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Synthesis and Structural Characterization of Tetranuclear Zinc(II) Complexes with a Linear Array

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1,3-Bis(salicylideneamino)-2-propanol (H_3salpro) and 1,3-bis(salicylideneamino)propane (H_2salpn) react with $Zn(ClO_4)_2 \cdot 6H_2O$ and pyrazole (Hpz) to give tetranuclear complexes with a linear Zn_4 array, $[Zn_4(Hsalpro)_2(pz)_2(Hpz)_2](ClO_4)_2$ (**1**) and $[Zn_4(salpn)_2(pz)_2(Hpz)_2]$ $(ClO_4)_2$ (**2**), which were characterized by infrared spectra and X-ray crystallography.

1,3-Bis(salicylideneamino)-2-propanol (H_3salpro) is a pentadentate Schiff-base ligand which affords dinuclear metal species by virtue of a bridging property of the central alcoholic-oxygen donor atom.[1,2] In the cases of nickel(II) and copper(II) systems, which favor a square-planar arrangement around the central metal atom, the two metal atoms are bridged by the deprotonated alcoholic oxygen and by an exogenous bridging ligand, such as pyrazolate anion, to form square-planar dinuclear metal complexes.[1] In the present study, we extended this to zinc(II) chemistry, which may be considered to favor a tetrahedral arrangement, in order to examine what kind of species can be isolated by a reaction with zinc(II) ion.

When H_3salpro was treated with zinc(II) perchlorate hexahydrate and pyrazole in methanol containing triethylamine, a zinc(II) complex, $[Zn_4(Hsalpro)_2(pz)_2(Hpz)_2](ClO_4)_2$ (**1**), was isolated as pale-yellow crystals. Unexpectedly, the complex has a novel tetranuclear structure. The X-ray crystallography of **1** reveals that a linear array of the four zinc atoms is formed by alternating di-μ-phenoxo-, di-μ-pyrazolato-, and di-μ-phenoxo-bridges (Fig. 1). The molecule has a crystallographic inversion center at the midpoint of the Zn2–Zn2′. In the asymmetric unit, the Schiff-base ligand H_3salpro is doubly-deprotonated and forms a distorted N_2O_2 plane with deviations within ±0.18 Å for the Zn1 atom. The Zn1 atom is situated on this basal plane by 0.39 Å toward the N5 atom of Hpz. The coordination geometry of the Zn1 atom can be essentially described as a distorted square pyramid. The perchlorate ion is located in the vicinity of the Zn1 atom with a Zn1–O4 distance of 3.21(3) Å. The splitting of the ν(Cl–O) bands (1106 and 1058 cm^{-1}) in the infrared spectrum of **1** suggests a semicoordination of the pechlorate ion. Thus, the coordination geometry of the Zn1 atom can also be regarded as a distorted octahedron. The two phenoxo-oxygen atoms act as bridging groups binding Zn1 and Zn2. The Zn1–Zn2 distance is 3.091(3) Å. The Zn2 atom takes a distorted tetrahedral arrangement with these phenoxo-oxygen atoms and two pyrazolato ions (pz), which act as bridging groups for the Zn2 and Zn2′ atoms. The Zn2–Zn2′ distance is 3.553(3) Å. One of the interesting features in **1** is the linear array of the square-pyramidal–tetrahedral–tetrahedral–square-pyramidal zinc atoms [Zn1–Zn2–Zn2′ 173.8(1)°]. We are unaware of such an example in zinc(II) coordination chemistry. It is noteworthy that the central alcoholic group of Hsalpro is not coordinated to any metal atom, and is directed to the protonated nitrogen atom (N6) of Hpz, forming a possible hydrogen bonding [O2–N6 3.30(4) Å]. The tortion angle N1–Zn1–N5–N6 is −10.8°, and the infrared spectrum of **1** shows a broad band due to ν(OH) at 3474 cm^{-1}. These facts are in accordance with the presence of hydrogen bonding.

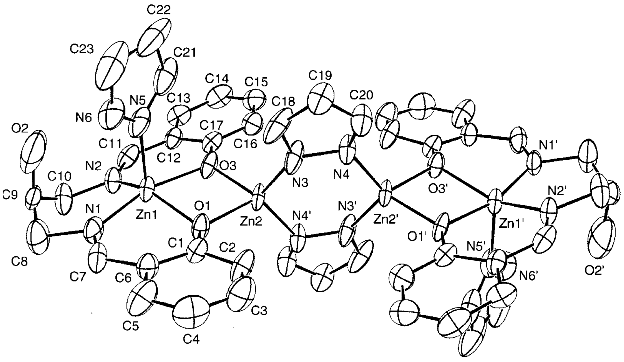

Fig. 1. Molecular structure of **1** showing the atom numbering scheme. The perchlorate ion is omitted for clarity. Selected bond distances (Å): Zn1–O1 2.06(1), Zn1–N1 1.97(2), Zn1–N2 2.07(2), Zn1–O3 2.10(2), Zn1–N5 2.08(2), Zn2–O1 1.99(2), Zn2–O3 2.00(1), Zn2–N3 1.92(2), Zn2–N4′ 1.97(2).

