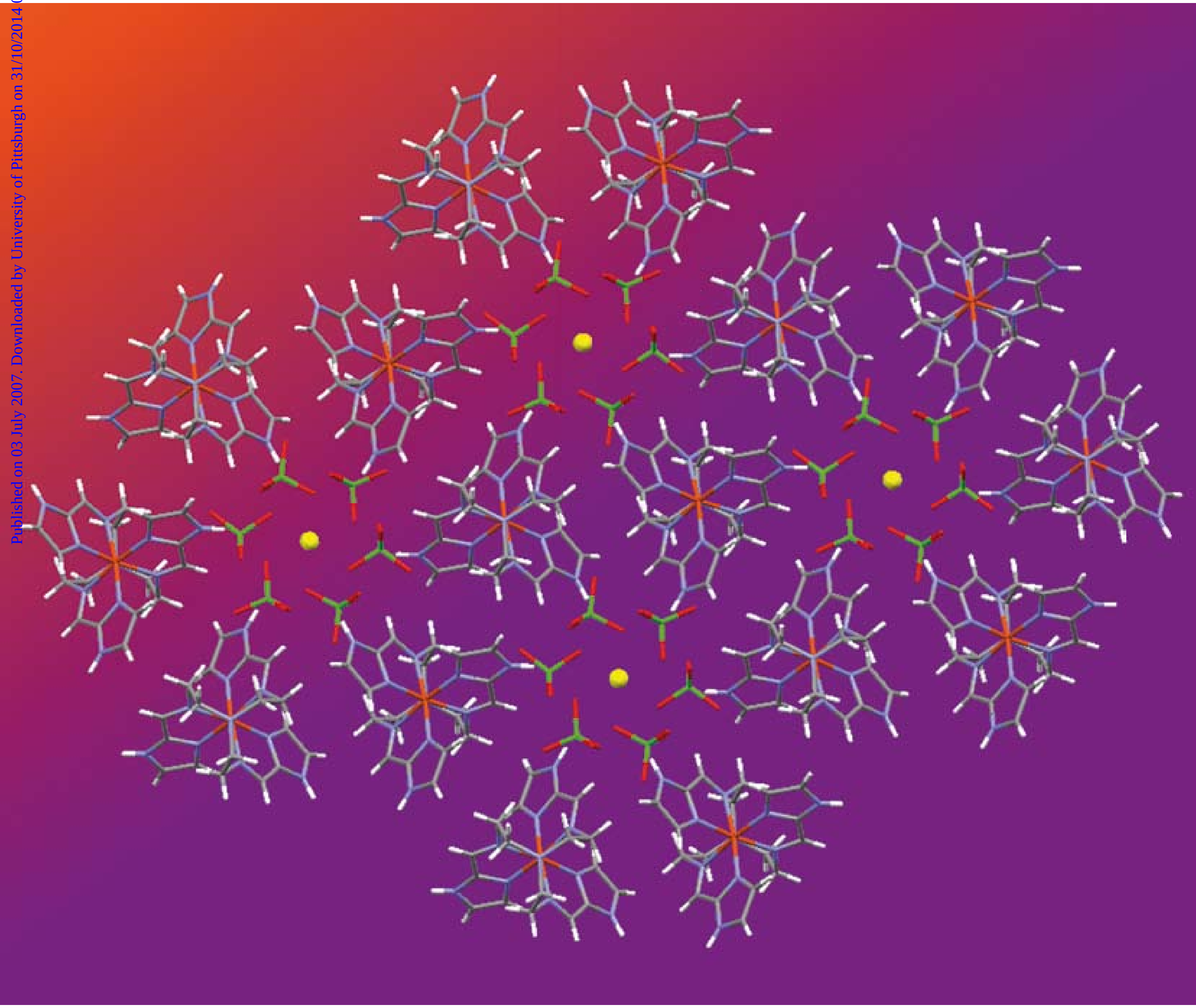
Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Number 37 | 7 October 2007 | Pages 4105–4228



ISSN 1477-9226

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1477-9226(2007)37;1-0

Supramolecular assemblies prepared from an iron(II) tripodal imidazole complex. A molecular scaffolding for the self assembly of icosahedral complexes of K^+, Rb^+, Cs^+ and NH_4^+ cations†‡

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Received 30th March 2007, Accepted 21st May 2007
First published as an Advance Article on the web 3rd July 2007
DOI: 10.1039/b704823h

The iron(II) complex of the 1 : 3 Schiff base condensate of tris(2-aminoethyl)amine (tren) with 2-imidazolecarboxaldehyde, H_3L^1, $[FeH_3L^1](ClO_4)_2$, was reacted with $MClO_4$ (M = K, Rb, Cs, and NH_4). The products were double salts of the formula $\{[FeH_3L^1](ClO_4)_2\}\cdot MClO_4$. The complexes have been characterized by Elemental Analysis, X-ray crystallography, ESMS, IR and Mössbauer spectroscopy. The resultant complexes are all trigonal, crystallize in $P\bar{3}$ and exhibit a hexameric structure in the extended lattice. The cations are located at the origin (0, 0, 0) and $c/2$ (0, 0, 0.5) on the c axis. The cations are twelve coordinate and exhibit a distorted icosahedral geometry formed by six bidentate perchlorate anions. The perchlorate anions are involved in extensive hydrogen bonding with the iron complexes, which are located at the vertices of the hexagon. Each perchlorate anion has five hydrogen bonds to three iron complexes. The iron complexes use the imidazole N*H* and imine N=C*H* as donors to the perchlorate oxygen atoms. The imidazole N*H* is a trifurcated donor and the imine C*H* is a bifurcated donor. The formation of the double salt and the accompanying hydrogen bonding results in a shift in the spin equilibrium of the parent iron(II) complex from 63% high spin, HS, and 37% low spin, LS, at 295 K to pure LS in the double salts. Attempts to incorporate sodium or silver in the above salts failed due to their size and oxidizing strength, respectively. The analogous manganese complex, $[MnH_3L^1](ClO_4)_2$, failed to give these double salts under identical reaction conditions. The lack of reactivity of $[MnH_3L^1](ClO_4)_2$ does not appear to be due to its solubility or geometric considerations of the hydrogen bonding donor site, but instead to the electronic differences between the high spin $[MnH_3L^1](ClO_4)_2$ and the spin crossover $[FeH_3L^1](ClO_4)_2$.

Introduction

An important class of ligands is the 1 : 3 Schiff base condensates of tris(2-aminoethyl)amine (tren), tris(2-aminoethyl)-methylammonium ion (*N*-Metren$^+$) or tris(3-aminopropyl)amine (trpn) with imidazole or pyrazole carboxaldehydes (Fig. 1). The remarkable versatility of these ligands is due to the fact that they can bind to metals in different oxidation states (M^{2+} or M^{3+}), protonation states (H_3L, H_2L^-, HL^{2-}, or L^{3-}), coordination numbers (6 or 7)[1] and conformations,[2] which allows for a wide variety of resultant complexes. Some of the significant areas of investigation utilizing these systems are spin crossover (SC),[3] proton coupled electron transfer (PCET),[4] and supramolecular chemistry.[5]

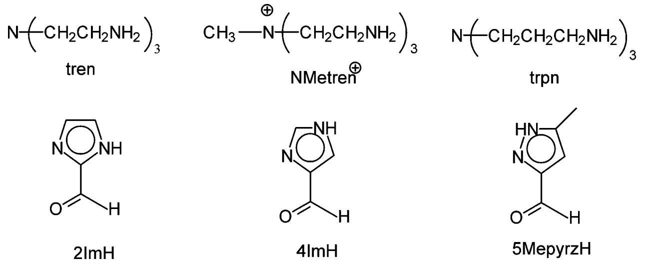

Fig. 1 Line drawings of tripodal ligand precursors. H_3L represents any tripodal Schiff base condensate. H_3L^1 is tren(2ImH)$_3$ (ImH = imidazole), H_3L^2 is tren(4ImH)$_3$, H_3L^3 is tren(5MepyrzH)$_3$, H_3L^4 is trpn(2ImH)$_3$ and H_3L^5 is *N*-Metren(2ImH)$_3^+$.

