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LETTER

Complexes of Group 12 metals with sterically-hindered thiolate ligands. The crystal and molecular structures of $[Zn_2(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_4]$ and $[CdI_2(2\text{-}SC_5H_3NH\text{-}6\text{-}SiMe_2Bu^t)_2]$

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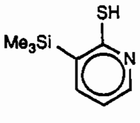
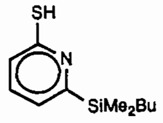
Introduction

Zinc–thiolate coordination chemistry has received considerable contemporary attention as a consequence of the presence of zinc–cysteine coordination in numerous metalloproteins [1–8]. As part of our extensive studies of the coordination chemistry of sterically-hindered thiolate ligands [9], we have synthesized and characterized the complexes of zinc, and of its congener cadmium, with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ (**A**) and $2\text{-}HSC_5H_3N\text{-}6\text{-}SiMe_2Bu^t$ (**B**).



A



B

Experimental

Reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with **A** in ethanol yields colorless crystals of $[Zn_2(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_4]$ (**1**) in 80% yield. Crystal data for $C_{32}H_{48}N_4Si_4S_4Zn_2$ (**1**): monoclinic space group $P2_1/c$, $a = 16.439(3)$, $b = 13.627(2)$, $c = 19.154(3)$ Å, $\beta = 96.69(1)°$, $V = 4261.4(11)$ Å^3, $Z = 4$, $D_{calc} = 1.338$ g cm^{-3}. Structure solution and refinement based on 2962 reflections with $I_o \geqslant 3\sigma(I_o)$ converged at $R = 0.048$.

Reactions of ZnX_2 precursors (X = Cl, I) with **B** in ethanol yield $[ZnX_2(2\text{-}SC_5H_3NH\text{-}6\text{-}SiMe_2Bu^t)_2]$ (X = Cl, **2a**; I, **2b**). *Anal.* Calc. for $C_{22}H_{38}N_2Si_2Cl_2Zn$: C, 45.0; H, 6.48; N, 4.77. Found: C, 44.7; H, 6.10; N, 4.92%.

Reaction of CdI_2 with **B** in ethanol yields the analogous species $[CdI_2(2\text{-}SC_5H_3NH\text{-}6\text{-}SiMe_2Bu^t)_2]$ (**3**). *Anal.* Calc. for $C_{22}H_{38}N_2Si_2S_2I_2Cd$: C, 32.3; H, 4.66; N, 3.43. Found: C, 31.9; H, 4.42; N, 3.21%. Crystal data for $C_{22}H_{38}N_2Si_2S_2I_2Cd$ (**3**): monoclinic space group $P2_1/c$, $a = 25.804(4)$, $b = 10.228(2)$, $c = 12.585(3)$ Å, $\beta = 104.01(1)°$, $V = 3222.6(11)$ Å^3, $Z = 4$, $D_{calc} = 1.682$ g cm^{-3}. Structure solution and refinement based on 2262 reflections with $I_o \geqslant 3\sigma(I_o)$ converged at $R = 0.048$.

Discussion

The structure of **1**, shown in Fig. 1, consists of discrete neutral binuclear units with the Zn centers in distorted tetrahedral $[ZnS_2N_2]$ environments. Each Zn atom coordinates to the sulfur and nitrogen donors of a terminally ligated 2-pyridinethiolate ligand and to the sulfur and nitrogen donors of two different (N, S)-bridging pyridinethiol groups, which results in an unusual eight-membered heterocyclic ring [Zn–S–C–N–Zn–S–C–N] which adopts a chair-like configuration. The binuclear Zn–thiolate complexes previously reported [7] are invariably dianionic species $[Zn_2(SR)_6]^{2-}$ with planar $[Zn_2S_2]$ bridge cores. Complex **1** provides a novel structural type for consideration as a possible coordination mode in zinc–cysteine proteins.

In attempting to prepare the analogous species with ligand **B**, only mononuclear complexes of the general type $[ZnX_2(2\text{-}SC_5H_3NH\text{-}6\text{-}SiMe_2Bu^t)_2]$ (X = Cl, **2a**; I, **2b**) could be isolated, presumably as a consequence of the steric influence of the bulky $SiMe_2Bu^t$ in the 6-position preventing coordination of the pyridyl nitrogen. Since **2a** and **2b** are neutral, the ligand must be present in the neutral 1H-2-pyridinethione form. This was confirmed by the structural analysis of the analogous cadmium complex $[CdI_2(2\text{-}SC_5H_3NM\text{-}6\text{-}SiMe_2Bu^t)_2]$ (**3**), whose structure is shown in Fig. 2. The isolation of neutral $[MX_2(HL)_2]$ complexes from the reactions of zinc and cadmium dications with **B**, rather than binuclear

