Bulky guanidinato and amidinato zinc complexes and their comparative stabilities†

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The preparation of a series of amidinato and guanidinato zinc halide complexes incorporating ligands of varying steric bulk is described, and their thermal stabilities compared. Salt elimination reactions between [M(Giso)] (M = K or Li; Giso = $[(ArN)_2CNCy_2]^-$, Ar = 2,6-diisopropylphenyl, Cy = cyclohexyl) and ZnX_2 (X = I or Br) have yielded the monomeric complexes [(Giso)ZnI] and $[(Giso)Zn(\mu\text{-}Br)_2Li(OEt_2)_2]$. Both have been crystallographically characterised and the former shown to slowly decompose in solution at ambient temperature to give the carbodiimide, ArN═C═NAr. In contrast, reactions between alkali metal complexes of a less bulky guanidinate, [M(Priso)] (Priso = $[(ArN)_2CNPr^i_2]^-$) and ZnX_2 have yielded $[(IZn)_2(\mu\text{-}NPr^i_2)\{\mu\text{-}N,N'\text{-}(NAr)_2CH\}]$ and $[(Priso)Zn(\mu\text{-}Br)_2Li(OEt_2)_2]$. The latter decomposes in solution at ambient temperature, generating ArN═C═NAr, which was also produced in the preparation of the former. Analogies are drawn between the decomposition of $[(Priso)Zn(\mu\text{-}Br)_2Li(OEt_2)_2]$ and the carbonic anhydrase catalysed dehydration of bicarbonate. Two bulky amidinato zinc complexes, $[\{(Piso)Zn(\mu\text{-}Br)\}_2]$ and $[Zn(Piso)_2]$ (Piso = $[(ArN)_2CBu^t]^-$) have been prepared, structurally characterised and shown to be markedly more thermally stable than the zinc guanidinate compounds. Attempts to reduce several of the zinc(II) halide complexes to dimeric zinc(I) compounds were so far unsuccessful, in all cases leading to the deposition of zinc metal.

Introduction

The coordination chemistry of anionic amidinate ($[R^1NC(R^2)NR^1]^-$, R^1, R^2 = H, alkyl, aryl, silyl *etc.*) and guanidinate ($[R^1NC(NR_2^2)NR^1]^-$) ligands is extensive and includes complexes incorporating metals from across the periodic table.[1] Such systems have found many applications in areas as diverse as catalysis,[2–4] materials science[5] and synthesis.[1] Despite this, the chemistry of zinc amidinate and guanidinate compounds is relatively poorly developed, though in recent years an increase in activity in the area has occurred.[1b] This is likely due to the realisation that mono(amidinato)- and mono(guanidinato)-zinc complexes have potential for use as catalysts in, for example, the ring opening polymerisation (ROP) of cyclic esters, *e.g.* D,L-lactide[6] and ε-caprolactone.[7] That said, they are generally not as effective for this purpose as are related β-diketiminato zinc complexes.[8] The reasons for these differences include the tendency of the amidinate or guanidinate complexes to undergo redistribution reactions, yielding bis(chelate) zinc complexes. In this respect, it has been shown that the extent of such redistribution reactions can be attenuated by increasing the steric bulk of the chelating ligand.[9]

We have developed a series of extremely bulky guanidinate ligands ($[(ArN)_2CNR_2]^-$ Ar = $C_6H_3Pr^i_2$-2,6; R = cyclohexyl (Giso) or Pr^i (Priso))[10] and have applied these to the stabilisation of metallacycles containing s-, p-, d- and f-block metals in low oxidation states and with low coordination numbers.[11,12] Throughout this work, the stabilising and coordinating properties of the ligands have been shown to be more akin to those of bulky β-diketiminates than less bulky guanidinates. Accordingly, we saw the opportunity to utilise our guanidinate ligands to prepare mono(guanidinato) zinc complexes which are very resistant towards redistribution reactions. We were particularly interested in preparing zinc(II) halide complexes, LZnX (L = bulky guanidinate, X = halide), which we saw as potential precursors to zinc(I) dimers, LZnZnL. This seemed a realistic prospect in light of the increasing number of kinetically stabilised Zn–Zn bonded complexes (including β-diketiminate coordinated examples[13]) that have populated the literature since Carmona's landmark preparation of [Cp*ZnZnCp*].[14] Moreover, given our prior preparation of a related stable guanidinato magnesium(I) dimer, [(Priso)MgMg(Priso)],[12e] and the well known chemical similarities between Mg and Zn, zinc(I) dimers were deemed viable synthetic targets. Herein, we report the synthesis and characterisation of several guanidinato zinc(II) complexes and compare their stability with that of related bulky amidinato zinc(II) compounds. In addition, we detail unsuccessful attempts to reduce these to zinc(I) dimers.

