derivatives. A structure with a boron cage in the 4′ position *viz* 4′-(*closo*-o-carboranyl)terpyridine also has this *tt* conformation.[23] This *trans* conformation of pyridine rings is also found in quaterpyridine[24] and a *para* substituted sexipyridine.[25]

The reasons for this order of conformational preference is clear from the geometry of the optimised structures (Fig. 4). In the *tt* form, the N–C–C–N torsion angles are both 180.0°. However in the *ct* form, while the *trans* torsion angle at −176.1° shows that the rings are close to being coplanar, the *cis* torsion angle at −43.0° shows that the rings are very much twisted away from planarity. This twist is caused by the repulsion between the two *ortho* hydrogen atoms and possibly also from electron–electron repulsion between the lone pairs on the nitrogen atoms. This pattern of conformational change is also observed in the *cc* form where the torsion angles are −47.9, 47.9°. Clearly, the *cis* arrangement reduces conjugation between the two rings and is particularly destabilised by repulsions between the *ortho* hydrogen atoms.

These calculations were carried out on the free ligands but it is possible that the conformational preferences may well change in the presence of hydrogen bond donors or acceptors. It is interesting that the *tt* form is the lowest energy conformation of neutral terpyridyl which is unsuitable for tridentate complexation with a metal atom. However it is possible that this conformation could be stabilised in polar solvents by the formation of intermolecular hydrogen bonds. Thus a water molecule could enter the cavity with the same arrangement as found for the $[H_2L^2]^{2+}\cdot H_2O$ cation found in **1** but with donor O–H · · · N instead of acceptor O · · · H–N hydrogen bonds [see Fig. 5(a)]. A precedence for this proposed structure is found for a crystal structure of terpyridyl co-crystallised with $[SnPh_3(NCS)(H_2O)]$.[26] This is the only crystal structure where an oligopyridine contains adjacent pyridine ligands in the *cis* conformation, but the conformation is stabilised by the formation of two hydrogen bonds to the water molecule which is situated in the terpyridine cavity as well as being bonded to the tin.

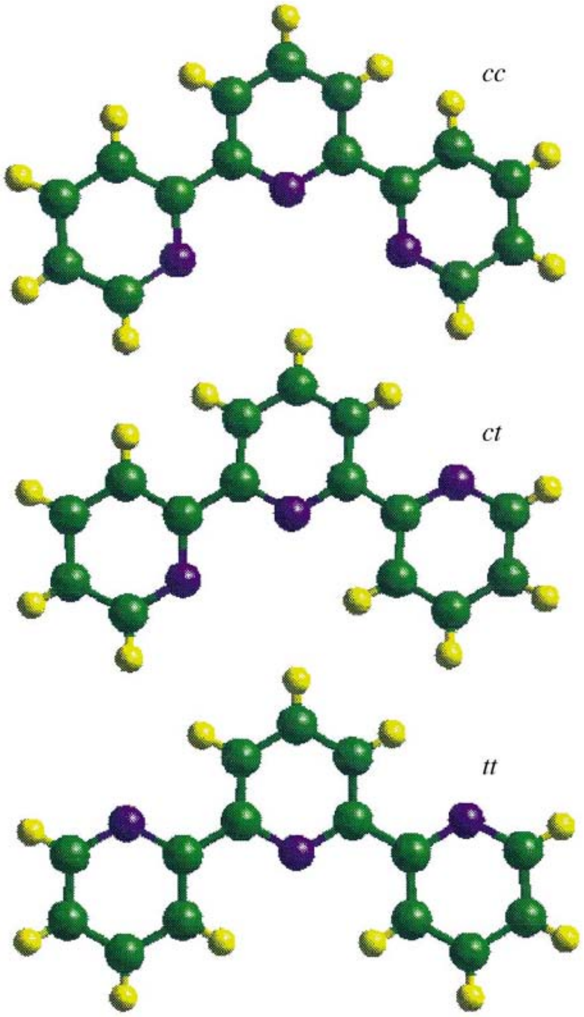


Fig. 4 The three conformations of L^2, *cis*,*cis* (*cc*), *cis*,*trans* (*ct*) and *trans*,*trans* (*tt*). Energies after geometry optimisation (au) and torsion angles (°) were for *cc* −737.798, −47.9, 47.9; for *ct* −737.807, −43.0, −176.1 and for *tt* −737.818, 180, 180.

In order to calculate the effect of the formation of this $L^2\cdot H_2O$ complex, a model structure was built using CERIUS2 [Fig. 5(a)] and subjected to optimisation in GAUSSIAN 94. Results show that the energy of the complex was 11.29 kcal mol^{-1}, lower than that of the L^2 and H_2O separated at infinity.

