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Transition metal complexes with thiosemicarbazide-based ligands. XLIII.[1] Chlorobis(3-methylisothiosemicarbazide-κ^2N^1,N^4)zinc(II) chloride

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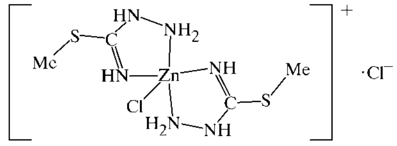
In the title compound, $[ZnCl(C_2H_7N_3S)_2]Cl$, the Zn^{II} ion is five-coordinated in a distorted trigonal–bipyramidal arrangement, with the hydrazine N atoms located in the apical positions. The structure is stabilized by N—H···Cl hydrogen bonds, which involve both the Cl atoms and all the hydrogen donors, except for one of the two thioamide N atoms. A comparison of the geometry of thiosemicarbazide and *S*-methylisothiosemicarbazide complexes with Zn^{II}, Cu^{II} and Ni^{II} shows the pronounced influence of the hydrogen-bond network on the coordination geometry of Zn^{II} compounds.

Comment

A number of complexes of transition metals and thiosemicarbazide (TSC) based ligands have found application in medicine, technology and analytical chemistry (Casas *et al.*, 2001). In recent years, interest in the crystal engineering of metal complexes has stimulated investigation of the means of engagement of thiosemicarbazide-based metal complexes in supramolecular structures (Burrows *et al.*, 1997; Allen *et al.*, 1999). The relatively rigid structure of metal–TSC chelate rings and the capacity of the ligand for hydrogen bonding make these molecules potentially important for the stabilization of supramolecular structures. In its complexes, TSC behaves as a chelating bidentate ligand coordinated through the terminal hydrazine N atom and the S atom. Upon methylation of the S atom, the manner of coordination of TSC changes, so that it coordinates through the thioamide N atom instead of S (Bogdanović *et al.*, 2001).

A comparison of the previously reported structures of the Ni^{II} (Obadović *et al.*, 1997; Bourosh *et al.*, 1987) and Cu^{II} (Gerbeleu *et al.*, 1987) complexes with *S*-methylisothiosemicarbazide (ITSC) and the corresponding TSC analogues (Campbell, 1975) shows that, in both types of compound, the geometry of the coordination polyhedron is similar. In order to investigate the influence of a different coordination mode on the geometry of the coordination polyhedron in the absence of ligand field stabilization energy, and also the packing characteristics of the corresponding compound, we have determined the crystal structure of the title complex, $[ZnCl(ITSC)_2]Cl$, (I).



(I)

To date, the crystal structures of two Zn^{II} complexes with TSC have been reported, namely tetrahedral $[Zn(TSC)Cl_2]$ (Cavalca *et al.*, 1960) and octahedral $[Zn(TSC)_3Cl_2]$ (Nardelli & Chierici, 1960). Since a different coordination mode of the ITSC ligand changes the arrangement of potential hydrogen-bond donors, it is expected that these changes will be reflected in the number and disposition of hydrogen bonds in the crystal structure.

The crystal structure of (I) consists of monomeric units comprising $[Zn(ITSC)_2Cl]^+$ and Cl$^-$ ions. The coordination geometry around the metal ion can be described as distorted trigonal–bipyramidal ($\tau = 0.72$; Addison *et al.*, 1984), with two thioamide N atoms and a Cl atom in the equatorial sites, and two hydrazine N atoms in the apical positions (Fig. 1). The differences between the Zn—N(hydrazine) and Zn—N(thioamide) bond lengths are more pronounced in this complex [0.234 (8) and 0.253 (8) Å] than in the previously reported Ni^{II} and Cu^{II} complexes with *S*-methylisothiosemicarbazide, where this difference is in the range 0.05–0.09 Å. Non-equivalence of the *M*—N1 and *M*—N4 bond lengths can be explained in terms of the different hybridization of the corresponding N atoms. In (I), this effect is strengthened, probably as a consequence of the different degree of contribution of the *p* orbitals in the equatorial and apical bonds of a trigonal bipyramid (Cotton & Wilkinson, 1967).