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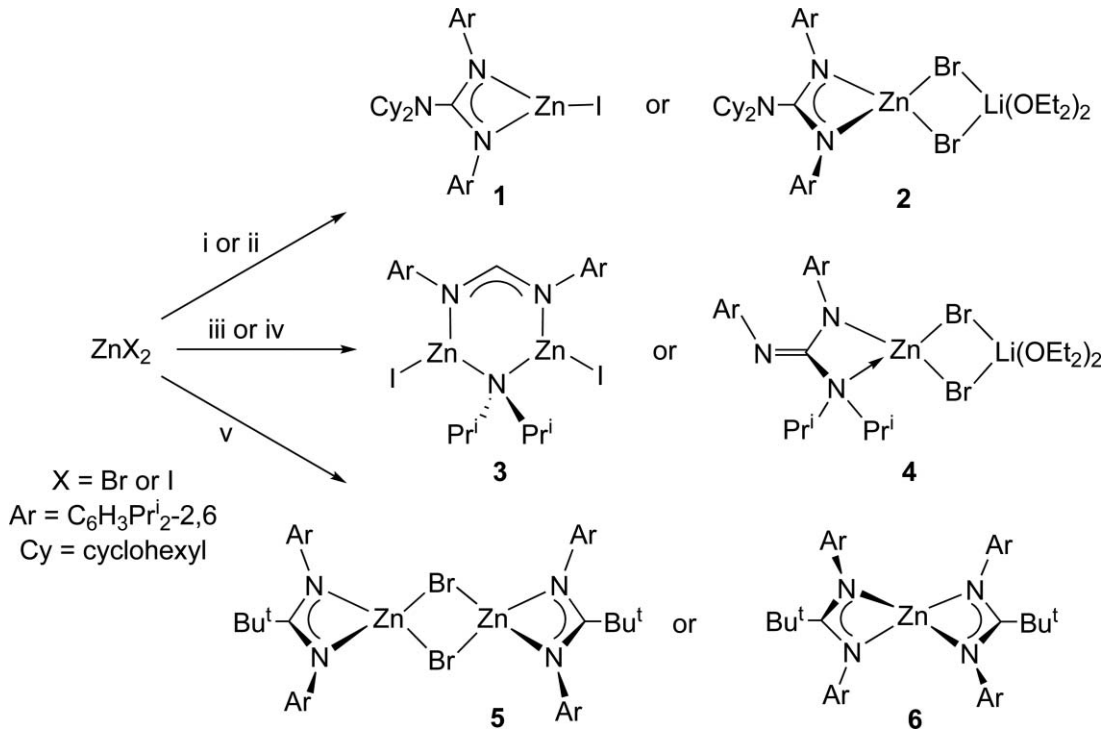

Scheme 1 i) THF, X = I, [K(Giso)], –KI; ii) Et_2O, X = Br, [Li(Giso)]; iii) THF, X = I, [K(Priso)], –KI; iv) Et_2O, X = Br, [Li(Priso)]; v) toluene–Et_2O or toluene, X = Br, [K(Piso)], –KBr.

Results and discussion

In prior studies we have had most success in stabilising low oxidation state metal complexes using the very bulky Giso ligand.[11] As a result, this was initially chosen for the preparation of potential zinc(II) halide precursors to the zinc(I) dimer [(Giso)ZnZn(Giso)]. The 1 : 1 reaction of [K(Giso)] with ZnI_2 afforded a low isolated yield of the monomeric complex, **1**, after recrystallisation from diethyl ether (Scheme 1).[15] Similarly, a moderate yield of the "ate" complex, **2**, was obtained from the reaction of [Li(Giso)] with $ZnBr_2$ in diethyl ether. Although both compounds are thermally stable in the solid state, in C_6D_6 solutions at ambient temperature compound **1** was found to very slowly decompose (over weeks) to yield product mixtures, the only identifiable component of which was the carbodiimide, ArN═C═NAr.[16]

Attempts to reduce **1** or **2** to [(Giso)ZnZn(Giso)] with KC_8 led instead to the deposition of zinc metal and product mixtures including significant amounts of ArN═C═NAr. We have recently shown that hydrocarbon soluble β-diketiminate stabilised magnesium(I) dimers can act as milder and more selective reducing agents than KC_8 and other alkali metal reagents in both organic[17] and organometallic synthesis.[18] Accordingly, the reaction of **2** with half an equivalent of [(^{Mes}Nacnac)MgMg(^{Mes}Nacnac)] (^{Mes}Nacnac = [{$(C_6H_2Me_3$-2,4,6)NC(Me)}$_2$CH]$^-$)[17a] was carried out in C_6D_6, though this also led to zinc metal deposition and a mixture of unidentifiable products. The mechanism of formation of the carbodiimide, and the fate of the NCy_2 (Cy = cyclohexyl) fragment in these reactions, are not known. In contrast, no reduction occurred in the reaction of **2** with Mg powder in THF. Instead, the diethyl ether ligands of the zinc complex exchanged with THF to yield [(Giso)Zn(μ-Br)$_2$Li(THF)$_2$], which is isostructural to **2** (see Supplementary Material).

The solution state spectroscopic data for **1** and **2** are consistent with their solid state molecular structures, which are depicted in Fig. 1 and 2. To the best of our knowledge there have been no prior structural characterisations of guanidinato zinc halide complexes, though several amidinato zinc halide structures have been reported.[9,19] All of these are dimeric and possess four-coordinate Zn centres. In contrast, the steric bulk of the delocalised Giso ligand in **1** leads to it being monomeric with a distorted trigonal planar zinc geometry. As a result, both the Zn–I and Zn–N distances in the compound and significantly shorter than the mean separations for such interactions (2.564 Å and 2.096 Å) in previously reported complexes.[20] The structure of compound **2** reveals it to be an "ate" complex with a distorted tetrahedral zinc geometry, very similar to that described for the closely related amidinate complex, [{Bu^{t}C(NCy)$_2$}Zn(μ-Br)$_2$Li(OEt$_2$)$_2$].[19a] Both the Zn–N (2.012 Å mean) and Zn–Br (2.415 Å mean) separations in that compound are comparable to those in **2**.

As the guanidinate ligand, Giso, was found to be apparently unsuitable for the stabilisation of a dimeric zinc(I) species, attention turned to the less bulky ligand, Priso. As already mentioned, this has been utilised in the preparation of the thermally very stable magnesium(I) dimer, [(Priso)MgMg(Priso)],[12e] *via* the potassium reduction of the magnesium(II) precursor, [(Priso)Mg(OEt$_2$)(μ-I)$_2$Mg(Priso)]. Attempts were made to synthesise a similar zinc(II) complex by the reactions of [K(Priso)] with ZnI_2 in THF, or [Li(Priso)] with $ZnBr_2$ in diethyl ether. These did not lead to ArN-,ArN-chelated products (*cf.* **1** and **2**), but instead reproducibly afforded low to moderate yields of the unexpected products, **3** and **4** (Scheme 1).

