Influence of Intramolecular Coordination on the Aggregation of Sodium Phenolate Complexes. X-ray Structures of [NaOC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_6$ and [Na(OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)(HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)]$_2$

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The structural characterization of two new sodium phenolate complexes, containing *ortho*-amino substituents, enables the influence of intramolecular coordination on the aggregation of sodium phenolate complexes to be determined. Crystals of hexameric [NaOC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_6$ (**1a**) are monoclinic, space group $P2_1/c$, with a = 11.668(4) Å, b = 18.146(4) Å, c = 14.221(5) Å, β = 110.76(3)°, V = 2815.5(16) Å^3, and Z = 2; R = 0.0736 for 2051 reflections with $I > 2.0\sigma(I)$. Complex **1a** contains a unique Na$_6$O$_6$ core, consisting of two face-fused cubes, with the *ortho*-amino substituent of each phenolate coordinating to a sodium atom. In addition, two of the phenolate ligands have an η^2-arene interaction with an additional sodium atom in the core. Crystals of dimeric [(NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)(HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)]$_2$ (**2b**) are triclinic, space group $P\bar{1}$, with a = 10.0670(8) Å, b = 10.7121(7) Å, c = 27.131(3) Å, α = 92.176(8)°, β = 99.928(8)°, γ = 106.465(6)°, V = 2752.1(4) Å^3, and Z = 2; R = 0.0766 for 5329 reflections with $I > 2.0\sigma(I)$. Dimeric complex **2b** contains two phenolate ligands, which bridge the two sodium atoms, each coordinating with one *ortho*-amino substituent to a sodium atom, while the second available *ortho*-amino substituent remains pendant. The coordination sphere of each sodium atom is completed by a (neutral) bidentate *O,N*-coordinated parent phenol molecule. The second *ortho*-amino substituent of this neutral phenol is involved in a hydrogen bridge with its acidic hydrogen. On the basis of these two new crystal structures and previously reported solid state structures for sodium phenolate complexes, it is shown that the introduction of first one and then two *ortho*-amino substituents into the phenolate ligands successively lowers the degree of association of these complexes in the solid state. In this process, the basic Na$_2$O$_2$ building block of the molecular structures remains intact.

Introduction

Although lithium and sodium phenolates are common starting materials for the preparation of transition metal phenolate complexes *via* transmetalation,[1] relatively little is known with respect to their structure either in solution[2,3] or in the solid state.[2,4–7] This is especially the case for sodium phenolate complexes.[2,47] Recently, we and others became interested in the use of phenolates containing *ortho*-amino substituents as ligands for main group, transition, and lanthanide metals.[6,8–13] From these studies it became apparent that such ligands show great versatility in bonding to metal centers (see Figure 1).

In the course of our work we have prepared a number of lithium and sodium complexes of monoanionic phenolate ligands depicted in Figure 1. As some interesting structures, both in solution and in the solid state, were already found,[2,5] we have continued to study the different bonding modes and the influence of intramolecular coordination on the aggregation state and structure of alkali metal phenolates.

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(1) (a) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159. (b) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. (c) Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 2.
(2) van der Schaaf, P. A.; Jastrzebski, J. T. B. H.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1993**, *32*, 4111.
(3) (a) Jackman, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 4177. (b) Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829. (c) Jackman, L. M.; Chen, X. *J. Am. Chem. Soc.* **1992**, *114*, 403.
(4) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1993**, *32*, 3041.
(5) van der Schaaf, P. A.; Hogerheide, M. P.; Grove, M. D.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1703.
(6) Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.
(7) Matilainen, L.; Leskelä, M.; Klinga, M. *J. Chem. Soc., Chem. Commun.* **1995**, 421.

(8) Hogerheide, M. P.; Wesseling, M.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1995**, *14*, 4483.
(9) Hogerheide, M. P.; Ringelberg, S. N.; Jastrzebski, J. T. B. H.; Boersma, J.; Spek, A. L.; van Koten, G. To be published.
(10) van der Schaaf, P. A.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1993**, *32*, 5108.
(11) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 4691.
(12) (a) Wehman, E.; van Koten, G.; Knotter, D. M.; Erkamp, C. J. M.; Mali, A. N. S.; Stam, C. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 370. (b) Tesh, K. F.; Hanusa, T. P. *J. Chem. Soc., Chem. Commun.* **1991**, 879. (c) Gultneh, Y.; Farooq, A.; Liu, S.; Karlin, K. D.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 3607. (d) Teipel, S.; Griesar, K.; Haase, W.; Krebs, B. *Inorg. Chem.* **1994**, *33*, 456.
(13) (a) Hogerheide, M. P.; Jastrzebski, J. T. B. H.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1994**, *33*, 4431. (b) Hogerheide, M. P.; Ringelberg, S. N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 1185.
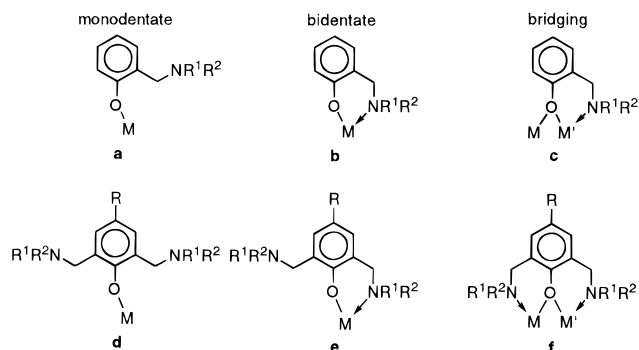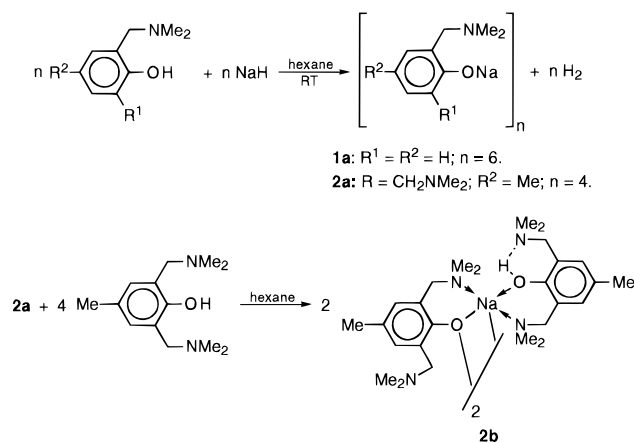
Figure 1. Phenolate ligands with potentially intramolecularly coordinating amino substituents and their previously reported coordination geometries: monodentate (**a**, **d**);[10,11] bidentate (**b**, **e**);[11–13] bridging between identical (M = M′)[1,14] or different (M ≠ M′)[15] metal centers (**c**, **f**).

