Angewandte Chemie

Coordination Modes

# Rhodizonate Metal Complexes with a 2D Chairlike $M_6$ Metal–Organic Framework: $[M(C_6O_6)(bpym)(H_2O)]\cdot n\,H_2O$[**]

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The chronological significance and interesting chemistry of the monocyclic oxocarbon dianions, $C_nO_n^{2-}$ ($n=3$, deltate; $n=4$, squarate; $n=5$, croconate; $n=6$, rhodizonate), which is a nonbenzenoid aromatic system, are well elaborated in numerous books and reviews.[1] Over the past four decades, focus on the whole family of the oxocarbon dianions has been directed towards their aromaticity and molecular symmetry. Theoretical approaches have indicated that the aromaticity decreases as the ring size increases. It is thus expected that rhodizonate ($C_6O_6^{2-}$) has only a small degree of aromatic character.[2] Accordingly, much research has been carried out on the exploitation of squarate ($C_4O_4^{2-}$) and croconate ($C_5O_5^{2-}$) ligands in the construction of versatile coordination polymeric architectures through various binding modes.[3–5] The existence of planar $D_{nh}$ structures has been established on metal salts or complexes chelated by squarate and croconate. Conversely, owing to their relative instability, structural information on complexes by using deltate and rhodizonate as the building ligands is obscure.[6–10] Thus far, just a few rhodizonate salts of $K_2C_6O_6$,[8] $Rb_2C_6O_6$[10] and some inclusion compounds of urea and thiourea[9] have been structurally well characterized. For example, rhodizonate conforms to nonplanar $D_{3d}$ and $C_2$ molecular geometries coexisting in $K_2C_6O_6$, a $D_{6h}$ geometry in $Rb_2C_6O_6$, $[n\mathrm{Bu_4N}]^+{}_2C_6O_6^{2-}\cdot 4\,\mathrm{PhNHCONH_2}$ and $[n\mathrm{Bu_4N}]^+{}_2C_6O_6^{2-}\cdot 2\,m\text{-}\mathrm{OHC_6H_4NHCONH_2}\cdot 2\,H_2O$, and a planar $C_{2v}$ molecular geometry in $[n\mathrm{Bu_4N}]^+{}_2C_6O_6^{2-}\cdot 2\,\mathrm{NH_2CONHCH_2CH_2NHCONH_2}\cdot 3\,H_2O$.[9] To the best of our knowledge, the crystal structure of a rhodizonate transition-metal complex, unfortunately, has not yet been reported. It is thus both fundamentally and practically important to explore rhodizonate transition-metal complexes and consequently to shed light on their corresponding binding modes and molecular symmetries. Herein, we report the first two rhodizonate

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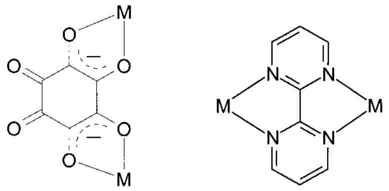
[**] This work was supported by the National Science Council, Taiwan, R.O.C. M = Cd, $n=1$; M = Mn, $n=2$; bpym = 2,2′-bipyrimidine.

DOI: 10.1002/ange.200460278

transition-metal complexes, $[Cd(C_6O_6)(bpym)(H_2O)]\cdot H_2O$ (**1**) and $[Mn(C_6O_6)(bpym)(H_2O)]\cdot 2H_2O$ (**2**), in which both rhodizonate and 2,2′-bipyrimidine (bpym) act as the bis-bidentate ligands (Scheme 1) to chelate the metal ions, thus forming a novel 2D chairlike $M_6$ metal–organic framework (MOF).



