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Ca(ɪɪ), Yb(ɪɪ) and Tm(ɪɪɪ) complexes with tri- and tetra-anions of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene†

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Reduction of [(dpp-bian)$^{2-}$M^{2+}(thf)$_4$] (M = Ca, 1; Yb, 6; dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) by alkali metals results in heterometallic, [(dpp-bian)$^{3-}$M^{2+}K$^+$(thf)$_2$]$_2$ (M = Ca, 2; Yb, 7), [(dpp-bian)$^{4-}$Ca^{2+}A$_2^+$(thf)$_4$]$_2$ (A = Na, 3; Li, 4; K, 5), [(dpp-bian)$^{4-}$Yb^{2+}K$_2^+$(thf)$_4$]$_2$ (8) and [(dpp-bian)$_2^{4-}$Yb$_3^{2+}$K$_2^+$(thf)$_8$] (9). The reduction of [(dpp-bian)TmBr(thf)$_n$] (*in situ*) affords [(dpp-bian)$^{4-}$Tm^{3+}Na$^+$(thf)$_2$]$_2$ (10).

Polyanions, molecules with high negative charges, can be sorted into two virtual classes dependent on the charge localization. The first one consists of molecules with repeating monoanionic units resulting from, for instance, deprotonation of OH groups.[1] The second one is signified by organic molecules that may reversibly accept electrons without changing their composition – so called electron reservoirs. Usually, the formation of such polyanions is accompanied by a change of skeletal bond lengths due to the population of the π* LUMOs. A well-known example here is naphthalene, which can be reduced by alkali metals to mono- or dianions.[2] Only a few sequences of anions of the second class have been reported so far. Inaccessibility of some members in the series is caused by disproportionation reactions that are dependent of both polyanions and cations. Thus, all the reactions of Li$^+$(C$_{10}$H$_8$)$^-$ with lanthanide halides lead to the lanthanide complexes with naphthalene dianions.[3] Also, Gambarotta, Budzelaar and co-workers have shown that reduction of α,α′-[2,6-iPr$_2$C$_6$H$_3$N=C(Me)]$_2$(C$_5$H$_3$N) using Li affords, independently of the reagent ratio, the Li salt of the trianion of the diiminopyridine as the only isolable product.[4] Among the electron reservoirs are polyaromatic hydrocarbons[5] and heterocyclic systems.[6] The metal complexes of tri-[4] and tetra-anionic[7] amido ligands derived from α,α′-[2,6-iPr$_2$C$_6$H$_3$N=C(Me)]$_2$(C$_5$H$_3$N) have been isolated. A difference between the first and second classes

of polyanions should be emphasized. Usually, an increase of the charge of the anion of the first class results in a significant increase of its reduction potential. This is not the case with the second class of polyanions that do not reveal any reductive properties. In 2003 we reported four-step reduction using sodium of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian). Sodium salts of four anions, (dpp-bian)$^{n-}$ (n = 1, 2, 3, and 4), have been isolated and structurally characterized.[8] Up to now over 100 examples of the main group metals, of the lanthanide and transition metals with the dpp-bian mono- and dianions have been reported. The presence of dpp-bian dianions in the main group metal complexes provides their unique reactivity[9] that otherwise would not be possible due to the redox-innocence of their cations. Recently we attempted preparation of the first lanthanide complexes with tri- and tetra-anions of dpp-bian. Besides the group 1 and 2 metals, the lanthanide ions can sustain a reduction power of (dpp-bian)$^{n-}$ (n = 3 or 4). We found that reduction of [(dpp-bian)$^{2-}$LaI(thf)$_2$]$_2$ using K in thf gives sandwich-like {[(dpp-bian)La(thf)][K(thf)$_3$]}$_2$, which consists of two dpp-bian tetraanions.[10] Here we report the synthesis and characterization of calcium, ytterbium and thulium complexes with tri- and tetraanions of dpp-bian.