In order to check a factor for a tetranuclear formation of this hydrogen bonding, a similar reaction of the related Schiff-base ligand without an alcoholic group, 1,3-bis(salicylideneamino)propane (H_2salpn), was performed; we obtained an $[Zn_4(salpn)_2(pz)_2(Hpz)_2](ClO_4)_2$ (**2**). The X-ray structure of **2** is very similar to that of **1**, as shown is Fig. 2. The salpn ligand forms a distorted N_2O_2 plane and gives a di-μ-phenoxo-bridged zinc(II) dinuclear unit, which is further connected to the other dinuclear zinc(II) unit by pyrazolato bridges. The Zn1–Zn2 and Zn2–Zn2′ distances are 3.082(1) and 3.533(1) Å, respectively. The Zn1–Zn2–Zn2′ angle is 174.21(3)°. The perclorate ion is weakly coordinated to the zinc atom with a Zn1–O5 distance of 3.389(9) Å. There are no significant differences between the two tetranuclear structures in **1** and **2**, except for the orientation of the axial pyrazole and possible hydrogen bonding between the uncoordinated alcoholic group and the pyrazole nitrogen in **1**. The molecular arrangements of **1** and **2** are quite unique in a family of tetranuclear zinc(II) compounds.[3] In these complexes, the inside zinc atoms take a tetrahedral coor-

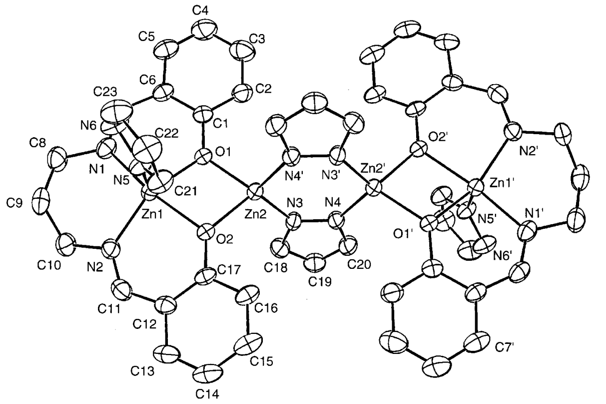

Fig. 2. Molecular structure of **2** showing the atom numbering scheme. The perchlorate ion is omitted for clarity. Selected bond distances (Å): Zn1–O1 2.023(4), Zn1–N1 2.047(6), Zn1–N2 2.014(6), Zn1–O2 2.056(5), Zn1–N5 2.088(5), Zn2–O1 1.958(5), Zn2–O2 1.951(4), Zn2–N3 1.954(5), Zn2–N4′ 1.972(6).

dination geometry in contrast to the square-pyramidal or octahedral geometry of the outside zinc atoms. This variable coordination geometries enable us to form linear tetranuclear metal species.

Experimental

Synthesis of 1. To a methanol solution containing H_3salpro (149 mg, 0.500 mmol), zinc(II) perchlorate hexahydrate (372 mg, 1.00 mmol), and pyrazole (102 mg, 1.50 mmol), a methanol solution of triethylamine (202 mg, 2.00 mmol) was added. The resulting solution was left standing for several days. Pale-yellow needles were deposited. These were collected by filtration and dried in vacuo. Yield, 129 mg. Found: C, 41.72; H, 3.60; N, 12.42%. Calcd for $C_{46}H_{46}Cl_2N_{12}O_{14}Zn_4$: C, 41.75; H, 3.50; N, 12.70%. IR(Nujol mull) 3474(br, OH); 3348(br, NH); 1623(s, C=N); 1106(s, ClO_4^-), 1058 cm^{-1} (s, ClO_4^-). Diffuse reflectance spectrum: λ_{max}/nm 340, 420sh.

