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New directions in amido–transition metal chemistry: the preparation and reaction of mixed amino–amido macrocyclic ligands

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The synthesis and reactivity of cyclam (1,4,8,11-tetraazacyclotetradecane) in which the donor atoms were amino–amido or exclusively amido groups with $ZrCl_4(thf)_2$ (thf = tetrahydrofuran) are described.

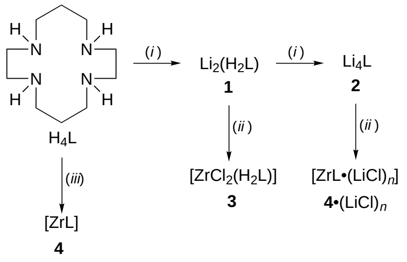
Polyaza macrocycles, though ligands *par excellence*, in co-ordination chemistry, have rarely been used in their deprotonated forms as amido ligands[1,2] or as ancillary ligands in organometallic chemistry for supporting organic functionalities. This is particularly surprising in light of the attention that has been addressed to the synthesis and use of amido and polyamido ligands in early-transition-metal chemistry.[3] Such macrocyclic polyamines have, in principle, a number of appealing advantages: (1) the variety and type of known ligands is vast and as a consequence it is possible to fine tune the properties of the target complex using variants such as the number and type of donor atoms, ring size and structural variations such as C or N alkylation; (2) by varying the number of amine *vs.* amido donors one is able to alter the overall charge of the molecule. This is a particularly useful feature which allows the preparation of organometallic fragments with sites that can be functionalised; (3) the macrocyclic effect should play an important role in the stabilisation of any resulting organometallic fragments.

We wish to illustrate these principles with the tetraaza macrocycle cyclam (1,4,8,11-tetraazacyclotetradecane H_4L)[4] and show how, in the appropriate form, it can be successfully reacted with early transition metals, illustrated here by zirconium(IV).

Scheme 1 outlines the synthesis and reactivity of the amido forms of H_4L. Addition of 2 or 4 equivalents of LiBu to a tetrahydrofuran (thf) solution of the amine gave the soluble dianionic $Li_2(H_2L)$ **1**† and insoluble tetraanionic Li_4L **2**‡ species respectively. Proton NMR spectra of the two species were identical and suggested a symmetrical complex with the two lithium cations most probably co-ordinated on opposite sides of the macrocycle,§ though the actual species in solution may be a higher order aggregate. This arrangement has been verified in the solid state for **1**, and is shown along with the most relevant parameters in Fig. 1.¶

The structure consists of two Li cations which interact with opposite sides of the N_4 core; the tetrahedral co-ordination sphere of each cation being provided by one amino and two adjacent amido nitrogen atoms and through the O(1) oxygen atom from one thf molecule. The Li–N bond distances fall in the usual range; those involving the N(2) amido nitrogen atoms [average 1.981(8) Å] being a little, but significantly, shorter than that involving the amino N(1) atom.

Both amido compounds **1** and **2** react cleanly with a number of transition metals. Here we illustrate their reaction with $ZrCl_4{\cdot}2thf$,‖ which was best achieved *in situ* and led, in both cases, to very soluble products. The LiCl by-product was easily removed in the case of compound **3** but could not be removed for **4**. Compound **4** however could be prepared salt free *via* $[Zr(NMe_2)_4]$.



Scheme 1 (*i*) 2LiBu thf, room temperature (r.t.); (*ii*) $ZrCl_4{\cdot}2thf$, thf, r.t.; (*iii*) $[Zr(NMe_2)_4]$ toluene, r.t.

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† Preparation of compound **1**. To a stirred slurry of cyclam (10 g, 50 mmol) in thf (500 cm^3) was added, over 30 min, a solution of LiBu (58.8 cm^3, 1.70 M in hexane). During this time the solid dissolved to give a light yellow solution. The mixture was stirred for a further 60 min and filtered, and the filtrate taken to dryness. The resulting cream-light tan coloured solid was triturated with hexane (300 cm^3), collected by filtration and dried *in vacuo* (75–90%). Crystals suitable for X-ray analysis were grown from dilute solutions of thf and were very susceptible to desolvation (Found: C, 56.40; H, 10.45; N, 25.10. $C_{10}H_{22}Li_2N_4$ requires C, 56.65; H, 10.45; N, 26.45%). ^1H NMR (C_5D_5N, 200 MHz): δ 3.79 (t, 4 H), 3.58 (t, 4 H), 3.00 (t, 4 H), 2.90 (t, 4 H) and 2.00 (br s, 4 H). Different batches did show residual thf (0–0.6 mol equivalent); no attempt was made to remove this solvent. IR (Nujol)/cm^{-1}: 3276s, 2669s, 1324s, 1151s, 1109s and 538m.