Compound **3** contains a Zn_2N_3C heterocycle in which the two zinc atoms are bridged by a formamidinate ligand and the amide anion, $NPr^i_2^-$. Clearly, this complex results from the cleavage of

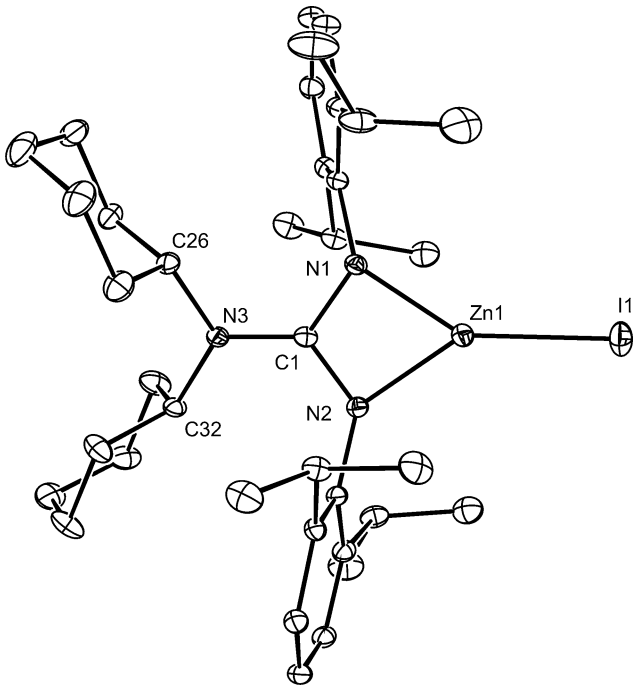

Fig. 1 Molecular structure of **1** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): I(1)–Zn(1) 2.4204(6), Zn(1)–N(1) 1.970(2), Zn(1)–N(2) 1.981(2), N(1)–C(1) 1.367(3), C(1)–N(2) 1.359(3), C(1)–N(3) 1.363(3), N(1)–Zn(1)–N(2) 68.50(9), N(1)–Zn(1)–I(1) 147.08(7), N(2)–Zn(1)–I(1) 144.29(7), N(2)–C(1)–N(1) 109.3(2).

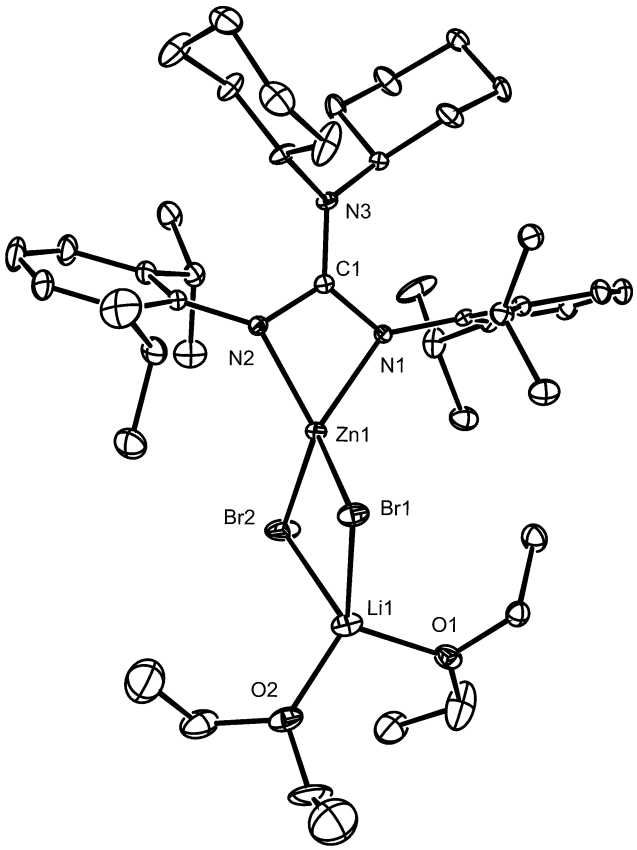

Fig. 2 Molecular structure of **2** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Br(1)–Zn(1) 2.4016(8), Br(1)–Li(1) 2.540(6), Br(2)–Zn(1) 2.3940(7), Br(2)–Li(1) 2.570(7), Zn(1)–N(2) 2.014(2), Zn(1)–N(1) 2.046(2), N(1)–C(1) 1.341(4), N(2)–C(1) 1.354(4), N(3)–C(1) 1.387(4), N(2)–Zn(1)–N(1) 66.01(10), Br(2)–Zn(1)–Br(1) 101.13(3), N(1)–C(1)–N(2) 110.3(3), O(2)–Li(1)–O(1) 108.3(6), Br(1)–Li(1)–Br(2) 92.90(19).

the C–NPr^i_2 bond of the Priso ligand, though the full mechanism of its formation is unknown at this stage. It is noteworthy, however, that an NMR spectroscopic analysis of the reaction mixture that gave **3** showed the presence of significant amounts of the carbodiimide, ArN═C═NAr, *i.e.* the same product that was generated from the slow thermal decomposition of **1**. Therefore, it seems likely that the reaction of [K(Priso)] with ZnI_2, initially yields a guanidinato zinc complex [{(Priso)ZnI}$_n$] (n = 1 or 2), which is less thermally stable than **1**, and decomposes *via* an amide extrusion process to give **3**, amongst other products. A very similar amide extrusion from an *in situ* generated guanidinato zinc aryloxide, [{$Me_2NC(NPr^i)_2$}ZnOAr′] (Ar′ = $C_6H_3Bu^t_2$-2,6), has been reported to give [(Ar′OZn)$_2$(μ-NMe_2){μ-*N*,*N*′-$(NPr^i)_2CNMe_2$}],[6] which contains a central Zn_2N_3C heterocycle reminiscent of that in **3**. This reaction was seen as having implications for the mechanisms of the metal catalysed guanylation of amines[21] and C═N bond metathesis of carbodiimides.[22]