Scheme 1. Preparation of the Sodium Phenolate Complexes

Here we report two new structures which, in combination with earlier reported solid state structures,[2,4] allow us to describe the effect of introducing first one and then two *ortho*-amino substituents on the aggregation of sodium phenolate complexes. In addition, one of these complexes shows that intramolecular hydrogen bonding in the parent bis(*ortho*-amino)-substituted phenol allows it to act as a bidentate neutral ligand.

Results

Syntheses and Properties. The parent phenols $HOC_6H_4(CH_2NMe_2)$-2 (**1**) and $HOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 (**2**) were prepared by reactions of phenol and *p*-cresol, respectively, with the appropriate amounts of dimethylamine and formaldehyde in water.[2] The corresponding sodium phenolates $[NaOC_6H_4(CH_2NMe_2)$-2$]_6$ (**1a**) and $[NaOC_6H_2(CH_2NMe_2)$-2,6-Me-4$]_4$ (**2a**) were obtained in (nearly) quantitative yield by reaction of the parent

phenol with NaH in hexane at room temperature, as described previously (see Scheme 1).[2] Complex **1a** is only sparingly soluble in aromatic solvents which hampered the determination of the aggregation state in solution. Moreover, no sharp melting point could be observed when tetrahydrofuran (THF) was used as the solvent during cryoscopic measurements.[2] Attempts to obtain crystals were also unsuccessful until we observed that the solubility of **1a** in aromatic solvents was increased when an excess of the parent phenol was present. Crystals obtained from these mixtures by slow diffusion of pentane into the aromatic solvents were found to be pure **1a**, as analyzed by NMR spectroscopy. The structure of the bis(*ortho*-amino)-complex **2a**, both in benzene solution (dimeric) and in the solid state (tetrameric), was reported previously.[2]

The new sodium phenolate−phenol complex $[(NaOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4$)(HOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4$)]_2$ (**2b**) was obtained in 70−80% yield by the addition of an excess of the parent phenol $HOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 (**2**) to a hexane solution of $[NaOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4$]_4$ (**2a**), followed by crystallization of the product at −30 °C (see also Scheme 1). Initial ^{1}H NMR analysis of the crystalline material showed the presence of one acidic proton for two phenolate moieties, while ^{13}C NMR showed two separate signals for C_{ipso}, indicating the presence of two different coordination geometries for the phenolate ligand in the complex.

In order to gain insight into the coordination mode(s) of the phenolate ligand and the coordination geometry around the metal center, the molecular structures of **1a** and **2b** were determined from X-ray structure determinations.

Structures in the Solid State. Crystals of $NaOC_6H_4(CH_2NMe_2)$-2 (**1a**) suitable for an X-ray structure determination were obtained from a pentane-layered toluene solution of the complex containing an excess of $HOC_6H_4(CH_2NMe_2)$-2 (**1**). The crystal structure determination shows the hexameric molecular structure to contain a unique Na_6O_6 core forming two face-fused cubes (see Figure 2), with an inversion point in the center of the fused

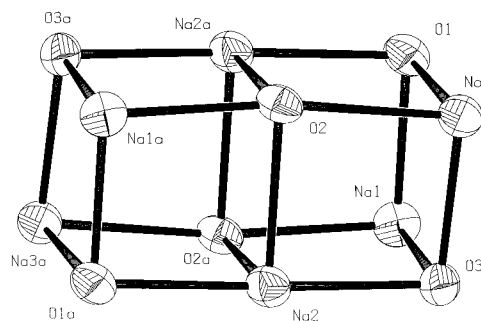**Figure 2.** ORTEP representation of the Na_6O_6 core structure (50% probability) of $[NaOC_6H_4(CH_2NMe_2)$-2$]_6$ (**1a**) forming two face-fused cubes.