The packing of the molecules in (I) is determined by relatively strong N—H···Cl hydrogen bonds (Ferari Belicchi *et al.*, 1992) (distance and angle ranges are 2.38–2.64 Å and 152–174°, respectively). Repeating pairs of molecules, connected by hydrogen bonds, form zigzag chains along the *b* axis [the symmetry codes of the interacting pairs are: (x, y, z) and $(-x, y+\frac{1}{2}, \frac{1}{2}-z)$, and $(\frac{1}{2}-x, -y, z+\frac{1}{2})$ and $(x+\frac{1}{2}, \frac{1}{2}-y, -z)$]. Crosslinking of these chains *via* N—H···Cl hydrogen bonds builds a complex three-dimensional net. The intermolecular hydrogen bonds which involve only cations can be described in graph-set notation (Etter, 1991; Bernstein *et al.*, 1995) as *C*(4)[Cl1, H2*A*, N1*A*, Zn1] (for molecules inside the chain) and *C*(5)[Cl1, H3, N2, N1, Zn1] (for molecules between the chains) (Fig. 2). The same pair of motifs is present in the structurally similar compound $[Zn(TzHy)_2Cl]Cl$ [TzHy is

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[1] Part XLII: Bogdanović *et al.* (2001).

(2-thiazolin-2-yl)hydrazine; Bernalte-Garcia *et al.*, 1997]. In both molecules, chemically equivalent types of atoms are arranged in the same way, forming the trigonal bipyramid.

It is interesting to note that, irrespective of the molar ratio of the reactants, the same bis(ligand) complex was obtained, while the reactions of $ZnCl_2$ and TSC yield two different structures, tetrahedral (mono) and octahedral (tris). It is difficult to determine the main factor which favours trigonal–bipyramidal coordination upon methylation of the S atom, bearing in mind that the steric requirements of both ligands are approximately the same and that the Zn^{II} ion has a preference for forming tetrahedral and octahedral structures. However, it should be noted that the bite angles of thiosemicarbazide and *S*-methylisothiosemicarbazide are more in accordance with trigonal–bipyramidal (where the chelate ring spans axial and equatorial positions) and octahedral symmetry than the tetrahedral arrangements.

One of the factors that we would like to stress is the different arrangement of the hydrogen bonds as a result of the different coordination mode. Considering the small bite angle of the TSC ligand, it is expected that bis-tetrahedral structures of this ligand will be rather distorted. In the case of the tetrahedral complex $[Zn(TSC)_2(NO_3)_2]$ (Tong *et al.*, 2000), due to the presence of the nitrate group as a counter-ion, complementary hydrogen-bond interactions are formed between the donor pair of cations, *i.e.* the hydrazine and thioamide N atoms of the TSC moiety, and the nitrate O atoms, as an acceptor pair. These interactions play an important role in the stabilization of $[Zn(TSC)_2(NO_3)_2]$. In the presence of a counter-ion with one donor site, stabilization through complementary hydrogen bonds is not possible. In mono-$Zn(TSC)Cl_2$, a different kind of tetrahedral structure is formed. Since only one molecule of the TSC ligand and two Cl atoms are involved in the formation of this complex, its tetrahedral geometry is less distorted. The positions of the H atoms in mono-$Zn(TSC)Cl_2$ have not been reported so we cannot analyze the role of the hydrogen bonds in the stabilization of this complex.

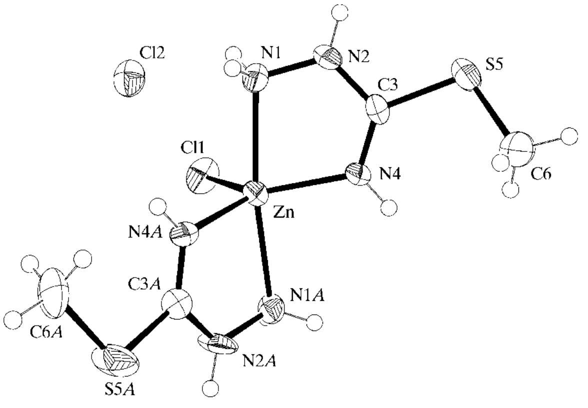

Figure 1
The molecular geometry and atom-labelling scheme for (I) with 50% probability displacement ellipsoids.

In contrast with TSC complexes, the coordination of ISTC through the hydrazine and thioamide N atoms reduces the ability of the latter atom to form a hydrogen bond. This may be the reason why, in (I), the pair of hydrazine N atoms plays a major role in the stabilization of the structure. One of the thioamide N atoms (N4*A*) forms an intramolecular hydrogen bond with the Cl^- anion, while the other (N4) is the only hydrogen-bond donor which is not involved in the hydrogen-bonding net. The closest acceptor, *viz.* the coordinated Cl atom, is at a distance of 3.01 Å from atom H4(N4)($-x - 1, y - \frac{1}{2}, \frac{1}{2} - z$). This contact could be categorized as a long intermolecular contact, since it exceeds the sum of the van der Waals radii for H and Cl atoms (Aullon *et al.*, 1998).