Water adducts built with the *ct* and *tt* structures proved not to be stable to geometry optimisation, no doubt because of the repulsions from adjacent C–H groups. In the *cc* L·H_2O complex, the structure maintains C_s symmetry, though this was not imposed. The N–C–C–N torsion angles at 42.0, −42.0° are only slightly reduced (by 5.9°) from values in the unhydrated form. The N···H and O···H distances are 2.2, 3.15 Å respectively with an O–H···N angle of 177.3°. This contrasts with torsion angles of 29.0, −18.0° and N···O distances of 2.80, 2.76 Å in ref. 26.

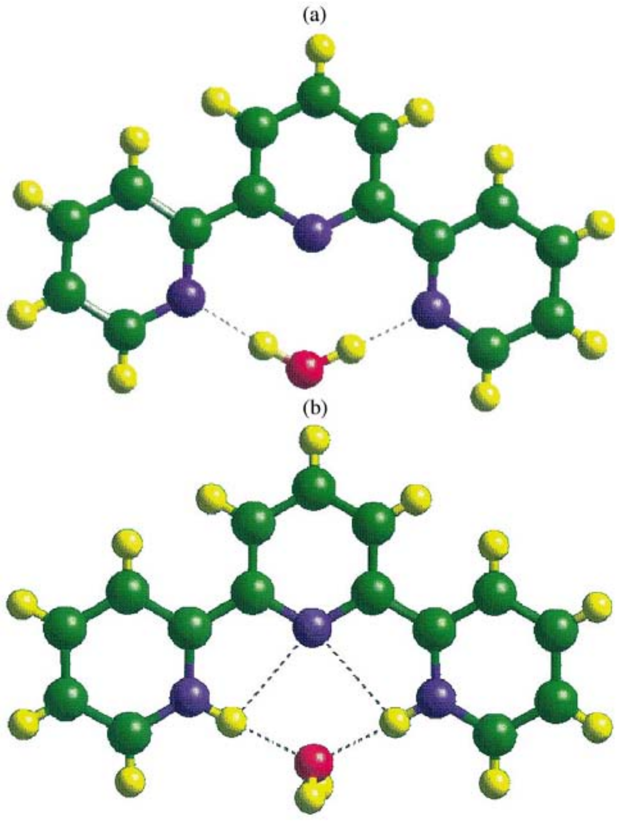


Fig. 5 The stabilisation of the *cis*,*cis* conformation by intramolecular hydrogen bonds with water molecules. Geometry optimisation *via* GAUSSIAN 94. (a) The *cc* form accepting hydrogen bonds from a water molecule; N–C–C–N torsion angles are −42.0, 41.9°. (b) The 2H-*cc*2 form donating hydrogen bonds to a water molecule; N–C–C–N torsion angles are −18.7, 18.7°. Hydrogen bonds shown as dotted lines. Carbon green, hydrogen yellow, nitrogen purple, oxygen red.

Monoprotonated $[HL^2]^+$. When L^2 is monoprotonated, then there are seven possible structures (Fig. 6) depending on the conformation and which nitrogen atom is protonated. There are two *cis*,*cis* structures; H-*cc*1, H-*cc*2 depending on whether N(11) or N(21) is protonated [N(11) is equivalent to N(31)]; three *cis*,*trans* structures H-*ct*1, H-*ct*2, H-*ct*3 dependent upon whether N(11), N(21) or N(31) is protonated; and two *trans*, *trans* structures H-*tt*1, H-*tt*2 dependent upon whether N(11) or N(21) is protonated. These seven structures were built with CERIUS2 and geometry optimised with GAUSSIAN 94 and the resulting structures are shown in Fig. 6. As with terpyridyl L^2, the energies of $[HL^2]^+$ can be correlated with two dominant structural features, one favourable and one unfavourable.

