Kinetically inert cryptate systems: solid state and solution NMR studies †

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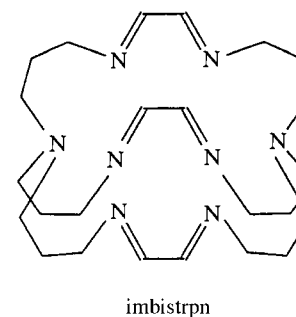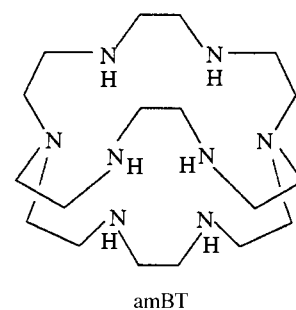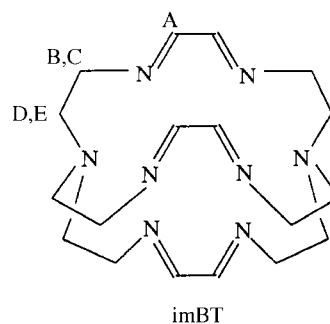[e] Department of Chemistry, University of Newcastle, Newcastle on Tyne, UK NE1 7RU
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Mononuclear cryptates of Pb^{2+}, Cd^{2+} and Hg^{2+} with the small host 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]-hexacosa-4,6,13,15,21,23-hexaene (imBT) showed satellite peaks in ^1H NMR solution spectra throughout the accessible (−40 to +70 °C) fluid range of solvents used indicating kinetic inertness toward decomplexation. Solid-state MAS NMR studies were made on these cryptates and on dinuclear silver(I) and copper(I) analogues, in the latter case establishing coupling of $^{63,65}Cu$ to ^{15}N. A crystal structure determination of the mercury cryptate showed a symmetrical six-co-ordinate site for Hg^{2+} with all imino nitrogens co-ordinated, consistent with the observation, for the isomorphous cadmium(II) complex, of a 13-line ^{113}Cd resonance in the CP MAS NMR spectrum.

The small 6-atom stranded cage systems sar and sep show notable kinetic stability when encapsulating first and second transition series cations,[1] but have not been widely used to host the larger heavy metal cations which are of environmental significance. Ligands which can ensure kinetic inertness of these cations are much sought after for the purpose of environmental remediation or for transport of radionuclide or other imaging agents.[2] The compound imBT, the small iminocryptand generated by the [2+3] Schiff-base condensation method[3] using tris(aminoethyl)amine and the 2-carbon dialdehyde, glyoxal, differs from sep only in the number of carbon atoms in the methylene capping units (two per strand *versus* one in sep). This iminocryptand has the right cavity size to ensure good fit of the larger main group cations, such as Cd^{2+}, Pb^{2+}, Hg^{2+}. In the case of the analogous aminocryptand, amBT (=imBT + 12H), it has been shown that high stability constants result from the good match of cation size and cavity dimensions.[4,5] However, the basicity[4] of the aminocryptand host ensures competition of protons for the sp^3 N-donor sites, which reduces the effectiveness of the hosts in acidic media, and can incidentally lead to lower kinetic stability.[6,7] Kinetic lability may be an advantage for some, *e.g.* analytical purposes, but is not desirable for environmental remediation applications. In a previous study involving imBT we observed unusual kinetic stability[8] for transition metal ions encapsulated in mononuclear fashion within the hexaimine cage; this stability appears to protect both cation and ligand in that the ligand appears stabilised against metal-assisted hydrolysis of C=N bonds which normally affects Schiff-base complexes of Lewis-acid cations. This hexaimino cryptand thus appears a promising host for the larger Group 11–14 cations.

imBT

amBT

imbistrpn

Table 1 Proton NMR spectra of imBT cryptates[a]

				δ		
Compound	ν/MHz	T/K	Solvent	H_A	H_B/H_C	H_D/H_E
imBT	500	300	CDCl$_3$	7.74 (s)	3.56 (s)	2.73 (br s)
		218	CDCl$_3$	7.75 (s)	3.78 (d),[b] 3.43 (t)[b]	3.09 (t),[b] 2.46 (d)[b]
1 [Pb(imBT)]$^{2+}$	500	300	CD$_3$CN	8.63 (s, sats)[c]	3.92 (t)[d]	2.91 (t)[d]
		240	CD$_3$CN	8.59 (s, sats)[c]	3.88 (t)[d]	2.86 (t)[d]
2 [Cd(imBT)]$^{2+}$	500	300	CD$_3$CN	8.24 (s, sats)[e]	3.81 (t),[f] 3.48 (d,[f] sats[g])	2.91 (d),[f] 2.73 (t)[f]
3 [Hg(imBT)]$^{2+}$	500	323	CD$_3$CN	8.25 (s, sats)[h]	3.58 (br s)	2.78 (br s)
		243	CD$_3$CN	8.19 (s, sats)[h]	3.61 (t),[b] 3.39 (d,[b] sats[i])	2.79 (d),[b] 2.62 (t)[b]
4 [Ag$_2$(imBT)]$^{2+j}$	300	243	CD$_3$CN	8.16 (s)	3.77 (t)[k]	2.79 (t)[k]
5 [Cu$_2$(imBT)]$^{2+j}$	500	298	CD$_3$CN	8.05 (s)	3.67 (t)[l]	3.0 (t)[l]
		233	CD$_3$CN	8.05 (s)	3.65 (br s)	3.15 (s), 3.04 (br s)
6 [Li(imBT)]$^{+}$	300	300	D$_2$O	7.72 (s)	3.7 (br s)	3.0 (br s), 2.6 (br s)

[a] Chemical shifts in ppm from TMS. [b] $^2J(H,H)_{ax/eq} \approx {}^3J(H,H)_{ax,ax'} \approx$ 12–13 Hz. [c] $^3J\{^{207}Pb,^1H\} \approx$ 13 Hz. [d] $^3J(H,H) \approx$ 10 Hz. [e] $^3J\{^{113,111}Cd,^1H\} \approx$ 40 Hz. [f] $^2J(H,H)_{ax/eq} \approx {}^3J(H,H)_{ax/ax'} \approx$ 13 Hz. [g] $^3J\{^{113,111}Cd,^1H\} \approx$ 25 Hz. [h] $^3J\{^{199}Hg,^1H\} \approx$ 152 Hz. [i] $^3J\{^{199}Hg,^1H\} =$ 85 Hz. [j] Refs. 9–11. [k] $^3J(H,H) \approx$ 5 Hz. [l] $^3J(H,H) \approx$ 6 Hz.

