Syntheses and crystal structure of $[Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]\cdot 2CH_3CN$, $[Na_4(\mu,\eta^2\text{-ddbfo})_4(CH_3CN)_4]$ and $[Zn_2(\mu,\eta^1\text{-ddbfo})_2Cl_2(py)_2]$ aggregates†

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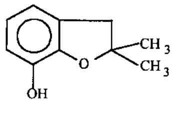
The synthesis, characterization and the X-ray structure of the three title complexes containing the 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide (ddbfo) ligand are reported. The structure of $[Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]$ includes four lithium and one zinc tetrahedral metal centers linked by μ-$O_{aryloxide}$ and μ_3-$O_{aryloxide}$ bridges. The crystals of $[Na_4(\mu_3,\eta^2\text{-ddbfo})_4(CH_3CN)_4]$ are composed of centrosymmetric cubic molecules. The crystal structure determination of compound $[Zn_2(\mu,\eta^1\text{-ddbfo})_2Cl_2(py)_2]$ shows it to be a centrosymmetric dimer, in which two ZnCl(py) units are linked by μ-$O_{aryloxide}$ oxygen atoms of η^1-ddbfo ligands.

Metal phenoxides, specifically those of zinc, are oligomeric or polymeric, and it is actually difficult to obtain simple mononuclear zinc phenoxide and alkoxide complexes.[1] Zinc alkoxide complexes are of interest either as precursors of new ZnO-containing materials[2] or as models of enzyme substrates that offer a free coordination site for incoming molecules.[3] To extend this chemistry we have attempted to synthesize new zinc species with the ddbfo (ddbfo = 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide) ligand. This ligand has attractive features. As it contains two oxygen donor atoms, ether and aryloxide, it can act not only as a chelate ligand by occupying two coordination sites on the metal but also as a tether between metal atoms to create multinuclear species.



ddbfoH

Herein, we report the syntheses and crystal structures of heteropentanuclear $[Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]$, tetranuclear $[Na_4(\mu,\eta^2\text{-ddbfo})_4(CH_3CN)_4]$ and dimeric $[Zn_2(\mu,\eta^1\text{-ddbfo})_2Cl_2(py)_2]$ complexes.

Experimental

Methods and materials

All the syntheses were performed under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under N_2 by conventional methods. Metallic sodium, LiBu, $ZnCl_2$, 2,3-dihydro-2,2-dimethyl-7-benzofuranol, THF, CH_3CN and pyridine were purchased from Aldrich. IR spectra were measured on a Perkin–Elmer 180 instrument in Nujol mulls.

Syntheses

$[Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]\cdot 2CH_3CN$ (1). To a solution of $ZnCl_2$ (0.27 g, 1.98 mmol) in CH_2Cl_2 (50 cm^3) was added Liddbfo (1.68 g, 9.9 mmol). The solution was heated for 2 h and a white solid precipitated. The solvent was removed *in vacuo* and the white solid was extracted with CH_3CN. LiCl was removed by filtering. When the filtrate was cooled at 253 K overnight, colorless crystals suitable for X-ray studies deposited. Anal. calcd for $C_{58}H_{67}ClLi_4N_4O_{10}Zn$: C, 63.83; H, 6.09; N, 5.05; Cl, 3.20. Found: C, 63.78; H, 6.13; N, 5.14; Cl, 3.26%. IR (Nujol): 316(w), 408(w), 464(m), 532(m), 580(m), 608(m), 746(vs), 786(m), 844(m), 872(vs), 968(w), 1034(vs), 1048(s), 1130(s), 1160(m), 1192(m), 1236(s), 1310(vs).

$[Na_4(\mu,\eta^2\text{-ddbfo})_4(CH_3CN)_4]$ (2). To a suspension of NaH (0.034 g, 1.5 mmol) in THF (50 cm^3) was added 2,3-dihydro-2,2-dimethyl-7-benzofuranol (0.25 g, 1.5 mmol) and the mixture was stirred for 2 h. The colorless solution was evaporated to dryness *in vacuo* and the residue extracted with CH_3CN. The filtrate deposited colorless crystals suitable for X-ray studies on cooling at 275 K. Anal. calcd for $C_{48}H_{52}N_4Na_4O_4$: C, 63.43; H, 6.21; N, 6.16. Found: C, 63.69; H, 6.31; N, 6.04%. IR (Nujol): 424(m), 484(m), 592(m), 714(m), 760(s), 786(m), 840(m), 876(s), 916(w), 968(w), 1034(s), 1052(m), 1074(s), 1132(m), 1160(s), 1184(w), 1232(w), 1286(w), 1318(s), 1480(s), 1568(m), 1598(s).

