O9—U1—N18	132.2 (3)	C47—N48—C49	119.2 (8)
O26—U1—O29	86.7 (3)	O2—C3—C4	127 (1)
O26—U1—O30	92.4 (3)	C42—C43—C44	121 (1)
O26—U1—N11	134.3 (3)	C43—C44—C45	121 (1)
O26—U1—N18	71.1 (3)	C44—C45—C46	119.0 (9)
O29—U1—O30	178.8 (3)	C45—C46—C47	121.1 (9)
O29—U1—N11	94.9 (3)	N48—C47—C42	117.1 (7)
O29—U1—N18	94.1 (3)	N48—C47—C46	123.1 (8)
O30—U1—N11	85.1 (3)	C42—C47—C46	119.8 (9)
O30—U1—N18	84.8 (3)	N48—C49—C50	127 (1)
N11—U1—N18	63.2 (2)	C49—C50—C51	117.1 (9)
O*W*31—U31—O39	75.2 (2)	C49—C50—C55	122.6 (9)
O*W*31—U31—O56	78.8 (2)	O2—C3—C8	110.9 (9)
O*W*31—U31—O59	90.6 (3)	C4—C3—C8	122 (1)
O*W*31—U31—O60	90.8 (4)	C3—C4—C5	120 (1)
O*W*31—U31—N41	146.0 (2)	C4—C5—C6	120 (2)
O*W*31—U31—N48	150.7 (3)	C5—C6—C7	120 (1)
O39—U31—O56	153.9 (2)	C6—C7—C8	122 (2)
O39—U31—O59	90.0 (3)	C6—C7—C10	119 (2)
O39—U31—O60	90.5 (3)	C8—C7—C10	119.9 (8)
O39—U31—N41	70.8 (2)	O9—C8—C3	120 (2)
O39—U31—N48	134.1 (2)	O9—C8—C7	123.3 (9)
O56—U31—O59	90.4 (3)	C3—C8—C7	116.2 (9)
O56—U31—O60	89.7 (3)	N11—C10—C7	127 (2)
O56—U31—N41	135.2 (2)	N11—C12—C13	122.5 (8)
O56—U31—N48	72.0 (2)	N11—C12—C17	116.2 (9)
O59—U31—O60	178.8 (3)	C13—C12—C17	121 (1)
O59—U31—N41	90.7 (3)	C12—C13—C14	118.6 (9)
O59—U31—N48	91.3 (3)	C13—C14—C15	120 (2)
C14—C15—C16	121 (1)	C34—C35—C36	120 (2)
C15—C16—C17	120 (1)	C35—C36—C37	121 (1)
N18—C17—C12	117.7 (9)	C36—C37—C38	119.4 (8)
N18—C17—C16	123.1 (8)	C36—C37—C40	117 (1)
C12—C17—C16	119.1 (9)	C38—C37—C40	123.3 (9)
N18—C19—C20	127 (1)	O39—C38—C33	118.3 (9)
C19—C20—C21	117 (1)	O39—C38—C37	124.1 (8)
C19—C20—C25	122.8 (9)	C33—C38—C37	117.5 (9)
C21—C20—C25	119.6 (9)	N41—C40—C37	124.7 (9)
C20—C21—C22	120 (2)	N41—C42—C43	124.2 (8)
C21—C22—C23	121 (2)	N41—C42—C47	116.5 (8)
C22—C23—C24	121 (1)	C43—C42—C47	119.3 (8)
O27—C24—C23	125.4 (9)	C51—C50—C55	120.1 (9)
O27—C24—C25	114.6 (9)	C50—C51—C52	121 (2)
C23—C24—C25	120 (2)	C51—C52—C53	120 (2)
O26—C25—C20	122.2 (8)	C52—C53—C54	121 (1)
O26—C25—C24	119.3 (9)	O57—C54—C53	122.9 (9)
C20—C25—C24	118.5 (9)	O57—C54—C55	115.4 (9)
O32—C33—C34	125.6 (9)	C53—C54—C55	122 (2)
O32—C33—C38	112.7 (9)	O56—C55—C50	124.1 (8)
C34—C33—C38	122 (2)	O56—C55—C54	118.3 (9)
C33—C34—C35	121 (1)	C50—C55—C54	117.3 (9)

