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Syntheses and crystal structures of lithium and niobium complexes containing a new type of monoanionic "scorpionate" ligand†

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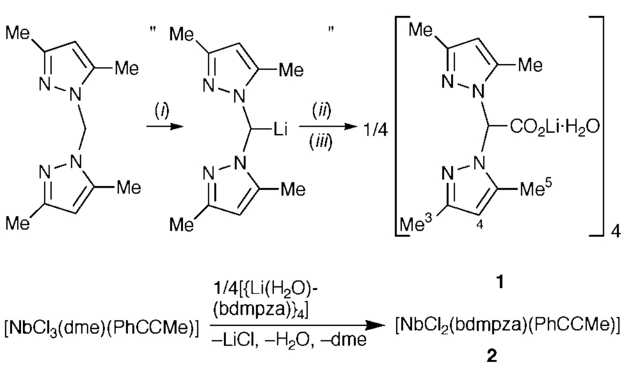
The synthesis of a novel lithium compound [{Li(H_2O)(bdmpza)}$_4$] [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate], containing a new "scorpionate" ligand, and its reaction with a niobium complex to give [$NbCl_3$(bdmpza)(PhC≡CMe)] have been reported.

Since the initial development of tris(pyrazolyl) borate or "scorpionate" ligands by Trofimenko in the late 1960's, a significant number of complexes of most metals of the periodic table have been prepared with these ligands.[1] As a result of our research in the field of niobium complexes with Tp or Tp* ligands [Tp = hydridotris(pyrazol-1-yl)borate or Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate], some of us reported the preparation of several complexes of the type TpNb(Cl)$_2$(RC≡CR′) (R = Ph, R′ = Me) or Tp*Nb(O)(Cl)(OR) (R = Me, Et).[2] We are now interested in the preparation of new facially-coordinating and monoanionic ligands, also called "scorpionate" ligands, with pyrazole rings in order to test their coordinative ability towards early transition metal centres. With this aim in mind, we have developed a synthetic route in order to isolate a useful lithium compound containing a new class of tridentate mixed functionalized ligand as a precursor for the introduction of this ligand into transition metal complexes. This ligand is related to the tris(pyrazolyl)methane ligand,[3] but with one of the pyrazole groups replaced by a carboxylate group. Thus, a mixture of a chilled (−70 °C) solution of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[4] in THF and 1 equiv of Bu^{n}Li, was treated with CO_2. This reaction gave rise to the lithium carboxylate compound **1** as an air-stable white solid in good yield (96%) after the appropriate work-up (see Scheme 1). Although the reaction was carried out under extreme anhydrous experimental conditions, the presence of adventitious moisture in the reaction mixture in the work-up procedure was probably responsible for the presence of the coordinated water molecule.