Reduction of dpp-bian with an excess of Ca metal in thf in the presence of a small amount of CaI$_2$ affords monomeric [(dpp-bian)$^{2-}$Ca^{2+}(thf)$_4$] (1).[11] Further reduction does not occur even during a prolonged reflux. In contrast, reduction of complex 1 with one equivalent of potassium metal easily proceeds in thf and results in the Ca/K salt of the dpp-bian trianion, [(dpp-bian)$^{3-}$Ca^{2+}K$^+$(thf)$_2$] (2). The use of two equivalents of sodium metal affords the Ca/Na salt of the dpp-bian tetraanion [(dpp-bian)$^{4-}$Ca^{2+}Na$_2^+$(thf)$_4$]$_2$ (3) (Scheme 1). Related to complex 3 derivatives [(dpp-bian)$^{4-}$Ca^{2+}A$_2^+$(thf)$_4$]$_2$ (A = Li, 4; and K, 5) have been prepared similarly. Crystalline 2, 3, 4 and 5 have been isolated in 19, 46, 44 and 62% yields correspondingly. Due to the presence of dpp-bian radical-trianion, complex 2 exhibits a well-resolved ESR signal, whose hyperfine coupling (hfc) constants indicate coupling of an unpaired electron to six naphthalene protons as well as to two ^{14}N and one ^{39}K nuclei (Fig. 1).

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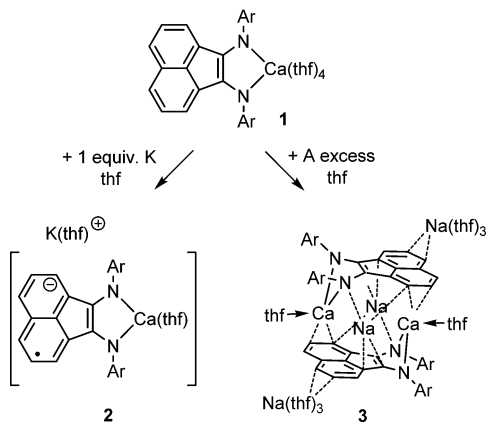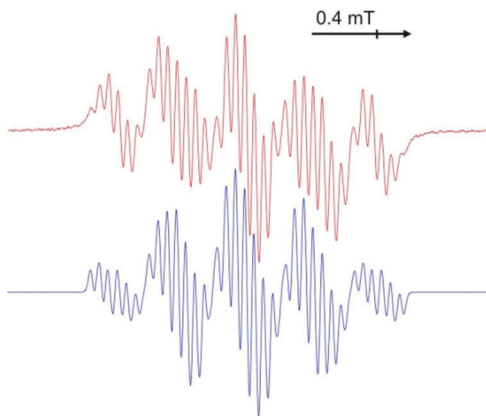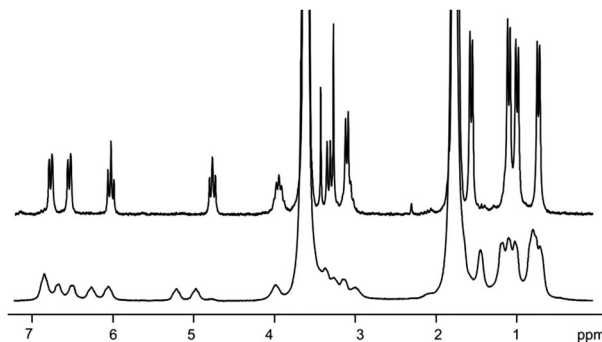
Scheme 1 Synthesis of calcium complexes **2** and **3**.

Fig. 1 ESR spectrum of **2** (thf, 298 K); red – experimental; blue – simulated: $g_i = 2.0028$, $a_H = 0.487$ ($1 \times {}^1H$), $a_H = 0.427$ ($1 \times {}^1H$), $a_H = 0.376$ ($1 \times {}^1H$), $a_H = 0.362$ ($1 \times {}^1H$), $a_H = 0.060$ ($1 \times {}^1H$), $a_H = 0.036$ ($1 \times {}^1H$), $a_N = 0.005$ ($2 \times {}^{14}H$), and $a_K = 0.060$ ($1 \times {}^{39}K$) mT.

Higher ${}^1H$ hfc constants compared with those of ${}^{14}N$ clearly indicate delocalization of the spin density mainly over the naphthalene fragment, thus approving the presence of dpp-bian trianions in complex **2**.

