One-dimensional Chain and Discrete Trinuclear Compounds Derived from Assembly Reaction of $[Mn(saltmen)(H_2O)]ClO_4$ and $K_2[Hg(CN)_4]$ {$saltmen^{2-}$ = *N*,*N'*-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato) dianion}

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The reaction of Mn(III) Schiff base complex $[Mn(saltmen)(H_2O)]ClO_4$ and $[Hg(CN)_4]^{2-}$ gave two distinct compounds with respect to the formula ratio of Mn/Hg and structures, one is a 1-D polymeric compound $[\{Mn(saltmen)(H_2O)\}\{Hg(CN)_3\}]_n$ and the other is a discrete trinuclear compound $[\{Mn(saltmen)(H_2O)\}_2\{Hg(CN)_4\}]$. These compounds were synthesized by making vary the ratio of mixing two building blocks.

Several synthetic strategies to obtain the multi-dimensional coordination polymers have been developed,[1] in which the method we used is the assembly reaction of a metal complex exhibiting donor coordination ability and a metal complex exhibiting acceptor coordination ability. We have been engaged in metal-complex based magnetic materials by this strategy, in which a series of hetero-metal assemblies has been synthesized by the use of $K_3[Fe(CN)_6]$ having donor coordination ability and Mn(III) quadridentate Schiff base complex having acceptor coordination ability at the apical sites and the assembly reaction of these building blocks gave their versatile extended-structures and magnetic properties.[2]

Tetracyanomercurate(II) is a tetrahedral type ligand-complex while hexacyanoferrate(III) is a octahedral type and mercurate(II) is labile kinetically and reactive and the elimination of cyanide ions occurs depending on the reaction conditions. The reaction of $K_2[Hg(CN)_4]$ and Mn(III) quadridentate Schiff base complex $[Mn(saltmen)(H_2O)]ClO_4$ in methanol / water solution gave two complexes $[\{Mn(saltmen)(H_2O)\}\{Hg(CN)_3\}]_n$ **1** and $[\{Mn(saltmen)(H_2O)\}_2\{Hg(CN)_4\}]\cdot 2MeOH$ **2**[3] as the rhombic black crystals suitable for X-ray crystallographic analysis.[4] The formulation of these complexes depends on the molar ratio in starting materials. The reaction in 1 : 1 $[Mn(saltmen)(H_2O)]^+$ / $[Hg(CN)_4]^{2-}$ molar ratio formed the neutral complex of $[\{Mn(saltmen)(H_2O)\}\{Hg(CN)_3\}]_n$ **1** by the elimination of one of the four cyanide ions of $[Hg(CN)_4]^{2-}$, while the elimination of cyanide ions did not occur at the reaction in 1 : 2 molar ratio and at this reaction, formed complex **2**. In any event, the reaction formed a neutral complex.

An ORTEP drawing of the dinuclear unit for compound **1** with the atom numbering scheme is given in Figure 1. The Hg atom is coordinated by carbon atoms of three different cyanide ligands, terminal, bridging to Mn atom, and intrachain bridging. Intrachain bridging cyanide ligand of the $[Hg(CN)_3]^-$ moiety bridges the Hg atom of the neighboring unit and as a result, the Hg atom has a four-coordinate tetrahedral geometry and giving an one-dimensional chain structure $(\text{-Hg-CN-})_n$ with bond distances of Hg-C(23) = 2.17(1) Å, Hg-N(5) = 2.51(1) Å, and C(23)-N(5) = 1.13(2) Å and angles of Hg-C(23)-N(5) = 167(1) °, C(23)-N(5)-Hg = 163(1) ° and C(23)-Hg-N(5) = 83.4(5) °. One cyanide ligand of the $[Hg(CN)_3]^-$ moiety bridges the Mn atom with bond distances of Hg-C(21) = 2.30(2) Å, Mn-N(3) = 2.29(1) Å, and C(21)-N(3) = 1.05(2) Å and angles of Hg-C(21)-N(3) = 168(1) ° and Mn-N(3)-C(21) = 140(1) °. The geometry of the Mn atom is roughly octahedral, the basal plane being occupied by N_2O_2 donor atoms of the quadridentate Schiff base $saltmen^{2-}$ ligand while the axial sites are occupied by the

