Synthesis and structure of arene soluble *N,N′*-bis(di-*tert*-butylsalicylidene)ethylenediamine yttrium complexes

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YCl_3 reacts with 1 and 2 equiv. of the dipotassium salt of *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (K_2salen′) and thf to form the arene soluble complexes, [(salen′)Y(μ-Cl)(thf)]$_2$ and (thf)$_2$K[Y(salen′)$_2$], respectively, which provide comparative structural information on the use of this ligand *vis-à-vis* bis(cyclopentadienyl) ligand sets.

Efforts to extend the range of ancillary solubilizing and stabilizing environments for yttrium and the lanthanide metals beyond the common cyclopentadienyl ligand and its analogs have led to the exploration of alternative, polydentate anionic ligands containing various combinations of oxygen and nitrogen donor atoms.[1] Among the ligands examined have been substituted Schiff base derivatives of *N,N′*-bis(salicylidene)-ethylenediamine (H_2salen), a ligand which has been successfully used with both main group and transition metals.[2–8] Salen derivatives are attractive since they can be prepared and derivatized easily and inexpensively[2] and even bi- and tridentate Schiff bases have been shown to be effective ligands for lanthanides.[3] Initial studies[6] of the di-*tert*-butyl substituted analog *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine, H_2salen′,[7] suggested that this ligand would be of limited use with the f-elements compared to cyclopentadienyl ligands since synthetic routes using common precursors such as YCl_3 and $Y[N(SiMe_3)_2]_3$, led to insoluble, presumably oligomeric complexes.[6] Only by use of the specialized silylamide, $[N(SiHMe_2)_2]^-$,[9] was a fully characterizable complex, (salen′)Y[N(SiHMe$_2$)$_2$](thf) **1** obtained.[6] We report here that by using the potassium salt, K_2salen′, obtained from H_2salen′ and KH, soluble complexes can be obtained directly from YCl_3.

YCl_3 reacts with 1 equiv. of K_2salen′ in thf over a 6 h period to form the arene soluble complex [(salen′)Y(μ-Cl)(thf)]$_2$ **2** which was identified by NMR and IR spectroscopy, elemental analysis,† and X-ray diffraction,‡ Fig. 1. Complex **2** crystallizes from benzene as a thf-solvated asymmetric dimer in which one salen′ ligand adopts a nearly planar orientation [Y(2)] and the other is non-planar.

Both yttrium ions in **2** have seven-coordinate distorted capped trigonal prismatic geometries, but Cl(1) occupies the capping position for the Y(1) trigonal prism and N(3) is the cap for Y(2). The distortions of the trigonal prisms also differ: the dihedral angles of the planes of the trigonal faces are 16.6° for Y(1) and 5.4° for Y(2). The salen′ ligand attached to Y(1) has a 119.8° dihedral angle between the planes of the phenyl rings, whereas the salen′ around Y(2) has a more planar orientation, with an 8.4° dihedral angle. The analogous angle in **1** is 108°.[6] In contrast, (salen′)InCl[8] is a monomer in which the salen′ donor atoms are planar. The monomeric structure may be more favorable for indium since it is less electropositive and *ca.* 0.1 Å smaller than yttrium.

Since **2** is similar to the important general class of bis(cyclopentadienyl) halide precursors $[(C_5H_4R)_2Y(\mu\text{-}Cl)]_2$, comparison of the structural parameters of the $[Y(\mu\text{-}Cl)]_2$ unit in **2** with those of the structurally characterized cyclopentadienyl examples in which R = H,[10] $SiMe_3$[11] and PPh_2,[12] allows evaluation of the salen′$^{2-}$ ligand set *vs.* two $C_5H_4R^-$ ligands. As shown in Table 1, the Y–Cl distances in **2** are larger than those

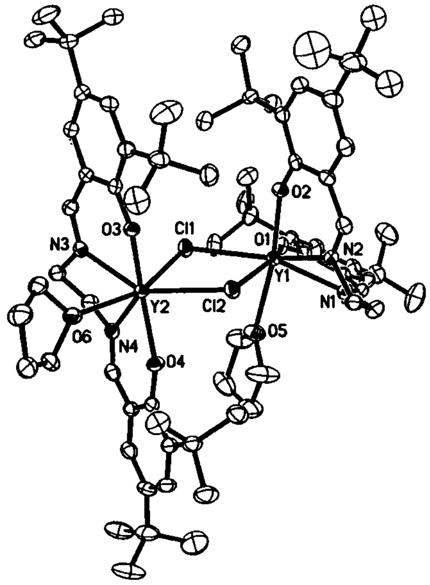

Fig. 1 Structure of [(salen′)Y(μ-Cl)(thf)]$_2$ **2** with thermal ellipsoids drawn at the 50% probability level.