The interest in SC systems[6] of d^4–d^7 first row complexes is partly attributed to the potential applications of molecules with two electronic ground states that are interconverted by changes in temperature, pressure, or light as memory devices[7] and switches.[8] The most important examples involve iron(II) (d^6, $^1A \rightleftharpoons {}^5T$) or iron(III) ($d^5$, $^2T \rightleftharpoons {}^6A$) complexes as the requirement for SC that the crystal field splitting parameter (Δ) equals the pairing energy is easily met with the iron species coupled to readily available ligands. The SC condition is met for iron(II) and iron(III) with ligands that have N_4O_2–N_6 donor sets.[9] It is possible to control the spin state of the iron complexes of tren simply by selecting an appropriate aldehyde for the Schiff base condensation which results in N_4O_2–N_6 donor sets.[10] The study of the SC iron(II) and iron(III) complexes of these ligands has focused on their structural,

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† CCDC reference numbers 628770, 630381, 631972, 635041, 635168 and 635260. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704823h

‡ Electronic supplementary information (ESI) available: Table of ESMS and IR values for the new complexes. See DOI: 10.1039/b704823h

magnetic, and Mössbauer properties.[11] All of the protonation and spin states of the iron(II) and iron(III) complexes of H_3L^2 have been investigated by DFT methods.[12]

PCET work has focused on the relationship between proton loss from an iron(II) complex, $[FeH_3L]^{2+}$, and aerial oxidation to give the neutral iron(III) complexes, [FeL].[13]

Supramolecular homo valence, $\{[Fe^{II}H_3L^2][Fe^{II}L^2]\}(BF_4)$, and hetero valence, $\{[Fe^{II}H_3L^2][Fe^{III}L^2]\}(BF_4)_2$, complexes[14] and both a mixed valence and mixed protonation, $\{[Fe^{II}H_2L^3][Fe^{III}HL^3]\}(ClO_4)_2$, complex[15] have been structurally and electronically characterized. The complexes utilizing H_3L^2 exist as hydrogen bound hexameric rings, while that of H_3L^3 is a discrete hydrogen bound pseudo dimer.

In addition to the other properties described above the iron(III) imidazolate complexes, [FeL], function as Lewis bases, binding metal containing Lewis acids through the imidazolate nitrogen atom.[16] A $[Co^{III}L]$ complex has been used as a hydrogen bonding acceptor in adducts with hydroquinone and resorcinol.[17] To date the use of these complexes as hydrogen bonding donors has not been fully investigated. A goal of this investigation was to determine if the adjacent imidazole N*H* and imine C*H* atoms of $[Fe^{II}H_3L^1]^{2+}$, which have the appropriate geometry (Fig. 2), could be used as a bidentate hydrogen bonding donor to anions or organic ligands.

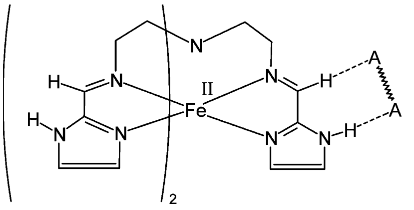

Fig. 2 Line drawing of $[Fe^{II}H_3L^1]^{2+}$ showing its potential role as a bidentate hydrogen bond donor.

The use of an imine proton, –N=C–*H*, as a hydrogen bond donor is non-conventional but there is a large body of data showing that C–H hydrogen bonds play an important role in chemistry and biology.[18] The classic example of a bidentate hydrogen bond donor is the guanidine group (or its protonated form) of arginine which complexes with dihydrogenphosphate.[19] Further synthetic work has resulted in hydrogen bonding donors that are more specialized.[20]

In this work double salts were prepared by the reaction of $[Fe^{II}H_3L^1](ClO_4)_2·H_2O$, **1**·$H_2O$, with $MClO_4$ (M = K, Rb, Cs, and NH_4). The resulting complexes, **1**·$MClO_4$, exhibit a number of supramolecular features including the observation that **1** functions as a bidentate hydrogen bond donor to the perchlorate anion.

Results and discussion

Molecular structure

The crystallographic data of **1**·$KClO_4$, **1**·$RbClO_4$, **1**·$CsClO_4$, **1**·NH_4ClO_4, and $[MnH_3L^1](ClO_4)_2$, **2**, are given in Table 1. Table 2 gives selected bond distances and angles for **1**·H_2O and the new complexes. The double salts all crystallize in $P\bar{3}$. The asymmetric unit contains one third of the iron complex, one perchlorate anion, and two independent cations. The structures of the metal(II) complex cation itself, the supramolecular features of the double salts, the relationship to a related structure, and relationship to $MClO_4$ structures will be discussed in the following sections.

Molecular structure: structure of complex metal cation, $[MH_3L^1]^{2+}$, M = Fe or Mn

The ORTEP diagrams of the iron cation of **1**·$KClO_4$ and the manganese cation of **2** are shown in Fig. 3. N_{ap} is the apical nitrogen atom of tren, N1 is the imine nitrogen atom, N2 is the metal bound imidazole nitrogen atom, N3 and H3B are the backside imidazole nitrogen atom and its proton and C3 and H3A are the imine carbon atom and its hydrogen atom.

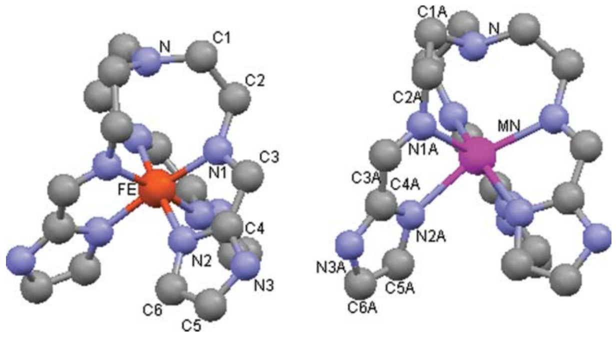

Fig. 3 Structure diagram of the $[FeH_3L^1]^{2+}$ cation of **1**·$KClO_4$ (left) and the $[MnH_3L^1]^{2+}$ cation of **2** (right). Hydrogen atoms have been omitted for clarity. For $[FeH_3L^1]^{2+}$ only the unique arm is labeled. For $[MnH_3L^1]^{2+}$ only arm "A" is labeled.

The structural signature[21] of spin states in these tripodal imidazole complexes are: 1) the M–$N_{imidazole}$ and M–N_{imine} bond distances (HS > 2.10 Å, LS < 2.00 Å); 2) the $N_{imidazole}$–M–N_{imine} bite angle (HS ~ 76°, LS ~ 81°); 3) the $N_{imidazole}$–M–N_{imine}′ *trans* angle (HS ~166°, LS ~ 175°); and 4) the M–N_{ap} distance (HS < 3.1 Å, LS > 3.1 Å). The metrical parameters of all the iron(II) complexes in the double salt are nearly identical to one another and the parent complex, **1**·H_2O and are consistent with a LS assignment. The values for **2** are consistent with a HS assignment for this metal. HS complexes have an "N in" conformation with a pyramidal N_{ap} pointed toward the metal atom and LS complexes have a planar N_{ap} conformation. Fig. 4 illustrates the two different conformations of N_{ap} for the $[FeH_3L^1]^{2+}$ cation of **1**·$KClO_4$ and the $[MnH_3L^1]^{2+}$ cation of **2**.

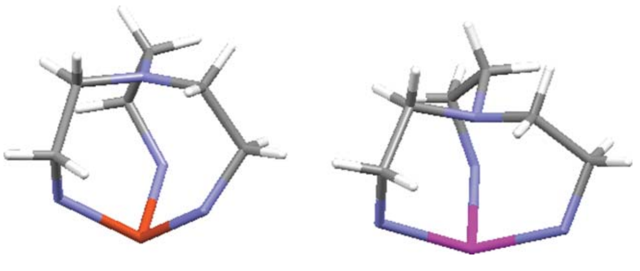

Fig. 4 The planar and "N in" tren conformations of $[FeH_3L^1]^{2+}$ in **1**·$KClO_4$ (left) and $[MnH_3L^1]^{2+}$ in **2** (right).

