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A zirconium zwitterion containing a caged amine H atom

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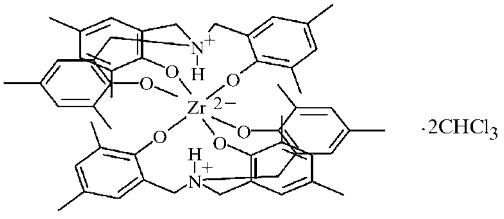
The crystallographically centrosymmetric zwitterion bis[tris(3,5-dimethyl-2-oxidobenzyl-κO)ammonium]zirconium(IV) crystallizes as the chloroform disolvate, $[Zr(C_{27}H_{31}NO_3)_2]\cdot 2CHCl_3$, with the two molecules of chloroform closely associated with two of the aromatic rings. The Zr atom has a distorted octahedral geometry with three phenoxy O atoms from each of the two ligands coordinated to it. Charge balance is maintained by protonation of each N atom, which then forms intramolecular hydrogen-bonding interactions to all three adjacent O atoms.

Comment

When two equivalents of tris(2-hydroxy-3,5-dimethylbenzyl)amine, $\{N(Y OH)_3\}$ (Y is CH_2Ph-3,5-Me_2), are added to $[Zr(O^nBu)_4]$ in CH_2Cl_2, a colourless air-stable precipitate appears in the solution after *ca* 10 min. Analytical data are consistent with two tris(phenoxide) ligands and one Zr atom. The complex is insoluble in CH_2Cl_2 but readily dissolves in $CHCl_3$ and was crystallized from the latter solvent as the chloroform disolvate, (I).



(I)

The structural arrangement in (I) is shown in Fig. 1. The Zr atom lies on a centre of symmetry surrounded by a distorted octahedral arrangement of six similar phenoxy O atoms, suggesting that this part of the complex has an overall formal charge of 2−, as might be expected for a $[Zr(OAr)_6]^{2-}$ dianion. However, whereas $[ZrCl_6]^{2-}$ is well known (*e.g.* $[NMe_4]_2[ZrCl_6]$; Morss *et al.*, 1991), $[Zr(OAr)_6]^{2-}$ is apparently not, the nearest equivalent being $[Zr(SAr)_6]^{2-}$ (Friese *et al.*, 2000). The alternative, whereby one of the phenoxy ligands