$[Zn_2(\mu,\eta^1\text{-ddbfo})_2Cl_2(py)_2]$ (3). To a solution of $ZnCl_2$ (0.31 g, 2.3 mmol) in THF (40 cm^3) was added pyridine (0.36 g, 4.6 mmol), then 2,3-dihydro-2,2-dimethyl-7-benzofuranol (0.34 cm^3, 2.3 mmol) and NaH (0.055 g, 2.3 mmol). The mixture was stirred for 24 h and a white solid precipitated. After the suspension was heated NaCl was filtered off. When the light violet solution was kept at low temperature colorless crystals suitable for X-ray studies deposited in 72% yield. Anal. calcd for $C_{30}H_{30}Cl_2N_2O_4Zn_2$: C, 52.51; H, 4.70; N, 4.08; Cl, 10.33. Found: C, 52.40; H, 4.73; N, 4.18; Cl, 10.07%. IR (Nujol): 344(s), 420(m), 472(w), 500(w), 624(w), 646(w), 698(s), 748(m), 756(s), 768(s), 776(s), 872(s), 1032(s), 1048(s), 1070(m), 1104(w),

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† Dedicated to Professor S. Pasynkiewicz on the occasion of his 70th birthday.

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1132(m), 1160(m), 1192(w), 1216(m), 1236(w), 1260(w), 1286(m), 1306(s), 1484(s), 1584(m), 1610(s).

Crystallographic structure determination

The crystal was sealed in a glass capillary under a dinitrogen gas stream. Preliminary examination and data collection were carried out on a KUMA KM-4 four-circle diffractometer[4] using graphite-monochromated Mo-Kα radiation. For all data Lorentz and polarization corrections were applied. An absorption correction following the ABSORB[5] procedure was also used for **3**: minimum and maximum absorption corrections were 0.651–1.322. The structures were solved by direct methods (SHELXS97) and refined on F^2 by full-matrix least-squares methods (SHELXL97).[6] The carbon-bonded hydrogen atoms were included in the calculated positions and refined using a riding model. The crystal data and some features of the structure refinement are summarized in Table 1.

CCDC reference number 440/182. See http://www.rsc.org/suppdata/nj/b0/b001832p/ for crystallographic files in .cif format.

Results and discussion

Exchange reactions between metal halides such as $ZnCl_2$ and lithium alkoxides are well known and give soluble heterometallic alkoxides of the type $Li_xZn(OMe)_{2+x}$.[2] Similar reaction of $Zn(OMe)_2$ with Li(OMe) in methanol gave a product corresponding to $Li_4Zn(OMe)_6$, but its X-ray structure is unknown.[7]

Treatment of $ZnCl_2$ with 5 equiv. of Li(ddbfo) in dichloromethane give an almost quantitative yield of product, which can be isolated as crystalline material from acetonitrile solution. Li(ddbfo) was obtained from the direct reaction of LiBu with ddbfoH in hexane.

$$ZnCl_2 + 5\,Li(ddbfo) + 4\,CH_3CN \rightarrow [Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]\cdot 2CH_3CN + LiCl \quad (1)$$

