Nonbridging and Monodentate Carboxylate Coordination of Calcium(2+) Through the Use of Intramolecular Hydrogen Bonding in a New Sterically Hindered Carboxylate Ligand

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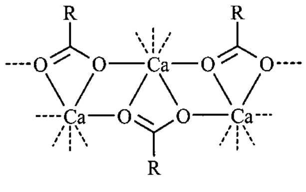
The sterically hindered carboxylate ligand 2,6-bis(2,2-dimethylpropionylamino)benzoic acid (**HL**) has been prepared. The two intramolecular hydrogen bonds in **HL** are exploited to restrict the corresponding carboxylate anion ($\mathbf{L}^-$) to nonbridging coordination and to preorganise its sterically bulky substituents proximal to the first and second coordination sphere of the bound metal ion. The crystal structures of the ligand anion as the ammonium salt $[NH_4][\mathbf{L}]$ and the distorted octahedral calcium complex $Ca\mathbf{L}_2(H_2O)_2$, in which $\mathbf{L}^-$ binds to the calcium(2+) ion in a monodentate, nonbridging mode, are described.

Introduction

Sterically hindered ligands are commonly used to control the coordination environment of metal ions, and hence their properties, through favouring lower coordination numbers and/or by preventing the unwanted formation of polynuclear species that often arise through ligand bridging.[1] This approach is particularly challenging for carboxylate ligands, nevertheless over recent years the application of this strategy has proven to be effective for the synthesis of some low molecular weight model compounds for transition metal ion sites in proteins, in which the role of the protein in providing a preorganised arrangement of carboxylate ligands at a metal ion binding site has been to some extent reproduced by the use of steric hindrance.[2] With sterically hindered carboxylate ligands the challenge is not primarily to limit coordination numbers, but rather to inhibit the strong natural tendency of the carboxylate group to bridge between two or more metal ions which results in the undesired formation of polymeric or highly polynuclear species. This is particularly problematic for the coordination chemistry of calcium(2+) which has an ionic radius of 0.99 Å, substantially larger than divalent transition metal ions [e.g., high-spin iron(2+), 0.78 Å], and as a consequence the triply bridging motif **I** and related structures are commonplace for simple carboxylate ligands.[3] In contrast, monodentate, nonbridging carboxylates are common ligands for calcium(2+) in proteins,[4] and although there are several examples of such calcium(2+) coordination for small molecules in the Cambridge Crystallographic Database,[5] these are all apparently serendipitous, arising unpredictably from the use of polydentate ligands and/or fortuitous packing arrangements.[6]



I

We wished to design a sterically hindered carboxylate ligand that specifically excludes the possibility of laterally bridging coordination to calcium(2+) or other metal ions. The sterically hindered 2,6-dialkyl- or 2,6-diarylbenzoic acid derivatives currently used for transition metal studies were not considered appropriate as the carboxylate group is free to rotate out of the plane of the aromatic ring and thus bridging is still allowed to occur.[2] The chosen design strategy was to use two intramolecular hydrogen bonds from adjacent amide groups to constrain the carboxylate group to be coplanar with the aromatic ring and therefore prevent lateral bridging to metal ions, whilst preorganising two sterically bulky groups proximal to the first and second coordination spheres of any bound metal ion. We herein report the synthesis of the *tert*-butyl-substituted ligand **HL**, the structure of its anion (as the ammonium salt) and its complexation with calcium(2+). Moreover, the straightforward synthesis of **HL** should allow the facile preparation of derivatives with a wide variety of R substituents, thus

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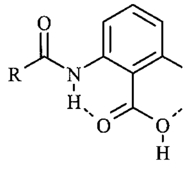
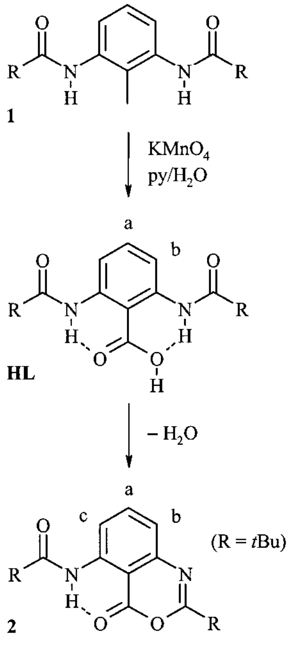
providing the opportunity for further control over the first and second coordination spheres of any metal ion and greater scope for the design of metallobiosite model complexes where restriction of the carboxylate coordination mode is required.