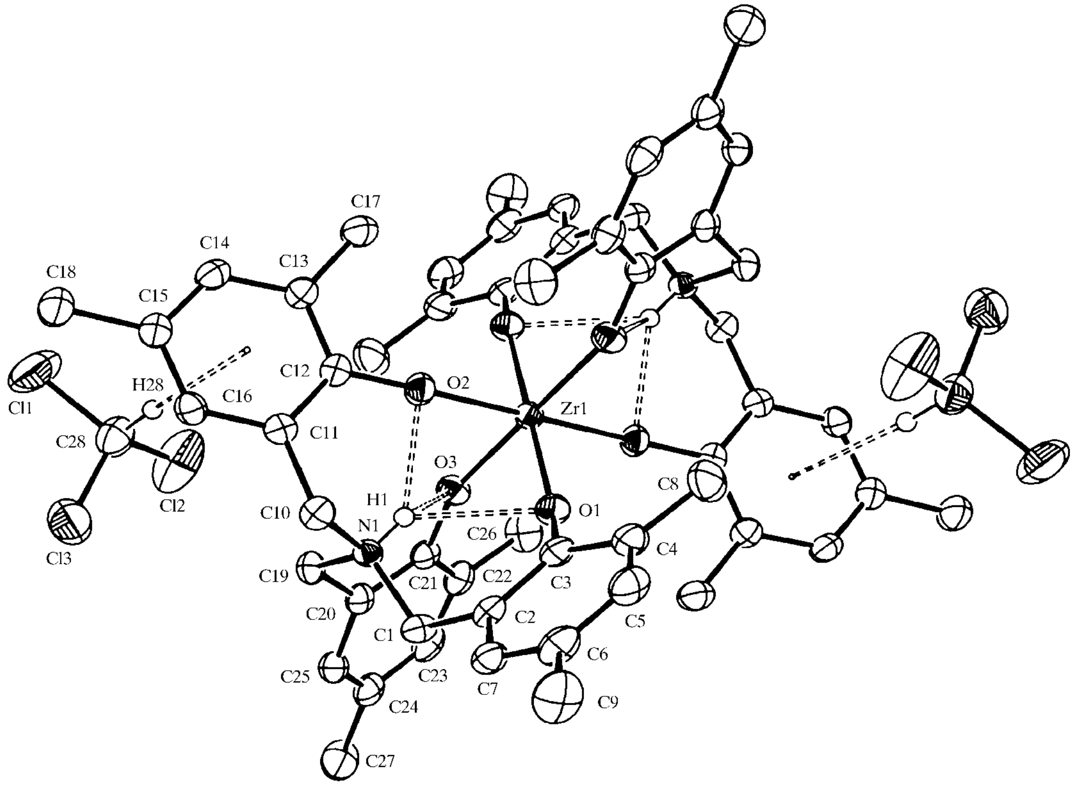


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

in each ligand is protonated, is inconsistent with the observed ^{1}H NMR spectrum, which shows a symmetrical complex. Inspection of the difference map in the vicinity of the donor O atoms also failed to show signs of any protonation. However, a potential site for the extra H atom was detected near the N atom of each ligand, giving the N atom a positive charge and thus maintaining charge balance. A similar structure has recently been reported for the zwitterion moiety when crystallized with toluene molecules of crystallization (Davidson *et al.*, 2003).

The Zr—O bond lengths in (I) [2.066 (2), 2.064 (2) and 2.049 (2) Å] are similar to those found in phenoxide complexes where the O→Zr π-donation is also spread over several O-atom donors, *e.g.* in [Zr(O-$C_6H_4NO_2$-4)(acac)$_3$], where the phenoxide Zr—O bond length is 2.045 (3) Å (Dinger & Scott, 2001), and in the toluene analogue of (I) (Davidson *et al.*, 2003), where corresponding values of 2.058 (2), 2.064 (2) and 2.057 (2) Å are observed. The Zr—O—C bond angles of 158.0 (2), 162.6 (2) and 160.3 (2)° in (I) do not differ greatly from those observed in [Ti(OCHMe$_2$){N(*Y*O)$_3$}] [*Y* is CH$_2$Ph-3,5-Me$_2$; Ti—O—C bond angles = 164.4 (6)°; Kol *et al.*, 2001] or in the toluene solvate of (I) [Zr—O—C bond angles = 157.2 (2), 154.5 (2) and 160.0 (2)°; Davidson *et al.*, 2003]. The N-bound H atom is trapped in a cage-like arrangement, at distances of 2.27, 2.12 and 2.29 Å from atoms O1, O2 and O3, respectively, such approaches being indicative of H⋯O hydrogen bonding. The H atom points directly at the Zr atom [Zr⋯H—N = 174 (2)°] at a distance of 2.76 (3) Å. The Zr⋯N separation is 3.603 (2) Å.

A further feature of the structure of (I) is the two chloroform molecules found associated with each Zr complex. In this respect, the current structure differs from that of the recently reported toluene-solvated zwitterion (Davidson *et al.*, 2003). The H atom of each chloroform molecule points directly at one of the benzene rings of each phenoxide moiety, approaching its C atoms at distances of 2.70, 2.74, 2.98, 3.09, 3.32 and 3.36 Å. The H⋯ring-centroid distance is 2.71 Å. A survey of the Cambridge Structural Database (Version 1.1; Allen, 2002) shows that a similar feature has been previously crystallographically characterized, but only in a few phenoxide complexes (Sudbrake & Vahrenkamp, 2001; Borgias *et al.*, 1984; Jimenez-Perez *et al.*, 2000; Liu *et al.*, 1992; Munoz-Hernandez *et al.*, 2000). There is NMR evidence for such an interaction in solution (Nishio *et al.*, 1995). This weak hydrogen-bond interaction provides a possible explanation as to why the complex is soluble in CHCl$_3$ but is almost completely insoluble in CH$_2$Cl$_2$.

Experimental

A solution of tetrabutoxyzirconium (0.5 g, 1.19 mmol; 0.63 g of an 80% *w*/*w* solution in butanol) in CH$_2$Cl$_2$ (25 ml) was added dropwise to a solution of tris(2-hydroxy-3,5-dimethylbenzyl)amine (0.95 g, 2.4 mmol) in CH$_2$Cl$_2$ (80 ml) and the mixture was stirred for 2 h. The colourless solid was filtered off, washed with CH$_2$Cl$_2$ (30 ml) and dried *in vacuo* (yield 1.0 g, 98%). Analysis for $C_{54}H_{62}N_2O_6Zr$, found: C 69.83, H 7.05, N 3.03%; calculated: C 70.02, H 6.75, N 3.02%. Spectroscopic analysis: ^{1}H NMR (400.13 MHz, CDCl$_3$, p.p.m.): 1.88 (*s*, 9H, 3Me), 2.10 (*s*, 9H, 3Me), 3.18 (*b*, 3H, 3CH), 4.67 (*b*, 3H, 3CH), 6.58 (*d*, $^3J_{\rm H-H}$ = 1.76 Hz, 3H, 3Me-H), 6.74 (*d*, $^3J_{\rm H-H}$ = 1.76 Hz, 3H, 3Me-H), 11.78, (*b*, 2H, 2NH); ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, p.p.m.): 16.4 (Me), 20.3 (Me), 56.1 (CH$_2$), 116.7 (*o*-C), 124.8 (*o*-C), 127.9 (C), 129.5 (C), 132.6 (C), 159.0 (*ipso*-C). Recrystallization of this product from dry chloroform in air gave colourless crystals of the CHCl$_3$ solvate, (I) (yield: 1.28 g, 100%). Analysis for $C_{56}H_{64}Cl_6N_2O_6Zr$, found: C 57.60, H 5.52, N 2.30%; calculated: C 57.73, H 5.54, N 2.40%.

