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Note

Crystal structures of aryloxide complexes of zinc embracing sodium aryl group interactions: $Na[Zn(2,6\text{-diphenylphenoxide})_3(H_2O)]$ and $Na[Zn_2(2,6\text{-diisopropylphenoxide})_4Cl]\cdot 3THF$

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Abstract

The addition of Na(2,6-diphenylphenoxide) to a diethyl ether solution of the monomeric $Zn(2,6\text{-diphenylphenoxide})_2(THF)_2$ derivative affords the trisphenoxide complex, $Na[Zn(2,6\text{-diphenylphenoxide})_3(H_2O)]$ (**1**). An X-ray crystal structure analysis of **1** reveals the zinc to possess a distorted tetrahedral geometry and that the sodium counterion is essentially six-coordinate, being bound to the three oxygen atoms of the aryloxide ligands and the aromatic carbon atoms of one of the phenyl substituents on each of these ligands. An additional zinc phenoxide complex, $Na[Zn_2(2,6\text{-diisopropylphenoxide})_4Cl]\cdot 3THF$ (**2**), was obtained during the synthesis of $Zn(2,6\text{-diisopropylphenoxide})_2(THF)_2$ in the presence of NaCl. The X-ray structure of **2** again shows the sodium ion to be six-coordinate, involved in an η^6-interaction with the phenoxide π-system and bound to two THF ligands and a chloride ion.

Keywords: Crystal structures; Zinc complexes; Aryloxide complexes

1. Introduction

Most metal phenoxides exist as aggregate, in particular as dimers, as discussed in the review by Malhotra and Martin [1]. For example, in complexes of zinc two phenoxide ligands often bridge the two metal centers in a μ_2-bonding mode. The coordination sphere of the zinc is completed with phenoxides and/or other ligands in the terminal positions of either two edge-sharing tetrahedral units [2]. Alternatively these complexes exist as dimers containing three-coordinate zinc centers [3]. Recently there has been renewed interest in phenoxides as ligands for both main group and transition metals. Specifically, monomeric metal alkoxides and phenoxides have been reviewed [4], and new synthetic procedures such as the use of metal bis(trimethylsilyl)amides as starting reagents have provided convenient routes to these complexes [3a,c,5].

When zinc phenoxides or alkoxides are prepared using alkali metal phenoxides or alkoxides, the alkali metal is sometimes incorporated into the solid-state structure, coordinated to one or more of the oxygen atoms [3a,d]. The term 'double alkoxides' refers to complexes which contain a single alkali metal associated with another metal alkoxide system, although alkali metals themselves form alkoxide complexes which are often oligiomeric or polymeric [6]. Early reports on the preparation of the 'double alkoxides', $K[Zn(OMe)_3]$, $K[Zn(ethylate)_3]$, $Na[Zn(isopropylate)_3]$ [7], and $Li[Zn(OMe)_3]$ [8] have not included structural data.

Our interest in complexes of zinc phenoxides stems from their effectiveness as catalysts for the co- and ter-polymerization of epoxides and carbon dioxide to afford polycarbonates [9]. During the synthesis of monomeric 2,6-disubstituted phenolate derivatives of zinc, two complexes were isolated in which a sodium cation was found not only to interact with the oxygen atoms, but also with the aromatic carbon atoms of the zinc coordinated phenoxide ligands. In this note, the synthesis and structural characterization of $Na[Zn(2,6\text{-diphenylphenoxide})_3(H_2O)]$ (**1**) and $Na[(Zn_2(2,6\text{-diisopropylphenoxide})_4Cl]\cdot 3THF$ (**2**) are reported. Complex **1** is unusual in that it is the first monomeric trisaryloxide zinc structure to be reported.

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2. Results and discussion

The complex, Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$, was prepared as previously reported [9] using the general synthetic route which involves the reaction of Zn[N(SiMe$_3$)$_2$]$_2$ with 2,6-disubstituted phenols containing bulky substituents [3a]. The monomeric trisphenoxide complex, Na[Zn(2,6-diphenylphenoxide)$_3$(H$_2$O)] (**1**), was isolated upon further reaction of the neutral zinc complex (dissolved in diethyl ether) with 1 equiv. of Na(2,6-diphenylphenoxide). X-ray quality crystals were grown from a diethyl ether solution of **1** maintained at −15°C.

In order to provide the first structural evidence for a monomeric trisaryloxide zinc complex, a single-crystal X-ray structure of **1** was carried out. The final atomic positional and isotropic displacement parameters are listed in Table 1. Selected bond distances and angles are presented in Table 2, and a thermal ellipsoid drawing is shown in Fig. 1. Complex **1** crystallizes in a *R*3 space group where the zinc and sodium atoms are on special positions with 1/3 of the complexes being unique. The remaining portion of the complex was generated by its inherent symmetry. The structure of **1** consists of discrete mononuclear units with distorted tetrahedral geometry about the zinc(II) center defined by three 2,6-diphenylphenoxide ligands and the aquo ligand. The zinc bound water molecule is not participating in any hydrogen-bonding interactions. The sodium counterion is essentially six-coordinate being bound to the three oxygen atoms of the aryloxide ligands and the aromatic carbon atoms of one of the phenyl substituents on each of the three phenoxide ligands.

