Inorg. Chem. **2008**, *47*, 2777−2785

Inorganic Chemistry
Article

Phosphonate- and Ester-Substituted 2-Cyanoethylene-1,1-Dithiolate Clusters of Zinc: Aerial CO$_2$ Fixation and Unusual Binding Patterns

Bijay Sarkar, **Ben-Jie Liaw**, **Ching-Shiang Fang**, and **C. W. Liu***

Department of Chemistry, National Dong Hwa University, Hualien 97401, Taiwan

Received October 27, 2007

Treatment of [Zn(tmeda)Cl$_2$] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with a phosphonate-substituted 2-cyanoethylene-1,1-dithiolato ligand in air yields a tetranuclear zinc−carbonate complex **1** having the formula of [Zn$_4$(tmeda)$_3$(μ_3-CO$_3$){S$_2$CC(CN)P(O)(OEt)$_2$}$_3$] in which four zinc atoms form a trigonal pyramid with the apical zinc atom in a hitherto unknown S$_3$O$_3$ coordination sphere. It is the first example of aerial CO$_2$ fixation to afford a metal–carbonato compound incorporating 1,1-ethenedithiolate ligands. In sharp contrast, reaction with an isobutyl ester-substituted 2-cyanoethylene-1,1-dithiolate forms a trimeric zinc complex [Zn(tmeda){S$_2$CC(CN)(CO$_2{}^i$Bu)}]$_3$, **2**, which does not contain the metal-bound carbonate. Compound **2** is the first example of a trinuclear zinc complex composed of four-, five-, and six-coordinated Zn atoms. The unsymmetrical ligand orientation around three zinc centers in **2** suggests that the other structural isomer, which would have an idealized C_3 axis, may exist. The reaction of the ethyl ester derivative of 2-cyanoethylene-1,1-dithiolate with [Zn(tmeda)Cl$_2$] affords [{Zn(tmeda)Cl}$_2$-{S$_2$CC(CN)(CO$_2$Et)}], **3**. The ester-functionalized 1,1-dithiolate ligands in compounds **2** and **3** display a bimetallic, triconnective coordination mode, which is rare for these types of ligands. Some probable intermediates generated from the formation of compound **1** have also been proposed.

Introduction

Despite the fact that the first structural report of a metal complex containing 1,1-ethenedithiolate ligand was published in 1966,[1] and that the metal complexes of this type of ligand have shown interesting photophysical properties,[2] 1,1-ethenedithiolate and its derivatives have received much less attention than their 1,2-isomers.[3] 1,1-Dithiolate ligands are well-known to form cluster compounds with group 11 metal ions.[4]The variable coordination modes (Scheme 1a−d) of the 1,1-ethenedithiolato ligands toward metal ions make it possible to form multinuclear clusters. With phosphonate-substituted 2-cyanoethylene-1,1-dithiolato ligands [S$_2$CC(CN)-P(O)(OEt)$_2$]$^{2-}$ (abbreviated as cpdt), a few more binding modes may exist as represented in Scheme 1e−h. Thus it is anticipated that several species with different nuclearity may coexist in solution. Hence determination of solid-state structure for the isolated compounds is the only way to rationalize the final outcome of the reaction in the solution state.

Although there are several reports on the metal complexes of symmetrical 1,1-dithiolate ligands [S$_2$C=C(X)$_2$]$^{2-}$,[5] such as *i*-MNT (2,2-dicyanoethylene-1,1-dithiolate),[6] only a limited number of structural reports are available for metal complexes containing unsymmetrically substituted 1,1-dithiolate ligands [S$_2$C=C(X)(Y)]$^{2-}$.[4g,h,7] Although researchers have explored the coordination chemistry with various

---

* E-mail: chenwei@mail.ndhu.edu.tw. Fax: +886-3-8633570.

(1) Fackler, J. P.; Coucouvanis, D. *J. Am. Chem. Soc.* **1966**, *88*, 3913.

(2) (a) Paw, W.; Cummings, S. D.; Mansour, M. A.; William, B.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125. (b) Vicente, J.; Chicote, M. T.; Gonzalez-Herrero, P.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Inorg. Chem.* **1999**, *38*, 5018. (c) Bevilacqua, J. M.; Zuleta, J. A.; Eisenberg, R. *Inorg. Chem.* **1993**, *32*, 3689. (d) Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bardaji, M. *Inorg. Chem.* **2004**, *43*, 7516. (e) Vicente, J.; González-Herrero, P.; Pérez-Cadenas, M.; Jones, P. G.; Bautista, D. *Inorg. Chem.* **2005**, *44*, 7200.

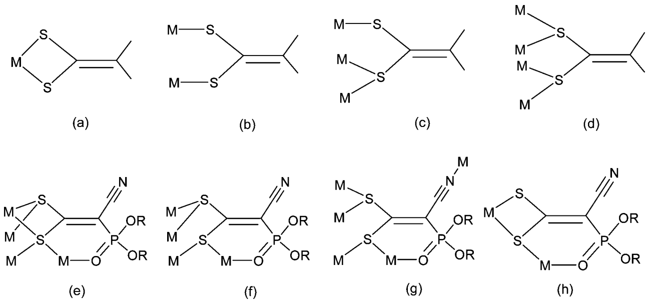
(3) Stiefel, E. I. *Prog. Inorg. Chem.* **2004**, *52*, 1–681.

(4) (a) Perruchas, S.; Boubekeur, K. *Dalton Trans.* **2004**, 2394. (b) Perruchas, S.; Boubekeur, K.; Auban-Senzier, P. *J. Mater. Chem.* **2004**, *14*, 3509. (c) Hanhui, Z.; Xiufen, Y. *Jiegou Huaxue* **1987**, *6*, 98. (d) Fackler, J. P.; Staples, R. J.; Assefa, Z. *J. Chem. Soc., Chem. Commun.* **1994**, 431. (e) Baudron, S. A.; Hosseini, M. W.; Kyritsakas, N. *New J. Chem.* **2006**, *30*, 1083. (f) Khan, M. N. I.; Wang, S.; Fackler, J. P. *Inorg. Chem.* **1989**, *28*, 3579. (g) Liu, C. W.; Liaw, B.-J. *Inorg. Chem.* **2000**, *39*, 1329. (h) Liu, C. W.; Liaw, B.-J.; Wang, J.-C.; Liou, L.-S.; Keng, T.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 1058.

(5) (a) Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bautista, D. *Eur. J. Inorg. Chem.* **2006**, 115. (b) Coucouvanis, D.; Hollander, F. J.; Caffery, M. L. *Inorg.Chem.* **1976**, *15*, 1853. (c) Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268. (d) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.

10.1021/ic702126k CCC: $40.75

Scheme 1. Schematic Representation of General Binding Modes for a 1,1-Ethenedithiolate Ligand (a−d) and Binding Modes for cpdt (e−h)



symmetrically or unsymmetrically substituted 1,1-ethenedithiolates previously, none of the complexations of these ligands has resulted in aerial CO_2 fixation. Even though our research group has reported silver[4g] and copper[4h] clusters with the cpdt ligand, none of the corresponding reactions produced a metal-bound carbonato complex.

Though it is possible to attain all of the binding modes represented in Scheme 1 for an ester-functionalized 1,1-dithiolate ligand, the majority of the studies on this type of ligand showed its coordination to metals through thiolate S atoms only, leaving the carbonyl O atom uncoordinated.[8] Only a few examples can be found where both thiolate S and carbonyl O are involved in the coordination toward the metal center.[9]

Herein we present the first example of aerial CO_2 fixation obtained via the complexation process between $[S_2CC(CN)P(O)(OEt)_2]^{2-}$ and $[Zn(tmeda)Cl_2]$ in THF under air to afford $[Zn_4(\mu_3\text{-}CO_3)(tmeda)_3\{S_2CC(CN)P(O)(OEt)_2\}_3]$, **1**. For the analogous ester-functionalized dithiolate ligand $[S_2CC(CN)(CO_2{}^i\text{Bu})]^{2-}$, hydration of CO_2 did not occur. Instead, the reaction yielded the trimeric zinc compound $[Zn(tmeda)\{S_2CC(CN)(CO_2{}^i\text{Bu})\}]_3$, **2**. All three ligands incorporated in **2** have a similar bonding mode, but the unsymmetrical ligand orientation around three zinc centers has yielded four-, five-, and six-coordinate zinc atoms in the structure. Interestingly, this leaves a possibility that the other structural isomer, which would contain three five-coordinate zinc atoms, may exist. A trinuclear zinc complex having four-, five-, and six-coordinate zinc atoms has not been reported prior to this work. In the case of an ethyl ester functionalized ligand $[S_2CC(CN)(CO_2Et)]^{2-}$, a dinuclear complex $[\{Zn(tmeda)Cl\}_2\{S_2CC(CN)(CO_2Et)\}]$, **3**, was obtained from a similar reaction. The dithiolate ligands in both **2** and **3** display a bimetallic-triconnective coordination mode where the carbonyl O atom of the ester is coordinated to the zinc center along with their thiolate S atoms. Due to the similarity in skeleton between ligands $[S_2CC(CN)P(O)(OEt)_2]^{2-}$ and $[S_2CC(CN)(CO_2Et)]^{2-}$, the compound **3** indeed provides insights regarding the structure of probable intermediates during the formation of **1**.