Table 1. Selected Bond Distances (Å) for $[NaOC_6H_4(CH_2NMe_2)$-2$]_6$ (**1a**)[a]

	Na(1) [4-coordinate]		Na(2) [5-coordinate]		Na(3) [6-coordinate]	
	Bonds to Sodium					
Na−(μ_3-O)	Na(1)−O(1)	2.240(5)	Na(2)−O(1)	2.344(5)	Na(3)−O(1)	2.309(5)
	Na(1)−O(3)	2.295(5)	Na(2)−O(3a)	2.302(5)	Na(3)−O(3)	2.234(5)
Na−(μ_4-O)	Na(1)−O(2a)	2.325(5)	Na(2)−O(2)	2.434(5)	Na(3)−O(2)	2.478(5)
			Na(2)−O(2a)	2.448(5)		
Na−N	Na(1)−N(2a)	2.447(5)	Na(2)−N(1)	2.494(6)	Na(3)−N(3)	2.410(6)
Na−C					Na(3)−C(21)	2.687(6)
					Na(3)−C(22)	2.744(6)
	Other Bonds					
C−O	C(11)−O(1)	1.311(8)	C(21)−O(2)	1.314(7)	C(31)−O(3)	1.334(7)

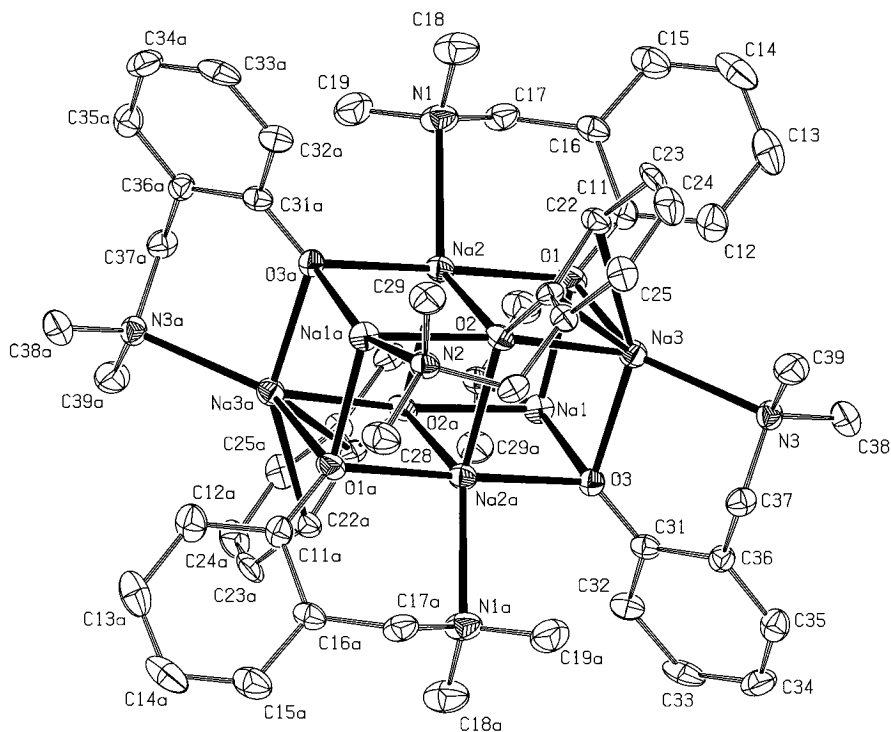[a] "a" indicates the symmetry operation $-x + 2$, $-y$, $-z + 1$.

Figure 3. ORTEP representation (30% probability) of $[NaOC_6H_4(CH_2NMe_2)-2]_6$ (**1a**) with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Angles (deg) for $[NaOC_6H_4(CH_2NMe_2)-2]_6$ (**1a**)[a]

Na–O–Na Angles			
Na(1)–O(1)–Na(2)	91.57(19)	Na(1)–O(1)–Na(3)	84.35(16)
Na(2)–O(1)–Na(3)	91.42(19)	Na(2)–O(2)–Na(3)	85.38(15)
Na(1a)–O(2)–Na(2)	89.26(16)	Na(2)–O(2)–Na(2a)	89.21(16)
Na(1a)–O(2)–Na(3)	169(2)	Na(2a)–O(2)–Na(3)	84.11(15)
Na(1a)–O(2)–Na(2a)	86.97(15)	Na(1)–O(3)–Na(3)	84.80(16)
Na(1)–O(3)–Na(2a)	93.34(17)	Na(2a)–O(3)–Na(3)	93.33(17)

O–Na–O Angles			
O(1)–Na(1)–O(3)	95.44(17)	O(1)–Na(1)–O(2a)	93.51(18)
O(2a)–Na(1)–O(3)	89.99(16)	O(1)–Na(2)–O(2)	91.61(16)
O(1)–Na(2)–O(2a)	87.86(15)	O(1)–Na(2)–O(3a)	178.18(17)
O(2)–Na(2)–O(2a)	90.79(15)	O(2)–Na(2)–O(3a)	87.15(16)
O(2a)–Na(2)–O(3a)	90.83(16)	O(1)–Na(3)–O(2)	91.34(17)
O(1)–Na(3)–O(3)	95.20(17)	O(2)–Na(3)–O(3)	91.67(16)

Na–O–C Angles			
Na(1)–O(1)–C(11)	144.1(4)	Na(2)–O(1)–C(11)	122.8(4)
Na(3)–O(1)–C(11)	102.8(3)	Na(2)–O(2)–C(21)	119.8(3)
Na(3)–O(2)–C(21)	84.3(3)	Na(1a)–O(2)–C(21)	106.1(3)
Na(2a)–O(2)–C(21)	147.6(3)	Na(1)–O(3)–C(31)	116.2(3)
Na(3)–O(3)–C(31)	124.2(3)	Na(2a)–O(3)–C(31)	132.2(4)