The lowest energy structures contain at least one pair of mutually *cis* nitrogen atoms of which one is protonated so that an energetically favourable intramolecular hydrogen bond interaction can be formed. Thus H-*cc*2 has the lowest energy with two such interactions, next lowest are H-*cc*1, H-*ct*1 and H-*ct*2 with one such interaction and the three highest energies are H-*ct*3, H-*tt*1 and H-*tt*2 with no such interactions. The unfavourable interaction occurs when the N–H is *cis* to one or two C–H bonds leading to H···H repulsion. Two of these interactions are found in H-*tt*2, and one in H-*tt*1, H-*ct*3 and H-*ct*2. It is interesting that this latter H-*ct*2 structure also has a favourable hydrogen bond interaction which more than compensates for this repulsion as the energy is one of the lowest found. Unfavourable *ortho* C–H interactions are also found in several of the structures. The geometry in the structures (Fig. 6) follow a regular logical pattern. For the *cis* N–C–C–N torsions, the angle is close to zero when a hydrogen bond is formed (*e.g.* 5.1 in H-*cc*1, −0.1 in H-*cc*2, 6.8 in H-*ct*1, −0.3° in H-*ct*2) but otherwise is twisted significantly to relieve steric strain (*e.g.* −28.6 in H-*cc*1, −37.2° in H-*ct*3). For the *trans* N–C–C–N torsions, the angle is only close to 180° in H-*tt*1 where there are no *ortho* repulsions but in all the other structures the absolute value of the angle ranges from 148.8 to 155.8°. There are other geometric changes concomitant with the formation of the intramolecular N–H···N hydrogen bonds. Thus in H-*ct*2 the

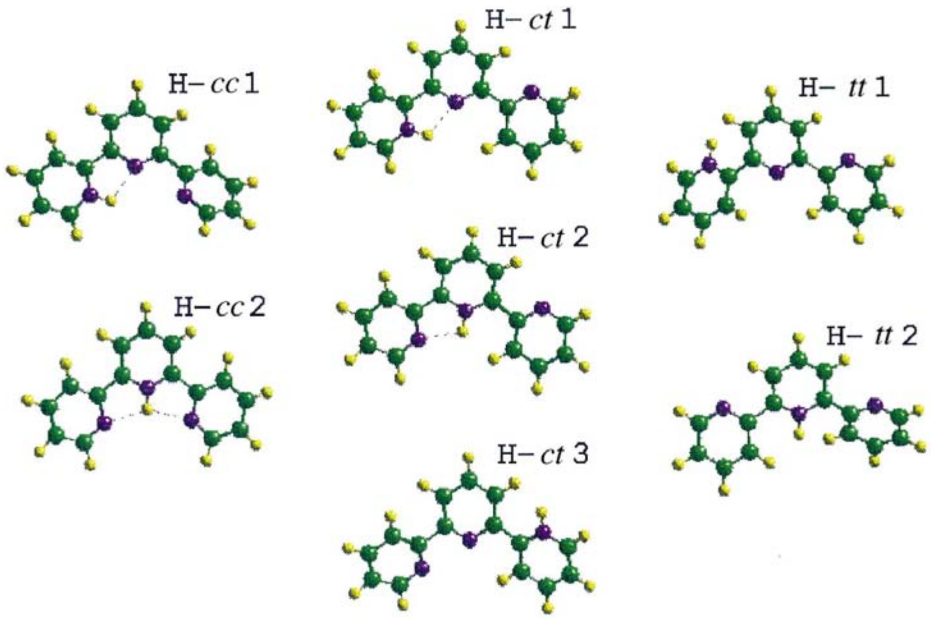


Fig. 6 The seven structures of $[HL^2]^+$ which are characterised by the conformation and the nitrogen that is protonated. Energies after geometry optimisation (au) and torsion angles (°) were for H-*cc*1 −738.202, −28.6, 5.1; for H-*cc*2 −738.215, −0.1, −0.1; for H-*ct*1 −738.203, 6.8, −163.8; for H-*ct*2 −738.206, −0.3, 155.8; for H-*ct*3 −738.189, −37.2, −154.8; for H-*tt*1 −738.195, −174.0, −148.8 and for H-*tt*2 −738.195, −150.0, −150.0. Hydrogen bonds shown as dotted lines. Carbon green, hydrogen yellow, nitrogen purple.

two C–C–N angles to the central pyridine atom are 115.1° to ring 1 to facilitate the hydrogen bond and 119.1° to ring 3 where there is no such hydrogen bond. The H···N distances are 2.07 Å in H-*cc*1, but 2.16 Å in H-*ct*2 and 2.12 Å in H-*ct*1, 2.10 Å in H-*ct*2. The N–H···N angles range from 105 to 108°, rather small compared to the usual angle for a hydrogen bond, but the calculations presented here clearly indicate that the hydrogen bonds are significant. There is a significant change in the N–C bond lengths when the nitrogen is protonated and increases of *ca.* 0.01 Å are observed. Thus in H-*cc*2, the C–N distances are 1.338 Å compared to 1.326 and 1.315 Å where the N is unprotonated.