Data were corrected for Lorentz and polarization effects. The unit cell contains two independent salophene–uranium–water complexes (1:1:1) and an isolated water molecule. The uranium cations were located by the Patterson method and the rest of the non-H atoms by successive Fourier syntheses. Weights for each reflection were calculated from $w = 4F_o/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined to be 0.04. In the difference Fourier map two peaks were found which were attributed to water O atoms. One of the O atoms (O*W*3) gave a reasonable displacement parameter; the displacement parameter for the other water O atom (O*W*4) became very large ($B > 20$) on refinement. From the large value of B, we concluded that the position of the second water molecule is only partially occupied (the latter has not been included in the formula). O*W*4 was refined isotropically, all other non-H atoms were refined anisotropically. H atoms were treated as riding on their parent atom at a distance of 0.95 Å, except for the water H atoms which were not located and therefore not included in the refinement. Calculations were performed using *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic Chloro[tris(2-aminoethyl)-amine]zinc(II) Chloride Trihydrate, $[ZnCl(C_6H_{18}N_4)]Cl.3H_2O$

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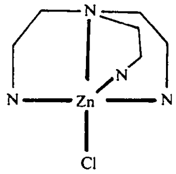
Abstract

The synthesis and the crystal and molecular structure of the five-coordinate racemic $[Zn(tren)Cl]Cl.3H_2O$ complex [tren = tris(2-aminoethyl)amine, $C_6H_{18}N_4$] are reported. The coordination polyhedron around

the Zn atom is approximately trigonal bipyramidal with the tetradentate tren ligand occupying three equatorial sites and one apical position, while the second apical position is occupied by a Cl^- ligand. The bond lengths and angles are in the normal range for this class of complexes, with the exception of the Zn—Cl distance [2.3552 (8) Å] which is rather long because of the involvement of the Cl atom in hydrogen bonds. The complex has also been studied by infrared and ^1H NMR spectroscopy, the results of which are discussed in connection with the results of the structure analysis.

Comment

In recent years a number of metal polyamine complexes of the type $[M(\text{polyamine})XY]^{n+}$, where $n = 0$, 1 or 2, $M = Cu^{2+}$, Ni^{2+}, Zn^{2+} or Rh^{2+}, polyamine = tris(2-aminoethyl)amine (tren) or triethylenetetraamine (trien), and X or $Y = H_2O$, Cl^-, Br^-, I^- or SCN^-, have been synthesized (Torres & Marzilli, 1991; Marzotto, Clemente, Ciccarese & Valle, 1993; Marzotto, Clemente & Valle, 1993) with the aim of obtaining highly selective coordination complexes able to bind particular and selected N atoms of DNA nucleobases (adenine, guanine, cytosine or thymine). In particular, we have already demonstrated that the octahedral $[Ni(tren)(H_2O)Cl]Cl.H_2O$ complex is able to bind selectivity to the N(3) atom of adenine (Marzotto, Clemente, Ciccarese & Valle, 1993). The title complex, (I), is one of a number of five-coordinate compounds of Zn with a trigonal-bipyramidal geometry. Orioli, Di Vaira & Sacconi (1966) reported the five-coordinate structure of bis(*N*-methylsalicylaldiminato)zinc(II) and Ciampolini & Nardi (1966*a*,*b*) studied the zinc(II) complex of the tetradentate amine $N[CH_2CH_2N(CH_3)_2]_3$, [tris(2-dimethylaminoethyl)amine, Me_6tren], in order to investigate the spectroscopic behaviour of these complexes. We have synthesized the title complex to test its behaviour towards DNA nucleobases, but this topic will be discussed elsewhere.



(I)

The crystal structure consists of $[Zn(tren)Cl]^+$ cations, Cl^- anions and water molecules connected by a network of hydrogen bonds. $[Zn(tren)Cl]^+$ has nearly trigonal-bipyramidal geometry with the three primary amine N atoms N(11), N(12) and N(13) in the equatorial positions and the tertiary amine N atom, N(10), and the Cl(1) ligand in the apical positions, as shown in Fig. 1. The bond lengths in the title complex are similar to those found in [Zn(tren)(NCS)](SCN) (Andreetti, Jain & Lingafelter, 1969); the only major difference seems to be in the Zn—N(10) distance [2.292 (4) compared with 2.265 (2) Å in the present complex]. The increase in bond length of 0.027 (6) Å is most likely due to the greater *trans* influence of NCS than Cl (Appleton, Clark & Manzer, 1973). The distances found by Di Vaira & Orioli (1968*b*) for $[Zn(Me_6tren)Br]Br$ [Zn—N(10) = 2.20 (2), Zn—$N(CH_3)_2$ = 2.11 (2) Å] are considerably different from those in the title complex, indicating some influence of the methyl groups. The value of the Zn—Cl bond length [2.3552 (8) Å], which is higher than the normal values {*e.g.* 2.170 (2) Å for [tris(4,5-diisopropylimidazol-2-yl)phosphine]dichlorozinc (Read & James, 1981) and 2.243 (2) and 2.160 (3) Å for [bis(4,5-diisopropylimidazol-2-yl)phosphinic acid]dichlorozinc hydrate (Ball, Brown & Cocho, 1984)}, most likely results from the participation of the Cl atom in hydrogen bonds (see below) similar to those observed in ammonium tetrachlorozincate(II) [Zn—Cl range 2.11–2.404 Å (Mikhail, 1980)].