Table 1
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1** [a]

	x	y	z	U_{eq} [b]
Zn(1)	0	0	8(1)	26(1)
Na(1)	0	0	1704(3)	33(1)
O(1)	−738(3)	−1166(3)	688(3)	25(1)
O(2)	0	0	−1218(7)	57(3)
C(1)	−1602(5)	−2563(5)	−190(5)	24(2)
C(2)	−2490(6)	−3408(6)	−372(5)	31(2)
C(3)	−3311(6)	−3683(6)	107(5)	32(2)
C(4)	−3359(6)	−3121(6)	769(5)	32(2)
C(5)	−2399(5)	−2279(5)	979(5)	25(2)
C(6)	−1555(6)	−2000(6)	501(5)	21(2)
C(7)	197(6)	−1882(6)	−401(6)	26(2)
C(8)	1006(6)	−1575(6)	−910(6)	38(2)
C(9)	890(6)	−1694(7)	−1754(7)	47(3)
C(10)	−49(8)	−2130(7)	−2092(6)	49(3)
C(11)	−849(8)	−2406(7)	−1586(6)	38(3)
C(12)	−732(6)	−2284(5)	−714(5)	25(2)
C(13)	−2954(7)	−1279(7)	1792(6)	41(2)
C(14)	−2898(9)	−740(7)	2474(8)	56(3)
C(15)	−2254(8)	−600(7)	3110(8)	58(3)
C(16)	−1661(8)	−984(7)	3046(6)	53(3)
C(17)	−1699(7)	−1526(7)	2359(5)	36(2)
C(18)	−2357(6)	−1696(6)	1714(6)	29(2)

[a] E.s.d.s are given in parentheses.

[b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2
Selected bond lengths (Å) [a] and angles (°) for **1** [b]

Zn(1)–O(1)	1.954(5)	Zn(1)–O(2)	1.976(12)
Zn(1)–Na(1)	2.733(6)	Na(1)–O(1)	2.301(6)
Na(1)–C(17)	2.774(9)	O(1)–C(6)	1.342(9)
O(1)1–Zn(1)–O(1)	91.6(2)	O(1)–Zn(1)–O(2)	124.1(2)
O(1)–Zn(1)–Na(1)	55.9(2)	O(2)–Zn(1)–Na(1)	180.0
O(1)–Na(1)–O(1)	75.0(2)	O(1)–Na(1)–Zn(1)	44.7(2)
O(1)–Na(1)–C(17)	71.9(2)	O(1)–Na(1)–C(17)	144.4(2)
O(1)–Na(1)–C(17)	108.1(2)	Zn(1)–Na(1)–C(17)	112.4(2)
C(17)–Na(1)–C(17)	106.4(2)	C(6)–O(1)–Zn(1)	129.1(5)
C(6)–O(1)–Na(1)	143.5(5)	Zn(1)–O(1)–Na(1)	79.5(2)
C(18)–C(17)–Na(1)	100.9(5)	C(16)–C(17)–Na(1)	92.4(6)

[a] E.s.d.s are given in parentheses.

[b] Symmetry transformations used to generate equivalent atoms: $-x+y$, $-x$, z.

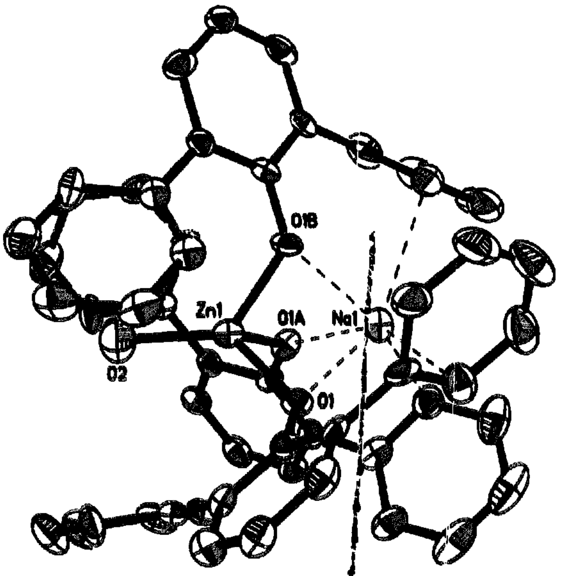

Fig. 1. Molecular structure of complex **1**, thermal ellipsoids at 50% probability.

