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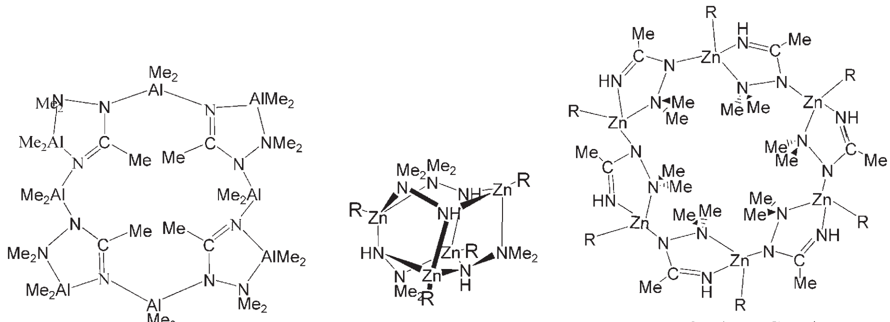
Alkylzinc Hydrazides: Self-Assembly of Hexanuclear Ring Systems in Acetonitrile

Mark R. J. Elsegood[b] **and Carl Redshaw***[a]

A number of groups have been investigating the reactivity of hydrazines towards Group 12 and 13 alkyl species, driven in-part by the desire to find new useful presursors for OMCVD. These studies have led to the isolation and structural characterization of a number of intriguing complexes.[1] The remarkable product of the reaction of trimethylaluminium, Me_3Al, with 1,1′-dimethylhydrazine, Me_2NNH_2, following work-up in acetonitrile is the calix[4]pyrrole-like ring system **1** (Scheme 1),[1b] which has prompted us to further explore the scope of this reaction for generating other novel main-group structural motifs. Both Mitzel and co-workers[1d] and ourselves[1e] have found that dialkylzinc reagents of the type R_2Zn, where R = methyl or ethyl, afford tetrametallic Zn_4N_8 cages of the form **2**; our work-up involved the use of excess acetonitrile, which under the conditions employed served only as the solvent of crystallization. However, we now find that on changing the substituent at zinc, and using more robust work-up conditions, the course of the reaction and resulting product structure can be dramatically changed, affording new zinc–nitrogen ring systems **3**.



1

2 (R = Me, Et)

3a ($R = C_6F_5$)
3b (R = Ph)
3c (R = Cl)
3d (R = Et)

Scheme 1.

Reaction of $(C_6F_5)_2Zn$[2] (2.1 equiv) with 1,1′-dimethylhydrazine in refluxing toluene results in, following work-up, **3a** in about 35 % yield. Small colorless prisms of **3a** suitable for an X-ray analysis using synchrotron radiation[3] were grown from solutions of acetonitrile on prolonged standing at −20 °C. The molecular structure of the acetonitrile solvate is shown in Figure 1; half the molecule and three acetonitriles of crystallization are unique.[4] The molecule sits on an inversion centre and is made up of six five-membered ZnN_3C rings linked via $(C_6F_5)Zn{-}N$ bonds. Each zinc is four-coordinate being bound to one amide nitrogen, a nitrogen of an imine and datively bonded to an NMe_2 group; the coordination geometry is completed by a C_6F_5 group. The six C_6F_5 rings are all virtually in the plane of the Zn_6 ring, which may in part be due to their involvement in off-set $C_6F_5{-}C_6F_5$ packing [shortest C···C contact 3.475 Å]. This π-stacking and the presence of six N−H···F hydrogen bonds [av H···F = 2.53 Å], gives rise to a 3D network; there is also hydrogen bonding between N(1)–H(1) and acetonitrile of crystallization [H···N = 2.42 Å]. A second crystallization afforded the solvate **3**·2 MeCN (**3a′**),[5] in which the acetonitrile molecules

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[a] Dr. C. Redshaw
School of Chemical Sciences and Pharmacy
The University of East Anglia
Norwich, NR4 7TJ (UK)
Fax: (+44) 1603 592003
E-mail: carl.redshaw@uea.ac.uk

[b] Dr. M. R. J. Elsegood
Chemistry Department
Loughborough University
Loughborough, Leicestershire, LE11 3TU (UK)