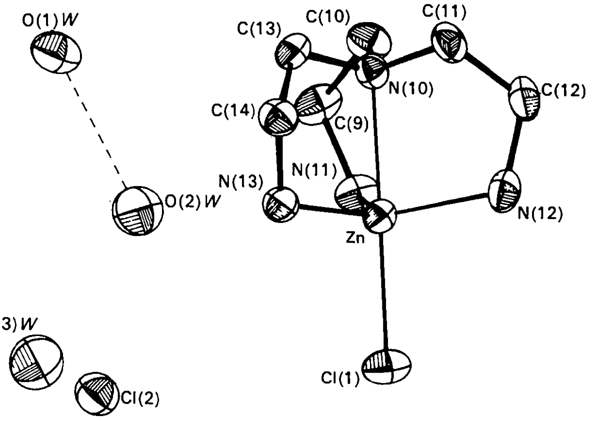


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of $[Zn(tren)Cl]Cl.3H_2O$ showing the numbering scheme used. H atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

The principal distortion of the coordination polyhedron from C_{3h} symmetry arises from the shift of the Zn atom out of the equatorial plane formed by the three N donor atoms in the direction of the Cl^- ligand by 0.25 Å. Thus, the three N(10)—Zn—NH_2 bond angles are all less than 90° [80.42 (9), 80.80 (9) and 81.13 (7)°] and the three NH_2—Zn—NH_2 angles are less than 120° [115.4 (1), 117.5 (1) and 119.62 (9)°]. Similar distortions are observed in other trigonal-bipyramidal complexes formed by the tren ligand, such as [Cu(tren)(NCS)](SCN) (Jain & Lingafelter, 1967) and [Zn(tren)(NCS)](SCN) (Andreetti, Jain & Lingafelter, 1969). The pointgroup symmetry of the complex is close to C_3, as seen in Fig. 2, which shows the structure viewed along the pseudo threefold axis. The axis also relates the three ethylenediamine chelate rings which have a *gauche* butane-like conformation (Corey & Bailar, 1959), as found for the tren complexes mentioned above.

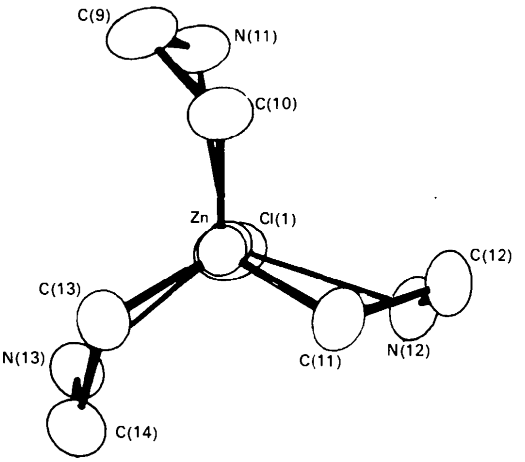


Fig. 2. The $[Zn(tren)Cl]^+$ cation viewed down the pseudo threefold axis with the chelate ring in the λ configuration.