Compound **4** is unstable in non-coordinating solvents at ambient temperature and rapidly decomposes to yield product mixtures, the main and only spectroscopically identifiable component of which is the carbodiimide, ArN═C═NAr. Like **2**, compound **4** is an "ate" complex, but in this case the guanidinate ligand chelates the Zn centre unsymmetrically through its amino and amide N-centres, leaving the imino fragment uncoordinated. This unusual guanidinate coordination mode has only been seen on one previous occasion in the titanium complexes, [{Ti[(NMe_2)(NPr^i)C═NPr^i]$_2$(μ-E)}$_2$] (*E* = O or S).[23] What is significant about the guanidinate coordination in **4** is that the complex appears "pre-organised" to heterolytically cleave its C–NPr^i_2 bond to generate the carbodiimide, ArN═C═NAr, and a zinc amide fragment. Indeed, the solid state structure of this complex (*vide infra*) reveals this bond to be significantly elongated (1.511(4) Å) in comparison to what would be expected for normal sp^2C–sp^3N single bonds (1.416 Å).[24] This, combined with the rather obtuse ArN═C═NAr angle (139.2(3)°), leads to the conclusion that **4** represents an intermediate, or "snapshot", in the aforementioned amide extrusion process. Interestingly, this process can be directly compared to the dehydration of bicarbonate, HCO_3^-, to yield CO_2, which is reversible and is extremely efficiently catalysed by Zn^{2+} in carbonic anhydrase (CA).[25] Many studies have suggested that the intermediate in this catalysed process contains the bicarbonate anion coordinated to the zinc centre in an κ^2-*O*,*O*′-fashion, *viz.* "-Zn{(OH)(O)C═O}" (*cf.* the -Zn{(NPr^i_2)(NAr)C═NAr} fragment in **4**).[25,26] Cleavage of the C–OH bond then occurs to give CO_2 and a zinc hydroxide moiety, "–Zn(OH)". This is equivalent to the aforementioned C–NPr^i_2 bond cleavage of **4**, which gives ArN═C═NAr (an isoelectronic analogue of CO_2), and an insoluble material which is presumably a zinc amide species, "–Zn(NPr^i_2)".

The stability of complexes of the type, [(Priso)ZnX] (X = halide), seems to be related to the nature of the zinc coordinated halide. No such species could be isolated for X = I, whereas a

related metastable "ate" complex, **4**, was isolable when X = Br. In contrast, we have previously prepared [{(Priso)ZnCl}$_2$],[27] which is very stable in solution and shows no signs of decomposition to give ArN═C═NAr. Although the solid state structure of this compound was not reported, solution NMR spectroscopic data for it suggest that the Priso ligand chelates the Zn centre through both NAr units. This preference for "normal" guanidinate coordination might explain the enhanced stability of the complex relative to **4** and the likely intermediate in the formation of **3**, *viz.* [{(Priso)ZnI}$_n$] (n = 1 or 2).

The solution state spectroscopic data for **3** are reminiscent of it retaining its solid state structure in solution. Due to the thermal instability of solutions of **4**, no NMR spectroscopic data could be obtained for this compound. Both **3** and **4** were crystallographically authenticated and their molecular structures are depicted in Fig. 3 and 4 respectively. That for **3** shows it to possess two distorted trigonal planar Zn centres with Zn–I and Zn–N distances close to those in **1**. As already mentioned, the central six-membered Zn_2N_3C ring of the compound is close to planar and resembles that in [(Ar′OZn)$_2$(μ-NMe$_2$){μ-*N*,*N*′-(NPr^i)$_2$CNMe$_2$}],[6] and the Be_2N_3C ring in [(ClBe)$_2${μ-N(SiMe$_3$)$_2$}{μ-*N*,*N*′-(NSiMe$_3$)$_2$CPh}].[28] The equivalent backbone C–N distances in the bridging formamidinate (Fiso) show it to be delocalised, as in other complexes bearing this ligand, *e.g.* [Zn(Fiso)$_2$].[29] The structure of the "ate" complex, **4**, has been briefly described above. It is somewhat related to **2**, except that the guanidinate ligand chelates the distorted tetrahedral zinc centre unsymmetrically through amide and tertiary amine N-centres, leaving an imine fragment uncoordinated. Although the N(3)–C(1) distance is very long for a single bond, the bond lengths within the N(2)–C(1)–N(1) fragment are consistent with partial delocalisation.

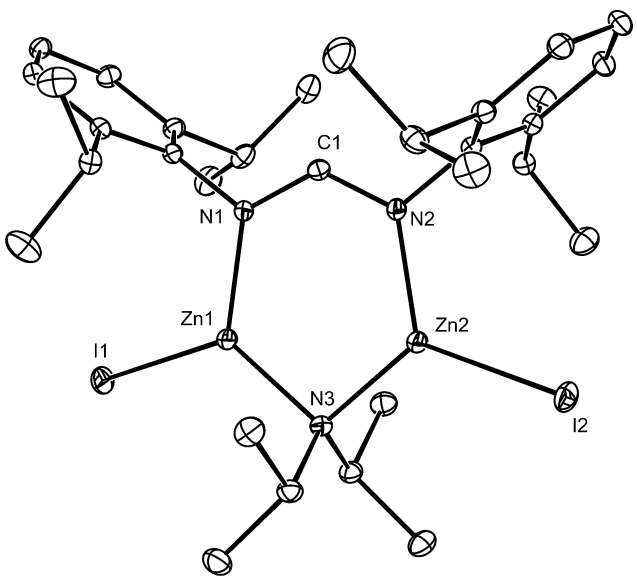

Fig. 3 Molecular structure of **3** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): I(1)–Zn(1) 2.4857(6), Zn(1)–N(1) 1.961(2), Zn(1)–N(3) 1.979(2), N(1)–C(1) 1.320(3), C(1)–N(2) 1.320(3), I(2)–Zn(2) 2.4892(6), Zn(2)–N(2) 1.960(2), Zn(2)–N(3) 1.978(2), N(1)–Zn(1)–N(3) 118.75(9), N(2)–Zn(2)–N(3) 119.09(9), C(1)–N(1)–Zn(1) 126.77(18), C(1)–N(2)–Zn(2) 126.43(18), N(1)–C(1)–N(2) 126.5(2), Zn(2)–N(3)–Zn(1) 101.11(10).