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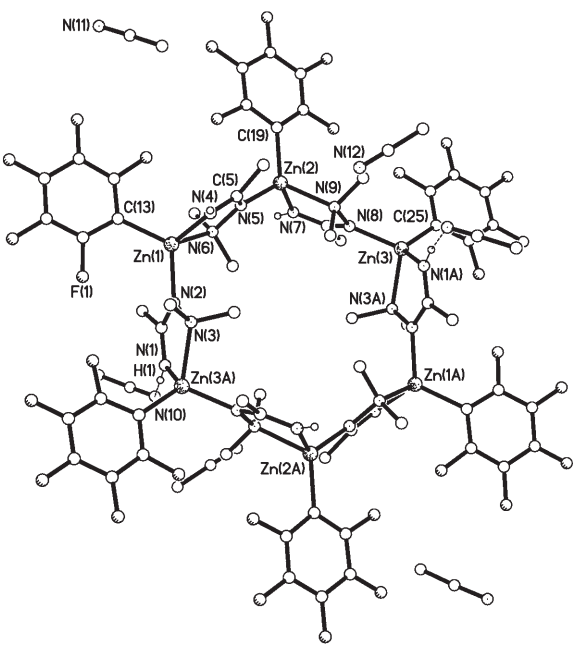

Figure 1. Molecular structure of **3a**. Selected bond lengths [Å] and angles [°]: Zn(1)–N(2) 2.022(2), Zn(1)–N(4) 1.972(2), Zn(1)–N(6) 2.164(2), Zn(1)–C(13) 2.032(3), N(5)–N(6) 1.459(3), N(4)–C(5) 1.315(3), N(5)–C(5) 1.329(3), N(5)–Zn(2) 2.0191(19); N(4)-Zn(1)-N(2) 116.07(8), N(4)-Zn(1)-C(13) 113.22(10), N(2)-Zn(1)-C(13) 118.13(9), N(4)-Zn(1)-N(6) 79.75(8). Symmetry operator A = −x, −y+1, −z+1.

(one unique) lie above and below the ring system, but are not involved in hydrogen bonding to N−H groups (Figure 2). However, the N−H groups at N(1) and N(9) form hydrogen bonds to F atoms on neighbouring molecules so that each Zn_6 ring forms a total of four hydrogen bonds (two as donor, two as acceptor). The C_6F_5 ring at Zn(1) π–π stacks with a C_6F_5 ring on Zn(2) of a neighbouring molecule and vice versa, whilst the ring at Zn(3) π-π stacks with a symmetry equivalent on a neighbouring molecule. As a consequence each Zn_6 ring forms six π–π stacking interactions, resulting in a supramolecular 3D network (see Supporting Information).

Similar use of Ph_2Zn[6] afforded, upon work-up, small colourless prisms (**3b**) suitable for X-ray analysis using synchrotron radiation in about 70% yield.[7] The structure of **3b** is shown in Figure 3, with selected bond lengths and angles given in the caption. One sixth of the hexameric molecule is unique, plus half a disordered acetonitrile. The 18-membered ring system is very similar to that observed for **3a/a′**; geometrical parameters associated with the ZnN_3C rings are also very similar to those of **3a/a′**(and **3c**). As in **3a/a′**, the aryl rings are virtually in the plane of the Zn_6 ring. Encouraged by the synthesis of the ring systems **3a,b**, we then investigated the reaction of the mixed alkyl-chloro reagent EtZnCl[8] with 1,1-dimethylhydrazine; a few drops of tetrahydrofuran were necessary to aid solubilization of the zinc reagent. Following work-up (acetonitrile) of the EtZnCl reaction, large colourless blocks of **3c**, suitable for single-crystal X-ray diffraction, formed in about 45% yield on cooling to ambient temperature.

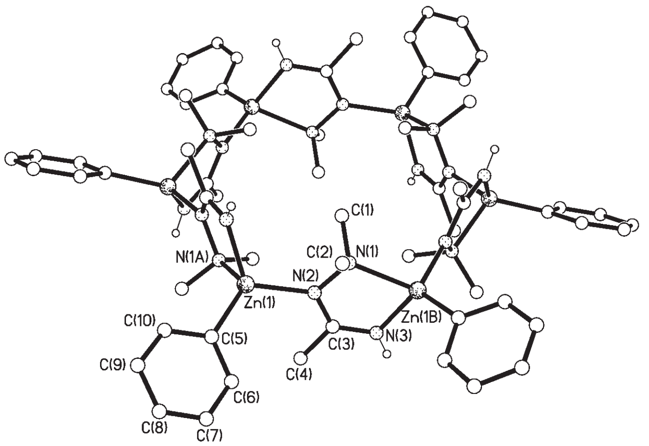

Figure 3. Molecular structure of **3b**. Selected bond lengths [Å] and angles [°]: Zn(1)–N(2) 2.047(2), Zn(1)–N(1A) 2.195(2), Zn(1)–N(3A) 1.986(2), Zn(1)–C(5) 1.986(3), N(1)–N(2) 1.460(3), N(2)–C(3) 1.328(3), N(3)–C(3) 1.320(3); N(1A)-Zn(1)-N(2) 105.20(8), N(3A)-Zn(1)-C(5) 116.46(10), N(2)-Zn(1)-C(5) 117.30(10), N(1A)-Zn(1)-N(3A) 78.35(8). Symmetry operators: A = y+1/3, −x+y+2/3, −z+2/3; B = x−y+1/3, x−1/3, −z+2/3.