Crystal data

[Zr($C_{27}H_{31}NO_3$)$_2$]·2CHCl$_3$
M_r = 1165.01
Monoclinic, $P2_1/c$
a = 11.3902 (2) Å
b = 13.9774 (1) Å
c = 18.0502 (2) Å
β = 104.134 (1)°
V = 2786.69 (6) Å^3
Z = 2
D_x = 1.388 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2–25°
μ = 0.54 mm^{-1}
T = 150 (2) K
Rectangular prism, colourless
0.40 × 0.24 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\rm min}$ = 0.814, $T_{\rm max}$ = 0.910
14 693 measured reflections
4880 independent reflections
3907 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045
$\theta_{\rm max}$ = 25.1°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.115
S = 1.04
4880 reflections
332 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 2.019P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.038
$\Delta\rho_{\rm max}$ = 0.95 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	2.066 (2)	O1—C3	1.340 (3)
Zr1—O2	2.064 (2)	O2—C12	1.342 (3)
Zr1—O3	2.049 (2)	O3—C21	1.333 (3)
O1—Zr1—O2	86.60 (7)	C21—O3—Zr1	160.29 (18)
O1—Zr1—O3	87.66 (8)	C19—N1—C1	112.7 (2)
O2—Zr1—O3	86.56 (7)	C19—N1—C10	112.8 (2)
C3—O1—Zr1	158.04 (17)	C1—N1—C10	112.5 (2)
C12—O2—Zr1	162.56 (17)		

All H atoms were included in calculated positions and refined using a riding model [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for CH$_2$, aromatic CH and chloroform atom H28, with C—H = 0.99, 0.95 and 1.00 Å, respectively; $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for the methyl H atoms, with C—H = 0.98 Å], except for atom H1, which was located from a difference Fourier synthesis and refined with N—H = 0.845 Å.

Acta Cryst. (2003). C**59**, m494–m496 Alastair J. Nielson *et al.* • [Zr($C_{27}H_{31}NO_3$)$_2$]·2CHCl$_3$ **m495**

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 2001); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1541). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Borgias, B. A., Cooper, S. R., Koh, Y. B. & Raymond, K. N. (1984). *Inorg. Chem.* **23**, 1009–1016.

Davidson, M. G., Doherty, C. L., Johnson, A. & Mahon, M. F. (2003). *Chem. Commun.* pp. 1832–1833.

Dinger, M. B. & Scott, M. J. (2001). *Inorg. Chem.* **40**, 856–864.

Farrugia, L. J. (2001). *ORTEP*-3 *for Windows*. Version 1.06. University of Glasgow, Scotland.

Friese, J. C., Krol, A., Puke, C., Kirschbaum, K. & Giolando, D. M. (2000). *Inorg. Chem.* **39**, 1496–1500.

Jimenez-Perez, V. M., Camacho-Camacho, C., Guizado-Rodriguez, M., Noth, H. & Contreras, R. (2000). *J. Organomet. Chem.* **614**, 283–293.

Kol, M., Shamis, M., Goldberg, I., Goldschmidt, Z., Alfi, S. & Hayut-Salant, E. (2001). *Inorg. Chem. Commun.* **4**, 177–178.

Liu, S., Gelmini, L., Rettig, S. J., Thompson, R. C. & Orvig, C. (1992). *J. Am. Chem. Soc.* **114**, 6081–6087.

Morss, L. R., Carnall, W. T., Williams, C. W., Fahey, J. A., Fuger, J., Meyer, G. & Irmler, M. (1991). *J. Less Common Met.* **169**, 1–8.

Munoz-Hernandez, M. A., Keizer, T. S., Parkin, S., Patrick, B. & Atwood, D. A. (2000). *Organometallics*, **19**, 4416–4421.

Nishio, M., Umezawa, Y., Hirota, M. & Takeuchi, Y. (1995). *Tetrahedron*, **51**, 8665–8701.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1995). *SMART* (Version 5.046) and *SAINT* (Version 5.01). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sudbrake, C. & Vahrenkamp, H. (2001). *Eur. J. Inorg. Chem.* pp. 751–754.

m496 Alastair J. Nielson *et al.* • $[Zr(C_{27}H_{31}NO_3)_2]\cdot 2CHCl_3$ *Acta Cryst.* (2003). C**59**, m494–m496