Preparation and Characterisation of Cd^{II}, Hg^{II} and Pb^{II} Complexes of a Macrodinucleating Hexaaza-dithiophenolate Ligand

Vasile Lozan[a] and Berthold Kersting*[a]

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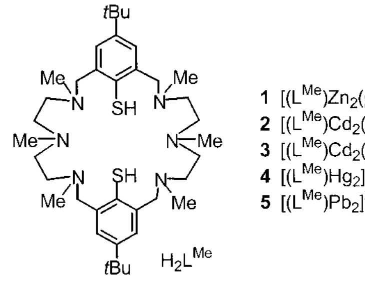
The ligating properties of a Robson-type 24-membered macrodinucleating hexaaza-dithiophenolate ligand towards the heavy metal ions Cd^{II}, Hg^{II} and Pb^{II} have been examined. The complexation of H_2L^{Me} with $CdCl_2$ or $Cd(OAc)_2$ in the presence of triethylamine leads to monocationic $[(L^{Me})Cd_2(\mu\text{-}L')]^+$ complexes bearing additional coligands [$L' = Cl^-$ (**2**) or OAc^- (**3**)]. With $Hg(OAc)_2$ and $Pb(OAc)_2$, the respective dicationic complexes $[(L^{Me})Hg_2]^{2+}$ (**4**) and $[(L^{Me})Pb_2]^{2+}$ (**5**) were obtained. The latter show no tendency to bind to further coligands. The crystal structure determinations of **2**·BPh_4 and **3**·BPh_4 revealed the presence of bowl-shaped, calixarene-like $[(L^{Me})Cd_2(\mu\text{-}L')]^+$ cations featuring six-coordinate Cd^{II} ions with N_3S_2Cl (**2**) or N_3S_2O (**3**) environments. The metal ions in the dications **4** and **5** display highly irregular N_3S coordination environments, presumably as a consequence of the steric constraints imposed by the rigid macrocyclic nature of $(L^{Me})^{2-}$. All complexes could also be fully characterised by ^1H and ^{13}C NMR spectroscopy. These results have thus established the ability of the macrodinucleating polyaza-dithiophenolate ligand to support the formation of stable dinuclear complexes of toxic heavy metals.

Introduction

It is well established that macrodinucleating ligands of the Robson type[1] are ideally suited to the formation of kinetically and thermodynamically stable complexes of the 3d elements.[2] Since these ligands also bind strongly to a range of toxic and precious heavy metal ions,[3−5] they may serve as complexing or extracting agents for biological, environmental or recycling purposes.[6−8] With regards to the soft characteristics of the heavy metal ions,[9] it could be advantageous to use macrocyclic ligands with mixed nitrogen-sulfur donor sets to improve their metal-ion selectivity. Consequently, a large number of N,S-based macrocycles have been reported and their binding properties towards environmentally important elements have been investigated.[10,11] To the best of our knowledge, the thiophenolate derivatives[12−14] of Robson-type macrocycles have not yet been tested in this respect. This led us to investigate the ligating properties of the dinucleating hexaaza-thiophenolate ligand $(L^{Me})^{2-}$ (see Scheme 1)[15,16] towards the metal ions Cd^{II}, Hg^{II} and Pb^{II}.

Herein we demonstrate that such metal ions can be readily accommodated in the two binding pockets of H_2L^{Me}. In each case we have obtained single crystals suitable for X-ray structure determinations. It has therefore been possible to study, in detail, the binding of the metal ions to the octadentate N_6S_2 macrocycle H_2L^{Me}. The results of IR and NMR spectroscopic investigations are also reported.



Scheme 1. Structure of the ligand H_2L^{Me}

Results and Discussion

Preparation

The synthesised compounds and their labels are collected in Scheme 1 with Scheme 2 depicting the synthetic procedures. The complexation reactions of the free macrocycle H_2L^{Me}·6HCl with $CdCl_2$, $Cd(OAc)_2$, $Hg(OAc)_2$ and $Pb(OAc)_2$ were all carried out in methanol in the presence of triethylamine. All reactions proceeded smoothly and produced clear solutions from which, upon addition of an excess of $LiClO_4$, the highly crystalline salts $[(L^{Me})Cd_2(\mu\text{-}Cl)]ClO_4$ (**2**·ClO_4), $[(L^{Me})Cd_2(\mu\text{-}OAc)]ClO_4$ (**3**·ClO_4), $[(L^{Me})Hg_2](ClO_4)_2$ (**4**·ClO_4) and $[(L^{Me})Pb_2](ClO_4)_2$ (**5**·ClO_4) precipitated in good to excellent yields. Complex **3** was also

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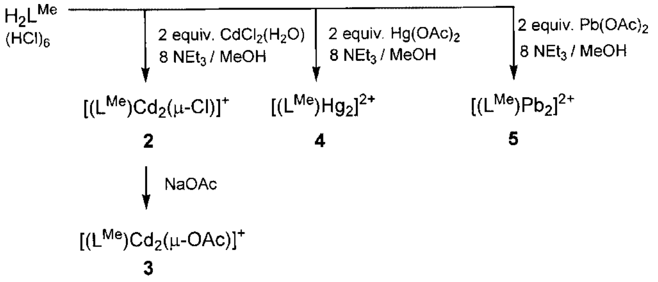
[a] Institut für Anorganische Chemie, Universität Leipzig
Johannisallee 29, 04103 Leipzig
Fax: (internat.) + 49-341-9736143
E-mail: b.kersting@uni-leipzig.de

accessible from $[(L^{Me})Cd_2(\mu\text{-}Cl)]ClO_4$ (**2**·ClO_4) and sodium acetate.



Scheme 2. Synthesis of complexes and their labels; the complexes were either isolated as ClO_4^- or BPh_4^- salts

The new compounds are colourless to pale-yellow solids and dissolve readily in polar protic solvents such as methanol or ethanol. With the exception of complex **2**, which fixes carbon dioxide from air to give the methyl carbonate complex $[(L^{Me})Cd_2(\mu\text{-}O_2COMe)]^+$, all compounds are stable in air both in solution and in the solid state. All compounds gave satisfactory elemental analyses and were characterised by spectroscopic methods (IR, ^1H and ^{13}C NMR spectroscopy) and X-ray crystallography.