The X-ray analysis[9] revealed that the structure of **3c** is again an 18-membered macrocycle closely related to that adopted

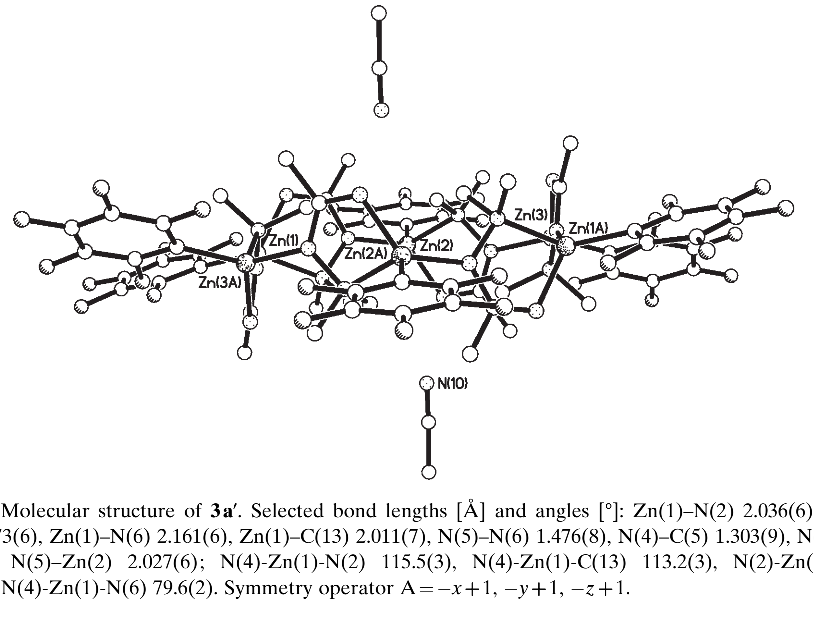

Figure 2. Molecular structure of **3a′**. Selected bond lengths [Å] and angles [°]: Zn(1)–N(2) 2.036(6), Zn(1)–N(4) 1.973(6), Zn(1)–N(6) 2.161(6), Zn(1)–C(13) 2.011(7), N(5)–N(6) 1.476(8), N(4)–C(5) 1.303(9), N(5)–C(5) 1.327(9), N(5)–Zn(2) 2.027(6); N(4)-Zn(1)-N(2) 115.5(3), N(4)-Zn(1)-C(13) 113.2(3), N(2)-Zn(1)-C(13) 118.0(3), N(4)-Zn(1)-N(6) 79.6(2). Symmetry operator A = −x+1, −y+1, −z+1.

by **3a/a′,b**. The hexa-nuclear ring sits on an inversion centre, and as in **3a/a′,b** the R groups, here chloro, are in the plane of the Zn_6 ring. There is one unique hydrogen bond, N–H···Cl, through which molecules of **3c** pair-up in head-to-tail fashion (Figure 4) to link three rings above and another three below by symmetry.

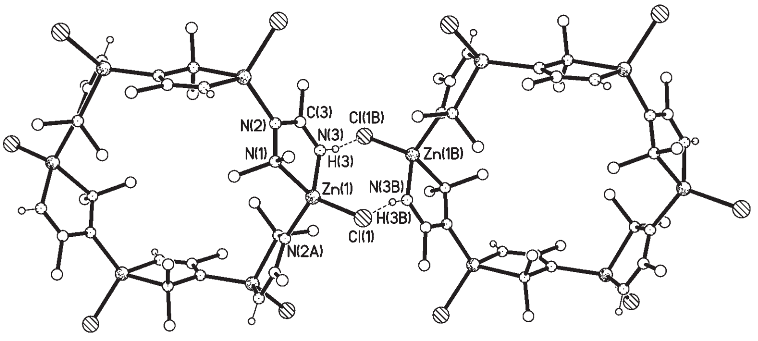

Figure 4. Molecular structure of **3c**. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.104(7), Zn(1)–N(3) 1.924(4), Zn(1)–N(2B) 2.035(7), Zn(1)–Cl(1) 2.2449(10), N(1)–N(2) 1.465(7), N(2)–C(3) 1.341(7), N(3)–C(3) 1.296(7); N(3)-Zn(1)-N(1) 81.79(18), N(1)-Zn(1)-Cl(1) 109.96(18), N(3)-Zn(1)-N(2B) 116.4(2). Symmetry operators $A = -x+2/3, -x+y+1/3, -z+4/3$, $B = -x+1/3, -y+5/3, -z+5/3$.