The angle between the aryloxide groups O(1)–Zn–O(1′) (91.6(2)°) is smaller than the angle between the fourth coordinated ligand, H$_2$O, and the aryloxides (124.1(2)°). The former angle is significantly reduced as compared to the angle between aryloxide groups in the related Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$ complex (136.2(2)°) [9]. This may be due to the interactions of the sodium ion with the oxygen atoms and η^1-hydrocarbon bonds of the phenyl-substituents of the phenoxide ligands; in effect, the sodium pulls the phenoxides closer together to satisfy its coordination requirement. Olefinic or aromatic η^1-systems often coordinate to alkali metals and the induced dipole interactions are not necessarily weak as noted by the similarity of the K^+ affinities for diethyl ether and benzene (93.3 and 80.3 kJ mol^{-1}, respectively) [10]. Both the Na–O bond (2.301(6) Å) and the Na–C bond (2.774(9) Å) fall within the range of reported lengths for similar sodium complexes (Na–O = 2.24–2.54 and Na–C(η^1) = 2.65–2.97 Å) [11].

The Zn–O–C(aryl) angle of 129.1(5)° falls within the range of those reported for other known Zn(II) aryloxides [2a,3,12]. The Zn–O(aryl) bond distance observed at 1.954(5) Å is somewhat longer than that of 1.864(4) Å found in the diaryloxide derivative, Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$. This may be due in part to increased steric crowding around the metal center. The Zn–O(H_2O) bond length (1.976(12) Å) is shorter than that noted for the coordinated THF ligands in the parent complex, Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$ (2.036(4) and 2.080(4) Å).

An additional zinc phenoxide complex, which has an incorporated sodium ion in its solid-state structure, was crystallized during our attempt to prepare Zn(2,6-diisopropylphenoxide)$_2$(THF)$_2$. In this instance 2,6-diisopropylphenol was added directly to a reaction mixture of $ZnCl_2$ and sodium bis(trimethylsilyl)amide in THF prior to the removal of the NaCl salt by filtration. The material which crystallized from THF/hexane at −15°C was found to be the Zn(2,6-diisopropylphenoxide)$_2$ dimer containing 1 mol of NaCl, Na[Zn$_2$(2,6-diisopropylphenoxide)$_4$Cl]·3THF (**2**). The desired Zn(2,6-diisopropylphenoxide)$_2$(THF)$_2$ complex has subsequently been prepared by removal of the precipitated sodium chloride salt preceding the addition of the phenol derivative, and its structure defined crystallographically [13].

Two independent molecules were observed in the unit cell of **2**; similar bond distances and angles are seen in the two independent molecules. The final atomic positional and isotropic displacement parameters are listed in Table 3, while Fig. 2 shows a thermal ellipsoid drawing of one molecule of **2**. Selected bond lengths and bond angles for **2** are listed in Table 4. This complex, which crystallized in the space group $Pna2_1$, has two inequivalent, pseudo-tetrahedral zinc environments. Zn(1) is coordinated to one terminal phenoxide, two bridging phenoxides and one THF. The Zn(1)–O(4) phenoxide bond length of 1.843(12) Å is essentially the same as the zinc phenoxide bonds in Zn(2,6-diisopropylphenoxide)$_2$(THF)$_2$ (1.846(11) and 1.856(13) Å) [13], while the two bridging phenoxides have slightly elongated bonds (1.954(12) and 1.982(11) Å). The Zn(1)–O(9) THF bond is also essentially the same as that seen in Zn(2,6-diisopropylphenoxide)$_2$(THF)$_2$. Zn(2) is also bound to one terminal phenoxide and two bridging phenoxides but has a chloride ligand replacing the solvent molecule in its coordination sphere. The sodium ion's η^6-interaction with the phenoxide π-system, however, reduced the Zn(2)–O(1)–C(1) angle slightly to 123.7(10)°. The coordination sphere of sodium is completed with two additional THF ligands and the chloride ion.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **2** [a]