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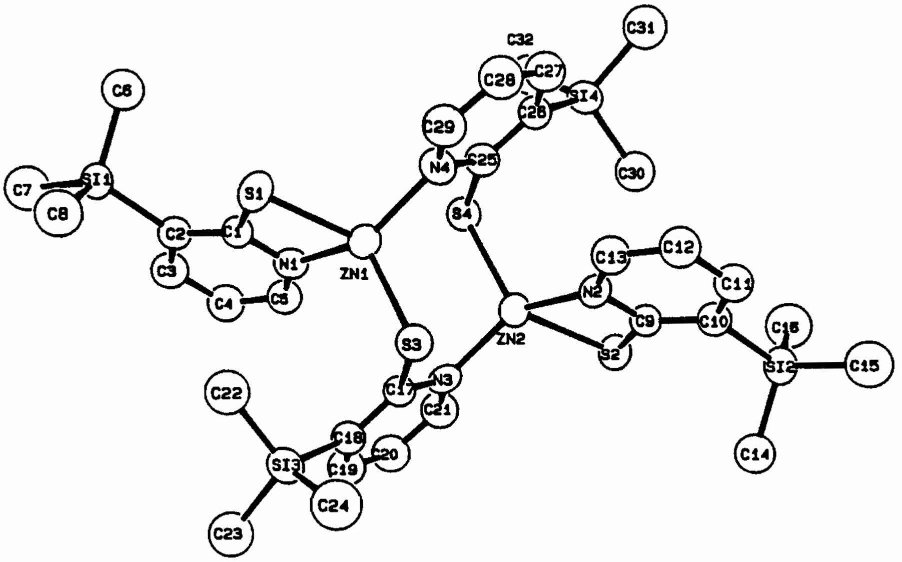

Fig. 1. ORTEP view of the structure of $[Zn_2(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_4]$ (1), showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Zn(1)–S(1), 2.405(3); Zn(1)–S(3), 2.337(3); Zn(1)–N(1), 2.072(6); Zn(1)–N(4), 2.066(7); Zn(2)–S(2), 2.410(3); Zn(2)–S(4), 2.335(3); Zn(2)–N(2), 2.055(6), Zn(2)–N(3), 2.032(7); S(1)–Zn(1)–S(3), 123.8(1); N(1)–Zn(1)–N(4), 141.7(3); S(1)–Zn(1)–N(1), 70.4(2); S(2)–Zn(2)–S(4), 123.9(1); N(2)–Zn(2)–N(4), 140.0(3); S(2)–Zn(2)–N(2), 69.9(2).

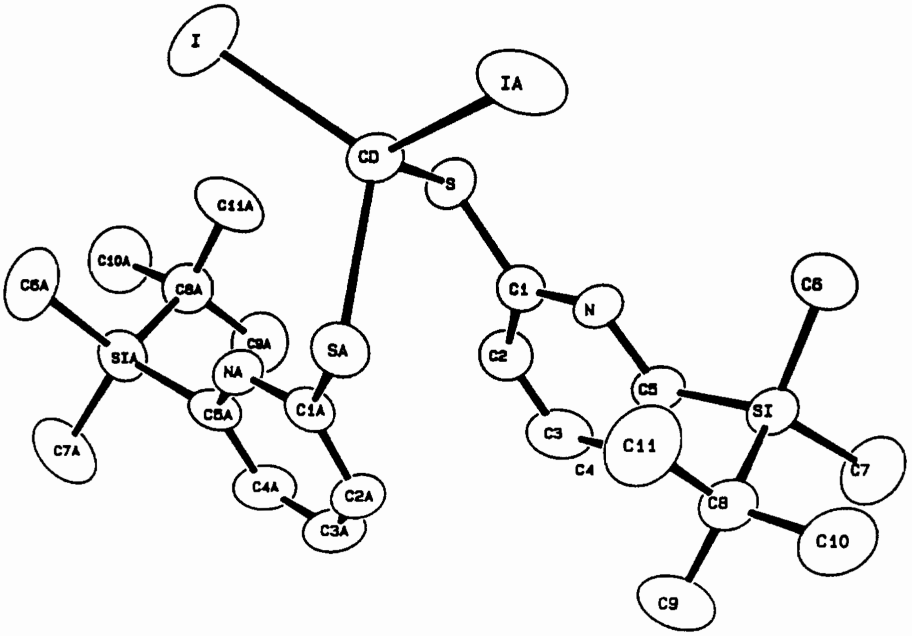

Fig. 2. ORTEP view of the structure of $[CdI_2(2\text{-}SC_5H_3NH\text{-}6\text{-}SiMe_2Bu^t)_2]$ (3). Selected bond lengths (Å) and angles (°): Cd–I, 2.7358(8); Cd–S, 2.558(2); S–C(1), 1.720(6); I–Cd–I(a), 119.30(4); I–Cd–S, 100.13(4); I–Cd–S(a), 116.70(4); S–Cd–S(a), 103.56(8).

thiolate bridged species or mononuclear $[ML_3]^{1-}$ or $[ML_4]^{2-}$ types, demonstrates the dramatic influence of substituents and their locations on the chemistry of the derivatized 2-pyridinethiol ligands.

Acknowledgement

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