

Design and Self-assembly of a Novel Tetranuclear Zinc(II) Complex *via* Reaction of 1,3-Thiazolidine-2- thione(tzdtH) with $\text{Zn}(\text{NO}_3)_2$ *

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Introduction

The self-assembly of clusters in inorganic systems is an interesting subject. The self-assembly of big molecules has been well established in biological systems^[1–5]. In addition, the coordination chemistry of metal-sulfur-nitrogen cluster complexes has been a very active and attracting field for many years as a result of the novelty and versatility of the crystal structures and reactivities of such clusters, as well as their potential applications as the models for the active sites in non-heme proteins^[6,7]. At the same time, there is currently considerable interest in the formation of metal complexes with heterocyclic ligands because of the diverse characteristics of ligands and their consequential wide range of applications^[8,9].

Many coordination complexes that are constructed from heterocyclic ligands and metal atoms have been synthesized by many methods^[10]. It is well known that 1,3-thiazolidine-2-thione(tzdtH) is a classical heterocyclic ligand^[7]. TzdtH has shown various monodentate, bridging, and chelating coordination models as a neutral ligand or as an anion with a deprotonated structure^[11]. In particular, the deprotonation of tzdtH produces the corresponding thionate anions, which are versatile bridging ligands.

The 1,3-thiazolidine-2-thionate anion[Fig. 1(A)] is typical of this kind of anions in the entire range of heterocyclic thionates. With three and seven electrons available for use in various ways that invariably involve the endocyclic nitrogen and exocyclic sulfur thioamide

atoms, the anion is an effective chelating ligand^[12]. The μ_2 -S[Fig. 1(B)] and μ_2 -S, N[Fig. 1(C), (E)] allow tzdtH to construct oligomer metal-organic complexes, such as the four isostructural tetranuclear clusters of Cu^I or Ag^I and the mixed metal tetranuclear cluster of Cu^I and Ag^I : $(\text{PPh}_3)_2\text{Ag}_4(\text{tzdt})_4$, $(\text{PPh}_3)_2\text{Cu}_4(\text{tzdt})_4$, $(\text{PPh}_3)_2\text{Ag}_2\text{Cu}_2(\text{tzdt})_4$, and $(\text{py})\text{Cu}_4(\text{tzdt})_4$ synthesized by John P. Fackler *et al.*^[3] with ligand tzdtH. In addition, $[\text{Os}_3\text{H}(\text{tzdt})(\text{CO})_{10}]$ and $\{[\text{Ni}(\text{OH})(\text{tzdt})(\text{py})]\}_4$ have also been synthesized^[13,14].

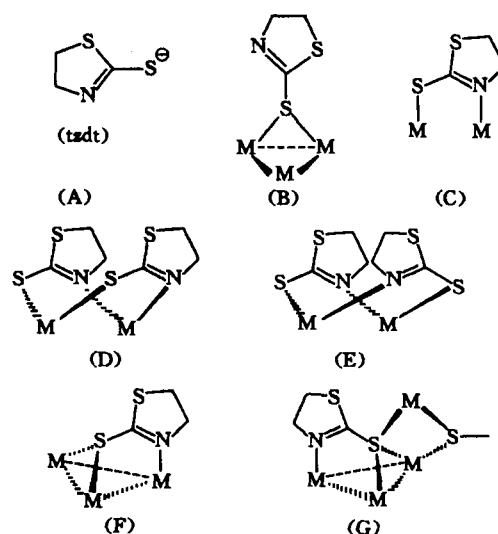


Fig. 1 1,3-Thiazolidine-2-thionate(tzdtH) and its coordination models(A–G)

In this study, 1,3-thiazolidine-2-thionate was chosen as the multifunctional coordination ligand on the

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basis of the considerations that it has exocyclic sulfur (S_{exo}) and endocyclic nitrogen (N_{endo}) donors that are at the meta position and allow tzdtH to form and support an isolated metal-ligand cluster in the coordination architecture. As a result, a blossom-shaped tetranuclear zinc cluster $[Zn_4(\mu_4-O)(tzdt)_6]$ was synthesized by the reaction of tzdtH with $Zn(NO_3)_2$ under a mild condition for the first time. It was characterized by means of IR spectrometry and elemental analyses. The crystal structure of $[Zn_4(\mu_4-O)(tzdt)_6]$ was determined by X-ray diffraction (XRD).