Experimental Section

The solvents used were purified following a standard protocol. All other chemicals purchased were used without further purification. $K_2S_2CC(CN)P(O)(OEt)_2$, $K_2S_2CC(CN)(CO_2{}^i\text{Bu})$, and $K_2S_2CC(CN)(CO_2Et)$ were synthesized as described in a literature report.[10] NMR spectra were recorded with a 300 MHz Bruker Advance DPX300 FT-NMR spectrometer. The $^{31}P\{^1H\}$ NMR spectra were referenced externally against 85% H_3PO_4 ($\delta = 0$ ppm). The elemental analyses were carried out on a Perkin-Elmer 2400 CHNS analyzer. Melting points were measured by using a Fargo melting point apparatus, MP-2D. The collections of single-crystal X-ray diffraction data were performed on a Bruker P4 for **1** and APEX-II diffractometers for **2** and **3** by using the 2θ-ω scan technique. Data reduction was performed with SAINT,[11] which corrects for Lorentz and polarization effects. A multiscan absorption correction based on Ψ scans (**1**) and SADABS (**2** and **3**) was applied. One of the chloride atoms in $CHCl_3$ in **2** is disordered, and two positions with equal occupancy were refined. The ethyl moiety in **3**, whose bond length is fixed at 1.500(5) Å and is refined isotropically, is severely disordered. The structure was solved by the use of direct methods, and the refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[12] incorporated in SHELXTL/PC V5.10.[13]

Synthesis of $[Zn_4(tmeda)_3(\mu_3\text{-}CO_3)\{S_2CC(CN)P(O)(OEt)_2)\}_3]$ (1). The $[Zn(tmeda)Cl_2]$ (0.38 g, 1.5 mmol) in 20 mL of THF was added to a solution of $K_2S_2CC(CN)P(O)(OEt)_2$ (0.31 g, 0.9 mmol) in THF (100 mL) in a 250 mL conical flask in open air. The solution was stirred at room temperature. After a few hours, white solids started to form. The reaction mixture was continually stirred for 7 days. The white solid was separated by filtration and extracted with dichloromethane to isolate the product from the KCl formed during the reaction. The dichloromethane was evaporated by using a rotavapor to obtain the product as a white solid. Single crystals suitable for X-ray crystallography were grown by diffusing hexane into a dichloromethane solution of the compound. Yield: 0.20 g (46.9%). Anal. Calcd for $C_{40}H_{78}N_9O_{12}P_3S_6Zn_4$: C, 33.71; H, 5.59; N, 8.85; S, 13.50. Found: C, 33.57; H, 5.43; N, 8.76; S, 13.34. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ in ppm: 21.3 (s, 3P). ^1H NMR (CD_2Cl_2) δ in ppm: 1.33 (m, 18H, $-OCH_2CH_3$), 2.58 (br s, 36H, $(CH_3)_2N-$), 2.69 (br s, 12H, $-NCH_2-$), 4.17 (m, 12H, $-OCH_2CH_3$). ^{13}C NMR (CD_2Cl_2) δ in ppm: 16.2 ($O-CH_2CH_3$), 47.1 (NCH_3), 56.7 (CH−-

---

(6) (a) McCandlish, L. E.; Bissel, E. C.; Coucouvanis, D.; Fackler, J. P., Jr; Knox, K. *J. Am. Chem. Soc.* **1968**, *90*, 7357. (b) Birker, P. J. M. W. L.; Verschoor, G. G. *J. Chem. Soc., Chem. Commun.* **1981**, 322. (c) Liu, C. W.; Staples, R. J.; Fackler, J. P. *Coord. Chem. Rev.* **1998**, *174*, 147. (d) Liu, C. W.; McNeal, C. J.; Fackler, J. P. *J. Cluster Sci.* **1996**, *7*, 385. (e) Dietrich, H.; Storck, W.; Manecke, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1036.

(7) (a) Alkam, H. H.; Kanan, K. M.; Hadjikostas, C. C. *Polyhedron* **2005**, *24*, 2944. (b) Lang, M. A.; Sunkel, K.; Ponikwar, W.; Beck, W. *Z. Naturforsch., B: Chem. Sci.* **2003**, *58*, 311. (c) Weigand, W.; Bosl, G.; Polborn, K. *Chem. Ber.* **1990**, *123*, 1339. . (d) Li, D.-C.; Feng, S.-C.; Dou, J.-M.; Wang, D.-Q. *Z. Kristallogr.* **2005**, *220*, 330.

(8) (a) Coucouvanis, D.; Hollander, F. J.; Pedelty, R. *Inorg. Chem.* **1977**, *16*, 2691. (b) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G. *Inorg. Chem.* **2003**, *42*, 4268. (c) Coucouvanis, D.; Kanodia, S.; Swenson, D.; Chen, S.-J.; Studemann, T.; Baenziger, N. C.; Pedelty, R.; Chu, M. *J. Am. Chem. Soc.* **1993**, *115*, 11271. (d) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 6193. (e) Huertas, S.; Hissler, M.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 1183.

(9) (a) Coucouvanis, D.; Swenson, D.; Baenziger, N C.; Pedelty, R.; Caffery; M. L, *J. Am. Chem. Soc.* **1977**, *99*, 8097. (b) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Pedelty, R.; Caffery, M. L.; Kanodia, S. *Inorg. Chem.* **1989**, *28*, 2829. (c) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1994**, *13*, 1257. (d) Vicente, J.; Chicote, M. T.; Martinez-Viviente, E.; Martinez-Martines, A. J.; Jones, P. G. *Inorg. Chem.* **2006**, *45*, 10434.

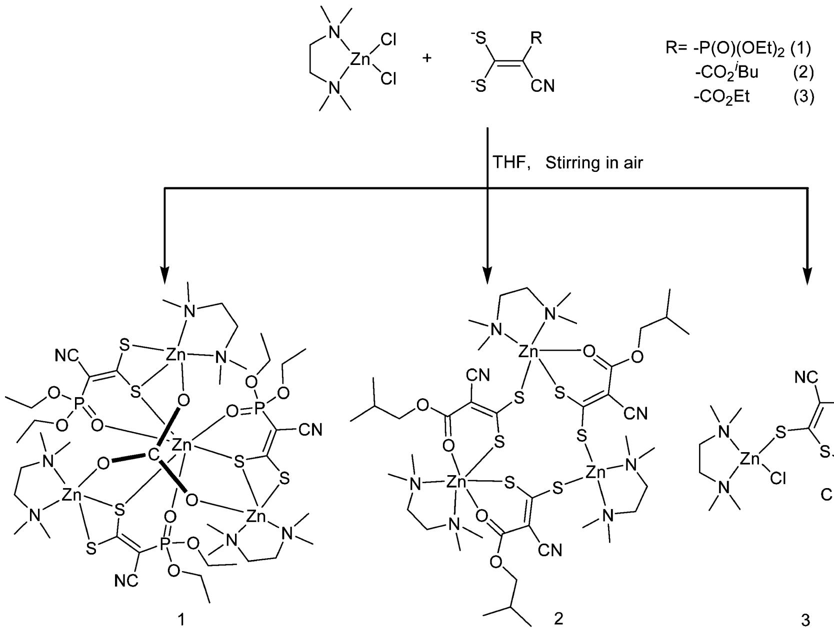
(10) Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1968**, *22*, 1107.

(11) *SAINT V4.043: Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

(12) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(13) *SHELXL 5.10: Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray System: Madison, WI, 1998.

Scheme 2. Schematic Representation of Formation of Neutral Complexes **1**, **2**, and **3** by the Reaction of [Zn(tmeda)Cl$_2$] with Unsymmetrically Substituted 1,1-Dithiolate Ligands



N), 62.9 (O−CH_2CH$_3$), 79.7 (*C*(CN)), 120.8 (−*C*N), 168.3 (CO_3^{2-}), 206.5 (*C*S$_2$). IR (cm^{-1}): ν_{CN} 2182, $\nu_{C=O}$ 1465; mp 248 °C (decomposed).