Compound **1** was characterized spectroscopically. The ^{1}H NMR spectrum of **1** shows four singlets, which are assigned to CH, H^4, Me^3 and Me^5 of the pyrazolyl rings. However, the signal corresponding to the H_2O was not observed in the spectrum. The ^{13}C-{H} NMR spectrum exhibits only one set of resonances, as would be expected for the presence of two equivalent pyrazolyl rings in the molecule. The more deshielded signal at δ 164.7 corresponds to the CO_2^- group. Finally, the ^{7}Li NMR spectrum exhibits a singlet at δ 1.50 for the lithium atom. The mass spectrum (FAB) of **1** indicates a tetranuclear formulation,‡ which was corroborated by means of an X-ray crystal structure determination.§ The structure of **1** is represented in Fig. 1. The complex consists of tetrameric units, with crystallographic C_2 symmetry, with a cubane-like[5] array in which the vertices are alternately occupied by four Li atoms and four bridging carboxylate groups. The two independent "scorpionate" ligands act in a tridentate fashion, bridging three Li atoms through the two oxygen atoms of the carboxylate and a nitrogen atom of a pyrazolyl ring. Each Li atom has a distorted tetrahedral coordination, binding two oxygen atoms from adjacent carboxylate groups, a nitrogen atom from a pyrazolyl ring and an oxygen atom from a water molecule. The oxygen atoms of each bridging carboxylate group are coordinated in a different manner to the lithium atoms, one with a normal geometry and bond distance [C2–O2–Li1* = 117.9(2)°, O2–Li1* = 1.934(4) Å; C2′–O1′–Li2 = 121.8(2)°, Li2–O1′ = 1.904(4) Å] and the other with a significant π bonding character and noticeable shortening of the bond distance [Li1–O1–C2 = 155.2(2)°, Li1–O1 = 1.877(4) Å; C2′–O2′–Li2* = 149.1(2)°, O2′–Li2* = 1.859(4) Å]. The Li–N bond lengths are longer than the Li–O ones and the Li1 and Li2 atoms are out of the mean plane of the coordinated pyrazolyl rings by 1.281(4) and 1.064(4) Å, respectively. Only one of the two pyrazolyl radicals of the "scorpionate" ligands is N-coordinated, so the *a* carbon atoms become chiral. However, in the tetramer both *R* and *S* configurations are present and the whole complex is therefore achiral (*meso* diastereoisomer).



Scheme 1 Summary of reactions leading to the compounds **1** and **2**. Reagents and conditions: (*i*) Bu^{n}Li, THF, −70 °C, 45 min under atmosphere of dry nitrogen, (*ii*) CO_2, THF, 0 °C, 1 h under atmosphere of dry nitrogen, (*iii*) crystallization from THF–hexane.

The stability and structure of **1** make it an appropriate precursor for the synthesis of new niobium(III) complexes containing the scorpionate ligand. Thus, the lithium compound **1** reacts at room temperature, in a 1 : 1 molar ratio (Scheme 1), with the complex [$NbCl_3$(dme)(PhC≡CMe)][6] (dme = 1,2-dimethoxyethane) in THF to give, after the appropriate work-up, the complex [$NbCl_2$(bdmpza)(PhC≡CMe)] **2** [bdmpza =

