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Synthesis and X-ray crystal structures of homotrimetallic Zinc Bisureate Complexes

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Alkane elimination reactions of the tethered bis(urea) proligand 1,4-(*t*-BuNHCONH)₂-C₄H₈ **1** with ZnR₂ (R = Me, Et, *n*-Pr) yielded trimetallic zinc complexes [RZn-1,4-(*t*-BuNHCONH)₂-C₄H₈]₂Zn (R

= Me **2**, Et **3**, *n*-Pr **4**). **2** - **4** were characterized by heteronuclear NMR (¹H, ¹³C) and IR spectroscopy, elemental analysis and single crystal X-ray diffraction.

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Introduction

Transition metal and main group metal complexes containing monoanionic N,N'-chelating substituents such as β-diketiminates **I**, amidinates **II** and guanidines **III** have been synthesized and structurally characterized in large number. Surprisingly, their N,O-chelating counterparts - ketiminates **IV**, amidates **V** and ureates **VI** - have been substantially less investigated.^[1]

Scheme 1. N,N'- and N,O-chelating substituents.

Urea H₂NC(O)NH₂, also known as carbamide or carbonyldiamide, whose synthesis by Wöhler represents the birth of organic chemistry,^[2] and its organic derivatives such as tetramethylurea have been widely used as neutral ligand in coordination chemistry. A large number of complexes of different main group metals, transition metals and lanthanides have been synthesized and structurally characterized.^[3] Metal urea complexes find different

applications and are typically used as fertilizers^[4] and in pharmaceutical application, e.g. a platinum-urea complex is an antitumor reagent.^[5] In addition, urea-based receptors are used for anion recognition due to their capability to form hydrogen-bonding interactions with a large number of different anions.^[6] Recently, oligoureases have received increasing interest due to their capability to serve as a helical platform for the fabrication of nanostructures in aqueous conditions.^[7]

Neutral urea typically serves as monodentate ligand and coordinates to the metal center by its oxygen atom (**A**), while the N,O-bidentate (**B**) and O-bridging coordination modes (**C**), which is observed in complexes with monovalent cations,^[8c,d] are less common.^[8] Comparable findings were made for N,N'-dimethylurea OC(NHMe)₂ and N,N'-tetramethylurea OC(NMe₂)₂.^[9] 27 hits were found in the Cambridge structural database for N,N'-dimethylurea OC(NHMe)₂ complexes and 48 hits for N,N'-tetramethylurea OC(NMe₂)₂ complexes. The urea ligands in these complexes exclusively bind in a monodentate coordination mode through the carbonyl oxygen atom (**A**).

Scheme 2. Binding modes observed in urea and ureate complexes.

In contrast, the number of complexes containing its deprotonated, monoanionic ureate ligand is significantly

lower. These complexes, which are of particular interest in bioinorganic chemistry, were obtained by metal-promoted deprotonation reactions and the resulting monoanionic ureate ligand was found to adopt μ_2 - $\kappa\text{N}:\kappa\text{O}$ - (**D**) and μ_3 - $\kappa\text{N}:\kappa\text{O}$ -bridging (**E**) as well as κ^2 -N,O-chelating (**F**) coordination modes.^[10] Moreover, metalation reactions of urea with alkali metal (Na – Cs) in liquid ammonia at temperatures below 50 °C yielded the corresponding alkali metal ureate complexes,^[11] whereas alkane elimination reactions of group 4 metal tetraalkyls with alkylated ureas gave the corresponding group 4 metal ureates.^[12] Compared to sterically analogous amidates, ureates are electron-rich ligands due to the electron-donating amino group attached to the central carbon atom. Therefore, the stabilization of such highly electropositive group 4 metals is reasonable.

In addition to as-described urea and ureate complexes, transition metal complexes of bis(ureas)^[13] and of tethered bis(ureates)^[14] have been reported. Compared to untethered bis(ureate) complexes, complexes containing tethered ligands often exhibit less fluxional behavior and coordination isomerism is also often suppressed.^[10d] Moreover, the steric accessibility of the metal center is typically increased by enforcing an equatorial disposition of the ligand. As a consequence, such complexes are of potential interest in catalysis and indeed, tethered bis(ureate) zirconium complexes showed an unprecedented reactivity in the intermolecular hydroamination of alkynes and the intramolecular hydroamination of alkenes. The catalytic activity of the alkyl-tethered bis(ureate) zirconium complex $\text{H}(\text{Me}_2\text{NZr}(\text{NMe}_2)_2\text{-}[\mu\text{-}1,3\text{-(NC(Ni-Pr}_2\text{O)}_2\text{CH}_2\text{CMe}_2\text{CH}_2)]$ was found to be significantly enhanced compared to untethered bis(ureate) complexes.^[14b,15] In addition, tethered bisureate ligands are of general interest since they in principle may give access to bimetallic complexes. Homo- and heterobimetallic complexes have received steadily increasing interest in recent years since the presence of two metal centers is a pre-requisite for possible beneficial cooperative effects.^[16]