[a] "a" indicates the symmetry operation $-x + 2, -y, -z + 1$.

face, and Na–O–Na and O–Na–O angles around 90 and 180° (see Table 2). The structure contains the phenolate ligands in two different coordination geometries, involving O-bridging between either three or four sodium atoms (see Figure 3). The four phenolate ligands with their oxygen atoms in one of the two outer Na_2O_2 faces [Na(1)O(1)Na(3)O(3) and Na(1a)O(1a)-Na(3a)O(3a)] are O-bridging between three sodium atoms and coordinate with their amino substituents to one of these sodium atoms. The coordination geometry around the oxygen atoms of these phenolate ligands is distorted tetrahedral. Each of the two phenolate ligands with their oxygen atoms in the inner Na_2O_2 face [Na(2)O(2)Na(2a)O(2a)] is O-bridging between four sodium atoms, coordinates with its amino substituent to one of these sodium atoms, and has an η^2-arene interaction with another. The coordination geometry around the oxygen atoms of these two phenolate ligands is distorted trigonal bipyramidal.

The bond length of 1.314(7) Å for O(2)–C(21) is comparable to the bond lengths of 1.311(8) and 1.334(7) Å for O(1)–C(11) and O(3)–C(31), respectively. These O–C bond lengths are normal for phenolates bonded to sodium.[2,4] As a result of the different coordination geometries of the phenolate ligands, the two sodium atoms in the inner face are five-coordinate, and the four sodium atoms in the two outer faces are either four- (Na(1) and Na(1a)) or six-coordinate (Na(3) and Na(3a)). The Na–O (range 2.234(5)–2.478(5) Å) and Na–N bond lengths (range 2.410(6)–2.494(6) Å) are close to those reported for other sodium phenolates (ranges 2.231(4)–2.417(2)[2,4] and 2.468(3)–2.664(5) Å,[2] respectively). The Na–C distances of 2.687(6) and 2.744(6) Å, involved in the η^2-arene interaction, are significantly shorter than the average Na–C bond length of 2.94-(11) Å for the η^6-arene interaction in $[NaOC_6H_4Me-4]_\infty$ (**3**).[4]

Crystals suitable for an X-ray structure determination of **2b** were obtained by cooling a concentrated hexane solution of **2a** containing a 2-fold excess of the free phenol **2** to −30 °C. The structure determination showed the dimeric structure of **2b** (see Figure 4) to consist of two sodium atoms, bridged by two phenolate ligands, resulting in a flat Na(μ-O)$_2$Na unit [maximum distance from the least-squares plane: 0.034(3) Å for O(3)] with all four angles near 90° and $\Sigma° = 359.80°$ (see Table 3). Each of the two phenolate ligands coordinates with one of its amino substituents to one of the sodium atoms, while its second amino substituent is pendant. The coordination sphere around each sodium is completed by an *O,N*-coordinated (neutral) phenol ligand, in which the acidic hydrogen forms a hydrogen bridge with the second amino substituent (O(1)–N(12) = O(4)–N(42) = 2.599(4) Å). This O–H⋯N bond is somewhat shorter than the range reported for organic compounds (2.62–2.93 Å),[14] indicating a strong bond. The Na–O distances in the flat Na-(μ-O)$_2$Na unit (2.216(3)–2.289(3) Å) are in the lower part of the ranges of those reported earlier (2.231(4)–2.417(2) Å)[2,4] and those found in **1a** (2.234(5)–2.478(5) Å). The Na–O bond

(14) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Reinhold Publishing Corp.: New York, 1960.
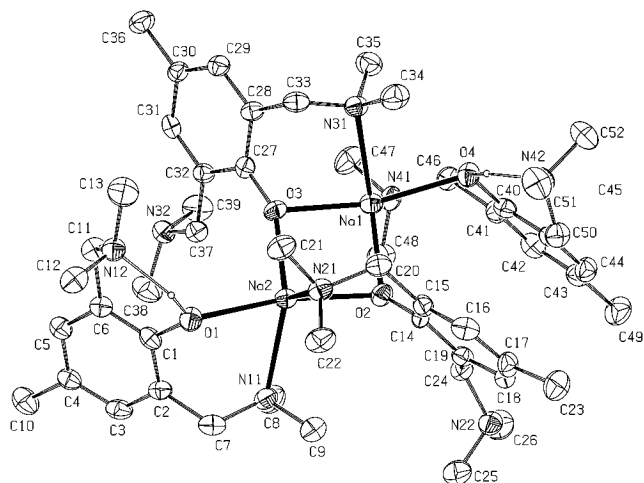
Figure 4. ORTEP representation (50% probability) of [(NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)(HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)]$_2$ (**2b**) with the adopted numbering scheme. All hydrogen atoms except those in the O—H···N bridges have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [(NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)(HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)]$_2$ (**2b**)