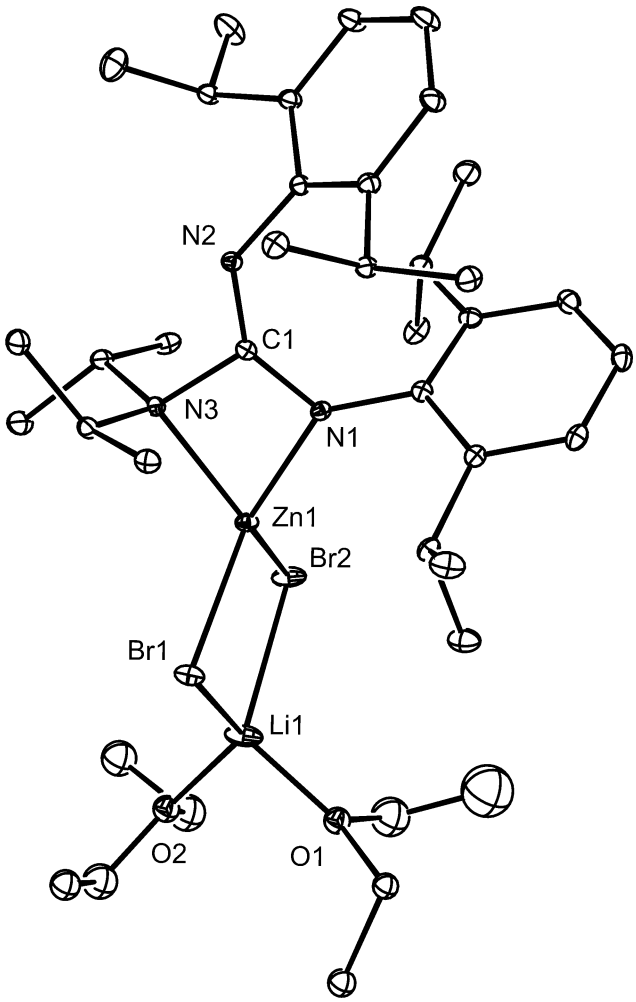

Fig. 4 Molecular structure of **4** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Br(1)–Zn(1) 2.4285(11), Br(1)–Li(1) 2.512(6), Br(2)–Zn(1) 2.4129(9), Br(2)–Li(1) 2.519(6), Zn(1)–N(1) 1.988(2), Zn(1)–N(3) 2.141(3), N(1)–C(1) 1.351(4), N(2)–C(1) 1.286(4), N(3)–C(1) 1.511(4), N(1)–Zn(1)–N(3) 66.87(10), Br(2)–Zn(1)–Br(1) 99.23(4), C(1)–N(1)–Zn(1) 99.51(18), C(1)–N(3)–Zn(1) 88.23(16), Br(1)–Li(1)–Br(2) 94.28(19), N(2)–C(1)–N(1) 139.2(3), N(2)–C(1)–N(3) 115.4(3), N(1)–C(1)–N(3) 105.4(2).

Considering that the bulky guanidinato zinc halide complexes were found to be less stable than expected, and not amenable for reduction to zinc(I) dimers, the possibility of using less bulky amidinato zinc halide species for this purpose was examined. The rationale here was that their amidinate ligands should not be susceptible to N–C cleavage reactions. The 1 : 1.1 reaction of [K(Piso)] (Piso = [(ArN)$_2$CBu^t]$^-$) with ZnBr$_2$ in a toluene–diethyl ether mixture afforded a moderate yield of the dimeric mono(chelate) complex, **5** (Scheme 1). In contrast, when the same reaction was carried out in toluene, the homoleptic complex, [Zn(Piso)$_2$] **6**, was generated in good yield, leaving significant amounts of unreacted ZnBr$_2$ in the product mixture. The homoleptic complex results from the latter reaction as the [K(Piso)] in the mixture preferentially reacts with initially formed **5** (to give **6**), rather than with toluene insoluble ZnBr$_2$ (to give more **5**). The diethyl ether present in the former reaction partially solubilises the ZnBr$_2$ reactant, leading to the competitive formation of **5**

over **6**. A number of attempts were made to reduce **5** with either KC_8, Na or [(Mes Nacnac)MgMg(Mes Nacnac)], but all led to the deposition of zinc metal and the formation of PisoH amongst other unidentifiable products.

The solution state data for **5** are very similar to those for [{(Piso)Zn(μ-Cl)$_2$}],[9] whilst those for **6** show it to have four chemically inequivalent sets of isopropyl methyl groups. This was thought to reflect steric crowding between the two Piso ligands. The solid state structures of **5** and **6** are shown in Fig. 5 and 6 respectively. Compound **5** is dimeric, through bridging bromides, and its crystal structure is isomorphous to the previously reported complex, [{(Piso)Zn(μ-Cl)$_2$}].[9] Like that compound, the NCN backbone of the Piso ligands are effectively delocalised and the zinc atom has a distorted tetrahedral coordination geometry. This is also the case for **6**, the structure of which closely resembles those of a number of other bis(chelate) zinc complexes, *e.g.* [Zn(Fiso)$_2$][29] and [Zn(Aiso)$_2$] (Aiso = (ArN)$_2$CMe$^-$).[9] The steric crowding in **6** most probably gives rise to the significant differences between its Zn–N bond lengths. This crowding and the dihedral angle between the two ZnN$_2$C least squares planes (59.7°), seemingly accounts for the four chemically inequivalent sets of isopropyl methyl resonances observed in the ^{1}H NMR spectrum of the compound.