Synthesis of 2. To a solution of H_2salpn (35 mg, 0.12 mmol) in methanol was added a methanol solution of zinc(II) perchlorate hexahydrate (86 mg, 0.23 mmol) and pyrazole (17 mg, 0.25 mmol). The resulting yellow solution was left standing for one week to give pale-yellow plates, which were collected by filtration and dried in vacuo over P_2O_5. Yield, 20 mg. Found: C, 42.80; H, 3.67; N, 12.81%. Calcd for $C_{46}H_{46}Cl_2N_{12}O_{12}Zn_4$: C, 42.78; H, 3.59; N, 13.02%. IR(Nujol mull) 3324(br, NH); 1620(s, C=N); 1112(s, ClO_4^-), 1058 cm^{-1}(s, ClO_4^-). Diffuse reflectance spectrum: λ_{max}/nm 340, 430sh.

Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyser. Infrared spectra were measured with a JASCO Infrared Spectrometer (Model IR 700) in the region 4000–400 cm^{-1} on KBr disks. The diffuse reflectance spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100).

X-Ray Crystal Structure Analyses. The crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation at 25 ± 1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \le 2\theta \le 30°$. Intensitiy data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods using the weighting scheme $w = 1/[\sigma^2(|F_0|) + (0.02|F_0|)^2 + 1.0]$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were not determined for **1** because of the paucity of data. For **2**, the hydrogen atoms were inserted at their calculated positions and fixed there. The temperature factors of oxygen atoms of the perchlorate ions (O6 for **1** and **2**) have rather high values possibly because of the partial disorder. All of the calculations were carried out on a Micro-VAXII computer using a Enraf-Nonius SDP program package.[4]

Crystallographic data: for **1**; $C_{46}H_{46}Cl_2Zn_4N_{12}O_{14}$, fw = 1323.4, triclinic, space group $P\bar{1}$, a = 9.627(8), b = 15.181(11), c = 9.366(7) Å, α = 102.14(6), β = 104.67(6), γ = 85.39(6)°, V = 1294.1(17) Å^3, Z = 1, D_m = 1.68, D_c = 1.70 g cm^{-3}, μ(Mo $K\alpha$) = 21.0 cm^{-1}, crystal dimensions 0.08×0.15×0.52 mm^3, 4572 reflections measured ($2\theta_{max}$ = 50°), 2130 [$I \ge 3\sigma(I)$] used in the refinement, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.117$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.133$. For **2**; $C_{46}H_{46}Cl_2N_{12}O_{12}Zn_4$, fw = 1291.4, triclinic, space group $P\bar{1}$, a = 9.646(4), b = 15.021(4), c = 9.356(3) Å, α = 103.44(2), β = 104.76(3), γ = 85.95(3)°, V = 1274.9(8) Å^3, Z = 1, D_m = 1.67, D_c = 1.68 g cm^{-3}, μ(Mo $K\alpha$) = 21.0 cm^{-1}, crystal dimensions 0.13 × 0.35 × 0.60 mm^3, 4476 reflections measured ($2\theta_{max}$ = 50°), 3225 [$I \ge 3\sigma(I)$] used in the refinement, R = 0.052, R_w = 0.056. The X-ray analyses data have been deposited as Document No. 74008 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; copies can be obtained upon request, free of charge, by quoting the publication citation and the deposition numbers 151555 and 151556.

References

1 a) W. Mazurek, B. J. Kennedy, K. S. Murray, J. O'Connor, J. R. Rodgers, M. R. Snow, A. G. Wedd, and P. R. Zwack, *Inorg. Chem.*, **24**, 3258 (1985). b) W. Mazurek, A. M. Bond, J. O'Connor, and A. G. Wedd, *Inorg. Chem.*, **25**, 906 (1986). c) Y. Nishida and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1986**, 2633. d) Y. Nishida and S. Kida, *Inorg. Chem.*, **27**, 447 (1988). e) M. Mikuriya, T. Sasaki, A. Anjiki, S. Ikenoue, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 334 (1992).

2 M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 1466 (1992).

3 a) M. J. Grannas, B. F. Hoskins, and R. Robson, *J. Chem. Soc., Chem. Commun.*, **1990**, 1644. b) A. Belforte, F. Calderazzo, U. Englert, and J. Strahle, *Inorg. Chem.*, **30**, 3778 (1991). c) E. Asato, H. Furutachi, T. Kawahashi, and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, **1995**, 3897. d) N. D. J. Branscombe, A. J. Blake, A. Marin-Becerra, W.-S. Li, S. Parsons, L. Ruiz-Ramirez, and M. Schroder, *Chem. Commun.*, **1996**, 2573. e) M.-L. Tong, H.-K. Lee, S.-L. Zheng, and X.-M. Chen, *Chem. Lett.*, **1999**, 1087. f) M. Mikuriya and K. Minowa, *Inorg. Chem. Commun.*, **3**, 227 (2000).

4 B. A. Frenz, "The SDP-User's Guide," Enraf-Nonius, Delft, The Netherlands (1985).