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3537/

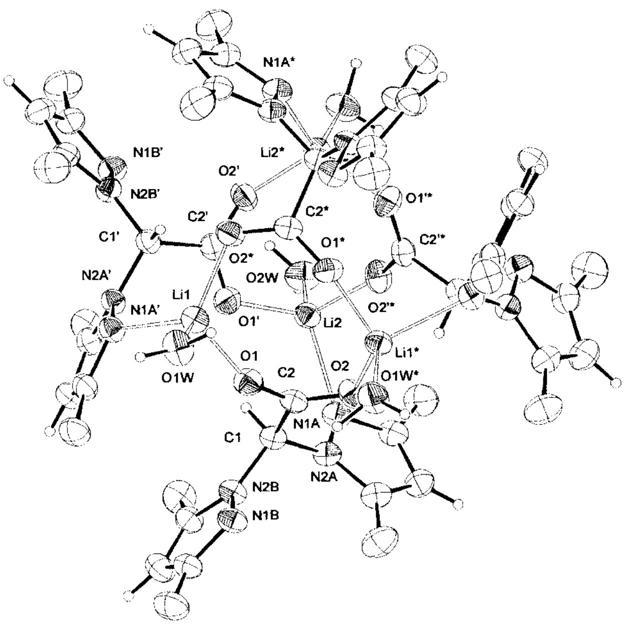

Fig. 1 View of complex **1** showing the tetrameric unit. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Li–O1 1.877(4), Li1–O1W 1.929(4), Li1–N1A′ 2.156(4), Li1–O2* 1.934(4), Li2–O1′ 1.904(4), Li2–O2W 1.929(4), Li2–N1A 2.163(4), Li2–O2′* 1.859(4), C2–O1 1.238(3), C2–O2 1.238(3), C2′–O1′ 1.250(3), C2′–O2′ 1.233(3); O1–C2–O2 128.4(2), O1′–C2′–O2′ 128.2(2), O1–Li1–O1W 106.5(2), O1–Li1–O2* 116.1(2), O1W–Li1–O2* 107.4(2), O1–Li1–N1A′ 99.0(2), O1W–Li1–N1A′ 112.6(2), O2*–Li1–N1A′ 115.0(2), O2′*–Li2–O1′ 115.1(2), O2′*–Li2–O2W 104.2(2), O1′–Li2–O2W 107.9(2), O2′*–Li2–N1A 100.2(2), O1′–Li2–N1A 113.1(2), O2W–Li2–N1A 116.0(2). Symmetry operator * $1 - x$, y, $3/2 - z$.

bis(3,5-dimethylpyrazol-1-yl)acetate], which was isolated as an orange solid.

The ^{1}H NMR spectrum of this complex exhibits two resonances for each of the H^4, Me^3 and Me^5 pyrazole protons, indicating that the two pyrazolyl rings from the bdmpza ligand are non-equivalent. These results agree with an octahedral structural disposition where the two pyrazolyl rings are located in *cis* and *trans* positions with respect to the alkyne ligand. In addition, the ^{13}C-{H} NMR spectrum of complex **2** exhibits two resonances for each of the different pyrazole carbon atoms (C^3, C^4, C^5, Me^3, Me^5). The more deshielded signal at δ 161.8 of the bdmpza ligand corresponds to the CO$_2^-$ group. The ^{13}C NMR resonances for the sp carbon atoms of the alkyne ligand appear at *ca.* δ 240, indicating that the alkyne ligand behaves as a four-electron donor.[7] This asymmetrical structural disposition means that the niobium is a chiral centre giving rise to two enantiomers which cannot be distinguished by means of NMR spectroscopy. However, we have confirmed the presence of these two enantiomers by addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of **2**. This process gives rise to the appearance in the ^{1}H NMR spectrum of two signals for each proton that are due to the two diastereoisomers from the corresponding two enantiomers.

In order to confirm the proposed structure for this complex, an X-ray crystal structure analysis was carried out.§ The geometry around the niobium atom is approximately octahedral with the metal atom surrounded by an N,N,O-coordinated "scorpionate" ligand, an alkyne and two chloride ligands. In the solid state, due to the centrosymmetric space group, both enantiomers are present and one of them, namely *OC*-6-32-C, is depicted in Fig. 2. The Nb atom is displaced by 0.3210(5) Å from the mean equatorial plane passing through Cl1, Cl2, N1B, O1 [maximum deviation 0.029(4) Å for N1B] towards the alkyne C3–C4 bond, whose projection onto the mean plane mentioned above is such as to bisect the N1B–Nb–O1 angle. The orientation of the alkyne C≡C triple bond is similar to that found in [TpNbCl$_2$(PhC≡CMe)][2] and in [Tp*NbCl$_2$(PhC≡CMe)],[8] as well as in other octahedral alkyne