It is interesting to deepen the discussion of the structures of the $[M(tren)X]X$ complexes, as they exhibit molecular chirality due to an axis of chirality coincident with the pseudo threefold axis mentioned above. Looking at the model along this threefold axis, one can also see three independent helical axes similar to those observed in 1,1,1-trimethoxymethane or in [4.4.4]propellane (Ermer, Gerdil & Dunitz, 1971). The $>N—CH_2—CH_2—NH_2$ chain assumes a *gauche* butane-type conformation with chirality described by λ or δ.* Since in the present complex three $>N—CH_2—CH_2—NH_2$ tren helical chains are present, four stereoisomers could, in theory, be found. Nevertheless, most likely for steric reasons, the chirality of one chain imposes the same chirality on the other two, so that, experimentally, only complexes having all three chains with the λ conformation ($\lambda\lambda\lambda$) or all three chains with the δ conformation ($\delta\delta\delta$) have been found. In fact the torsion angles for metal–tren and metal–Me$_6$tren (where metal = Zn^{2+}, Cu^{2+} or Ni^{2+}) complexes have equal helicity for a given complex, as shown in Table 3. Moreover, both chiral forms, $\lambda\lambda\lambda$ and $\delta\delta\delta$, exist in the present complex as the space group is centrosymmetric. Such behaviour has been observed previously for only two complexes in the space group *Pbca*: [Zn(tren)(NCS)](SCN) (Andreetti, Jain & Lingafelter, 1969) and [Ni(Me$_6$tren)(NCS)](SCN).H_2O (Dapporto & Gatteschi, 1973). Table 3 also shows that complexes crystallizing in non-centrosymmetric space groups which belong to the enantiomorphous crystal classes 222 or 23 and show optical activity, show only one chiral form, $\lambda\lambda\lambda$ or $\delta\delta\delta$. However, since the absolute configuration of these optically active complexes was not determined, any chirality assignment is undefined even though resolution into the two forms has occurred. Table 3 also shows that the absolute values of the three torsion angles in all of the complexes are similar, with the exception of those in [Ni(Me$_6$tren)(NCS)](SCN).H_2O. An immediate explanation of this is not easy. In fact, two of the torsion angles are very small and result in short van der Waals contacts (< 2.36 Å) involving the methylene H atoms, particularly those bonded to C(6).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Zn	0.86943 (1)	−0.03581 (3)	0.81700 (2)	0.0286 (1)
Cl(1)	0.91245 (4)	0.22512 (7)	0.90761 (5)	0.0442 (2)
Cl(2)	1.11714 (4)	0.37023 (9)	0.64021 (5)	0.0496 (2)
N(10)	0.8321 (1)	−0.2941 (2)	0.7365 (1)	0.0312 (4)
N(11)	0.8291 (1)	0.0529 (2)	0.6619 (2)	0.0364 (5)
N(12)	0.7711 (1)	−0.1071 (3)	0.9077 (2)	0.0403 (6)
N(13)	0.9866 (1)	−0.1606 (2)	0.8419 (1)	0.0342 (5)
C(9)	0.8295 (2)	−0.0910 (3)	0.5835 (2)	0.0410 (7)
C(10)	0.7887 (2)	−0.2515 (3)	0.6277 (2)	0.0397 (6)
C(11)	0.7747 (1)	−0.3803 (3)	0.8058 (2)	0.0406 (7)
C(12)	0.7172 (1)	−0.2471 (3)	0.8518 (2)	0.0422 (7)
C(13)	0.9136 (1)	−0.3903 (3)	0.7318 (2)	0.0365 (6)
C(14)	0.9767 (1)	−0.3501 (3)	0.8307 (2)	0.0370 (6)
O(1)*W*	1.0719 (2)	−0.2927 (3)	0.4858 (2)	0.0578 (7)
O(2)*W*	1.0627 (2)	−0.0388 (3)	0.6519 (2)	0.069 (1)
O(3)*W*	0.8745 (2)	−0.2676 (4)	1.1046 (2)	0.077 (1)

Table 2. *Selected geometric parameters* (Å, °)