With Anionic Phenolate Ligands			
Distances			
Na(1)—O(2)	2.253(3)	Na(1)—N(31)	2.564(4)
Na(1)—O(3)	2.269(3)	Na(2)—N(21)	2.490(4)
Na(2)—O(2)	2.289(3)	C(14)—O(2)	1.302(5)
Na(2)—O(3)	2.216(3)	C(27)—O(3)	1.300(5)
Angles			
Na(1)—O(2)—Na(2)	89.46(12)	Na(1)—O(2)—C(14)	129.2(3)
Na(1)—O(3)—Na(2)	90.89(11)	Na(1)—O(3)—C(27)	115.1(2)
O(2)—Na(1)—O(3)	89.51(10)	Na(2)—O(2)—C(14)	122.3(3)
O(2)—Na(2)—O(3)	89.94(12)	Na(2)—O(3)—C(27)	153.6(3)
With Neutral Phenolate Ligands			
Distances			
Na(1)—O(4)	2.374(3)	C(1)—O(1)	1.371(5)
Na(2)—O(1)	2.413(3)	C(40)—O(4)	1.373(5)
Na(1)—N(41)	2.509(4)	O(1)-H···N(12)	2.599(4)
Na(1)—N(11)	2.513(4)	O(4)-H···N(42)	2.599(4)
Angles			
Na(1)—O(4)—C(40)	116.2(2)	Na(2)—O(1)—C(1)	119.0(3)

lengths connected with the neutral, bidentate ligands are in the upper part of these ranges. The Na—N distances (range 2.490-(4)—2.564(4) Å) are slightly longer than those found in **1a** (range 2.410(6)—2.494(6) Å). The O—C bond lengths in the anionic phenolate ligands (1.302(5) and 1.300(5) Å) are comparable to those in **1a** and slightly shorter than those in the neutral ligands (1.371(5) and 1.373(5) Å).

Discussion

If we compare the solid state structure of the sodium *o*-aminophenolate **1a** with the extended array structure of the parent sodium phenolate {[[NaOC$_6$H$_4$Me-4]$_2$]}$_\infty$ (**3**)[4] in Figure 5, we can clearly see the effect of the introduction of an *ortho*-amino substituent on the structure and aggregation state of sodium phenolate complexes. In **3**, the η^6-arene interaction of the phenolate ligands with sodium plays a crucial role. It restricts the structure of the resulting coordination polymer to a one-dimensional stack of [NaOC$_6$H$_4$Me-4]$_2$ units and prevents the formation of a fully extended three-dimensional network. In **1a**, the intramolecular coordination of the amino substituent partly replaces the role of the η^6-arene interaction in **3** in
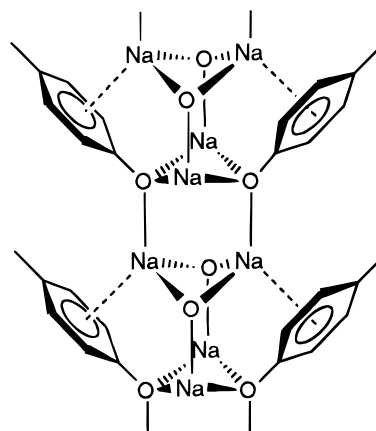

Figure 5. Schematic representation of part of the extended array structure of [NaOC$_6$H$_4$Me-4]$_\infty$ (**3**). The aryl systems of the phenolate ligand in each second Na$_2$O$_2$ layer have been omitted for clarity.
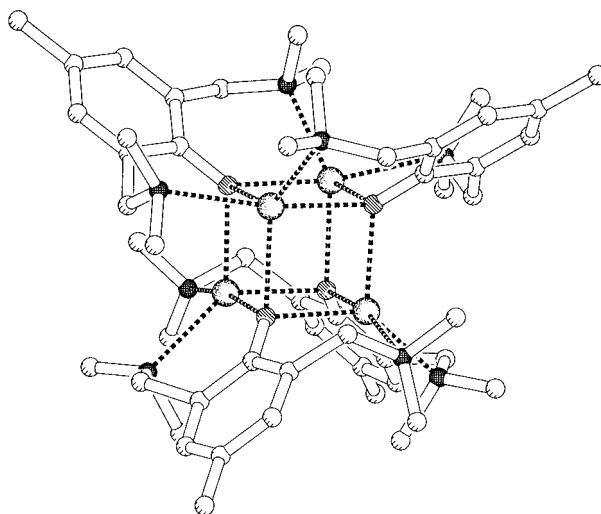

Figure 6. PLUTON drawing of [NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$_4$ (**2a**). Hydrogen atoms have been omitted for clarity. Adapted from ref 2.

completing the coordination sphere around sodium: only one sodium atom in each outer face in the solid state structure of **1a** still maintains an η^2-arene interaction to complete its coordination sphere. As a result of the almost complete disappearance of the η^6-arene interaction, which in **3** results in nonplanar Na$_2$O$_2$ units, the deviation from square planar has now become minimal for the Na$_2$O$_2$ units in the structure of **1a**. This results in additional Na—O interactions between the Na$_2$O$_2$ units in **1a** as compared to those in **3**. These additional Na—O interactions, together with the intramolecular coordination of the amino substituents, result in a reduction of the number of Na$_2$O$_2$ units in the array from unlimited (in **3**) to 3. The phenolate ligands with their oxygen atoms in the outer Na$_2$O$_2$ faces in **1a** still bridge between three sodium atoms (as in **3**) with a distorted tetrahedral geometry around oxygen. In contrast, the oxygen atoms in the inner Na$_2$O$_2$ face now bridge four sodium atoms with a distorted trigonal bipyramidal coordination geometry.