HL (R = *t*Bu)

Results and Discussion

The carboxylic acid **HL** was readily prepared in 41% yield by the oxidation of the aromatic methyl group of diamide **1**[7] with potassium permanganate in aqueous pyridine at reflux (Scheme 1).[12] The two intramolecular hydrogen bonds in **HL** would be expected to stabilise the corresponding carboxylate anion, but less so than for 2,6-dihydroxybenzoic acid (vide supra).[13] In nonprotogenic solvents (e.g., chloroform) the carboxylic acid **HL** was found readily to eliminate water over several hours to form the benzoxazine **2**. ^{1}H and ^{13}C NMR spectroscopy showed that in chloroform an equilibrium (1:2) mixture of **HL**/**2** (and water) was formed after approximately 24 h. Pure **2** could be obtained in quantitative yield by the deliberate dehydration of a toluene solution of **HL** with excess acetic anhydride. Under mildly basic conditions in the presence of water both **HL** and **2** were found to rapidly reform the carboxylate anion **L**$^-$.



Scheme 1

The structure of the carboxylate anion **L**$^-$ is revealed by the single-crystal X-ray structure determination of the ammonium salt **3** (Figure 1). As expected, there are intramolecular hydrogen bonds between the two amide N−H groups and the carboxylate oxygen atoms. The X-ray diffraction data were of sufficient quality for the amide N−H hydrogen atoms to be located in the difference Fourier map and freely refined; the N−H bond lengths of 0.90(3) Å indicate that there is no significant lengthening of the N−H bonds compared with the expected value of 0.85−0.90 Å, as determined by X-ray diffraction.[5] In addition, the N(1)···O(1) and N(2)···O(2) distances of 2.564(3) and 2.571(3) Å are relatively long, and the N(1)−H(1)···O(1) and N(2)−H(2)···O(2) angles of 142(2) and 147(3)° are significantly more acute than the usual range of 160−180° for strong hydrogen bonds. Furthermore, the carboxylate and two amide groups are slightly twisted out of the plane of the central aromatic ring with torsional angles between the respective pairs of least-squares planes of 21.3(1), 10.6(1) and 18.7(1)°. All these structural parameters suggest that these hydrogen bonds are weaker than in the near-planar 2,6-dihydroxybenzoate anion (Table 1),[13] and indicate that **HL** should be a weaker acid than 2,6-dihydroxybenzoic acid. However, the most important effect of these hydrogen bonds is that they successfully preorganise the planar, *trans*-primary-amide groups and therefore position the bulky *tert*-butyl groups to restrict coordination to the carboxylate group. In the lattice of **3** the packing of the carboxylate anions leaves cavities that are each occupied by a pair of ammonium counterions, with an inter-ammonium cation (N···N) distance of 3.675(3) Å, which, although short, is typical for ammonium carboxylate structures.[14] This electrostatically unfavourable arrangement is compensated for by the formation of hydrogen bonds to all four of the ammonium N−H bonds, thus the two ammonium ions are imprisoned in a cage of eight appropriately positioned hydrogen bond acceptor oxygen atoms (Figure 2, Table 2).