Interestingly, use of $ZnCl_2$ in an analogous fashion resulted only in the formation of the complex $[ZnCl_2(NH_2NMe_2)_2]$, the structure of which contains four unique H-bonds resulting in chains of molecules along *a*.[10]

Given the ease of formation of **3a/a′–c**, we decided to revisit the Zn_4N_8 cage **2** and subject it to nitrile under more forcing conditions (reflux, 48 h). Analysis of the resulting pale yellow precipitate was consistent with formation of a **3**-type structure, and indeed single crystal X-ray analysis (Figure 5) revealed the analogous ethyl derivative (**3d**) of **3a/a′–c**.[11] Again the molecule sits on an inversion centre, and in this case the ethyl groups are very much in the plane of the ring.

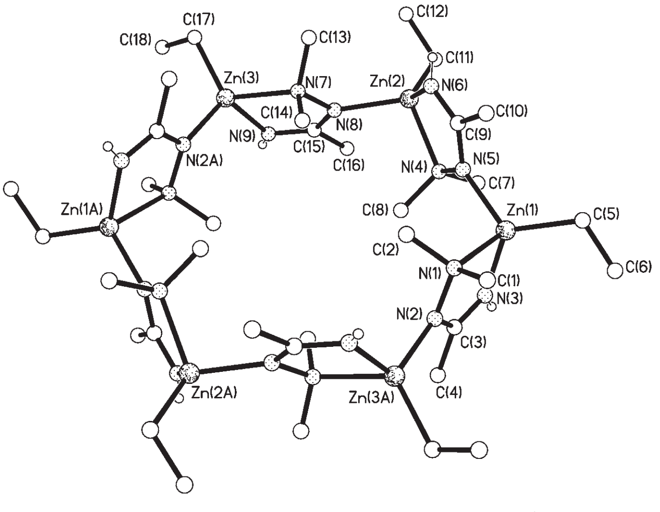

Figure 5. Molecular structure of **3d**. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.2063(16), Zn(1)–N(3) 1.9791(18), Zn(1)–N(5) 2.0669(16), N(1)–N(2) 1.464(2), N(2)–C(3) 1.330(2), C(3)–N(3) 1.315; N(1)-Zn(1)-N(3) 77.55(6), N(1)-Zn(1)-(N5) 104.26(6), Zn(1)-N(1)-N(2) 109.44(11). Symmetry operator $A = -x+1, -y+1, -z+1$.

The formation of the ring systems herein can therefore be described in terms of an initial deprotonation reaction, affording tetrameric Zn_4N_8 type systems, which upon addition of acetonitrile undergo tautomerism to afford the type **3** ring structures. In complexes of type **3**, in the IR spectrum, νNH and ν(C=N) appear in the regions 3320–3410 cm^{-1} and 1540–1570 cm^{-1}, respectively. However, ^1H NMR studies were hampered by the poor solubility of **3b–d** in hydrocarbons, arenes and halogenated solvents.

Complete hydrolysis of ring systems **3** readily releases acetamide hydrazones of the form $[R,R'NN{=}C(Me)NH_2]$ in good yield; the procedure starting from the appropriate hydrazine can be carried out in one-pot if required.[12] Crystal structure determinations of the ligand $R = Me$, $R' = Ph$, reveal both tetragonal and monoclinic polymorphs with hydrogen-bonded chains.[13] Such ligands have attracted little attention in the literature, despite appearing to be attractive synthons for organic synthesis.[14, 15]

In conclusion, the reaction of zinc aryls, $(C_6F_5)_2Zn$ or Ph_2Zn, or the zinc alkyl halide EtZnCl with 1,1′-dimethylhydrazine affords, upon work-up (acetonitrile), a new class of 18-membered zinc–nitrogen macrocycles. Furthermore, this same class of macrocycle is available via previously reported Zn_4N_8-type cages on treatment with MeCN under forcing conditions. Further studies are in progress to explore and extend the synthetic scope of this reaction and the chemistry of the resulting macrocycles.