Discussion

The complexation of imBT with main group cations is easily achieved, simply by treating a solution of the ligand with the metal salt. Apart from the disilver(I)[9] and dicopper(I) salts,[10] (see Fig. 9) which adopt different co-ordination sites (two sets of N$_3$ and N$_4$ donors respectively) the cryptates are obtained as mononuclear complexes (Table 1). Studies of solution complexation thermodynamics with both amBT and imBT are underway;[12] our main concern in this paper is to report the characterisation of the isolated reaction products of imBT with heavy metal cations and to examine these products to obtain qualitative information on their tendency to decomplexation in solution. NMR spectroscopy is a valuable source of data on the rates of dynamic processes, and as most of the target cations in this study are diamagnetic we have looked at the way in which their ^{1}H NMR solution spectra vary with temperature. A study of the spectrum of the 'free' ligand imBT was also undertaken. For comparison, we have examined the MAS solid state spectra of these cryptates and the parent ligand.

Solution ^{1}H NMR studies

The 'free' ligand ^{1}H NMR spectrum at ambient temperature in CDCl$_3$ indicates fluxionality of conformation. Three single resonances are seen, corresponding to the imino signal H$_A$, a single broadened methylene H$_{B,C}$ and a very broad methylene H$_{D,E}$ resonance (Table 1). As the temperature is lowered the methylene resonances develop (by 263 K) into four single broad resonances and finally (by 218 K) into a nicely resolved doublet, triplet, triplet, doublet pattern corresponding to separate H$_B$, H$_C$, H$_D$ and H$_E$ resonances (Fig. 1). Owing to coincidental near equality of the larger geminal and vicinal methylene coupling constants ($^3J_{ax,ax'} \approx {}^2J_{ax,eq} \approx$ 12–13 Hz, while $^3J_{ax,eq}$ and $^3J_{eq,eq'}$ are much smaller at $\approx$2–3 Hz) there is accidental simplification of the spectrum as frequently found in other iminocryptand systems.[13,14] From the coalescence temperature and separation of coalescing resonances, the activation enthalpy for interconversion of conformation is estimated as $\approx$53.7 kJ mol^{-1}, i.e. intermediate between those ($\approx$56;[14] 47 kJ mol^{-1}[15]) found earlier for two 'free' iminocryptand ligands of this series. The good solubility of imBT in non-polar solvents allowed observation of ^{13}C NMR in CDCl$_3$ solution; a simple three line spectrum corresponding to equivalence of the three strands and both ends is observed at 300 K.

Within the series of mononuclear imBT cryptates, the pattern of ^{1}H NMR spectra observed depends on the relative mobility or rigidity of the cryptand skeleton. When the relatively large cation Pb^{2+} is encapsulated within imBT only a sharply resolved triplet, triplet methylene spectrum illustrating equivalence of the H$_B$/H$_C$ and H$_D$/H$_E$ pairs due to rapid interconver-
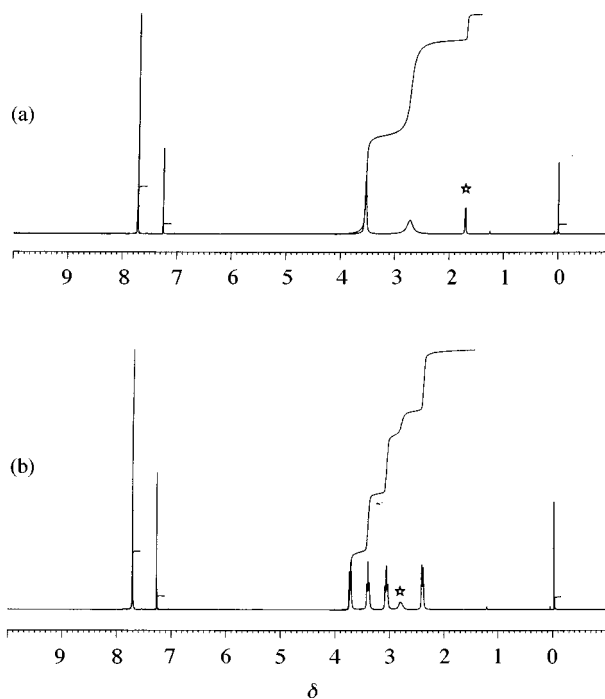
Fig. 1 The 500 MHz ^{1}H NMR spectra (CDCl$_3$) of imBT (a) at 300 and (b) at 218 K. ☆ = Solvent impurity.

sion of configurations on the NMR timescale, is observed at any temperature in CD$_3$CN solution (Table 1). At 220 K the spectrum obtained in d^6-acetone showed loss of triplet coupling, but no differentiation of the methylene axial and equatorial resonances. With Pb(amBT)$^{2+}$[5] such differentiation starts to appear in the complex broad 223 K spectrum, most obviously in the central glyoxal-derived proton resonance which splits to a doublet deriving from the onset of geminal coupling as the temperature is lowered.[5]