Table 1 Crystallographic data for new complexes

	1·$KClO_4$	**1**·$RbClO_4$	**1**·$CsClO_4$
Empirical formula	$C_{18}H_{24}Cl_3FeKN_{10}O_{12}$	$C_{18}H_{24}Cl_3FeN_{10}O_{12}Rb$	$C_{18}H_{24}Cl_3CsFeN_{10}O_{12}$
M/g mol^{-1}	773.77	820.14	867.58
Temperature/K	173(2)	173(2)	173(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}$	$P\bar{3}$	$P\bar{3}$
Unit cell dimensions:			
a/Å	13.389(2)	13.4744(8)	13.5022(13)
b/Å	13.389(2)	13.4744(8)	13.5022(13)
c/Å	9.174(3)	9.3487(11)	9.5419(13)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
Volume/Å^3	1424.4(6)	1469.9(2)	1506.5(3)
Z	2	2	2
Abs. coeff./mm^{-1}	1.037	2.508	2.033
F(000)	788	824	860
Crystal size/mm^3	0.46 × 0.41 × 0.26	0.54 × 0.45 × 0.32	0.42 × 0.36 × 0.12
θ range/°	2.83 to 29.80	2.18 to 30.83	2.13 to 30.75
Index ranges	$-18 \le h \le 18$ $-18 \le k \le 14$ $-12 \le l \le 12$	$-18 \le h \le 18$ $-18 \le k \le 18$ $-12 \le l \le 13$	$-19 \le h \le 19$ $-17 \le k \le 19$ $-13 \le l \le 13$
Reflections collected	16 177	16 933	16 336
Independent reflections	2718	2919	2978
$R1$	0.0245	0.0233	0.0381
$wR2$	0.0672	0.0571	0.0989
GOF on F^2	1.057	1.039	1.128

	1·NH_4ClO_4	**1**·NH_4ClO_4	**2**
Empirical formula	$C_{18}H_{28}Cl_3FeN_{11}O_{12}$	$C_{18}H_{28}Cl_3FeN_{11}O_{12}$	$C_{18}H_{24}Cl_2MnN_{10}O_8$
M/g mol^{-1}	752.71	752.71	634.31
Temperature/K	173(2)	293(2)	173(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Orthorhombic
Space group	$P\bar{3}$	$P\bar{3}$	$Pna2_1$
Unit cell dimensions:			
a/Å	13.4838(4)	13.5873(4)	9.7997(9)
b/Å	13.4838(4)	13.5873(4)	16.6091(16)
c/Å	9.3520(6)	9.3764(6)	16.0430(15)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	90
V/Å^3	1472.51(11)	1499.11(11)	2611.2(4)
Z	2	2	4
Abs. Coeff./mm^{-1}	0.863	0.848	0.774
F(000)	772	772	1300
Crystal size/mm^3	0.44 × 0.39 × 0.10	0.44 × 0.39 × 0.10	0.60 × 0.07 × 0.06
θ range/°	1.74 to 30.68	2.17 to 30.64	1.76 to 29.51
Index ranges	$-17 \le h \le 18$ $-18 \le k \le 18$ $-13 \le l \le 13$	$-18 \le h \le 18$ $-18 \le k \le 17$ $-13 \le l \le 13$	$-13 \le h \le 12$ $-22 \le k \le 22$ $-15 \le l \le 22$
Reflections collected	16 951	17 231	21 315
Independent reflections	2884	2929	5817
$R1$	0.0270	0.0333	0.0326
$wR2$	0.0742	0.0967	0.0702
GOF on F^2	1.069	1.044	1.032

Molecular structure: supramolecular considerations

The packing diagram of the double salt (Fig. 5) showing the location of the cations on the c axis is the first step in understanding the supramolecular features exhibited by these complexes.

These features include the organization of six perchlorate anions around the cation to give a distorted icosahedral complex, the size selectivity of the cation binding site and the hydrogen bonding arrangement between the perchlorate anions and the trifurcated imidazole N*H* and bifurcated imine C*H* hydrogen bond donors of **1**. The extended molecular lattice of the double salts is shown in Fig. 6.

The overall structure contains edge sharing hexagons. At the center of each hexagon there is a cation that electrostatically holds

Table 2 Selected bond and non-bonded distances (Å) and angles (°) for a) $\mathbf{1}\cdot H_2O^a$ b) $\mathbf{1}\cdot KClO_4{}^b$, c) $\mathbf{1}\cdot RbClO_4{}^b$, d) $\mathbf{1}\cdot CsClO_4{}^b$, e) $\mathbf{1}\cdot NH_4ClO_4{}^b$ at 173 K f) $\mathbf{1}\cdot NH_4ClO_4{}^b$, at 293 K and g) $[MnH_3L^1](ClO_4)_2$, **2**. The labeling scheme employed for the arms of the tren complexes is N_{ap}(C1–C2–N1=C3(H)(2-ImH))$_3$. N2 is the metal bound imidazole nitrogen atom

	a	b	c	d	e	f	g
T/K	100	173	173	173	173	293	173
M–N_{ap} non-bonded	3.436	3.350	3.376	3.386	3.380	3.368	2.813
H–H non-bonded	2.769	2.886	2.869	2.909	2.908	2.895	2.775
$N_{imidazole}$ *H* to C_{imine} *H*	2.817	—	—	—	—	—	2.778
	2.863	—	—	—	—	—	2.771
Average	2.816	2.886	2.869	2.909	2.908	2.895	2.775
M–N1 (imine)	1.974(2)	1.9624(10)	1.9740(12)	1.978(2)	1.9751(10)	1.9766(12)	2.247(2)
	1.976(2)	—	—	—	—	—	2.267(2)
	1.989(2)	—	—	—	—	—	2.295(2)
Average	1.980	1.9624	1.9740	1.978	1.9751	1.9766	2.270
M–N2 (imidazole)	1.958(2)	1.9432(10)	1.9552(11)	1.957(2)	1.9578(10)	1.9612(11)	2.277(2)
	1.967(2)	—	—	—	—	—	2.292(2)
	1.968(2)	—	—	—	—	—	2.309(2)
Average	1.964	1.9432	1.9552	1.957	1.9578	1.9612	2.293
M1–O1[c]	NA	3.0351(13)	3.0416(12)	3.160(3)	3.036	3.086	NA
Average		3.0351	3.0416	3.160	3.036	3.086	
M1–O3[c]	NA	2.9451(12)	3.0287(12)	3.135(2)	3.039	3.047	NA
Average		2.9451	3.0287	3.135	3.039	3.047	
M2–O2[c]	NA	2.9432(11)	3.1238(14)	3.241(3)	3.126	3.137	NA
Average		2.9432	3.1238	3.241	3.126	3.137	
M2–O3[c]	NA	2.9438(12)	3.0402(12)	3.169(2)	3.037	3.061	NA
Average		2.9438	3.0402	3.169	3.037	3.061	
N1–M–N2 (bite)	80.68(9)	81.08(4)	81.03(5)	81.08(9)	81.08(4)	80.91(5)	73.66(8)
	80.89(9)	—	—	—	—	—	72.82(7)
	80.75(8)	—	—	—	—	—	72.58(7)
Average	80.77	81.08	81.03	81.08	81.08	80.91	73.02
N1–M–N2′ (*trans*)	173.99(8)	173.02(4)	172.82(5)	172.80(10)	172.91(4)	172.97(5)	159.48(8)
	171.92(9)	—	—	—	—	—	157.86(8)
	173.67(9)	—	—	—	—	—	156.26(8)
Average	173.19	173.02	172.82	172.80	172.91	172.97	157.87
C1–N_{ap}-C1′	120.6(2)	119.843(13)	119.856(15)	119.85(3)	119.848(13)	119.81(2)	112.9(2)
	119.4(2)	—	—	—	—	—	112.0(2)
	119.9(2)	—	—	—	—	—	112.3(2)
Average	120.0	119.84	119.856	119.85	119.848	119.81	112.4

[a] Ref. 13*a*. [b] Only one value is given for each of the three tren arms due to symmetry. [c] Each M–O (M = K, Rb, Cs, and N from NH_4^+) distance has 6 identical values due to symmetry. O1 and O2 are bound only to M1 and M2, O3 is bound to both M1 and M2. For NH_4^+ the N to O distance is a non-bonded distance.

six perchlorates in place. These in turn are hydrogen bound to the iron complexes.

