

Siloxide Complexes of Chromium(II), Manganese(II), Cobalt(II), and Chromium(III) Incorporating Potassium(I)

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Heteroleptic ate complexes of the type $K[M\{N(SiMe_3)_2\}_2\{OSi(O^tBu)_3\}]$ ($M = Cr, Mn, Co$) were synthesized by adding one equivalent of the potassium salt $KOSi(O^tBu)_3$ to the bis(trimethylsilyl)amide precursors $[Cr\{N(SiMe_3)_2\}_2(thf)_2]$, $[Mn\{N(SiMe_3)_2\}_2(thf)]$ and $[Co\{N(SiMe_3)_2\}_2(thf)]$, respectively. Surprisingly, the reaction of $CrCl_3(thf)_3$ with only two equivalents of $KOSi(O^tBu)_3$ yielded the homoleptic ate complex $K[Cr\{OSi(O^tBu)_3\}_4]$. The compounds were characterized by elemental analysis and DRIFT spectroscopy as well as X-ray crystallography.

Key words: Siloxides, Silylamides, Transition Metals, Alkali Metals, Ate Complexes

Introduction

Ate complexes of the type $(AM)[M(L)_x]$ or $[(AM)(do)_n][M(L)_x(do)_m]$ ($AM =$ alkali metal, $M =$ transition metal, $L =$ negatively charged ligand, $do =$ neutral donor molecule) are often undesired reaction products, and subsequent separation of the alkali metal salt is not easily accomplished. Nevertheless, some ate complexes have been put to use. One well-known example is the application of lithium trialkylmanganates $LiMnR_3$ ($R =$ alkyl), *e. g.* for the addition of alkyl groups to unsaturated carbonyl derivatives or chiral acylsilanes [1, 2], for cyclization reactions [3], mediation of carbon-carbon bond formations [4], and as initiators for methyl methacrylate polymerization [5]. Ate complexes with silylamide and siloxide ligands are, however, less explored. Recently, we reported on the purposeful synthesis and characterization of silylamide ate complexes of the divalent transition metals chromium, manganese, iron, and cobalt [6]. Heterobimetallic bis(trimethylsilyl)amide compounds have also been synthesized for group 2 metals and lanthanides [7–14]. For the redox-active 4f element cerium it has been shown that ate complexes of the types $(thf)Li[Ce\{N(SiHMe_2)_2\}_4]$

and $[KCe\{N(SiHMe_2)_2\}_4]_n$ drive the formation of the homoleptic complex $[Ce\{N(SiHMe_2)_2\}_4]$ *via* $Ph_3CCl/PhICl_2/C_2Cl_6$ -promoted oxidation/ligand redistribution and separation of alkali metal halide [15, 16].

Molecularly well-defined metal siloxide complexes have been studied since the late 1950s for a better understanding of main group and transition metal-based $M-O-Si$ linkages, a prevailing structural motif in naturally abundant silicates [17–19]. When it comes to siloxide ate complexes, several chromium(II) and vanadium(III) derivatives have been synthesized and structurally characterized, for example ion-separated $[Na(dibenzo-18-crown-6)][Cr(OSi^tBu)_3]$ and $[Li(thf)_4][V(OSiPh_3)_4(thf)_2]$ as well as ligand-bridged $(C_6H_6)Na[CrCl(OSi^tBu)_2]$ and $(thf)_2LiV(OSiMe_2^tBu)_4$ [20, 21]. The homoleptic uranium(III) siloxide ate complex $[K(18-crown-6)][U\{OSi(O^tBu)_3\}_4]$ was shown to react with azides to form uranium(V) imides [22]. Heteroleptic lanthanide ate complexes $[Na(12-crown-4)_2][M\{N(SiMe_3)_2\}_3(OSiMe_3)]$ ($M = Sm, Eu, Yb, Lu$) [23] as well as $[Li(thf)_4][Nd\{N(SiMe_3)_2\}_3(OSiMe_3)]$ [24] have been reported in the literature. Karl *et al.* investigated the (ring opening) polymerization of methylmethacrylate and

norbornene with the samarium and the ytterbium derivatives but found that both are rather poor catalysts [23]. Also, a few monometallic mixed siloxide bis(trimethylsilyl)amide complexes have been structurally characterized, namely $[Y(OSi^tBuAr_2)\{N(SiMe_3)_2\}_2]$ ($Ar = o\text{-}C_6H_4(CH_2NMe_2)$) [25], $[Pb\{N(SiMe_3)_2\}(\mu\text{-}OSiMe_3)]_2$ [26], $[Zn\{N(SiMe_3)_2\}(\mu\text{-}OSiR_3)]_2$ ($R = Et, ^iPr$) [27], and $[N(SiMe_3)_2]_2Fe_2\{\mu\text{-}OSi(Me)_2SiMe_3\}_4Fe$ [28]. Heteroleptic $[Ga\{N(SiMe_3)_2\}(OSiMe_3)_2(py)]$ and $[N\equiv Mo\{N(SiMe_3)_2\}(OSiMe_3)_2]$ have been applied as precursors for metal nitride phases [29, 30]. The latter can also be utilized as a precatalyst for alkyne metathesis reactions [31–34]. Particularly, silanol $HOSi(O^tBu)_3$ has been employed to model the grafting of organometallics onto silica materials, emulating both siloxy and siloxane sites [35–39]. Representative examples of silylamide-based surface organometallic chemistry include the grafting of $[Ba\{N(SiHMe_2)_2\}_2(thf)_4]$ onto MCM-41 [40] or $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ onto $SiO_2\text{-}700$ [41]. In the latter case, reaction with one equivalent of $HOSi(O^tBu)_3$ yielded only the product of the Schlenk equilibrium, $[Ca\{OSi(O^tBu)_3\}_2]$ [41], whereas for the barium compound, heteroleptic $[Ba_3\{\mu_2\text{-}OSi(O^tBu)_3\}_2\text{-}$