Synthesis of [Zn(tmeda){S$_2$CC(CN)(CO$_2{}^i$Bu)}]$_3$ (2). [Zn(tmeda)Cl$_2$] (0.25 g, 1 mmol) in 10 mL of THF was added to a solution of K$_2$S$_2$CC(CN)(CO$_2{}^i$Bu) (0.29 g, 1 mmol) in THF (25 mL) and stirred at room temperature in a 100 mL conical flask. After a few hours, white solid started to form. It was continually stirred for 2 days. The solid was separated by filtration and extracted with dichloromethane to isolate the product from the salt formed during the reaction. The dichloromethane was evaporated using a rotavapor to obtain the product as a white solid. Single crystals suitable for X-ray crystallography were grown by diffusing hexane into a solution of this compound in CHCl$_3$. Yield: 0.24 g (63.4%). Anal. Calcd for $C_{42}H_{75}N_9O_6S_6Zn_3$: C, 42.37; H, 6.35; N, 10.59; S, 16.16. Found: C, 42.14; H, 6.19; N, 10.42; S, 16.80. ^{1}H NMR (CDCl$_3$) δ in ppm: 0.98 (m, 18 H, −OCH$_2$CH(C*H*$_3$)$_2$), 1.86 (m, 3H, −OCH$_2$C*H*(CH$_3$)$_2$), 2.60 (br s, 36H, (C*H*$_3$)$_2$NCH$_2$−), 2.72 (br s, 12H, (CH$_3$)$_2$NC*H*$_2$−), 3.95 (m, 6H, −OC*H*$_2$CH(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$) δ in ppm: 18.9 (−OCH$_2$CH(*C*H$_3$)$_2$), 27.9 (−OCH$_2$*C*H(CH$_3$)$_2$), 48.1 ((*C*H$_3$)$_2$NCH$_2$−), 56.7 ((CH$_3$)$_2$N*C*H$_2$−), 70.9 (−O*C*H$_2$CH(CH$_3$)$_2$), 92.7 (−*C*(CN)), 120.7 (−*C*N), 169.3 (*C*═O), 206.7 (−*C*S$_2$). IR (cm^{-1}): ν_{CN} 2179, mp 225 °C (decomposed).

Synthesis of [{Zn(tmeda)Cl}$_2${S$_2$CC(CN)(CO$_2$Et)}] (3). [Zn(tmeda)Cl$_2$] (0.25 g, 1 mmol) in 10 mL of THF was added to a solution of K$_2$S$_2$CC(CN)(CO$_2$Et) (0.13 g, 0.5 mmol) in 10 mL of THF and stirred at room temperature in a 100 mL conical flask. After a few hours, white solid started to form. It was continually stirred for 1 day. The white solid was isolated by filtration and extracted with dichloromethane to separate the product from the salt formed during the reaction. The dichloromethane was evaporated using a rotavapor, and the product was obtained as a white solid. Single crystals suitable for X-ray crystallography were grown by diffusing hexane into a CH$_2$Cl$_2$ solution of this compound. Yield: 0.14 g (45.2%). Anal. Calcd for $C_{18}H_{37}Cl_2N_5O_2S_2Zn_2$: C, 34.79; H, 6.00; N, 11.27; S, 10.32. Found: C, 34.35; H, 5.85; N, 10.91; S, 10.38; ^{1}H NMR (CDCl$_3$) δ in ppm: 1.29 (t, $^3J_{HH}$ = 7.2 Hz, 3H, −OCH$_2$C*H*$_3$), 2.59 (br s, 24H, (C*H*$_3$)$_2$NCH$_2$−), 2.71 (br s, 8H, (CH$_3$)$_2$NC*H*$_2$−), 4.28 (q, $^3J_{HH}$ = 7.2 Hz, 2H, −OC*H*$_2$CH$_3$). ^{13}C NMR (CDCl$_3$) δ in ppm: 15.3 (−OCH$_2$*C*H$_3$), 46.7 ((*C*H$_3$)$_2$NCH$_2$−), 55.6 ((CH$_3$)$_2$N*C*H$_2$−), 55.6 (−O*C*H$_2$CH$_3$), 93.1 (*C*(CN)), 119.7 (−*C*N), 167.1 (*C*═O), 206.1 (*C*S$_2$). IR (cm^{-1}): ν_{CN} 2177, mp 216 °C.

Results and Discussions

[Zn(tmeda)Cl$_2$] reacted with each of the following three unsymmetrically substituted 1,1-ethenedithiolate ligands [S$_2$CC(CN)P(O)(OEt)$_2$]$^{2-}$, [S$_2$CC(CN)(CO$_2{}^i$Bu)]$^{2-}$, and [S$_2$CC(CN)(CO$_2$Et)]$^{2-}$ in different stoichiometric amounts in THF under ambient conditions to afford compounds **1**, **2**, and **3**, respectively (Scheme 2). Each of the three complexes was precipitated from the reaction mixture as a white solid and was extracted with dichloromethane to separate it from the KCl which formed during the reaction. Single crystals suitable for X-ray crystallography could be grown by diffusing hexane into either CH$_2$Cl$_2$ (for compounds **1** and **3**) or CHCl$_3$ (for compound **2**). Structural elucidations confirmed that compounds **1**, **2**, and **3** have the formula of [Zn$_4$(tmeda)$_3$(μ_3-CO$_3$){S$_2$CC(CN)P(O)(OEt)$_2$}$_3$], [Zn(tmeda){S$_2$CC(CN)CO$_2{}^i$Bu}]$_3$, and [{Zn(tmeda)Cl}$_2${S$_2$CC(CN)(CO$_2$Et)}], respectively. Crystallographic data for **1**−**3** are represented in Table 1.

Structural Description of 1. Tetranuclear zinc cluster **1** (Figure 1), which is composed of three, five-coordinate zinc atoms and a six-coordinate zinc atom, crystallizes in the $R\bar{3}$ space group. The selected bond lengths and bond angles are presented in Table 2. Four zinc atoms form a trigonal pyramid with six-coordinate Zn1 at the vertex. The basal plane of the pyramid comprises three, five-coordinate zinc (Zn2) atoms. The length of the basal edge (Zn2···Zn2 distance = 4.726 Å) is slightly shorter than the vertical edge of the pyramid, 4.815 Å. Each cpdt ligand links the apical zinc (Zn1) atom and one of the zinc (Zn2) atoms at the basal plane. One of the thiolate S atoms (S1) of each cpdt acts as a bridging atom between the zinc atom (Zn1) at the vertex and one of the basal zinc atoms (Zn2). For each cpdt ligand, the other S atom (S2) is terminally chelated to a Zn2, whereas

Table 1. Crystallographic Data for $[Zn_4(tmeda)_3(\mu_3\text{-}CO_3)\{S_2CC(CN)P(O)(OEt)_2\}_3]$ (**1**), $[Zn(tmeda)\{S_2CC(CN)(CO_2{}^iBu)\}]_3$ (**2**), and $[\{Zn(tmeda)Cl\}_2\{S_2CC(CN)(CO_2Et)\}]$ (**3**)

	1	**2**·$CHCl_3$	**3**
empirical formula	$C_{40}H_{78}N_9O_{12}P_3S_6Zn_4$	$C_{43}H_{76}Cl_3N_9O_6S_6Zn_3$	$C_{18}H_{37}Cl_2N_5O_2S_2Zn_2$
fw	1423.86	1309.95	621.29
crystal symmetry	trigonal	monoclinic	orthorhombic
space group	$R\bar{3}$	$P2_1/c$	$P2_12_12_1$
a, Å	19.7070(19)	11.2262(6)	11.1470(4)
b, Å	19.7070(19)	37.6188(18)	14.0317(7)
c, Å	27.670(4)	14.6704(6)	18.9209(9)
α, deg	90	90	90
β, deg	90	94.458(2)	90
γ, deg	120	90	90
V, Å^3	9306.3(18)	6176.8(5)	2959.4(2)
Z	6	4	4
T, K	293(2)	298(2)	298(2)
ρ_{calcd}, g/cm^3	1.524	1.409	1.394
μ, mm^{-1}	1.886	1.536	1.964
$R1^a$	0.0609	0.0640	0.0646
$wR2^b$	0.1253	0.1568	0.1505
GOF	1.060	0.927	0.963
$\Delta\rho_{max}$, e Å^{-3}	0.757	0.827	0.690
$\Delta\rho_{min}$, e Å^{-3}	−0.672	−1.051	−0.376
Flack parameter			0.01(2)

^{a} $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

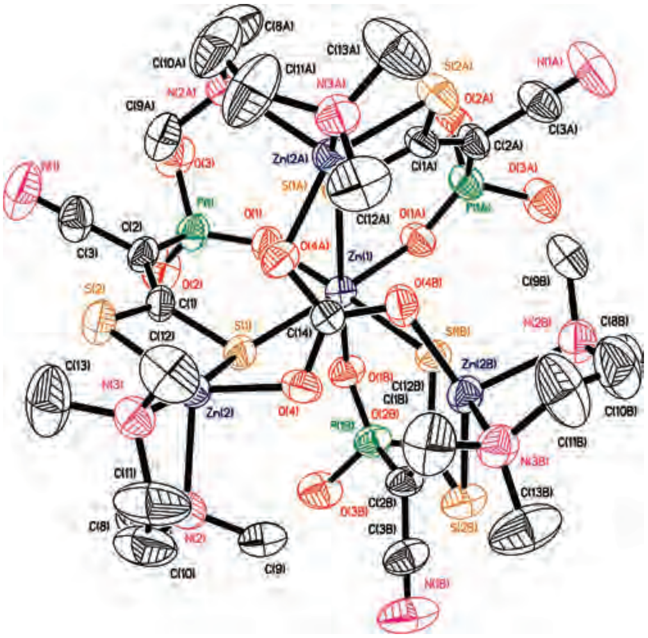


Figure 1. Thermal ellipsoid (50% probability) drawing of $[Zn_4(tmeda)_3(\mu_3\text{-}CO_3)\{S_2CC(CN)P(O)(OEt)_2\}_3]$ (**1**). The ethyl groups have been omitted for clarity.