The Cd^{2+} cation, being smaller and more tightly co-ordinated, is expected, on encapsulation, to generate a less mobile cryptate system. With imBT as with amBT[4,5] even at 295 K, sharply resolved ^{1}H resonances are observed in CD$_3$CN solution [Fig. 2(a)] for the Cd^{2+} cryptate demonstrating the absence of any dynamic process rapid on the NMR timescale. The methylene cap spectrum takes the form of a simple triplet, doublet, doublet, triplet pattern deriving once more from accidental equivalence of geminal $^2J_{ax,eq}$ and vicinal $^3J_{ax/ax'}$ proton coupling constants; relative chemical shifts for axial(triplet) and equatorial(doublet) resonances are reversed for the convergent cryptate conformation compared with the divergent conform-
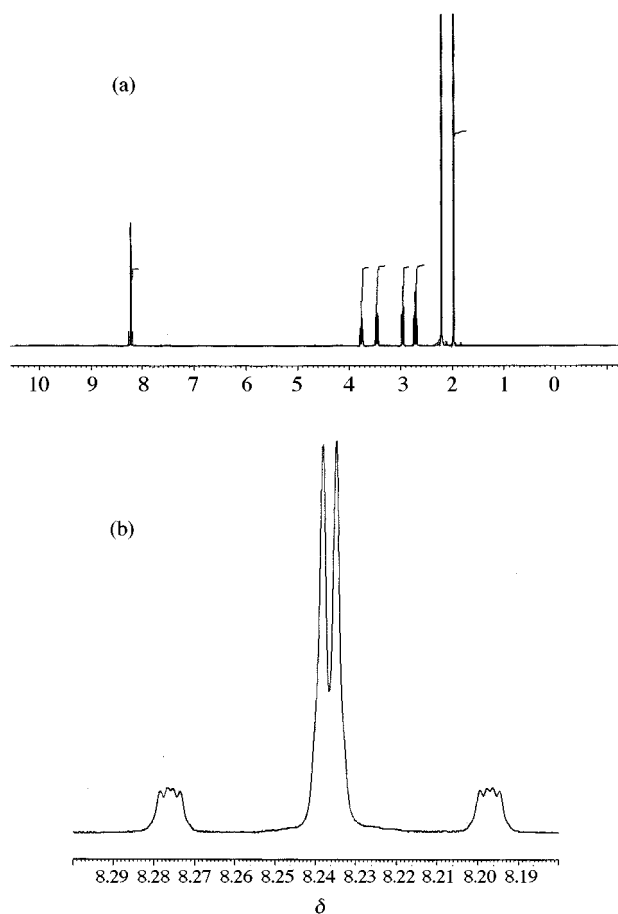
Fig. 2 (a) The 500 MHz ^{1}H NMR spectrum of [Cd(imBT)]$^{2+}$ at 300 K. (b) The ^{111}Cd and ^{113}Cd satellites resolved on the imino resonance in [Cd(imBT)]$^{2+}$.

ation of the free cryptand. Well defined satellite peaks with couplings $^3J(^1H,^{113,111}Cd)$ and $^3J(^1H,^{207}Pb)$ are seen on the high frequency imino CH resonance. This testifies to kinetic stabilisation against decomplexation, as even in the fluxional Pb^{2+} cryptate system it appears that rapid exchange of cation between the solvated and cryptated situation is absent. The remarkably well resolved ^{1}H NMR spectrum of the cadmium cryptate **2** allows observation of satellite peaks even in the methylene spectrum, on the doublet arising from the equatorial proton α to the imino nitrogen. When examined under high resolution, satellite peaks for the imine (C)H resonance (which takes the form of a closely spaced doublet due to a small four-bond coupling to the equatorial proton adjacent to the imino N) are seen to consist of two sets of doublets [Fig. 2(b)] arising from separately resolved coupling to ^{111}Cd and ^{113}Cd. (The coupling constant $^3J(^1H,^{111}Cd)$ at 38.5 Hz compares with $^3J(^1H,^{113}Cd)$ at 40.2 Hz, mirroring the 0.96:1 proportion of gyromagnetic ratios.)

In the case of the amBT cryptate of mercury(II), [Hg(amBT)]$^{2+}$, the complex and overlapped methylene signal was only partly assignable,[16] but changes on lowering temperature indicated that, as with Pb^{2+}, differentiation of axial and equatorial signals starts to appear around the lower temperature fluid limit of the CD$_3$CN solvent. The mercury(II) iminocryptate **3**, reported here, shows much simpler ^{1}H NMR spectra (Fig. 3), similar to those of **2**. Differentiation of axial and equatorial protons is manifest (at room temperature and below) in the doublet, triplet, triplet, doublet methylene pattern which also demonstrates equivalence of the three cryptand strands. On the imino CH signal, ^{199}Hg satellites are clearly observed with a large (152 Hz) coupling constant, much larger, in comparison with the cadmium analogue, than expected on gyromagnetic ratio considerations alone. As X-ray powder
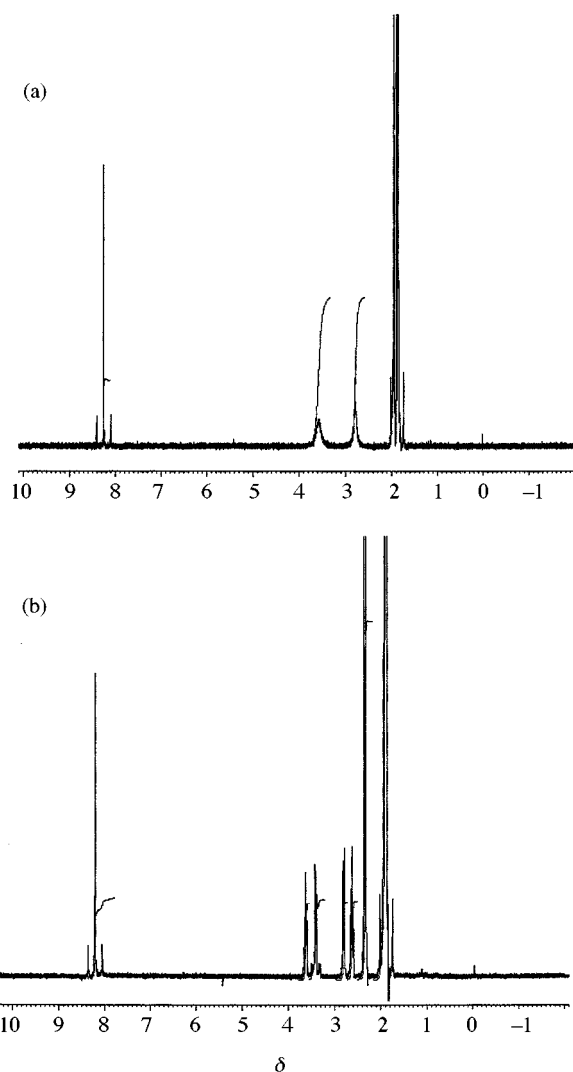
Fig. 3 The 500 MHz ^{1}H NMR spectra of [Hg(imBT)]$^{2+}$ at (a) 323 and (b) 240 K.

patterns (see Experimental section) are consistent with close similarity in the co-ordination site used for this pair of cryptates, then the relatively large $^3J(^1H, ^{199}Hg)$ coupling constant may be taken to suggest appreciable covalence in the Hg–N coordinate bond. This coupling persists even at temperatures above 300 K where differentiation of the axial and equatorial signals has been lost, its observation demonstrating that at least one Hg–N$_{imine}$ bond is retained during whatever dynamic process is responsible for loss of axial and equatorial differentiation. In other words, the dynamic process responsible for fluxionality resides in ligand conformational change rather than cation decomplexation. $^3J(^1H, ^{199}Hg)$ satellites are also seen on the equatorial methylene doublet centred at δ 3.39; as in the analogous Cd^{2+} case, this coupling constant is just over half the value for the three-bond coupling to the imino C–H proton.