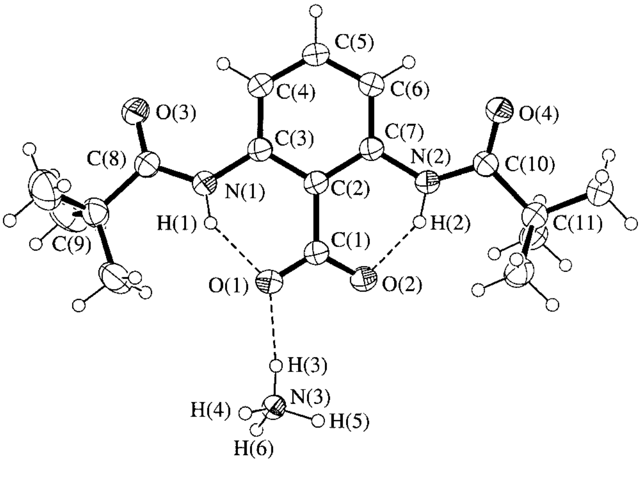


Figure 1. ORTEP[18] view of the molecular structure of **3** with thermal ellipsoids shown at 40%; hydrogen bonds are denoted by dashed lines; selected bond lengths [Å]: C(8)−N(1) 1.344(3), C(8)−O(3) 1.228(3), C(10)−N(2) 1.342(3), C(10)−O(4) 1.222(3)

Table 1. Structural parameters related to the intramolecular hydrogen bonding of the carboxylate group in **3** and **4**

Compound	$\{ArCO_2^-\}$[a]	**3**	**4**
Hydrogen-bonding geometry	(X = O)	(X = N)	(X = N)
X(1)−H(1), X(2)−H(2) [Å]	0.81(2), 0.83(2)	0.90(3), 0.90(4)	0.88(3), 0.90(3)
H(1)···O(1), H(2)···O(2) [Å]	1.78(2), 1.77(2)	1.79(3), 1.77(4)	1.93(3), 1.88(3)
X(1)···O(1), X(2)···O(2) [Å]	2.511(2), 2.542(2)	2.564(3), 2.571(3)	2.683(2), 2.622(2)
X(1)−H(1)···O(1), X(2)−H(2)···O(2) [°]	149(2), 153(2)	142(3), 147(3)	142(2), 138(2)
O(5)−H(3) [Å]	–	–	0.88(3)
H(3)···O(2) [Å]	–	–	1.82(3)
O(5)···O(2) [Å]	–	–	2.671(2)
O(5)−H(3)···O(2) [°]	–	–	162(3)
Carboxylate group geometry			
C(1)−O(1), C(2)−O(2) [Å]	1.283(2), 1.260(2)	1.235(3), 1.248(3)	1.270(2), 1.255(2)
C(1)−C(2) [Å]	1.481(2)	1.519(3)	1.519(2)
$Ar-CO_2^-$ torsional angle [°]	1.4(1)	21.3(1)	33.6(1)

[a] 2,6-Dihydroxybenzoate anion, ref.[13]

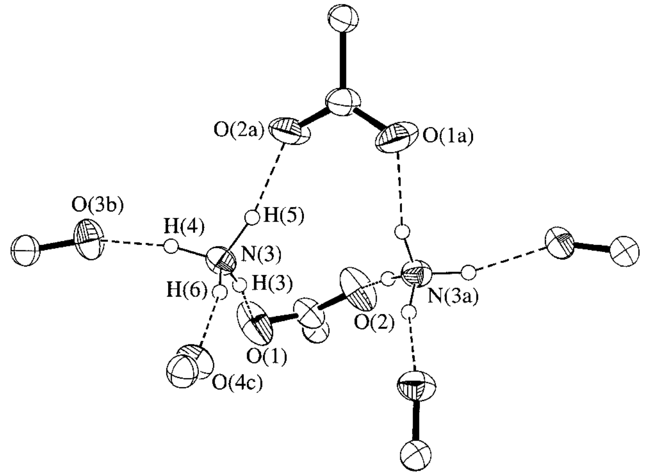


Figure 2. ORTEP[18] view of the ammonium cation hydrogen-bonding environment in **3** with thermal ellipsoids shown at 40%; hydrogen bonds are denoted by dashed lines; the majority of the ligand structures have been omitted for clarity; symmetry transformations: a: 2 − *x*, 1 − *y*, *z*; b: 3/2 − *x*, 1/2 + *y*, *z*; c: *x*, 1/2 + *y*, 1/2 + *z*

Table 2. Hydrogen-bonding geometry of the ammonium cation in **3**

D−H···A[a]	D−H	H···A	D···A	∠D−H···A
N(3)−H(3)···O(1)	0.90(3)	1.83(3)	2.713(3)	166(3)
N(3)−H(4)···O(3b)	0.99(3)	1.79(3)	2.750(3)	160(2)
N(3)−H(5)···O(2a)	1.00(3)	1.77(3)	2.749(3)	168(3)
N(3)−H(6)···O(4c)	0.95(3)	1.85(3)	2.776(3)	166(3)

[a] Symmetry transformations: a: 2 − *x*, 1 − *y*, *z*; b: 3/2 − *x*, 1/2 + *y*, *z*; c: *x*, 1/2 + *y*, 1/2 + *z*.