We are generally interested in the synthesis and solid state structures of homo- and heteroleptic zinc complexes containing N,N'-chelating β -diketiminates^[17] and amidinates,^[18] as well as of N,O-chelating ketoiminates^[19] and their potential capability to serve as catalyst in the ROP of *rac*-lactide^[20] Moreover, we recently reported on the synthesis and solid state structures of tethered bisamidinate alane complexes.^[21] These studies prompted our interest towards tethered bis(ureate) complexes and we herein report on reactions of the bis(urea) 1,4-(*t*-BuNHCONH)₂-C₄H₈ **1** with three zinc dialkyls ZnR₂, yielding homotrimetallic zinc bis(ureate) complexes of the general type [RZn-1,4-(*t*-BuNHCONH)₂-C₄H₈]₂Zn (R = Me **2**, Et **3**, *n*-Pr **4**). To the best of our knowledge, compounds **2-4** represent the first zinc complexes containing tethered bisureate ligands. The solid-state structures of **1-4** were determined by single crystal X-ray diffraction.

Results and Discussion

The starting tethered bis(urea) ligand 1,4-(*t*-BuNHCONH)₂-C₄H₈ **1** was synthesized according to literature method and identified by NMR (¹H, ¹³C) and IR spectroscopy.^[22] Single crystals of **1** were obtained upon storage of a solution in CHCl₃ at –30 °C after 12 h.

The bond length and angle of the other independent molecules of **1** are comparable and can be found in the SI. The model suggests that the packing is dominated by the R₁(6) motif of hydrogen bonds commonly found in RHNCONHR (see Scheme 3). Strings of these motifs along <210> appear to be present. However, considering the limited quality of the model, we do not consider it appropriate to discuss the packing in further detail.

The general synthesis of the zinc complexes is shown in Scheme 4. **2-4** were obtained from reactions of **1** with the corresponding zinc dialkyl ZnR₂ (R = Me, Et, *n*-Pr) in 2:3 molar ratio. Reactions with 1:1 and 1:2 molar ratio also exclusively yielded **2-4** in addition to non-reacted **1** and ZnR₂, respectively. In addition, analogous reactions at 80 °C also proceeded only with formation of **2-4**, proving the thermal stability of these compounds in solution.

Scheme 4. Synthesis of **2-4**.

2-4 are soluble in common organic solvents such as toluene and THF. ¹H and ¹³C NMR spectra of **2-4** in non-coordinating (C₆D₆) and coordinating solvents (THF-*d*₈) are comparable, each showing the expected resonances due to the *t*-Bu groups and the C₄H₄ bridging unit of the ureate ligand as well as the alkyl group bonded to the Zn atom (R = Me **2**, Et **3**, *n*-Pr **4**) in a 2:3 molar ratio. These findings doesn't surprise since we did not expect any coordination of the solvent molecule (thf) to the zinc atoms, which adopts tetrahedral coordination spheres. In addition, each ¹H NMR spectra also exhibits two additional resonances of equal intensity for the remaining N-H groups at δ_H 3.8 and 4.7, respectively. Temperature-dependent ¹H NMR spectroscopy studies gave no indication for any type of dynamic properties of **2-4**, since only some line broadening at lower temperatures (-80 °C) was observed. We therefore believe that **2-4** adopt the same structures as observed in the solid state. The NMR spectroscopy findings were confirmed by IR spectroscopy. The IR spectra of **2-4** each display rather broad absorption bands due to the symmetric and asymmetric stretching vibrations of the remaining N-H groups. The carbonyl stretching vibrations are found at 1558 cm⁻¹ (**2**), 1580 cm⁻¹ (**3**) and 1582 cm⁻¹ (**4**), respectively, which are shifted to lower frequencies compared to those observed for **1** (1638 cm⁻¹). The stretching frequency of the carbonyl vibration of urea (NH₂)₂CO is at 1686 cm⁻¹, which is shifted to a lower frequency number compared to that observed for acetone (1715 cm⁻¹), which contains a "true" C=O double bond. This shift is caused by the delocalization of the π electron density within the N₂CO core, resulting in a reduction of the double bond character to roughly 60%.