Experimental Section

All manipulations were performed under N_2 using standard Schlenk techniques and dried, deoxygenated solvents. Complexes **3a/a′–c** were prepared by heating Me_2NNH_2 (16.6 mmol) with two equivalents of the appropriate alkylzinc reagent under reflux in toluene (toluene/THF, 10:1 was used for alkylzinc halides) for 12 h. Volatile components were removed in vacuo, MeCN (30 mL) was added and stirring was continued for 12 h. In the case of **3d**, work-up involved refluxing for 48 h. The products were obtained by extraction into warm acetonitrile. Small colourless prisms were obtained on prolonged standing at −20 °C (**3a/a′**, **3d**) or ambient temperature (**3b**, **3c**).

For **3a**: Yield: 35 %; m. p. > 320 °C (decomp. ca. 280 °C); ^1H NMR (CD_3CN, 400 MHz, 348 K): $\delta = 3.89$ (s, 1H, NH), 3.66 (s, 1H, NH), 3.50 (s, 1H, NH), 3.34 (s, 1H, NH), 3.14 (s, 6H, CMe), 3.05 (s, 6H, CMe), 3.00 (s, 1H, NH), 2.89–2.87 (overlapping s, 10H, N*H*, C*Me*, N*Me*$_2$), 2.69 (s, 6H, NMe_2), 2.58 (s, 6H, NMe_2), 2.49 (s, 6H, NMe_2), 2.42 (s, 6H, NMe_2), 2.33 (s, 6H, N*Me*$_2$), −0.38 ppm (bs, 3H, MeCN); ^{19}F NMR (CD_3CN, 282 MHz, 300 K): $\delta = -114.87$ (m, *o*-F, 3F), −115.71 (m, *o*-F, 3F), −116.19 (m, *o*-F, 3F), −116.53 (m, *o*-F, 3F), −156.92 (t, *J*, *p*-F, 1F), 159.00 (t, J 18.5 Hz, p-F, 2F), 159.74 (t, J 19.8 Hz, p-F, 2F), 160.55 (t, J 19.8 Hz, p-F, 1F), −163.84 (overlapping m, m-F, 6F), −164.35 (m, m-F, 6F), −164.88 ppm (m, m-F, 6F); IR: $\tilde{\nu}=3406$ (m), 3208 (w), 2287 (w), 2252 (w), 1681 (w), 1635 (s), 1564 (s), 1533 (s), 1504 (s), 1446 (bs), 1373 (s), 1275 (m), 1339 (s), 1275 (s), 1254 (s), 1096 (s), 1174 (s), 1095 (s), 1053 (s), 994 (m), 948 (s), 865 (s), 823 (s), 796 (s), 766 (m), 716 (m), 685 (m), 601 (m) cm^{-1}; MS (FAB): 2119 ([M^+−3MeCN]), 1997 ([M^+−6MeCN]), 1895 ([M^+−6MeCN−Me$_2$NNC(Me)NH$_2$]), 1729 ([M^+−6MeCN−Me$_2$NNC(Me)NH$_2$−C$_6$F$_5$]), 1561 ([M^+−6MeCN−Me$_2$NNC(Me)NH$_2$−2C$_6$F$_5$]); elemental analysis calcd (%) for $C_{60}H_{60}N_{18}F_{30}Zn_6$ (sample dried in vacuo for 12 h): C 36.11, H 3.03, N 12.64; found: C 36.11, H 3.06, N 12.51. For **3b**: Yield: 68%; m. p > 320°C; IR: $\tilde{\nu}=3356$ (m), 2454 (w), 2395 (w), 2196 (w), 1962 (w), 1948 (w), 1884 (w), 1870 (w), 1822 (w), 1762 (w), 1583 (bs), 1298 (m), 1261 (s), 1243 (m), 1217 (bm), 1187 (m), 1172 (s), 1094 (s), 1068 (s), 1022 (s), 1000 (s), 983 (m), 955 (m), 904 (w), 874 (m), 851 (w), 802 (s), 760 (w), 724 (s), 703 (s), 650 (m), 615 (s) cm^{-1}; MS (MALDI, solvent-free): 866 ([M^+−3MeCN−2Zn−2PhH−2Me$_2$NNC(Me)NH$_2$]), 801 ([M^+−3MeCN−3Zn−2PhH−2Me$_2$NNC(Me)NH$_2$]), 745 ([M^+−3MeCN−3Zn−3PhH−2Me$_2$NNC(Me)NH$_2$]); elemental analysis calcd (%) for $C_{66}H_{99}N_{21}Zn_6$: C 50.20, H 6.32, N 18.63; found: C 50.12, H 6.36, N 18.52. For **3c**: Yield: 45%; m. p > 320°C; IR: $\tilde{\nu}=3320$ (s), 2484 (w), 2253 (w), 1567 (s), 1260 (s), 1242 (s), 1224 (m), 1175 (s), 1094 (s), 1010 (s), 959 (s),873 (m), 796 (s), 751 (m), 702 (w), 679 (m), 620 (s) cm^{-1}; MS (MALDI, solvent-free): 1026 ([M^+−Zn−Me$_2$NNC(Me)NH$_2$]); elemental analysis calcd (%) for $C_{24}H_{48}N_{18}Cl_6Zn_6$: C 24.15, H 4.05, N 21.13; found: C 24.24, H 4.17, N 21.03. For **3d**: Yield near quantitative (> 95%); m. p > 320°C; IR: $\tilde{\nu}=3330$ (m), 3175 (m), 2154 (s), 1541 (s), 1260 (s), 1209 (s), 1169 (s), 1094 (s), 1015 (s), 967 (s), 862 (m), 800 (m), 739 (m), 640 (w) cm^{-1}; MS (MALDI, solvent-free): 1067 ([M^+−Zn−Me$_2$NNC(Me)NH$_2$]), 1037 ([M^+−Zn−Me$_2$NNC(Me)NH$_2$−Et]), 1009 ([M^+−Zn−Me$_2$NNC(Me)NH$_2$−2Et]); elemental analysis calcd (%) for $C_{36}H_{90}N_{18}Zn_6$: C 37.03, H 7.77, N 21.60; found: C 36.96, H 7.93, N 21.53. For [ZnCl$_2$(NH$_2$NMe$_2$)$_2$]: Yield 47%; m. p ca. 220°C (decomp); IR: $\tilde{\nu}=3239$ (w), 3172 (w), 2361 (w), 2322 (w), 1593 (s), 1558 (w), 1540 (w), 1298 (m), 1261 (s), 1220 (w), 1163 (w), 1150 (m), 1088 (m), 1014 (s), 872 (w), 803 (s), 724 (m), 708 (m), 668 (w) cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 298 K): $\delta=4.21$ (bs, 4H, NH$_2$), 2.33 ppm (s, 12H, NMe$_2$). EI-MS: 136.5 ([M^+−2H$_2$NMe$_2$]), 124.6 ([M^+−2Cl−H$_2$NMe$_2$]); elemental analysis calcd (%) for $C_4H_{16}N_4Cl_2Zn$: C 18.73, H 6.29, N 21.85; found: C 18.79, H 5.43, N 21.98.