Table 1 Structural data on complexes containing the $[Y(\mu\text{-}Cl)]_2$ unit

Formula	Coordination number	Y–Cl/Å	Y–Cl–Y/°	Cl–Y–Cl/°	Ref
[(salen′)Y(μ-Cl)(thf)]$_2$	7	2.734(1)– 2.759(1)	102.60(3) 103.13(3)	76.34(3) 76.52(3)	This work
$[Cp_2Y(\mu\text{-}Cl)]_2$	8	2.677(3) 2.691(3)	98.58(4)	81.44(4)	10
$[(Me_3SiC_5H_4)_2Y(\mu\text{-}Cl)]_2$	8	2.684(1) 2.704(1)	98.4(1)	81.6(1)	11
syn-$[(Ph_2PC_5H_4)_2Y(\mu\text{-}Cl)]_2$	8	2.655(2) 2.680(2)	97.19(7) 97.43(7)	82.34(7) 82.99(7)	12
anti-$[(Ph_2PC_5H_4)_2Y(\mu\text{-}Cl)]_2$	8	2.657(2) 2.657(2)	99.30(7)	80.69(7)	12

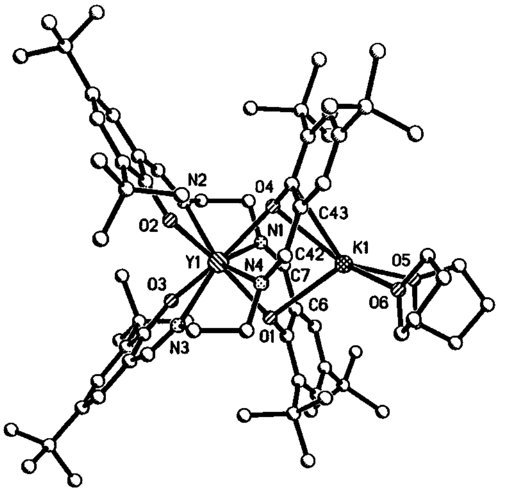

Fig. 2 Ball-and-stick model (for clarity) of $(thf)_2K[(salen')_2Y]$ **3**.

in the $[(C_5H_4R)_2Y(\mu\text{-}Cl)]_2$ complexes, even though **2** is formally seven coordinate and the other complexes are eight coordinate. This difference is accompanied by slightly smaller Cl–Y–Cl angles and slightly larger Y–Cl–Y angles.

Reaction of 2 equiv. of K_2salen′ with YCl_3 also provides an arene soluble product, $(thf)_2K[(salen')_2Y]$ **3**. The coordination environment in **3** (Fig. 2) differs from the 'sandwich' type of coordination which has been postulated for lanthanide complexes containing two disalicylidene-1,2-phenylenediamine ligands.[4] The yttrium in **3** is surrounded by a distorted eight-coordinate square antiprismatic coordination geometry with the N(2) and O(2) of one salen′ ligand and the N(3) and O(3) of the other ligand in one square face and the other donor atoms of the two ligands, N(1), N(4), O(1) and O(4), in the other square face. The dihedral angles between the arene rings in the salen′ ligands are similar: 20.9 and 22.5°. The Y–O distances [2.245(4)–2.356(3) Å] in this eight-coordinate complex are larger than those [2.143(2) and 2.16 Å] in seven-coordinate **2** and six-coordinate **1**, respectively. The Y–N distances [2.556(4)–2.618(4) Å] are also larger than the largest Y–N distances in **2** and **1** [2.492(3) and 2.44 Å, respectively].

The potassium in **3** is coordinated to two thf oxygen atoms at distances of 2.608(6) and 2.683(3) Å and an oxygen atom from each salen′ at 2.720(4) and 2.724(4) Å. The next closest distances involve C(48) [3.141(5) Å] and C(1) [3.180(5) Å], both of which are comparable to the potassium–phenyl carbon distance of 3.191(5) Å in $KBPh_4$.[13] The potassium distances to N(4) [3.245(5) Å], N(1) [3.362(4) Å], C(43) [3.431(5) Å], C(42) [3.434(5) Å], C(6) [3.454(5) Å] and C(7) [3.464(5) Å] are longer, but are within the 3.288(9)–3.534(13) Å range of K-donor atom long distance interactions cited in potassium aryloxide literature.[14] The structure of **3** demonstrates the flexibility of the salen′ ligand: two of these large ligands can be accommodated at one yttrium center and can incorporate a counter-cation to make an arene soluble product. The cyclopentadienyl analog, which would be a $[(C_5H_4R)_4Y]^-$ complex, is not known for yttrium.[15]

These results show that the salen′ ligand is viable both synthetically and structurally for metals the size of yttrium. This ligand can take the place of two cyclopentadienyl ligands in a chloride complex to provide a bridged species with slightly modified structural parameters as well as a bis(salen′) complex which has no cyclopentadienyl analog. Electronically, this salen′ should be quite different from cyclopentadienyl ligand sets and the ramifications of this difference are under investigation.