the phosphonyl oxygen (O1) atom is coordinated to Zn1 atom. The chelate-bridging binding pattern of the thiolate sulfur atoms coupled with the oxygen atom of the phosphonyl group yields a new bonding mode (bimetallic, tetraconnective) for the cpdt ligand (Scheme 1h).[4g,h,14] On the other hand, the carbonate anion, which adopts a μ_3-bridging mode, caps the three Zn2 atoms in the basal plane of the pyramid. The carbon and oxygen atoms of the carbonate are located at 0.481 and 0.496 Å below the basal plane, respectively. The Zn2−$O_{carbonate}$ distance is 1.996(5) Å, which is normal for a μ_3-carbonate anion coordinated to a zinc center.[15]

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Zn_4(tmeda)_3(\mu_3\text{-}CO_3)\{S_2CC(CN)P(O)(OEt)_2\}_3]$ (**1**)^a

Zn(1)-O(1)	2.077(5)	Zn(1)-S(1)	2.493(2)
Zn(2)−O(4)	1.996(5)	Zn(2)−N(2)	2.135(6)
Zn(2)−N(3)	2.185(6)	Zn(2)−S(2)	2.351(2)
Zn(2)−S(1)	2.652(2)	O(4)−C(14)	1.276(5)
O(1A)−Zn(1)−O(1)	90.24(19)	O(1A)−Zn(1)−S(1)	177.64(14)
O(1)−Zn(1)−S(1)	87.59(13)	O(1B)−Zn(1)−S(1)	90.70(15)
S(1)−Zn(1)−S(1A)	91.50(7)	S(1)−Zn(1)−S(1B)	91.50(7)
O(4)−Zn(2)−N(2)	97.8(2)	O(4)−Zn(2)−N(3)	95.7(2)
N(2)−Zn(2)−N(3)	84.1(2)	O(4)−Zn(2)−S(2)	145.39(15)
N(2)−Zn(2)−S(2)	113.35(19)	N(3)−Zn(2)−S(2)	102.03(18)
O(4)−Zn(2)−S(1)	91.19(15)	N(2)−Zn(2)−S(1)	97.99(18)
N(3)−Zn(2)−S(1)	172.50(18)	S(2)−Zn(2)−S(1)	70.51(7)
C(1)−S(1)−Zn(1)	114.1(2)	C(1)−S(1)−Zn(2)	82.4(2)
Zn(1)−S(1)−Zn(2)	138.76(9)	C(1)−S(2)−Zn(2)	91.9(2)
P(1)−O(1)−Zn(1)	138.6(3)	C(14)−O(4)−Zn(2)	113.9(3)
C(9)−N(2)−Zn(2)	109.1(5)	C(8)−N(2)−Zn(2)	111.5(5)
C(10)−N(2)−Zn(2)	105.9(5)	C(13)−N(3)−Zn(2)	112.1(5)
C(11)−N(3)−Zn(2)	101.7(5)	C(12)−N(3)−Zn(2)	113.3(5)

^{a} Symmetry transformation used to generate equivalent atoms: A $-y+2, x-y+1, z$; B $-x+y+1, -x+2, z$.

The coordination geometry around Zn1 is distorted octahedral with bond angles around Zn1 ranging from 87.59(13) to 177.64(14)°. Each of the three cpdt ligands donates one bridging S atom (S1) and phosphonyl oxygen atom (O1) to the Zn1. Thus the O_3S_3 coordination sphere in a facial conformation is revealed around the apical zinc atom. *To the best of our knowledge, no example where Zn is coordinated by three oxygen and three sulfur atoms has been reported.* Zn1−O bond lengths of 2.077(5) Å are similar to those reported for polymeric $[Zn\{HN(CH_2PO_3H)_3(H_2O)_3\}]_n$.[16]

For five-coordinate species, the value of the angular geometric parameter (τ_5) which can be defined by the equation $\tau_5 = (\beta - \alpha)/60°$ (where β = the largest angle, α = the second largest angle around the central atom) should be unity for trigonal bipyramidal geometry and zero for square pyramidal geometry

---

[14] Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949.

[15] Kong, L.-Y.; Zhang, Z.-H.; Zhu, H.-F.; Kawaguchi, H.; Okamura, T.; Doi, M.; Chu, Q.; Sun, W.-Y.; Ueyama, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4352.

[16] Demadis, K. D.; Katarachia, S. D.; Koutmos, M. *Inorg. Chem. Commun.* **2005**, *8*, 254.

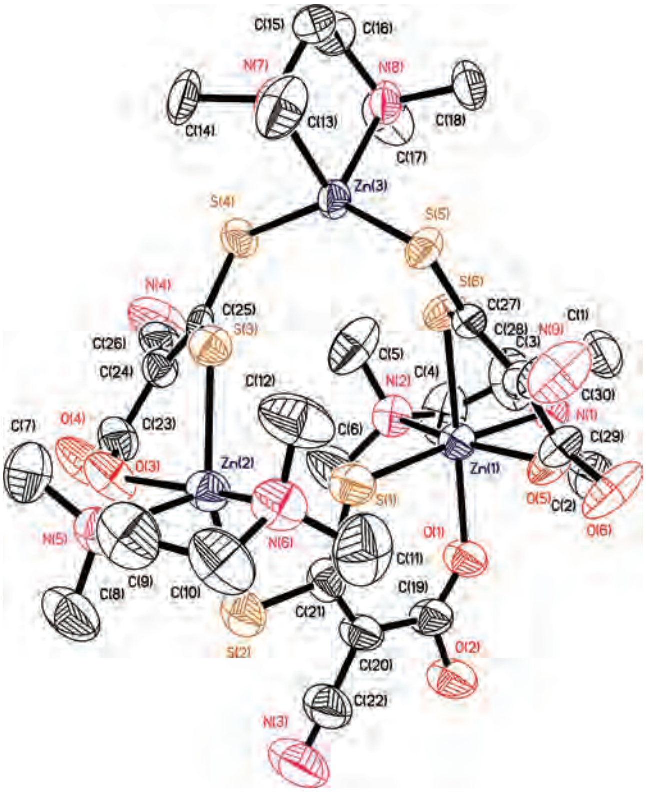


Figure 2. Thermal ellipsoid (50% probability) drawing of the [Zn(tmeda){$S_2CC(CN)(CO_2{}^iBu)$}]$_3$ (**2**). The isobutyl groups have been omitted for clarity.

in an idealized case.[17] The largest (β) and second largest (α) angles around Zn2 in **1** are 172.50(18) and 145.39(15)°, respectively. By applying the above concept, the coordination geometry around Zn2 centers ($\tau_5 = 0.45$, more closer to zero) can be better described as distorted square pyramidal rather than trigonal bipyramidal. S1 and S2 of a cpdt, O4 of the carbonate, and N3 of the tmeda moiety constitute the basal plane of the square pyramid, whereas N5 of the tmeda is situated at the vertex of the square pyramid. The bond angles around the Zn2 ranging from 70.51(7) to 172.50(18)° indicate the square pyramidal geometry is highly distorted. The bridging S1 atom is closer to the Zn1 compared to the Zn2, as evidenced by the shorter bond length of 2.493(2) Å for Zn1−S1, in comparison with 2.652(2) Å for Zn2−S1. The bond length between the chelating sulfur S2 and Zn2 is 2.351(2) Å. These distances are comparable to the reported Zn−S bond lengths, 2.698(1) and 2.308(1) Å, in the compound Zn[*i*-MNT](3-MePy)$_3$.[18] The S1−Zn2−S2 bond angle, 70.51(7)°, is also comparable to the reported bond angle of 71.86(3)° for a 1,1-dithiolate chelated to the zinc atom in Zn[*i*-MNT](3-MePy)$_3$.[18] The Zn−N bond lengths, 2.135(6) and 2.185(6) Å, are in the range of reported value for those in Zn[$SC(Me)_2CH_2N(Me)CH_2$]$_2$[19a] and $ZnS_4[MeN(C_2H_4NMe_2)_2]$.[19b] Besides, all three five-coordinate zinc atoms (Zn2) have retained the chelating tmeda moiety, while six-coordinate Zn1 has lost its tmeda from its precursor.