***Scheme 1.*** The bis-bidentate bridging mode of rhodizonate and bpym.

The preparation of **1** and **2** was carried out by the treatment of $Cd(NO_3)_2\cdot 4H_2O$ (or $MnCl_2\cdot 4H_2O$) with 2,2′-bipyrimidine (bpym) and $Na_2C_6O_6$ in an aqueous solution under acidic conditions (pH ~ 4.4) for a period of several days to yield deep-green crystals. Single-crystal X-ray diffraction studies revealed that the molecular structure of rhodizonate in both complexes has a nonplanar $C_2$ symmetry. As depicted in Figure 1, all cadmium centers in compound **1** are seven-coordinate.[11] The geometric environment of each Cd atom is in a distorted pentagonal bipyramidal (O(7)-Cd(1)-N(2) 164.3(2)°), coordinated by two nitrogen atoms of bpym ligands, four oxygen atoms of two $C_6O_6^{2-}$ ligands and one water molecule. Each rhodizonate adopts a bis-bidentate ($\mu_4$) bridging mode (Scheme 1) through four adjacent oxygen atoms and links two crystallographically identical Cd ions, thus forming a 1D polymeric zigzag chain (Figure 2a). It is noteworthy that this is the first structure ever reported in which $C_6O_6^{2-}$ acts as a bridging ligand bonded with the metal ion. Adjacent chains are then mutually linked by the bridge of bpym ligands that adopt a bis-bidentate binding mode to form a novel 2D MOF (Figure 2b) with a chairlike $\{Cd_6\}$ skeleton as the building unit (Figure 2c). Each $\{Cd_6\}$ unit is composed of six Cd ions, four rhodizonates and two bpym ligands. The Cd···Cd separations through $C_6O_6^{2-}$ and bpym bridges are 7.321(3) and 6.257(1) Å, respectively. Despite the differing

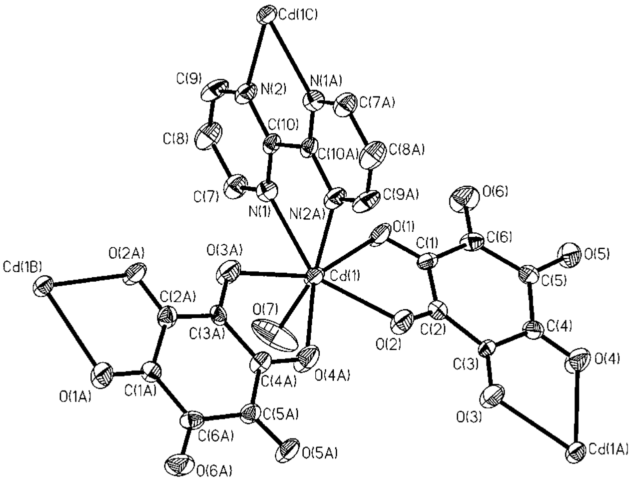


***Figure 1.*** ORTEP drawings of the coordination of the cadimum center in **1** (thermal ellipsoids set at 50% probability, all H atoms and solvated water molecular omitted for clarity).