Zn—Cl(1)	2.3552 (8)	Zn—N(10)	2.265 (2)
Zn—N(11)	2.064 (2)	Zn—N(12)	2.076 (3)
Zn—N(13)	2.050 (2)	N(10)—C(10)	1.471 (3)
N(10)—C(11)	1.468 (3)	N(10)—C(13)	1.475 (3)
N(11)—C(9)	1.472 (3)	N(12)—C(12)	1.484 (3)
N(13)—C(14)	1.469 (3)	C(9)—C(10)	1.518 (3)
C(11)—C(12)	1.514 (4)	C(13)—C(14)	1.508 (3)
N(12)—Zn—N(13)	119.62 (9)	N(11)—Zn—N(13)	117.5 (1)
N(11)—Zn—N(12)	115.4 (1)	N(10)—Zn—N(13)	80.42 (9)
N(10)—Zn—N(12)	80.80 (9)	N(10)—Zn—N(11)	81.13 (7)
Cl(1)—Zn—N(13)	97.41 (8)	Cl(1)—Zn—N(12)	98.79 (7)
Cl(1)—Zn—N(11)	101.55 (6)	Cl(1)—Zn—N(10)	177.15 (6)
Zn—N(10)—C(13)	106.2 (2)	Zn—N(10)—C(11)	106.3 (1)
Zn—N(10)—C(10)	105.9 (1)	C(11)—N(10)—C(13)	112.5 (2)
C(10)—N(10)—C(13)	112.3 (2)	C(10)—N(10)—C(11)	113.0 (2)
Zn—N(11)—C(9)	109.9 (1)	Zn—N(12)—C(12)	110.5 (2)
Zn—N(13)—C(14)	111.6 (2)	N(11)—C(9)—C(10)	109.7 (2)
N(10)—C(10)—C(9)	110.2 (2)	N(10)—C(11)—C(12)	110.0 (2)
N(12)—C(12)—C(11)	109.8 (3)	N(10)—C(13)—C(14)	110.2 (2)
N(13)—C(14)—C(13)	109.3 (2)		

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* We use the symbols λ or δ (Commission on the Nomenclature of Inorganic Chemistry, 1970) for the left-handed and the right-handed helix, respectively, formed by a helical array of four atoms. Thus, λ and δ correspond respectively to the $-\tau$ and $+\tau$ torsion angles of Klyne & Prelog (1960). Cahn, Ingold & Prelog (1966), Prelog & Helmchen (1982); more recently Dodziuk & Mirowicz (1990) proposed the use of the *M* and *P* symbols which are equivalent to λ and δ.

Table 3. *Torsion angles* (φ_1, φ_2, φ_3) *in five-coordinate metal*–tren *and metal*–Me_6tren *complexes* (°) (*metal* = Zn^{II}, Cu^{II}, Ni^{II} *or* Co^{II})

	Space group	φ_1	φ_2	φ_3	Mean value
$[Zn(tren)Cl]Cl.3H_2O^a$	*P*2₁/*a*	± 53.0 (3)	± 54.0 (3)	± 54.2 (3)	± 53.7 (3)
$[Zn(tren)(NCS)](SCN)^b$	*Pbca*	± 33.4 (12)	± 37.5 (8)	± 43.6 (11)	± 38.2 (10)
$[Cu(tren)(NCS)](SCN)^c$†	$P2_12_12_1$	− 49.3 (4)	− 50.2 (4)	− 52.8 (5)	− 50.8 (4)
$[Cu(tren(NH_3)](ClO_4)_2^d$†	$P2_13$	− 48.8 (5)	− 48.8 (5)	− 48.8 (5)	− 48.8 (5)*
$[Ni(Me_6tren)(NCS)](SCN).H_2O^e$	*Pbca*	± 8.4 (30)	± 17.1 (30)	± 58.2 (20)	± 28.1 (30)
$[Zn(Me_6tren)Br]Br^f$†	$P2_13$	− 55.8 (20)	− 55.8 (20)	− 55.8 (20)	− 55.8 (20)*
$[Co(S\text{-}tan)(NCS)](ClO_4)^g$	$P2_12_12_1$	+ 46.1 (19)	+ 51.1 (20)	+ 55.1 (20)	+ 50.8 (20)

References: (*a*) present paper; (*b*) Andreetti, Jain & Lingafelter (1969); (*c*) Jain & Lingafelter (1967); (*d*) Duggan, Ray, Hathaway, Tomlinson, Brint & Pelin (1980); (*e*) Dapporto & Gatteschi (1973); (*f*) Di Vaira & Orioli (1968*a*,*b*) (the corresponding complexes of Ni^{II}, Cu^{II}, Mn^{II} and Fe^{II} exhibit very similar torsion angles); (*g*) Shunji, Hiroshi, Soichiro & Izumi (1985) [S-tan = $Me_2NCH_2CH(Me)N(CH_2CH_2NMe_2)_2$].

* Complexes in the cubic space group ($P2_13$) have all three torsion angles equal as the molecular and crystallographic C_3 axes are coincident.

† Complexes crystallizing in non-centrosymmetric space groups (which belong to the enantiomorphous crystal classes 222 or 23, with optical activity) show negative torsion angles. Since the absolute configuration of these optically active complexes has not been determined, the − sign or the + sign are equally probable.

