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Dichlorobis[1-methyl-3-(prop-2-enyl)-imidazole-2(3*H*)-thione-*S*]zinc(II)

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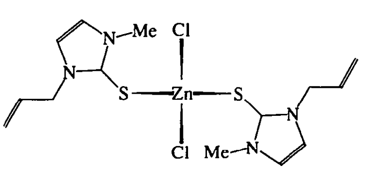
Abstract

The crystal structure of the title compound, $[ZnCl_2(C_7H_{10}N_2S)_2]$, shows a discrete molecular structure with tetrahedral geometry around the zinc ion. The mean Zn—Cl and Zn—S distances are 2.259 (7) and 2.372 (4) Å, respectively. Bond angles around the zinc ion range from 102.8 (1) to 113.7 (1)°. Ring distances and angles in the ligand compare favorably with literature values of analogous compounds, and the mean C—S bond distance of 1.71 (1) Å is close to the average distance of 1.72 Å observed for several dialkylimidazolethione complexes of main group and transition metal halides.

Comment

The title compound, $[ZnCl_2(mpit)_2]$, where mpit is 1-methyl-3-(prop-2-enyl)imidazole-2(3*H*)-thione, was reported in an earlier study (Williams, Ly, Mudge, Van-Derveer & Jones, 1994) as the first metal halide complex to be prepared from this new sterically hindered dialkylimidazolethione. The compound, (I), was included in a study that reinvestigated the so-called 'thioamide' vibrational mode assignments given in the literature.



(I)

The discrete molecular nature and observed tetrahedral geometry about the zinc ion in (I) (Fig. 1) are expected based on reported physical properties and on known structures of previously reported bis(dialkylimidazolethione)dihalometal(II) complexes (Kheddar, Protas, LeBaccon, Guglielmetti & Guerchais, 1976). The mean Zn—S distance of 2.372 (4) Å compares favorably with the value of 2.35 (1) Å reported for bis(thiourea)dichlorozinc(II), but the mean Zn—Cl distance of 2.259 (7) Å is significantly shorter than that reported for the dichlorozinc–thiourea complexes [2.35 (1) Å] cited above (Kunchur & Truter, 1958). A greater covalent character of the Zn—Cl bond in $[ZnCl_2(mpit)_2]$ is indicated since the bond length lies closer to the sum of the covalent radii (2.19 Å) than to the sum of the ionic radii (2.55 Å) (Huheey, Keiter & Keiter, 1993).

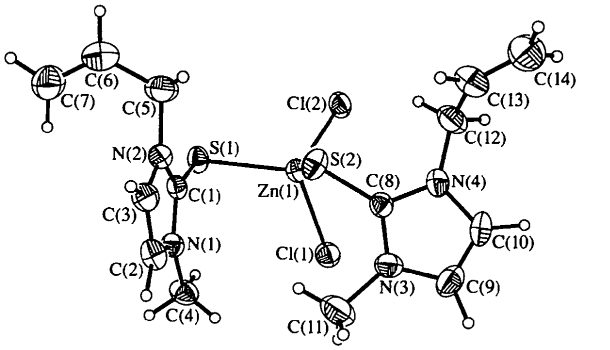


Fig. 1. View of the molecular unit of $[ZnCl_2(mpit)_2]$. Displacement ellipsoids are shown at 40% probability levels.

Bond angles around the zinc ion range from 102.8 (1) to 113.7 (1)°. Large deviations from the ideal value of 109.5° are probably due to packing restraints of the bulky dialkylimidazolethione ligands since the bond-angle range of 107.3–111.5° for bis(thiourea)dichlorozinc(II) does not show as great a deviation from the ideal (Kunchur & Truter, 1958).