	x	y	z	U_{eq} [b]
Zn(1)	7043(1)	6604(2)	0	37(1)
Zn(2)	7859(1)	5862(2)	−478(1)	39(1)
Na(1)	9126(3)	4412(6)	−687(2)	64(3)
Cl(1)	8356(2)	4611(4)	−230(2)	59(2)
Zn(3)	9703(1)	−890(2)	−2731(1)	42(1)
Zn(4)	10501(1)	−1566(2)	−3241(1)	38(1)
Na(2)	8398(3)	543(7)	−2483(3)	61(2)
Cl(2)	9148(2)	329(5)	−2945(2)	66(2)
O(1)	8043(5)	6078(10)	−955(3)	46(3)
C(1)	8442(6)	5574(15)	−1115(5)	42(5)
C(2)	8378(7)	4558(15)	−1240(5)	49(6)
C(3)	8784(8)	4081(14)	−1401(5)	60(6)
C(4)	9262(8)	4593(15)	−1431(5)	71(7)
C(5)	9297(6)	5631(16)	−1337(5)	55(6)
C(6)	8908(7)	6121(14)	−1157(5)	47(5)
C(7)	7854(8)	4014(15)	−1221(6)	61(7)
C(8)	7506(7)	4382(18)	−1505(5)	76(8)
C(9)	7906(8)	2749(16)	−1207(6)	72(7)
C(10)	8927(10)	7254(17)	−1073(6)	53(6)
C(11)	9339(11)	7930(2)	−1193(7)	112(11)
C(12)	9010(10)	7364(17)	−654(6)	72(9)
O(2)	7738(5)	7033(10)	−123(3)	40(4)
C(13)	7944(7)	8011(14)	−42(5)	32(4)
C(14)	8206(7)	8137(19)	274(6)	54(6)
C(15)	8394(9)	9160(2)	342(7)	80(8)
C(16)	8304(9)	10050(2)	147(7)	81(8)
C(17)	8076(7)	9911(15)	−159(7)	53(6)
C(18)	7882(6)	8865(18)	−269(6)	52(6)
C(19)	8341(10)	7165(19)	498(5)	63(7)
C(20)	8826(9)	6640(2)	−396(8)	151(15)
C(21)	8287(12)	7420(2)	897(6)	110(12)
C(22)	7582(9)	8771(15)	−636(6)	65(7)
C(23)	7867(9)	9313(17)	−941(6)	85(9)
C(24)	7041(7)	9213(17)	−584(5)	56(6)
O(3)	7121(4)	5607(9)	−397(3)	31(3)
C(25)	6763(6)	4994(15)	−572(4)	34(5)
C(26)	6497(7)	5514(15)	−854(4)	41(5)
C(27)	6152(7)	4958(17)	−1049(5)	56(6)
C(28)	6099(8)	3870(2)	−989(7)	82(8)
C(29)	6393(8)	3379(17)	−718(7)	69(7)
C(30)	6712(7)	3926(14)	−504(6)	45(5)
C(31)	6535(9)	6732(16)	−913(5)	73(7)
C(32)	6892(7)	6969(16)	−1224(5)	59(6)
C(33)	5985(9)	7207(16)	−1000(6)	90(9)
C(34)	6958(8)	3379(17)	−215(6)	61(6)
C(35)	6609(9)	3041(18)	77(6)	94(9)
C(36)	7306(10)	2476(18)	−315(8)	87(10)
O(4)	6551(5)	7636(9)	42(4)	48(4)
C(37)	6202(7)	7840(16)	284(5)	36(5)
C(38)	6291(7)	8453(16)	582(6)	57(6)
C(39)	5918(9)	8643(16)	842(5)	65(7)
C(40)	5441(10)	8256(16)	799(6)	75(8)
C(41)	5318(8)	7633(15)	514(6)	59(6)
C(42)	5679(7)	7380(14)	252(6)	48(6)
C(43)	5576(7)	6680(15)	−57(5)	52(5)
C(44)	5040(7)	6671(18)	−184(7)	113(11)
C(45)	5766(7)	5523(15)	−5(6)	62(6)
C(46)	6843(8)	8937(17)	624(6)	58(7)
C(47)	7026(10)	9070(2)	986(7)	109(11)
C(48)	6852(9)	9990(2)	411(7)	97(9)

(continued)

Table 3 (*continued*)