Table 4. *Infrared spectra* (cm^{-1}) *of free* tren *and* $[Zn(tren)Cl]Cl.3H_2O$

tren^a	$[Zn(tren)Cl]Cl.3H_2O$	Band assignment
	3482*sh*, 3431*s*,*b*	ν(O—H)
3350*s*, 3270*s*, 3180*m*	3319*sh*, 3302*ms*, 3289*ms*, 3219*s*,*b*, 3150*m*	$\nu(NH_2)$
2930*s*, 2855*s*, 2800*s*	2953*m*, 2922*ms*, 2872*m*, 2854*w*	$\nu(CH_2)$
	1647*ms*	δ(H—O—H)
1590*s*,*b*	1605*ms*	$\delta(NH_2)$
	1499*w*, 1484*w*	
1455*m*	1470*m*, 1458*m*	$\delta(CH_2)$
1390*w*, 1365*sh*, 1348*m*	1411*w*, 1397*w*, 1375*vw*, 1365*m*	$\gamma(CH_2)$
1304*m*	1320*m*	$\gamma(NH_2)$
1270*m*, 1230*w*	1286*w*, 1273*w*, 1261*w*, 1247*w*	(CH_2) twist
	1128*w*	
1090*m*, 1070*m*, 1035*s*	1116*m*, 1084*s*, 1061*m*	ν(C—N)
1020*sh*, 902*s*,*b*	1013*m*, 994*m*	(NH_2) twist
865*s*,*b*, 840*sh*	902*w*, 885*m*, 862*w*, 801*w*	
765*sh*, 730*w*	746*w*, 695*sh*	$\rho(CH_2)$
	667*w*, 621*w*	$\rho(NH_2)$
	581*w*, 552*w*, 549*m*	
	450*s*,*b*	$\nu(Zn—N_{tren})$
	363*m* 330*w*	
	301*w*, 278*m*	ν(Zn—Cl)

Reference: (*a*) Ficheux & Morris (1978).

The distance between the amino N atom N(13) and the atom O(2)*W* of a water molecule is 2.911 (2) Å and the distance between O(2)*W* and H(1)N13 is 2.00 (2) Å. The bond angle N(13)—H(1)N13···O(2)*W* is 167.6 (4)°. These values suggest the formation of a strong hydrogen bond between N(13) and O(2)*W*. A similar hydrogen bond is formed between N(12) and O(3)*W* [N(12)···O(3)*W* = 3.021 (2), O(3)*W*···H(1)N12 = 2.12 (2) Å, N(12)—H(1)N12···O(3)*W* = 176.6 (7)°]. Moreover, the Cl(1) atom is involved in two hydrogen bonds: O(3)*W*···Cl(1^{i}) = 3.351 (3), H(1)O3*W*···Cl(1^{i}) = 2.30 (5) Å, O(3)*W*—H(1)O3*W*···Cl(1^{i}) = 174.4 (4)°, and N(13)···Cl(1^{i}) = 3.344 (1), H(2)N13···Cl(1^{i}) = 2.56 (2) Å, N(13)—H(2)N13···Cl(1^{i}) = 158 (1)° [symmetry code: (i) $2 - x$, $-y$, $2 - z$.] The participation of the Cl(1) atom (bound to Zn) in hydrogen bonds with water O(3)*W* and amino N(13) atom donors can account for the rather long Zn—Cl(1) distance observed. Also, a medium strength hydrogen bond involves the Cl(2) anion and N(11) [N(11)···Cl(2^{ii}) = 3.329 (2), H(1)N11···Cl(2^{ii}) = 2.69 (5) Å, N(11)—H(1)N11···Cl(2^{ii}) = 159.9 (7)°; symmetry code: (ii) $-\frac{1}{2} + x$, $\frac{1}{2} - y$, z]. Finally, there is a rather short hydrogen bond between the two water molecule O atoms O(1)*W* and O(2)*W* with O(1)*W*···O(2)*W* = 2.851 (2) Å. Other hydrogen bonds involving H_2O, Cl(2) and amine N atoms are also present.