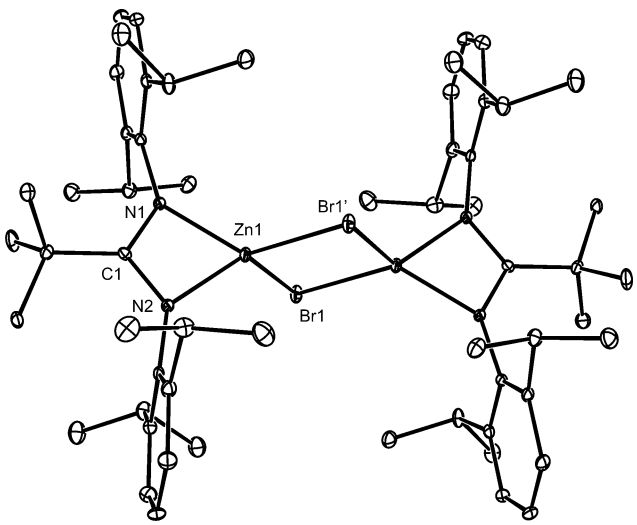

Fig. 5 Molecular structure of **5** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Br(1)–Zn(1) 2.4352(4), Zn(1)–N(1) 1.996(2), Zn(1)–N(2) 2.003(2), Zn(1)–Br(1)′ 2.4182(4), N(1)–C(1) 1.343(4), C(1)–N(2) 1.345(4), N(1)–Zn(1)–N(2) 66.64(10), Br(1)′–Zn(1)–Br(1) 97.524(14), N(1)–C(1)–N(2) 109.6(2). Symmetry operation: ′–x+1, –y+2, –z.

Conclusion

In summary, a variety of bulky amidinato and guanidinato zinc halide complexes have been prepared and their thermal stabilities compared. The guanidinato complexes are generally susceptible to decomposition *via* amide extrusion reactions, yielding the carbodiimide, ArN═C═NAr. This is more so for complexes bearing the less bulky ligand, Priso, than those incorporating the more sterically demanding guanidinate, Giso. Analogies have been drawn between the decomposition of the guanidinato zinc halide

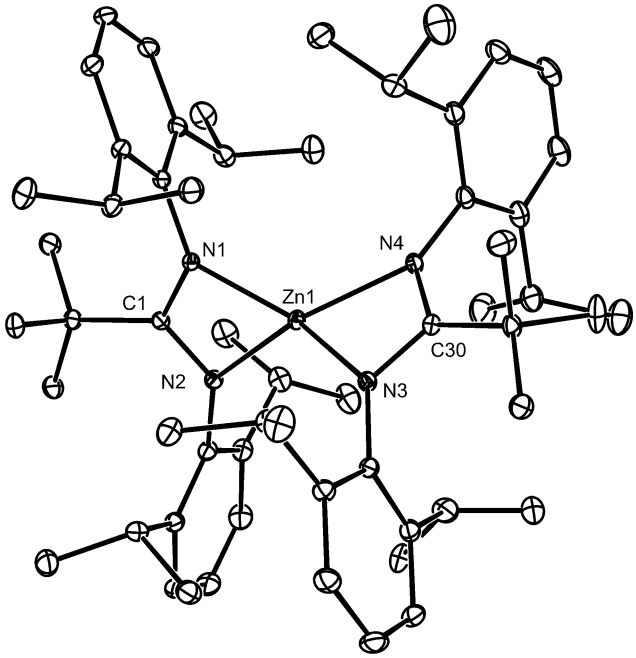

Fig. 6 Molecular structure of **6** (25% thermal ellipsoids are shown; hydrogens omitted). Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.0005(14), Zn(1)–N(3) 2.0143(14), Zn(1)–N(4) 2.1452(14), Zn(1)–N(2) 2.1564(14), N(1)–C(1) 1.354(2), N(2)–C(1) 1.325(2), N(3)–C(30) 1.345(2), N(4)–C(30) 1.334(2), N(1)–Zn(1)–N(2) 63.65(6), N(3)–Zn(1)–N(4) 63.88(6), N(2)–C(1)–N(1) 110.09(13), N(4)–C(30)–N(3) 110.63(14).

complexes and the carbonic anhydrase catalysed dehydration of bicarbonate, which yields CO_2. In contrast, the thermal stability of a less bulky amidinato zinc bromide complex was found to be greater than that of its guanidinato counterparts. Attempts to reduce several of the zinc(II) halide complexes reported here to dimeric zinc(I) compounds were unsuccessful, in all cases leading to the deposition of zinc metal.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. THF, hexane and toluene were distilled over molten potassium, while diethyl ether was distilled over a Na/K alloy. Melting points were determined in sealed glass capillaries under argon or dinitrogen and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. The microanalysis was obtained from Medac Ltd. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DXP300 or DPX400 spectrometers and were referenced to the resonances of the solvent used. [K(Giso)],[12g] [K(Priso)],[10] K[(Piso)],[12b] GisoH[10] and PrisoH[10] were prepared using variations of literature procedures. [Li(Giso)] and [Li(Priso)] were prepared *in situ* by treating diethyl ether solutions of either GisoH or PrisoH with one equivalent of a 1.6 M solution of LiBu^n in hexanes.[10] All other reagents were used as received.