	x	*y*	*z*	U_{eq} [b]
O(5)	9531(5)	−1225(10)	−2271(3)	52(4)
C(49)	9132(7)	−779(16)	−2110(5)	41(5)
C(50)	8660(8)	−1310(17)	−2067(5)	55(6)
C(51)	8253(8)	−800(2)	−1892(5)	65(7)
C(52)	8317(8)	212(18)	−1747(5)	53(6)
C(53)	8764(8)	706(16)	−1791(5)	60(6)
C(54)	9190(7)	293(17)	−1968(5)	49(6)
C(55)	9682(8)	780(2)	−2002(6)	69(7)
C(56)	9677(7)	1994(16)	−1949(6)	72(7)
C(57)	10055(9)	435(18)	−1732(7)	109(10)
C(58)	8620(10)	−2416(16)	−2242(8)	64(8)
C(59)	8244(9)	−3111(19)	−1996(7)	111(10)
C(60)	8467(10)	−2436(18)	−2585(8)	89(11)
O(6)	9813(4)	−2035(10)	−3082(3)	27(3)
C(61)	9586(8)	−3028(16)	−3113(5)	37(5)
C(62)	9681(7)	−3832(16)	−2887(5)	45(6)
C(63)	9439(10)	−4807(15)	−2948(6)	73(8)
C(64)	9131(10)	−4920(2)	−3219(8)	102(10)
C(65)	9066(8)	−4163(18)	−3482(6)	64(7)
C(66)	9270(7)	−3201(17)	−3419(5)	41(5)
C(67)	9187(8)	−2373(16)	−3688(6)	45(6)
C(68)	9135(12)	−2686(19)	−4040(6)	102(11)
C(69)	8716(10)	−1760(2)	−3612(7)	109(10)
C(70)	10035(8)	−3697(15)	−2590(4)	46(6)
C(71)	9856(8)	−4212(19)	−2237(6)	88(8)
C(72)	10573(7)	−4118(16)	−2677(5)	57(5)
O(7)	10436(5)	−560(10)	−2861(3)	42(3)
C(73)	10760(7)	80(16)	−2692(6)	49(3)
C(74)	10779(7)	1187(16)	−2749(6)	57(3)
C(75)	11132(8)	1818(18)	−2552(6)	67(3)
C(76)	11434(8)	1364(19)	−2309(6)	74(6)
C(77)	11443(9)	249(18)	−2247(6)	78(6)
C(78)	11112(8)	−443(18)	−2446(5)	58(6)
C(79)	10461(7)	1698(16)	−3019(5)	48(5)
C(80)	10094(10)	2571(15)	−2872(8)	92(11)
C(81)	10777(10)	2112(19)	−3319(6)	94(8)
C(82)	11123(7)	−1589(18)	−2386(5)	53(6)
C(83)	10829(8)	−1790(16)	−2062(5)	68(7)
C(84)	11652(8)	−1990(2)	−2344(6)	88(8)
O(8)	11020(5)	−2510(9)	−3338(4)	43(4)
C(85)	11299(8)	−2565(14)	−3636(5)	40(6)
C(86)	11740(8)	−2000(17)	−3644(5)	51(6)
C(87)	12031(9)	−2035(18)	−3967(7)	68(7)
C(88)	11865(11)	−2530(2)	−4252(8)	97(10)
C(89)	11436(11)	−3084(19)	−4232(6)	86(9)
C(90)	11110(9)	−3185(16)	−3912(5)	58(6)
C(91)	11931(7)	−1343(15)	−3349(6)	60(6)
C(92)	12516(8)	−1333(18)	−3304(7)	110(9)
C(93)	11752(8)	−181(17)	−3379(6)	79(8)
C(94)	10618(11)	−3820(2)	−3862(7)	99(11)
C(95)	10698(11)	−4840(19)	−3660(7)	98(10)
C(96)	10399(10)	−4110(2)	−4247(7)	121(12)
O(9)	7085(5)	5705(11)	457(3)	57(4)
C(97)	7441(6)	4889(14)	565(4)	57(6)
C(98)	7474(9)	4960(2)	950(4)	108(10)
C(99)	7102(9)	5716(19)	1057(4)	81(8)
C(100)	6773(7)	5820(2)	754(4)	85(9)
O(10)	10367(5)	−656(10)	−3690(3)	48(4)
C(101)	9940(6)	69(15)	−3734(4)	53(6)
C(102)	9810(7)	0(2)	4108(5)	92(9)
C(103)	10286(8)	−200(2)	−4274(5)	99(9)
C(104)	10609(7)	−700(2)	−4015(5)	95(10)
O(11)	8239(8)	2275(12)	−2571(6)	107(8)
C(105)	8202(15)	2660(2)	−2927(6)	210(2)
C(106)	7857(13)	3580(2)	−2906(7)	184(19)
C(107)	7952(15)	4020(17)	−2575(8)	155(17)
C(108)	8144(15)	3150(2)	−2370(6)	186(19)
O(12)	9291(7)	2637(11)	−638(5)	92(7)
C(109)	9077(10)	1961(18)	−383(8)	157(15)
C(110)	9385(13)	1000(2)	−390(10)	240(3)
C(111)	9717(16)	1050(2)	−672(11)	270(3)
C(112)	9711(12)	2132(19)	−784(9)	200(2)
O(13)	9867(5)	4987(12)	−457(4)	80(5)
C(113)	9923(7)	4870(2)	−91(5)	99(9)
C(114)	10455(8)	4600(2)	−22(5)	96(9)
C(115)	10727(6)	4910(3)	−321(6)	124(12)
C(116)	10351(7)	5120(2)	−591(5)	110(10)
O(14)	7618(5)	122(14)	−2738(5)	93(5)
C(117)	7494(10)	−500(2)	−3038(6)	173(17)
C(118)	6954(10)	−300(3)	−3121(7)	150(15)
C(119)	6805(12)	540(3)	−2913(12)	250(3)
C(120)	7151(11)	450(4)	−2614(8)	250(3)
O(15)	10943(13)	−6050(3)	−1421(10)	169(18)
C(121)	11487(14)	−6080(3)	−1356(8)	85(15)
C(122)	11730(11)	−5840(3)	−1689(9)	69(12)
C(123)	11332(15)	−5600(4)	−1918(8)	111(18)
C(124)	10931(13)	−5280(3)	−1678(12)	130(2)

[a] E.s.d.s are given in parentheses.

[b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3. Experimental

3.1. General procedures

All reactions were carried out under an inert atmosphere with degassed solvents. NMR spectra were collected using a Varian XL-200E spectrometer. All chemicals were obtained commercially and used without further purification. Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$ was prepared as previously reported [9].

3.2. Preparation of Na(2,6-diphenylphenoxide)

Equimolar amounts of NaOH (0.08 g, 2 mmol) and 2,6-diphenylphenol (0.5 g, 2 mmol) were refluxed in diethyl ether (25 ml) until the sodium hydroxide was consumed, being replaced with a white slurry. The solvent was then removed and the precipitate washed with additional diethyl ether to remove water. It was then dried in vacuo.