In contrast to the mercury cryptate **3**, the silver(I) analogue **4**, even at low temperature in CD$_3$CN solution, shows simple ^{1}H NMR methylene spectra which do not differentiate the axial and equatorial protons, although one methylene resonance is severely broadened in the 250 K 500 MHz spectrum. One possibility is that this apparent simplicity derives from a rapid dynamic process averaging out conformational and co-ordination differences in solution. The solid state ^{13}C NMR spectra (qv) are complex however and consistent with the crystal structure (see Fig. 9) of the disilver cryptate.[9] This structure is not compatible with the simple ^{1}H NMR solution spectrum observed. The absence of three-bond coupling from

Table 2 Solid state spectra of cryptates

Compound	Spectrum	ν/MHz	Reference	δ		Comment
				Imino carbon	Methylene carbons	
imBT	^{13}C	75.4	TMS	164.7 (s), 163.6 (sh)	60.0, 59.2; 57.4, 52.7	
1				161.6 (vbr)	58.1, 53.7 (sh, vbr)	vbr noisy spectrum
2				160.0, 158.6	57.6, 59.9; 55.6, 54.8	
3				157.5, 156.4	58.0, 56.9; 55.0, 54.3	
4				168.2, 165.1, 164.4, 161.0, 152.0	58.3, 54.4, 52.7, ≈51.7 (sh)	
5				155.9	61.7, 52.4	
6				163.3; 162.0 (sh)	58.8, 54.0 (br)	Fairly broad spectrum
				Imino nitrogens	Bridgehead nitrogens	
imBT	^{15}N	30.4	NH$_4$NO$_3$	≈−17.5 (sh), −18.4, −21.7	−347.6, −348.6	
1				−34.3, −43.2 (br)	−336.8, −343.7	br, weak, spectrum
2				−74.3, −75.8	−355.4, −358.9	
3				−67.3, −70.0	−355.0, −357.9	
4				−47.6, −51.5 (sh), −69.5, −76.8, −84.13	−347.0	Weak, noisy
5				−91.1, −95.1, −99.5, −104.9	−347.9	
5				−88.3, −93.6, −100.9, −109.5	−348.4	
6				−26.5, −37.6 (br)	−347.3	br, weak
				Ionic perchlorate	Low symmetry perchlorate	
1	^{35}Cl	29.4	1 M NaCl	1003.9	996.8 (br)	
2				999.5	990.0 (br)	
3				1000.5	≈992 (vbr)	
6				986.7, 975.5		Quadrupole-split peaks, equal height and width
				Metal nuclei		
2	^{113}Cd	66.6	CdMe$_3$	93.7, 13 lines		$^{1}J(^{14}$N, ^{113}Cd) = 85 Hz
3	^{199}Hg	53.6	HgMe$_2$	−1884.5		
5	^{65}Cu	79.5		No observable spectrum		
6	^{7}Li	116.6	1 M LiCl	0.2		

the metal cation to the imino CH proton, which as $^{3}J[^{109,107}$Ag,^{1}H] has been seen as a small (≈5–12 Hz) splitting in *all* other disilver cryptates of the series,[3,13] and is noted above for the appropriate magnetic isotope in **1**–**3**, suggests that the solution dynamic process in **4** involves breaking of Ag$^+$–imine links. Addition of 'free' ligand imBT to the disilver cryptate solution confirms this suggested lability, as the observed spectrum of the mixture shows no sign of the characteristic free imBT resonances, merely a shifting of the resonance position of the methylene triplets toward the 'free' ligand values, consequent upon the operation of averaging effects.

For the dicopper(I) cryptate **5** the comparison with cryptates of larger cations such as Cd^{2+}, or indeed with dicopper(I) cryptates of larger hosts,[13] highlights the low temperature required for differentiation of axial and equatorial protons in the ^{1}H NMR spectrum (<250 K) as surprising. There is no evidence of lability in this case, as on addition of free imBT the broad cryptand spectrum is merely superposed on the unaltered cryptate spectrum. The rationalisation of the triplet, triplet pattern methylene spectrum in this case appears to be that the donor disposition necessary for dinuclearity[3] in this small cryptate necessitates a more open conformation of the methylene cap, thus generating greater mobility of conformation. The more flexible trpn-capped analogue, [Cu$_2$(imbistrpn)]$^{2+}$, whose ligand is more tightly co-ordinated, being more flexible, does indeed show[11] differentiation of axial and equatorial methylene protons at ambient temperatures.

Owing to the similarity of cation size and charge of Li$^+$ and Cu$^+$, an attempt was made to encapsulate lithium in both mononuclear and dinuclear modes. However, the monolithium hexahydrate product **6** was obtained independent of stoichiometry used. The ^{1}H NMR of **6** in D$_2$O solution is very broad and resonance positions differ only slightly from those of the

free cryptand, suggesting that this cation may be exchanging with solvent.

Solid state NMR spectra

Comparison with spectra obtained in the solid state should establish the presence or absence of decomplexation equilibria in solution. However this comparison poses difficulty in some cases, as proton spectra are unmanageably broad and complex in the solid state, while the solubility required for ^{13}C NMR spectra is often lacking in the cryptate systems.

The best resolved spectra were obtained for the cryptates of cadmium(II), mercury(II), silver(I) and copper(I), which also presented the sharpest ^{1}H NMR solution spectra. With the mercury cryptate **3**, MAS spectra were obtained for ^{13}C, ^{15}N, ^{199}Hg, as well as for ^{35}Cl in the counter ion (Table 2). In the ^{13}C spectrum each of the expected three resonances consists of two closely spaced lines of equal intensity, although the differences in siting of methylene and imino carbons shown by the crystal structure are on the margins of significance. (Comparison of the powder diffraction pattern for the bulk sample of **3** with that generated from the single crystal data confirmed that the sample used for MAS studies is isomorphous with the crystal.) The observed splitting is consistent with the 3-fold symmetry of the carbon where each atom along an individual strand is crystallographically independent. It is surprising however that such marginally significant crystallographic differences between the two ends of the cryptate appear to ensure appreciable splitting of resonances in the MAS spectra.