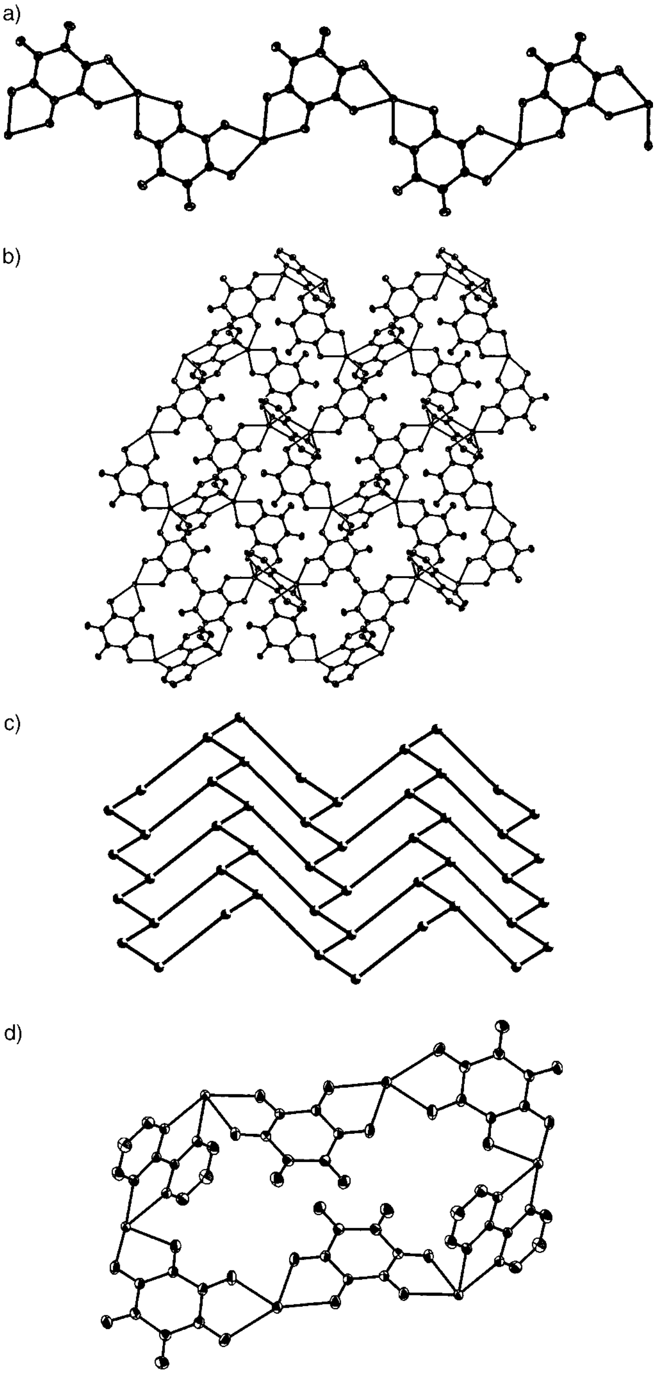


***Figure 2.*** a) A zigzag chain formed by the bridge of Cd with $C_6O_6^{2-}$. b) The 2D metal organic framework through the connectivity of Cd and $C_6O_6^{2-}$, bpym ligands, and c) the schematic representation of chairlike $\{Cd_6\}$ unit, the blue line through bpym bridge and the red line via $C_6O_6^{2-}$ bridge. d) The chairlike building unit composed of six $Cd^{II}$ ions, four $C_6O_6^{2-}$, and two bpym ligands (water molecules omitted for clarity).

numbers of lattice water molecules, the molecular structure of compound **2** is almost the same as that of compound **1** and has a 2D chairlike {Mn$_6$} MOF constructed through the linkages of Mn ions with bis-bidentate (μ$_4$) bridging the $C_6O_6^{2-}$ and bis-bidentate bpym.[11] The geometric environment of each Mn atom is also in a distorted pentagonal bipyramidal (O(7)-Cd(1)-N(2) 167.77(7)°) coordinated by two nitrogen atoms from bpym ligands, four oxygen atoms from two $C_6O_6^{2-}$ ligands, and an oxygen atom from a water molecule (Figure 3). The Mn⋅⋅⋅Mn separations through $C_6O_6^{2-}$ and bpym bridges are 7.177(3) and 6.061(1) Å, respectively.

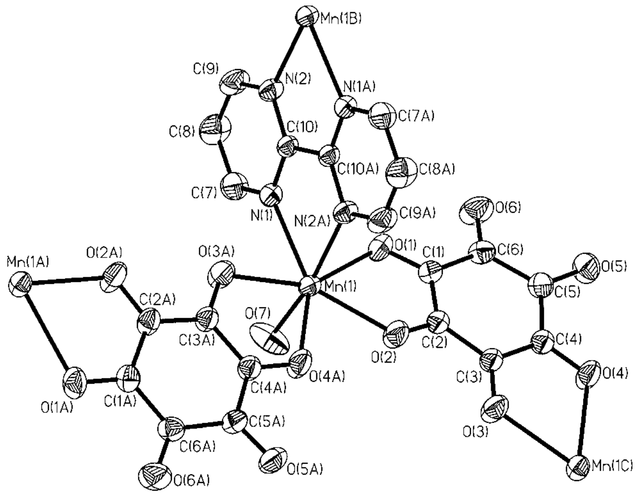


***Figure 3.*** ORTEP drawings of the coordination of manganese ion in **2** (thermal ellipsoids set at 50% probability, all H atoms and solvated water molecular omitted for clarity).