1

The solid-state structure of **1** shown in Fig. 1 consists of the $[Li_4Zn(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]$ species and two CH_3CN solvent molecules of crystallization. Selected bond lengths are given in Table 2. The structure of **1** includes four lithium and one zinc tetrahedral metal centers linked by μ- and μ_3-aryloxide bridges. The environments of the lithium atoms are not equivalent. The coordination sphere of Li(1) is completed by an ether oxygen atom O(10), two aryloxide μ_3-O(11) and μ_3-O(41) oxygen atoms of ddbfo as well as nitrogen atom N(1) of CH_3CN. Likewise, Li(2) is surrounded by an ether O(20) oxygen, aryloxide μ-O(21), μ_3-O(11) oxygens and a nitrogen N(2) atom. In contrast, Li(3) is linked by an ether O(30) oxygen atom and three aryloxide μ-O(31), μ_3-O(11) and μ_3-O(41) oxygen atoms, while the coordination sphere of Li(4) is completed by two ether O(40) and O(50) oxygen atoms and two aryloxide μ_3-O(41), μ-O(51) oxygens of the coordinated ddbfo ligands. The zinc atom is surrounded by μ-O(21), μ-O(31) and μ-O(51) bridging oxygen atoms and one chlorine atom.

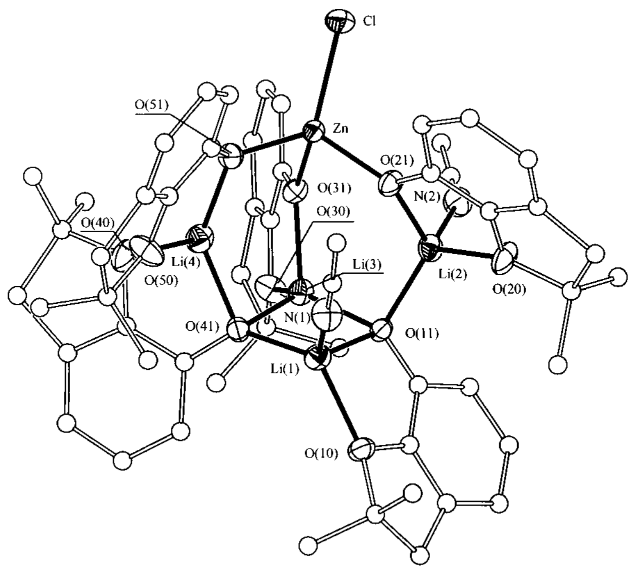

Fig. 1 The molecular structure of **1** with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radius.

To understand the transformation of Li(ddbfo) and $ZnCl_2$ into **1**, it is important to determine the crystal structure of Li(ddbfo). Unfortunately, up to now we have not been able to obtain the lithium aryloxide species in a crystalline form. Thus, the sodium species **2** was obtained from the direct reaction of NaH and ddbfoH in THF and recrystallized from CH_3CN.

Table 1 Crystal data and structure refinement details for complexes **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{58}H_{67}ClLi_4N_4O_{10}Zn$	$2(C_{48}H_{56}N_4Na_4O_8)$	$C_{15}H_{16}ClNO_2Zn$
Formula weight	1108.74	1817.86	343.11
T/K	299(1)	298(1)	299(1)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	11.818(2)	9.988(2)	9.855(4)
b/Å	23.435(5)	18.643(4)	8.836(5)
c/Å	21.975(4)	28.848(6)	18.068(6)
α/°		84.29(3)	
β/°	96.92(3)	84.32(3)	99.99(4)
γ/°		76.00(3)	
U/Å^3	6042(2)	5170.6(19)	1549.5(12)
Z	4	2	4
μ/mm^{-1}	0.507	0.107	1.757
No. of data collected	6898	7022	2650
No. of data refined	6646	6406	2505
$R_1{}^a$	0.0387	0.0395	0.0261
$wR_2{}^b$	0.1057	0.1069	0.0755

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond lengths [Å] for complexes **1**, **2** and **3**