The MAS CP ^{15}N NMR spectrum also appears as two pairs of signals arising from inequivalent bridgehead- and imino-N resonances. Direct polarisation ^{199}Hg spectroscopy shows a single broad resonance at δ −1884 *vs.* HgMe$_2$; there is a large
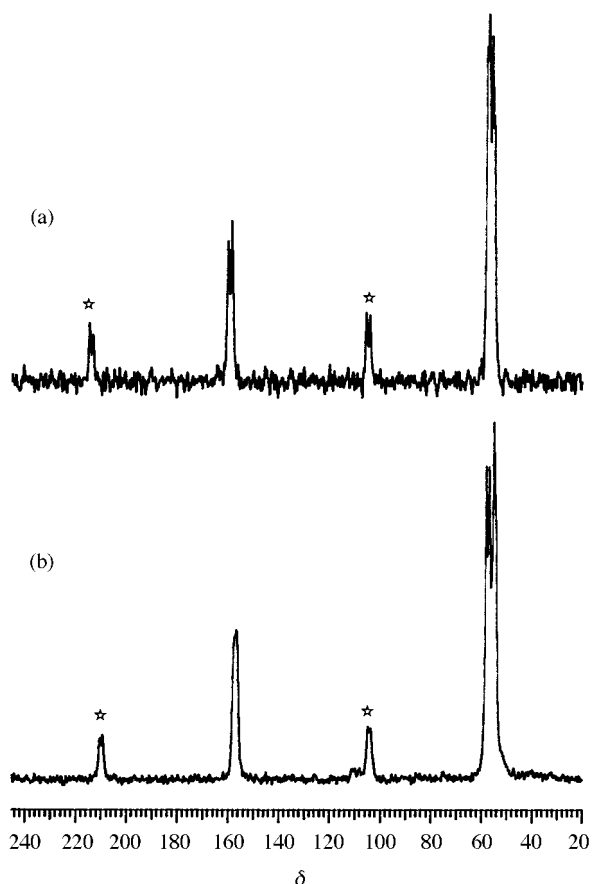
Fig. 4 The ^{13}C CP MAS NMR spectra of (a) [Cd(imBT)]$^{2+}$ and (b) [Hg(imBT)]$^{2+}$. Spinning sidebands indicated by ☆.

Fig. 5 The ^{15}N CP MAS NMR spectra of (a) [Cd(imBT)]$^{2+}$ and (b) [Hg(imBT)]$^{2+}$. Spinning sidebands indicated by ☆.

>500 Hz half-width of the signal, arising most probably from residual dipolar coupling between ^{199}Hg and ^{14}N. Another broad feature appears in the ^{35}Cl spectrum, which consists of a reasonably sharp signal superposed on a second broad resonance in the region of δ 1000 *vs.* 1 M NaCl.

Spectra of the cadmium cryptate, **2**, are very similar to those of **3** as X-ray powder patterns require, although they are in general sharper for the cadmium than for the mercury cryptate. Comparison with **3** reveals a slight high frequency (low-field) shift in the imino-carbon ^{13}C resonance of **2** (Fig. 4) and a small low frequency (high-field) shift of the imino-nitrogen ^{15}N resonance (Fig. 5). The doublet appearance of all these signals is maintained for **2**. The resonance of the metal nucleus is not merely broadened as for the mercury cryptate but appears in the ^{113}Cd NMR (Fig. 6) as a nicely resolved 13-line signal resulting from coupling to the six equivalent imino nitrogen $I = 1$ ^{14}N nuclei. In the ^{35}Cl NMR again the perchlorate exhibits one sharp resonance close to δ 1000 and another broader one centered ≈10 ppm to lower frequency.

All the spectra for complex **1** are seriously broadened in comparison to those of the cadmium and mercury analogues. The ^{13}C and ^{35}Cl resonances are at much the same chemical shift as for **2** and **3**, while the imino ^{15}N signal is significantly shifted compared to these, moving >25 ppm to higher frequency.

The 'free' ligand, imBT·H$_2$O, ^{13}C NMR spectrum is somewhat broader than those of the cadmium or mercury cryptates, **2** and **3**, and appears less well resolved, but like these shows two imino-carbon signals separated by around 100 Hz. The methylene resonances, partly because of increased breadth of signal but also in consequence of "co-ordination" shifts which move the C_D and C_E resonances in opposite directions, are spread over nearly 500 Hz in place of the ≈200–250 Hz seen for the cadmium and mercury cryptates. Compared to the CDCl$_3$
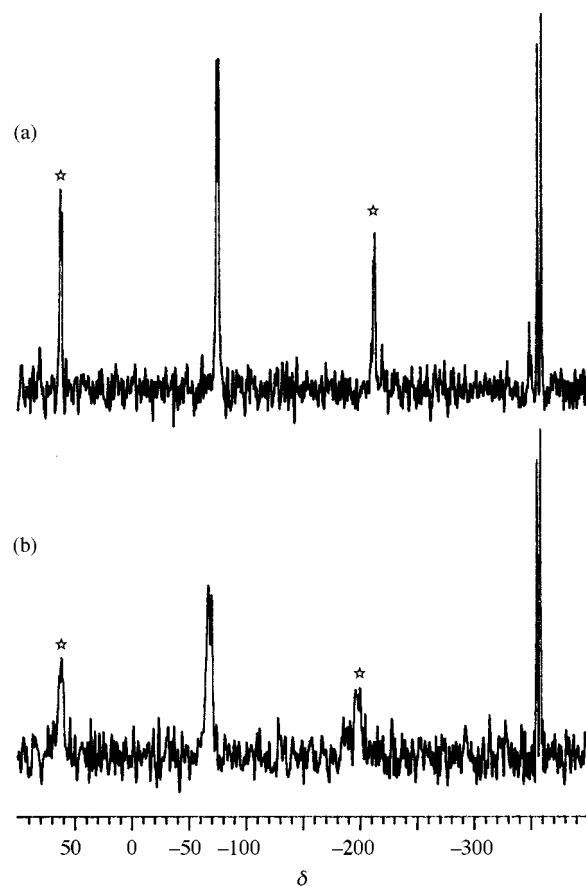