The ${}^1H$ NMR spectra of compounds **3**, **4** and **5** (ESI,† Fig. S1 and S2) are similar. Delocalization of a formal 2− charge over the naphthalene fragment causes a strong high field shift of the signals of three pairs of naphthalene protons (a pseudo triplet at 5.0–4.5 ppm and two doublets at 3.8–3.4 and 3.3–3.0 ppm) in comparison with those signals in complex **1** (7.5–5.7 ppm).[11]

Ca(II) and Yb(II) complexes are often isostructural due to similarity of their ionic radii, 1.00 and 1.02 Å, respectively.[12] An analog of complex **1**, compound [(dpp-bian)${}^{2-}$Yb^{2+}(thf)$_4$] (**6**), has been prepared by reacting ytterbium and dpp-bian in the presence of a catalytic amount of YbI$_2$ in thf. By analogy with complex **1** the *in situ* reduction of complex **6** with potassium, depending on the reagent ratio, produces either [(dpp-bian)${}^{3-}$Yb^{2+}K${}^+$(thf)$_2$] (**7**) or [(dpp-bian)${}^{4-}$Yb^{2+}K$_2$${}^+(thf)_4$]$_2$ (**8**). Compounds **7** and **8** have been isolated as dark crystals from benzene and thf in 27 and 64% yields correspondingly. Due to the presence of the dpp-bian trianion, complex **7** reveals an ESR signal (ESI,† Fig. S3),

whose hfc constants ($g_i = 2.00406$; $a_H = 0.482$ ($1 \times {}^1H$), $a_H = 0.427$ ($1 \times {}^1H$), $a_H = 0.376$ ($1 \times {}^1H$), $a_H = 0.362$ ($1 \times {}^1H$), $a_H = 0.060$ ($1 \times {}^1H$), $a_H = 0.036$ ($1 \times {}^1H$), $a_N = 0.005$ ($2 \times {}^{14}N$), $a_K = 0.060$ ($1 \times {}^{39}K$), $a_{Yb} = 0.05$ ($1 \times {}^{173}Yb$), and $a_{Yb} = 0.18$ ($1 \times {}^{171}Yb$) mT) are very similar with those of complex **2**. The only difference between the spectra of **2** and **7** is connected with the hfc to ytterbium isotopes in **7**. Also, the ${}^1H$ NMR spectrum of diamagnetic **8** (Fig. 2) is very similar to that of calcium analog **5**.

Attempted X-ray single crystal analyses of **7** and **8** failed. But, looking over crystals of complex **8** a single crystal of a new compound has been found and measured. The X-ray study has shown compound [(dpp-bian)$_2$${}^{4-}Yb_3$${}^{2+}K_2$${}^+(thf)_8$] (**9**), which was then isolated in a 65% yield from the reaction of a mixture **6** + YbI$_2$ with an excess of potassium in thf (Scheme 2).

The ${}^1H$ NMR spectrum of compound **9** (Fig. 2) is remarkably different from that of **8**. The former consists of a doubled signal set. Broadening of all the signals in the spectrum of **9** can be explained by a slow migration of ytterbium and potassium cations in the space between two dpp-bian ligands.

To test whether dpp-bian may stabilize divalent thulium we attempted reduction of a dpp-bian thulium(III) complex with sodium metal. Starting [(dpp-bian)TmBr(thf)$_n$] has been prepared by reacting an excess of thulium with dpp-bian in the presence of 0.5 molar equivalent of 1,2-dibromostilbene in thf. Refluxing the mixture for several hours resulted in a deep blue solution of [(dpp-bian)TmBr(thf)$_n$]. Stirring of this solution using sodium for eight hours was accompanied by a color change from deep blue to green and finally to red brown. Product [(dpp-bian)${}^{4-}$Tm^{3+}Na${}^+$(thf)]$_2$ (**10**) was isolated from toluene in 46% yield as dark crystals (Scheme 3).