Acknowledgements

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Keywords: macrocycles · self-assembly · structure elucidation · zinc

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[4] Crystal data for **3a**: $C_{60}H_{60}F_{30}N_{18}Zn_6\cdot 6\,(C_2H_3N)$, $M_r=2241.80$, triclinic, space group $P\bar{1}$, colourless, $0.31\times 0.08\times 0.06$ mm^3, $a=13.430(3)$, $b=13.724(3)$, $c=13.924(3)$ Å, $\alpha=77.127(3)$, $\beta=69.501(3)$, $\gamma=71.711(3)°$, $V=2264.0(9)$ Å^3, $T=120(2)$ K, $Z=1$, $\rho_{\text{calcd}}=1.644$ g cm^{-3}, $\mu=1.681$ mm^{-1}, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monchromator, $\lambda=0.6897$ Å, 24895 reflections measured, 13540 unique ($R_{\text{int}}=0.0280$) which were used in all calculations. The final $wR2=0.1240$ (all data) and $R1=0.0414$ (for 5915 data with $F^2>2\sigma(F^2)$), 607 parameters, largest difference map features within ±0.970 e Å^{-3}. [16]

[5] Crystal data for **3a'**: $C_{60}H_{60}F_{30}N_{18}Zn_6\cdot 2\,(C_2H_3N)$, $M_r=2077.59$, triclinic, space group $P\bar{1}$, colourless, $0.18\times 0.07\times 0.02$ mm^3, $a=13.521(4)$, $b=13.569(4)$, $c=13.938(4)$ Å, $\alpha=100.378(4)$, $\beta=116.933(4)$, $\gamma=107.888(4)°$, $V=2010.1(10)$ Å^3, $T=150(2)$ K, $Z=1$, $\rho_{\text{calcd}}=1.716$ g cm^{-3}, $\mu=1.884$ mm^{-1}, data collected on a Bruker APEX 2 CCD diffractometer, $\lambda=0.71073$ Å, 15882 reflections measured, 7048 unique ($R_{\text{int}}=0.1094$) which were used in all calculations. The final $wR2=0.1273$ (all data) and $R1=0.0581$ (for 3475 data with $F^2>2\sigma(F^2)$), 561 parameters, largest difference map features within ±0.550 e Å^{-3}.[16]