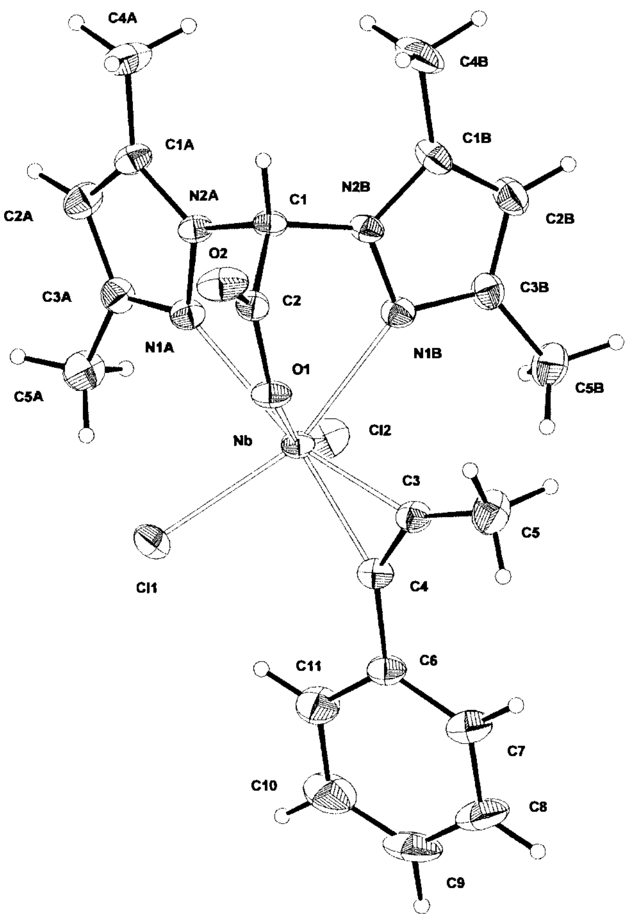

Fig. 2 Structure of **2** (30% probability ellipsoids). Selected bond lengths (Å) and angles (°): Nb–N1A 2.377(4), Nb–N1B 2.263(3), Nb–O1 2.098(3), Nb–C3 2.053(5), Nb–C4 2.055(4), Nb–Cl1 2.404(1), Nb–Cl2 2.377(1), C3–C4 1.293(5), C2–O2 1.209(5), C2–O1 1.295(5); N1A–Nb–N1B 78.6(1), N1A–Nb–O1 80.3(1), N1B–Nb–O1 78.4(1), O1–Nb–Cl2 159.0(1), N1B–Nb–Cl1 159.3(1), N1B–Nb–Cl2 85.8(1), O1–Nb–Cl1 87.2(1), Cl1–Nb–Cl2 104.03(5), N1A–Nb–Cl1 84.5(1), N1A–Nb–Cl2 83.2(1), N1A–Nb–C3 158.6(1), N1A–Nb–C4 164.5(1), C3–Nb–C4 36.7(2), C4–C3–C5 142.9(5), C3–C4–C6 142.8(5), Nb–C3–C5 145.3(3), Nb–C4–C6 145.6(3), O1–C2–O2 124.5(4), Nb–O1–C2 128.4(3).

complexes of niobium, for example: [NbCl$_3$(PhC≡CPh)(THF)$_2$], [NbCl$_3$(PhC≡CMe)(THF)$_2$], [NbCl$_4$(PhC≡CPh)(THF)]$^-$.[9] The phenyl group of the alkyne points towards the chlorine atoms, whereas in the aforementioned Tp and Tp* niobium complexes it is directed to the opposite side. The planar NbC5C3C4C6 moiety is practically orthogonal to the mean equatorial plane [dihedral angle: 89.06(7)°]. The metal–carbon bond lengths [2.053(5), 2.055(4) Å], as well as the alkyne bond length [1.293(5) Å], are similar to those found in the compounds mentioned above. The bond lengths indicate the existence of an M–C single bond and a C–C bond order greater than 2.[9,10] The *trans* influence of the alkyne bond is observed in all the complexes considered. The complexes are joined to give a dimeric unit by two weak centrosymmetric hydrogen bonds C1–H1 ··· O2 ($1 - x$, $-y$, $-z$).

In conclusion, we have explored a method for the synthesis of a novel lithium compound containing a new scorpionate ligand. This compound is an excellent precursor for the introduction of this ligand in transition metal complexes. This has been confirmed by reaction with a niobium complex. We are extending our work to include the coordination chemistry of this new ligand with other oxophilic metal centres and in the preparation of new related lithium compounds using the synthetic route described.