Single crystals of **2-4** were obtained upon storage of solutions in fluorobenzene/Et₂O at -30 °C after 5 days (**2**) or in toluene/Et₂O at 0 °C after 24 h (**3**, **4**). **2** crystallizes in the monoclinic space group *P*2₁/*n* with the molecules placed on

the two-fold axis. **3** is possibly isostructural to **2**, but the best model available uses the triclinic space group *P*-1 with one molecule in the asymmetric unit. Though quantitative results of this model should be taken with care, the connectivity is reliable. **4** crystallizes in the monoclinic space group *P*2₁/*c* with the molecules placed on the general position.

The solid state structures of **2-4** are very similar. The four monoanionic ureate units serve as μ₂-κN:κO bridging units between the central zinc atom (Zn1) and one of the outer Zn atoms (Zn2, Zn2'), resulting in a μ₄-κN:κO:κN:κO-coordination mode of each bisureate ligand. The central tetrahedrally coordinated zinc atom (Zn1) binds to four nitrogen atoms of two dianionic bis(ureate) ligands (**2**: N3, **3**: N2/N7, **4**: N2/N6), which are directly bonded to the linking alkyl chain. Each Zn1 atom of **2-4** consequently adopts a κ⁴(N,N,N,N) coordination mode. The two bisureate ligands are further connected via two zinc atoms (Zn2, Zn2'), which bind to one nitrogen and two oxygen atoms in a κ³(N,O,O) coordination environment and to one additional alkyl group. The Zn atoms adopt slightly distorted tetrahedral coordination spheres and the bond angles deviate by about ±15° from the ideal tetrahedral angle.

Figure 2. Solid state structure of **2**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels; Non NH hydrogen atoms omitted for clarity. The two ligands are highlighted in red and blue. The red one and the not labeled ZnR group are generated via 2-fold rotational symmetry.

Figure 3. Solid state structure of **3**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels; Non NH hydrogen atoms omitted for clarity. The two ligands are highlighted in red and blue.

Figure 4. Solid state structure of **4**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels; Non NH hydrogen atoms and second orientation of disordered parts omitted for clarity. The two ligands are highlighted in red and blue.

Table 1. Selected bond lengths [Å] of **1** - **4**.

	1	2	3	4
Zn1-N2	-	1.9741(19)	2.064(5)	2.0715(12)
Zn1-N3	-	2.0592(19)	1.980(5)	1.9779(12)
Zn1-N6	-	-	1.977(5)	2.0612(12)
Zn1-N7	-	-	2.049(5)	1.9810(13)
Zn2-C15/29	-	1.964(3)	1.977(6)	1.9846(16)
Zn2/3-O1	-	2.0154(16)	2.020(4)	2.0163(11)
Zn2/3-O2	-	2.0259(15)	2.001(4)	2.0145(11)
Zn2/3-N3/6/7	-	2.1145(19)	2.119(5)	2.1272(13)
Zn3-C31/32	-	-	1.972(6)	2.007(8)
Zn2/3-O3	-	-	2.011(4)	2.0086(11)
Zn2/3-O4	-	-	2.024(4)	2.0117(11)
Zn2/3-N2	-	-	2.102(5)	2.1126(13)
N1-C1/5	1.351(7)	1.370(3)	1.356(7)	1.346(2)
N2-C1/5	1.352(5)	1.325(3)	1.362(7)	1.3679(19)
O1-C1/5	1.236(4)	1.272(3)	1.264(8)	1.2609(18)
N3-C6/10	1.338(5)	-	1.332(8)	1.3209(19)
N4-C6/10	1.346(5)	-	1.368(8)	1.3715(19)
O2-C6/10	1.237(4)	-	1.272(7)	1.2755(18)