The structure of **4** (Figure 3) shows that the carboxylate ligand is bound to the calcium ion in the desired monodentate and nonbridging manner, and that the calcium ion is restricted to six coordination and a distorted octahedral geometry. Indeed, the "average" coordination environment for calcium(2+) in proteins is octahedral, and moreover with a mixture of carboxylate, peptide carbonyl and water ligands,[4] coincidently very similar to the specific structure described here. The average Ca−O bond length is 2.359 Å, only slightly longer than the value of 2.337 Å found for the comparable, unhindered octahedral complex $Ca(acac)_2(H_2O)_2$.[15] The Ca−O(1) distance is the longest in the calcium coordination sphere in **4**, 2.3830(11) Å, presumably due to the steric congestion of the carboxylate group, and the carboxylate is clearly monodentate with a very long Ca(1)···O(2) distance of 3.7205(12) Å. It is particularly noteworthy that this coordination mode is preferred over a more symmetrical bidentate coordination, or the formation of simple second coordination sphere $[Ca(H_2O)_n]^{2+}$ hydrogen-bonded salts of the ligand anion. One possible reason for the stability of **4** is that the long Ca−O(1) bond is supported by a strong hydrogen bond between the adjacent water ligand and the nonbound carboxylate oxygen atom

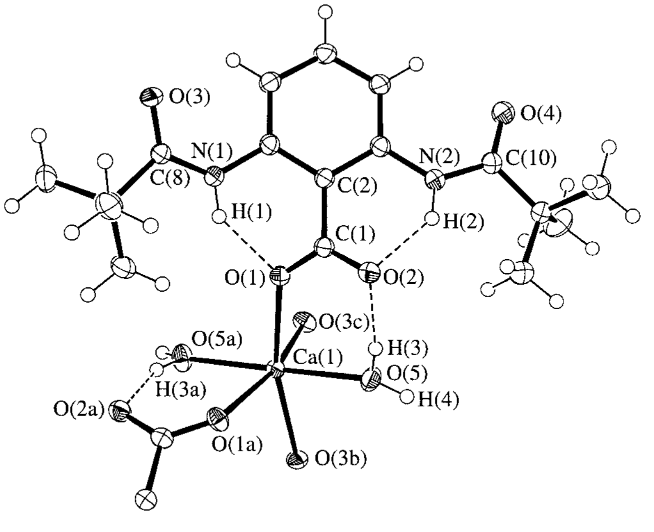


Figure 3. ORTEP[18] view of the structure of **4** with thermal ellipsoids shown at 50%; hydrogen bonds are denoted by dashed lines; for clarity only one ligand is shown in its entirety; selected bond lengths [Å] and angles [°]: Ca(1)−O(1) 2.3830(11), Ca(1)−O(5) 2.3378(11), Ca(1)−O(3b) 2.3560(11), C(8)−N(1) 1.349(2), C(8)−O(3) 1.241(2), C(10)−N(2) 1.362(2), C(10)−O(4) 1.232(2); O(1)−Ca(1)−O(5) 80.45(4), O(1)−Ca(1)−O(1a) 93.16(6), O(1)−Ca(1)−O(3b) 164.67(4), O(3b)−Ca(1)−O(3c) 90.37(6), O(3b)−Ca(1)−O(5) 84.29(4), O(5)−Ca(1)−O(5b) 177.44(7); symmetry transformations: a: 3 − *x*, *y*, 3/2 − *z*; b: 1/2 + *x*, 1/2 + *y*, *z*; c: 5/2 − *x*, 1/2 + *y*, 3/2 − *z*