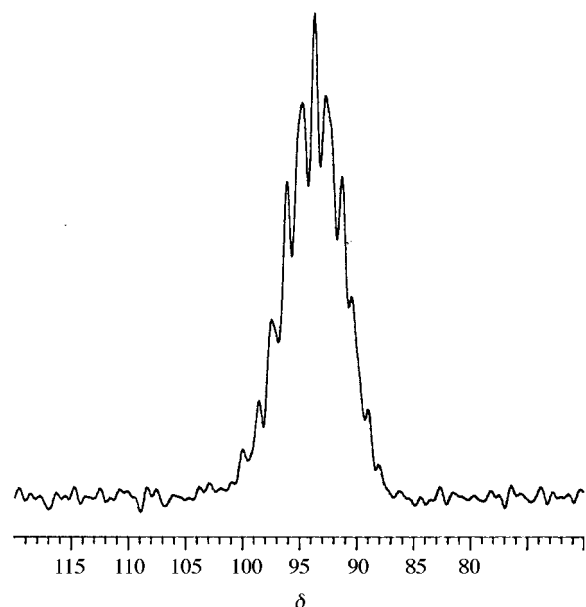**Fig. 6** The ^{113}Cd CP MAS NMR spectrum of [Cd(imBT)]$^{2+}$.

solution spectrum of imBT, the higher frequency resonance of each pair appears close to the chemical shift seen in the simpler solution spectrum (which has just three ^{13}C resonances at δ 163.058, 59.061 and 52.953). The CP MAS ^{15}N NMR spectrum of imBT is weak but shows the usual N-bridgehead signal centered around δ -350, together with an imino-N resonance which takes the form of three lines in the δ -18 to -22 region. This demonstrates, first, that the bridgehead-N resonance is relatively uninfluenced by change from divergent to convergent conformation, and secondly that the imino-N

shift is, in contrast, sensitive to conformational and co-ordination effects in the co-ordinated ligand. As the crystal structure[17] of imBT shows no difference between strands or ends of the cryptand, the splitting of the imino-N resonance may derive from hydrogen-bonding effects in this hydrated form of the 'free' ligand.

Dicopper(I) and disilver(I) cryptates

These complexes are of interest because the simplicity of their ^{1}H NMR solution spectra suggested the possibility of dissociation in solution, generating ligand spectra which are time-averaged between the co-ordinated and unco-ordinated situations. In the case of the disilver(I) cryptate **4** the general difference in complexity between solid state and solution spectra supports this idea. For the imino carbon in the ^{13}C CP MAS spectrum, five clear resonances are observed in the solid state, with the chance that a sixth is concealed in the over-lapping signals. The closest pair of signals are separated by ≈70 Hz, too large for $^2J(^{13}$C, ^{107,109}Ag) coupling: given the small gyromagnetic ratio of the ^{109,107}Ag isotopes, couplings to silver nuclei in these systems are expected to be unresolvable. So the supposition is that the signals observed in the solid state repre-sent 6 inequivalent imine positions, perhaps arising from two sets of resonances from 3 inequivalent carbons, one set from each of the two cations existing independently in the unit cell.[9] The methylene carbon resonances consist of four rather broad maxima, which may derive from differences in the two ends of the cryptand host or in the two different cations in the unit cell, but the envelope may conceal a more complex pattern, resulting from the expression of both these differences and more. The ^{15}N CP MAS spectrum is relatively weak and noisy but shows equivalence of both N_{br} resonances which appear as a sharp singlet at δ −347 vs. NH_4NO_3. The imino-N resonances, on the other hand, appear as a set of at least 5 resonances in the range δ −47 to −85 with smallest separation of the order of 108 Hz.

In the case of the dicopper(I) complex, **5**, the ^{13}C CP MAS NMR spectrum is simple and similar to the CD_3CN solution spectrum, showing in this case that the solution conformation is no different from that revealed in the crystal structure (see Fig. 9). In both solid state and CD_3CN solution spectra, just one sharp imino-C signal at $\delta \approx 155$ and a pair of methylene resonances at $\delta \approx 51$–52 and ≈ 61.5 [Fig. 7(a)] are observed, confirming the X-ray finding that the two ends and three strands of the cryptand are equivalent.

The ^{15}N NMR spectrum is more complex however, and the origin of this complexity can be unambiguously attributed by running the spectrum at two different frequencies. The spec-trum of the imino-N [Fig. 7(b)] at both 30.4 and 20.3 MHz takes the form of a well defined four-line resonance centered near δ 100. The different chemical shifts of the four resonances at these two frequencies (Table 2), together with insensitivity to spectrometer frequency of the spacing in Hz of the four-line pattern, means that they must be attributed to coupling of ^{15}N to the $I = 3/2$ copper nuclei. We know of no previously reported observation of ^{15}N, ^{63,65}Cu coupling with which our observed coupling may be compared, but ongoing work[11] on similar iminopodates of copper(I) indicates that ^{15}N, ^{63,65}Cu couplings of the order of 120–180 Hz are general in copper(I) imino complexes. The N_{br} signal appears as a singlet at δ −348 in both 20 and 30 MHz spectra providing a good check on con-sistency of instrumental parameters. This value is very close to those (δ −347) seen for the free cryptand or cryptates **3** and **4** where this donor is unco-ordinated, confirming that co-ordination of N_{br} in **5** has had little effect on its chemical shift. In contrast, however, the ^{15}N chemical shift of the imino N is significantly more negative for this cryptate than for any other imBT derivative, suggesting that back bonding from copper(I) cations to the imino-π system has increased electron density on the N-donor.
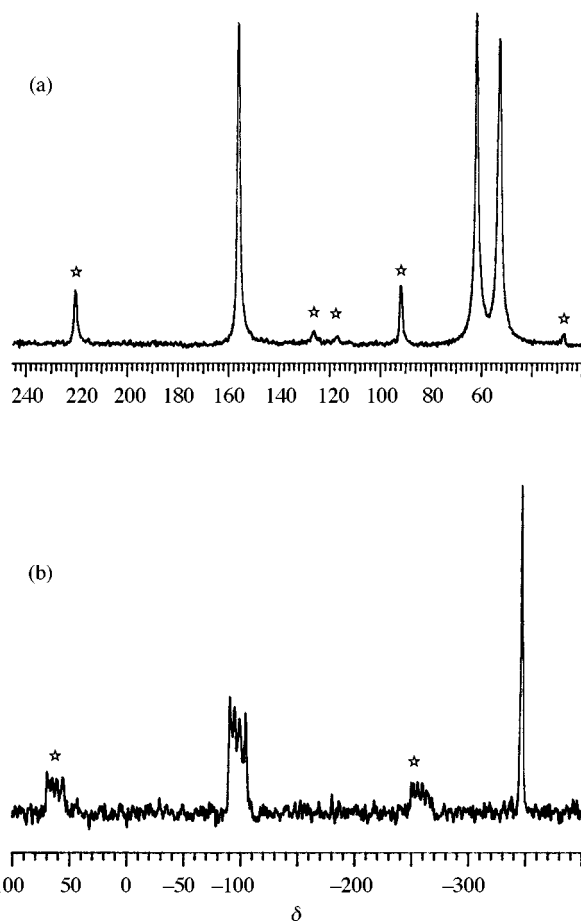
Fig. 7 The CP MAS NMR spectra of $[Cu_2(imBT)]^{2+}$ (a) ^{13}C and (b) ^{15}N. Spinning sidebands indicated by ☆.