The C_3^i (S_6) axis at the center of the hexagon is the *c* axis of the cell. The two independent cations are located on the *c* axis at the origin (0, 0, 0) and *c*/2 (0, 0, 0.5) and alternate positions. Midway between adjacent cation positions are three symmetry related perchlorate anions. The three chlorine atoms form an equilateral triangle perpendicular to the *c* axis. The orientation of the oxygen atoms of the perchlorate anion is approximately tetrahedral with O1 and O2 above and below the chlorine plane and bound to a single cation while O3 is in the chlorine plane (displaced 0.074 Å) and bridges both cation positions. O4 is also in the plane (displaced 0.054 Å) of the three chlorine atoms but directed away from the *c* axis and is thus not bound to the metals. Progressing down the *c* axis the next grouping of three perchlorate anions is related to the first by inversion symmetry, C_3^i (S_6). This is illustrated in Fig. 7 and 8.

Fig. 9 illustrates different representations of the potassium coordination sphere in $\mathbf{1}\cdot KClO_4$. The potassium cation has an approximate octahedral array of six chlorines around it, which are outside of a bonding interaction. Each perchlorate anion acts as a bidentate donor to the metal resulting in a distorted icosahedron. An icosahedral cage can be illustrated by connecting the coordinated oxygen atoms. Each of the six perchlorate anions contributes two oxygen atoms to the distorted icosahedron. The average O–O distance is 3.184 Å. The icosahedron is not regular due primarily to the short O–O non-bonded distance of the bidentate perchlorate anions. The icosahedral arrangement is similar to that of $Ce(NO_3)_6{}^{2-}$ found in $Ce(NH_4)_2(NO_3)_6$.[22]

The size of the cation is very important in the formation of double salts of this structure. The sum of the ionic radii[23] of the CN = 12 potassium cation (1.78 Å) and oxide (1.28 Å) is 3.06 Å, which very closely matches the average K–O distance of 2.9668(12) Å. The analogous sums for rubidium (CN = 12, 1.86 Å) and caesium (CN = 12, 2.02 Å) are 3.14 and 3.30 Å respectively. The observed average Rb–O and Cs–O distances are 3.0586(12) and 3.176(3) Å. These distances suggest that in terms of size considerations alone the match of the cation size with the icosahedral binding site is potassium > rubidium > caesium. This trend should not be over-interpreted due to the fact that the cage is not a rigid species as the twelve vertices are non-bonded interactions rather than covalent bonds as in the icosahedral $B_{12}H_{12}{}^{2-}$ anion or the C_{60} icosahedral complexes of potassium or rubidium.[24] Thus, the cage is capable of expanding or contracting

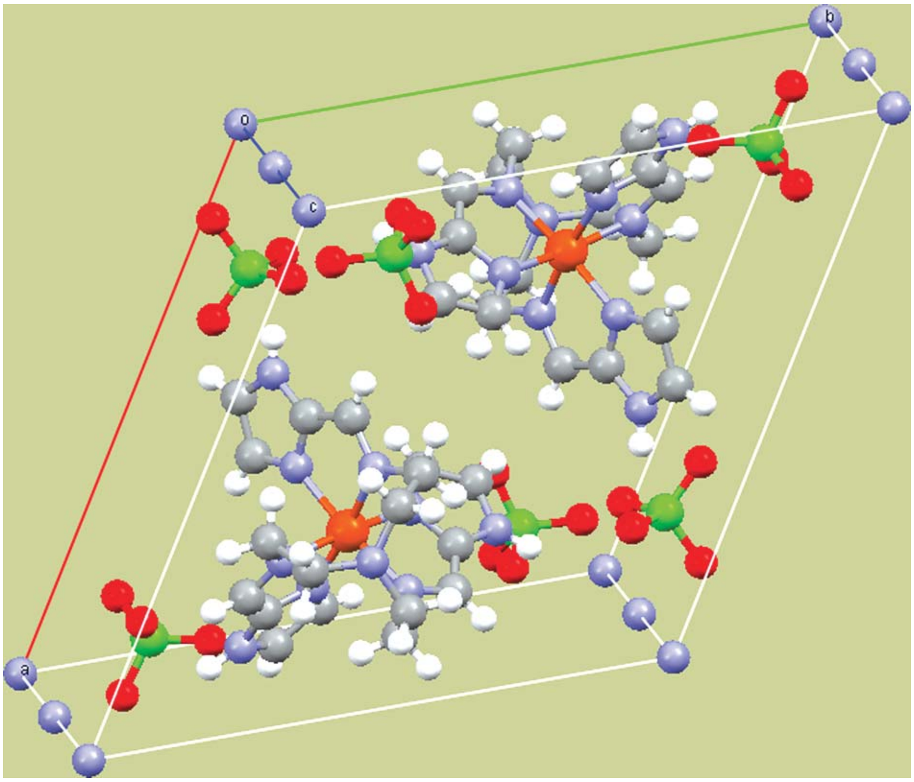

Fig. 5 The unit cell of **1**·NH_4ClO_4 at 293 K.

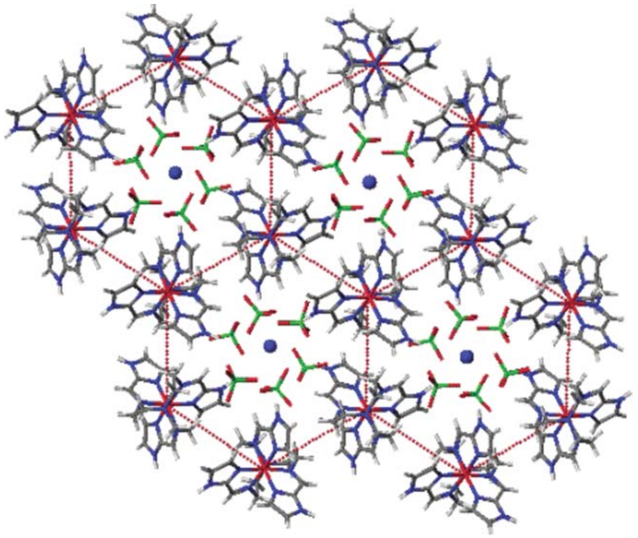

Fig. 6 The molecular lattice of **1**·$KClO_4$. The view is of the extended *ab* plane. The dashed lines connecting the iron atoms serve to highlight the hexameric pattern. Adjacent iron complexes are of opposite chirality and orientation, Fe eclipsing N_{ap} or the reverse.

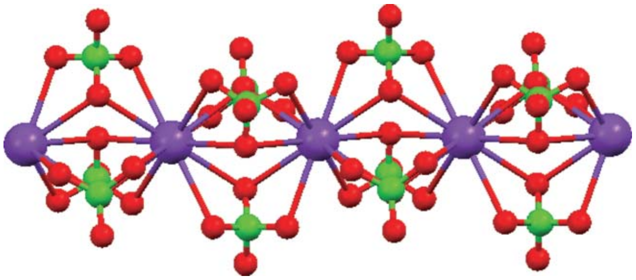

Fig. 7 The extended *c* axis of **1**·$KClO_4$. Alternate metal sites are identical.

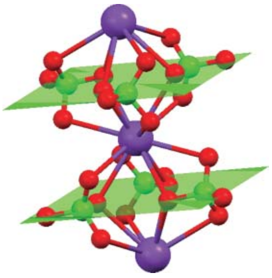

Fig. 8 The planes of the three chlorine atoms between the metal positions in **1**·$KClO_4$.

to accommodate slight differences in cation size. However, this ability to expand or contract has limits. The sum of the oxide radius with the small sodium ion (CN = 12, 1.53 Å) is 2.81 Å, which is ~0.2 Å shorter than the observed K–O distance in the smallest cage. Contraction of the cage to accommodate the small sodium cation is not observed and may be due to strong repulsive forces between the perchlorate anions. Expansion of the cage to accommodate the larger rubidium or caesium ions is more easily accomplished.