The solid state structure of the sodium bis(*o*-amino)phenolate **2a** (reproduced in Figure 6) shows that introduction of a second *ortho*-amino substituent leads to complete replacement of the arene interactions by intramolecular coordination. This results in a further restriction in the stacking of Na$_2$O$_2$ units from 3 (in **1a**) to 2. It is of interest to note that, in this complex, in contrast to **1a**, both amino substituents coordinate to the sodium atoms in the Na$_2$O$_2$ unit of which the phenolate oxygen is part. As a

Table 4. Crystallographic Data for **1a** and **2b**

	1a	**2b**
formula	$C_{54}H_{72}N_6Na_6O_6$	$C_{52}H_{86}N_8Na_2O_4$
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.668(4)	10.0670(8)
b, Å	18.146(4)	10.7121(7)
c, Å	14.221(5)	27.131(3)
α, deg		92.176(8)
β, deg	110.76(3)	99.928(8)
γ, deg		106.465(6)
V, Å^3	2815.5(16)	2752.1(4)
D_{calc}, g cm^{-3}	1.226	1.126
Z	2	2
μ, cm^{-1}	1.2	0.9
T, K	150	150
λ(Mo Kα), Å	0.710 73	0.710 73
final R^a	0.0736	0.0766
final $R_{w2}{}^b$	0.1887	0.2048

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_{w2} = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

Table 5. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **1a**

atom	x	y	z	U_{eq},^{a} Å^2
Na(1)	0.1365(2)	−0.05282(12)	0.3838(2)	0.0352(8)
Na(2)	0.0383(2)	0.08813(12)	0.4792(2)	0.0325(8)
Na(3)	0.2494(2)	−0.03229(12)	0.6114(2)	0.0329(8)
O(1)	0.2266(4)	0.0449(2)	0.4769(3)	0.0363(17)
O(2)	0.0593(3)	0.0161(2)	0.6288(3)	0.0311(12)
O(3)	0.1483(3)	−0.1268(2)	0.5178(3)	0.0321(14)
N(1)	0.1160(5)	0.2102(3)	0.4475(3)	0.047(2)
N(2)	−0.1000(4)	0.0132(3)	0.7889(3)	0.0326(17)
N(3)	0.3972(4)	−0.1189(3)	0.7148(3)	0.0337(17)
C(11)	0.3272(6)	0.0844(3)	0.5084(4)	0.033(2)
C(12)	0.4385(6)	0.0539(4)	0.5686(5)	0.049(3)
C(13)	0.5461(7)	0.0966(6)	0.6059(6)	0.062(4)
C(14)	0.5434(8)	0.1704(6)	0.5813(7)	0.065(4)
C(15)	0.4357(7)	0.2002(5)	0.5212(7)	0.055(3)
C(16)	0.3283(6)	0.1612(6)	0.4830(5)	0.036(2)
C(17)	0.2170(7)	0.1951(4)	0.4102(6)	0.044(3)
C(18)	0.1558(7)	0.2625(4)	0.5306(6)	0.063(3)
C(19)	0.0134(7)	0.2408(4)	0.3637(6)	0.062(3)
C(21)	0.1332(5)	0.0388(3)	0.7173(4)	0.028(2)
C(22)	0.2336(5)	0.0858(3)	0.7267(5)	0.035(2)
C(23)	0.3168(6)	0.1060(4)	0.8185(5)	0.044(3)
C(24)	0.3065(7)	0.0787(4)	0.9063(5)	0.048(3)
C(25)	0.2075(6)	0.0359(4)	0.8993(5)	0.040(3)
C(26)	0.1213(5)	0.0150(3)	0.8087(4)	0.0294(19)
C(27)	0.0139(6)	−0.0294(3)	0.8069(5)	0.034(2)
C(28)	−0.1991(7)	−0.0353(5)	0.7877(7)	0.053(3)
C(29)	−0.0827(6)	0.0673(4)	0.8699(5)	0.048(3)
C(31)	0.1961(5)	−0.1937(3)	0.5187(4)	0.030(2)
C(32)	0.1606(7)	−0.2373(4)	0.4326(5)	0.038(2)
C(33)	0.2118(7)	−0.3063(4)	0.4340(6)	0.048(3)
C(34)	0.2978(7)	−0.3337(4)	0.5187(6)	0.047(3)
C(35)	0.3296(6)	−0.2917(4)	0.6037(5)	0.040(3)
C(36)	0.2823(5)	−0.2235(3)	0.6079(4)	0.030(2)
C(37)	0.3161(6)	−0.1824(4)	0.7046(5)	0.035(2)
C(38)	0.5103(7)	−0.1418(5)	0.7010(7)	0.054(3)
C(39)	0.4285(7)	−0.0866(4)	0.8160(5)	0.050(3)

^{a} U_{eq} is one-third of the trace of the orthogonalized **U** tensor.

result, the solid state structure of **2a** can be seen as a dimer of Na$_2$O$_2$ units, which is supported by the observation that the molecular weight measured for **2a** in benzene solution is in agreement with the formulation [NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$_2$.^{2} This reflects the fact that, for **2a**, containing the bis-(*ortho*) chelating ligand, the coordination number of sodium in the [NaOAr]$_2$ unit is 4 [coordination numbers of sodium vary from 4 to 6 with 5 as the most preferred],^{15} while for complexes

(15) (a) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169. (b) Fenton, D. E. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 3.