The Zn-N bond lengths (Table 1) of the threefold-coordinated nitrogen atoms (**2**: N2, **3**: N3/N6, **4**: N3/N7) to the central Zn atom (Zn1) are about 8 pm shorter compared to those of the fourfold-coordinated nitrogen atoms (**2**: N3, **3**: N2/N7, **4**: N2/N6), that adopt bridging positions between Zn1 and Zn2/Zn2'. The longest Zn-N bonds are observed for the Zn atoms (Zn2/Zn3) to the bridging nitrogen atoms (**2**: N3, **3**: N2/N7, **4**: N2/N6), which are approx. 14 pm longer and within the typical range observed for rather dative Zn-N bonds. As was expected, the C-O and C-N bond length within the ligands was found to increase as a consequence of

the coordination to the Zn atoms. The Zn-O bond lengths are almost identical and range from 2.00 to 2.02 Å, as is typically observed for Zn-O single bonds. Changes in the bond angles are neglectable (Table 2). The two terminal amide groups (*t*-BuNH) of each bis(ureate) ligand are not involved in the coordination to the metal centers and one would expect the hydrogen atoms to engage in hydrogen bonding. However, since possible acceptors for hydrogen bonds are located in the center of the molecule or are sterically unavailable, no hydrogen bond formation is observed. Despite the different steric demand of the alkyl groups, the overall conformation of the molecules is in good approximation unaltered (see Figure 5).

Figure 5. Overlay of the solid state structures of **2** (red) **3** (blue) and **4** (green).

Table 2. Selected bond angles [°] of **1** - **4**.

	1	2	3	4
N2-Zn1-N3	-	97.25(8)	95.9(2)	97.18(5)
N2-Zn1-N3'/N6	-	110.29(8)	111.4(2)	115.45(5)
N2-Zn1-N2'/N7	-	123.53(12)	119.3(2)	114.47(5)
N3-Zn1-N3'/N6	-	119.99(11)	125.2(2)	113.71(5)
N3-Zn1-N7	-	-	109.5(2)	119.35(5)
N6-Zn1-N7	-	-	97.4(2)	97.88(5)
Zn1-N2/6-Zn3	-	90.79(7)	90.85(18)	92.48(5)
Zn1-N7/2-Zn2	-	-	92.3(2)	91.91(5)
O1-Zn2/3-O2	-	98.94(6)	97.24(18)	103.00(4)
N1-C1/5-N2	114.2(3)	119.8(2)	121.0(6)	121.15(13)
N1-C1/5-O1	123.6(4)	117.5(2)	118.6(5)	118.54(14)
N2-C1/5-O1	122.1(4)	122.7(2)	120.4(5)	120.30(13)

Conclusions

1 is a powerful starting reagent for the synthesis of zinc complexes, which were obtained by alkane elimination of the corresponding zinc dialkyls ZnR₂. Only the two N-H groups of each bis(urea) ligands, which are directly bonded to the linking alkyl chain, are metalated, resulting in the

formation of the homotrimetallic zinc ureate complexes of the general type $[\text{RZn-1,4-}(t\text{-BuNHCON})_2\text{-C}_4\text{H}_8]_2\text{Zn}$ ($\text{R} = \text{Me}$ **2**, Et **3**, $n\text{-Pr}$ **4**). These complexes each contain three tetrahedral coordinated zinc atoms, whose coordination environment differs: two Zn atoms are coordinated by one alkyl group as well as two oxygen and one nitrogen atom of the dianionic bis(ureate) ligand (RZnNO_2 coordination), whereas the central zinc atom is coordinated by four N atoms of two ureate ligands (ZnN_4 coordination). Further reactions of **1** and comparable derivatives with other transition metal and main group metal complexes will be performed in due course in order to prove their general applicability for the formation of metal complexes of the desired type. Moreover, the applicability of **2** - **4** to serve as catalyst in the ring opening polymerization (ROP) of cyclic esters such as lactide is currently under investigation.

Experimental Section

All manipulations were performed in a glovebox under argon atmosphere or by using standard Schlenk techniques. Solvents were carefully dried with Na/K and degassed prior to use. 1,4- $[\text{t-BuN(H)CONH}]_2\text{-C}_4\text{H}_8$ **1**^[21] and ZnR_2 ($\text{R} = \text{Me}$, Et , $n\text{-Pr}$) were prepared according to literature methods.^[25] NMR spectra were recorded at 25 °C with a Bruker DMX 300 spectrometer (^1H : 300 MHz; ^{13}C : 75 MHz) and are referenced to internal CDCl_3 (^1H : $\delta = 7.26$ ppm; ^{13}C : $\delta = 77.2$ ppm). IR spectra were recorded with an ALPHA-T FT-IR spectrometer equipped with a single-reflection ATR sampling module, which is placed in an argon filled glovebox. Melting points were measured in sealed capillaries. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen.