[6] ZnPh$_2$ was prepared via BPh$_3$ in a manner analogous to (C$_6$F$_5$)$_2$Zn.

[7] Crystal data for **3b**: $C_{60}H_{90}N_{18}Zn_6\cdot 3\,(C_2H_3N)$, $M_r=1578.88$, trigonal, space group $R\bar{3}$, colourless, $0.15\times 0.14\times 0.06$ mm^3, $a=20.7641(19)$, $c=14.8997(14)$ Å, $V=5563.3(8)$ Å^3, $T=150(2)$ K, $Z=3$, $\rho_{\text{calcd}}=1.414$ g cm^{-3}, $\mu=1.962$ mm^{-1}, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monchromator, $\lambda=0.6904$ Å, 12594 reflections measured, 4056 unique ($R_{\text{int}}=0.0673$) which were used in all calculations. The final $wR2=0.1651$ (all data) and $R1=0.0562$ (for 3264 data with $F^2>2\sigma(F^2)$), 145 parameters, largest difference map features within ±0.737 e Å^{-3}. The molecule of MeCN is two-fold disordered.[16]

[8] A. Guerrero, D. L. Hughes, M. Bochmann, *Organometallics* **2006**, *25*, 1525.

[9] Crystal data for **3c**: $C_{24}H_{60}Cl_6N_{18}Zn_6\cdot C_7H_8$, $M=1297.95$, space group trigonal, $R\bar{3}m$, colourless, $0.90\times 0.88\times 0.53$ mm^3, $a=21.8080(11)$, $c=9.9724(11)$ Å, $V=4107.4(5)$ Å^3, $T=150(2)$ K, $Z=3$, $\rho_{\text{calcd}}=1.574$ g cm^{-3}, $\mu=2.92$ mm^{-1}, data collected on a Bruker APEX 2 CCD diffractometer, $\lambda=0.71073$ Å, 14410 reflections measured, 1270 unique ($R_{\text{int}}=0.0264$) which were used in all calculations. The final $wR2=0.0953$ (all data) and $R1=0.0328$ (for 1102 data with $F^2>2\sigma(F^2)$), 79 parameters, largest difference map features within ±1.143 e Å^{-3}. Platon squeeze[17] recovers sufficient electrons for one molecule of toluene (disordered over a symmetry element) per Zn$_6$ unit. The Zn and Cl atoms are ordered, the ligand exhibits two-fold disorder.[16]

[10] Crystal data for [ZnCl$_2$(NH$_2$NMe$_2$)$_2$]: $C_4H_{16}Cl_2N_4Zn$, $M_r=256.48$, space group monoclinic, $P2_1/n$, colourless, $0.53\times 0.02\times 0.02$ mm^3, $a=7.733(6)$, $b=8.342(6)$, $c=16.203(12)$ Å, $\beta=93.348(8)$, $V=1043.5(13)$ Å^3, $T=150(2)$ K, $Z=4$, $\rho_{\text{calcd}}=1.633$ g cm^{-3}, $\mu=2.818$ mm^{-1}, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monchromator, $\lambda=0.6904$ Å, 6451 reflections measured, 1488 unique ($R_{\text{int}}=0.1530$) which were used in all calculations. The final $wR2=0.1913$ (all data) and $R1=0.0740$ (for 1488 data with $F^2>2\sigma(F^2)$), 105 parameters, largest difference map features within ±1.468 e Å^{-3}.[16]

[11] Crystal data for **3d**: $C_{36}H_{90}N_{18}Zn_6$, $M_r=1167.48$, space group orthorhombic, $Pbca$, colourless, $0.92\times 0.37\times 0.36$ mm^3, $a=15.6487(4)$, $b=15.5532(4)$, $c=23.3257(6)$ Å, $V=5677.2(3)$ Å^3, $T=150(2)$ K, $Z=4$, $\rho_{\text{calcd}}=1.366$ g cm^{-3}, $\mu=2.535$ mm^{-1}, data collected on a Bruker SMART 1000 CCD diffractometer, $\lambda=0.71073$ Å, 47095 reflections measured, 6992 unique ($R_{\text{int}}=0.0212$) which were used in all calculations. The final $wR2=0.0814$ (all data) and $R1=0.0283$ (for 5915 data with $F^2>2\sigma(F^2)$), 292 parameters, largest difference map features within ±1.142 e Å^{-3}. Analysis of the voids in the structure with

