Synthesis and structural characterization of lanthanide complexes with the di- or tri-anionic diguanidinate ligand: new insight into the flexibility and distinct reactivity of the linked diguanidinate ligand†

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Unprecedented disproportionation and deprotonation of the linked diguanidinate ligand have been established, demonstrating, for the first time, that the number and distribution of negative charges on the diguanidinate ligand are tunable, and representing a new and efficient method for synthesis of linked diguanidinate di- and tri-anion complexes.

Guanidinate anions comprise a class of ligand currently finding many applications in coordination and organometallic chemistry,[1] and more recently as ancillary ligands[2] or as intermediates[3] in catalytic cycles. Desirable attributes of these ligands include their compatibility with a remarkably wide range of metal-ion requirements from all parts of the periodic table, tunable steric profile through directed variation of the substituents on the nitrogen atoms as well as their ability to function as spectator ligands in analogy with well precedented ligands such as cyclopentadienyl. Controlling the metal coordination environment and reactivity through modification of supporting ligation is an important strategy in organometallic chemistry. Considerable interest has focused on the tailoring of two independent monoanion ligands to a defining and constraining linked dianion ligand for further perfecting the versatility of these ligands.[4–7] Such concepts have been elegantly applied to *ansa*-metallocene complexes[4] and other anionic functionalities including aryloxides,[5] amidinates[6] and amidates.[7] However, there are few reports employing linked diguanidinate dianion analogues, and all those complexes were prepared from the corresponding diguanidine starting material.[8] Therefore, it is highly desirable to develop new routes to novel linked diguanidinate complexes.

On the other hand, there is currently considerable interest in studying the reactivities of the Ln–N bond of lanthanide amides due to their applications in organic synthesis and catalysis.[4a] Nonetheless, research efforts are primarily focused on non-linked amido lanthanide complexes.[9] To our knowledge, the regioselective reaction involving the linked diamido ligand in organolanthanide chemistry has remained unexplored to date, probably due to the lack of suitable complexes. In most cases, the linked diamido ligands are only typically ancillary ligands which stabilize and construct but do not participate in organometallic reactions.[10] The long-term goal of our research program over the years has been the development of insertion chemistry of organolanthanide complexes for chemical transformations of practical significance.[11] To probe the extent of these reactions and to develop a new method for the construction of support ligands in organolanthanide chemistry, we are interested in further revealing the possibility of insertion based on the linked diamido ligand and examining the versatility of the guanidinate ligand system. Herein we report the reaction of a pyridyldiamido lanthanide complex with carbodiimide, leading to a series of novel di- or tri-anionic diguanidinate-bridged binuclear and polynuclear lanthanide complexes. These results represent the first example that the number and distribution of negative charges on the linked diguanidinate ligand are tunable from double monoanionic units, through mixed neutral/dianionic isomer to mixed monoanionic/dianionic counterpart, and provide a new and efficient method for synthesis of linked diguanidinate dianion and trianion complexes.

Complex **1** was prepared in 67% yield by the protonolysis of Cp_3Yb with 0.5 equiv. of 2,6-diaminopyridine ($2,6\text{-}(H_2N)_2C_5H_3N$) in THF at room temperature. Then, it was reacted with two equiv. of diisopropylcarbodiimide ($^{i}PrN{=}C{=}N^{i}Pr$) in THF at 0 °C to give **2**, indicating that carbodiimide inserts into each the N–H bond of two amido groups of **1**. Interestingly, when a THF solution of **2** was kept at room temperature for two weeks, it was slowly converted into the unusual guanidine-substituted dianionic guanidinate complex **3** *via* an unprecedented disproportionation of the diguanidinate ligand (Scheme 1). To our knowledge, a mixed neutral guanidine/dianionic guanidinate metal complex has not yet been reported.