Spectroscopic Characterisation

Infrared Spectroscopy

The infrared spectra of all compounds are dominated by the absorptions of the $[(L^{Me})M_2]^{2+}$ fragments and the counterions (ClO_4^- or BPh_4^-).[17] The IR spectrum of **3**·ClO_4 shows two bands at 1577 and 1422 cm^{-1} which can be assigned to the asymmetric [$\nu_{asym}(OAc^-)$] and symmetric stretching modes [$\nu_{sym}(OAc^-)$] of the acetate group, respectively.[18] These values are very similar to those of the zinc complex $[(L^{Me})Zn_2(\mu\text{-}OAc)]^+$ (**1**),[16] indicating that the acetate group in the cadmium complex **3** is also in the $\mu_{1,3}$-bridging mode. The IR spectra of complexes **4** and **5** lack these two bands which is in good agreement with the presence of unligated $[(L^{Me})M_2]^{2+}$ dications. The IR spectra of **4** and **5** were otherwise not very informative with regards to the compositions and structures of the complexes.

NMR Spectroscopy

All of the new complexes were further characterised by ^1H and ^{13}C NMR spectroscopy. Table 1 lists selected NMR spectroscopic data for complexes **2**–**5**. The data for complex **1** have been reported previously and are included for comparative purposes. As can be seen, the ^1H NMR spectroscopic data of the acetato-bridged complexes **1** and **3** are very similar. Both complexes display only one set of signals, indicating that both exist as single isomers in solution. Furthermore, the four aromatic protons (ArH), the methyl protons on the benzylic nitrogens ($N^{Bz}CH_3$), the methyl protons on the central amine nitrogen of the linking diethylene triamine units (NCH_3) and the *tert*-butyl protons [$C(CH_3)_3$] appear as singlets, indicative of C_{2v} symmetry for the $[(L^{Me})M_2(\mu\text{-}OAc)]^+$ cations in solution. This is further supported by the fact that the $[(L^{Me})M_2]^{2+}$ fragments give rise to only eleven ^{13}C signals (7 for the aliphatic and 4 for the aromatic carbon atoms). Of note is the appearance of the ^1H NMR signals for the methyl protons of the acetato coligands in **1** and **3** at δ = 0.85 and δ = 0.98 ppm, respectively. The signals are shifted considerably to high-field compared with the value recorded for free sodium acetate in the same solvent (δ = 1.83 ppm). This provides strong

Table 1. Selected ^1H and ^{13}C NMR spectroscopic data for complexes **1**–**5**

	1[a][b]	**2**[a]	**3**[a]	**4**[a]	**5**[a]
ArH	7.13 s	7.20 s	7.12 s	7.36 d, 7.31 d 7.27 d, 7.26 d	7.69 d 7.45 d
NCH_3	2.92 s	2.84 s	2.84 s	2.80 s, 2.57 s 2.42 s, 2.33 s	3.33 s
$N^{Bz}CH_3$	2.48 s	2.33 s	2.36 s	2.31 s, 2.24 s	2.40 s, 2.27 s
*t*Bu	1.28 s	1.26 s	1.23 s	1.23 s, 1.19 s	1.36 s
OAc	0.85 s	–	0.98 s	–	–
$C^{arom.}$	145.7 142.5 136.8 134.3	147.1 141.8 135.8 131.0	146.4 141.5 136.1 130.5	151.3, 149.9 137.5, 137.4 136.9, 136.7 135.3, 134.1 133.9, 133.7 133.6, 132.6	151.2 139.9 139.1 138.7 131.4 130.8
CH_2	64.2 59.2 57.9	63.8 60.8 58.0	63.0 60.4 57.9	66.8, 64.5, 63.3 62.9, 62.0, 60.0 58.6, 57.3, 55.6 54.9, 52.0, 51.3	64.3, 63.2 60.5, 59.7 57.1, 56.7
NCH_3	49.8 46.7	50.1 46.0	50.3 46.7	49.7, 49.3, 46.4 46.3, 46.2, 44.9	48.1, 43.8, 39.9
$C(CH_3)_3$	34.4	34.7	34.7	35.2, 35.1	35.1
$C(CH_3)_3$	31.8	31.6	31.6	31.4, 31.3	31.8

[a] All spectra were recorded in CD_3CN at ambient temperature. [b] ^{13}C NMR spectroscopic data recorded for the BPh_4^- salt in $CDCl_3$.

evidence that the coordinated acetate groups sense the ring-currents of the two flanking phenyl rings of $(L^{Me})^{2-}$. As can be seen from Figure 2 (see below), the methyl protons of the acetate groups are positioned in the binding cavity of the $[(L^{Me})M_2]^{2+}$ fragment slightly above the centre of the two phenyl rings in the shielded region. Since the angle between the phenyl rings in the zinc complex **1** (80.0°)[16] is much smaller than in the cadmium complex **3** (94.4°), the distance of the methyl protons to the centre of the phenyl rings is smaller in the former and hence the shielding effect is more pronounced in this compound. These spectroscopic findings thus clearly show that the coligands in **1** and **3** remain attached to the metal ions in solution with retention of their solid-state structures.

The ^{1}H NMR spectroscopic data of the dicadmium complex **2** are very similar to those of **3**. Again, the ArH, $N^{Bz}CH_3$, NCH_3 and $C(CH_3)_3$ protons all appear as well-resolved singlets. Likewise, there are only eleven signals in the ^{13}C spectrum. On the basis of these data, one can also conclude the existence of C_{2v} symmetry in the $[(L^{Me})Cd_2(\mu\text{-}Cl)]^+$ cation. The most striking feature in the ^{1}H NMR spectrum of **2**·ClO_4 is the rare observation of satellites for the $ArCH_2N$ and the $N^{Bz}CH_3$ protons that presumably arise from three-bond $^1H-^{111,113}Cd$ couplings $[^3J(^{111,113}Cd-^1H)$ = 4.6 Hz and 4.0 Hz, respectively].[19] This reflects kinetic inertness of the complex cation in solution as well as a degree of covalency in the Cd−ligand bonds. Similar findings have been observed for other cadmium complexes of macrocyclic ligands.[10,20]

The ^{13}C NMR spectroscopic data of the mercury complex **4** differ significantly from those of the compounds above and, as we will show below, this complex exhibits C_1 symmetry in the solid state. This symmetry arises because of different configurations for the two chiral amine donors in the two opposing diethylene triamine units [e.g. (*R*)-N(1), (*R*)-N(3) vs. (*S*)-N(4), (*R*)-N(6), see Figure 3 below]. This in turn renders all carbon atoms of the present complex chemically inequivalent and, given that its solid-state structure is maintained in solution, a total of 34[21] resonances (12 aromatic C atoms, 4 benzylic C atoms, 8 ethylene C atoms, 4 *tert*-butyl C atoms and 6 *N*-methyl C atoms) are, in principle, observable. The experiment clearly shows that this is indeed the case (see Table 1). At 75 MHz, the differences in the ^{13}C chemical shift values are sufficiently large for all the expected 34 resonances to be resolved. The 12 aromatic carbon atoms resonate in the region $\delta = 150-120$ and the 22 aliphatic carbon atoms can be observed between 70 and 30 ppm. The fact that **4** is a C_1-symmetric species is also supported by ^{1}H NMR spectroscopy. In the case of the benzylic CH_2 and the ethylenic CH_2 protons the chemical shift differences are too small for full resolution of all expected 16 resonances. However, the expected 14 signals for the four aromatic protons, the four CH_3 groups on the benzylic nitrogen atoms, the two CH_3 groups on the central amine N atoms of the diethylene triamine units and the two *tert*-butyl groups are all observable with the correct intensity ratios. It can therefore be concluded that **4** maintains its solid-state structure in solution.