The structure of **1** can also be delineated as the existence of three mononuclear units of [Zn(tmeda){$S_2CC(CN)P(O)(OEt)_2$}] being held together by one Zn^{2+} and a $CO_3{}^{2-}$ anion from two sides represented in Scheme 5. A 3-fold symmetry axis passes through the Zn1 and C14 of the carbonate, which is perpendicular to the plane composed of three Zn2 atoms.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of [Zn(tmeda){$S_2CC(CN)(CO_2{}^iBu)$}]$_3$ (**2**)

Zn(1)−O(1)	2.147(4)	Zn(1)−O(5)	2.162(4)
Zn(1)−N(2)	2.208(5)	Zn(1)−N(1)	2.223(5)
Zn(1)−S(1)	2.4232(17)	Zn(1)−S(6)	2.4980(16)
Zn(3)−N(8)	2.161(5)	Zn(3)−N(7)	2.222(5)
Zn(3)−S(4)	2.3119(15)	Zn(3)−S(5)	2.3177(15)
Zn(2)−N(5)	2.216(5)	Zn(2)−N(6)	2.258(6)
Zn(2)−O(3)	2.294(5)	Zn(2)−S(2)	2.357(2)
Zn(2)−S(3)	2.3694(18)		
O(1)−Zn(1)−O(5)	87.72(17)	O(1)−Zn(1)−N(2)	91.80(19)
O(5)−Zn(1)−N(2)	165.38(18)	O(1)−Zn(1)−N(1)	91.98(17)
O(5)−Zn(1)−N(1)	84.19(17)	N(2)−Zn(1)−N(1)	81.22(19)
O(1)−Zn(1)−S(1)	84.45(12)	O(5)−Zn(1)−S(1)	94.84(13)
N(2)−Zn(1)−S(1)	99.66(14)	N(1)−Zn(1)−S(1)	176.34(14)
O(1)−Zn(1)−S(6)	166.38(13)	O(5)−Zn(1)−S(6)	83.67(12)
N(2)−Zn(1)−S(6)	99.19(14)	N(1)−Zn(1)−S(6)	97.60(13)
S(1)−Zn(1)−S(6)	85.78(6)	N(8)−Zn(3)−N(7)	83.7(2)
N(8)−Zn(3)−S(4)	100.49(13)	N(7)−Zn(3)−S(4)	103.02(13)
N(8)−Zn(3)−S(5)	111.20(13)	N(7)−Zn(3)−S(5)	99.16(14)
S(4)−Zn(3)−S(5)	142.96(6)	N(5)−Zn(2)−N(6)	82.1(2)
N(5)−Zn(2)−O(3)	82.1(2)	N(6)−Zn(2)−O(3)	163.2(2)
N(5)−Zn(2)−S(2)	100.94(16)	N(6)−Zn(2)−S(2)	99.56(17)
O(3)−Zn(2)−S(2)	88.84(14)	N(5)−Zn(2)−S(3)	109.29(16)
N(6)−Zn(2)−S(3)	97.74(16)	O(3)−Zn(2)−S(3)	82.37(13)
S(2)−Zn(2)−S(3)	146.87(7)	C(27)−S(5)−Zn(3)	97.07(18)
C(25)−S(4)−Zn(3)	105.19(19)	C(27)−S(6)−Zn(1)	108.39(19)
C(21)−S(1)−Zn(1)	115.4(2)	C(25)−S(3)−Zn(2)	108.8(2)
C(21)−S(2)−Zn(2)	99.2(2)	C(23)−O(3)−Zn(2)	124.9(4)
C(19)−O(1)−Zn(1)	139.2(4)	C(29)−O(5)−Zn(1)	132.9(4)
C(10)−N(6)−Zn(2)	102.0(5)	C(12)−N(6)−Zn(2)	112.6(5)
C(11)−N(6)−Zn(2)	112.9(5)	C(9)−N(5)−Zn(2)	105.7(4)
C(7)−N(5)−Zn(2)	113.1(4)	C(8)−N(5)−Zn(2)	109.4(4)
C(1)−N(1)−Zn(1)	113.0(4)	C(2)−N(1)−Zn(1)	111.8(4)
C(3)−N(1)−Zn(1)	104.8(4)	C(4)−N(2)−Zn(1)	106.4(4)
C(6)−N(2)−Zn(1)	113.3(5)	C(5)−N(2)−Zn(1)	110.9(4)
C(17)−N(8)−Zn(3)	113.7(4)	C(16)−N(8)−Zn(3)	103.9(4)
C(18)−N(8)−Zn(3)	110.6(4)	C(15)−N(7)−Zn(3)	104.6(4)
C(13)−N(7)−Zn(3)	111.2(4)	C(14)−N(7)−Zn(3)	110.6(4)

Structural Description of 2. The trinuclear zinc complex **2** (Figure 2), which crystallizes in the monoclinic $P2_1/c$ space group, is composed of a four-coordinate, a five-coordinate, and a six-coordinate zinc. The structure contains a solvated chloroform molecule in the asymmetric unit. The selected bond lengths and bond angles are presented in Table 3. The structure analysis reveals each dithiolate ligand connects two zinc atoms via its sulfur atoms, while the ester carbonyl oxygen is coordinated to one of these two zinc centers. Thus the binding mode of the ligands is bimetallic triconnective. The carbonyl oxygen atom O1 of the ligand [$S_2CC(CN)(CO_2{}^iBu)$]$^{2-}$ which connects Zn1 and Zn2 is coordinated to Zn1; the carbonyl oxygen atom O3 of the second ligand which bridges Zn2 and Zn3 is bound to Zn2; however, the O5 of the third ligand which is connected to Zn1 and Zn3 is coordinated to Zn1. All three zinc centers have retained the chelating tmeda moiety.

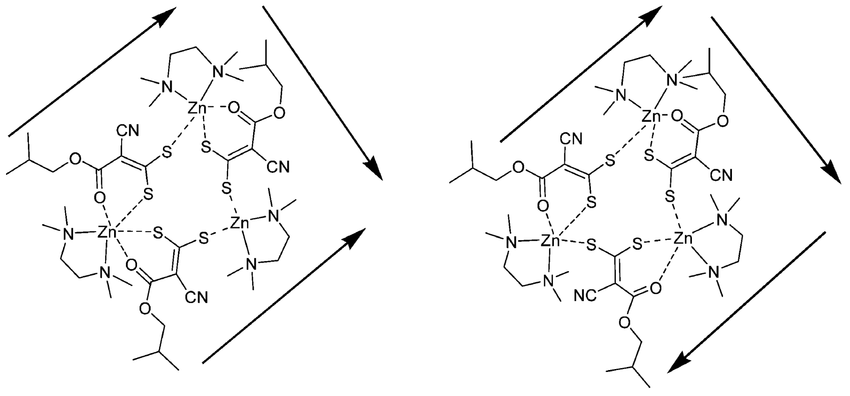
Two thiolate S atoms (S1 and S6), two carbonyl O atoms (O1 and O5) from two [$S_2CC(CN)(CO_2{}^iBu)$]$^{2-}$ ligands, and two N atoms (N1 and N2) from a tmeda unit are coordinated to Zn1 in a distorted octahedral geometry. The bond angles around Zn1 ranging from 81.22(19) to 176.34(14)° confirm the distortion from ideal octahedral geometry. The Zn2 has

---

(17) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijin, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(18) Xiong, R.-G.; Liu, C.-M.; You, X.-Z.; Huang, X.-Y. *Polyhedron* **1997**, *16*, 1637.

Scheme 3. (a) Schematic Representation of **2**, (b) The Probable Structural Isomer of Compound **2**: Arrowheads Designate the Sulfur End of the Ligand and Tails Represent the Ester End



(a) (b)

a coordination sphere of N_2S_2O with a distorted square pyramidal geometry. The angular geometric parameter ($\tau_5 = 0.27$) around Zn2 justifies the geometry as distorted square pyramidal instead of trigonal bipyramidal. Two thiolate sulfurs S2 and S3 from two ligands, one carbonyl oxygen O3, and a tmeda nitrogen N6 constitute the basal plane of the square pyramid with the other N5 atom of the tmeda in the vertex of the pyramid. Bond angles around Zn2 range from 82.1(2) to 163.2(2)°. The Zn3 has a N_2S_2 coordination environment. Recently, Houser's research group has proposed an angular geometric index (τ_4) for a four-coordinate metal center which is defined by the equation $\tau_4 = [360 - (\alpha + \beta)]/141$ (α and β are the largest and the second largest angles around the metal).[20] Depending on the value of τ_4, the geometry of the four-coordinate center can be described as tetrahedral ($\tau_4 = 1$), trigonal pyramidal ($\tau_4 = 0.85$), seesaw ($\tau_4 = 0.64, 0.50, 0.18, 0.07$), and square planar ($\tau_4 = 0$). The τ_4 value for Zn3 is calculated to be 0.75 (α and β were 142.96 and 111.2°, respectively). So the geometry around Zn3 can be best described as distorted trigonal pyramidal. The distortion can be understood from the bond angles around Zn3 ranging from 83.7(2) to 142.96(6)°. The Zn3 is surrounded by S4 and S5 from two ligands and tmeda nitrogen atoms N7 and N8 without further coordination to carbonyl oxygen atom.

