Dimeric complexes of lithium and sodium forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure†‡

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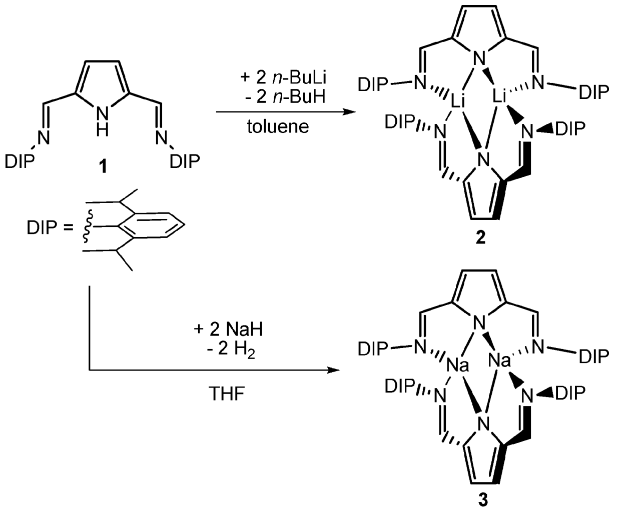
The reaction of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}-pyrrole (DIP$_2$-pyr)H with *n*BuLi and NaH resulted in the dimeric lithium and sodium compounds [(DIP$_2$-pyr)M]$_2$ (M = Li, Na). In the solid-state both compounds exhibit diamond-shaped M$_2$N$_2$ cores, in which the metal atoms are tetra-coordinated. The structures consist of four five membered rings forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure for each compound.

We and other groups recently reported that 2,5-bis(*N*-aryliminomethyl)pyrrolyls serve as unique monoanionic nitrogen ligands in coordination chemistry. Homoleptic and heteroleptic complexations were observed. The first complexes in this area were some actinide complexes in which the 2,5-bis(aryliminomethyl)pyrrole structural motif was part of a larger oligodentate macrocyclic ligand.[1–3] Later, some macrocyclic multinuclear nickel compounds were reported.[4,5] In 2000, Bochmann *et al.*[6] introduced the tridentate 2,5-bis(aryliminomethyl)pyrrolyl ligand in transition metal chemistry. Today aluminium,[7] group 4,[6] iron,[6] chromium,[8] copper,[9] and rare earth metal complexes[10–12] are known. Some of them had been used as catalysts for the polymerization of ε-caprolactone[10] and ethene,[6] and for the oligomerization of ethene and propene to linear and branched products.[6] In most of the cases the ligand binds in a tridentate fashion with the two Schiff-base nitrogen atoms and the pyrrolyl moiety onto the metal centers. In the few cases in which steric crowding is observed a didentate binding mode was also observed.

We were working for some time with the sterically very demanding ligand 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole, (DIP$_2$-pyr)H (**1**) (Scheme 1).[11,12] As reported earlier compound **1** was synthesized by condensation of pyrrole-2,5-dicarbaldehyde with 2,6-diisopropylaniline. Two pathways for the metal complex synthesis were established. The first one is an amine or alkane elimination reaction starting from a homoleptic amido complex such as [Ln{N(SiMe$_3$)$_2$}$_3$] or alkyl compounds such as AlMe$_3$. The second one is a salt metathesis reaction using the lithium[6,8,12] and potassium[11,12] derivatives of compound **1**. These alkaline metal salts of compound **1** have already been established as useful transfer reagents but have never been studied in detail. Herein we report on the synthesis and for the first time also on the solid-state structures of the lithium and the hitherto unknown sodium derivative of compound **1**. Both compounds form dimeric complexes in the solid-state.

Reaction of compound **1** with *n*BuLi in toluene resulted in the dimeric lithium compound [(DIP$_2$-pyr)Li]$_2$ (**2**) (Scheme 1).§ Compound **2**, which was reported earlier as a monomeric species,[8] was fully characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single crystal X-ray diffraction. Even though compound **2** is a dimer in the solid-state, only one set of signals is observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra. In the ^{1}H NMR one doublet at δ 1.18 ppm and clear septet at δ 3.22 ppm are observed for the isopropyl groups, indicating that the 2,6-diisopropylaniline moieties of the ligand can freely rotate in solution. This is in contrast to many other metal complexes ligated by (DIP$_2$-pyr)$^-$, in which the isopropyl CH$_3$ signals are split into two sets of doublets as a consequence of restricted rotation about the N–C$_{ipso}$ bond.[11,12] Only one signal for the imino N=CH moieties at δ 8.18 ppm is seen by using C$_6$D$_6$ as the solvent. In contrast a multiplet is observed in THF-d_8 at δ 7.95 ppm. We suggest that a symmetric coordination of the ligand is observed in an apolar solvent, whereas an interaction with the solvent takes place in THF-d_8.