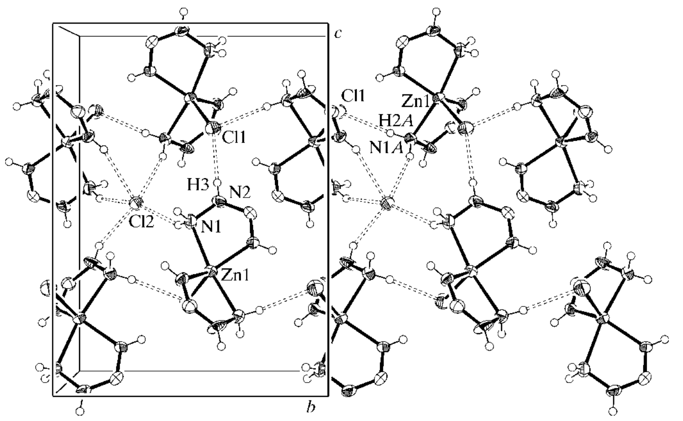

Figure 2
The crystal structure of (I) viewed down the *a* axis, showing the formation of hydrogen-bonded zigzag chains. The $S(CH_3)$ group has been omitted for clarity.

Experimental

White monocrystals of complex (I) were obtained by the reaction of EtOH solutions of stoichiometric amounts of $Zn(OAc)_2\cdot 2H_2O$ and *S*-methylisothiosemicarbazide hydrogen iodide, and an excess of $LiCl_2$.

Crystal data

$[ZnCl(C_2H_7N_3S)_2]Cl$
$M_r = 346.6$
Orthorhombic, $P2_12_12_1$
$a = 9.402$ (2) Å
$b = 10.121$ (3) Å
$c = 13.710$ (3) Å
$V = 1304.6$ (6) Å^3
$Z = 4$
$D_x = 1.765$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.8$–$17.4°$
$\mu = 2.59$ mm^{-1}
$T = 293$ (2) K
Cube, white
$0.24 \times 0.23 \times 0.22$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4392 measured reflections
3730 independent reflections
1913 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.095$

$\theta_{\max} = 30°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 3.1%

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Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.124$
$S = 0.98$
3730 reflections
136 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Absolute structure: Flack (1983); 1561 Friedel pairs
Flack parameter = 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Zn1—N4	1.989 (6)	Zn1—N1*A*	2.244 (6)
Zn1—N4*A*	1.991 (6)	Zn1—Cl1	2.296 (2)
Zn1—N1	2.223 (5)		
N4—Zn1—N4*A*	126.2 (2)	N1—Zn1—N1*A*	169.3 (2)
N4—Zn1—N1	77.4 (2)	N4—Zn1—Cl1	124.9 (2)
N4*A*—Zn1—N1	101.8 (2)	N4*A*—Zn1—Cl1	108.9 (2)
N4—Zn1—N1*A*	94.0 (2)	N1—Zn1—Cl1	93.8 (2)
N4*A*—Zn1—N1*A*	77.9 (2)	N1*A*—Zn1—Cl1	96.5 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*A*···Cl2	0.86	2.55	3.328 (6)	152
N2—H3···Cl1$^{\rm i}$	0.86	2.38	3.238 (6)	174
N2*A*—H3*A*···Cl2$^{\rm ii}$	0.86	2.38	3.188 (7)	156
N1—H1···Cl2$^{\rm iii}$	0.90	2.52	3.321 (6)	149
N1*A*—H2*A*···Cl1$^{\rm iv}$	0.90	2.49	3.385 (6)	172
N1—H2···Cl2	0.90	2.42	3.265 (6)	156
N1*A*—H1*A*···Cl2$^{\rm iv}$	0.90	2.64	3.509 (6)	162

Symmetry codes: (i) $-\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $-\frac{3}{2} - x, -y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, -\frac{1}{2} - y, -z$; (iv) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

H atoms were positioned geometrically at distances of 0.96, 0.90 and 0.86 Å from their parent C, Nsp^3 and Nsp^2 atoms, respectively, and their isotropic displacement parameters were fixed at 1.5 and 1.2 times the equivalent isotropic displacement parameter of their parent C and N atoms, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988); data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1563). Services for accessing these data are described at the back of the journal.

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