General procedure for the synthesis of **2-4**.

A suspension of 1,4- $[\text{t-BuNHCONH}]_2\text{-C}_4\text{H}_8$ **1** (0.7 mmol, 0.2 g) in 10 mL of toluene was cooled to -30 °C and ZnR_2 (1.1 mmol; $\text{R} = \text{Me}$ 0.11 g, Et 0.14 g, $n\text{-Pr}$ 0.16 g) was slowly added via syringe. The resulting suspension was slowly warmed to ambient temperature, upon which a smooth gas evolution was observed, and stirred for additional 15 h. The solvent and unreacted ZnR_2 was removed in vacuo, yielding **2-4** as colorless crystalline powders. Single crystals of **2** were obtained after storage of a solution of **2** in fluorobenzene/ Et_2O at -30 °C for 5 days, whereas single crystals of **3** and **4** were obtained from solutions in toluene/ Et_2O at 0 °C after 24 h.

[MeZn-1,4-}(t\text{-BuNHCON})_2\text{-C}_4\text{H}_8]_2\text{Zn 2}. Yield: 0.52 g (93 %).

Mp.: 220 °C (dec.). Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{62}\text{N}_8\text{O}_4\text{Zn}_3$ (795.09 g/mol): C, 44.80 (45.32); H, 7.99 (7.86); N, 13.95 (14.09) %. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ -1.03 (s, 6 H, ZnMe), 1.27 (s, 20 H, CMe_3 , CH_2), 1.29 (s, 20 H, CMe_3 , CH_2), 1.54 (m, 2 H, CH_2), 1.72 (t, $^3J_{\text{HH}} = 12.55$ Hz, 2 H, CH_2), 1.92 (t, $^3J_{\text{HH}} = 12.80$ Hz, 2 H, CH_2), 2.57 (t, $^3J_{\text{HH}} = 12.04$ Hz, 2 H, CH_2), 2.94-3.02 (m, 6 H, CH_2), 3.83 (s, 2 H, NH), 4.66 (s, 2 H, NH). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ -20.5 (ZnMe), 27.3 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 47.8 (NCMe_3), 47.9 (NCMe_3), 50.4 (NCMe_3), 51.2 (NCMe_3), 162.0 (CO), 166.6 (NCN). IR (v, cm^{-1}): 3365, 2963, 2937, 2856, 1632, 1558, 1525, 1451, 1360, 1327, 1277, 1242, 1214, 1193, 1152, 1051, 972, 933, 786, 774, 749, 631, 453, 419 cm^{-1} .

[EtZn-1,4-}(t\text{-BuNHCON})_2\text{-C}_4\text{H}_8]_2\text{Zn 3}. Yield: 0.55 g (95 %).

Mp.: > 220 °C (dec.). Elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{66}\text{N}_8\text{O}_4\text{Zn}_3$ (823.14 g/mol): C, 46.50 (46.69); H, 8.01 (8.08); N, 13.57 (13.61) %. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ -0.03 (quart, $^3J_{\text{HH}} = 8.10$ Hz, 4 H, ZnCH_2CH_3), 1.20 (t, $^3J_{\text{HH}} = 8.11$ Hz, 6

H, ZnCH_2CH_3), 1.27 (s, 18 H, CMe_3), 1.30 (s, 18 H, CMe_3), 1.35 (m, 4 H, CH_2), 1.51 (m, 2 H, CH_2), 1.70 (t, $^3J_{\text{HH}} = 12.59$ Hz, 2 H, CH_2), 1.90 (t, $^3J_{\text{HH}} = 12.80$ Hz, 2 H, CH_2), 2.56 (t, $^3J_{\text{HH}} = 12.14$ Hz, 2 H, CH_2), 2.98-3.02 (m, 6 H, CH_2), 3.82 (s, 2 H, NH), 4.66 (s, 2 H, NH). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ -4.6 (ZnCH_2CH_3), 13.6 (ZnCH_2CH_3), 27.3 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 47.8 (NCMe_3), 48.0 (NCMe_3), 50.4 (NCMe_3), 51.1 (NCMe_3), 162.0 (CO), 166.8 (NCN). IR (v, cm^{-1}): 3444, 2996, 2963, 2929, 2835, 2803, 1581, 1514, 1486, 1441, 1392, 1355, 1336, 1312, 1271, 1239, 1211, 1138, 1119, 1078, 1056, 1044, 1020, 983, 932, 901, 831, 797, 645, 598, 578, 525, 434 cm^{-1} .