The Zn−S bond distances are in the range from 2.3119(15) to 2.4980(16) Å in structure **2**. These distances are comparable to those observed in the compound Zn(*i*-MNT)(3-MePy)$_3$.[18] The Zn−N bond lengths ranging from 2.161(5) to 2.258(6) Å in compound **2** are in the range of reported values for those in the zinc complexes, $Zn[SC(Me)_2CH_2N(Me)CH_2]_2$[19a] and $ZnS_4[MeN(C_2H_4NMe_2)_2]$.[19b] The Zn−O bond distances are in the range of 2.147(4) to 2.294(5) Å, which are also comparable to the reported value for Zn−O distances in [(beppa)Zn](ClO$_4$)$_2$ (beppa = *N*-bis-2-(ethylthio)ethyl-*N*-(6-amino-2-pyridylmethyl)amine)[21a] and in $[Zn(C_5H_4NCO_2CH_3)_2Br_2]$.[21b]

Although the binding mode for each ester-substituted 2-cyanoethylene-1,1-dithiolate ligand in **2** is the same, the orientation of the ligands surrounding the trinuclear zinc units is different. Two ligands have the same direction; however, the third one is in the opposite way, as shown in a simplified diagram Scheme 3a, where arrowheads designate the sulfur end of the ligand and tails represent the ester end. This implies that the other structural isomer, which would have all three ligands oriented in the same direction around the trinuclear zinc complex, may exist. Such a structural isomer represented in Scheme 3b will have an idealized C_3 axis and contain three, five-coordinate zinc atoms. The formation of structural isomers due to different arrangement of the ligands can be understood from a recent result published by Sordo et al. on the structure of silver(I) sulfanylcarboxylates.[22]

Structural Description of 3. The dinuclear zinc complex **3** isolated from the reaction of $K_2S_2CC(CN)(CO_2Et)$ and $[Zn(tmeda)Cl_2]$ has the molecular formula of $[\{Zn(tmeda)Cl\}_2\{S_2CC(CN)(CO_2Et)\}]$. It crystallizes in the orthorhombic $P2_12_12_1$ space group (Figure 3). The selected bond lengths and angles are presented in Table 4. Two sulfur atoms of the dithiolate ligand connect two Zn(tmeda)Cl fragments by the replacement of one of the chlorides from the precursor. The carbonyl oxygen of the ligand is terminally coordinated to Zn2. So this binding mode generates one four-coordinate and one five-coordinate zinc centers in the compound **3**. The two largest angles around the five-coordinate Zn2 center are 165.1(4) and 126.9(3)°. Interestingly, the angular geometric parameter (τ_5) concerning the Zn2 is 0.64, which justifies the coordination geometry of this zinc center and can be better described as distorted trigonal bipyramidal rather than square pyramidal. Thus Zn2 adopts a distorted *tbp* geometry where the axial positions are occupied by the carbonyl oxygen atom O1 and one of the tmeda nitrogen atoms N3, and the equatorial positions are occupied by the other tmeda nitrogen N4, a thiolate sulfur S1, and one chlorine atom Cl2. Bond angles around the Zn2 center are in the range of

---

(19) (a) Grapperhaus, C. A.; Mullins, C. S.; Kozlowski, P. M.; Mashuta, M. S. *Inorg. Chem.* **2004**, *43*, 2859. (b) Pafford, R. J.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 1974.

(20) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955.

(21) (a) Berreau, L. M.; Makowska-Grzyska, M. M.; Arif, A. M. *Inorg. Chem.* **2000**, *39*, 4390. (b) Gonzàlez-Duarte, P.; March, R.; Pons, J. *Polyhedron* **1996**, *15*, 2747.

(22) Barreiro, E.; Casas, J. S.; Couce, M. D.; Sánchez, A.; Seoane, R.; Sordo, J.; Varela, J. M.; Vázquez-López, E. M. *Dalton Trans.* **2007**, 3074.

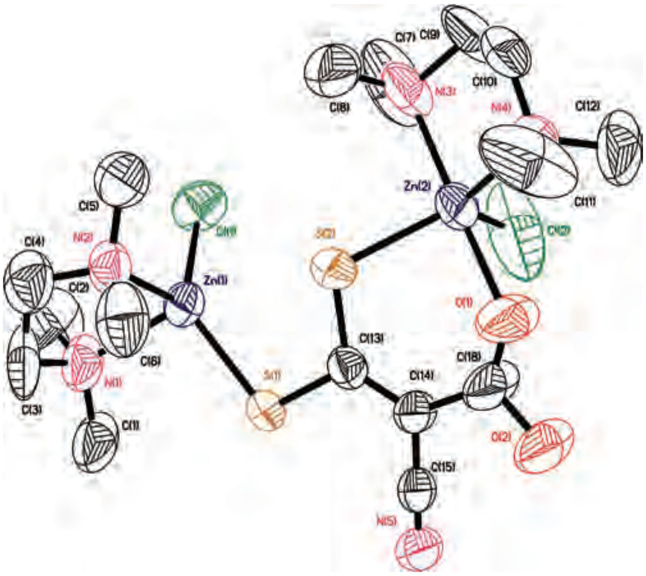


Figure 3. Thermal ellipsoid (50% probability) drawing of [{Zn(tmeda)Cl}$_2${S$_2$CC(CN)(CO$_2$Et)}] (**3**). The ethyl groups have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [{Zn(tmeda)Cl}$_2${S$_2$CC(CN)(CO$_2$Et)}] (**3**)

Zn(1)−N(2)	2.092(7)	Zn(1)−N(1)	2.198(8)
Zn(1)−Cl(1)	2.223(3)	Zn(1)−S(1)	2.306(2)
Zn(2)−N(4)	2.108(7)	Zn(2)−N(3)	2.186(9)
Zn(2)−Cl(2)	2.235(4)	Zn(2)−O(1)	2.242(9)
Zn(2)−S(2)	2.335(3)		
N(2)−Zn(1)−N(1)	86.6(3)	N(2)−Zn(1)−Cl(1)	108.2(2)
N(1)−Zn(1)−Cl(1)	104.5(3)	N(2)−Zn(1)−S(1)	119.4(2)
N(1)−Zn(1)−S(1)	99.3(2)	Cl(1)−Zn(1)−S(1)	127.49(9)
N(4)−Zn(2)−N(3)	83.9(3)	N(4)−Zn(2)−Cl(2)	111.6(3)
N(3)−Zn(2)−Cl(2)	99.8(3)	N(4)−Zn(2)−O(1)	85.4(3)
N(3)−Zn(2)−O(1)	165.1(4)	Cl(2)−Zn(2)−O(1)	93.8(4)
N(4)−Zn(2)−S(2)	126.9(3)	N(3)−Zn(2)−S(2)	96.5(2)
Cl(2)−Zn(2)−S(2)	120.46(12)	O(1)−Zn(2)−S(2)	81.6(3)
C(13)−S(1)−Zn(1)	100.1(3)	C(13)−S(2)−Zn(2)	105.2(3)
C(1)−N(1)−Zn(1)	114.2(6)	C(2)−N(1)−Zn(1)	115.4(8)
C(3)−N(1)−Zn(1)	100.5(6)	C(12)−N(4)−Zn(2)	108.7(7)
C(10)−N(4)−Zn(2)	106.3(6)	C(11)−N(4)−Zn(2)	112.9(7)
C(8)−N(3)−Zn(2)	112.9(7)	C(9)−N(3)−Zn(2)	101.6(6)
C(7)−N(3)−Zn(2)	114.3(9)	C(18)−O(1)−Zn(2)	123.0(8)
C(4)−N(2)−Zn(1)	104.5(6)	C(5)−N(2)−Zn(1)	112.3(5)
C(6)−N(2)−Zn(1)	111.7(5)		

81.6(3)−165.1(4)° and reveal the distortion from an ideal *tbp* geometry. On the other hand, Zn1 has a distorted trigonal pyramidal geometry ($\tau_4 = 0.80$) with N$_2$SCl coordination sphere where two N atoms are donated by the tmeda and a thiolate sulfur by the ligand [S$_2$CC(CN)(CO$_2$Et)]$^{2-}$. Bond angles around Zn1 range from 86.6(3) to 127.49(9)°. The Zn−S distances of 2.335(3) and 2.306(2) Å are comparable to those observed in the compound Zn(*i*-MNT)(3-MePy)$_3$.[18] The Zn−N bond lengths range from 2.092(7) to 2.198(8) Å and the Zn−O bond distance is 2.242(9) Å, which are comparable with those reported for the Zn−N[19] and Zn−O bonds.[21]