‡ Preparation of compound **2**. The deprotonated compound was prepared in a similar manner to **1** except that 4 equivalents of LiBu were added. The resulting pyrophoric off-white solid analysed as follows (Found: C, 57.80; H, 9.80; N, 15.25. $C_{10}H_{20}Li_4N_4{\cdot}1.5thf$ requires C, 57.85; H, 9.70; N, 16.90%). ^1H NMR (C_5D_5N, 200 MHz; sparingly soluble): δ 4.03 (t, 4 H), 3.83 (m, 10 H), 3.24 (t, 4 H), 3.12 (t, 4 H), 2.25 (br s, 4 H) and 1.80 (m, 6 H). IR (Nujol)/cm^{-1}: 2669m, 1097m. Batches containing 3 mol equivalents of thf were also observed as evidenced by ^1H NMR.

§ In the case of compound **2** this most probably does not represent the bulk of the reaction due to the insolubility of the product.

¶ Crystal data: $C_{10}H_{22}Li_2N_4{\cdot}2C_4H_8O$ **1**, $M = 356.4$, monoclinic, space group $P2_1/c$, $a = 9.237(2)$, $b = 14.789(3)$, $c = 8.729(2)$ Å, $\beta = 117.84(1)°$, $U = 1054.4(4)$ Å^3, $Z = 2$, $D_c = 1.123$ g cm^{-3}, $F(000) = 392$, Cu-Kα ($\lambda = 1.541\ 78$ Å), $\mu = 5.31$ cm^{-1}, crystal dimensions 0.12 × 0.44 × 0.82 mm. The structure was solved by direct methods using SHELXS 86[6] and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from a Fourier-difference map and introduced as fixed contributors in the last stage of refinement ($U_{iso} = 0.05$ Å^2). For 821 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 133$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140°$) and corrected for absorption the final R is 0.053 ($wR2 = 0.161$ for the 1373 reflections having $I > 0$ used in the refinement).

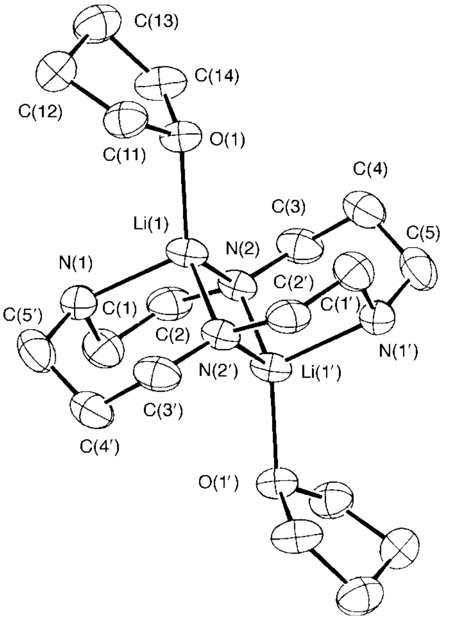

Fig. 1 An ORTEP[5] drawing of complex **2** (50% probability ellipsoids). Selected bond distances (Å) and angles (°): Li(1)–O(1) 1.965(5), Li(1)–N(1) 2.036(7), Li(1)–N(2) 1.986(8), Li(1)–N(2′) 1.977(7); N(2)–Li(1)–N(2′) 106.9(3), N(1)–Li(1)–N(2′) 99.9(3), N(1)–Li(1)–N(2) 89.8(3). Prime denotes a transformation of $-x, 1-y, -z$

The crystal structure of compound **3** is shown in Fig. 2 along with the relevant structural parameters.** The zirconium atom has an octahedral co-ordination environment with the two chloride atoms occupying *cis* sites. The Zr–N(1) and Zr–N(4) bond distances [average value 2.074(7) Å] are in agreement with the values reported in the literature for Zr–N (amide) distances and, as expected, are remarkably shorter than the distances involving the amino N(2) and N(3) nitrogen atoms distances [average value 2.362(8) Å].[7] The Zr–Cl bonds [average value 2.507(2) Å] fall in the upper range of values observed for six-co-ordinated zirconium complexes.