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Notes and references

† Addition of YCl_3 (975 mg, 5 mmol) to a stirred solution of K_2salen′ (2.69 g, 4.74 mmol, from KH and H_2salen′ in thf) in 70 mL of thf caused the white suspension of K_2salen′ to disappear immediately. A clear yellow solution with white insoluble material began to form. After 6 h, the reaction mixture was filtered and the solvent was removed by rotary evaporation to give an oil. Trituration with hexanes generated a yellow powder and removal of the volatiles by rotary evaporation left **2** as a yellow powder (3.10 g, 90%). $\delta_H(C_4D_8O$, 400 MHz) 8.25 (s, 2H), 7.36 (d, J 2.8, 2H), 7.03 (d, J 2.4, 2H), 3.89 (br, 4H), 1.45 (s, 18H), 1.25 (s, 18H); $\delta_C(C_4D_8O$, 100 MHz) 169.5, 129.4, 130.5, 63.3, 30.3, 31.9. Isopiestic molecular weight in thf: calc. 1357; found, 1190. IR(KBr): 2953s, 2861m, 1738m, 1716m, 1620s, 1533m, 1461m, 1435m, 1410m, 1353w, 1256w, 1200w, 1159w, 1102w, 1159w, 1102w, 1056w, 1025w cm^{-1}. Anal. Calc. for $C_{36}H_{54}N_2O_3YCl$: C, 62.92; H, 7.85; N, 4.07. Found: C, 62.80; H, 7.62; N, 3.97%.

Following the procedure above, addition of YCl_3 (150 mg, 0.77 mmol) to K_2salen′ (929 mg, 1.6 mmol) gave **3** as a dark orange powder (820.9 mg, 95%). $\delta_H(C_4D_8O$, 500 MHz) 8.14 (s, 2H), 7.07 (d, J 2.75, 2H), 6.80 (s, J 2.75, 2H), 4.29 (br, 4H), 1.26 (s, 18H), 1.14 (s, 18H); $\delta_C(C_4D_8O$, 125 MHz) 169.3, 128.2, 130.7, 64.3, 30.3, 32.0. IR(KBr): 2955s, 2860m, 1625m, 1530s, 1437m, 1408m, 1349w, 1308w, 1261m, 1197w, 1161w, 1056m br, 797m cm^{-1}. Anal. Calc. for $C_{80}H_{124}KN_4O_8Y$: C, 68.73; H, 8.94; N, 4.01. Found: C, 68.24; H, 8.94; N, 3.84%.

‡ *Crystallographic data*: $\mathbf{2}\cdot 2.5C_7H_8$: $C_{72}H_{108}N_4O_6Y_2Cl_2\cdot 2.5C_7H_8$, M = 1604.68, monoclinic, space group $P2_1/n$, a = 14.4421(7), b = 21.3531(10), c = 29.7693(14) Å, β = 103.333(1)°, V = 8932.9(7) $Å^3$, Z = 4, T = 158 K, μ = 1.403 mm^{-1}, Mo-Kα radiation, graphite monochromator. The raw frame data were processed using SAINT and SADABS and subsequent calculations were carried out with SHELXTL. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. At convergence, $wR2$ = 0.1492 and GOF = 1.028 for 900 variables refined against 21112 unique data [as comparison, for refinement on F, $R1$ = 0.0618 for those 13184 data with $I > 2.0\sigma(I)$].

3: $C_{80}H_{124}KN_4O_8Y$, M = 1397.84, space group $P2_1/n$, a = 16.3521(9), b = 25.6261(14), c = 19.1803(10) Å, β = 97.7470(10), V = 7964.0(7), Z = 4, T = 158 K, μ = 0.838 mm^{-1}, Mo-Kα radiation, graphite monochromator. Data analysis was as above. At convergence, $wR2$ = 0.2546 and GOF = 1.031 for 747 variables refined against all 18592 unique data [as comparison, for refinement on F, $R1$ = 0.1038 for those 10540 data with $I > 2.0\sigma(I)$]. CCDC 182/1125.

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