There is very little experimental evidence on $[HL^2]^+$ that can be correlated with these calculations. There is only one crystal structure containing $[HL^2]^+$, *viz* the salt with $[CF_3SO_3]^-$ [13] and this has the H-*ct*1 structure. However the structure of diprotonated quinquepyridinium which has the *cis*,*trans*,*trans*,*cis* conformations shows the outer two nitrogens to be protonated so that the structure contains two moieties equivalent to the H-*ct*1 structure.[27] As is apparent from the energy values in Table 4, this H-*ct*1 structure is not the lowest energy structure, but unlike the more favourable H-*cc*2 and H-*ct*2 structures, it retains the possibility of being able to form intermolecular hydrogen bonds. Indeed in the two crystal structures, this is precisely what is found, that the protonated nitrogen atom forms an intramolecular hydrogen bond but also an intermolecular hydrogen bond to the anion in the crystal. The anion is situated well away from the cavity (Fig. 7) and calculations show that this anion (or indeed any other) could not form stable hydrogen bonds to the protonated central nitrogen atom as occurs in H-*cc*2 and H-*ct*2. We conclude, therefore, that in the presence of solvents and/or anions which can accept hydrogen bonds that the H-*ct*1 structure is more likely to be found in preference to H-*cc*2 and H-*ct*2 despite these having lower energies in the gas phase.

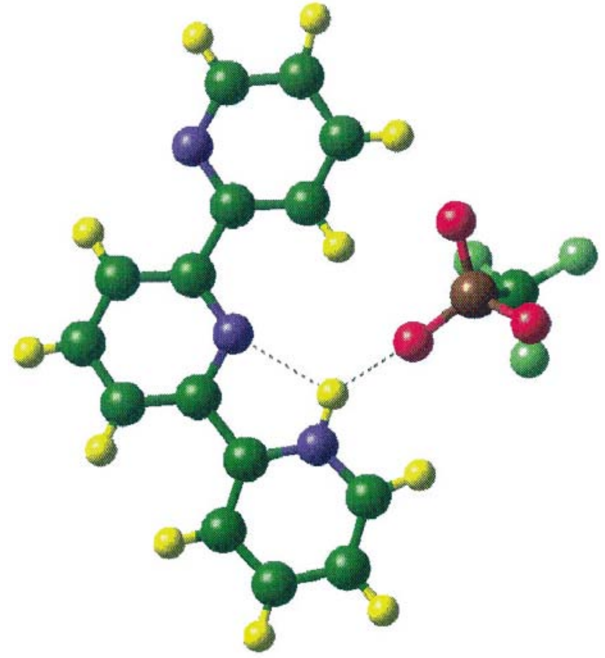


Fig. 7 The structure of $[HL^2]^+[CF_3SO_3]^-$ showing the intermolecular hydrogen bond between N–H and an oxygen atom in the anion.[13] Sulfur brown, oxygen red, carbon green, fluorine light green, nitrogen purple, hydrogen yellow.

Diprotonated $[H_2L^2]^{2+}$. For $[H_2L^2]^{2+}$ there are also seven different structures. There are two with the *cis*,*cis* conformation called 2H-*cc*1 [with N(11) and N(21) protonated], and 2H-*cc*2 [with N(11) and N(31) protonated]; three with the *cis*,*trans* conformation; 2H-*ct*1 [N(11), N(21) protonated], 2H-*ct*2 [N(11), N(31) protonated] and 2H-*ct*3 [N(21), N(31) protonated] and two with the *trans*,*trans* conformation; 2H-*tt*1 [N(11), N(21) protonated] and 2H-*tt*2 [N(11), N(31) protonated].

Models were built with CERIUS2 and then geometry optimised with GAUSSIAN 94 and the results are given in Table 4 and illustrated in Fig. 8. The same two structural features are crucial to determining the relative energy values, thus lower energy structures contain intramolecular hydrogen bonds and higher energy structures N–H···C–H repulsions. There are more of these latter types of repulsion in the diprotonated structures than in the monoprotonated structures and there is also the possibility of N–H···N–H repulsions. The C–H···C–H repulsions are present in all structures but seem to be less important, possibly because the electrostatic repulsions between hydrogen atoms is less.

Because of these *ortho–ortho* repulsions only three structures contain intramolecular hydrogen bonds 2H-*cc*2, 2H-*ct*2 and 2H-*cc*1 and these together with 2H-*tt*2 have the lowest energies. The lowest energy conformation (2H-*cc*2) is also observed in the two crystal structures reported above. In this structure the