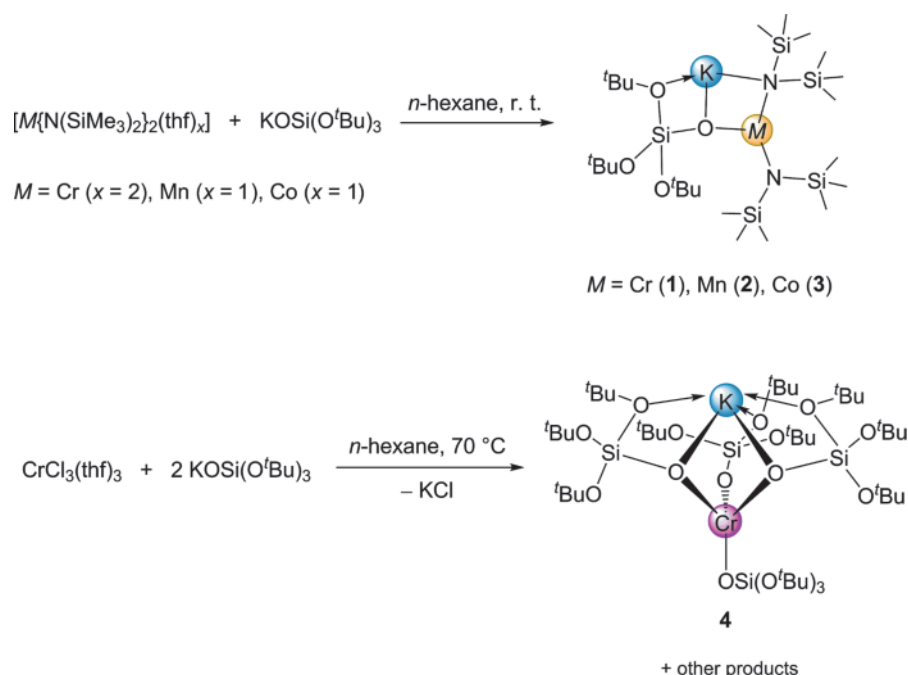
$\{\mu_3\text{-}OSi(O^tBu)_3\}\{\mu_2\text{-}N(SiHMe_2)_2\}\{N(SiHMe_2)_2\}_2]$ could be obtained [40].

In this work, we report on the synthesis of heterobimetallic mixed tris(*tert*-butoxy)siloxide bis(trimethylsilyl)amide complexes of the divalent transition metals chromium, manganese, and cobalt as well as a homoleptic chromium(III) tris(*tert*-butoxy)siloxide ate complex and their characterization by DRIFT spectroscopy and X-ray crystallography.

Results and Discussion

Ate complexes $K[M\{N(SiMe_3)_2\}_2\{OSi(O^tBu)_3\}]$ of Cr(II) (1), Mn(II) (2), and Co(II) (3) were synthesized by adding one equivalent of $KOSi(O^tBu)_3$ to the corresponding M (II) bis(trimethylsilyl)amide complexes in *n*-hexane (Scheme 1). Surprisingly, the reaction of activated $CrCl_3(thf)_3$ with two equivalents of $KOSi(O^tBu)_3$ resulted in the homoleptic siloxide ate complex $K[Cr\{OSi(O^tBu)_3\}_4]$ (4, Scheme 1).

Compounds 1–3 are heterobimetallic complexes with one tris(*tert*-butoxy)siloxy and two bis(trimethylsilyl)amido ligands (Fig. 1). The complexes are isostructural with 3-coordinate transition metal centers in a distorted trigonal-planar coord-



Scheme 1. Synthesis of siloxide ate complexes of Cr(II) (1), Mn(II) (2), Co(II) (3), and Cr(III) (4).