The case for the ammonium ion in **1**·NH_4ClO_4 is quite different from the other double salts due to both size and symmetry considerations. The size of the ammonium cation is 1.51 Å,[23] which is approximately the same size as sodium, and therefore

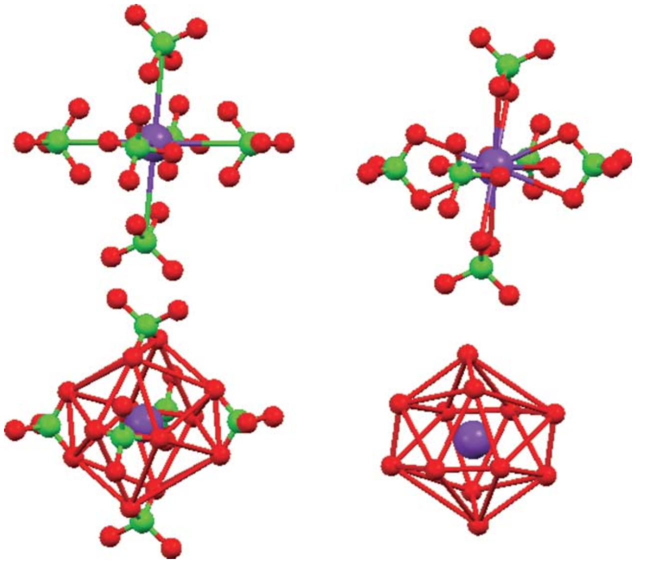

Fig. 9 Coordination of the potassium ion by the six perchlorate anions. Top left shows the octahedral arrangement of the chlorine atoms around the potassium. Top right shows the CN = 12 potassium ion. Bottom left draws in the oxygen–oxygen non-bonded distances to show the framework of the distorted icosahedron. Bottom right is the same as bottom left but eliminates the chlorine and oxygen atoms not bound to potassium.

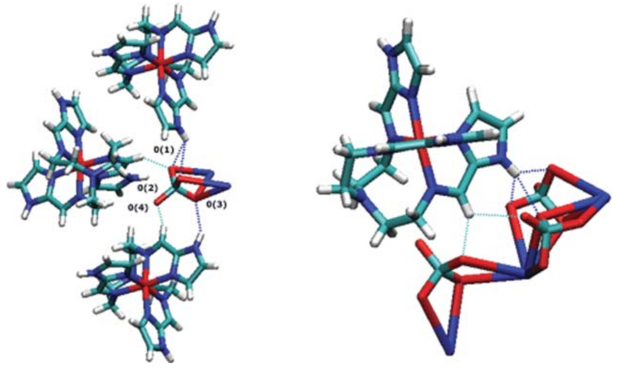

Fig. 10 The hydrogen bonding arrangement between one perchlorate anion and three $[FeH_3L^1]^{2+}$ complexes (left) and one $[FeH_3L^1]^{2+}$ complex and three perchlorate anions (right). The numbering scheme used for the four perchlorate oxygen atoms O(1)–O(4) in Table 3 is illustrated in the left side view.

does not seem a good candidate for analogous coordination by perchlorate anions. This ignores hydrogen bonding considerations that are present with ammonium but are lacking with the alkali metal cations. The average observed non-bonded N–O distance in **1**·NH_4ClO_4 at 293 K is 3.08 Å, which is quite similar to the average K–O distance of 2.9668(12) Å observed in **1**·$KClO_4$. The non-bonded N–O distance in a N–H · · · O hydrogen bonding interaction can easily be ~3.0 Å as is observed in **1**·NH_4ClO_4. The symmetry problem for the ammonium ion is more complex. The cation positions are on the *c* axis, which has C_3^{i} (S_6) symmetry. This poses no problem for the spherical alkali metal cations but does for the tetrahedral ammonium ion, which lacks this symmetry element. The resolution of this dilemma is discussed in the section describing the structures of the simple $MClO_4$.

Extending outward from the *c* axis is the hydrogen bonding interaction between the perchlorate anions and the iron complex cations. Examination of Fig. 6 reveals that one perchlorate anion is adjacent to one arm of each iron complex cation. However each perchlorate anion (and each arm of an iron complex ion) is within hydrogen bonding distance of the ions to either side. Thus each perchlorate anion is hydrogen bound to three adjacent iron complex cations and each arm of an iron complex cation is hydrogen bound to three adjacent perchlorate anions as is illustrated in Fig. 10. Thus, one iron complex has fifteen hydrogen bonds to nine perchlorate anions.

The hydrogen bonding scheme is complex in that it involves both traditional $N_{\mathrm{imidazole}}$–H · · · O and non traditional C_{imine}–H · · · O hydrogen bonding. In addition both bifurcated and trifurcated hydrogen bonds are present. It is clear from Fig. 10 (left view) that $[FeH_3L^1]^{2+}$ can function as a bidentate hydrogen bonding donor to a single perchlorate anion. Table 3 summarizes the hydrogen bonding data, which are remarkably similar from one complex to another despite the difference in the size of the central cation on the *c* axis. Non-traditional hydrogen bonds have been well established crystallographically[18] and the values observed here are well within range for weak hydrogen bonding interactions. A key element in non-traditional hydrogen bonds is the activation of a C–*H* bond, in this case the imine bond, by either hybridization or bonding to electronegative substituents.[25] Both bifurcated[18] and trifurcated donors are observed in the present system. Trifurcated N–H donors,[26] while rare, have been established in other reports involving nucleotides,[27] bis(2-pyridylmethyl)amine,[28] tren,[29] and imidazole.[30] There is a report of a diazabicyclo[2.2.2]octane-1,4-diium salt that contains both trifurcated N–H and C–H donors.[31] The perchlorate anion in the double salts is tethered to its bonding site in a remarkable fashion with five hydrogen bonding interactions and four electrostatic bonds. Although in this case the binding site was self-assembled,[32] it is reminiscent of ligands designed for this purpose[33] or of the anion binding site in transferrin.[34]

Molecular structure: relationship to structure of $[Fe^{II}H_3L^2][Fe^{III}L^2](BF_4)_2$ in *P*3

These hexameric structures bear some similarity to an isomeric iron complex of H_3L^2 (Fig. 1). The related complex is not a double salt but a mixed valence compound of formula $[Fe^{II}H_3L^2][Fe^{III}L^2](BF_4)_2$.[14] This complex crystallizes in *P*3 rather than $P\bar{3}$. Both space groups are non-centrosymmetric but the former contains only a single enantiomer (racemic conglomerate, resolved at the level of the crystal) and has chiral recognition[35] while the latter contains both enantiomers and is a racemic compound. Both systems exhibit a hexameric arrangement of iron complexes in which adjacent complexes differ in their alignment of the Fe–N_{ap} axis, imidazole rings pointed up or down. At low temperature both systems have a *c* axis of comparable length, 9.40 Å for the mixed valence species and 9.17–9.54 Å for the double salts. This distance is approximately the width of the isomeric iron complexes. The reason for the variation in length of the *c* axis in the double salts is that the size of the cation that is on this axis varies from the relatively small potassium (*c* = 9.17 Å) to the larger caesium (*c* = 9.54 Å). Both systems have a central cavity in the middle of the hexamer, which is the *c* axis. In the mixed valence species the cavity contains the tetrafluoroborate anions whereas