Table 6. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for **2b**

atom	x	y	z	U_{eq}, Å^2
Na(1)	0.9607(2)	0.44155(14)	0.22076(6)	0.0277(5)
Na(2)	0.9115(2)	0.22304(14)	0.29824(6)	0.0268(5)
O(1)	0.9578(3)	0.1749(3)	0.38458(11)	0.0306(12)
O(2)	0.8637(3)	0.2229(3)	0.21265(10)	0.0284(11)
O(3)	0.9938(3)	0.4393(2)	0.30556(10)	0.0279(11)
O(4)	0.9886(3)	0.4765(3)	0.13680(10)	0.0299(11)
N(11)	0.6908(3)	0.0522(3)	0.30866(12)	0.0306(12)
N(12)	1.1546(3)	0.3069(3)	0.45828(12)	0.0309(12)
N(21)	1.1081(3)	0.1403(3)	0.28103(12)	0.0292(12)
N(22)	0.5160(3)	−0.0118(3)	0.10659(13)	0.0326(12)
N(31)	1.2099(3)	0.6026(3)	0.24235(12)	0.0279(12)
N(32)	0.7138(3)	0.5548(3)	0.38423(12)	0.0294(12)
N(41)	0.7691(3)	0.5434(3)	0.19065(12)	0.0295(12)
N(42)	1.1255(3)	0.3713(3)	0.08291(13)	0.0323(12)
C(1)	0.8629(4)	0.1814(4)	0.41452(15)	0.0263(12)
C(2)	0.7266(4)	0.0966(4)	0.40123(15)	0.0272(12)
C(3)	0.6304(4)	0.1037(4)	0.4316(2)	0.0307(14)
C(4)	0.6659(4)	0.1901(4)	0.47419(15)	0.0285(12)
C(5)	0.8027(4)	0.2728(4)	0.48649(15)	0.0271(12)
C(6)	0.9017(4)	0.2712(4)	0.45681(15)	0.0263(12)
C(7)	0.6914(4)	−0.0041(4)	0.3571(2)	0.0339(14)
C(8)	0.5739(4)	0.1053(4)	0.2962(2)	0.0425(17)
C(9)	0.6832(5)	−0.0484(4)	0.2703(2)	0.0402(17)
C(10)	0.5604(4)	0.1961(5)	0.5066(2)	0.0401(16)
C(11)	1.0467(4)	0.3677(4)	0.4682(2)	0.0295(12)
C(12)	1.1807(4)	0.2212(4)	0.4965(2)	0.0363(16)
C(13)	1.2854(4)	0.4050(5)	0.4543(2)	0.0515(18)
C(14)	0.8836(4)	0.1348(4)	0.18271(13)	0.0241(12)
C(15)	1.0140(4)	0.1045(4)	0.18812(14)	0.0263(12)
C(16)	1.0339(4)	0.0140(4)	0.1552(2)	0.0324(14)
C(17)	0.9295(4)	−0.0525(4)	0.11454(15)	0.0303(12)
C(18)	0.8007(4)	−0.0263(4)	0.10958(15)	0.0297(12)
C(19)	0.7748(4)	0.0623(4)	0.14251(14)	0.0250(12)
C(20)	1.1320(4)	0.1776(4)	0.23095(15)	0.0308(12)
C(21)	1.2258(4)	0.2177(4)	0.3188(2)	0.0382(16)
C(22)	1.0956(5)	0.0020(4)	0.2843(2)	0.0412(16)
C(23)	0.9577(5)	−0.1431(5)	0.0762(2)	0.0448(17)
C(24)	0.6359(4)	0.0927(4)	0.13500(15)	0.0276(12)
C(25)	0.4773(5)	−0.1209(5)	0.1367(2)	0.0458(17)
C(26)	0.3975(4)	0.0391(4)	0.0917(2)	0.0479(16)
C(27)	1.0353(4)	0.5538(4)	0.33061(14)	0.0229(12)
C(28)	1.1681(4)	0.6460(4)	0.32867(14)	0.0245(12)
C(29)	1.2096(4)	0.7667(4)	0.35679(14)	0.0265(12)
C(30)	1.1276(4)	0.8044(4)	0.38677(14)	0.0251(12)
C(31)	0.9973(4)	0.7148(4)	0.38817(14)	0.0255(12)
C(32)	0.9501(4)	0.5930(4)	0.36093(14)	0.0236(12)
C(33)	1.2616(4)	0.6112(4)	0.29660(15)	0.0288(14)
C(34)	1.3096(5)	0.5674(4)	0.2152(2)	0.0425(17)
C(35)	1.1931(5)	0.7273(4)	0.2267(2)	0.0372(16)
C(36)	1.1740(4)	0.9363(4)	0.4169(2)	0.0350(16)
C(37)	0.8089(4)	0.4977(4)	0.36238(15)	0.0267(12)
C(38)	0.5966(4)	0.4532(5)	0.3954(2)	0.0448(16)
C(39)	0.6588(5)	0.6379(4)	0.3496(2)	0.0403(17)
C(40)	0.8701(4)	0.4260(4)	0.10025(14)	0.0256(12)
C(41)	0.7555(4)	0.4749(4)	0.10050(15)	0.0293(12)
C(42)	0.6356(4)	0.4231(4)	0.0634(2)	0.0315(12)
C(43)	0.6274(4)	0.3267(4)	0.0268(2)	0.0321(12)
C(44)	0.7442(4)	0.2824(4)	0.0273(2)	0.0318(12)
C(45)	0.8657(4)	0.3298(4)	0.06360(15)	0.0272(12)
C(46)	0.7639(4)	0.5824(4)	0.13938(15)	0.0297(12)
C(47)	0.7871(5)	0.6586(4)	0.2251(2)	0.0422(17)
C(48)	0.6387(5)	0.4436(4)	0.1950(2)	0.0417(17)
C(49)	0.4959(4)	0.2738(5)	−0.0134(2)	0.0446(16)
C(50)	0.9870(4)	0.2733(4)	0.0652(2)	0.0337(14)
C(51)	1.2351(5)	0.3073(5)	0.0955(2)	0.0470(17)
C(52)	1.1605(5)	0.4643(5)	0.0457(2)	0.0451(17)

^{a} U_{eq} is one-third of the trace of the orthogonalized **U** tensor.