The presence of the paramagnetic thulium ion prevented characterization of complex **10** *via* ESR and NMR spectroscopy. Compound **10** has been characterized by elemental analysis and IR spectroscopy, and its crystal structure has been determined

Fig. 2 ${}^1H$ NMR spectra (thf-d$_8$) of **8** (top) and **9** (bottom).
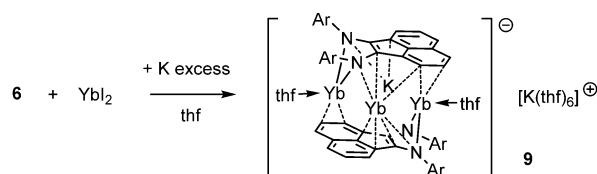
Scheme 2 Synthesis of ytterbium complex **9**.
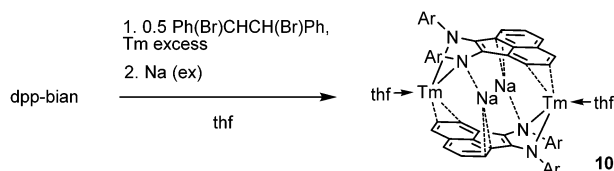
Scheme 3   Synthesis of thulium complex 10.

by the single crystal X-ray analysis. Once isolated, complexes 2–5 and 7–10 display a good solubility in thf and dme. In contrast they are almost insoluble in hexane and diethyl ether.

Molecular structures of 3, 9 and 10 have been determined by single crystal X-ray analysis and are depicted in Fig. 3, 4 and 5 correspondingly. All three complexes exhibit a similar structural motif: dpp-bian tetraanions are positioned parallel to each other with a head-to-tail orientation. Smaller distances between the dpp-bian planes in 10 (3.5 Å) in comparison with those values in 3 (3.9 Å) and 9 (3.8 Å) reflect smaller ionic radii
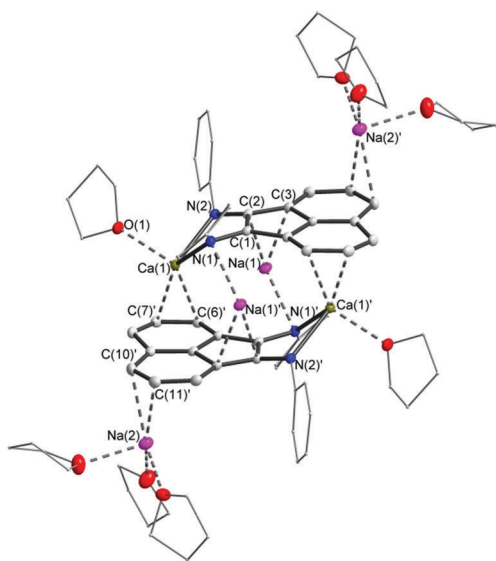
Fig. 3   Molecular structure of complex 3. Isopropyl groups are omitted for clarity. Thermal ellipsoids show a 50% probability.
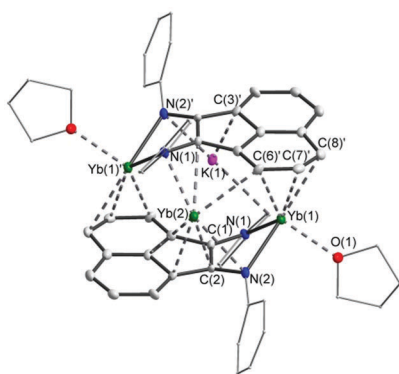
Fig. 4   Molecular structure of complex 9. Isopropyl groups and cation [K(thf)$_6$] are omitted for clarity. Thermal ellipsoids show a 30% probability.
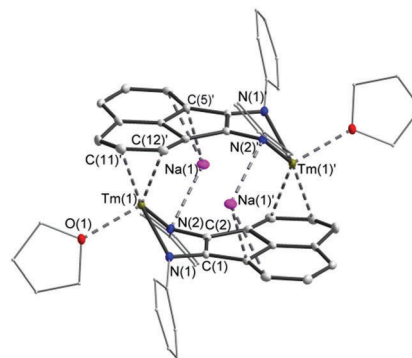
Fig. 5   Molecular structure of complex 10. Isopropyl groups are omitted for clarity. Thermal ellipsoids show a 30% probability.

of Tm(III) (0.88 Å) in comparison with that of Ca(II) (1.0 Å) and Yb(II) (1.02 Å).[13] In [(dpp-bian)$^{4-}$Na$_4^+$(thf)$_4$]$_2$[8] the distance between the planes of dpp-bian ligands is *ca.* 4.3 Å. Molecules of 3, 9 and 10 lie on the crystallographic inversion centre.