The lead complex **5** displays only half as many ^{13}C NMR signals as **4** but the total number of 17 resonances is still larger than the 11 resonances observed for **3**, indicating symmetry higher than C_1 but lower than C_{2v}. The ^{1}H NMR spectroscopic data suggest that it is C_2 symmetry which was observed in the solid state. The higher symmetry of **5** (relative to **4**) is easily detectable in the identical configurations for the four benzylic amine nitrogen donors in the two opposing diethylene triamine units [e.g. (*S*)-N(1), (*S*)-N(3), (*S*)-N(4), and (*S*)-N(6), see Figure 4, below]. In summary, the NMR spectroscopic investigations have clearly established that all complexes exist as discrete and stable species in solution.

X-ray Crystallography

Further confirmation regarding the composition and structures of the complexes was provided by X-ray diffraction studies. Single crystals of X-ray quality were obtained for the tetraphenylborate salts of **2**−**4** and for the diperchlorate salt of **5**. The molecular structures of the complexes are displayed in Figures 1−4 and selected bond lengths and angles are given in Tables 2 and 3.

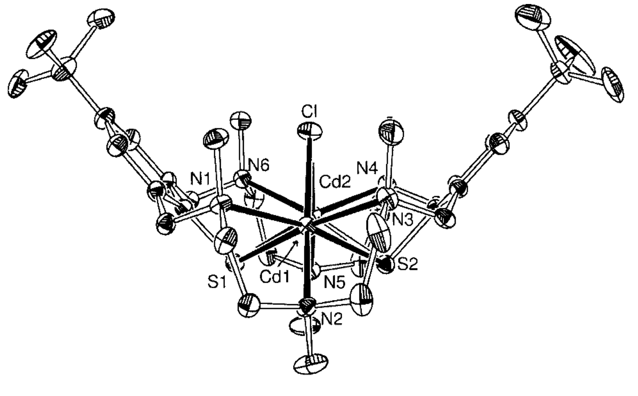


Figure 1. Molecular structure of the cation **2**; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity

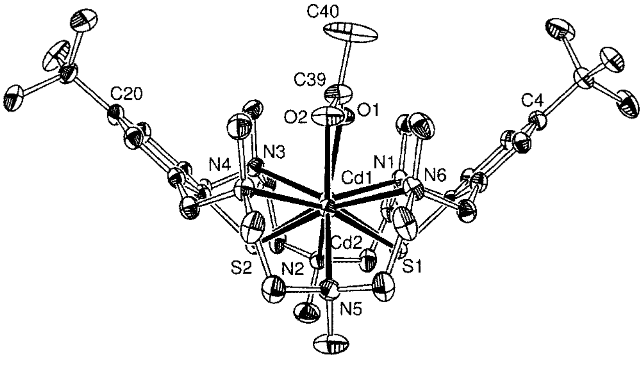


Figure 2. Molecular structure of the cation **3**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity

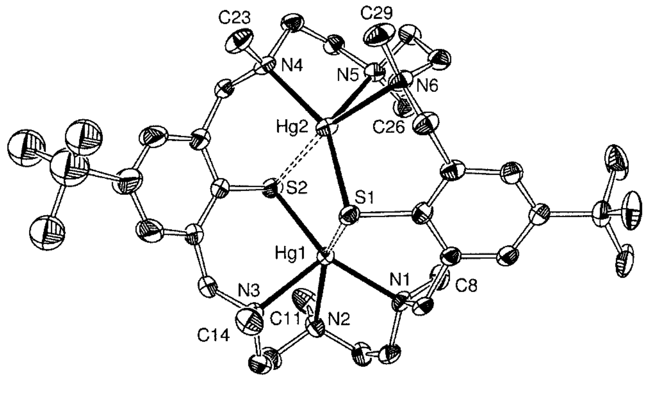


Figure 3. Molecular structure of the dication **4**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity

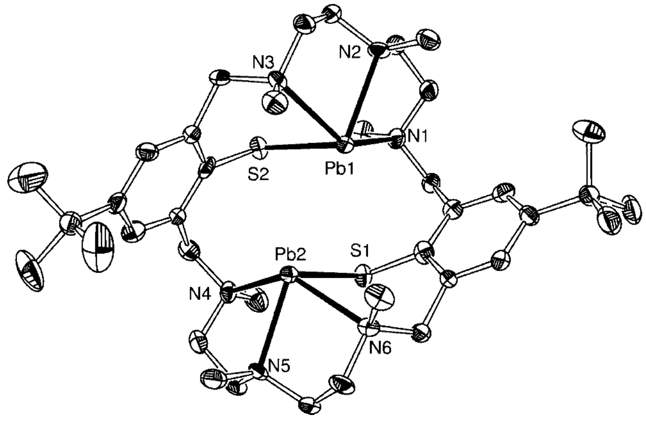


Figure 4. Molecular structure of the dication **5**; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity

Description of the Crystal Structures

[(L^{Me})Cd$_2$(μ-Cl)]BPh$_4$·1.5MeOH (2·BPh$_4$·1.5MeOH)

This salt crystallises in the triclinic space group $P\bar{1}$. The structure revealed the presence of discrete dinuclear [(L^{Me})Cd$_2$(μ-Cl)]$^+$ cations, tetraphenylborate anions and methanol solvate molecules. The dicadmium complex exhibits idealized C_{2v} symmetry as was established by NMR spectroscopy. As can be seen in Figure 1, the cadmium(II) ions are coordinated in a distorted octahedral fashion by three *facially* oriented nitrogen atoms, two bridging thiophenolate sulfur atoms and a bridging halide ion. The minimum and maximum deviations from the ideal 90° and 180° bond angles of a perfect octahedron are −14.8° for N(1)−Cd(1)−N(2) and −10.4° for Cl−Cd(2)−N(5), respectively. The mean cadmium−ligand bond lengths (Cd−N 2.421 Å, Cd−S 2.677 Å, Cd−Cl 2.703 Å) show no unusual features and compare well with those in **3** (see below) and related complexes with mixed N and S ligation.[20,22] It is also worth mentioning that the macrocycle in **2** adopts the "conical" calixarene-like conformation which differs from the alternative "partial cone" conformation seen in the related complexes [(L^{Me})M$_2$(μ-Cl)]$^+$ of the lighter 3d elements Co^{II}, Ni^{II} and Zn^{II}.[15,24] The preference of the latter for adopting the "partial cone" conformation is presumably due to the smaller ionic radii of these metal ions (Co^{II}: 0.885 Å, Ni^{II}: 0.83 Å, Zn^{II}: 0.88 Å vs. 1.06 Å for Cd^{II})[23] and presumably also due to the rigid nature of the 24-membered macrocycle.