3.3. Preparation of Na[Zn(2,6-diphenylphenoxide)$_3$·H_2O] (1)

A white, cloudy solution of Zn(2,6-diphenylphenoxide)$_2$(THF)$_2$, (0.3 g, 0.43 mmol), Na(2,6-diphenylphenoxide), (0.12 g, 0.43 mmol) and 20 ml of diethyl ether was stirred

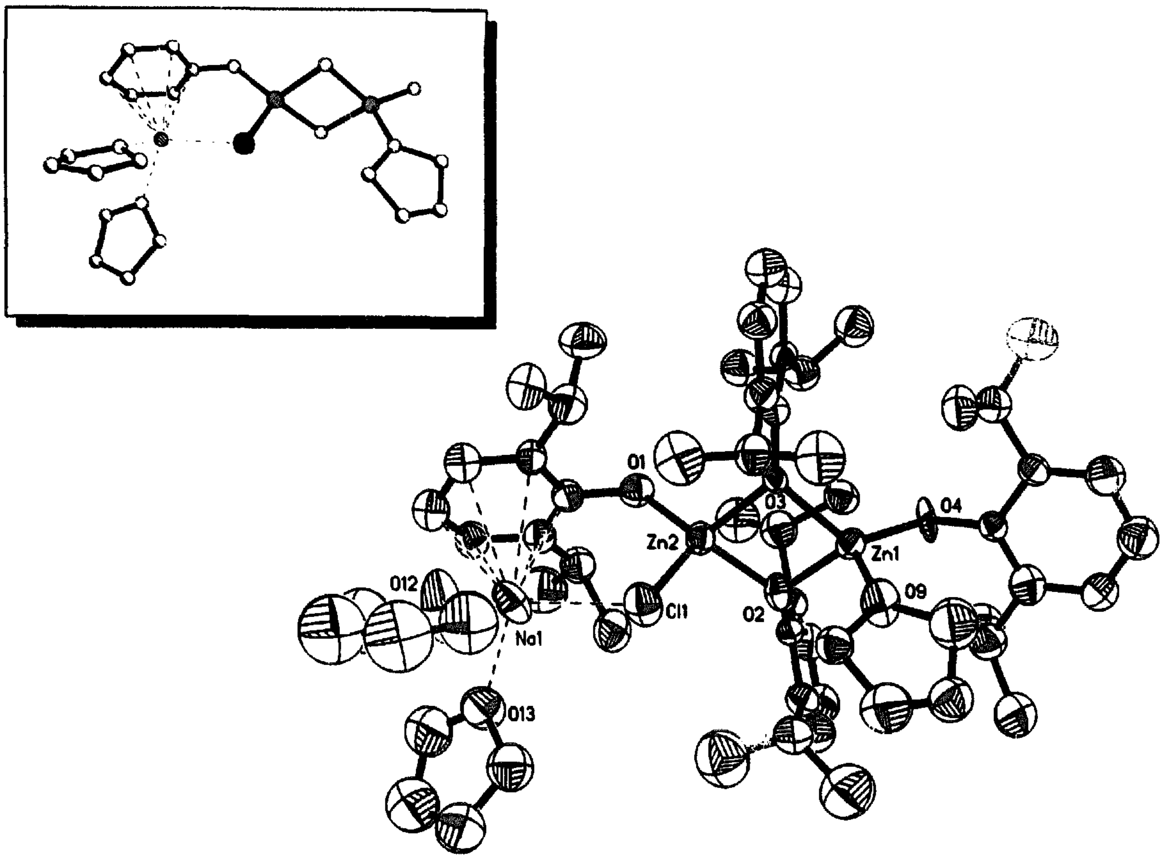

Fig. 2. Molecular structure of complex 2, thermal ellipsoids at 50% probability. The insert illustrates a ball and stick drawing where the substituted phenyl groups are omitted for clarity.

for 2 h. The solvent was then removed and the product extracted with 10 ml of benzene. The solvent was again removed under vacuum, leaving a white solid (70% yield). Crystals of X-ray quality were grown at −15°C from a portion of the initial diethyl ether solution of the complex. ^{1}H NMR (C_6D_6, ppm): 6.91 (t), 7.18 (m), 7.48 (d). *Anal.* Calc. for $C_{54}H_{41}O_4NaZn$: C, 77.00; H, 4.91. Found: C, 80.04; H, 5.99%. If two benzene molecules (the solvent used in the extraction) are included, the calculated C = 79.39 and H = 5.35 are in much better agreement.

3.4. *Na[Zn$_2$(2,6-diisopropylphenoxide)$_4$Cl]·3THF (2)*

0.50 g of $ZnCl_2$ was combined with 1.40 g of sodium bis-trimethylsilylamide and was refluxed in 20 ml of tetrahydrofuran. 1.30 g of 2,6-diisopropylphenol were added via syringe. After stirring overnight the precipitated sodium chloride was removed by filtration through celite. The resulting light green solution was concentrated to half its original volume and 25 ml of hexane was added. The solution was placed in the freezer. 1.0 g (24.5% yield) of product were isolated. *Anal.* Calc. for $C_{60}H_{92}O_7Zn_2ClNa$: C, 64.66; H, 8.32. Found: C, 62.44; H, 8.32%. The inclusion of two water molecules leads to C = 62.63 and H = 8.41, which is in better agreement with the observed analysis.