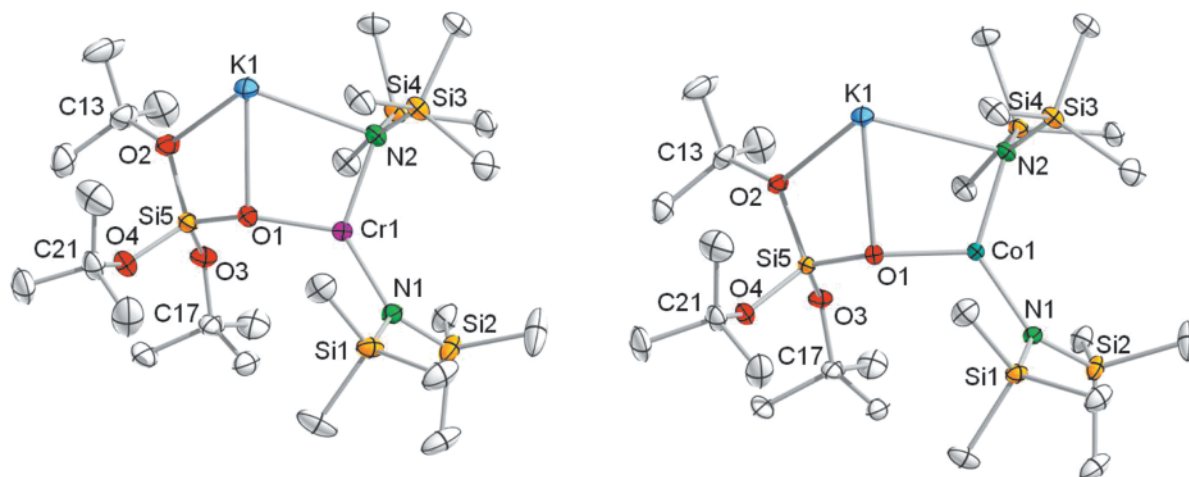


Fig. 1 (color online). Molecular structures of complexes **1** (left) and **3** (right), ellipsoids are set at the 50% level, hydrogen atoms and secondary intermolecular interactions are omitted for clarity.

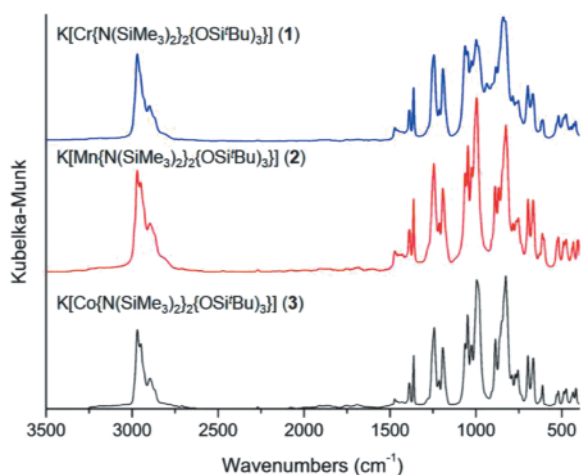


Fig. 2 (color online). DRIFT spectra of compounds **1–3**.

dination geometry. The potassium centers are also 3-coordinate and interact with a *tert*-butoxy group in addition to one siloxy and one amido moiety. The isostructurality is also displayed in the DRIFT spectra of the three complexes that differ only very slightly (Fig. 2).

In general, complex **2** features the largest metal center (Mn(II) high-spin configuration) and hence exhibits the longest $M1-N$ and $M1-O1$ bonds, whereas complex **3** with the smallest Co(II) center shows the shortest bonds (Table 1). The $K1-N2$ bonds are very sim-

ilar for **2** and **3**, while the shortest bond is observed for chromium-containing **1**. The longest $K1-O1$ bond is found in the cobalt(II) complex (**3**) whilst the shortest $K1-O1$ bond is located in the chromium(II) complex (**1**). The longest $M1 \cdots K1$ distance is observed for **1** followed by **2** and **3**. The bonding angles of the three isotopic complexes are more or less the same (Table 1).

As aforementioned, mixed siloxide bis(trimethylsilyl)amide ate complexes are known for lanthanides. For example, the separated ion pair $[Li(thf)_4][Nd\{N(SiMe_3)_2\}_3\{OSiMe_3\}]$ resulted from the reaction of $LiOSiMe_3$ with $Nd\{N(SiMe_3)_2\}_3$ [24]. Some years later, complexes of the type $[Na(12-crown-4)_2][M\{N(SiMe_3)_2\}_3\{OSiMe_3\}]$ were obtained upon the reaction of $NaOSiMe_3$ with $M\{N(SiMe_3)_2\}_3$ in the presence of 12-crown-4 ($M = Sm, Eu, Yb, Lu$) [23]. In the case of complexes **1–3**, ion separation cannot be observed. Instead, X-ray crystallography revealed that the “molecules” $K[M\{N(SiMe_3)_2\}_2\{OSi(O^tBu)_3\}]$ arrange in an infinite chain-like structure involving $K \cdots CH_3Si$ intermolecular secondary interactions (Fig. 3). Short potassium-carbon contacts of 3.244(1) Å for the chromium complex **1**, 3.269(1) Å for the manganese complex **2**, and 3.293(1) Å for the cobalt complex **3** can be observed (*cf.* Fig. 3). Similar interactions between potassium and methyl groups of two adjacent molecules were found for $K[Sm\{N(SiMe_3)_2\}_3]$ leading to a two-dimensional network (shortest $K \cdots C$: 3.190(6) Å) [12]. The authors state that the intermolecular interactions stabi-