In comparison with complexes of alkaline earth metals and lanthanides(II) with [dpp-bian]$^{2-}$ atoms Ca(1) and Yb(1) in 3 and 9 deviate remarkably from the plane N(1)–C(1)–C(2)–N(2): the angles between the latter plane and the planes N(1)–M–N(2) in 3 and 9 are 36.66(7) and 40.8(4)° correspondingly (*cf.* [(dpp-bian)Ca(thf)$_4$],[11] 12.0°; and [(dpp-bian)Yb(dme)$_2$],[13] 13.3°). A higher degree of bending of the metallacycles in compounds 3 and 9 as compared to mononuclear species [(dpp-bian)Ca(thf)$_4$] (1)[11] and [(dpp-bian)$^{2-}$Yb^{2+}(dme)$_2$][13] may indicate a strong bonding of Ca and Yb cations to the neighboring naphthalene fragments. On the contrary, the corresponding interplanar angles in 10 (50.0(2)°) and [(dpp-bian)$^{2-}$La^{3+}(thf)Cp★][10] (50.2°) are practically the same.

Complexes 10 and {[(dpp-bian)La(thf)][K(thf)$_3$]}$_2$,[10] both consisting of two dpp-bian tetraanions, two rare earth metal ions and two alkali metal cations reveal rather different structures: in 10 the alkali metal cations are located between two polycyclic planes, while in the lanthanum complex they prefer outer coordination above and below the polyanionic core. But for all that the interplaner distance in the lanthanum complex is much larger (4.33 Å) than in the thulium complex 10 (3.5 Å). It is worth noting that in the complexes 3, 9 and 10 the internal alkali metal cations do not coordinate solvent molecules. The same is true for atom Yb(2) in complex 9, which is free of coordinating solvent. This is not the case for complex [(dpp-bian)$^{4-}$Na$_4^+$(thf)$_4$]$_2$[8] in which internal sodium cations coordinate thf molecules as expected. Lowered coordination numbers are also observed for Ca and Yb cations in compounds 3 and 9. Each coordinates only one thf molecule, while in starting complexes 1 and 6 the metal centers are surrounded by four thf donors. To achieve a normal coordination number of six by Ca and Yb centers in 3 and 9 one should consider one of the naphthalene rings acting as a six-electron donor. The Ca–N and Yb–N distances in 3 (aver. 2.357 Å) and 9 (aver. 2.346 Å) are slightly shorter compared with those in their precursors [(dpp-bian)Ca(thf)$_4$][11] (aver. 2.389 Å) and [(dpp-bian)Yb(dme)$_4$][13] (aver. 2.355 Å).

Two kinds of metal complexes of [(dpp-bian)$^{4-}$] were reported so far: (i) the homometallic derivative, [(dpp-bian)$^{4-}$Na$_4$$^{1+}$];[8] and (ii) the heterometallic complex formed by the combination of +3 and +1 metal cations, [(dpp-bian)$^{4-}$La^{3+}K^{1+}].[10] In this communication we report the synthesis and structural characterization of dpp-bian tri- and tetraanions surrounded simultaneously with mono- and divalent cations, *e.g.* [K$^+$Yb^{2+}] and [Na$_2$$^+$Ca^{2+}]. We have found that polyvalent cations (M^{2+} or M^{3+}) primarily coordinate the N atoms of the diimine fragment. But all the cations present provide for the assembly of the two tetraanions in a sandwich like structure *via* numerous interactions with the dpp-bian ligands. Depending on the distance between the sandwich decks in the complexes, the reported alkali metal cations may either occupy an inner space between the ligands or surround the sandwich core. We believe that this kind of molecule may find further application, for instance as multi-electron reducing agents in organic synthesis or precursors of stoichiometric mixed metal oxides and other inorganic functional materials.

Conflicts of interest

There are no conflicts to declare.

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