The monolithium cryptate **6** shows a broad ^{13}C NMR spec-trum with imino resonance close to δ 163, and a pair of methyl-ene resonances at δ 59 and 54, similar to the situation in **5**. The ^{15}N spectrum shows the N_{br} signal as the usual sharp singlet at $\delta \approx 348$, but the weak, broad imino nitrogen resonance lies well downfield of that for any cryptate examined, indeed closer to the position for the 'free' ligand imBT suggesting adoption of a mainly exclusive co-ordination site, in contrast to the inclusive sites universally adopted in other azacryptates studied to date.[3] A strong ^{7}Li signal at δ 0.157 vs. 1 M LiCl confirms the presence of lithium, but the complexity of the ^{35}Cl resonance and the small co-ordination shift of the ^{15}N imino signal suggest that perchlorate O may be playing a role in co-ordination of this cation, together most likely with some of the solvate water molecules.

X-ray crystallography of complex 3

The $[Hg(imBT)]^{2+}$ cation and the two independent perchlorate anions each lie on 3-fold axes and do not interact with one another. The Hg^{2+} ion sits at the approximate center of the cryptand ligand and is co-ordinated to the six imino donors but not to the bridgehead amines (Fig. 8). The co-ordination geo-metry is closer to octahedral than trigonal prismatic, and the relative rotation of the two sets of imine nitrogen donors is 38.5(1)°. The torsion angle between the two imine groups in each chain is small [N11–C3–C4–N12 4.46(1.19)°], suggesting that no significant distortion is imposed on the ligand and resulting in a small ligand bite angle (N11–Hg–N12 68.63°). The distances from the Hg^{2+} cation to the six imino-N donors and the two unco-ordinated N_{br} atoms fall into two sets: Hg–N_{im} 2.409(8); Hg–N_{br} 3.17(3) and Hg–N_{im} 2.427(7); Hg–N_{br} 2.98(4) which are differentiated by less than the 3σ test of significance. Nonetheless, these apparent differences may need
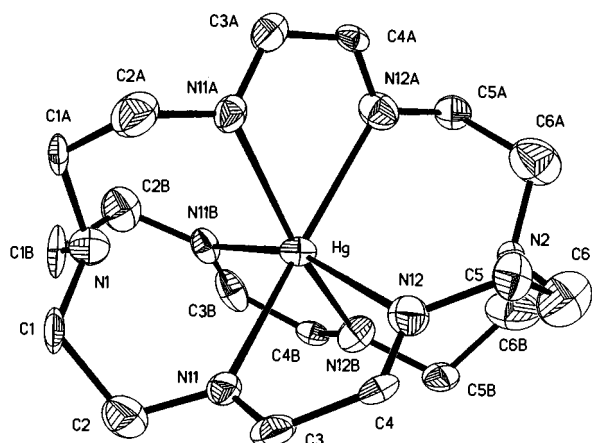
Fig. 8 Structure of [Hg(imBT)][ClO$_4$]$_2$ **3**. Selected distances: Hg–N$_{im}$ 2.409(8), 2.427(7); Hg–N$_{br}$ 3.17(3), 2.98(4) Å. A threefold rotation axis runs through N1, Hg and N2.

to be invoked as the origin of the two sets of ^{13}C and ^{15}N NMR resonances seen in the solid state MAS NMR spectra.

This structure is similar to that adopted in other mono-nuclear cryptates of this host[8,18,19] where the cation adopts a central position, though in the gadolinium case the cation[19] co-ordinates the bridgehead nitrogens in addition to the six imino nitrogens. The two dinuclear cryptates structurally character-ised have adopted very different binding strategies as shown in Fig. 9; the series of structures illustrate the various ligation possibilities available which allow adoption of co-ordination numbers 3–8.
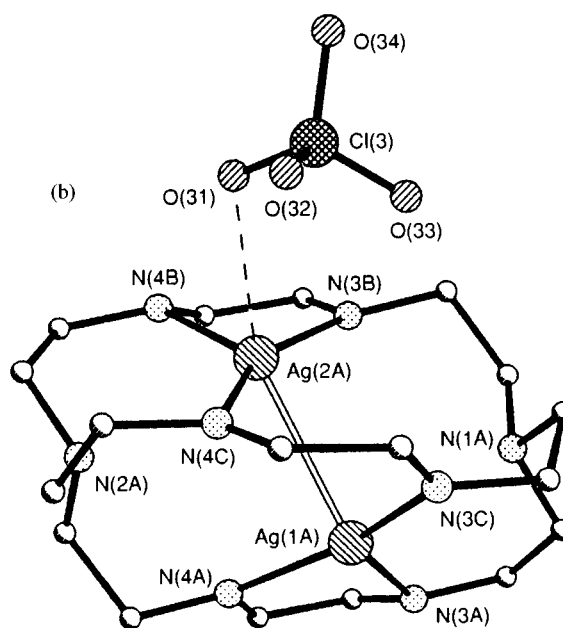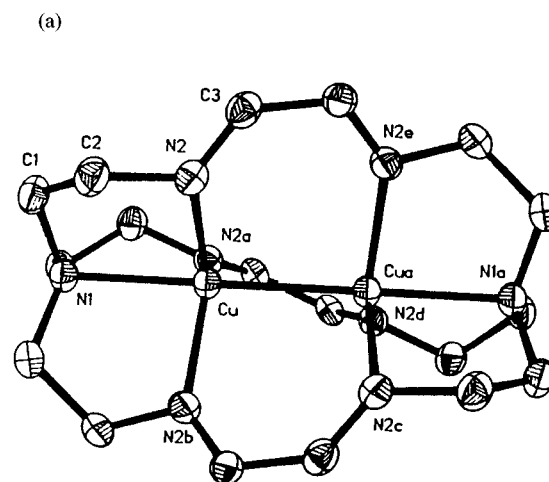
Conclusion