Compound **2** crystallizes in the monoclinic space group $C2/c$ with two independent dimeric molecules in the unit cell (Fig. 1). Two ligands are coordinating two lithium atoms each by the pyrrolyl and the Schiff-base nitrogen atoms exhibiting a diamond-shaped Li$_2$N$_2$ core. The pyrrolyl unit is μ-coordinated



Scheme 1

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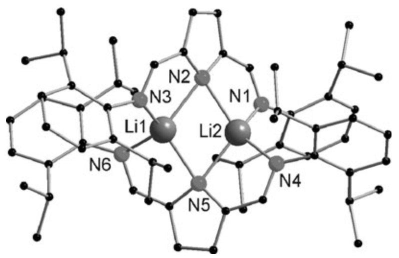

Fig. 1 Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Shown is only one of two independent molecules. Selected bond lengths [Å] or angles [°]: Li1–N2 2.1934(4), Li1–N3 2.0265(3), Li1–N5 2.2019(5), Li1–N6 2.0244(4), Li2–N1 2.0194(4), Li2–N2 2.1994(5), Li2–N4 2.0464(4), Li2–N5 2.1612(4), Li3–N7 2.0501(4), Li3–N8 2.1919(4), Li3–N10 2.0611(4), Li3–N11 2.2103(4), Li4–N8 2.1738(4), Li4–N9 2.0502(4), Li4–N11 2.1650(4), Li4–N12 2.0217(4), Li1–L2 2.5653(5), Li3–Li4 2.5587(5); N2–Li1–N3 86.663(12), N2–Li1–N6 130.540(14), N2–Li1–N5 107.574(15), N3–Li1–N5 138.780(15), N3–Li1–N6 114.43(2), N5–Li1–N6 85.814(13), N1–Li2–N2 86.007(12), N1–Li2–N4 116.83(2), N1–Li2–N5 131.918(15), N2–Li2–N4 133.36(2), N4–Li2–N5 86.209(12), N5–Li2–N2 108.823(15), N7–Li3–N10 117.73(2), N7–Li3–N8 86.221(12), N7–Li3–N11 133.565(15), N8–Li3–N10 133.301(15), N8–Li3–N11 107.184(15), N10–Li3–N11 85.318(12), N8–Li4–N9 86.085(12), N8–Li4–N11 109.486(15), N8–Li4–N12 131.839(15), N9–Li4–N11 131.731(15), N9–Li4–N12 117.56(2), N11–Li4N12 86.125(13).

in between the two lithium atoms. The whole structure consists of four five-membered rings forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure. This kind of structural motif is very rare in lithium chemistry and was to the best of our knowledge only reported three times beforehand.[13–15] The distance between the two lithium atoms is 2.5653(5) Å. In compound **2** both lithium atoms are distorted tetrahedral coordinated by the (DIP$_2$-pyr)$^-$ ligand. The bite angle of each metallacyclopentane ring is smaller than in an ideal tetrahedral geometry (*e.g.* N1–Li2–N2 86.007(12)°, N2–Li1–N3 86.663(12)°).

Reaction of compound **1** with sodium hydride in THF resulted after workup in the new dimeric sodium compound [(DIP$_2$-pyr)Na]$_2$ (**3**) (Scheme 1) as yellow crystals. As observed for compound **2** one set of signals is observed for the (DIP$_2$-pyr)$^-$ ligands in the ^{1}H and ^{13}C{^{1}H} NMR spectra showing a clearly resolved doublet at δ 1.22 ppm and a septet at δ 3.26 ppm for the isopropyl groups. In contrast to some lanthanide complexes no rotation around the N–C$_{\text{ipso}}$ bond is observed.[11,12] The symmetric coordination of the ligand is also supported by the fact that only one signal for the imino N=CH moieties at δ 7.98 ppm is seen.

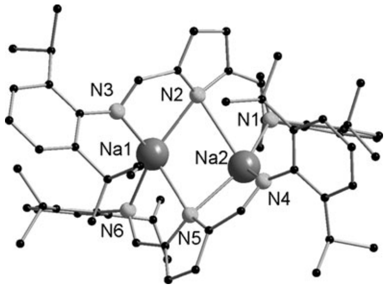

Fig. 2 Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: Na1–N2 2.451(3), Na1–N3 2.369(3), Na1–N5 2.513(3), Na1–N6 2.382(3), Na2–N1 2.413(3), Na2–N2 2.800(4), Na2–N4 2.404(3), Na2–N5 2.492(3), Na1–Na2 3.045(2); N2–Na1–N3 77.65(11), N2–Na1–N5 107.71(11), N2–Na1–N6 148.89(12), N3–Na1–N5 119.51(12), N3–Na1–N6 129.42(12), N5–Na1–N6 74.44(11), N1–Na2–N2 70.69(11), N1–Na2–N4 132.28(12), N1–Na2–N5 150.05(11), N2–Na2–N4 107.04(11), N2–Na2–N5 98.30(11), N4–Na2–N5 77.21(10).