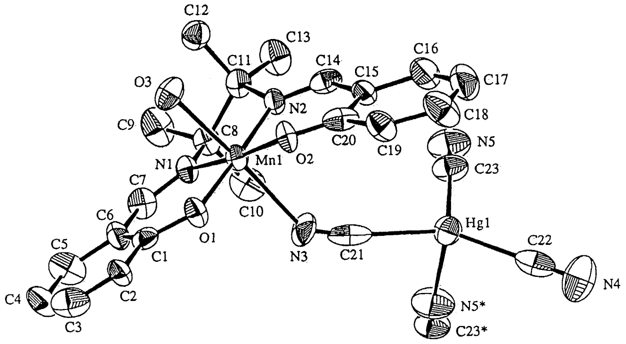

Figure 1. ORTEP drawing of a dinuclear unit for **1**. The selected bond distances (Å) and angles (°) are as follows; Hg-C21 = 2.30(2), Hg-C22 = 2.23(2), Hg-C23 = 2.17(1), Hg-N5* = 2.51(1), Mn-N3 = 2.29(1), Mn-O3 = 2.260(8), N3-C21 = 1.05(2), N4-C22 = 1.09(2), N5-C23 = 1.13(2), Hg-C21-N3 = 168(1), Hg-C22-N4 = 175(1), Hg-C23-N5 = 167(1), Hg-N5*-C23* = 163(1), Mn-N3-C21 = 140(1), O3-Mn-N3 = 170.0(4).

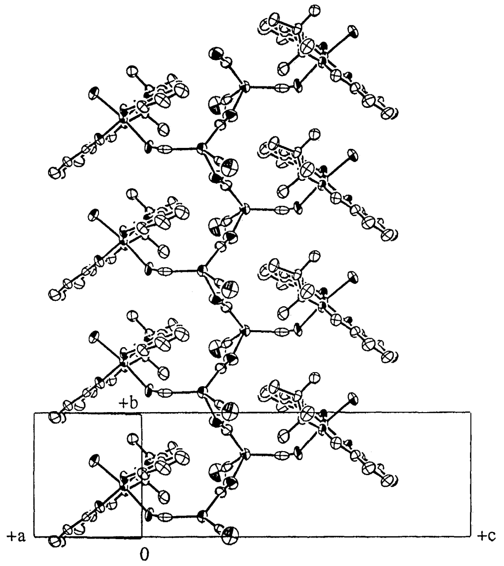

Figure 2. Projection perpendicular to the *b*-axis for **1**, showing an one-dimensional chain structure consisted of the Hg atoms bridged by cyanide ligands.

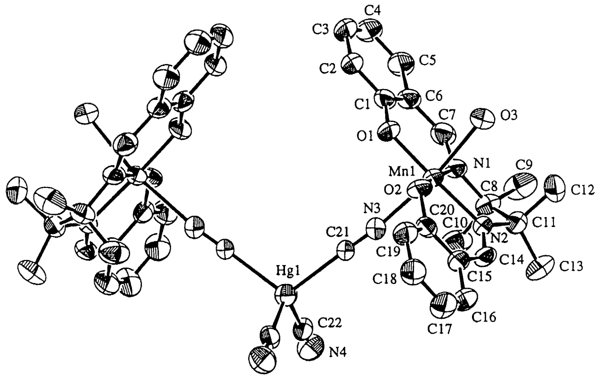

Figure 3. ORTEP drawing of a trinuclear structure for **2**. The selected bond distances (Å) and angles (°) are as follows; Hg-C21 = 2.233(9), Hg-C22 = 2.116(9), Mn-N3 = 2.295(7), Mn-O3 = 2.369(6), N3-C21 = 1.109(9), N4-C22 = 1.14(1), Hg-C21-N3 = 178.4(9), Hg-C22-N4 = 178.1(8), Mn-N3-C21 = 173.4(8), O3-Mn-N3 = 170.4(2).

nitrogen atom of the cyanide ligand and the oxygen atom of the water [Mn-O(3) = 2.260(8) Å, N(3)-Mn-O(3) = 170.0(4) °]. The crystal structure projected perpendicular to the *b* -axis is given in Figure 2, showing a "tree-type" one-dimensional chain structure consisted of Hg atoms bridging by cyanide ligands.

An ORTEP drawing of the trinuclear molecule of compound **2** with the atom numbering scheme is given in Figure 3. Since the space group is *C2/c* and the unit cell contains four trinuclear molecular units, the unsymmetrical unit is one half of a trinuclear unit and the Hg atom must occupy the special positions (0, y, -1/4). The Hg atom in the unit is coordinated by carbon atoms of two different pairs of cyanide ligands which are terminal and bridging to Mn atom and it has a four-coordinate tetrahedral geometry. Two cyanide ligands of the $[Hg(CN)_4]^{2-}$ moiety bridge the Mn atom with bond distances of Hg-C(21) = 2.233(9) Å, Mn-N(3) = 2.295(7) Å, and C(21)-N(3) = 1.109(9) Å and angles of Hg-C(21)-N(3) = 178.4(9) ° and Mn-N(3)-C(21) = 173.4(8) °. The geometry of the Mn atom is roughly octahedral similarly to complex **1**, the basal plane being occupied by N_2O_2 donor atoms of the quadridentate Schiff base saltmen^{2-} ligand while the axial sites are occupied by the nitrogen atom of the cyanide ligand and the oxygen atom of the water [Mn-O(3) = 2.369(6) Å, N(3)-Mn-O(3) = 170.4(2) °].