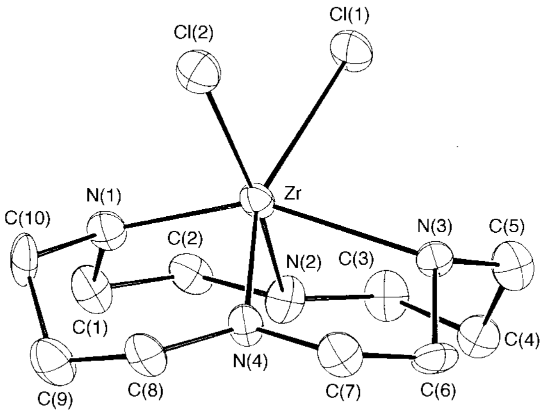

Fig. 2 An ORTEP drawing of complex **3** (50% probability ellipsoids). Selected bond distances (Å) and angles (°): Zr–Cl(1) 2.523(2), Zr–Cl(2) 2.490(2), Zr–N(1) 2.073(7), Zr–N(2) 2.347(8), Zr–N(3) 2.377(6), Zr–N(4) 2.075(6); N(3)–Zr–N(4) 74.6(2), N(2)–Zr–N(4) 99.3(3), N(2)–Zr–N(3) 80.5(2), N(1)–Zr–N(4) 91.4(3), N(1)–Zr–N(3) 149.4(3), N(1)–Zr–N(2) 75.1(3), Cl(1)–Zr–Cl(2) 89.3(1)

These compounds exemplify a new direction in the use of amido ligands and, in particular, in the form of a macrocycle. The ability to alter the charge of the ligand by altering the amido–amine ratio is particularly appealing. This was demonstrated in their reaction with zirconium(IV). In the case of compound **3** two *cis* sites capable of being functionalised are left for subsequent reactivity. We believe that this type of fragment will be a good 'non Cp_2M-' ($Cp = \eta$-C_5H_5) candidate because, unlike the related organometallic chemistry of [(tmtaa)ZrR_2] (R = Me or $PhCH_2$; H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyl-dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine), competing *intra* and *inter* alkyl migration is not possible.[8] Our chemistry with compound **4** centres on its ability to act as a carrier of alkali metals in non-polar solvents, indeed this was partly alluded to above.

Acknowledgements

We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-40268.94) for financial support.

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Received 12*th May* 1997; *Communication* 7/03263C

|| Preparation of compound **3**. To a stirred slurry of cyclam (5.0 g, 25.0 mmol) in thf (300 cm^3) was added, over 30 min, a solution of LiBu (29.4 cm^3, 1.70 M) in hexane. The solution was stirred for 60 min, filtered, and to the resulting light brown solution was added solid $ZrCl_4$·2thf (9.43 g, 25.0 mmol). The mixture was then left stirring for 4 h to finally give a red-brown cloudy solution. The mixture was filtered and the solvent removed *in vacuo*. Hexane (200 cm^3) was added to aid transfer to an extraction filter and the brown solid extracted with dichloromethane (200 cm^3, *ca.* 1 h, 55 °C) to give a red-brown solution and a pale brown solid left on the filter. The filtrate was taken to dryness and the resulting pale brown solid washed with hexane (100 cm^3) and dried *in vacuo* (60–75%) (Found: C, 33.40; H, 6.20; N, 14.50. $C_{10}H_{22}Cl_2N_4Zr$ requires C, 33.20; H, 6.15; N, 15.55%). ^1H NMR (CD_2Cl_2, 200 MHz): δ 4.10–2.60 and 2.15–1.50 (complex CH_2 region). This spectrum is more simple, though still complex, after fractional crystallisation. X-Ray quality crystals were obtained at −20 °C (2 weeks) after 2 recrystallisations in pyridine.

** Crystal data: $C_{10}H_{22}Cl_2N_4Zr\cdot 1.5C_5H_5N$ **3**, $M = 479.1$, orthorhombic, space group $P2_12_12$, $a = 11.841(3)$, $b = 19.002(4)$, $c = 9.443(3)$ Å, $U = 2124.7(10)$ Å^3, $Z = 4$, $D_c = 1.498$ g cm^{-3}, $F(000) = 988$, Cu-Kα ($\lambda = 1.541\,78$ Å), $\mu = 67.72$ cm^{-1}, crystal dimensions 0.10 × 0.17 × 0.48 mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from a Fourier-difference map and introduced as fixed contributors in the last stage of refinement ($U_{iso} = 0.05$ Å^2). For 1701 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 133$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140°$) and corrected for absorption the final R is 0.043 ($wR2 = 0.119$ for the 2133 reflections having $I > 0$ used in the refinement). Since the space group is polar, the crystal chirality was tested by inverting all the coordinates ($x, y, z \longrightarrow -x, -y, -z$) and refining to convergence again. The resulting R values ($R = 0.048$, $wR2 = 0.133$) indicated the original choice should be considered the correct one. All calculations were carried out on a Quansan Personal Computer equipped with an Intel Pentium processor. CCDC reference number 186/585.