[n-PrZn-1,4-}(t\text{-BuNHCON})_2\text{-C}_4\text{H}_8]_2\text{Zn 4}. Yield: 0.56 g (95 %).

Mp.: > 220 °C (dec.). Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{68}\text{N}_8\text{O}_4\text{Zn}_3$ (849.18 g/mol): C, 48.03 (48.09); H, 8.04 (8.07); N, 13.15 (13.20) %. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 0.09 (t, $^3J_{\text{HH}} = 7.34$ Hz, 4 H, $\text{ZnCH}_2\text{CH}_2\text{CH}_3$), 0.94 (t, $^3J_{\text{HH}} = 7.21$ Hz, 6 H, $\text{ZnCH}_2\text{CH}_2\text{CH}_3$), 1.27 (s, 18 H, CMe_3), 1.29 (s, 18 H, CMe_3), 1.30-1.33 (m, 4 H, CH_2), 1.51 (m, 2 H, CH_2), 1.57 (sext, $^3J_{\text{HH}} = 7.34$ Hz, 4 H, $\text{ZnCH}_2\text{CH}_2\text{CH}_3$, 2 H, CH_2), 1.71 (t, $^3J_{\text{HH}} = 12.55$ Hz, 2 H, CH_2), 1.90 (t, $^3J_{\text{HH}} = 12.80$ Hz, 2 H, CH_2), 2.56 (t, $^3J_{\text{HH}} = 11.98$ Hz, 2 H, CH_2), 2.95-3.05 (m, 6 H, CH_2), 3.82 (s, 2 H, NH), 4.65 (s, 2 H, NH). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 7.8 ($\text{ZnCH}_2\text{CH}_2\text{CH}_3$), 21.1 ($\text{ZnCH}_2\text{CH}_2\text{CH}_3$), 22.4 (CH_3), 27.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 30.0 (CH_2), 47.8 (NCMe_3), 48.0 (NCMe_3), 50.3 (NCMe_3), 51.1 (NCMe_3), 162.0 (CO), 166.5 (NCN). IR (v, cm^{-1}): 3442, 2963, 2930, 2868, 2811, 1582, 1513, 1486, 1442, 1394, 1362, 1309, 1260, 1243, 1212, 1199, 1178, 1119, 933, 865, 796, 763, 699, 657, 643, 531, 502, 433, 384 cm^{-1} .

Single crystal X-ray diffraction. Crystallographic data of **1-4**, which were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK α radiation, $\lambda = 0.71073$ Å) at 100(1) K (**3**, **4**) and 180(1) K (**1**, **2**), are summarized in Table S1 (SI). The solid-state structures of **1-4** are shown in Figures 1-4, bond lengths and angles of **1-4** are summarized in Table 1. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).^[26,27] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. In **1** a part of one independent molecule is disordered over two positions. To avoid correlations in the final refinement the occupancies were fixed at 0.2 and 0.8. In **3** the model was refined as pseudo-merohedrally twinned by two-fold rotation about a . The metrics of the unit cell suggests that it might be isostructural to **2** and indeed it may be solved in monoclinic $P2_1/n$. The systematic extinctions for an n glide-plane symmetry are not full-filled and R_{int} is ~24%. The final $R1$ and $wR2$ values of the model are 30% and 67% respectively. However, a closer inspection of the reciprocal suggests that several highly overlapping twin components may be present. Any attempts to separate them failed. Thus the triclinic model is the best available. It should be noted that quantitative results may be unreliable. In **4** the NH hydrogen atoms could be identified in the difference Fourier synthesis and were refined freely with its NH distance restrained to 0.87 Å (DFIX). One of the propyl groups was disordered over two positions. RIGU restraints were applied to the atomic displacement parameters of the corresponding atoms. The crystallographic data of **1-4** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1572048 (**1**), CCDC-1572049 (**2**), CCDC-1572050 (**3**) and CCDC-1572051 (**4**). Copies of the data can be obtained free of charge on application to CCDC,

Supporting Information (see footnote on the first page of this article): A CIF file giving X-ray crystallographic data of **1-4**, spectroscopic details (^1H , ^{13}C NMR; IR) and crystallographic details of **1-4**.

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