The solid-state structure of compound **3** was established by single crystal X-ray diffraction. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ having two molecules of **3** and three molecules of toluene in the unit cell (Fig. 2). As observed for the lithium derivative **2**, compound **3** forms a dimeric structure with a diamond-shaped Na$_2$N$_2$ core in the solid-state. The whole structure again can be best described as four five-membered rings, which are fused together forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure. This kind of structural motif was to the best of our knowledge not described previously in the literature for sodium. The five-membered metallacycles are formed by pyrrolyl and the Schiff-base function, which chelate the sodium atoms. The pyrrole function of each ligand also bridges two sodium atoms, which have a distance of Na1–Na2 3.045(2) Å. The sodium atoms are distorted tetrahedral coordinated but the distortion is significantly larger than in compound **2**. This is a result of the larger ionic radius of the sodium ion compared to the lithium ion (*e.g.* N1–Na2–N2 70.69(11)°, N2–Na1–N3 77.65(11)°). The (DIP$_2$-pyr)$^-$ ligands are arranged almost perpendicular to each other. Even though lithium and sodium cations have a quiet different ionic radius, the structures of compound **2** and **3** are related but not isostructural. The bond valence sums indicate a closed coordination sphere for both compounds.[16]

In conclusion we have prepared the dimeric lithium and sodium compounds [(DIP$_2$-pyr)M]$_2$ (M = Li, Na) by a deprotonation reaction of 2,5-bis{*N*-(2,6-diisopropylphenyl)-iminomethyl}-pyrrole (DIP$_2$-pyr)H with *n*BuLi and NaH, respectively. In the solid-state both compounds exhibit a diamond-shaped M$_2$N$_2$ core, in which the metal atoms are tetra coordinated. The structures consist of four five membered rings forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure for each compound. This kind of structural motif is very rare for lithium and hitherto unknown for sodium compounds.

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References

§ *Preparation of* **2**: (DIP$_2$-pyr)H (**1**) (883 mg, 2.00 mmol) was dissolved in toluene (20 ml) and cooled to −78 °C. *n*BuLi (2.5 M, 0.8 ml, 2.04 mmol) was added slowly and the solution was stirred for 3 h at ambient temperature. The solvent was evaporated *in vacuo* and the residue was washed with pentane. The product was dried *in vacuo* giving a pale yellow powder. Yield: 655 mg, 1.46 mmol, 73%. Single crystals were obtained by crystallization from hot toluene. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ = 1.18 (d, 24H, CH(CH_3), $J_{\text{H,H}}$ = 6.9 Hz), 3.22 (sept, 4H, CH(CH$_3$), $J_{\text{H,H}}$ = 6.9 Hz), 6.71 (m, 2H, 3,4-pyr), 6.89–7.03 (m, 2H, *p*-Ph), 7.10–7.13 (m, 4H, Ph), 7.95 (m, 2H,