O(2) (Table 1); thus the carboxylate group is effectively acting as a bidentate ligand to a Ca−OH_2 group. Indeed, several similar structural motifs have been described over recent years in the transition metal chemistry of sterically hindered carboxylate ligands,[2] and in calcium(2+) coordination chemistry.[16] The coordination sphere of the calcium ion is completed by one amide carbonyl group from each of two equivalent neighbouring molecules, and the Ca(1)−O(3a) bond length of 2.3560(11) Å and Ca(1)−O(3a)−C(8a) angle of 169.98(11)° are typical of a predominantly electrostatic interaction with the metal ion. This interaction also results in a slight perturbation of the amide group with a longer C(8)=O(3) distance of 1.241(2) Å and shorter C(8)−N(1) distance of 1.349(2) Å compared to 1.232(2) and 1.362(2) Å, respectively for the other, noncoordinated amide group. Similar to as described above for **3**, the carboxylate and two amide groups in **4** are twisted out of the plane of the central aromatic ring. The torsional angles between the respective pairs of least-squares planes of 33.6(1), 25.0(1) and 10.1(1)° show that the ligand in **4** has larger distortions from planarity than in **3**, particularly with regard to the carboxylate group. For **3** and **4** these variations in torsional angles probably primarily arise from different packing effects and bonding requirements of the ammonium and calcium(2+) ions, respectively.

In conclusion, the sterically hindered ligand **HL** designed for nonbridging coordination to metal ions has been successfully prepared and its desired mode of coordination structurally characterised for a mononuclear calcium(2+) complex. The coordination chemistry of **HL** and related ligands with transition metal and lanthanide ions is currently under investigation.[17]

Experimental Section

General: *N*-[3-(2,2-Dimethylpropionylamino)-2-methylphenyl]-2,2-dimethylpropionamide (**1**) was prepared from 2,6-diaminotoluene and trimethylacetyl chloride by a literature method.[7] Elemental analyses were obtained with a Fisons EA1108 CHNS analyser. IR spectra were recorded as KBr disks with a Perkin−Elmer Paragon-100 FT-IR spectrophotometer. NMR spectra were recorded using a Jeol JNM-LA400 spectrometer at room temperature (20 °C) and are reported relative to tetramethylsilane. Mass spectra were recorded with a Finnigan 1200 (EI) mass spectrometer.

2,6-Bis(2,2-dimethylpropionylamino)benzoic Acid (HL): Potassium permanganate (4.75 g, 30 mmol) and diamide **1** (4.35 g, 15 mmol) in pyridine/water (1:1, 150 mL) was heated at reflux with constant stirring for 2 h, or until the purple colour of the permanganate had disappeared. The reaction mixture was allowed to cool to room temperature, water (250 mL) added, then the solution filtered to remove the dark brown precipitate of hydrated manganese dioxide. The pale yellow filtrate was concentrated to near dryness under reduced pressure and water (150 mL) added. The insoluble residue of unchanged **1** was filtered off, concentrated hydrochloric acid (20 mL) added to the filtrate and the precipitate of **HL** extracted into dichloromethane (3 × 40 mL). The dichloromethane extracts were combined, dried ($MgSO_4$), filtered, and the solvents evaporated to dryness under reduced pressure. Yield: 2.55 g (53%). The product was sufficiently pure for subsequent use, but an analytically pure sample could not be obtained by recrystallisation due to the facile conversion of **HL** to *N*-(2-*tert*-butyl-4-oxo-4*H*-benzo[*d*][1,3]oxazin-5-yl)-2,2-dimethylpropionamide (**2**). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, CH_3), 7.20 (br. s, 1 H, CO_2H), 7.49 (t, ^3J = 8.3 Hz, 1 H, H^a), 8.26 (d, ^3J = 8.3 Hz, 2 H, H^b), 10.44 (s, 2 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.6, 40.3, 106.8, 117.1, 134.3, 140.9, 169.6, 177.5 ppm. IR (KBr): $\tilde{\nu}$ = 3407 (m), 2970 (m), 2874 (w), 1694 (s), 1636 (m), 1610 (m), 1582 (s), 1514 (s), 1464 (s), 1368 (m), 1294 (m), 1222 (s), 1163 (m), 1125 (w), 812 (m), 785 (m), 752 (m), 701 (w), 420 cm^{-1} (w). MS (EI): *m*/*z* (%) = 320 (14) [M^+], 302 (26) [$M^+ - H_2O$].