Solid state NMR spectra obtained for this series of imBT cryptates are in general of high quality, allowing an extensive multinuclear study. Well resolved coupling between ^{15}N and encapsulated metal ion in the case of dicopper(I) and mono-cadmium(II) cryptates testifies to high symmetry and strong interaction in these cases, which also show the largest ^{15}N co-ordination shifts. Comparison of solution and solid state NMR confirms the existence of decomplexation equilibria in CD$_3$CN solutions of the disilver(I) but not the dicopper(I) cryptate. The observation of satellite peaks, including separately resolved ^{111}Cd and ^{113}Cd satellites, in CD$_3$CN solution, confirms the absence of decomplexation equilibria for mercury, cadmium and lead cryptates. Overall the MAS data illustrate the poten-tial value of this technique in furnishing information on struc-ture and bonding in co-ordination compounds.

Experimental

Cryptate syntheses

[M(imBT)][ClO$_4$]$_2$·nH$_2$O (M = Pb, n = 0 1; M = Cd, n = 1 2; M = Hg, n = 0 3). To 1 mmol of imBT in 25 cm^3 CHCl$_3$ was added 1 mmol of the metal salt in 25 cm^3 MeCN–EtOH with stirring at 40 °C. Yellow crystals of product were obtained in 60–70% yield on cooling in ice. Complex **1**: FAB MS m/z 665 (100) and 566 (43%) [Found (Calc.): C, 28.40 (28.28); H, 3.97 (3.95); N, 14.45 (14.66)%]. Complex **2**: FAB MS m/z 571 (100) and 470 (98%) [Found (Calc.): C, 32.89 (32.29); H, 4.49 (4.78); N, 16.60 (16.74)%]. Complex **3**: obtained analogously, using mercury(II) perchlorate trihydrate and recrystallisation from MeCN; FAB MS m/z 659 (50) and 558 (30%) [Found (Calc.): C, 28.66 (28.52); H, 3.88 (3.99); N, 14.59 (14.58)%].

[Ag$_2$(imBT)][ClO$_4$]$_2$ 4 and [Cu$_2$(imBT)][ClO$_4$]$_2$ 5. These com-plexes were obtained, as described elsewhere,[9,11,18] on treatment of imBT in CHCl$_3$ with the appropriate metal salt in 1:2

stoichiometry. Complex **4**: FAB MS m/z 465 (100) and 673 (15%) [Found (Calc.): C, 28.23 (27.96); H, 3.90 (3.91); N, 14.22 (14.49)%].

[Li(imBT)]ClO$_4$·6H$_2$O 6. To a stirred solution of imBT (1 mmol in 30 cm^3 CHCl$_3$) was added 1 mmol of LiClO$_4$ in 10 cm^3 MeCN and the white microcrystalline solid filtered off on standing. FAB MS m/z 365 (100) and 359 (20%) [Found (Calc.): C, 37.83 (37.79); H, 7.43 (7.40); N, 19.63 (19.59)%].

CAUTION: although all perchlorates must be treated as potentially explosive, and the quantities indicated in the syntheses described should not be exceeded, we experienced no problems in working with these complexes in the manner described.

X-Ray crystallography

Crystal data. [Hg(imBT)][ClO$_4$]$_2$, C$_{18}$H$_{30}$Cl$_2$HgN$_8$O$_8$, colour-less plate, dimensions 0.16 × 0.12 × 0.05 mm, hexagonal, space group $P6_3$, a = 8.9482(1), c = 18.3758(1) Å, U = 1274.23(2) Å^3, Z = 2, μ = 6.309 mm^{-1}, $F(000)$ = 744.

Data were collected at 160(2) K using a Siemens SMART CCD diffractometer with synchrotron radiation (λ = 0.6870 Å, SRS station 9.8[20] at Daresbury Laboratory). A hemisphere of data (4494 reflections, θ_{max} = 27.26°) was collected using 0.15° ω

Fig. 9 Structures of (a)[10] [Cu$_2$[(imBT)][ClO$_4$]$_2$ and (b)[9] [Ag$_2$(imBT)]-[ClO$_4$]$_2$.

scans over approximately 4 h. Data were corrected for Lorentz-polarisation effects and for the decay of the incident beam. The structure was solved by direct methods (TREF) and refined by full matrix least squares on F^2, using all 1724 independent reflections ($R_{int} = 0.0718$). All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions with isotropic displacement parameters riding on U_{ij} of their carrier atoms. The refinement, on 112 parameters, converged with $wR2 = 0.1232$, goodness of fit = 1.049 (all data) and conventional $R1 = 0.0471$ (2σ data). The only significant residual peaks in the electron density map were close to the Hg atom. All programs used in the structure refinement are contained in the SHELXL 97 package.[21]

CCDC reference number 186/1249.

See http://www.rsc.org/suppdata/dt/1999/229/ for crystallographic files in .cif format.

X-Ray powder patterns of complexes **2** and **3** were obtained using a Siemens D5000 instrument over 5 h at ambient temperature. The close similarity of the *d* values invited their description as isomorphous; however a few small but significant differences can be discerned ($2\theta = 4$–40): **3**, 9.2807, 7.9121, 7.2817, 6.0109, 4.8619, 4.6203, 4.5544, 4.4273, 4.0868, 3.9895, 3.8587, 3.6274, 3.3468, 3.2422, 3.0787, 2.9987, 2.9421, 2.8356, 2.6946, 2.6277, 2.5501, 2.5268, 2.5021, 2.3185, 2.2790 and 2.2121; **4**, 9.4017, 7.8966, 7.2497, 6.0297, 4.8875, 4.5293, 4.4147, 4.0817, 4.0227, 3.8597, 3.6224, 3.3839, 3.2621, 3.0091, 2.9324, 2.6802, 2.6204, 2.5703, 2.5369, 2.3250, 2.2649 and 2.2091 Å. Plots of powder diffraction data are available as SUP 57463.

NMR measurements

The solid state NMR spectra were obtained using a Varian Unityplus spectrometer and Doty Scientific MAS probes. All measurements were made at ambient probe temperature. Spectrometer operating frequencies are given in Table 2. Referencing (Table 2) was to an external sample in all cases. One ^{15}N spectrum was recorded using a Chemagnetics spectrometer operating at 20.29 MHz.

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