Preparation of [(Giso)ZnI] 1. A solution of [K(Giso)] (1.82 g, 3.13 mmol) in THF (20 cm^3) was added over 5 min to a solution of ZnI_2 (1.0 g, 3.13 mmol) in THF (20 cm^3) at −78 °C. The reaction mixture was warmed to room temperature to yield a pale yellow solution. Volatiles were removed *in vacuo*, the residue washed with hexane (10 cm^3) and extracted into diethyl ether (30 cm^3). Filtration and cooling to −30 °C overnight yielded colourless crystals of **1** (0.54 g, 24%). Mp: 175–185 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.62–0.71 (m, 4 H, CH_2), 0.84–1.01 (m, 8H, CH_2), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.67–1.42 (m, 8 H, CH_2), 3.60 (m, 2 H, Cy–CH), 3.62 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 6.89–7.29 (m, 6 H, Ar–H); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ = 20.2 (CH_2), 23.9 (CH(CH_3)$_2$), 24.9 (CH_2), 25.7 (CH(CH_3)$_2$), 27.2 (CH(CH$_3$)$_2$), 34.2 (CH_2), 59.3 (Cy–CH), 122.2, 123.7, 140.7, 141.9 (Ar–C), 168.1 (NCN); IR ν/cm^{-1} (Nujol): 1612 m, 1583 m, 1244s,1018s, 893 m, 865 m, 770 m, 722m; MS/EI m/z (%): 733.3 (M^+, 4), 608.2 (MH^+ − I, 6), 500.5 (GisoH$^+$-Pr^i, 80); acc. mass MS (EI) m/z: calc for $C_{37}H_{56}IN_3Zn$: 733.2805, found: 733.2809.

Preparation of [(Giso)Zn(μ-Br)$_2$Li(OEt$_2$)$_2$] 2. A solution of [Li(Giso)] (1.50 g, 2.73 mmol) in diethyl ether (25 cm^3) was added to a slurry of $ZnBr_2$ (0.71 g, 3.15 mmol) in diethyl ether (15 cm^3) at −60 °C, over 5 min. The reaction mixture was warmed to room temperature, filtered, and the filtrate cooled to −30 °C to give colourless crystals of **2**. Concentration of the supernatant solution to *ca.* 12 cm^3, and cooling to −30 °C yielded a second crop of **2** (1.30 g, 52%). Mp: 196–202 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.70–1.15 (m, 20 H, OCH$_2$CH_3, Cy–CH_2), 1.25–1.38 (m, 8 H, Cy–CH_2), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.57 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.65–1.77 (m, 4 H, Cy–CH_2), 3.41–3.48 (m, 10 H, OCH_2CH$_3$, Cy–CH), 3.58 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 6.99–7.23 (m, 6 H, ArH); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 22.9, 23.0, 25.1, 25.6, 27.0, 28.0 (2 × CH_2, 2 × CH(CH_3)$_2$, 1 × CH(CH$_3$)$_2$, 1 × OCH$_2$CH_3), 35.1 (CH_2), 59.4 (Cy–CHN), 68.0 (OCH_2CH$_3$), 123.2, 123.4, 143.4, 143.9 (ArC), CN_3 not observed; IR ν/cm^{-1} (Nujol): 1612 s 1583 s, 1454 s, 1326 s, 1258 s, 1183 m, 1150 m, 1093 s, 1066 s, 1021 s, 954 m, 898 s, 835 m, 795 s, 770 m, 750s.

Preparation of [(IZn)$_2$(μ-NPr$^i_2$){μ-*N*,*N*′-(NAr)$_2$CH}] 3. A solution of [K(Priso)] (1.57 g, 3.13 mmol) in THF (20 cm^3) was added over 5 min to a solution of ZnI_2 (1.0 g, 3.13 mmol) in THF (20 cm^3) at −78 °C. The reaction mixture was warmed to room temperature, then volatiles were removed *in vacuo*. The residue was washed with hexane (10 cm^3) and extracted into diethyl ether (20 cm^3). Filtration, concentration and cooling to −30 °C overnight yielded colourless crystals of **3** (0.67 g, 51% based on ZnI_2). Mp = 197–203 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, NCH(CH_3)$_2$), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 3.34 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 3.77 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, NCH(CH$_3$)$_2$), 7.03–7.29 (m, 6 H, ArH), 7.54 (s, 1 H, NCH); ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ = 22.9 (CH(CH_3)$_2$), 23.1 (CH(CH_3)$_2$), 24.1 (NCH(CH_3)$_2$), 28.5 (CH(CH$_3$)$_2$), 49.9 (NCH(CH$_3$)$_2$), 123.8, 125.2, 141.8, 143.7 (Ar–C), 167.1 (NCN); IR ν/cm^{-1} (Nujol): 1593 m, 1254 s, 1174 s, 1130 s, 1054 m, 932 m, 805 m, 761m; MS/EI m/z (%): 845.1 (M^+, 7), 366.2 (FisoH$^+$, 80); acc. mass MS (EI) m/z: calc for $C_{31}H_{49}I_2N_3Zn_2$: 845.0593, found: 845.0584; anal. calc. for $C_{31}H_{49}I_2N_3Zn_2$: C 43.89%, H 5.82%, N 4.95%, found: C 43.50%, H 5.99%, N 4.63%.

Preparation of [(Priso)Zn(μ-Br)$_2$Li(OEt$_2$)$_2$] 4. A solution of [Li(Priso)] (1.48 g, 3.15 mmol) in diethyl ether (40 cm^3) was added over 5 min to a slurry of $ZnBr_2$ (0.79 g, 3.51 mmol) in diethyl ether (10 cm^3) at −30 °C. The reaction mixture was warmed to room temperature, whereupon it was concentrated to *ca.* 20 cm^3, filtered, and cooled to −30 °C yielding colourless crystals of **4**. Concentration of the supernatant solution to *ca.* 8 cm^3, and cooling to −30 °C yielded a second crop of **4** (1.21 g, 46%). Mp: decomp. above 65 °C; IR ν/cm^{-1} (Nujol): 2174 s, 1611 s 1580 s, 1460 s, 1341 s, 1256 m, 1185 m, 1154 m, 1094 m, 1062 s, 1003 m, 975 m, 914 m, 828 m, 798 m, 767 m, 752 s. NMR spectroscopic data could not be obtained for the compound as it rapidly decomposes when dissolved in non-coordinating deuterated solvents.