***N*-(2-*tert*-Butyl-4-oxo-4*H*-benzo[*d*][1,3]oxazin-5-yl)-2,2-dimethylpropionamide (2):** In nonaqueous solutions (e.g., chloroform) **HL** was found to eliminate water over a period of a few hours to give an equilibrium mixture of **HL**, the benzoxazine **2** and water. The deliberate dehydration of **HL** with excess acetic anhydride in toluene gave a near quantitative yield of pure **2**. A sample for analysis was recrystallised from petroleum ether (boiling range 60−80 °C) as colourless needles. $C_{17}H_{22}N_2O_3$ (302.37): calcd. C 67.53, H 7.33, N 9.26; found C 67.49, H 7.46, N 9.25. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9 H, CH_3), 1.40 (s, 9 H, CH_3), 7.26 (d, ^3J = 8.2 Hz, 1 H, H^b), 7.75 (t, ^3J = 8.2 Hz, 1 H, H^a), 8.79 (d, ^3J = 8.2 Hz, 1 H, H^c), 11.39 (s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.5, 27.6, 37.8, 40.6, 103.9, 118.2, 120.8, 137.9, 141.6, 147.1, 162.5, 167.2, 178.5 ppm. IR (KBr): $\tilde{\nu}$ = 3298 (w), 2968 (m), 1716 (m), 1698 (s), 1645 (m), 1610 (m), 1580 (s), 1542 (m), 1475 (m), 1291 (m), 1182 (m), 1157 (s), 1049 (m), 914 (w), 817 (s), 715 (m), 690 (m), 556 cm^{-1} (w). MS (EI): *m*/*z* (%) = 302 (31) [M^+], 245 (100) [$M^+ - C_4H_9$].

Ammonium 2,6-Bis(2,2-dimethylpropionylamino)benzoate, $[NH_4]L$ (3): Carboxylic acid **HL** (0.96 g, 3 mmol) and potassium hydroxide (0.16 g, 2.9 mmol) were dissolved in methanol/water (1:1, 40 mL). Concentrated aqueous ammonia (20 mL) was added, the solution filtered and allowed to concentrate slowly. Large, colourless, X-ray quality crystals of **3** were obtained after 2−3 d. Yield: 0.56 g (55%). $C_{17}H_{27}N_3O_4$ (337.42): calcd. C 60.51, H 8.07, N 12.45; found C 60.35, H 8.32, N 12.32. ^1H NMR (400 MHz, $[D_6]$DMSO): δ = 1.20 (s, 18 H, CH_3), 7.14 (t, ^3J = 8.2 Hz, 1 H, H^a), 7.24 (br. s, 4 H, NH_4^+), 8.21 (d, ^3J = 8.2 Hz, 2 H, H^b), 14.04 (br. s, 2 H, NH) ppm. ^{13}C NMR (100.6 MHz, $[D_6]$DMSO): δ = 27.5, 111.5, 113.1, 129.1, 141.6, 171.3, 176.3 (the *t*Bu peak at ca. 40 ppm is masked by the solvent peak). IR (KBr): $\tilde{\nu}$ = 3080 (m), 2970 (m), 2155 (w), 1943 (w), 1654 (m), 1611 (m), 1580 (s), 1473 (s), 1433 (s), 1362 (s), 1252 (m), 916 (w), 839 (m), 785 (m), 709 (w), 548 (w), 421 cm^{-1} (w).