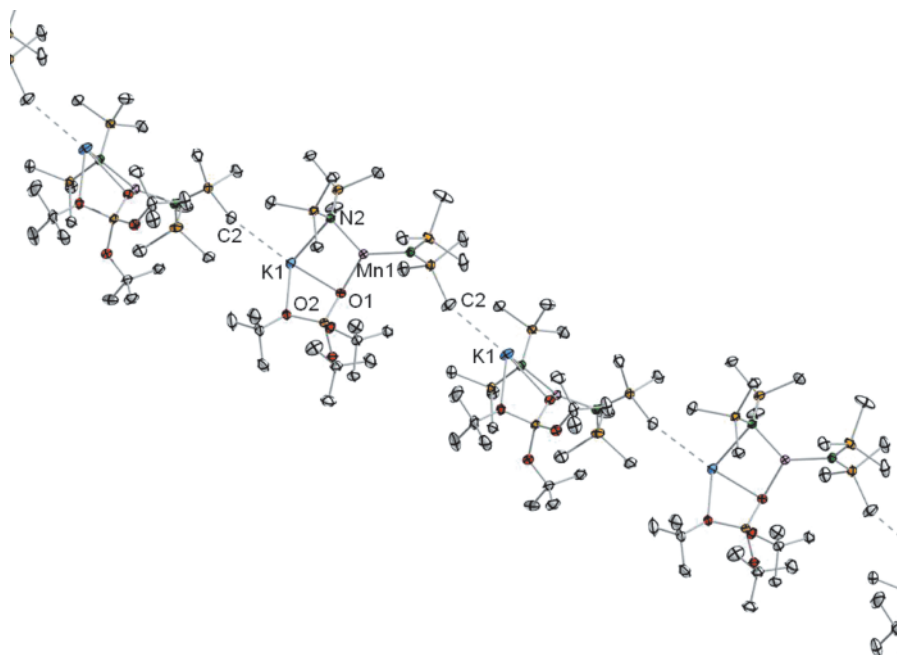


Fig. 3 (color online). Chain-like solid-state structure of complex **2** with potassium-carbon intermolecular interactions, ellipsoids are set at the 50% level.

Table 1. Selected interatomic distances (Å) and angles (deg) for **1**, **2** and **3** with estimated standard deviations in parentheses.

	1 (<i>M</i> = Cr)	2 (<i>M</i> = Mn)	3 (<i>M</i> = Co)
Distances			
<i>M1</i> – <i>N1</i>	1.9988(9)	2.0248(8)	1.9384(9)
<i>M1</i> – <i>N2</i>	2.0598(8)	2.0846(8)	1.9794(9)
<i>M1</i> – <i>O1</i>	1.9568(7)	1.9928(7)	1.9215(7)
<i>K1</i> – <i>N2</i>	2.8363(9)	2.8753(8)	2.8752(9)
<i>K1</i> – <i>O1</i>	2.6376(7)	2.6757(7)	2.6821(8)
<i>K1</i> – <i>O2</i>	2.6675(8)	2.6737(7)	2.6590(8)
<i>M1</i> ... <i>K1</i>	3.5121(3)	3.4671(3)	3.3933(3)
Angles			
<i>N1</i> – <i>M1</i> – <i>N2</i>	129.06(3)	130.54(3)	128.98(4)
<i>N1</i> – <i>M1</i> – <i>O1</i>	130.39(3)	123.28(3)	121.82(4)
<i>N2</i> – <i>M1</i> – <i>O1</i>	100.05(3)	105.13(3)	108.56(3)
<i>M1</i> – <i>N2</i> – <i>K1</i>	90.23(3)	87.17(3)	86.62(3)
<i>M1</i> – <i>O1</i> – <i>Si5</i>	142.72(5)	140.32(4)	141.66(5)
<i>O1</i> – <i>Si5</i> – <i>O2</i>	103.52(4)	103.75(3)	103.66(4)
<i>O1</i> – <i>K1</i> – <i>O2</i>	57.28(2)	56.98(2)	57.90(2)
<i>O1</i> – <i>K1</i> – <i>N2</i>	68.34(2)	71.27(2)	69.39(2)
<i>O2</i> – <i>K1</i> – <i>N2</i>	108.21(3)	109.07(2)	107.75(3)

lize the Sm(II)/N(SiMe₃)₂ system, enabling the sublimation of the complex in contrast to monometallic [Sm{N(SiMe₃)₂}₂(thf)₂], which disproportionates at elevated temperatures. Forbes *et al.* also obtained polymeric chain structures as well as dimers for a range

of magnesium(II) and zinc(II) bis(trimethylsilyl)amide complexes. The bridging occurs *via* potassium-methyl interactions with K...C contacts between 3.128 and 3.418 Å [42].

A monometallic mixed bis(trimethylsilyl)amide tris(*tert*-butoxy)siloxide of manganese(II), [Mn{N(SiMe₃)₂}{OSi(O^{*t*}Bu)₃}]₂, has recently been synthesized by our group [43]. The Mn1–N1 bond (2.003(2) Å) in the monometallic complex is slightly shorter than the Mn1–N bonds in **2**. The elongated bonds in the ate complex might be due to the inter- and intramolecular interactions of the silylamido groups with adjacent potassium atoms. In spite of the involvement of O1 in a bond with K1 in compound **2**, the Mn1–O bonds in [Mn{N(SiMe₃)₂}{OSi(O^{*t*}Bu)₃}]₂ are longer (2.187(2), 2.035(2) Å), which could be induced by the bridging character of these oxygen atoms.