[(L^{Me})Cd$_2$(μ-OAc)]BPh$_4$·2MeCN·MeOH (3·BPh$_4$·2MeCN·MeOH)

The crystal structure determination of the title compound showed the structure of the dinuclear [(L^{Me})Cd$_2$(μ-OAc)]$^+$ complex to be isostructural with the zinc complex [(L^{Me})Zn$_2$(μ-OAc)]$^+$ (**1**).[16] The hexaaza-dithiophenolate ligand assumes a bowl-shaped "calixarene-like" conformation which is typical for carboxylato-bridged complexes of this ligand.[24] The acetate ion bridges the two cadmium ions in a symmetrical fashion [O(1)−C(39) 1.222(4) Å, O(2)−C(39) 1.232(4) Å] with a Cd···Cd distance of 3.402(2) Å. It is deeply buried in the binding cavity of the [(L^{Me})Cd$_2$]$^{2+}$ fragment. As a consequence, its methyl protons are positioned above the centre of the two phenyl rings in the shielding region. The angle between the planes through the two phenyl rings of 94.4° is larger than in **1** (80.0°). This explains why the acetate protons in **1** experience a larger high-field shift compared with those in **3** (vide supra). The average Cd−N bond length of 2.439 Å is normal for six-coordinate cadmium complexes with amine donor ligands.[25,26] The same holds for the average Cd−S distance of 2.669 Å and the average Cd−O distance of 2.238 Å.[27,28] As expected, the metal-ligand bond lengths in **3** are larger than those in **1**. The mean difference of 0.13 Å is close to the difference between the ionic radii of the two elements.

[(L^{Me})Hg$_2$](BPh$_4$)$_2$·MeCN [4·(BPh$_4$)$_2$·MeCN]

The crystal structure determination of **4**·(BPh$_4$)$_2$·MeCN unambiguously confirmed the identity of the dimercury(II) complex **4**. Its molecular structure is illustrated in Figure 3. The [(L^{Me})Hg$_2$]$^{2+}$ dication bears no additional coligands and has an intramolecular Hg···Hg separation of 3.725(1) Å. The Hg^{II} ions are surrounded by three nitrogen and two sulfur donor atoms from (L^{Me})$^{2-}$ in highly irregular N$_3$S$_2$ coordination environments (coordination number of Hg^{II}: 4 + 1). The intramolecular separations Hg(1)···S(1) of 2.897(2) Å and Hg(2)···S(2) of 3.313(2) Å are much longer than the other two Hg−S distances of 2.383 and 2.395 Å, indicating that the latter exhibit more covalent character while the former are more electrostatic in nature. The diethylene triamine units are *facially* coordinated with one large and two smaller N−Hg−N bond angles, this being the most commonly observed situation in complexes with this tridentate unit.[29] The Hg−N bond lengths (mean value: 2.413 Å) are somewhat longer in comparison with the more covalent Hg−S bonds but are similar to those in related mercury complexes.[30,31] In [Hg(en)$_2$](ClO$_4$)$_2$ for example (en = ethylene diamine), an average Hg−N distance of 2.32 Å has been reported.[32]

Table 2. Selected bond lengths [Å] and angles [°] in the cations $[(L^{Me})Zn_2(OAc)]^+$ (**1**), $[(L^{Me})Cd_2(Cl)]^+$ (**2**), $[(L^{Me})Cd_2(OAc)]^+$ (**3**)

	1	2	3
	M = Zn, X = Y = O	M = Cd, X = Y = Cl	M = Cd, X = Y = O
M(1)−X	2.026(2)	2.682(1)	2.245(2)
M(1)−N(1)	2.379(2)	2.453(3)	2.474(3)
M(1)−N(2)	2.202(2)	2.424(3)	2.436(3)
M(1)−N(3)	2.316(2)	2.410(4)	2.408(3)
M(1)−S(1)	2.551(1)	2.653(1)	2.654(1)
M(1)−S(2)	2.515(1)	2.699(2)	2.677(1)
M(2)−Y	2.027(2)	2.723(1)	2.230(2)
M(2)−N(4)	2.314(2)	2.441(3)	2.467(3)
M(2)−N(5)	2.219(2)	2.388(3)	2.411(3)
M(2)−N(6)	2.388(2)	2.409(3)	2.442(3)
M(2)−S(1)	2.572(1)	2.696(1)	2.698(1)
M(2)−S(2)	2.508(1)	2.659(1)	2.645(1)
M−N[a]	2.303	2.421	2.439
M−X[a]	2.027	2.703	2.238
M−S[a]	2.536	2.677	2.669
M(1)−S(1)−M(2)	84.00(4)	77.78(4)	78.92(4)
M(1)−S(2)−M(2)	86.05(3)	77.63(4)	79.46(4)
M(1)−μCl−M(2)	−	76.83(4)	−
N(1)−M(1)−N(2)	78.92(8)	75.17(11)	75.22(9)
N(1)−M(1)−N(3)	98.84(7)	99.40(12)	101.87(9)
N(2)−M(1)−N(3)	80.98(9)	76.48(12)	75.99(9)
N(4)−M(2)−N(5)	80.23(7)	75.97(12)	75.84(10)
N(4)−M(2)−N(6)	99.00(7)	99.77(12)	103.53(10)
N(5)−M(2)−N(6)	79.05(7)	76.83(12)	76.31(9)
C(4)···C(20)	9.404	9.824	10.247
Ph/Ph[b]	80.0	83.7	94.4
M···M	3.427(1)	3.358(1)	3.402(2)

[a] Average values. [b] Angle between the normals of the planes of the two aryl rings.