Commonly the carbonyl O atom of the ester does not bind to the metal center in most of the reported structures incorporating ester-functionalized 1,1-dithiolates. Only a few examples besides compounds **2** and **3**, which display a bimetallic, triconnective coordination mode, are known. The first one was reported by Coucouvanis et al. in the decanuclear copper cluster where two Cu$_4$ tetrahedra were connected by two copper atoms via the oxygen and sulfur atoms of the 2,2-dicarbo-*tert*-butoxyethylene-1,1-dithiolate ligand.[9a] Adams et al. reported a dirhenium carbonyl complex bridged by an ester-functionalized 1,1-dithiolate which acts as an *S*,*S* and *S*,*O* donor.[9c] A similar connective pattern was also observed in a trinuclear Pd^{II} compound containing 2,2-diacetyl-1,1-ethenedithiolato ligands.[9d]

It is worthwhile to mention that most of the reported zinc complexes containing 1,2- or 1,1-ethenedithiolate ligands are mononuclear. Only one binuclear zinc complex incorporating 1,1-ethenedithiolate is reported.[23] In the case of 1,2-ethenedithiolate, only three structural reports of a binuclear zinc compound are known.[24] Compounds **1** and **2** are the first examples of a multinuclear zinc complex incorporating ethenedithiolates where the nuclearity exceeds 2. Finally, structurally characterized metal complexes with 2-(alkoxycarbonyl)-2-cyanoethene-1,1-dithiolate as the sulfur donor ligand are even rare. The compound Pt(COD)[S$_2$CC(CN)(CO$_2$Et)][2c] is the only one being reported prior to structures **2** and **3**. On the other hand, for mimicking the active site of the Zn-containing enzyme carbonic anhydrase,[25] researchers have synthesized plenty of zinc complexes where Zn is coordinated to carbonate[26] or methylcarbonate[27] by fixation of aerial CO$_2$, but only a few of them are tetranuclear species besides the compound **1**.[28]

Spectroscopy. Compound **1** exhibits chemical shifts at 2.58 and 2.69 ppm for methyl and methylene protons of tmeda and at 1.33 and 4.17 ppm for methyl and methylene protons of an ethoxy group of the dithiolate ligand in the ^{1}H NMR spectrum. The multiplet nature of the ethoxy protons in compound **1** could be due to the unresolved coupling by the phosphorus nuclei. The proton integration indicates that both tmeda and dithiolate ligands are present in 1:1 ratio in compound **1**. In the ^{31}P NMR spectrum, a single resonance

---

(23) Xiong, R.-G.; Zuo, J.-L.; You, X.-Z. *Inorg. Chem.* **1997**, *36*, 2472.

(24) (a) Wang, Q. H.; Long, D. L.; Hu, H.-M.; Cui, Y.; Huang, J.-S. *J. Coord. Chem.* **2000**, *49*, 201. (b) Liu, C.-M.; Zhang, D.-Q.; Song, Y.-L.; Zhan, C.-L.; Li, Y.-L.; Zhu, D.-B. *Eur. J. Inorg. Chem.* **2002**, 1591.

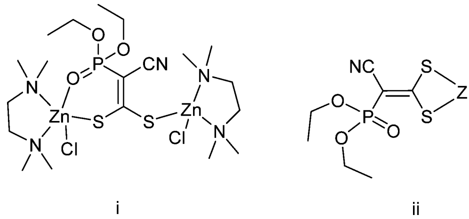
(25) Stryer, L. In *Biochemistry*, 3rd ed.; W. H. Freeman & Co., New York, 1988.

(26) (a) Kajiwara, T.; Yamamchi, T.; Kido, H.; Kawabata, S.; Kuroda, R.; Ito, T. *Inorg. Chem.* **1993**, *32*, 4990. (b) Allred, R. A.; McAlexander, L. H.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2002**, *41*, 6790. (c) Meyer, F.; Rutsch, P. *Chem. Commun.* **1998**, 1037. (d) Alsfasser, R.; Ruf, M.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 703. (e) Schrodt, A.; Neubrand, A.; van Eldik, R. *Inorg. Chem.* **1997**, *36*, 4579. (f) Trösch, A.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 2305. (g) Bazzicalupi, C.; Bencini, A.; Bencini, A.; Bianchi, A.; Corana, F.; Fusi, V.; Giorgi, C.; Paoli, P.; Paoletti, P.; Valtancoli, B.; Zanchini, C. *Inorg. Chem.* **1996**, *35*, 5540.

(27) (a) Kato, M.; Ito, T. *Inorg. Chem.* **1985**, *24*, 509. (b) Brombacher, H.; Vahrenkamp, H. *Inorg. Chem.* **2004**, *43*, 6042. (c) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911. (d) Alsfasser, R.; Ruf, M.; Trofimenko, S.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 703.

(28) (a) Adams, H.; Bradshaw, D.; Fenton, D. E. *J. Chem. Soc., Dalton Trans.* **2001**, 3407. (b) Döring, M.; Ciesielski, M.; Walter, O.; Görls, H. *Eur. J. Inorg. Chem.* **2002**, 1615. (c) Fondo, M.; García-Deibe, A. M.; Bermejo, M. R.; Sanmartín, J.; Llamas-Saiz, A. L. *J. Chem. Soc., Dalton Trans.* **2002**, 4746. (d) Bauer-Siebenlist, B.; Meyer, F.; Vidovic, D.; Pritzkow, H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2152. (e) Fondo, M.; García-Deibe, A. M.; Ocampo, N.; Sanmartín, J.; Bermejo, M. R. *Dalton Trans.* **2004**, 2135.

Scheme 4. Schematic Representation of the Two Probable Intermediates Formed in the Reaction of cpdt with [Zn(tmeda)Cl_2]



at 21.3 ppm is observed for the phosphonate moiety. The ^{13}C NMR spectrum of the complex **1** shows chemical shifts corresponding to the carbon atoms of tmeda (47.1 and 56.7 ppm), ethoxy group (16.2 and 62.9 ppm), cyanide (120.8 ppm), and ethene moiety (79.7 and 206.5 ppm) of the dithiolate ligand along with a peak at 168.3 ppm, which could be reasonably assigned as the carbonate carbon bound to zinc atoms.[15]

Besides the tmeda protons, which are observed in the normal range as those in compound **1**, compound **2** shows the proton chemical shifts for isobutyl groups at 0.98, 1.86, and 3.95 ppm corresponding to CH_3, CH, and CH_2, respectively, whereas **3** shows a chemical shift for its methyl and methylene protons at 1.29 and 4.28 ppm for the ethyl group. The proton integration further reveals that tmeda and the isobutyl group exist in 1:1 ratio in **2**, whereas a 2:1 ratio between tmeda and the ethyl moiety is observed in **3**. Due to several multiple, overlapping peaks revealed in the ^1H NMR spectrum, all efforts were unsuccessful to resolve the probable isomer of **2**. In addition, the line shape of proton chemical shifts observed from the tmeda moiety is broad for all three compounds, which may be attributed to the intrinsic nature of the coordinated tmeda protons in complexes.[29]

Carbons of the isobutyl group in **2** exhibit peaks at 18.9, 27.9, and 70.9 ppm in the ^{13}C NMR spectrum. Chemical shifts for tmeda carbons in **2** and **3** are observed at 48.1, 56.7 ppm and 46.1, 55.6 ppm, respectively. Cyanide and its adjacent carbons showed chemical shifts at 120.7, 92.7 ppm and 119.7, 93.1 ppm for **2** and **3**, respectively. Resonance frequency for the carbonyl carbon was at 169.3 and 167.1 ppm for **2** and **3**, respectively. The chemical shift for quaternary carbon of CS_2 is observed at 206.7 and 206.1 ppm for **2** and **3**, respectively.