Preparation of [{(Piso)Zn(μ-Br)}$_2$] 5. A solution of [K(Piso)] (1.00 g, 2.18 mmol) in toluene–diethyl ether (1 : 1, 40 cm^3) was added to a slurry of $ZnBr_2$ (0.54 g, 2.40 mmol) in toluene–diethyl ether (1 : 1, 40 cm^3) at −80 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resultant mixture was filtered, concentrated to *ca.* 25 cm^3 and cooled to −30 °C to yield colourless crystals of **5**. Concentration of the supernatant to *ca.* 10 cm^3 and cooling yielded another crop of **5** (0.75 g, 60%). Mp: 306–308 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.93 (s, 18 H, C(CH_3)$_3$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$), 3.64 (sept, $^3J_{HH}$ = 6.8 Hz, 8 H, CH(CH$_3$)$_2$), 6.94–7.31 (m, 12 H, ArH); ^{13}C{H}NMR (75.5 MHz, 298 K, C_6D_6): δ = 22.6 (CH(CH_3)$_2$), 26.8 (CH(CH_3)$_2$), 28.9 (CH(CH$_3$)$_2$), 30.3 (C(CH_3)$_3$), 42.2 (C(CH$_3$)$_3$), 123.5, 125.3, 142.3, 143.7 (Ar–C), 178.9 (NCN); IR (Nujol) ν/cm^{-1}: 1616 m, 1586 m, 1462 s, 1364 m, 1331 m, 1261 m, 1179 m, 1098 s, 1054 m, 933 m, 801 s, 757 s; MS (EI 70 eV), m/z (%): 521.2 ((M/2)$^+$ -Pr^i, 4), 420.6 (PisoH$^+$, 16), 244.1 (ArNCBu^{t+}, 100).

Preparation of [Zn(Piso)$_2$] 6. A slurry of [K(Piso)] (0.99 g, 2.16 mmol) in toluene (25 cm^3) was added to a suspension of $ZnBr_2$ (0.52 g, 2.31 mmol) in toluene (15 cm^3) at ambient temperature and the mixture stirred vigorously overnight. The resultant mixture was filtered, the filtrate concentrated to *ca.* 15 cm^3 and then cooled to 4 °C, affording colourless crystals of **6**·(toluene)$_{1.5}$ (0.62 g, 55%). Mp: 280–284 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.42 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 0.87 (s, 18 H, C(CH_3)$_3$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 3.24 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 3.78 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 6.89–7.08 (m, 12 H, ArH); ^{13}C{H} NMR (75.5 MHz, C_6D_6, 298 K): δ = 23.0 (CH(CH_3)$_2$), 23.1 (CH(CH_3)$_2$), 23.2 (CH(CH_3)$_2$), 25.4 (CH(CH_3)$_2$), 28.4 (CH(CH$_3$)$_2$, 28.6 (CH(CH$_3$)$_2$), 30.6 (C(CH_3)$_3$), 42.3 (C(CH$_3$)$_3$), 123.4, 124.8, 142.9, 144.0 (Ar–C), 178.1 \28;NCN); IR (Nujol) ν/cm^{-1}: 1616 m, 1586 m, 1462 s, 1366 m, 1312 m, 1253 m, 1173 s, 1096 m, 1044 m, 965 m, 933 m, 802 s, 760 s; MS (EI 70 eV), m/z (%): 902.7 (M^+, 12), 859.6 (M^+ − Pr^i, 10), 845.6 (M^+ -C$_4$H$_9$, 46), 244.1 (ArNCBu^{t+}, 100); acc. mass, m/z (EI): calc for $C_{58}H_{86}N_4Zn$: 902.6138; found 902.6152.

Table 1 Crystal data for compounds **1–6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**·(toluene)$_{1.5}$
Empirical formula	$C_{37}H_{56}IN_3Zn$	$C_{45}H_{76}Br_2LiN_3O_2Zn$	$C_{31}H_{49}I_2N_3Zn_2$	$C_{39}H_{68}Br_2LiN_3O_2Zn$	$C_{58}H_{86}Br_2N_4Zn_2$	$C_{68.5}H_{98}N_4Zn$
FW	735.12	923.22	848.27	843.09	1129.87	1042.88
T/K	150(2)	123(2)	150(2)	123(2)	123(2)	123(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.659(2)	19.350(4)	12.980(3)	9.3323(19)	10.0698(30	12.650(3)
b/Å	18.297(4)	19.897(4)	12.870(3)	14.519(3)	10.7948(4)	12.723(3)
c/Å	19.481(4)	12.633(3)	21.640(4)	18.076(4)	14.8844(7)	19.058(4)
α (°)	90	90	90	66.40(3)	105.869(2)	100.62(3)
β (°)	105.17(3)	103.02(3)	93.42(3)	85.15(3)	102.254(2)	90.59(3)
γ (°)	90	90	90	75.77(3)	106.999(2)	92.15(3)
V/Å^3	3666.8(13)	4738.7(16)	3608.7(13)	2175.3(8)	1411.22(9)	3012.3(10)
Z	4	4	4	2	1	2
Density (calcd)/Mg m^{-3}	1.332	1.294	1.561	1.287	1.329	1.150
μ(Mo-Kα)/mm^{-1}	1.539	2.241	3.062	2.434	2.304	0.451
F(000)	1528	1944	1688	884	592	1134
No. of reflections collected	15002	17945	14940	15510	21361	27427
No. of independent reflections (R_{int})	7927 (0.0348)	10313 (0.0335)	7856 (0.0268)	8431 (0.0316)	6293 (0.0508)	14451 (0.0245)
Final R_1 ($I > 2\sigma(I)$) and wR_2 indices (all data)	$R_1 = 0.0405$	$R_1 = 0.0469$	$R_1 = 0.0290$	$R_1 = 0.0416$	$R_1 = 0.0399$	$R_1 = 0.0417$
	w$R_2 = 0.0944$	w$R_2 = 0.1071$	w$R_2 = 0.0650$	w$R_2 = 0.1059$	w$R_2 = 0.0819$	w$R_2 = 0.1110$

X-Ray crystallography

Crystals of **1–6** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[30] using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. Details of the modelling of disorder in the crystal structures of 2, 4 and 6 can be found in their CIF files. Crystal data, details of data collections and refinement are given in Table 1.

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