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Notes and references

‡ Selected data. **1**: ^{1}H NMR (DMSO, 295 K), δ 6.35 (s, 1 H, CH), 5.72 (s, 2 H, H^4), 2.03 (s, 6 H, Me^3), 2.25 (s, 6 H, Me^5). ^{13}C-{^{1}H} (DMSO), δ 73.9 (s, CH), 140.1 (s, C^3), 105.1 (s, C^4), 145.2 (s, C^5), 11.5 (s, Me^3), 13.4 (s, Me^5), 164.7 (s, CO_2^-). ^{7}Li NMR (DMSO), δ 1.50 (s). IR (Nujol mull), 1557 ν(C=N), 1651 $\nu_{as}(CO_2^-)$, 1461 $\nu_s(CO_2^-)$ cm^{-1}. Mass spectrum (FAB (*m*/*z* assignment, % intensity): 769 [$Li_4(bdmpza)_3$], 20; 515 [$Li_3(bdmpza)_2$], 19; 261 [$Li_2(bdmpza)$], 100. Analysis for $C_{48}H_{68}Li_4N_{16}O_{12}$ found (calc.): C, 52.64 (52.94); H, 6.46 (6.28); N, 20.23 (20.58%). **2**: ^{1}H NMR (CD_2Cl_2, 295 K), δ 6.78 (s, 1 H, CH), 6.12 (s, 1 H, H^4), 6.10 (s, 1 H, H$^{4'}$), 1.93 (s, 3 H, Me^3), 2.60 (s, 3 H, Me$^{3'}$), 2.51 (s, 3 H, Me^5), 2.55 (s, 3 H, Me$^{5'}$), 7.49–7.39 (m, 5 H, PhC≡), 3.25 (s, ≡CMe). ^{13}C-{^{1}H} (CD_2Cl_2), δ 68.1 (s, CH), 155.1, 154.8, 142.2, 141.8 (all s, C$^{3\text{ or }3'}$ or C$^{5\text{ or }5'}$), 109.4, 109.3 (all s, C$^{4\text{ or }4'}$), 15.4 (s, Me^3), 15.2 (s, Me$^{3'}$), 11.2 (s, Me^5), 11.6 (s, Me$^{5'}$), 161.8 (s, CO_2^-), 137.4, 128.9, 131.1, 130.5 (all s, PhC≡), 22.9 (s, ≡CMe), 248.6, 232.6 (all s, C≡C). IR (Nujol mull), 1554 ν(C=N), 1676 $\nu_{as}(CO_2^-)$, 1454 $\nu_s(CO_2^-)$, 369, 323 ν(Nb–Cl) cm^{-1}. Mass spectrum (FAB) (*m*/*z* assignment, % intensity) 527 [M], 18; 492 $[M - Cl]^+$, 100. Analysis for $C_{21}H_{23}Cl_2N_4NbO_2$ found (calc.): C, 47.98 (47.83); H, 4.51 (4.39); N, 10.32 (10.62%).

§ Crystal data for complex **1**: $C_{48}H_{68}Li_4N_{16}O_{12}$, $M = 1088.94$, monoclinic, *C*2/*c*, $a = 27.355(8)$, $b = 8.966(3)$, $c = 25.515(8)$ Å, $\beta = 114.28(2)°$, $U = 5704(3)$ Å^3, $Z = 4$, $\mu = 0.757$ mm^{-1}, $T = 293$ K. $R_1 = 0.0598$ for 5365 unique reflections. The hydrogen atoms of the water molecules were located from the difference map and refined isotropically. Crystal data for complex **2**: $C_{21}H_{23}Cl_2N_4NbO_2 \cdot CH_2Cl_2$, $M = 612.17$, monoclinic, *C*2/*c*, $a = 19.242(7)$, $b = 8.024(3)$, $c = 34.146(10)$ Å, $\beta = 91.30(2)°$, $U = 5271(3)$ Å^3, $Z = 8$, $\mu = 0.889$ mm^{-1}, $T = 293$ K. $R_1 = 0.0484$ for 7677 unique reflections. One solvation molecule of CH_2Cl_2 per unit formula was located in the lattice. CCDC reference number 186/1649. See http://www.rsc.org/suppdata/dt/1999/3537/ for crystallographic files in .cif format.

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