The solid-state structure of K[Cr{OSi(O^{*t*}Bu)₃}₄] (**4**, Fig. 4) revealed that three siloxy ligands interact with the potassium center forming a “basket” for the latter, while the fourth ligand points in the opposite direction. Two independent molecules are located in the asymmetric unit, of which molecule **2** exhibits two alternating positions for the potassium atom in a ratio of K2A = 0.88 : 0.12 (Fig. 4, right).

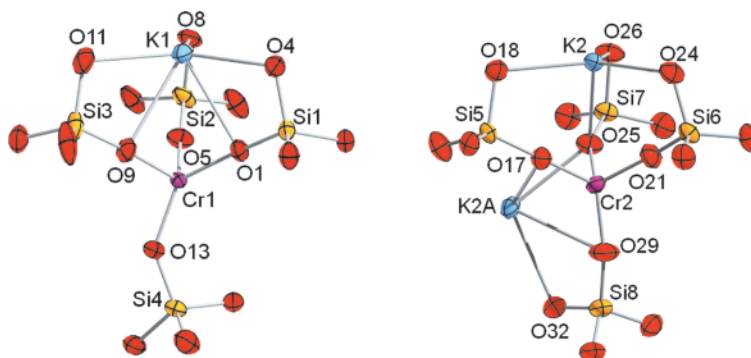


Fig. 4 (color online). Molecules 1 (left) and 2 (right) in the solid-state structure of complex **4**, ellipsoids are set at the 50% level, *tert*-butyl groups are omitted for clarity.

The potassium atom K1 is bonded to three *tert*-butoxy and two siloxy moieties and thus is five-coordinate. In contrast, K2 in molecule 2 shows only four K2–O bonds. This finding could arise from the existence of the alternative potassium atom position K2A. If only contacts shorter than the sum of the van der Waals radii (2.7 Å) are taken into account, K2A would solely interact with O25 (2.659(5) Å, Table 2). The distances to O17, O29 and O32, though, are only slightly longer with 2.933(4), 2.995(5) and 2.896(5) Å, respectively.

The bond from Cr2 to the terminal ligand O29 (1.805(2) Å) is the shortest Cr–O siloxy bond in both molecules and is significantly shorter than the corresponding terminal Cr1–O13 bond (1.851(2) Å, Table 2). The longest chromium-oxygen bond can be found in molecule 1 for Cr1–O1 (Table 2). The other chromium-oxygen bonds range from 1.838(2) to 1.856(2) Å. The terminal Cr1–O13 bond in molecule 1 exhibits the same length as the shortest Cr–O bond observed for the monometallic siloxide complex [Cr{OSi(O^tBu)₃}₃(thf)₂] (1.851(2), 1.860(2) and 1.895(2) Å) [44].

The contacts of K1 and K2 to the oxygen atoms of the *tert*-butoxy groups are shorter than to the siloxy moieties (Table 2). The distance Cr2...K2 is slightly shorter than Cr...K1, but both are longer than Cr2...K2A (Table 2). All-in-all, it is clear that the presence of K2A influences the structure of molecule 2 to a certain extent, and hence the molecules exhibit different bond lengths and angles.

The structural motif found in molecule 1 is already known in literature, although these examples, Na[Pb{OSi(O^tBu)₃}₃] and K[Sn{OSi(O^tBu)₃}₃], in-

Table 2. Selected interatomic distances (Å) and angles (deg) for both independent molecules of **4** with estimated standard deviations in parentheses.

	4 (Molecule 1)		4 (Molecule 2)	
Distances				
Cr1–O1	1.878(2)	Cr2–O17	1.856(2)	
Cr1–O5	1.843(2)	Cr2–O21	1.838(2)	
Cr1–O9	1.844(2)	Cr2–O25	1.849(2)	
Cr1–O13	1.851(2)	Cr2–O29	1.805(2)	
K1–O1	2.830(2)	K2–O18	2.658(2)	
K1–O4	2.680(2)	K2–O24	2.672(2)	
K1–O8	2.657(2)	K2–O25	2.862(2)	
K1–O9	2.848(2)	K2–O26	2.670(2)	
K1–O11	2.670(2)	–	–	
–	–	K2A–O25	2.659(5)	
Cr1...K1	3.2412(6)	Cr2...K2	3.2295(6)	
–	–	Cr2...K2A	2.785(4)	
Angles				
O1–Cr1–O5	96.07(8)	O17–Cr2–O21	101.95(8)	
O1–Cr1–O9	100.02(7)	O17–Cr2–O25	98.23(8)	
O1–Cr1–O13	132.57(7)	O17–Cr2–O29	122.30(9)	
O5–Cr1–O9	105.14(8)	O21–Cr2–O25	102.76(8)	
O5–Cr1–O13	118.41(7)	O21–Cr2–O29	112.4(1)	
O9–Cr1–O13	100.92(7)	O25–Cr2–O29	116.4(1)	
–	–	O25–Cr2–K2A	66.5(1)	
O1–K1–O4	55.12(5)	O25–K2–O26	54.82(5)	
O9–K1–O11	54.56(6)	–	–	
O4–K1–O8	116.21(6)	O18–K2–O24	123.56(6)	
O8–K1–O11	115.61(7)	O24–K2–O26	120.83(6)	
O11–K1–O4	127.97(8)	O26–K2–O18	115.22(6)	
–	–	O25–K2A–Cr2	39.63(7)	
–	–	O32–K2A–Cr2	87.8(1)	
–	–	O25–K2A–O32	104.8(1)	

volve divalent metal centers, and hence the fourth and terminal siloxy ligand is absent [45]. Interestingly, complex K[Cr{OSi(O^tBu)₃}₄] (**4**) was obtained with an substoichiometric amount of KOSi(O^tBu)₃ while

Table 3. Selected interatomic distances (Å) and angles (deg) for molecule 1 of complex **4**, $K[Sn\{OSi(O^tBu)_3\}_3]$ [45], and $Na[Pb\{OSi(O^tBu)_3\}_3]$ [45] (labeling in parentheses) with estimated standard deviations in parentheses. (*M* = metal, *AM* = alkali metal).