3.5. *X-ray crystallographic study of 1*

Crystal data and details of the data collection are given in Table 5. A colorless plate (0.3 × 0.3 × 0.1 mm) of **1**, was mounted on a glass fiber with epoxy cement at room temperature and cooled to 163 K in a N_2 cold stream. Preliminary examinations and data collections were performed on a Rigaku AFC5R X-ray diffractometer (oriented graphite monochromator). Cell parameters, which were calculated from the least squares fitting of the setting angles for 25 reflections, indicated acceptable crystal quality. ω scans for several intense reflections indicated acceptable crystal quality. Data for **1** was collected for $5.0 \geq 2\theta \geq 50.0°$ at 163 K. Three control reflections, collected every 150 reflections, showed no significant trends. Background measurements were performed by stationary crystal and stationary counter techniques at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were to 1432 reflections. A semi-empirical absorption correction was applied. Totals of 1069 unique reflections with $|I| > 2.0\sigma(I)$ were used in further calculations. The structures were solved by direct methods (SHELXS, SHELXTL-PLUS) [14]. Full matrix least squares refinement yielded $(I \geq \sigma(I))$, $R_F = 0.056$ and $R_W = 0.093$ (SHELXL-93) [14]. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral-atom

Table 4
Selected bond lengths [Å] and bond angles [°] for **2** [a]

Zn(1)–O(2)	1.954(12)	Na(1)–O(13)	2.25(2)
Zn(1)–O(3)	1.982(11)	Na(1)–Cl(1)	2.677(10)
Zn(1)–O(4)	1.843(12)	Na(1)–C(1)	2.84(2)
Zn(1)–O(9)	2.085(11)	Na(1)–C(6)	2.87(2)
Zn(2)–O(1)	1.904(12)	Na(1)–C(4)	2.87(2)
Zn(2)–O(2)	2.033(13)	Na(1)–C(2)	2.88(2)
Zn(2)–O(3)	1.982(11)	Na(1)–C(3)	2.90(2)
Zn(2)–Cl(1)	2.258(6)	Na(1)–C(5)	2.95(2)
Na(1)–O(12)	2.30(2)		
O(1)–C(1)–Na(1)	117.7(11)	C(3)–C(2)–Na(1)	76.9(12)
C(2)–C(1)–Na(1)	77.9(12)	C(1)–C(2)–Na(1)	74.1(11)
C(6)–C(1)–Na(1)	76.9(10)	C(7)–C(2)–Na(1)	122.9(14)
O(4)–Zn(1)–O(9)	110.6(6)	C(2)–C(3)–Na(1)	75.7(12)
O(2)–Zn(1)–O(9)	107.7(6)	C(4)–C(3)–Na(1)	74.8(12)
O(3)–Zn(1)–O(9)	106.6(5)	C(5)–C(4)–Na(1)	79.8(13)
O(1)–Zn(2)–O(3)	114.8(5)	C(3)–C(4)–Na(1)	76.9(11)
O(1)–Zn(2)–O(2)	124.9(5)	C(4)–C(5)–Na(1)	73.1(12)
O(3)–Zn(2)–O(2)	82.1(5)	C(6)–C(5)–Na(1)	72.8(11)
O(1)–Zn(2)–Cl(1)	110.8(4)	C(5)–C(6)–Na(1)	79.9(12)
O(3)–Zn(2)–Cl(1)	112.4(4)	C(1)–C(6)–Na(1)	74.5(10)
O(2)–Zn(2)–Cl(1)	108.9(4)	C(10)–C(6)–Na(1)	126.4(14)
O(13)–Na(1)–O(12)	97.1(7)	C(13)–O(2)–Zn(1)	123.9(11)
O(13)–Na(1)–Cl(1)	111.4(5)	C(13)–O(2)–Zn(2)	137.7(10)
O(12)–Na(1)–Cl(1)	100.4(5)	Zn(1)–O(2)–Zn(2)	95.9(6)
O(13)–Na(1)–C(1)	127.0(6)	C(25)–O(3)–Zn(1)	130.9(9)
O(12)–Na(1)–C(1)	132.3(7)	C(25)–O(3)–Zn(2)	132.3(9)
Cl(1)–Na(1)–C(1)	81.5(4)	Zn(1)–O(3)–Zn(2)	96.6(5)
O(13)–Na(1)–C(6)	99.9(6)	C(37)–O(4)–Zn(1)	132.9(13)
O(12)–Na(1)–C(6)	145.8(7)	C(116)–O(13)–Na(1)	133.5(13)
Cl(1)–Na(1)–C(6)	100.8(4)	C(113)–O(13)–Na(1)	116.1(12)
C(1)–Na(1)–C(6)	28.7(5)	C(112)–O(12)–Na(1)	124.6(13)
O(13)–Na(1)–C(4)	104.7(6)	C(109)–O(12)–Na(1)	125.1(13)
(12)–Na(1)–C(4)	97.7(7)	C(100)–O(9)–Zn(1)	126.0(12)
Cl(1)–Na(1)–C(4)	136.9(5)	C(97)–O(9)–Zn(1)	131.4(10)
C(1)–Na(1)–C(4)	57.8(5)	C(6)–Na(1)–C(4)	49.2(5)
O(13)–Na(1)–C(2)	148.2(6)	C(4)–Na(1)–C(3)	28.4(5)
O(12)–Na(1)–C(2)	104.4(7)	C(2)–Na(1)–C(3)	27.4(4)
Cl(1)–Na(1)–C(2)	87.7(4)	O(13)–Na(1)–C(5)	91.6(6)
C(1)–Na(1)–C(2)	27.9(4)	O(12)–Na(1)–C(5)	123.4(7)
C(6)–Na(1)–C(2)	50.2(5)	Cl(1)–Na(1)–C(5)	127.8(4)
C(4)–Na(1)–C(2)	49.9(5)	C(1)–Na(1)–C(5)	48.8(5)
O(13)–Na(1)–C(3)	132.8(6)	C(6)–Na(1)–C(5)	27.3(5)
O(12)–Na(1)–C(3)	89.6(7)	C(4)–Na(1)–C(5)	27.1(4)
Cl(1)–Na(1)–C(3)	113.2(5)	C(2)–Na(1)–C(5)	57.0(6)
C(1)–Na(1)–C(3)	48.6(5)	C(3)–Na(1)–C(5)	48.2(5)
C(6)–Na(1)–C(3)	57.3(5)	Zn(2)–Cl(1)–Na(1)	103.1(3)