Table 3. Selected bond lengths [Å] and angles [°] in $[(L^{Me})Hg_2]^{2+}$ (**4**) and $[(L^{Me})Pb_2]^{2+}$ (**5**)

4		5	
Hg(1)···S(1)	2.897(2)	Pb(1)···S(1)	3.465(3)
Hg(1)−S(2)	2.383(2)	Pb(1)−S(2)	2.640(3)
Hg(1)−N(1)	2.276(5)	Pb(1)−N(1)	2.584(10)
Hg(1)−N(2)	2.566(5)	Pb(1)−N(2)	2.427(9)
Hg(1)−N(3)	2.449(5)	Pb(1)−N(3)	2.552(10)
Hg(2)−S(1)	2.395(2)	Pb(2)−S(1)	2.554(3)
Hg(2)···S(2)	3.313(2)	Pb(2)···S(2)	3.824(3)
Hg(2)−N(4)	2.269(5)	Pb(2)−N(4)	2.591(10)
Hg(2)−N(5)	2.401(5)	Pb(2)−N(5)	2.403(8)
Hg(2)−N(6)	2.517(5)	Pb(2)−N(6)	2.600(9)
Hg(1)···Hg(2)	3.725(1)	Pb(1)···Pb(2)	3.4192(8)
Hg−N[a]	2.413	Pb−N[a]	2.526
Hg−S[a]	2.389	Pb−S[a]	2.597
N(1)−Hg(1)−N(2)	76.17(18)	N(1)−Pb(1)−N(2)	71.0(3)
N(1)−Hg(1)−N(3)	108.91(19)	N(1)−Pb(1)−N(3)	137.0(3)
N(2)−Hg(1)−N(3)	73.24(17)	N(2)−Pb(1)−N(3)	74.1(3)
N(4)−Hg(2)−N(5)	78.36(18)	N(4)−Pb(2)−N(5)	73.8(3)
N(4)−Hg(2)−N(6)	108.81(18)	N(4)−Pb(2)−N(6)	139.3(3)
N(5)−Hg(2)−N(6)	73.83(18)	N(5)−Pb(2)−N(6)	74.5(3)

[a] Average values.

It should be noted that the configurations of the benzylic nitrogen atoms in the opposing diethylene triamine are different. Thus, the configurations are (*R*)-N(1) and (*R*)-N(3) for one diethylene linker, whereas they are (*S*)-N(4) and (*R*)-N(6) for the other. The differences in the secondary Hg···S interactions [i.e. Hg(2)···S(2), Hg(2)···S(1)] are, at least in part, a consequence of these different N configurations. They are also responsible for the C_1 symmetry of the $[(L^{Me})Hg_2]^{2+}$ dication.

$[(L^{Me})Pb_2](ClO_4)_2\cdot MeCN$ [$\mathbf{5}\cdot(ClO_4)_2\cdot MeCN$]

This structure contains discrete $[(L^{Me})Pb_2]^{2+}$ cations, perchlorate anions and acetonitrile solvate molecules. Figure 4 shows the structure of the cation **5** together with the atomic numbering scheme. Similar to **4**, the dication is not bound to any further coligands. Complex **5** exhibits no crystallographically imposed symmetry but has idealized C_2 symmetry. The coordination environment of each lead(II) ion consists of three tertiary amine donors and one thiophenolate sulfur atom. The coordination geometry is best considered as distorted square pyramidal, with the lead ion sitting ca 1.3 Å above the plane formed from the four donor atoms [mean deviation from the planes N(1)N(2)N(3)S(2): 0.32 Å, N(4)N(5)N(6)S(1): 0.31 Å]. The empty space above the lead(II) ion on the apex of the pyramid is indicative of a stereochemically active lone pair as in PbO (yellow modification).[33] In contrast to the dimercury complex **4**, the diethylene triamine units bind in a meridional fashion which results in larger N(1)−Pb(1)−N(3) [137.0(3)°] and N(4)−Pb(2)−N(6) [139.3(3)°] angles. This has also been observed in lead complexes of macrodinucleating polyazaphenolate ligands.[34] The average Pb−N bond length of

2.526 Å is normal for lead(II) complexes.[35,36] The same is true for the Pb−S distances.

Conclusion

The main findings of the present work can be summarised as follows: a) The 24-membered hexaaza-dithiophenolate macrocycle H_2L^{Me} supports the formation of dinuclear complexes of Cd^{II}, Hg^{II} and Pb^{II}. b) The complexes dissolve in organic solvents without decomposition. c) The dicadmium complexes $[(L^{Me})M_2(\mu\text{-}L')]$ differ from the Hg and Pb complexes in that they bind additional coligands. This offers the opportunity to selectively recognise or separate Cd from a mixture of the three elements. d) The structures of $[(L^{Me})Hg_2]^{2+}$ and $[(L^{Me})Pb_2]^{2+}$ have clarified the binding preferences of the two toxic heavy metal ions towards the donors of H_2L^{Me}. This can now be used as a guide for fine-tuning the ligand to achieve high metal-ion selectivity. Current studies in this laboratory are focusing on the determination of the complex stability constants and on methods of metal-ion extraction.

Experimental Section

General: Unless otherwise noted, the preparations of the metal complexes were carried out under argon using standard Schlenk techniques. The compound $H_2L^{Me}\cdot 6HCl$ was prepared as described in the literature.[15,37] All other compounds and reagents were purchased. Melting points were determined in capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Bruker AVANCE DPX-200 or a Varian 300 unity spectrometer. Elemental analyses were performed with a Vario EL analyser (Elementaranalysensysteme GmbH). IR spectra were recorded with a Bruker VECTOR 22 FT-IR spectrometer as KBr pellets.

Safety Note: *Caution; perchlorate salts of transition metal complexes are hazardous and may explode; only small quantities should be prepared and great care should be taken!*