As the bis-bidentate (μ$_4$) binding mode of rhodizonate found in **1** and **2** is novel, it is of fundamental importance to examine the correlation between molecular symmetry and π-electron delocalization around the six-membered ring. The measured dimensions of the $C_6O_6^{2-}$ species in **1** and **2** conform nearly to a $C_2$ molecular symmetry, which corresponds to a diketone character (Figure 4). The mean deviations of carbon atoms from planarity are 0.071 and 0.054 Å for **1** and **2**, respectively, which are obviously larger than those of 0.020 and 0.010 Å in the inclusion compounds incorporating tetra-*n*-butylammonium rhodizonate and urea derivatives.[9] Moreover, the deviations of most oxygen atoms (see the numbers shown in Figure 4) in $C_6O_6^{2-}$ are larger than 0.1 Å, thus indicating a nonplanar molecular geometry. Notably, the C–C bond lengths—1.501(7) Å in **1**, 1.492(3) Å in **2**—between two nonbonded C=O groups are close to being single bond in character, and they are also larger than other C–C bond lengths—1.453(7)–1.468(7) Å in **1** and 1.443(3)–1.481(3) Å in **2**—for a $C_2$ molecular symmetry (Figure 4). This result implies that when $C_6O_6^{2-}$ acts as a bridging ligand, the π-electron delocalization in the six-membered ring of dianion is less extensive than that of its free ion in rhodizonate salts.[7–9] The nonplanar molecular geometry in $C_6O_6^{2-}$ seems to be in accordance with this theoretical prediction.[2] Thus the present finding provides direct, valuable information on the molecular geometry of rhodizonate when it is being used as a coordinating ligand. Finally, our preliminary results revealed that **1** in DMSO has an absorption band maximized at 490 nm. Upon excitation, **1** gave rise to an emission band maximum at 590 nm with decent quantum efficiency (≈0.05). Thus, the associated luminescence property for both complexes and magnetic phenomena for **2** should be of great interest. Investigations on detailed physical/photophysical properties of these complexes is currently in progress.

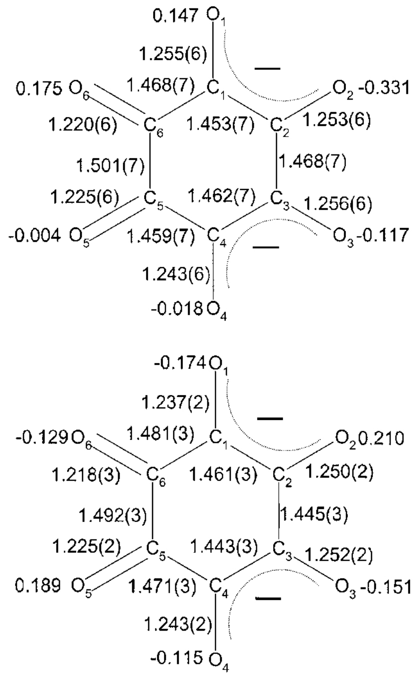


***Figure 4.*** Deviations of the oxygen atoms from the least-square plane of C6, and C–C, C–O bond lengths of the rhodizonate dianion with the $C_2$ molecular geometry in **1** (top) and **2** (bottom).

## Experimental Section

General: All chemicals were of reagent grade and were used as commercially obtained without further purification. Elementary analyses (carbon, hydrogen, and nitrogen) were performed by using a Perkin–Elmer 2400 elemental analyzer. IR spectra were recorded on a KBr disc with a Nicolet Fourier Transform IR, MAGNA-IR 500 spectrometer in the range of 500–4000 cm$^{-1}$.