The infrared absorption spectrum of $[Zn(tren)Cl]Cl.3H_2O$ is compared with that of the free tren ligand in Table 4. Remarkable differences are observed, particularly in the $\nu(NH_2)$ (3319–3150 cm^{-1} for the complex) and $\nu(CH_2)$ (2953–2854 cm^{-1} for the complex) stretching regions and in the $\delta(NH_2)$ (1605 cm^{-1} for the complex) and $\delta(CH_2)$ (1470–1458 cm^{-1} for the complex) bending regions. Differences are also found in the $\gamma(CH_2)$ (1411–1365 cm^{-1} for the complex) and $\gamma(NH_2)$ (1320 cm^{-1} for the complex) frequencies. The strong broad band centred at 450 cm^{-1} is assigned to $\nu(Zn—N_{tren})$ in agreement with previous work, in which a similar band at 440 cm^{-1} for the pentacoordinate [Zn(tren)Br]Br and [Zn(tren)(NCS)](SCN) complexes and at 469 cm^{-1} for the tetracoordinate (tetrahedral) complex $[Zn(tren)](ClO_4)_2$, were identified (Cayley & Hague, 1971). Two vibrational frequencies occur at 301 and 278 cm^{-1}, in the region in which Krishnan & Plane (1966) assigned the Zn—Cl stretching mode for the $Zn(en)Cl_2$ complex, where the Zn^{II} atoms are bridged by ethylenediamine (en) ligands.

^1H NMR spectra of the $[Zn(tren)Cl]Cl.3H_2O$ complex show the presence of a broad peak with two maxima centred at 2.73 and 2.79 p.p.m., shifted downfield by approximately 0.15 p.p.m. with respect to the resonance peaks of the free tren ligand, indicating that the Zn–tren complex is also stable in solution. Furthermore, like $Zn(tren)Br_2$ and $Zn(trien)Cl_2$, for which conductivity measurements in methanol clearly support the presence of a 1:1 electrolyte (Cayley & Hague, 1971), it is very like that one Cl^- ion is still bonded to the Zn atom.

Experimental

The title complex was prepared as follows: 1.15 μm^3 (7.5 mmol) of tren dissolved in 20 μm^3 of ethanol was added to 100 μm^3 of an ethanol solution containing 1.022 g (7.5 mmol) of $ZnCl_2$. White crystals were obtained after four weeks by slow evaporation of the ethanol solution at 293 K. Analysis: calculated for $C_6H_{24}Cl_2N_4O_3Zn$, C 21.41, H 7.19, N 16.65, Cl 21.07%; found, C 21.73, H 7.25, N 16.69, Cl 20.95%. Infrared spectra were measured as KBr pellets or Nujol mulls with a 5Sxc FT-IR (20 far IR) Nicolet spectrometer. ^{1}H NMR measurements were recorded on a Jeol FT spectrometer model FX 90Q, at 296 K in tetradeuteromethanol, CD_3OD. Chemical shifts in δ (p.p.m.) have been quoted downfield from tetramethylsilane (TMS).

Crystal data

[ZnCl($C_6H_{18}N_4$)]Cl.3H_2O
$M_r = 336.56$
Monoclinic
$P2_1/a$
$a = 15.556$ (3) Å
$b = 7.682$ (2) Å
$c = 12.384$ (2) Å
$\beta = 96.80$ (2)°
$V = 1469.5$ (5) Å^3
$Z = 4$
$D_x = 1.520$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 8.9$–$11.2°$
$\mu = 2.078$ mm^{-1}
$T = 293$ K
Prism
0.20 × 0.20 × 0.10 mm
White

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3686 measured reflections
3538 independent reflections
3042 observed reflections $[F_o > 7\sigma(F_o)]$
$R_{\rm int} = 0.146$

$\theta_{\rm max} = 28.05°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 150 reflections intensity variation: insignificant

Refinement

Refinement on F
$R = 0.040$
$wR = 0.044$
$S = 0.697$
3042 reflections
241 parameters
H atoms refined isotropically

$w = 1/[\sigma^2(F) + 0.006960F^2]$
$(\Delta/\sigma)_{\rm max} = 0.30$
$\Delta\rho_{\rm max} = 0.8$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.8$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76

A suitable crystal for data collection was mounted on a glass capillary and thinly coated with diluted polystyrene cement. Lorentz and polarization corrections were applied. The structure was solved by the standard Patterson method and successive Fourier maps. The structure was refined by full-matrix least squares using anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms. Torsion angles were calculated following the right-hand rule (see Klyne & Prelog, 1960) and standard deviations following the method of Stanford & Waser (1972). All calculations were performed with *SHELX*76 (Sheldrick, 1976) and the molecular illustration was drawn using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Bis(2,6-di-*tert*-butyl-4-methylphenolato)-samarium(II) Complex, [Sm(OAr)$_2$(thf)$_3$].-thf