$[(L^{Me})Cd_2(\mu\text{-}Cl)]ClO_4$ ($2\cdot ClO_4$): To a suspension of $H_2L^{Me}\cdot 6HCl$ (890 mg, 1.00 mmol) in methanol (40 mL) was added solid $CdCl_2\cdot H_2O$ (403 mg, 2.00 mmol). A solution of triethylamine (808 mg, 8.00 mmol) in methanol (2 mL) was then added to give a colourless solution. After stirring at room temperature for 3 h, solid $LiClO_4\cdot 3H_2O$ (2.50 g, 15.6 mmol) was added to give the perchlorate salt $2\cdot ClO_4$ as a white microcrystalline solid. This material was filtered, washed with cold ethanol (5 mL) and diethyl ether (5 mL), and dried in vacuo. Yield 876 mg (85%). M.p. 302−303 °C (decomposes without melting). IR (KBr pellet): $\tilde{\nu}$ = 3446 s br, 2958 s, 2865 s, 1630 m, 1457 s, 1394 w, 1365 m, 1314 m, 1291 m, 1267 m, 1234 m, 1203 w, 1168 w, 1158 w, 1100 vs. [$\nu(ClO_4)$], 1046 s, 1012 w, 1000 w, 978 m, 928 m, 910 m, 887 m, 815 s, 802 m, 746 m, 686 w, 664 w, 624 s, 593 w, 555 w, 484 w cm^{-1}. ^1H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 7.20 (s, 4 H, ArH), 4.70 [d, ^2J = 11.5, $^3J(^{111,113}Cd\text{-}^1H)$ = 4.6 Hz, 4 H, $ArCH_2$], 3.42 (m, 4 H, NCH_2), 3.24 (m, 4 H, NCH_2), 2.88−2.78 (m, 4 H +4 H, NCH_2+$ArCH_2$), 2.84 (s, 6 H, NCH_3), 2.50 (m, 4 H, NCH_2), 2.33 [s, $^3J(^{111,113}Cd\text{-}^1H)$ = 4.6 Hz, 12 H, $BzNCH_3$], 1.26 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (75.42 MHz, $[D_3]CH_3CN$, 25 °C, TMS): δ = 147.1, 141.8, 135.8 (CH), 131.0 (CH) (aromatic carbon atoms), 63.8, 60.8, 58.0 (all CH_2), 50.1, 46.0 (all NCH_3), 34.7 [$C(CH_3)_3$], 31.6 [$C(CH_3)_3$] ppm. $C_{38}H_{64}Cd_2Cl_2N_6O_4S_2$ (1028.81): calcd. C 44.36, H 6.27, N 8.17, S 6.23; found C 43.92, H 6.12, N 8.00, S 5.77. The tetraphenylborate salt, $[(L^{Me})Cd_2(\mu\text{-}Cl)]BPh_4$ ($2\cdot BPh_4$), was prepared by adding a solution of $NaBPh_4$ (198 mg, 0.580 mmol) in methanol (3 mL) to an argon-purged solution of $1\cdot ClO_4$ (103 mg, 0.100 mmol) in methanol (50 mL). The resultant colourless precipitate was isolated by filtration, washed with 5 mL of cold methanol and dried in air. Yield 112 mg (90%). M.p. 293−294 °C (decomp.). IR (KBr pellet): $\tilde{\nu}$ = 3053 m, 3032 w, 2996 w, 2964 s, 2925 w, 2900 w, 2862 m, 2835 w, 2807 w, 1477 m, 1457 s, 1425 m, 1394 m, 1365 m, 1352 w, 1313 m, 1290 m, 1267 m, 1232 m, 1203 w, 1181 w, 1170 w, 1157 m, 1131 w, 1114 w, 1083 s, 1044 s, 1011 w, 1000 w, 981 w, 927 w, 910 m, 887 m, 844 m, 815 m, 802 m, 734 s, 705 s [$\nu(BPh_4^-)$], 625 m, 612 m, 555 w, 475 w cm^{-1}. The tetraphenylborate salt was additionally characterised by X-ray crystallography.

$[(L^{Me})Cd_2(\mu\text{-}OAc)]ClO_4$ ($3\cdot ClO_4$): To a solution of $2\cdot ClO_4$ (103 mg, 0.100 mmol) in methanol (50 mL) was added a solution of sodium acetate (12.3 mg, 0.150 mmol) in methanol (5 mL). After the reaction mixture had been stirred for 3 h, a solution of $LiClO_4\cdot 3H_2O$ (802 mg, 5.00 mmol) in methanol (2 mL) was added. The resultant colourless microcrystalline solid was isolated by filtration, washed with methanol and dried in air. Yield 91 mg (86%). M.p. 352−353 °C (decomp.). IR (KBr, pellet): $\tilde{\nu}$ = 2960 s, 2900 m, 2865 s, 2837 sh, 2806 m, 1577 s [$\nu_{as}(OAc^-)$], 1456 s, 1422 s [$\nu_s(OAc^-)$], 1396 w, 1365 m, 1314 w, 1293 m, 1267 m, 1230 m, 1203 m, 1170 w, 1155 w, 1093 vs. [$\nu(ClO_4^-)$], 1044 s, 1012 w, 1000 w, 981 w, 925 w, 911 m, 884 m, 816 s, 802 m, 744 m, 684 w, 654 m, 624 s, 596 w, 555 w, 535 w cm^{-1}. ^1H NMR (200 MHz, $[D_3]CH_3CN$, 25 °C, TMS): δ = 7.12 (s, 4 H, ArH), 4.54 (d, ^2J = 11.5 Hz, 4 H, $ArCH_2$), 3.40 (m, 4 H, CH_2), 3.18 (m, 4 H, CH_2), 2.84 (s, 6 H, NCH_3), 2.82 (m, 4 H, CH_2), 2.74 (d, 4 H, $ArCH_2$), 2.48 (m, 4 H, CH_2), 2.36 (s, 12 H, NCH_3), 1.23 (s, 18 H, CH_3), 0.98 (s, 3 H, O_2CCH_3) ppm. ^{13}C NMR (75.42 MHz, $[D_3]CH_3CN$, 25 °C, TMS): δ = 176.3 (OAc), 146.4, 141.5, 136.1, 130.5, 63.0 (CH_2), 60.4 (CH_2), 57.9 (CH_2), 50.3 (NCH_3), 46.7 (NCH_3), 34.7 (C), 31.6 [$C(CH_3)_3$], 23.2 (OAc) ppm. The tetraphenylborate salt, $[(L^{Me})Cd_2(\mu\text{-}OAc)]BPh_4$ ($3\cdot BPh_4$), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of $3\cdot ClO_4$ (103 mg, 0.100 mmol) in methanol (50 mL). The resultant colourless solid was recrystallised from a mixed acetonitrile/methanol (1:1) solvent system. Yield 116 mg (91%). M.p. 304−305 °C (decomp.). IR (KBr pellet): $\tilde{\nu}$ = 3055 m, 3034 m, 2908 sh, 2963 s, 2924 m, 2899 m, 2866 m, 2836 m, 2804 w, 1576 s [$\nu_{asym}(OAc^-)$], 1476 w, 1455 s, 1425 s [$\nu_{sym}(OAc^-)$], 1395 w, 1364 w, 1353 w, 1313 w, 1291 w, 1267 w, 1230 w, 1203 w, 1181 w, 1170 w, 1155 m, 1133 w, 1116 w, 1082 s, 1045 s, 1012 w, 996 w, 981 w, 924 m, 911 m, 886 m, 842w, 815 s, 800 m, 744 m, 734 s, 704 s [$\nu(BPh_4^-)$], 653 w, 625 m, 612 m, 594 w, 556 w cm^{-1}. $C_{64}H_{87}BCd_2N_6O_2S_2$ (1272.18): calcd. C 60.42, H 6.89, N 6.61, S 5.04; found C 60.24, H 6.72, N 6.47, S 4.94. This salt was additionally characterised by X-ray crystallography.