Table 3 Hydrogen bond distances (Å) and angles (°) for **1**·MClO$_4$[a]. N3 is the free imidazole nitrogen atom, H(3B) is its proton, C(3) is the imine carbon atom and H(3A) is its proton. The four perchlorate oxygen atoms O1–O4 are labeled in Fig. 10

		d(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1·KClO$_4$	N(3)–H(3B)···O1	0.86	2.63	3.2016	124.8
	N(3)–H(3B)···O2	0.86	2.48	3.0781	127.1
	N(3)–H(3B)···O3	0.86	2.17	2.9229	146.7
	C(3)–H(3A)···O1	0.93	2.34	3.095	138.7
	C(3)–H(3A)···O4	0.93	2.68	3.122	110.2
1·RbClO$_4$	N(3)–H(3B)···O1	0.76	2.73	3.240	126.9
	N(3)–H(3B)···O2	0.76	2.61	3.1236	127
	N(3)–H(3B)···O3	0.76	2.29	2.959	147
	C(3)–H(3A)···O1	0.95	2.35	3.1267	138.9
	C(3)–H(3A)···O4	0.95	2.719	3.1439	107.9
1·CsClO$_4$	N(3)–H(3B)···O1	0.88	2.62	3.260	130.0
	N(3)–H(3B)···O2	0.88	2.54	3.185	130.5
	N(3)–H(3B)···O3	0.88	2.29	2.974	134.9
	C(3)–H(3A)···O1	0.95	2.38	3.153	138.6
	C(3)–H(3A)···O4	0.95	2.79	3.166	104.5
1·NH$_4$ClO$_4$ (173 K)	N(3)–H(3B)···O1	0.88	2.62	3.2278	126.6
	N(3)–H(3B)···O2	0.88	2.51	3.1333	128.6
	N(3)–H(3B)···O3	0.88	2.22	2.9589	141.6
	C(3)–H(3A)···O1	0.95	2.35	3.1336	139.3
	C(3)–H(3A)···O4	0.95	2.72	3.1467	107.8
1·NH$_4$ClO$_4$ (293 K)	N(3)–H(3B)···O1	0.86	2.67	3.264	127.8
	N(3)–H(3B)···O2	0.86	2.59	3.187	127.9
	N(3)–H(3B)···O3	0.86	2.25	2.978	143.2
	C(3)–H(3A)···O1	0.93	2.39	3.150	139.4
	C(3)–H(3A)···O4	0.93	2.76	3.175	108.5

[a] Only one value is given for each of the three tren arms due to symmetry.

in the double salt the cavity contains the alkali cations and the perchlorate anions. In the double salt there is a high degree of order and occupancy on the *c* axis. Not surprisingly the *a* axis is larger in the double salts (13.4–13.6 Å) than in the mixed valence complex (11.9 Å) as the double salts must accommodate both a larger number of atoms and larger atoms than are required to fit in the cavity of the mixed valence species.

Molecular structure: relationship to MClO$_4$ structures

The structures of MClO$_4$ (M = K, Rb, Cs, and NH$_4$) have been solved in the orthorhombic space group *Pnma*.[36] The coordination of the metal cations to the perchlorates is quite different from the distorted icosahedron described above. Each metal ion bonds to seven (not six) perchlorate anions and is twelve coordinate. This is achieved by bonding to two bidentate perchlorate anions in a very asymmetric mode (3.453(3) and 2.862(3) Å), to two bidentate perchlorate anions in a moderately asymmetric mode (3.153(2) and 2.884(3) Å), to a single bidentate perchlorate anion in a symmetric mode (2.983(3) Å) and to two monodentate perchlorate anions (2.877(4) and 2.870(4) Å). The orientation of the seven perchlorate chlorine atoms around the potassium is a distorted monocapped octahedron with the two monodentate perchlorate anions occupying the capping position and one of the four equatorial positions as shown in Fig. 11.

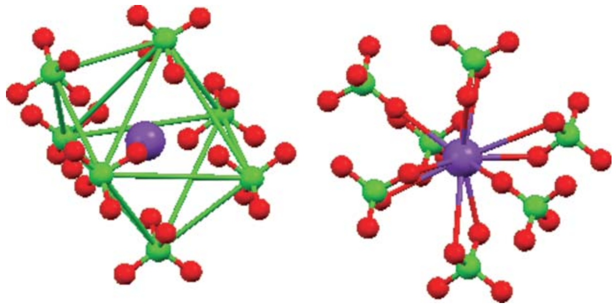

Fig. 11 The coordination of the potassium cation by perchlorate anions in *Pnma* KClO$_4$. The left view shows the distorted monocapped octahedral arrangement of the seven chlorine atoms around the potassium and the right view shows the distorted CN = 12 structure.

The structure of NH$_4$ClO$_4$ has been the subject of several investigations due to the use of this salt in propellants and explosives and possible errors in early reports.[37] At room temperature the hydrogen atoms of the ammonium ion are not located due to rotational disorder. The structure of ND$_4$ClO$_4$ has been determined at 20 and 70 K by neutron diffraction and is depicted in Fig. 12. Under these conditions the positions of the deuterium atoms are located and the structure is simply a tetrahedral ND$_4^+$ ion hydrogen bound to four different perchlorate anions. The same problem of rotational disorder is observed in the 293 K structure of **1**·NH$_4$ClO$_4$. At this temperature the nitrogen atom of the ammonium ion was located on the *c* axis but the hydrogen atoms were not located, presumably due to rotational disorder, just as was the case for NH$_4$ClO$_4$. At 173 K a single hydrogen atom and nitrogen atom were located for each cation site.

The symmetry of the space group represents this cation as an octahedral species (*i.e.* $N(H_6)_{.666}^{+}$). Obviously there is no octahedral ammonium cation and its representation in the solution is simply the result of symmetry considerations. The cations are found on the *c* axis, which has C_3^{i} (S_6) symmetry. If the cations are spherical as are the alkali metal cations or achieve spherical symmetry due to rapid rotational disorder (NH$_4^+$ at 293 K) then there is no symmetry problem. However if the cation loses

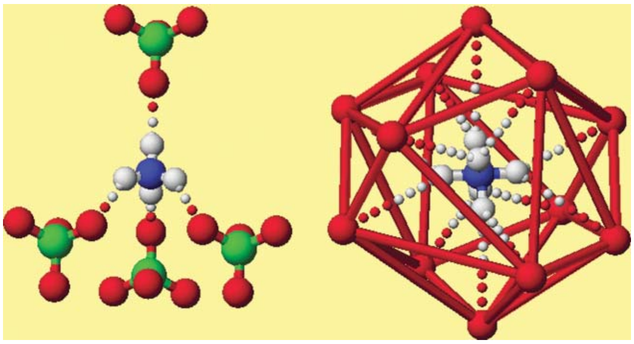

Fig. 12 The structure of ND_4ClO_4 at 70 K (left) and the ammonium ion of **1**·NH_4ClO_4 at 173 K in its icosahedral array of perchlorate anions (right). The N–O non-bonded distance indicates that the nitrogen atom of the ammonium cation is within hydrogen bonding distance to all twelve of the oxygen atoms of the six bidentate perchlorate anions.

spherical symmetry due to loss of rotational disorder (NH_4^+ at 173 K) then there is a problem if the cation lacks the necessary symmetry associated with its position as is the case here. The ammonium cation is tetrahedral and has a C_3 and S_4 axis but no S_6 axis. In this case the symmetry dilemma was solved by the representation of the ammonium cation as the octahedral, $N(H_6)_{.666}^+$, which has the required S_6 symmetry element. Each hydrogen atom located with the nitrogen atom of the two cation sites on the *c* axis in **1**·NH_4ClO_4 at 173 K acts as a bifurcated donor to two different perchlorate oxygen atoms. The hydrogen bonding interactions for the two nitrogen atoms of the ammonium cations, N1A and N2A, and the perchlorate oxygen atoms are *d*(D-H) (0.74 and 0.74 Å) *d*(H···A) (2.45 and 2.50 Å), *d*(D···A) (3.04 and 3.13 Å) and ∠DHA (138 and 143°) and *d*(D–H) (0.78 and 0.78 Å) *d*(H···A) (2.37 and 2.58 Å), *d*(D···A) (3.04 and 3.04 Å) and ∠DHA (144 and 119°) respectively. This indicates that the nitrogen atoms of the ammonium ions are within hydrogen bonding interactions of all twelve oxygen atoms of the six bidentate perchlorate anions that surround it. The ammonium cation and its surrounding six perchlorate anions are shown in Fig. 12. It needs to be emphasized that this representation does not imply an octahedral ammonium cation but simply is a result of the symmetry of the cation sites. However, Fig. 12 does correctly illustrate that the central nitrogen atom of the ammonium cation is within hydrogen bonding distance of all twelve perchlorate oxygen atoms. There are other ligand systems developed to encapsulate an ammonium cation that also utilize its tendency to form hydrogen bonds.[38]