Furthermore, it was found that under the heating condition (about 70 °C), **3** could undergo the partial cyclopentadiene elimination to give a rare linear tetrametallic complex **4**. Complex **4** represents the first example of linked diguanidinate trianion complexes. These results demonstrate that the intramolecular proton transfer reaction can take place not only between guanidinate groups but also between the guanidine substituent and cyclopentadienyl co-ligand. To the best of our knowledge, these types of multiple N–H activations are unique; previously, the linked diguanidinate ligand bound to Ta, Ti and Zr metals is stable.[8] The selective abstraction of ligand from organometallic complexes is a challenge to address in their preparation and in their potential competence as intermediates in catalytic cycles. Although the linked dianion ligands bearing the same functionality have been investigated extensively in organometallic chemistry, no example of isomerization concentrating two individual negative

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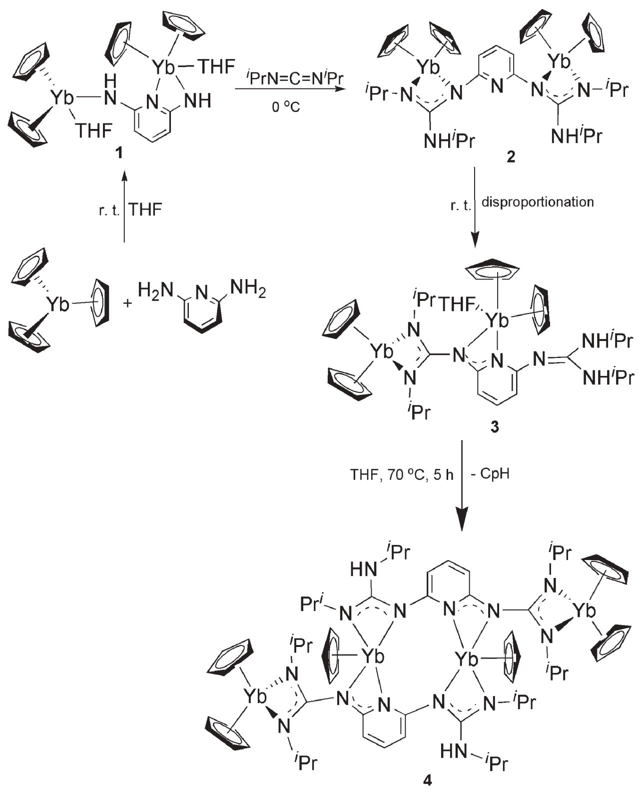

Scheme 1

charges on one functional group is known so far. The present results represent a good example that the binding mode of bifunctional ligand from double monoanionic units, through mixed neutral/dianionic isomer to mixed monoanionic/dianionic counterparts is tunable, and highlight distinctive fluxional structures of linked di(trisubstituted-guanidinate) complexes beyond that possible with the traditional linked dicyclopentadienyl, diamidinate, diamido and diaryloxide analogues, owing to the presence of reactive NH groups.

Complexes **1–4** were characterized by elemental analysis, spectroscopic properties, which were in good agreement with the proposed structures. Complexes **1**, **3** and **4** were further confirmed by the X-ray single crystal structural determination.‡ Unfortunately, due to the poor crystal quality of **2**, satisfactory data could not be obtained.

Fig. 1 clearly confirms that **3** contains two $^iPrN=C=N^iPr$ molecules that have been activated and inserted into two original N–H bond of **1** followed by the self-protonation, in which the newly formed hybrid guanidine–guanidinate dianion ligand acts as a tetradentate bridge to connect the two Cp_2Yb units through four N atoms. The two Yb centers possess different coordination environments with Yb(1) being nine-coordinated to two η^5-Cp groups, one THF oxygen and two nitrogen atoms from pyridyl and guanidinate bridges, respectively, to give a pseudo-triangle bipyramid geometry; while the Yb(2) atom is coordinated by two η^5-Cp groups and one η^2-guanidinate ligand and its formal coordination number is eight. The bond parameters suggest that negative charges of the dianionic guanidinate ligand are delocalized on the two linkage amidinate units bonded to Yb due to the conjugation effect of the pyridyl substituent, which is different from the observations in other known dianionic guanidinate complexes.[12] The average Yb(1)–N distance of 2.384(4) Å is longer than the average Yb(2)–N distance of 2.281(4) Å due to the higher coordination number.