$[(L^{Me})Hg_2](ClO_4)_2$ [$4\cdot(ClO_4)_2$]: To a suspension of $H_2L^{Me}\cdot 6HCl$ (890 mg, 1.00 mmol) in methanol (40 mL) was added a solution of $Hg(CH_3COO)_2$ (637 mg, 2.00 mmol) in methanol (10 mL). A solution of triethylamine (808 mg, 8.00 mmol) in methanol (5 mL) was then added to give a colourless solution. The reaction mixture was stirred for 12 h after which time a solution of $LiClO_4\cdot 3H_2O$ (802 mg, 5.00 mmol) in methanol (2 mL) was added. The resultant colourless microcrystalline solid was isolated by filtration, washed with methanol and dried in air. Yield 901 mg (71%). M.p. 246−247 °C (decomp). IR (KBr pellet): $\tilde{\nu}$ = 2958 s, 2902 w, 2864 s, 1463 m, 1394 w, 1366 m, 1307 w, 1290 w, 1266 w, 1231 m, 1202 w, 1183 w, 1143 m, 1119 s, 1107 s, 1088 s [ν(ClO_4^-)], 1045 w, 1022 w, 1010 w, 991 w, 960 w, 948 w, 927 w, 910 m, 901 m, 889 m, 810 m, 796 m, 782 w, 753 w, 742 w, 685 w, 630 m, 624 s. ^{1}H NMR (300 MHz, [D$_3$]CH_3CN, 25 °C, TMS): δ = 7.36 (d, ^4J = 2.3 Hz, 1 H, ArH), 7.31 (d, ^4J = 2.3 Hz, 1 H, ArH), 7.27 (d, ^4J = 2.3 Hz, 1 H, ArH), 7.26 (d, ^4J = 2.3 Hz, 1 H, ArH), 4.91 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 4.74 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 4.26 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 4.20 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 3.71 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 3.44 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 3.38 (d, ^2J = 12.0 Hz, 1 H, ArCH_2), 3.25−2.50 (m, 1 H +16 H, ArCH_2 + NCH_2CH_2N), 2.80 (s, 3 H, NCH_3), 2.57 (s, 3 H, NCH_3), 2.42 (s, 3 H, NCH_3) 2.33 (s, 3 H, NCH_3) 2.31 (s, 3 H, NCH_3) 2.24 (s, 3 H, NCH_3), 1.23 (s, 9 H, CH_3), 1.19 (s, 9 H, CH_3) ppm. ^{13}C{^{1}H} NMR (75.42 MHz, [D$_3$]CH_3CN, 25 °C, TMS): δ = 151.3, 149.9, 137.5, 137.4, 136.9, 136.7, 135.3, 134.1, 133.9, 133.7, 133.6, 132.6 (aromatic carbon atoms), 66.8, 64.5, 63.3, 62.9, 62.0, 60.0, 58.6, 57.3, 55.6, 54.9, 52.0, 51.3 (all CH_2), 49.7, 49.3, 46.4, 46.3, 46.2, 44.9 (all NCH_3), 35.2, 35.1 [$C(CH_3)_3$], 31.4, 31.3 [C(CH_3)$_3$] ppm. The tetraphenylborate salt, [(L^{Me})Hg_2](BPh_4)$_2$ [**4**·(BPh_4)$_2$], was prepared by adding a solution of $NaBPh_4$ (342 mg, 1.00 mmol) in methanol (3 mL) to a solution of [(L^{Me})Hg_2](ClO_4)$_2$ (127 mg, 0.100 mmol) in methanol (50 mL). The resultant colourless solid was isolated by filtration, washed with 5 mL of cold methanol, and dried in air. Yield 150 mg (88%). M.p. 170−171 °C (decomp.). IR (KBr pellet): ṽ = 3054 s, 3034 s, 2997 m, 2982 m, 2961 s, 2927 w, 2903 w, 2864 m, 2808 w, 1579 w, 1559 w, 1476 m, 1460 s, 1439 sh, 1425 m, 1396 m, 1375 w, 1364 m, 1351 w, 1307 w, 1285 w, 1265 m, 1229 m, 1202 w, 1183 w, 1157 m, 1133 m, 1111 w, 1087 m, 1063 m, 1042 m, 1032 m, 1009 vw, 992 w, 961 vw, 951 vw, 911 m, 890 m, 845 m, 810 m, 797 w, 784 w, 749 sh, 735 s, 706 s [ν(BPh_4)], 625 m, 613 s cm^{-1}.

[(L^{Me})Pb_2](ClO_4)$_2$ [5·(ClO_4)$_2$]: To a suspension of H_2L^{Me} 6HCl (890 mg, 1.00 mmol) in methanol (40 mL) was added a solution of $Pb(CH_3COO)_2 \cdot 3H_2O$ (759 mg, 2.00 mmol) in methanol (20 mL). A solution of triethylamine (808 mg, 8.00 mmol) in methanol (5 mL) was then added to give a pale yellow solution. After stirring for 12 h, a solution of $LiClO_4 \cdot 3H_2O$ (802 mg, 5.00 mmol) in methanol (5 mL) was added. The resultant pale-yellow precipitate was isolated by filtration, washed with methanol and dried in air. Yield 1.03 g (80%). M.p. 346−347 °C (decomp.). IR (KBr pellet): ṽ = 2955 s, 2901 m, 2862 s, 2810 m, 1459 m, 1396 w, 1364 m, 1304 w, 1296 w, 1259 w, 1228 w, 1203 w, 1175 w, 1144 m, 1107 sh, 1091 vs [ν(ClO_4^-)], 1045 w, 1000 w, 958 w, 927 w, 918 w, 888 w, 811 m, 797 m, 759 m, 625 s, 460 w cm^{-1}. ^{1}H NMR (300 MHz, [D$_3$]CH_3CN, 25 °C, TMS): δ = 7.69 (d, ^4J = 2.2 Hz, 2 H, ArH), 7.45 (d, ^4J = 2.2 Hz, 2 H, ArH), 4.92 (d, ^2J = 13.2 Hz, 2 H, ArCH_2), 4.59 (d, ^2J = 11.7 Hz, 2 H, ArCH_2), 4.29 (d, ^2J = 13.2 Hz, 2 H, ArCH_2), 3.88 (d, ^2J = 11.6 Hz, 2 H, ArCH_2), 3.86−2.92 (m, 16 H, NCH_2), 3.33 (s, 6 H, NCH_3), 2.40 (s, 6 H, NCH_3), 2.27 (s, 6 H, NCH_3), 1.36 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (75.42 MHz, [D$_3$]CH_3CN, 25 °C, TMS): δ = 151.2, 139.9, 139.1, 138.7, 131.4, 130.8 (aromatic carbon atoms), 64.3, 63.2, 60.5, 59.7, 57.1, 56.7 (all CH_2), 48.1, 43.8, 39.9 (all NCH_3), 35.1 [$C(CH_3)_3$], 31.8 [C(CH_3)$_3$] ppm. $C_{38}H_{64}Cl_2N_6O_8Pb_2S_2$ (1282.39): calcd. C 35.59, H 5.03, N 6.55, S 5.00; found C 35.49, H 5.21, N 6.33, S 4.69.