Synthesis

The synthesis of the double salts was achieved by reaction of **1**·H_2O in methanol with $MClO_4$ or MCl and $NaClO_4$ (excess) (M = K, Rb, Cs, or NH_4). The existence of these adducts in solution has not been demonstrated. The yield of the double salt followed the trend K > Rb > Cs. Whether this is due to solubility considerations or the match of metal size with its six surrounding perchlorate anions is uncertain. Sodium does not form a double salt under these conditions and all that is isolated with sodium in the absence of other alkali metal cations is **1**·H_2O. One reason for the failure of sodium to form a double salt is that sodium is simply too small to fit in the distorted icosahedral binding site formed by the six perchlorate anions. Alternately the high solubility of sodium perchlorate relative to the other alkali metal perchlorates in methanol may be responsible for the double salt not precipitating. Since ammonium perchlorate, which has high solubility in methanol, does form a double salt under these conditions it seems that the size of the cation, not its solubility, is the primary criterion for determining if the reaction will produce a double salt.

There are several structural elements in the double salts that could be altered in an attempt to produce analogous complexes. These are the central cation, the metal in the imidazole complex, the anion and the exact imidazole ligand utilized. Any central cation in analogous complexes would have to be an M^+ as any other valence would alter the empirical formula of the double salt, which would likely preclude crystallization in $P\bar{3}$. Further it should have an ionic radius (for CN = 12) close to that of K^+, Rb^+, or Cs^+. This restricts possibilities greatly but Ag^+, Au^+, Hg^+ and Tl^+ are possibilities. The reaction of **1**·H_2O with silver perchlorate in methanol was attempted and resulted in an immediate color change from red to green–dark blue and precipitation of a fine blue powder which was not further characterized. Silver(I) is a fairly strong oxidizing agent as are Au^+ and Hg^+. Reaction of these ions with the iron(II) of **1**·H_2O may result in oxidation and decomposition of the complex. Thus, in addition to size and charge, the redox properties of the central metal must be considered.

Seemingly the most innocent substitution would be replacement of the iron(II) in the complex with another metal(II) such as Mn(II), Ni(II), or Cu(II). The reactions of $[MH_3L^1](ClO_4)_2$ (M = Mn, Ni and Cu), generated *in situ*, with potassium perchlorate were attempted but failed to give the double salt under analogous reaction conditions. The failure of $[MH_3L^1](ClO_4)_2$ (M = Mn, Ni, Cu) to form analogous double salts could be attributed to differences in solubility, geometry of the bidentate hydrogen bonding donor site, complex acidity or electronic effects between $[MH_3L^1](ClO_4)_2$ (M = Mn, Ni, Cu) and **1**.

While solubility can never be underestimated it does not seem important here as in general the $[MH_3L](ClO_4)_2$ complexes are fairly soluble in methanol and both **1**·H_2O and **2** (only other complex of H_3L^1 isolated in pure form to date) are freely soluble in methanol. The structure of $[MnH_3L^1](ClO_4)_2$, **2**, was determined as part of this work to examine the difference in the non-bonded $N_{imidazole}$–*H* to C_{imine}–*H* distance with the $[FeH_3L^1]^{2+}$ cation. The average $N_{imidazole}$–*H* to C_{imine}–*H* distance (Table 2) in the double salts is 2.893 Å while that in $[MnH_3L^1]^{2+}$ is 2.775 Å. Given the variation in weak hydrogen bond distances and angles this does not seem significant enough to impact the ability of $[MnH_3L^1]^{2+}$ to function as a hydrogen bonding donor to the perchlorate anion. The imidazole protons in **2** are less acidic than those of **1** based on reactivity toward sodium hydroxide.[21] However, this does not imply that **2** is unable to act as a hydrogen bond donor.

There is a significant electronic difference between **1**·H_2O (SC at 295 K) and **2** (HS). As the imidazole proton begins to function more as a hydrogen donor it pushes the spin equilibrium more to the LS side (see Mössbauer section), which results in increasing the acidity of the imidazole proton and a further push to the LS side. Thus there is a reinforcing feedback. There are other examples of this type of feedback in which an iron(II) SC system reversibly shifts from HS to LS on proton removal/addition.[39] With **2** there is no spin equilibrium involved, which may explain its lack of reactivity.

Replacement of the ligand itself must involve changes only to the tren framework as the bidentate hydrogen bonding donor ability is only possible with 2-imidazolecarboxaldehyde. Substitution of trpn (H_3L^4), Nmetren$^+$ (H_3L^5) or others for tren in H_3L^1 (Fig. 1) and other anions for perchlorate is being investigated.

Preliminary characterization

The simplest evidence of reaction is the hexagonal shape of the double salts, which easily differentiates them from those of the starting complex, **1**·H_2O, are elongated rectangular crystals. The IR spectra of **1** and its adducts show the characteristic absorption bands attributable to the imidazole ν_{N-H} (3100–3400 cm^{-1}), and perchlorate ν_{Cl-O} (1147–1154 and 625 cm^{-1}). The position of the imine band, ~1577 cm^{-1}, correlates with the spin state.[40] The molecular ion of the iron complex in the double salts, **1**·$MClO_4$, was identified by ESMS. However there were no ions identifiable as containing the alkali metal (K, Rb, or Cs) or ammonium cation so this method was not useful in uniquely identifying a particular double salt.

Mössbauer

Mössbauer data (Fig. 13) were collected on the double salts, **1**·$MClO_4$, at 295 K and subjected to Lorentzian analysis. **1**·H_2O at 295 K is SC as there are doublets corresponding to the HS and LS iron(II) states. In contrast the spectra of the double salts, **1**·$MClO_4$, consist of a single doublet which is consistent with LS iron(II). This indicates that formation of the double salt shifts the position of the $LS(^1A) \rightleftharpoons HS(^5T)$ equilibrium of **1**·H_2O from mostly HS (62.8%) entirely to the LS side. The dramatic shift in the equilibrium is likely due to the extensive hydrogen bond donation of **1** to the perchlorate anions in **1**·$MClO_4$. If a SC complex acts as a hydrogen bond donor the ligand field of the complex increases and the SC equilibrium shifts to the LS side. The stabilization of a LS state of a complex in which the ligand that acts as a hydrogen bond donor has been observed with other SC iron(II) complexes.[41] At room temperature **1**·H_2O is involved in a spin equilibrium, $LS(^1A) \rightleftharpoons HS(^5T)$, and as it crystallizes to form the double salts the equilibrium is shifted entirely to the LS side due to the extensive hydrogen bond donation of $[FeH_3L^1]^{2+}$ to the perchlorate anions. The Mössbauer spectra of **1**·$RbClO_4$ and **1**·NH_4ClO_4 are essentially identical in appearance to that of **1**·$KClO_4$ depicted in Fig. 13. However the spectrum of **1**·$CsClO_4$ is asymmetric with greater intensity in the lower velocity line.

Conclusion

These double salts provide exciting new supramolecular systems that are examples of self organization controlled by electrostatic and hydrogen bonding. A cation of appropriate size organizes six bidentate perchlorate anions around it to form a distorted icosahedral complex. The six perchlorate anions in turn form a complex series of hydrogen bonds with bifurcated imine C*H* and trifurcated imidazole N*H* hydrogen donors of the tripodal iron complex. The iron atoms of the complexes are at the vertices of the edge sharing hexameric rings. The formation of the double salts shifts the SC equilibrium of the parent complex to pure LS. Extension of this type of self assembled supramolecular system to other combinations of central cation, surrounding anion and/or organic hydrogen bonding acceptors, and metal complex are underway to determine the interplay of size, coordination number, and hydrogen bonding. With an understanding of these factors applications of these systems to selective bonding of cations, anions and/or organic ligands is possible.