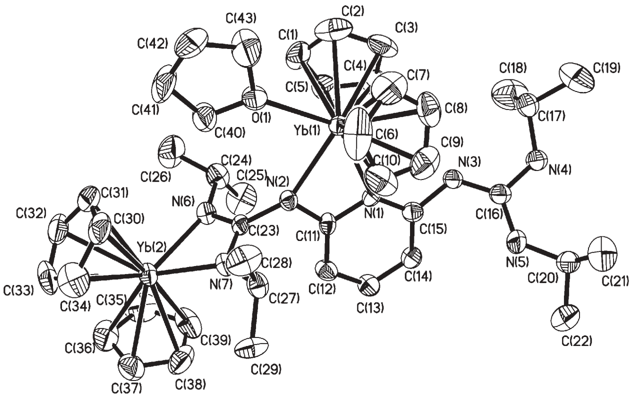

Fig. 1 Thermal ellipsoid (30%) plot of complex **3**. Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.374(4), Yb(1)–N(2) 2.395(4), Yb(1)–O(1) 2.419(4), Yb(2)–N(7) 2.281(4), Yb(2)–N(6) 2.282(5), N(2)–C(23) 1.409(6), N(6)–C(23) 1.345(6), N(7)–C(23) 1.321(7), N(1)–C(11) 1.378(6), N(2)–C(11) 1.363(7), N(3)–C(15) 1.384(7), N(3)–C(16) 1.307(8), N(4)–C(16) 1.350(7), N(5)–C(16) 1.347(8), N(2)–C(11)–N(1) 111.1(5), N(7)–C(23)–N(6) 113.9(5), N(7)–C(23)–N(2) 124.6(5), N(6)–C(23)–N(2) 121.5(5), N(3)–C(16)–N(5) 125.5(6), N(3)–C(16)–N(4) 118.0(6), N(5)–C(16)–N(4) 116.4(6), N(1)–C(15)–N(3) 114.5(5) C(16)–N(3)–C(15) 121.6(5).

The X-ray crystal structure of **4** (Fig. 2) definitively proves that the original hybrid guanidine–guanidinate dianion ligand has transformed to trianionic diguanidinate along with the elimination of cyclopentadiene. The four Yb ions are linked by double pyridyldiguanidinate trianion bridges in a μ-η^2:η^2:η^2 coordinated fashion to form an unusual linear tetrametallic complex. The four Yb atoms are located in two different coordinated environments.