N=CH) ppm. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C):[12] δ = 1.05 (d, 24H, CH(CH_3)$_2$, $J_{H,H}$ = 6.4 Hz), 3.16 (sept, 4H, CH(CH_3)$_2$, $J_{H,H}$ = 6.4 Hz), 6.90 (s, 2H, 3,4-pyr), 7.31 (m, 6H, Ph), 8.18 (s, 2H, N=CH). ^{13}C{^{1}H} NMR (THF-d_8, 100.4 MHz, 25 °C): δ = 24.1 (CH(CH_3)$_2$), 28.1 (CH(CH_3)$_2$), 117.2 (3,4-pyr), 123.2 (Ph), 123.7 (Ph), 139.5 (2,5-pyr), 144.3 (Ph), 151.3 (Ph), 160.5 (N=CH) ppm. ^{7}Li{^{1}H} NMR (C_6D_6, 400 MHz, 25 °C): 3.6 ppm. (**2**) $C_{30}H_{38}N_3Li$ (447.58): calcd C, 80.50, H, 8.56, N, 9.39%; found C, 80.09, H, 8.54, N, 9.09%. *Preparation of* **3**: THF (40 ml) was added to a mixture of (DIP$_2$-pyr)H (**1**) (883 mg, 2.00 mmol) and NaH (53 mg, 2.20 mmol) and the reaction mixture was refluxed for 4 h. After cooling to ambient temperature the excess of NaH was filtered off and the solvent was removed *in vacuo*. The residue was washed with pentane and dried *in vacuo*, to obtain the product as pale yellow powder. Yield: 735 mg, 1.59 mmol, 79%. Single crystals were obtained by crystallisation from hot toluene. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ = 1.22 (d, 24H, CH(CH_3), $J_{H,H}$ = 6.9 Hz), 3.26 (sept, 4H, CH(CH_3), $J_{H,H}$ = 6.9 Hz), 6.76 (s, 2H, 3,4-pyr), 6.99–7.04 (m, 2H, *p*-Ph), 7.12–7.15 (m, 4H, Ph), 7.98 (s, 2H, N=CH) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.4 MHz, 25 °C): δ = 23.8 (CH(CH_3)$_2$), 28.1 (CH(CH_3)$_2$), 117.0 (3,4-pyr), 122.9 (Ph), 123.2 (Ph), 139.2 (2,5-pyr), 144.5 (Ph), 152.4 (Ph), 160.5 (N=CH) ppm. (**3**) $C_{30}H_{38}N_3Na$ (463.63): calcd C, 77.72, H, 8.26, N, 9.06%; found C, 77.71, H, 8.43, N, 8.52%. *Crystal data for* **2**: $C_{60}H_{76}Li_2N_6$, M = 895.07, monoclinic, space group $C2/c$ (no.15), a = 77.222(15) Å, b = 15.608(3) Å, c = 18.684(4) Å, β = 96.85(3)°, V = 22 359(8) Å^3, T = 200(2) K, Z = 16, μ(MoKα) = 0.062 mm^{-1}, 45 705 reflections measured, 18 020 independent reflections (R_{int} = 0.0924). The final R_1 values were 0.0910 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.2499 (all data). The goodness of fit on F^2 was 0.995. CCDC 753230. *Crystal data for* **3**: $C_{70\cdot 50}H_{88}N_6Na_2$ (**3**·1.5 toluene) M = 1065.45, triclinic, space group $P\bar{1}$ (no.2), a = 11.205(2) Å, b = 12.304(3) Å, c = 24.047(5) Å, α = 83.20(3)°, β = 80.33(3)°, γ = 80.59(3)°, V = 3210.2(11) Å^3, T = 200(2) K, Z = 2, μ(MoKα) = 0.076 mm^{-1}, 26 156 reflections measured, 12 534 independent reflections (R_{int} = 0.0724). The final R_1 values were 0.0699 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1976 (all data). The goodness of fit on F^2 was 1.003. CCDC 753231.

1 J. L. Sessler, A. E. V. Gorden, D. Seidel, S. Hannah, V. Lynch, P. L. Gordon, R. J. Donohoe, C. D. Tait and D. W. Keogh, *Inorg. Chim. Acta*, 2002, **341**, 54–70.

2 J. L. Sessler, T. D. Mody, M. T. Dulay, R. Espinoza and V. Lynch, *Inorg. Chim. Acta*, 1996, **246**, 23–30.

3 J. L. Sessler, T. D. Mody and V. Lynch, *Inorg. Chem.*, 1992, **31**, 529–531.

4 A. Y. Chernyadyev, Y. A. Ustynyuk, G. G. Aleksandrov, A. A. Sidorov, V. M. Novotortsev, V. N. Ikorskii, S. E. Nefedov, I. L. Eremenko and I. I. Moiseev, *Russ. Chem. Bull.*, 2001, **50**, 1336–1338.

5 A. Y. Chernyady′′ev, Y. A. Ustynyuk, O. V. Yazev, E. A. Kataev, M. D. Reshetova, A. A. Sidorov, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, S. E. Nefedov, I. L. Eremenko and I. I. Moiseev, *Russ. Chem. Bull.*, 2001, **50**, 2445–2450.

6 D. M. Dawson, D. A. Walker, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2000, 459–466.

7 Y. Matsuo, H. Tsurugi, T. Yamagata, K. Tani and K. Mashima, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1965–1968.

8 B. A. Salisbury, J. F. Young, G. P. A. Yap and K. H. Theopold, *Collect. Czech. Chem. Commun.*, 2007, **72**, 637–648.

9 B. B. Wayland, J. A. Charlton and Y. Ni, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1999, **40**, 307–308.

10 Y. Matsuo, K. Mashima and K. Tani, *Organometallics*, 2001, **20**, 3510–3518.

11 N. Meyer, J. Jenter, P. W. Roesky, G. Eickerling and W. Scherer, *Chem. Commun.*, 2009, 4693–4695.

12 N. Meyer, M. Kuzdrowska and P. W. Roesky, *Eur. J. Inorg. Chem.*, 2008, 1475–1479.

13 P.-C. Kuo, J.-C. Chang, W.-Y. Lee, H. M. Lee and J.-H. Huang, *J. Organomet. Chem.*, 2005, **690**, 4168.

14 S. J. Trepanier and S. Wang, *Organometallics*, 1993, **12**, 4207.

15 G. L. J. vanVliet, F. J. J. deKanter, M. Schakel, G. W. Klumpp, A. L. Spek and M. Lutz, *Chem.–Eur. J.*, 1999, **5**, 1091.

16 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192–197.