	4 (Molecule 1)	$K[Sn\{OSi(O^tBu)_3\}_3]$	$Na[Pb\{OSi(O^tBu)_3\}_3]$
Distances			
<i>M1</i> – <i>O1</i>	1.878(2)	2.058(6)	2.14(2)
<i>M1</i> – <i>O5</i> (<i>O2</i>)	1.843(2)	2.038(5)	2.12(2)
<i>M1</i> – <i>O9</i> (<i>O3</i>)	1.844(2)	2.054(6)	2.15(2)
<i>AM1</i> – <i>O1</i>	2.830(2)	2.822(6)	2.50(1)
<i>AM1</i> – <i>O4</i> (<i>O6</i>)	2.680(2)	2.730(6)	2.52(2)
<i>AM1</i> – <i>O8</i> (<i>O7/O9</i>)	2.657(2)	2.704(7)	2.86(2)
<i>AM1</i> – <i>O9</i> (<i>O3</i>)	2.848(2)	2.797(6)	2.62(2)
<i>AM1</i> – <i>O11</i> (<i>O12</i>)	2.670(2)	2.730(8)	2.46(2)
<i>M1</i> ... <i>AM1</i>	3.2412(6)	3.483(2)	3.150(6)
Angles			
<i>O1</i> – <i>M1</i> – <i>O5</i> (<i>O2</i>)	96.07(8)	89.6(2)	86.4(6)
<i>O1</i> – <i>M1</i> – <i>O9</i> (<i>O3</i>)	100.02(7)	89.8(3)	87.7(5)
<i>O5</i> (<i>O2</i>)– <i>M1</i> – <i>O9</i> (<i>O3</i>)	105.14(8)	88.6(3)	86.9(6)
<i>O1</i> – <i>AM1</i> – <i>O4</i> (<i>O6</i>)	55.12(5)	54.4(2)	60.3(4)
<i>O9</i> (<i>O3</i>)– <i>AM1</i> – <i>O11</i> (<i>O12</i>)	54.56(6)	54.4(2)	58.7(4)

the literature examples were intentionally synthesized with an excess of $MOSi(O^tBu)_3$ (*M* = Na, K).

For the tin(II) compound [45], the contacts of the alkali metal to the oxygen atoms of the *tert*-butoxy groups are closer than those to the siloxide oxygen atoms, which has also been observed in **4** (Table 3). This is not the case for $Na[Pb\{OSi(O^tBu)_3\}_3]$ [45], in which the longest sodium–oxygen bond is found with one of the *tert*-butoxy groups ($Na1-O9 = 2.86(2)$ Å). In **4**, the potassium atom is only five- and four-coordinate, whereas the alkali metal centers in the lead(II) and tin(II) complexes are six-coordinate. The bonds that include chromium, lead and tin are of course affected by the different cation sizes, showing an enlargement as the ionic radius increases (Table 3).

Two more tris(*tert*-butoxy)siloxide ate complexes have been described in literature, although they have not been structurally characterized. The titanium(III) complex $Li[Ti\{OSi(O^tBu)_3\}_4]$ probably obtains a similar structure as **4** [46]. Hexameric $[NaCu\{OSi(O^tBu)_3\}_2]_6$ has been investigated by thermal analysis [47].

Conclusion

The heteroleptic ate complexes $K[M\{N(SiMe_3)_2\}_2\{OSi(O^tBu)_3\}]$ (*M* = Cr, Mn, Co) could be synthesized in moderate yields from the bis(trimethylsilyl)amide complexes and $KOSi(O^tBu)_3$. The complexes turned out to be isostructural, which can also be derived

from the DRIFT spectra. X-Ray crystal structure analyses further revealed that the monomers arrange in polymeric chains, that are built through interactions between the potassium centers and the methyl groups of adjacent bis(trimethylsilyl)amido ligands. This phenomenon has also been reported for heterobimetallic bis(trimethylsilyl)amide complexes. The homoleptic siloxide ate complex $K[Cr\{OSi(O^tBu)_3\}_4]$ was unexpectedly obtained *via* salt metathesis from $CrCl_3(thf)_3$ and two equivalents of the potassium salt $KOSi(O^tBu)_3$. The potassium atoms are embedded by three siloxy ligands interacting with *tert*-butoxy groups as well as siloxy moieties. This structural motif is literature-known for divalent lead and tin tris(*tert*-butoxy)siloxide ate complexes, which have, in contrast, been synthesized with an excess of $MOSi(O^tBu)_3$ (*M* = Na, K). X-Ray structure analysis of $K[Cr\{OSi(O^tBu)_3\}_4]$ further revealed two independent molecules in the asymmetric unit, one of which exhibiting an alternative position for the potassium atom, which affects the coordination of the other potassium atom as well as the bond lengths and angles within the whole molecule.