Crystal Structure Determinations: Single-crystals suitable for X-ray structural analyses were grown by recrystallisation from methanol (**2**·BPh_4·1.5MeOH), acetonitrile [**4**·(BPh_4)$_2$·MeCN, **5** (ClO_4)$_2$·MeCN] or a mixed acetonitrile/methanol solvent system (**3** BPh_4·2MeCN·MeOH). The crystals were mounted on glass fibres using perfluoropolyether oil. Intensity data were collected at 210(2) K using a Bruker SMART CCD diffractometer. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT and corrected for absorption using SADABS[38] (transmission factors: 1.00−0.95 for **2**·BPh_4, 1.00−0.85 for **3**·BPh_4, 1.00−0.64 for **4**·(BPh_4)$_2$ and 1.00−0.70 for **5**·(ClO_4)$_2$]. The structures were solved by direct methods using the program SHELXS-86[39] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[40] The SHELXTL version 5.10 program package was used for the structure solutions and

Table 4. Crystallographic data for **2**·BPh_4·1.5MeOH, **3**·BPh_4·2MeCN·MeOH, **4**(BPh_4)$_2$MeCN, **5**(ClO_4)$_2$MeCN

	2	**3**	**4**	**5**
Empirical formula	$C_{63.50}H_{90}BCd_2ClN_6O_{1.50}S_2$	$C_{69}H_{97}BCd_2N_8O_3S_2$	$C_{88}H_{107}B_2Hg_2N_7S_2$	$C_{40}H_{67}Cl_2N_7O_8Pb_2S_2$
M_r (gmol^{-1})	1296.60	1386.28	1749.73	1323.41
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	13.717(3)	14.661(3)	15.857(2)	16.333(3)
b [Å]	16.016(3)	16.726(3)	27.246(4)	14.428(3)
c [Å]	16.650(3)	17.348(3)	19.388(3)	22.556(5)
α [°]	110.49(3)	112.80(3)	90	90
β [°]	91.15(3)	110.47(3)	97.944(3)	94.32(3)
γ [°9	108.21(3)	95.46(3)	90	90
V [Å^3]	3220.2(11)	3540.6(11)	8296(2)	5300(2)
Z	2	2	4	4
$d_{calcd.}$ [gcm^{-3}]	1.337	1.300	1.401	1.658
Crystal size [mm]	0.25 × 0.25 × 0.25	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
μ(Mo-K_α) [mm^{-1}]	0.811	0.708	3.794	6.575
2θ limits [°]	2.64−56.64	2.74−57.68	2.60−57.84	2.89−59.66
Measured refl.	29690	32216	51765	48229
Independent refl.	15205	16591	19837	13351
Observed refl.[a]	7769	11397	11519	6018
No. of parameters	721	754	920	549
$R1$[b] ($R1$ all data)	0.0400 (0.1021)	0.0364 (0.0645)	0.0460 (0.0916)	0.0537 (0.1628)
$wR2$[c]($wR2$ all data)	0.0760 (0.0913)	0.0915 (0.1039)	0.1126 (0.1251)	0.1263 (0.1628)
Max, min peaks (eÅ^{-3})	0.703, −0.611	0.776, −0.670	5.333; −1.498	1.623; −1.951

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

refinements.[41] PLATON was used to search for higher symmetry.[42] ORTEP3 was used for generating the ORTEP diagrams.[43] Unless otherwise noted, the anisotropic thermal parameters of all nonhydrogen atoms were refined. Hydrogen atoms were included in calculated positions with their bond lengths and thermal parameters 1.2 times (1.5 times for CH_3 groups) the thermal parameter of the atoms to which they are attached. Selected details of the data collection and refinements are given in Table 4. In the crystal structure of **2**·BPh_4·1.5MeOH one *tert*-butyl group was found to be disordered over two positions. A split atom model was applied for the disordered *t*Bu groups. The site occupancies of the two orientations were refined as 0.67(1)/0.33(1) [for C(36a/c), C(37a/c), C(38a/c)]. In the crystal structure of **3**·BPh_4·2MeCN·MeOH the methanol solvent molecule of crystallisation was found to be disordered over two positions. The site occupancies of the two orientations were fixed at half occupancy. The C and O atoms of this molecule were refined isotropically. In the crystal structure of **4**·$(BPh_4)_2$·MeCN, the *tert*-butyl groups were found to be disordered over two positions. A split atom model was applied for these alkyl groups. The site occupancies of the two orientations were refined as 0.66(3)/0.34(3) [for C(32a/c), C(33a/c), C(34a/c)] and 0.56(2)/0.44(2) [for C(36a/c), C(37a/c), C(38a/c)]. The non-hydrogen atoms of the disordered *t*Bu groups and the acetonitrile solvate molecule were refined isotropically. No hydrogen atoms were calculated for these two residues. In the crystal structure of **5**·$(ClO_4)_2$, the acetonitrile molecule of solvation and one of the two perchlorate anions were found to be disordered over two positions. The site occupancy factors of the two orientations of the acetonitrile molecule were fixed at 0.50 and its C and N atoms were refined isotropically. No hydrogen atoms were calculated for the MeCN molecule. The site occupancy factors of the two orientations of the perchlorate anion were refined as 0.68(2) and 0.32(2) for O(5)O(6a)O(7a)O(8a) and O(5)O(6b)O(7b)O(8b). These atoms could not be refined anisotropically and, for this reason, were treated as isotropic scatterers. CCDC-243454 (**2**), -243455 (**3**), -243456 (**4**) and -243457 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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