Complex **1**			
Zn–Cl	2.2231(12)	Li(2)–O(21)	1.925(8)
Zn–O(21)	1.934(3)	Li(2)–N(2)	2.053(8)
Zn–O(31)	1.972(3)	Li(3)–O(11)	1.890(7)
Zn–O(51)	1.945(3)	Li(3)–O(30)	1.960(7)
Li(1)–O(10)	2.006(7)	Li(3)–O(31)	1.983(7)
Li(1)–O(11)	1.993(7)	Li(3)–O(41)	1.927(7)
Li(1)–O(41)	1.889(7)	Li(4)–O(40)	1.960(8)
Li(1)–N(1)	2.018(8)	Li(4)–O(41)	1.988(8)
Li(2)–O(11)	1.888(7)	Li(4)–O(50)	2.106(9)
Li(2)–O(20)	2.005(7)	Li(4)–O(51)	1.881(8)
Complex **2**			
Na(1)–O(41)	2.305(4)	Na(3)–O(11)	2.270(4)
Na(1)–O(21)	2.309(4)	Na(3)–O(21)	2.312(4)
Na(1)–O(11)	2.340(4)	Na(3)–O(30)	2.392(4)
Na(1)–O(10)	2.373(4)	Na(3)–O(31)	2.399(4)
Na(1)–N(1)	2.441(6)	Na(3)–N(3)	2.487(7)
Na(2)–O(31)	2.255(4)	Na(4)–O(31)	2.323(4)
Na(2)–O(41)	2.283(4)	Na(4)–O(11)	2.345(4)
Na(2)–O(21)	2.360(4)	Na(4)–O(41)	2.349(4)
Na(2)–O(20)	2.379(4)	Na(4)–O(40)	2.380(4)
Na(2)–N(2)	2.556(7)	Na(4)–N(4)	2.459(6)
Complex **3**			
Zn–O(11)	1.961(2)	Zn–O(11′)	2.027(2)
Zn–N	2.014(2)	Zn–Cl	2.1762(12)

Primed atoms are related to unprimed ones by: $-x, -y, -z$.

$$4\,\mathrm{NaH} + 4\,\mathrm{ddbfoH} + 4\,\mathrm{CH_3CN} \rightarrow [\mathrm{Na_4}(\mu_3,\eta^2\text{-ddbfo})_4(\mathrm{CH_3CN})_4] + 2\,\mathrm{H_2} \quad (2)$$

2

The crystals of **2** are composed of tetranuclear centrosymmetric cubic $[Na_4(\mu_3,\eta^2\text{-ddbfo})_4(CH_3CN)_4]$ molecules. The X-ray structure is shown in Fig. 2 and selected bond lengths are in Table 2. Each of the five-coordinate sodium atom is surrounded by three μ_3-$O_{aryloxide}$ oxygen atoms, an ether oxygen atom of the ddbfo ligand and a nitrogen atom of a coordinated CH_3CN molecule. The structure of the cube **2** is similar to those observed previously.[8]

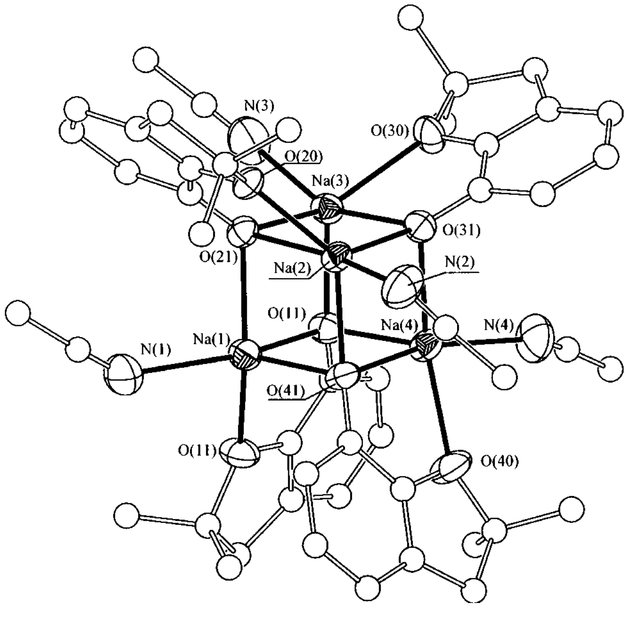

Fig. 2 The molecular structure of **2** with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radius.