Experimental Section

General Information. All reactions were carried out under a dry argon atmosphere using standard Schlenk or glove box techniques (MBraun, MB250B, < 0.1 ppm H_2O , O_2). The solvents were dried over Grubbs columns (MBraun,

Solvent Purification System) and stored inside a glove-box. Elemental analyses were carried out on an Elementar Vario MICRO cube instrument. DRIFT spectra were measured on a Thermo Scientific Nicolet6700 FTIR spectrometer using KBr powder and a DRIFT cell equipped with KBr windows. The spectra were recorded with 256 scans from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} . Manganese(II) chloride (97%), cobalt(II) chloride (99%), chromium(II) chloride (97%), chromium(III) chloride (99.9%), and 1,1,1,3,3,3-hexamethyldisilazane (98%) were purchased from ABCR. Potassium bis(trimethylsilyl)amide (sublimed at 130°C under high vacuum prior to use), HOSi(O^{*t*}Bu)₃ (99.999%) and *n*-butyllithium (2.5 M in hexane) were obtained from Sigma-Aldrich. CrCl₃(thf)₃ [48], [Cr{N(SiMe₃)₂}₂(thf)₂] [49], [Mn{N(SiMe₃)₂}₂(thf)] [50, 51], and [Co{N(SiMe₃)₂}₂(thf)] [52, 53] were synthesized according to literature procedures. KOSi(O^{*t*}Bu)₃ was generated by stirring HOSi(O^{*t*}Bu)₃ and KN(SiMe₃)₂ in *n*-hexane.

K[Cr{N(SiMe₃)₂}₂{OSi(O^{*t*}Bu)₃}] (1)

[Cr{N(SiMe₃)₂}₂(thf)₂] (99 mg, 0.19 mmol) was dissolved in *n*-hexane to give a blue solution. KOSi(O^{*t*}Bu)₃

(58 mg, 0.19 mmol) in *n*-hexane was added, and the light-green solution was stirred for 1.5 h. Removing the solvent and crystallization at −40°C from *n*-hexane gave turquoise crystals. Yield: 91 mg, 76%. – C₂₄H₆₃N₂O₄Si₅KCr (675.31): calcd. C 42.69, H 9.40, N 4.15; found C 42.47, H 8.70, N 4.20. – DRIFT (KBr): $\nu = 2970$ (m), 2900 (w), 1472 (w), 1387 (w), 1362 (m), 1245 (m), 1213 (w), 1191 (m), 1063 (s), 1049 (s), 1025 (m), 998 (s), 936 (m), 884 (m), 842 (s), 785 (m), 753 (m), 698 (m), 669 (m), 612 (w), 520 (w), 477 (w) cm^{-1} .

K[Mn{N(SiMe₃)₂}₂{OSi(O^{*t*}Bu)₃}] (2)

[Mn{N(SiMe₃)₂}₂(thf)] (113 mg, 0.25 mmol) was dissolved in *n*-hexane to give a rose solution. KOSi(O^{*t*}Bu)₃ (77 mg, 0.25 mmol) in *n*-hexane was added, and the colorless solution was stirred for 3 h. Removing the solvent and crystallization at −40°C from *n*-hexane gave colorless crystals. Yield: 115 mg, 67%. – C₂₄H₆₃N₂O₄Si₅KMn (678.25): calcd. C 42.50, H 9.36, N 4.13; found C 42.53, H 8.45, N 4.20. – DRIFT (KBr): $\nu = 2971$ (m), 2951 (m), 2897 (w), 1472 (w), 1387 (w), 1245 (s), 1213 (w), 1192 (m), 1063 (m), 1047 (s), 1025 (m), 996 (s), 888 (m), 867 (m), 826 (s), 783

Table 4. Crystal structure data for **1–4**.