Synthesis of [Cd($C_6O_6$)(bpym)($H_2O$)]·$H_2O$ (**1**): A solution (4 mL) of sodium rhodizonate ($Na_2C_6O_6$, 21.4 mg, 0.1 mmol) was added to a solution (4 mL) of Cd($NO_3$)$_2$·4$H_2O$ (30.9 mg, 0.1 mmol) and 2,2′-bipyrimidine (15.8 mg, 0.1 mmol) at room temperature to give a dark-brown solution. Deep-green crystals were obtained after several days in a yield of about 23%. IR (KBr pellet): $\tilde{\nu}$ = 3441 (m, br), 3054 (m, sharp), 1648 (m, sharp), 1604 (m, sharp), 1569 (s, sh), 1548 (vs, sharp), 1520 (vs, sharp), 1505 (vs, sharp), 1411 (s, sharp), 1216 (m, sharp), 1093 (m, sharp), 1052 (m, sharp), 1022 (m, sharp), 814 (m, sharp), 755 (m, sharp), 722 (m, sharp), 670 (m, sharp) cm$^{-1}$. Elemental analysis calcd (%) for $C_{10}H_7CdN_2O_8$ ($M_r$ = 395.58): C 30.33, N 7.07, H 1.76; found: C 29.91, N 6.90, H 1.72.

Synthesis of [Mn($C_6O_6$)(bpym)($H_2O$)]·2$H_2O$ (**2**): A solution (2 mL) of sodium rhodizonate ($Na_2C_6O_6$, 21.4 mg, 0.1 mmol) was added to a solution (4 mL) of $MnCl_2$ (19.7 mg, 0.1 mmol) and 2,2′-

bipyrimidine (15.8 mg, 0.1 mmol) at room temperature to give a dark-brown solution. Red-brown crystals were obtained after several days in a yield of about 34%. IR (KBr pellet): $\tilde{\nu}$ = 3564 (m, sharp), 3509 (m, sharp), 3457 (m, br), 3317 (m, br), 3098 (m, sharp), 1633 (s, sharp), 1568 (s, sharp), 1537 (s, sharp), 1485 (vs, br), 1411 (s, sharp), 1357 (m, sharp), 1216 (m, sharp), 1062 (m, sharp), 1026 (m, sharp), 757 (m, sharp), 671 (m, sharp), 563 (m, sharp) cm$^{-1}$. Elemental analysis (%) calcd for $C_{10}H_9MnN_2O_9$ ($M_r$ = 356.13): C 33.69, N 7.86, H 2.44; found: C 33.67, N 7.52, H 2.52.

Received: April 9, 2004 [Z460278]

**Keywords:** cadmium · coordination modes · manganese · O ligands

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[11] Crystal data for **1**: $C_{10}H_7CdN_2O_8$, $M_r$ = 395.58, monoclinic, space group $P2_1/n$, $a$ = 7.4250(5), $b$ = 13.9423(9), $c$ = 11.9924(8) Å, $\beta$ = 93.279(1)°, $V$ = 1239.4(1) Å$^3$, $Z$ = 4, $\mu$ = 1.807 mm$^{-1}$, $\rho_{calcd}$ = 2.120 g cm$^{-3}$, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, GOF = 1.244, $R1$ ($wR2$) = 0.0570 (0.1096) [2473 observed ($I > 2\sigma(I)$)] for 2873 ($R_{int}$ = 0.0455) independent reflections out of a total of 11716 reflections with 190 parameters. Crystal data for **2**: $C_{10}H_9MnN_2O_9$, $M_r$ = 356.13, monoclinic, space group $P2_1/n$, $a$ = 8.3746(6), $b$ = 13.6660(9), $c$ = 11.3170(8) Å, $\beta$ = 94.469(1)°, $V$ = 1291.3(2) Å$^3$, $Z$ = 4, $\mu$ = 1.076 mm$^{-1}$, $\rho_{calcd}$ = 1.832 cm$^{-3}$, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, GOF = 1.031, $R1$ ($wR2$) = 0.0365 (0.0973) [2676 observed ($I > 2\sigma(I)$)] for 2956 ($R_{int}$ = 0.0258) independent reflections out of a total of 12615 reflections with 199 parameters. Data collection was performed at 298(2) K on a Bruker SMART ApexCCD diffractometer with graphite-monochromated MoKα radiation. The structure was solved by direct methods by using SHELXTL program[12] and extended by using Fourier techniques. CCDC-236318 (**1**) and CCDC-236317 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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