[a] E.s.d.s are given in parentheses.

scattering factors were taken from the International Tables for X-ray Crystallography.

Table 5
Crystallographic data

	1	**2**
Empirical formula	$C_{54}H_{39}NaO_4Zn$	$C_{124}H_{192}C_{12}Na_2O_{14.50}Zn_4$
Formula weight	840.21	2264.08
Crystal system	rhombohedral	orthorhombic
Space group	*R*3	$Pna2_1$
V (Å^3)	3500(2)	12656(13)
Z (Z')	3	4 (8)
D_{calc} (g cm^{-3})	1.196	1.188
a (Å)	15.836(3)	26.17(2)
b (Å)		12.666(9)
c (Å)	16.116(6)	38.18(2)
T (K)	163(2)	293(2)
μ(Mo Kα) (mm^{-1})	0.579	0.854
Wavelength (Å)	0.71073	0.71073
R_F (%) [a]	5.6	8.8
$wR(F^2)$ (%) [b]	9.3	14.0

[a] $R_F = \Sigma |F_o - F_c| / \Sigma F_o$.

[b] $wR(F^2) = \{[\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma (wF_o^4)]\}^{1/2}$.

3.6. X-ray crystallographic study of **2**

Crystal data and details of the data collection are given in Table 5. A colorless block (0.3×0.3×0.3 mm) of **2**, was mounted on a glass fiber at room temperature. Preliminary examination and data collection was performed on a Nicolet R3m/v X-ray diffractometer (Mo Kα, λ = 0.71073 Å) at 293(2) K. Data collection methods and parameters are identical to that described in complex **1**. Lorentz and polarization corrections were applied to 11 283 reflections. An empirical absorption correction was applied. A total of 11 283 unique observed reflections, with $|I| \geq 2.0\sigma(I)$ were used in further calculations. Systematic absences for **2** indicated two possible space groups, $Pna2_1$ and *Pnma*. An examination of the distribution of intensities favored the non-centrosymmetric space group $Pna2_1$. Attempts to solve the structures in *Pnma* failed. The non-centrosymmetric space group was chosen and the structure solution and refinement were undertaken. Two unique molecules of **2** and one molecule of THF were located in the unique volume of the unit cell, indicating a Z' = 8. The structure was solved by direct methods (SHELXS, SHELXTL-PLUS) [14]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded ($|I| \geq 2.0\sigma(I)$), R = 0.0882, R_w = 0.1396 and S = 1.024 (SHELXL-93) [14]) at convergence. Large thermal parameters were seen for terminal carbon atoms and atoms of the THF moities. This was not considered unusual because of the nature of these atoms and the motion expected in the structure. It is certain that some disorder exists in the moieties; however, the exact modeling of the disorder is not considered critical to the conclusions drawn in this manuscript. Hydrogen atoms ride upon the adjacent attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography.

4. Supplementary material

Tables of atomic coordinates, anisotropic thermal parameters, complete bond lengths and bond angles and H atom coordinates for complexes **1** and **2** with complete atomic labeling schemes (32 pages) are available from the authors on request.

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