Ring distances and angles in the ligand compare favorably with literature values for analogous compounds (Kheddar *et al.*, 1976; Williams, Poor, Ramirez & Heyl, 1988). Of prime interest is the mean C—S bond distance of 1.71 (1) Å, which is close to the average distance of 1.72 Å observed for several dialkylimidazolethione complexes of main group and transition metal halides (Williams *et al.*, 1988). This gives additional support for assigning IR peaks around 1150–1180 cm^{-1} to the carbon–sulfur stretch, ν(C=S), the frequency of which is a point of considerable disagreement in the literature (Williams *et al.*, 1994). The isolated double-bond mean distance in the propenyl group [1.27 (1) Å for C(6)—C(7) and C(13)—C(14)] stands in marked contrast to the more delocalized double bonds in the heterocyclic ring [1.34 (1) Å for C(2)—C(3) and C(9)—C(10)]. These distances lend support to the assignments for the different CH deformation modes in the IR spectrum of $[ZnCl_2(mpit)_2]$, with the propenyl modes in the 900–1000 cm^{-1} region and the *cis*-olefinic ring modes around 700–800 cm^{-1} (Williams *et al.*, 1994).

Experimental

The synthesis of $[ZnCl_2(mpit)_2]$ has been reported elsewhere (Williams *et al.*, 1994). Crystals suitable for study were obtained by slow evaporation from CH_2Cl_2.

Crystal data

$[ZnCl_2(C_7H_{10}N_2S)_2]$
$M_r = 444.73$
Monoclinic
$P2_1/n$
$a = 14.0082\ (8)$ Å
$b = 10.803\ (1)$ Å
$c = 14.581\ (1)$ Å
$\beta = 116.625\ (8)°$
$V = 1972.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.50$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.61–14.74°$
$\mu = 1.73$ mm^{-1}
$T = 295$ K
Parallelepiped
0.23 × 0.21 × 0.20 mm
Colorless

Data collection

Rigaku AFC-7 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{min} = 0.38$, $T_{max} = 0.71$
3833 measured reflections
3467 independent reflections

1935 reflections with $F > 6\sigma(F)$
$R_{int} = 0.020$
$\theta_{max} = 25°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: ±2%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.044$
$S = 1.85$
1935 reflections
209 parameters
H atoms calculated; $U_H = 0.147\ (9)$ Å^2

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

Table 1. *Selected geometric parameters (Å, °)*

Zn(1)—Cl(1)	2.264 (3)	Zn(1)—S(2)	2.370 (2)
Zn(1)—Cl(2)	2.254 (2)	S(1)—C(1)	1.719 (6)
Zn(1)—S(1)	2.374 (3)	S(2)—C(8)	1.708 (9)
Cl(1)—Zn(1)—Cl(2)	109.9 (1)	Cl(2)—Zn(1)—S(2)	113.0 (1)
Cl(1)—Zn(1)—S(1)	113.7 (1)	S(1)—Zn(1)—S(2)	102.8 (1)
Cl(2)—Zn(1)—S(1)	110.7 (1)	Zn(1)—S(1)—C(1)	96.3 (3)
Cl(1)—Zn(1)—S(2)	106.6 (1)	Zn(1)—S(2)—C(8)	99.3 (2)

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined with a group displacement parameter as riding groups.

Data collection: Rigaku AFC-7 software. Cell refinement: Rigaku AFC-7 software. Data reduction: *TEXSAN* (Swepston, 1993). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1991). Molecular graphics: *SHELXTL-Plus*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1301). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The *isonido*-Metalladicarbaborane [1,1,1-H{P(CH$_3$)$_3$}$_2$-6-Cl-1,2,4-IrC$_2$B$_8$H$_9$]

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Abstract

A single-crystal diffraction study of the title iridadicarbaundecaborane species, 6-chloro-1,1-bis(trimethylphosphine-*P*)-1-*endo*-H-2,3-dicarba-1-irida-*isonido*-undecaborane(12), $[IrH(PMe_3)_2(C_2B_8H_9Cl)]$ or $[(PMe_3)_2(H)IrC_2B_8H_9Cl]$, shows that it has an *isonido*-type structure with a four-membered Ir1–C2–C4–B7 open face. The presence of the chlorine substituent on vertex B6 suggests that the compound is formed *via* a simple ligand elimination and intrafacial addition of the metal vertex to a neighbouring boron vertex in the probable precursor compound *nido*-$[(PMe_3)_2(CO)IrC_2B_8H_{10}Cl]$.

Comment

In the course of our investigations of heteroatom additions to metallaborane clusters to give metalla-