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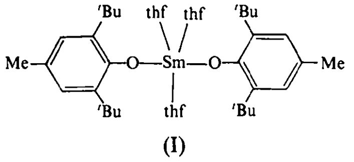
Abstract

The title complex, bis(2,6-di-*tert*-butyl-4-methylphenolato-*O*)tris(tetrahydrofuran-*O*)samarium tetrahydrofuran solvate, [Sm($C_{15}H_{23}O$)$_2$(C_4H_8O)$_3$].-C_4H_8O, has distorted trigonal bipyramidal geometry around the Sm^{II} atom. The O(2), O(3) and O(4) atoms of the thf ligands form a plane and the O(1) and O(5) atoms of the aryl groups occupy the apical sites. The Sm—OAr distances Sm—O(1) and Sm—O(5) are 2.318 (7) and 2.290 (9) Å, respectively.

Comment

Divalent samarium complexes are strong reducing agents and structurally defined soluble Sm^{II} complexes are rare (Bel'sky, Gunko, Bulychev, Sizov & Soloveichik, 1990; Evans, Bloom, Hunter & Atwood, 1981; Evans, Drummond, Zhang & Atwood, 1988; Evans, Grate, Choi, Bloom, Hunter & Atwood, 1985). We are interested in the chemical behaviour of Sm^{II} complexes having different ligands. In studying the structures of Sm^{II} complexes with low coordination numbers, the crystal structure of the title compound, (I), obtained from the reaction of (ArO)$_2$SmCl (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) with Na, has been determined. The molecular structure is shown in Fig. 1.



(I)

The title compound consists of one Sm atom, two OAr ligands, three thf ligand molecules and another tetrahydrofuran molecule as a solvent in the unit cell. The coordination number of Sm^{II} is five and, to our knowledge, this is the first X-ray structure determination of a five-coordinate Sm^{II} complex. The coordination polyhedron of the Sm^{II} atom is a distorted trigonal bipyramid. The triangular plane is formed by the thf O(2), O(3) and O(4) atoms; the Sm atom is 0.0046 Å above the plane and the aryloxide O(1) and O(5) atoms occupy the apical sites. This mode of coordination is different from that of the related Yb^{II} compound [Yb(OAr)$_2$(thf)$_3$] (Deacon, Hitchcock, Holmes, Lappert, Mackinnon & Newnham, 1989) which has distorted square-pyramidal coordination. The average Sm—OAr distance is 2.304 (8) Å. The Sm—O(2)(thf) and Sm—O(3)(thf) [2.581 (10) and 2.580 (10) Å, respectively] distances are almost the same, but the Sm—O(4)(thf) distance [2.614 (11) Å] is slightly longer.

The bond angles O(1)—Sm—O(5), O(2)—Sm—O(3), O(2)—Sm—O(4) and O(3)—Sm—O(4) are 156.7 (6), 175.7 (5), 85.7 (5) and 90.0 (4)°, respectively.

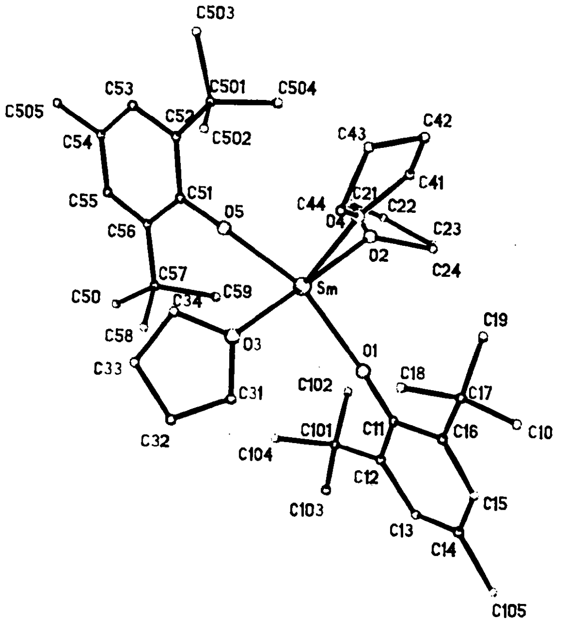


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme.

Experimental

All manipulations were carried out under argon by Schlenk techniques. Crystals were obtained by the reaction of equimolar amounts of (ArO)$_2$SmCl and Na in tetrahydrofuran, followed by crystallization from the toluene–tetrahydrofuran solvent mixture at 268 K. A suitable crystal was sealed in a thin-walled glass capillary for crystal structure determination.