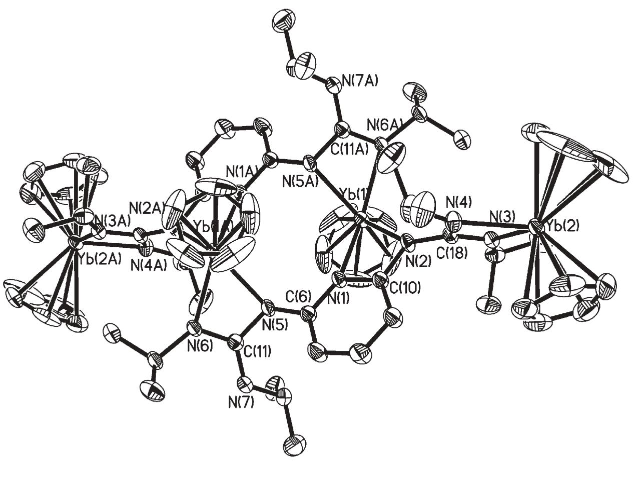

Fig. 2 Thermal ellipsoid (30%) plot of complex **4**. Selected bond lengths (Å) and angles (°): Yb(1)–N(2) 2.272(5), Yb(1)–N(6A) 2.309(4), Yb(1)–N(5A) 2.315(5), Yb(1)–N(1) 2.355(5), Yb(2)–N(4) 2.264(5), Yb(2)–N(3) 2.276(5), N(5)–C(11) 1.393(7), N(6)–C(11) 1.310(8), N(7)–C(11) 1.350(8), N(2)–C(18) 1.405(7), N(3)–C(18) 1.316(7), N(4)–C(18) 1.353(7), N(1)–C(10) 1.348(7), N(2)–C(10) 1.381(7); N(6)–C(11)–N(7) 124.2(6), N(6)–C(11)–N(5) 113.0(5), N(7)–C(11)–N(5) 122.7(6), N(3)–C(18)–N(4) 113.7(6), N(3)–C(18)–N(2) 123.2(5), N(4)–C(18)–N(2) 123.1(6), C(10)–N(2)–C(18) 117.3(5), N(1)–C(6)–N(5) 115.3(5). Letter A indicates the following symmetry transformation: 1 − *x*, 2 − *y*, 1 − *z*.

Atoms Yb(1) and Yb(1A) are coordinated by four chelating nitrogen atoms and one Cp group, respectively, to give a pseudo-trigonal bipyramid geometry, while both Yb(2) and Yb(2A) are coordinated by two nitrogen atoms of guanidinate and two Cp groups to form a distorted octahedral geometry. The distances within and between the ligands are as expected.

In summary, we have identified that the pyridyldiamido ligand bound to the lanthanide metal can undergo a clean tandem diguanylation/isomerization to afford a variety of novel linked diguanidinate complexes, such as the first examples of linked diguanidinate trianion complex and mixed neutral guanidine/dianionic guanidinate complex. These results provide a clear insight into the role of the flexibility and remarkable reactivity of linked diguanidinte ligands, and demonstrate, for the first time, that the diguanidinate dianion ligand can undergo disproportionation and deprotonation which are impossible for other homotopic linked bifunctional ligands R^-–Z–R^- (R = cyclopentadienyl, aryloxide, amidinate, amidate, and amido). Furthermore, our results provide a new route for preparation of linked diguanidinate complexes under mild conditions. Further investigation of this ligand system, including its transformation to monoanionic and tetraanionic counterparts, is in progress.[13]

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Notes and references

‡ *Crystal data*: for **1**, $C_{33}H_{41}N_3O_2Yb_2$, M = 857.77, monoclinic, space group $P2_1/c$, a = 15.286(5), b = 13.357(4), c = 15.847(5) Å, β = 100.134(4)°, V = 3185.2(16) Å^3, D_c = 1.789 g cm^{-3}, Z = 4, μ = 5.868 mm^{-1}. 13125 data collected, 5604 unique data (R_{int} = 0.0071), 3905 data with $I > 2\sigma(I)$, R_1 = 0.0374, wR_2 = 0.0732. CCDC 630571. For **3**: $C_{46}H_{68}N_7OYb_2$, M = 1081.15, monoclinic, space group $P2_1/c$, a = 18.734(7), b = 9.805(4), c = 26.843(10) Å, β = 108.652(5)°, V = 4672(3) Å^3, D_c = 1.537 g cm^{-3}, Z = 4, μ = 4.019 mm^{-1}. 18894 data collected, 8232 unique data (R_{int} = 0.0456), 6216 data with $I > 2\sigma(I)$, R_1 = 0.0383, wR_2 = 0.0780. CCDC 630572. For **4**: $C_{68}H_{94}N_{14}Yb_4$, M = 1799.73, monoclinic, space group $P2_1/c$, a = 13.906(5), b = 16.461(5), c = 15.924(5) Å, β = 98.049(5)°, V = 3609(2) Å^3, D_c = 1.656 g cm^{-3}, Z = 2, μ = 5.182 mm^{-1}. 16386 data collected, 7080 unique data (R_{int} = 0.0434), 5167 data with $I > 2\sigma(I)$, R_1 = 0.0344, wR_2 = 0.0757. CCDC 630573. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618151a

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13 Similar chemistry has been observed with metallic Er and Y as well as dicyclohexyl carbodiimide in our laboratory and the results will be published later.