Calcium Bis[2,6-bis(2,2-dimethylpropionylamino)benzoate] Dihydrate, $CaL_2(H_2O)_2$ (4): Carboxylic acid **HL** (0.96 g, 3 mmol) and potassium hydroxide (0.16 g, 2.9 mmol) were dissolved in water (45 mL). A solution of calcium acetate monohydrate (0.24 g, 1.5 mmol) in water (5 mL) was added and the resulting solution was filtered. Large, colourless, X-ray quality crystals of **4** were obtained after 3−4 d. Yield: 0.68 g (63%). $C_{34}H_{50}CaN_4O_{10}$ (714.87): calcd. C 57.13, H 7.05, N 7.84; found C 56.97, H 7.01, N 7.66. ^1H NMR (400 MHz, $[D_6]$DMSO): δ = 1.21 (s, 18 H, CH_3), 3.35 (br. s, 2 H, H_2O), 7.16 (t, ^3J = 8.3 Hz, 1 H, H^a), 8.22 (d, ^3J = 8.3 Hz, 1 H, H^b), 13.85 (br. s, 2 H, NH) ppm. ^{13}C NMR (100.6 MHz, $[D_6]$DMSO): δ = 27.5, 111.0, 113.2, 129.4, 141.7, 172.2, 176.3 (the *t*Bu peak at ca. 40 ppm is masked by the solvent peak). IR (KBr): $\tilde{\nu}$ = 3398 (m), 3133 (m), 2967 (m), 1652 (m), 1626 (m), 1591 (m), 1480 (s), 1441 (m), 1360 (s), 1306 (m), 1252 (m), 1172 (m), 991 (w), 917 (w), 831 (m), 783 (m), 747 (m), 640 (w), 549 (w), 416 cm^{-1} (w).

Crystal Structure Determinations: Data were collected at 150(2) K employing a wavelength of 0.71073 Å (Mo-K_α) with a Stoe IPDS

Table 3. Crystal data and structure refinement for **3** and **4**

Compound	**3**	**4**
Empirical formula	$C_{17}H_{27}N_3O_4$	$C_{34}H_{50}CaN_4O_{10}$
M_r [g mol^{-1}]	337.42	714.86
Crystal system	orthorhombic	orthorhombic
Space group	*Aba*2	*C*222$_1$
a [Å]	20.6625(17)	12.6255(6)
b [Å]	11.3308(10)	13.7423(8)
c [Å]	17.0301(12)	21.4274(11)
V [Å^3]	3987.1(6)	3717.7(3)
Z, $D_{\text{calcd.}}$ [g cm^{-3}]	8, 1.124	4, 1.277
μ(Mo-K_α) [mm^{-1}]	0.080	0.228
F(000)	1456	1528
Crystal dimensions [mm]	0.40 × 0.35 × 0.20	0.60 × 0.50 × 0.40
$\theta_{\min}/\theta_{\max}$ [°]	1.97/29.74	2.90/34.85
h, k, l ranges	−28/24, −15/15, −23/21	−20/20, −21/21, −33/34
Collected/unique reflections	14100/2928	28175/8040
Restraints, parameters	1, 242	0, 241
$T_{\min}/T_{\max}$	−	0.8410/0.9402
R_{int}	0.0842	0.0500
Goodness-of-fit on F^2	0.924	1.116
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0480$, $wR_2 = 0.1137$	$R_1 = 0.0555$, $wR_2 = 0.1469$
R indices (all data)	$R_1 = 0.0617$, $wR_2 = 0.1214$	$R_1 = 0.0586$, $wR_2 = 0.1516$
Flack parameter	−	0.00(3)
Largest difference peak/hole [e·Å^{-3}]	0.232/−0.220	0.602/−0.552

II image plate diffractometer. Space groups were determined by an examination of the systematic absences in the data, and their correct identification was confirmed by the successful solution and refinement of the structures. Solutions were provided by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[8] Numerical absorption corrections were applied to **4** using X-RED/X-SHAPE.[9] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions with U_{iso} set at 1.2 times the U_{eq} of the parent atom, and methyl groups were allowed to rotate about their X−C bonds; the positions of all N−H and O−H groups were freely refined. The analysis of the structures was carried out with PLATON[10] and WinGX.[11] Details are given in Table 3. Supplementary data for **3** and **4** are available free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk], quoting the deposition numbers CCDC-239602 and -239601, respectively.

Acknowledgments

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