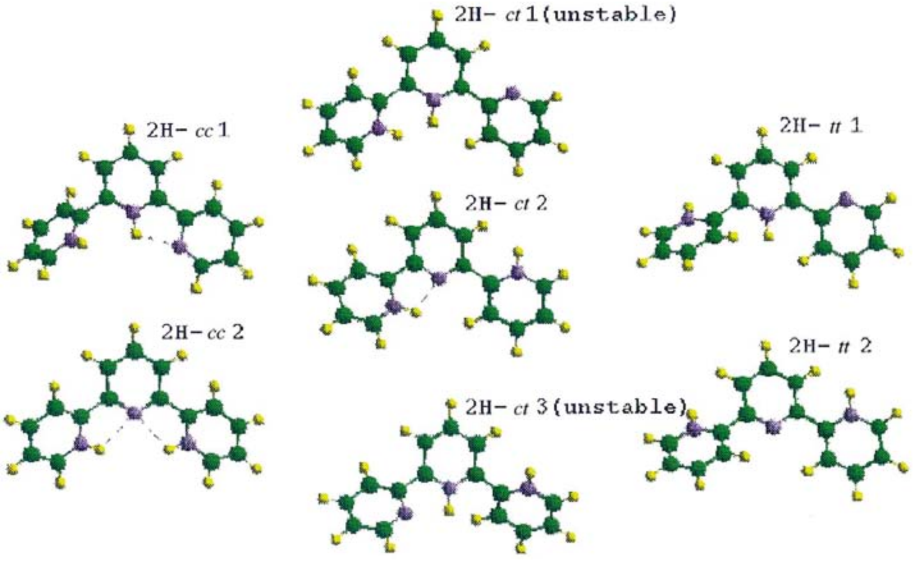


Fig. 8 The seven structures of $[H_2L^2]^{2+}$ which are characterised by the conformation and the nitrogen that is protonated. Energies after geometry optimisation (au) and torsion angles (°) were for 2H-*cc*1 −738.456, 0.6, 58.7; for 2H-*cc*2 −738.486, −28.3, −28.3; for 2H-*ct*1 unstable; 2H-*ct*2 −738.484, 12.8, −139.1; for 2H-*ct*3 unstable; for 2H-*tt*1 −738.444, −130.5, −155.1 and for H-*tt*2 −738.479, −145.0, −145.0. Hydrogen bonds shown as dotted lines. Carbon green, hydrogen yellow, nitrogen purple.

N–C–C–N torsion angles are −28.3° and the N–H···N distance is 2.43 Å. This compares with torsion angles of 0.4, 6.0; −3.3, 0.5; −1.9, 0.1° in **1** and 10.8, −3.7° in **2** and distances of 2.28–2.34 Å in the two structures (though it must be borne in mind that these are calculated hydrogen positions from the crystal structure determinations) and indeed to the 2.16 Å observed in the 1H-*cc*1 structure. The distance in 2H-*ct*2 is also large by comparison at 2.37 Å. It seems likely that the ligand in the crystal structures is more planar because of the intermolecular hydrogen bonds formed to the nitrate. In order to test this proposition, we carried out a GAUSSIAN 94 geometry optimisation of a water molecule contained within the cavity of the 2H-*cc*2 structure [Fig. 5(b)]. On optimisation the two torsion angles had decreased to 18.7 and −18.7° and the two H···N distances reduced to 2.13, 2.13 Å. Results show that the energy of the complex was 18.72 kcal mol^{-1}, lower than that of $[H_2L^2]^{2+}$ and H_2O separated at infinity. We conclude that in the case of the diprotonated $[H_2L^2]^{2+}$ the gas phase preference for the 2H-*cc*2 structure is enhanced in solution and that this is likely to be the only diprotonated species present.

The conformation found in the 2H-*cc*1 structure is particularly interesting as it contains a N–H···N–H repulsion which is alleviated with a torsion angle of 58.7° while the second *cis* interaction contains a N–H···N attraction and the torsion angle remains close to zero at 0.6°. Of the other structures 2H-*ct*1 and 2H-*ct*3 proved not to be stable to geometry optimisation and reverted to the 2H-*tt*1 structure. The 2H-*tt*2 structure contains no hydrogen bonds but has a relatively low energy because there are no significant *ortho* repulsions. The 2H-*tt*1 structure has the highest energy of all because of significant repulsions between N–H and C–H in the cavity.

Conclusion

Theoretical calculations have shown that the lowest energy conformation of the terpyridyl ligand is the *trans*,*trans* form. However *cis* forms are stabilised on protonation by the formation of weak intramolecular N–H···N hydrogen bonds. It is likely that the lowest energy forms in solution for the protonated and diprotonated forms are the H-*ct*1 and 2H-*cc*2. These results are consistent with evidence from crystal structure determinations presented here and from the literature. It is suggested that any theory of extraction based on the ion-pair mechanism must be consistent with the presence of these cations both of which will be stabilised by the formation of intermolecular hydrogen bonds to solvent and/or accompanying anions.

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