Experimental

Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN. Mass spectral analyses were obtained from HT Laboratories, San Diego, CA. Tris(2-aminoethyl)amine, 2-imidazolecarboxaldehyde, rubidium perchlorate, rubidium chloride, caesium perchlorate, caesium chloride, and ammonium perchlorate were obtained from Aldrich. Sodium perchlorate monohydrate, potassium chloride, and potassium perchlorate were obtained from Fisher. **1**·H_2O[13] and **2**[21] were prepared as described previously. Crystals of **2** were grown from methanol. All solvents were of reagent grade and used without further purification.

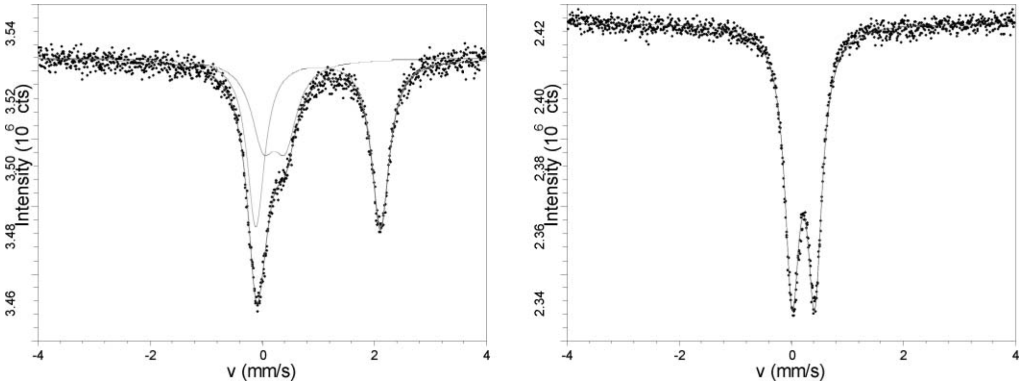

Fig. 13 Mössbauer spectra at 295 K of **1**·H_2O (left) and **1**·$KClO_4$ (right). The spectrum of **1**·H_2O was fitted to two doublets (IS = 0.21, QS = 0.39 mm s^{-1}, 37.2% and IS = 1.00, QS = 2.22 mm s^{-1}, 62.8%). These are assigned as LS and HS iron(II) respectively. Paired values of IS and QS for **1**·$MClO_4$ are M = NH_4 (0.29, 0.35 mm s^{-1}), M = K (0.29, 0.37 mm s^{-1}), M = Rb (0.29, 0.36 mm s^{-1}) and M = Cs (0.29, 0.35 mm s^{-1}); IS = isomer shift, QS = quadrupole splitting.

Spectra‡

The ^{57}Fe Mössbauer spectra were recorded from powdered samples with a constant acceleration MS1200 Ranger Scientific spectrometer and a *ca.* 1.85 GBq ^{57}Co–Rh source. The sample thickness was ~50–80 mg cm^{-2}. The line width of the calibration spectrum was 0.29 mm s^{-1}. The chemical isomer shift data are quoted relative to the centroid of the metallic iron spectrum at room temperature. The data were analyzed by a constrained least squares fit to Lorentzian shaped lines. IR spectra were obtained as KBr pellets on a Perkin Elmer 1600 FT IR spectrometer.

Structure determinations†

Crystal data for all complexes were collected on a Bruker Apex 2 diffractometer. All structures were solved using the direct methods program SHELXS-97.[42] All non-solvent heavy atoms were located using subsequent difference Fourier syntheses. The structures were refined against F^2 with the program SHELXL,[43] in which all data collected were used including negative intensities. All non-solvent heavy atoms were refined anisotropically. All hydrogen atoms were located by Fourier difference except for the ammonium hydrogen atoms in **1**·NH_4ClO_4 at 293 K. The hydrogen atom of the ammonium cation for this complex was located at 173 K.

Syntheses

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Synthesis of [FeH_3L^1](ClO_4)$_2$·NH_4ClO_4, 1·NH_4ClO_4. Ammonium perchlorate (0.074 g, 0.631 mmol) was added as a solid to a refluxing solution of **1**·H_2O (0.200 g, 0.315 mmol) in methanol (50 ml). The dark red solution was set aside to concentrate. After 2 d, dark red crystals (0.128 g, 54%) suitable for X-ray diffraction were removed by suction filtration. Elemental analysis calcd for $C_{18}H_{28}N_{11}Cl_3FeO_{12}$, **1**·$NH_4ClO_4$: C 28.72, H 3.75, N 20.47. Found: C 28.70, H 3.55, N 20.31.

Synthesis of [FeH_3L^1](ClO_4)$_2$·$KClO_4$, 1·$KClO_4$. 2-Imidazolecarboxaldehyde (0.129 g, 1.34 mmol) and tren (0.065 g, 0.45 mmol) were refluxed in methanol (10 ml) for 12 min to give a yellow solution. $FeCl_2$·$4H_2O$ (0.089 g, 0.45 mmol) was added as a solid and the solution turned dark red. The mixture was refluxed for a further 10 min and potassium chloride (0.033 g, 0.44 mmol) was added as a solid. An excess of sodium perchlorate monohydrate (0.254 g, 1.81 mmol) in methanol (10 ml) was added. The dark red solution was set aside to concentrate. After 7 d dark red crystals (0.254 g, 73.2%) suitable for X-ray diffraction were removed by suction filtration. Elemental analysis calcd for $C_{18}H_{24}N_{10}Cl_3FeKO_{12}$, **1**·$KClO_4$: C 27.94, H 3.13, N 18.10. Found: C 27.40, H 2.94, N 17.59.

Synthesis of [FeH_3L^1](ClO_4)$_2$·$RbClO_4$, 1·$RbClO_4$. 2-Imidazolecarboxaldehyde (0.197 g, 2.05 mmol) and tren (0.100 g, 0.685 mmol) were refluxed in methanol (20 ml) for 30 min to give a yellow solution. $Fe(ClO_4)_2$·$6H_2O$ (0.249 g, 0.685 mmol) was added in methanol (10 ml). The mixture was refluxed for 10 min and rubidium perchlorate (0.381 g, 2.06 mmol) was added as a solid at reflux. The dark red solution was set aside to concentrate. After a day a mixture of dark red crystals and white solid (0.655 g) was removed by filtration. The mixture was recrystallized from methanol (60 ml) and hot filtered to remove the white solids. Concentration of the filtrate yielded dark red crystals of **1**·$RbClO_4$ (0.169 g, 30%). A second crop (0.094 g) was obtained a day later. Elemental analysis calcd for $C_{18}H_{24}N_{10}Cl_3FeO_{12}Rb$, **1**·$RbClO_4$: C 26.36, H 2.95, N 17.08. Found: C 26.48, H 3.07, N 17.03.

Synthesis of [FeH_3L^1](ClO_4)$_2$$CsClO_4$, 1·$CsClO_4$. 2-Imidazolecarboxaldehyde (0.197 g, 2.05 mmol) and tren (0.100 g, 0.685 mmol) were refluxed in methanol (20 ml) for 30 min to give a yellow solution. $Fe(ClO_4)_2$·$6H_2O$ (0.249 g, 0.685 mmol) was added in methanol (10 ml). The mixture was refluxed for 10 min and caesium perchlorate (0.478 g, 2.06 mmol) was added as a solid at reflux. The dark red solution was set aside to concentrate. After a day a mixture of dark red crystals and white solid (0.657 g) was removed by filtration. The mixture was recrystallized from methanol (60 ml) and hot filtered to remove the white solids. Concentration of the filtrate yielded dark red crystals of **1**·$CsClO_4$ (0.035 g, 5.9%). Elemental analysis calcd for $C_{18}H_{24}N_{10}Cl_3CsFeO_{12}$, **1**·$CsClO_4$: C 24.92, H 2.79, N 16.14. Found: 25.25 C, 2.97 H, 16.02 N.

Acknowledgements

CUA aid to GB on 350010 is gratefully acknowledged.

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