A Plausible Formation Pathway of 1. Due to the various binding modes of functionalized 1,1-ethenedithiolates (Scheme 1), it is anticipated that several species may coexist in the reaction mixture. The compound **3** isolated from the reaction mixture of $[S_2CC(CN)(CO_2Et)]^{2-}$ and [Zn(tmeda)Cl_2] is a compound, which can be considered as an intermediate because the labile chlorides are not fully substituted. Presumably, this type of intermediate should have formed during the reaction of cpdt with [Zn(tmeda)Cl_2]. When the reaction is performed by utilizing *cpdt* ligand under inert atmosphere, two chemical shifts at 21.3 and 9.5 ppm were observed in the ^{31}P NMR spectrum. In addition, MALDI-TOF mass spectrometry shows a peak at *m/z* 432.6 corresponding to [Zn(tmeda){$S_2CC(CN)P(O)(OEt)_2$}]. Compound **1** showed only one peak at 21.3 ppm in the ^{31}P NMR spectrum. Obviously, this resonance frequency was due to the phosphorus nuclei attached to an oxygen atom, which further coordinated to the zinc center. Therefore, we can assume the reaction carried out under anaerobic conditions might generate species that contains the O atom of the phosphonyl moiety coordinated to Zn and displayed a peak at 21.3 ppm in the ^{31}P NMR spectrum. This species could be isostructural with **3**; however, instead of carbonyl oxygen coordinated to Zn, it would have P=O coordinated to Zn. A probable structure of this intermediate [{Zn(tmeda)Cl}$_2${$S_2CC(CN)P(O)(OEt)_2$}] (i) is drawn in Scheme 4. The other product, which shows a chemical shift at 9.5 ppm, must have a structure where the P=O fragment does not coordinate to the Zn. The compound [Pt(Ph_2phen)(cpdt)][30] reported by Eisenberg contains a cpdt ligand coordinated to Pt^{II} by two S atoms with the P=O moiety dangling. The ^{31}P NMR spectrum exhibited a chemical shift at 12.6 ppm in acetone-d_6 for the platinum compound, which was comparable to the one at 9.5 ppm in $CDCl_3$. Thus a new structure, based on both mass spectrum and the ^{31}P NMR spectrum, was proposed to be [Zn(tmeda){$S_2CC(CN)P(O)(OEt)_2$}] (ii) (Scheme 4). Because the solubility of both (i) and (ii) is much higher in chloroform in comparison with compound **1**, which is sparingly soluble in chloroform, we believe that neither (i) nor (ii) (generated under the N_2 atmosphere) is compound **1**. Moreover, the species (i) and (ii) were formed under carbonate-free anaerobic conditions. It was only on exposure to air that the species originally generated under an inert atmosphere of N_2 showed a diminishing peak at 9.5 ppm in the ^{31}P NMR spectrum with respect to time and finally yielded compound **1** whose identity was confirmed with X-ray diffraction.

Therefore, if we consider that the carbonate incorporated into the cluster **1** is generated by the hydration of aerial CO_2, and the intermediates (i) and (ii) form initially in the reaction media, a formation pathway can be proposed as demonstrated in Scheme 5. The presence of the potassium salt of the cpdt induces basicity in the reaction medium. Furthermore, it has been widely recognized that the activated Zn−OH moiety is the key species to perform CO_2 hydration in basic medium.[31] In the basic reaction condition, one of the zinc atoms of the intermediate (i) can be hydroxylated to form another transient intermediate (iii) containing Zn−OH. Eventually, nucleophilic attack by the coordinated hydroxide of (iii) on the aerial CO_2 followed by stepwise addition of two molecules of (ii) and elimination of the tmeda moiety will lead to the formation of a tetranuclear zinc complex **1**. That the same cpdt ligand did not hydrate aerial CO_2 in the presence of copper and silver indicates the special role of the zinc element, which may be correlated to the zinc-containing enzyme, carbonic anhydrase.[25] On the other hand, aerial CO_2 fixation did not take place when the ester-functionalized dithiolate was reacted with the same zinc complex [Zn(tmeda)Cl_2]. Thus a minute difference in electromeric effects for the P=O fragment of the cpdt ligand

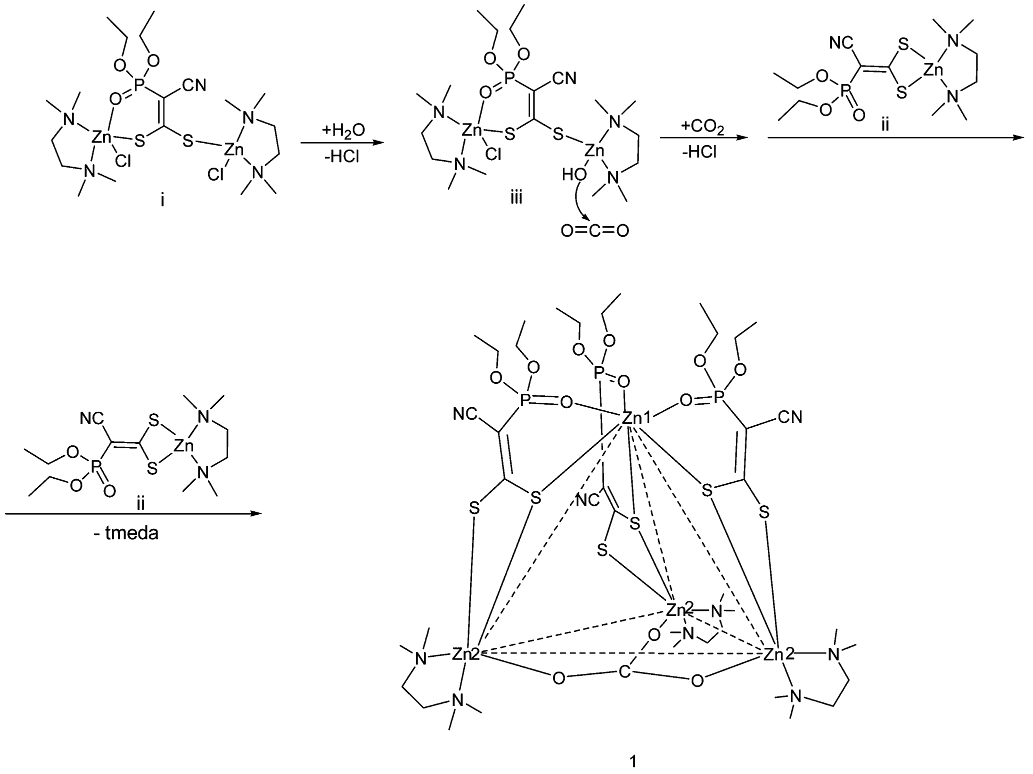
---

(29) Andrieu, J.; Dietz, J.; Poli, R.; Richard, P. *New J. Chem.* **1999**, *23*, 581.

(30) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 2913.

(31) (a) Adams, H.; Bradshaw, D.; Fenton, D. E. *J. Chem. Soc., Dalton Trans.* **2001**, 3407. (b) Parkin, G. *Chem. Commun.* **2000**, 1971.

Scheme 5. Probable Formation Pathway of the Compound **1**: Broken Line Indicates the Trigonal Pyramid Formed by Four Zn Centers



relative to the carbonyl of the ester moiety in $[S_2CC(CN)(CO_2{}^iBu)]^{2-}$ and $[S_2CC(CN)(CO_2Et)]^{2-}$ might exhibit some special effect.

Conclusion

Three unsymmetrically substituted 2-cyanoethylene-1,1-dithiolate ligands have been utilized to explore the coordination chemistry of zinc. Besides the dithiolate sulfur atoms, the P═O moiety in cpdt and the carbonyl O atom in $[S_2CC(CN)(CO_2{}^iBu)]^{2-}$ and $[S_2CC(CN)(CO_2Et)]^{2-}$ are also involved in the coordination sphere around zinc atoms. The compound **1**, containing metal-bound carbonate, exhibits the first example of CO_2 fixation anchored by a 1,1-ethenedithiolate ligand. Structural elucidation of **1** demonstrates a unique zinc center (Zn1) with S_3O_3 coordination sphere. The formation of compound **2** via assembly of three units of both $[S_2CC(CN)(CO_2{}^iBu)]^{2-}$ and Zn−tmeda moiety has demonstrated the first trinulcear zinc compound containing four-, five-, and six-coordinated zinc atoms. Surprisingly, the asymmetric orientation of three dithiolate ligands around zinc centers in **2** leads us to propose that the other structural isomer having a C_3 symmetry axis may be present in the bulk. Unfortunately, repeated efforts were not successful to isolate it. On the other hand, **3**, a dinuclear zinc compound with a bridging ethyl ester functionalized 1,1-ethenedithiolate, has been isolated in a similar reaction. Owing to the presence of chloride ion in each zinc center, it was thought that **3** could be a probable intermediate during the formation of a higher nuclearity zinc complex. A detailed structural comparison between compounds **1** and **3** leads us to propose the probable intermediate (i) during the formation of compound **1**. An extrapolation of results from both mass spectrum and ^{31}P NMR study of the products from the reaction of the cpdt ligand with $[Zn(tmeda)Cl_2]$ under anaerobic condition also supported the hypothesis of the probable intermediates (i) and (ii) that eventually leads us to sketch the plausible reaction pathway for the formation of compound **1**. An interesting structural observation of the five-coordinate environments at the metal centers of compounds **1**–**3** is the variation of the geometry as revealed by the angular geometric parameter (τ_5). The five-coordinate zinc centers in **1** and **2** have a distorted square pyramidal geometry, whereas in **3**, the five-coordinate geometry is distorted trigonal bipyramidal.

Acknowledgment. We thank reviewers' comments, and the National Science Council of Taiwan (NSC 96-2113-M-259-004) for the financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC702126K