Platon[17] reveals only 15 electrons per cell spread over four voids each with a volume of about 77 Å^3, thus there are very few, if any, solvent molecules in these voids.[16]

[12] Me,PhNN = C(Me)NH$_2$ was isolated from a "one-pot" synthesis starting from Me,PhNNH$_2$ and Et$_2$Zn using excess H$_2$O; our studies of Me,PhNNH$_2$ derived ring systems will be published separately.

[13] Crystal data for Me,PhNN=C(Me)NH$_2$, tetragonal polymorph: $C_9H_{13}N_3$, $M_r = 163.22$, space group tetragonal, $P4_32_12$, colourless, $0.30 \times 0.28 \times 0.24$ mm3, $a = 7.0680(4)$, $c = 37.975(4)$ Å, $V = 1897.1(3)$ Å^3, $T = 150(2)$ K, $Z = 8$, $\rho_{calcd} = 1.143$ g cm^{-3}, $\mu = 0.072$ mm^{-1}, data collected on a Bruker APEX 2 CCD diffractometer, $\lambda = 0.71073$ Å, 18083 reflections measured, 1346 unique ($R_{int} = 0.0490$) which were used in all calculations. The final $wR2 = 0.0776$ (all data) and $R1 = 0.0309$ (for 1183 data with $F^2 > 2\sigma(F^2)$), 118 parameters, largest difference map features within ± 0.130 e Å^{-3}. Crystal data for Me,PhNN = C(Me)NH$_2$, monoclinic polymorph: $C_9H_{13}N_3$, $M_r = 163.23$, space group monclinic, $C2/c$, colourless, $0.54 \times 0.12 \times 0.10$ mm^3, $a = 20.4094(16)$, $b = 9.1514(7)$, $c = 10.0458(8)$ Å, $\beta = 99.959(2)$, $V = 1848.0(3)$ Å^3, $T = 150(2)$ K, $Z = 8$, $\rho_{calcd} = 1.173$ g cm^{-3}, $\mu = 0.074$ mm^{-1}, data collected on a Bruker SMART 1000 CCD diffractometer, $\lambda = 0.71073$ Å, 7883 reflections measured, 2218 unique ($R_{int} = 0.0246$) which were used in all calculations. The final $wR2 = 0.1029$ (all data) and $R1 = 0.0407$ (for 1627 data with $F^2 > 2\sigma(F^2)$), 117 parameters, largest difference map features within ± 0.220 e Å^{-3}.[16]

[14] See for example, *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Elsevier, Amsterdam, **1996**.

[15] A search (23/10/06) of the Cambridge Structural data base on the backbone C$_2$NNC(C)NH$_2$ shows no hits for this type of hydrazone, though the motif does appear in a number of ring systems giving 19 hits. The following most closely resemble the type of hydrazone reported herein a) P. Prusiner, M. Sundaralingam, T. Ito, T. Sakurai, *Acta Crystallogr. Sect. B* **1976**, *32*, 853; b) M. Kimura, I. Okabayashi, N. Yasuoka, *Chem. Pharm. Bull.* **1984**, *32*, 318; c) M. Sbit, L. Dupont, O. Dideberg, M. Goblet, J. V. Dejardin, *Acta Crystallogr. Sect. C* **1988**, *44*, 909; d) R. M. Claramunt, P. Cozzini, P. Domiano, J. Elguero, I. Forfar, A. Fruchier, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1875; e) V. A. Makarov, V. A. Tafeenko, V. G. Granik, *Khim. Geterotsikl. Soedin.* **1998**, 1676; f) K. Martens, H. Dehne, H. Reinke, *Synthesis* **2001**, 696; g) X. L. Ren, C. Wu, F. Z. Hu, X. M. Zou, H. Y. Yang, *Chin. J. Chem.* **2004**, *22*, 194; h) J. Marek, Z. Travnicek, P. Cankar, *Acta Crystallogr. Sect. E* **2006**, *62*, o848.

[16] CCDC-671200, CCDC-671201, CCDC-671202, CCDC-671203, CCDC-671204, CCDC-671205, CCDC-671206, and CCDC-671207 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

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