Experimental

All the chemicals purchased were of reagent grade without further purification prior to use. Colorless crystals of $[Zn_4(\mu_4-O)(tzdt)_6]$ were obtained by the reaction of tzdtH and $Zn(NO_3)_2 \cdot 4H_2O$. A mixture of $Zn(NO_3)_2 \cdot 4H_2O$ (0.063 g, 0.25 mmol) and tzdtH (0.059 g, 0.05 mmol) was placed in a test tube containing chloroform (5 mL). The test tube was placed into a glass bottle that contained a mixture of ethanol (10 mL) and Et_3N (3 mL). The bottle was sealed and then kept in an ice box ($-2\text{ }^\circ\text{C}$) for about a month, and colorless crystals of $[Zn_4(\mu_4-O)(tzdt)_6]$ were obtained.

The speed of volatilization of Et_3N in the reaction was a key point for the formation of $[Zn_4(\mu_4-O)(tzdt)_6]$ because the coordination cluster was prepared at a lightly raised pH value and under a weakly alkaline condition.

The crystal structure of $[Zn_4(\mu_4-O)(tzdt)_6]$ was determined by single-crystal XRD. In addition, $[Zn_4(\mu_4-O)(tzdt)_6]$ was characterized by means of elemental analyses and IR spectrometry. The XRD data were collected on a Bruker SMART APEX-CCD diffractometer with Mo $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least squares on the basis of F^2 using the SHELXTL-97 software package. The elemental analyses were performed on a Perkin-Elmer 240 element analyzer. The IR spectra were obtained on a Nicolet Impact 410 FTIR spectrometer with KBr pellets. Elemental analysis (%), calc. (found): C 21.91 (21.95), H 2.45 (2.49), N 8.51 (8.57).

Results and Discussion

The IR spectrum of the tetranuclear complex provides the evidence for the existence of the corresponding thionate anions of tzdtH in the complex. Significant perturbation of the ligand thioamide bands (at 1514, 1297, 1048 and 694 cm^{-1}), particularly those of thioamide at 1514 and 694 cm^{-1} , can also be observed in

the IR spectrum of the complex. This observation is consistent with the coordination of the exocyclic sulfur and endocyclic nitrogen atoms of the deprotonated ligands to the zinc (II) atoms.

A suitable single crystal of the title compound was selected and mounted on a glass fiber. The intensity data were collected on a Bruker SMART APEX-CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073\text{ nm}$) at 298 K. A total of 7130 reflections were collected with 2704 unique reflections. The zinc and sulfur atoms were first located and the carbon, nitrogen, and oxygen atoms were found from the final difference Fourier maps and refined anisotropically. The hydrogen atoms of the heterocyclic rings were placed geometrically. Further details of the X-ray structural analysis are shown in Table 1 (CCDC reference number 293631).

Table 1 Crystal data and structure refinement for $[Zn_4(\mu_4-O)(tzdt)_6]$

Empirical formula	$C_{18}N_6O_{12}Zn_4$
Formula weight	345.73
T/K	293(2)
λ/nm	0.071073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 1.1638(2)\text{ nm}$, $\alpha = 90^\circ$ $b = 1.6357(3)\text{ nm}$, $\beta = 103.64^\circ$ $c = 1.8916(4)\text{ nm}$, $\gamma = 90^\circ$
V/nm^3	3.4993(12)
Z	11
$D_{\text{calc}}/(\text{Mg} \cdot \text{m}^{-3})$	1.805
Absorption coefficient/ mm^{-1}	2.255
$F(000)$	1936
θ range for data collection/ $^\circ$	1.67 to 27.48
Limiting indices	$0 \leq h \leq 15$, $0 \leq k \leq 21$, $-24 \leq l \leq 23$
Reflections collected/unique	7130/7130 [$R(\text{int}) = 0.0000$]
Completeness to $\theta = 27.48$	88.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7130/0/351
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0888$, $wR_2 = 0.2301$
R indices (all data)	$R_1 = 0.2044$, $wR_2 = 0.2623$
Largest diff. peak and hole/ ($e \cdot \text{nm}^{-3}$)	1.559 and -0.782

The novel tetranuclear zinc cluster $[Zn_4(\mu_4-O)(tzdt)_6]$ as shown in Fig. 2 is an asymmetric unit with a blossom structure (Figs. 3, 4). There are six tzdtH ligands in the blossom core. Each tzdtH ligand coordinates to two zinc atoms by the exocyclic sulfur and deprotonated endocyclic nitrogen atoms. The crystal unit contains four zinc atoms that are bridged by μ_4-O (O_2 comes from hydroxide ion^[13]) to form a Zn_4O core. Each organic ligand coordinates to two zinc atoms

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