1a and **3** the coordination numbers in the [NaOAr]$_2$ unit would be very unfavorable at 3 and 2, respectively. The flexibility of the bis(*ortho*) chelating phenolate [OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$^-$ is illustrated by the fact that the core structure of **2a** in the solid state is identical to that of [Na(OC$_6$H$_4$Me-4)(DME)]$_4$

(DME = dimethoxyethane),[4] where the oxygen donor atoms of DME are not connected to the aryl system of the phenolate ligands as is the case with the nitrogen donor atoms in **2a**. Similar parallels between complexes where donor functions are connected to a phenolate ligand at the metal center and phenolate complexes containing a free donor molecule were recently also observed for aluminum phenolates.[8]

A final example of the gradual breakdown of the polymeric structure of **3** is the formation of **2b** when the potentially tridentate parent phenol is added to a solution of **2a** in hexane. In that case, either the tetrameric structure of **2a** (as present in the solid state) is broken up or the formation of tetramers upon crystallization is prevented by the presence of the coordinating phenol.[16] The unique neutral, bidentate coordination mode of the bis(*ortho*-amino)-substituted phenol in the solid state structure of **2b** causes one of the two amino substituents of the anionic ligand to become pendant, resulting in two five-coordinate sodium atoms. This illustrates that the addition of a third (inter- or intramolecular) coordinating function can ultimately break down the number of Na_2O_2 units to 1, without disrupting this basic Na_2O_2 building block of complex **3**.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk techniques in an atmosphere of dry, oxygen-free dinitrogen. Solvents were carefully dried and distilled prior to use. $HOC_6H_4(CH_2NMe_2)$-2 (**1**) and $HOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 (**2**), as well as their sodium salts $NaOC_6H_4(CH_2NMe_2)$-2 (**1a**) and $NaOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 (**2a**), were synthesized according to literature procedures.[2] Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany. ^{1}H and ^{13}C NMR data were collected on Bruker AC200 and AC300 instruments.

[(NaOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)(HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)]$_2$ (2b). To a solution of **2a** (4.40 g; 18.01 mmol based on monomer) in 40 mL of hexane was added at room temperature an excess of **2** (8.0 g; 36 mmol). Cooling this solution to −30 °C for several weeks afforded the product as colorless crystals in 70−80% yield (based on **2a**).

^{1}H NMR data for **2b** (C_6D_6, 300 MHz, 297 K): δ 10.83 (s, 1 H, O*H*); 6.94 (s, 4 H, Ar *H*); 3.46 (br, 8 H, C*H$_2$*N); 2.25 (s, 6 H, *p-Me*); 1.99 (br, 24 H, N*Me$_2$*). ^{13}C NMR data for **2b** (C_6D_6, 75 MHz, 297 K): δ 166.87 (C_{ipso}); 156.69 (C_{ipso}); 133.74, 129.88, 124.40, 118.34 (Ar *C*); 63.95, 60.94 (*C*H$_2$N); 45.26 (N*Me$_2$*); 20.75 (*p-Me*). Anal. Calcd for $C_{26}H_{43}N_4O_2Na$: C, 66.92; H, 9.29; N, 12.01. Found: C, 66.97; H, 9.26; N, 12.02.

X-ray Data Collection and Structure Refinement for 1a and 2b. Colorless crystals of **1a** and **2b** were sampled directly into a viscous oil, glued on top of a glass fiber, and transferred into the cold nitrogen stream on an Enraf-Nonius Cad4T rotating-anode diffractometer for data collection. Accurate unit cell parameters were derived from the setting angles (SET4) of 25 well-centered reflections in the range 9 < θ < 16° for both **1a** and **2b**. All data were collected with $\omega/2\theta$ scan mode. Crystal data and details on data collection and refinement are collected in Table 4. Data were corrected for Lp effects, for the observed linear decay of the reference reflections, and for absorption (DIFABS;[17] correction ranges 0.570−2.332 and 0.862−1.081 for **1a** and **2b**, respectively). The structures were solved using direct methods (SHELXS86)[18] and subsequent difference Fourier techniques. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93).[19] Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with fixed isotropic thermal parameters related to the value of the equivalent isotropic thermal parameter of their carrier atoms by factors of 1.5 and 1.2 for the methyl hydrogen atoms and the other hydrogen atoms, respectively. Positional parameters are listed in Tables 5 and 6 for **1a** and **2b**, respectively. Neutral-atom scattering factors and anomalous-dispersion corrections were taken from ref 20. All calculations were carried out on a DEC5000 cluster. Geometrical calculations and ORTEP drawings were done with PLATON.[21]

Supporting Information Available: Tables of anisotropic thermal parameters, all H atom parameters, bond lengths and angles, and crystal data for **1a** and **2b** (25 pages). Ordering information is given on any current masthead page.

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(16) We have no data to ascertain whether complex **2a** is either dimeric or tetrameric in hexane solution.

(17) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(18) Sheldrick, G. M. *SHELXS86. Program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1986.
(19) Sheldrick, G. M. *SHELXL93. Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1993.
(20) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
(21) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.