	1	2	3	4
Empirical Formula	C ₂₄ H ₆₃ N ₂ O ₄ Si ₅ KCr	C ₂₄ H ₆₃ N ₂ O ₄ Si ₅ KMn	C ₂₄ H ₆₃ N ₂ O ₄ Si ₅ KCo	C ₄₈ H ₁₀₈ O ₁₆ Si ₄ KCr
<i>M_r</i>	675.31	678.25	682.24	1144.80
<i>T</i> , K	120(2)	100(2)	100(2)	123(2)
Crystal size, mm ³	0.58 × 0.50 × 0.39	0.43 × 0.29 × 0.17	0.50 × 0.19 × 0.16	0.56 × 0.27 × 0.17
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.2101(7)	12.1399(2)	12.1136(4)	23.0324(9)
<i>b</i> , Å	17.491(1)	17.4597(3)	17.4684(6)	25.033(1)
<i>c</i> , Å	19.289(1)	19.3963(4)	19.2473(6)	25.221(1)
β , deg	104.817(2)	105.063(1)	105.672(1)	111.022(1)
<i>V</i> , Å ³	3982.3(4)	3970.0(1)	3921.4(2)	13573.3(9)
<i>Z</i>	4	4	4	8
<i>D</i> _{calcd.} , g cm ^{−3}	1.13	1.14	1.16	1.12
μ (MoK α), mm ^{−1}	0.6	0.6	0.7	0.4
<i>F</i> (000), <i>e</i>	1464	1468	1476	4984
<i>hkl</i> range	−16 ≤ <i>h</i> ≤ +16 −23 ≤ <i>k</i> ≤ +22 −25 ≤ <i>l</i> ≤ +25	−16 ≤ <i>h</i> ≤ +16 −23 ≤ <i>k</i> ≤ +23 −25 ≤ <i>l</i> ≤ +25	−16 ≤ <i>h</i> ≤ +16 −23 ≤ <i>k</i> ≤ +23 −25 ≤ <i>l</i> ≤ +25	−30 ≤ <i>h</i> ≤ +30 −32 ≤ <i>k</i> ≤ +32 −33 ≤ <i>l</i> ≤ +33
Refl. measured	90 746	79 812	72 337	194 344
Refl. unique	9899	9840	9739	32 399
<i>R</i> _{int}	0.0221	0.0310	0.0262	0.0493
Param. refined	355	355	355	1423
2 ϑ _{max} , deg	56.56	56.56	56.56	55.79
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^{a,b}	0.0259/0.0656	0.0243/0.0575	0.0216/0.0547	0.0567/0.1558
GoF (<i>F</i> ²) ^c	1.055	1.056	1.032	1.037
$\Delta\rho$ _{fin} (max/min), <i>e</i> Å ^{−3}	0.34/−0.26	0.32/−0.23	0.38/−0.20	2.44/−1.56

^a $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $F_o > 2\sigma(F_o)$; ^b $wR(F^2) = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{}$; ^c $\text{GoF} = \frac{[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}}{[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$.

(w), 765 (w), 753 (w), 696 (m), 667 (m), 614 (w), 521 (w), 489 (w), 433 (w), 406 (w) cm^{-1} .

K[Co{N(SiMe₃)₂}₂{OSi(O^tBu)₃}] (3)

[Co{N(SiMe₃)₂}(thf)] (109 mg, 0.24 mmol) was dissolved in *n*-hexane to give a dark-green solution. KOSi(O^tBu)₃ (73 mg, 0.24 mmol) in *n*-hexane was added, and the turquoise solution was stirred for 1.5 h. Removing the solvent and crystallization at -40°C from *n*-hexane gave turquoise crystals. Yield: 127 mg, 78%. – C₂₄H₆₃N₂O₄Si₅KCo (682.24): calcd. C 42.25, H 9.31, N 4.11; found C 42.39, H 8.73, N 4.15. – DRIFT (KBr): $\nu = 2970$ (m), 2950 (m), 2897 (w), 1472 (w), 1387 (w), 1243 (m), 1214 (w), 1192 (m), 1063 (m), 1048 (s), 1025 (m), 995 (s), 887 (m), 827 (s), 790 (w), 755 (w), 697 (m), 666 (m), 613 (w), 521 (w), 488 (w), 575 (w), 435 (w), 418 (w) cm^{-1} .

K[Cr{OSi(O^tBu)₃}]₄ (4)

CrCl₃(thf)₃ (102 mg, 0.27 mmol) was suspended in *n*-hexane, and KOSi(O^tBu)₃ (164 mg, 0.54 mmol) in *n*-hexane was added. The violet suspension turned deep blue and was heated to 70°C for 20 h. After centrifugation and filtration, the solvent was removed yielding a pale-violet solid, which gave dark-blue crystals upon recrystallization at -40°C from *n*-hexane. Yield: 77 mg, 52% (based on KOSi(O^tBu)₃). – C₄₈H₁₀₈O₁₆Si₄KCr (1144.80): calcd. C 50.36, H 9.51; found C 50.51, H 9.55. – DRIFT (KBr): $\nu = 2971$ (s), 2929 (m), 2904 (sh), 2870 (w), 1472 (w), 1387 (m), 1363 (s), 1240 (m),

1215 (m), 1192 (s), 1049 (vs), 1026 (s), 1006 (s), 986 (s), 962 (s), 910 (w), 825 (m), 700 (m), 646 (w), 516 (w), 496 (m), 481 (w), 434 (w) cm^{-1} .

X-Ray crystal structure determinations

Crystals of **1** to **4** were grown by standard techniques from saturated solutions using *n*-hexane at -40°C . Single crystals suitable for X-ray diffraction were selected in a glove box and coated with Paratone-N (Hampton Research). Data collection for **1**, **2** and **3** was performed on a Bruker SMART APEX II diffractometer using multilayer monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). X-Ray diffraction data for **4** were collected on a Bruker SMART 2 K CCD diffractometer using graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) performing 180° ω -scans in four orthogonal ϕ -positions. Raw data for all crystals were collected by using the programs COSMO [54] or SMART [55] and integrated and reduced with the program SAINT [56]. Corrections for absorption effects were applied with SADABS [57]. The structures were solved by Direct Methods and refined with standard difference Fourier techniques (SHELXS/SHELXL) [58]. Details of the crystal structure determination are given in Table 4. All plots were generated utilizing the programs DIAMOND 3.2i [59] and POV-RAY [60].

CCDC codes 1017280 (**1**), 1017281 (**2**), 1017282 (**3**), and 1017283 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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