These new complexes **1** and **2** can be synthesized by treatment of mixing two building blocks and have different dimensional structures, complex **1** being one-dimensional polymeric structure and complex **2** being discrete trinuclear structure. The formation of these complexes is highly dependent on the reactivity of metal ion or metal complex as a building block and the coordination behavior of Hg(II) cyanide compound in this work is very similar to it of Cd(II) cyanide compound.[5]

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References and Notes

1 See for examples: a) B. F. Abrahams, B. F. Hoskins, D. M. Michail, and R. Robson, *Nature*, **369**, 727 (1994); b) S. R. Batten, B. F. Hoskins, and R. Robson, *Angew. Chem., Int. Ed. Engl.*, **34**, 820 (1995); c) S. Subramanian, and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, **34**, 2127 (1995); d) M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994); e) S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo, and M. Katada, *Inorg. Chem.*, **35**, 4449 (1996); f) K. Inoue, and H. Iwamura, *J. Am. Chem. Soc.*, **116**, 3173 (1994); g) M. Ohba, H. Okawa, T. Ito, and A. Ohto, *J. Chem. Soc., Chem. Commun.*, **1995**, 1545.

2 a) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, and C. Floriani, *Angew. Chem., Int. Ed. Engl.*, **34**, 1446 (1995); b) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, and C. Floriani, *J. Am. Chem. Soc.*, **118**, 981 (1996); c) N. Re, E. Gallo, C. Floriani, H. Miyasaka, and N. Matsumoto, *Inorg. Chem.*, **35**, 5964 (1996); d) N. Re, E. Gallo, C. Floriani, H. Miyasaka, and N. Matsumoto, *Inorg. Chem.*, **35**, 6004 (1996); e) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, and C. Floriani, *Inorg. Chem.*, in press (1997).

3 The crystals of compounds **1** and **2** were prepared by mixing the starting materials $[Mn(saltmen)(H_2O)]ClO_4$ and $K_2[Hg(CN)_4]$ in the molar ratio of 1 : 1 (0.5 mmol : 0.5 mmol) and 2 : 1 (1.0 mmol : 0.5 mmol), respectively, in methanol / watrer solution and standing for several days at the room temperature. The magnetic moment (μ_{eff}) per Mn at room temperature: **1**, 5.15 μ_B; **2**, 5.12 μ_B (paramagnetic behavior).

4 Crystal data for $[\{Mn(saltmen)(H_2O)\}\{Hg(CN)_3\}]_n$ **1** : $C_{23}H_{24}N_5O_3MnHg$, F.W. = 674.00, monoclinic, $P2_1/n$ (#14) with a = 11.531(2) Å, b = 7.220(4) Å, c = 29.639(5) Å, β = 90.85(1) °, V = 2467(1) Å^3, Z = 4, D_{calc} = 1.814 g/cm^3, μ(MoKα) = 67.76 cm^{-1}. Crystal data for $[\{Mn(saltmen)(H_2O)\}_2\{Hg(CN)_4\}]\cdot 2MeOH$ **2**: $C_{46}H_{56}N_8O_8Mn_2Hg$, F.W. = 1159.46, monoclinic, $C2/c$ (#15) with a = 24.285(4) Å, b = 12.467(4) Å, c = 19.921(3) Å, β = 127.251(9) °, V = 4800(1) Å^3, Z = 4, D_{calc} = 1.604 g/cm^3, μ(MoKα) = 37.76 cm^{-1}. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation(λ = 0.71069 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 20±1 °C using ω-2θ scan technique to a maximum 2θ value of 50.0° at a scan speed of 16.0 °/min (in omega). Of the 4983 reflections which were collected, 4732 were unique, of which 3823 observed reflections (I>3.00σ(I)) were employed for **1** and of the 4548 reflections which were collected, 4432 were unique, of which 3565 observed reflections (I>3.00σ(I)) were employed for **2**, where the unweighted and weighted agreement factors of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are used. The structures were solved by direct methods (SHELXS86). Final refinement yielded R = 0.045 and R_w = 0.069 for **1** and R = 0.052 and R_w = 0.050 for **2**.

5 T. Iwamoto and co-workers and R. Robson et al. have revealed a lot of the multi-dimensional compounds consisting of Cd(II) cyanide compounds and several metal ions and, similarly to Hg(II) cyanide compound, revealed a variety of reactivity and coordination geometry of Cd(II) ion. See for examples: a) T. Soma, H. Yuge, and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, **33**, 1665 (1994); b) T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, **1994**, 1029; c) B. F. Hoskins, R. Robson, and N. V. Y. Scarlett, *J. Chem. Soc., Chem. Commun.*, **1994**, 2025; d) B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson, and E. E. Sutherland, *J. Chem. Soc., Chem. Commun.*, **1994**, 1049.