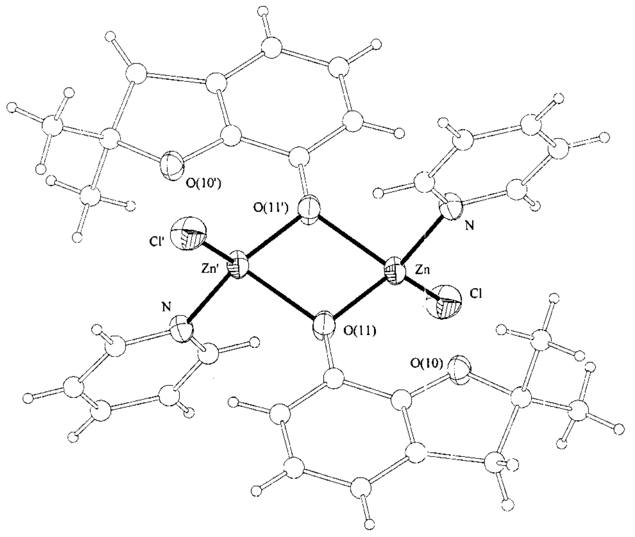

Fig. 3 The molecular structure of **3** with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C and H atoms are represented by circles of an arbitrary radius. Primed atoms are related to unprimed by: $-x, -y, -z$.

Unfortunately, the product of the reaction of $ZnCl_2$ and **2** in tetrahydrofuran is insoluble and up to now was impossible to obtain in a crystalline form. However, the reaction of $ZnCl_2$ with **2** and pyridine in THF produced a white precipitate, which contained **3**. The bulky pyridine ligand was used to favor the formation of soluble species and prevent aggregation.

$$4\,\mathrm{ZnCl_2} + \mathbf{2} + 4\,\mathrm{py} \rightarrow 2\,[\mathrm{Zn_2}(\mu,\eta^1\text{-ddbfo})_2\mathrm{Cl_2}(\mathrm{py})_2]$$

3

$$+ 4\,\mathrm{NaCl} + 4\,\mathrm{CH_3CN} \quad (3)$$

A crystal structure determination of **3** showed it to be a centrosymmetric dimer, in which two Zn(py)Cl units are linked by μ-aryloxide oxygen atoms of η^1-ddbfo ligands, as illustrated in Fig. 3. Selected bond lengths are given in Table 2. The zinc centers present slightly distorted tetrahedral environments, being coordinated by two μ-$O_{aryloxide}$ oxygen O(11) and O(11′) atoms, a pyridine nitrogen and a chlorine atom. The two ether oxygen atoms of bridging μ,η^1-ddbfo ligands are uncoordinated and thus the zinc atoms remain four-coordinate. The Zn_2O_2 core is planar (maximum deviation 0.01 Å). The average Zn–μ-$O_{aryloxide}$ distance is 1.987(5) Å in **3**; whereas the corresponding bond distances found in $Na[Zn_2(2,6\text{-diisopropylphenoxide})_4Cl)]$ average 1.851(13) Å[9] and the Zn–O bond lengths in $[Zn(2,6\text{-di-}tert\text{-butylphenoxide})_2(THF)_2]$ average 1.887(6) Å.[10] The N and Cl atoms are located 2.013(7) and 2.176(3) Å away from the zinc atoms, respectively. These distances are similar to those found in $[ZnCl_2(py)_2]$.[11]

Conclusions

The solid-state structures offer little assistance in the understanding of the reaction pathways involved in the formation of **1**–**3**. The course of reactions 1 and 3 demonstrates that in $ZnCl_2$ only one chloride atom is substituted by the aryloxide group and species **1** and **3** are formed. Similar behavior towards phenoxides is shown in the reactions of dialkylzinc[12] or trialkylaluminium[13] with phenols, which stop at the monoalkyl stage to give, for example, $[ZnEt(BHT)]_4$ and [AlEt(BHT)] (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide), respectively. This is in contrast to dialkylmagnesium, which forms $Mg(OAr)_2$ cleanly.[14] However, zinc dialkoxides could be prepared by the direct reaction of zinc dichloride with an appropriate lithium alkoxide.[11] We believe that the Li(ddbfo) species has a similar Li_4O_4 core[15] to that of **2** and is probably an intermediate in the formation of species **1**. We suppose that substitution of one chlorine in $ZnCl_2$ by a ddbfo ligand leads first to the formation of a ZnCl(ddbfo) intermediate, which reacts further with a Li_4O_4 moiety to destroy the cubic structure and yield $[Li_4Zn(\mu_3, \eta^2\text{-ddbfo})_2(\mu, \eta^2\text{-ddbfo})_3Cl(CH_3CN)_2]$.

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