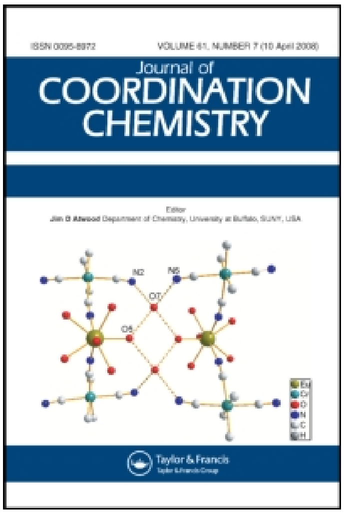

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Self-assembled hybrid water-chloride-ethanol chain in Schiff base Co(III) complex: synthesis, structure, and properties

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Self-assembled hybrid water–chloride–ethanol chain in Schiff base Co(III) complex: synthesis, structure, and properties

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A new Co(III) complex, $[CoL_2]\cdot(Cl)(EtOH)(H_2O)_2$ (**1**) with tridentate 5-bromo-*N*-(8-quinolyl) salicylaldimine (HL) has been synthesized and structurally characterized. The Co(III) is coordinated by two tridentate Schiff-base ligands and the CoN_4O_2 core shows distorted octahedral coordination geometry. A hybrid water chain is formed by self-assembly of octameric water–chloride–ethanol clusters $[(H_2O)_4(Cl)_2(EtOH)_2]^{2-}$ consisting of cyclic chair-like hexamer and two dangling water molecules. These hybrid water clusters occupy voids in the crystals and display extensive H-bonding interactions with the host complexes, thus playing a key role in the formation of 3-D structure.

Keywords: Self-assembly; Hybrid water chain; Hydrogen bonds; Crystal structure; Cobalt complex

1. Introduction

Considerable attention has been devoted to theoretical and experimental investigation of small water clusters [1, 2]. These studies facilitate understanding of the structures and functions of liquid water and ice [3]. Recent studies have led to the characterization of several water clusters in various crystal hosts. Notable among these are hexamers [4] and octamers [5]. While these studies have significantly advanced in understanding the structure of several discrete water clusters, how these clusters link themselves to form a large network is still a challenging scientific endeavor [2d, 6].

However, in contrast to the research on structural characterization of water clusters, the investigation of hybrid water clusters composed of hydrogen-bonded water associations with other solvents, counterions, or small molecules has received less attention [7]. In particular, there are only a few reports on experimental identification and analysis of discrete water–chloride clusters or hydrogen-bonded networks between water of crystallization and chloride counterions in crystalline materials [8, 9]. These reports are also believed to provide a contribution toward the understanding of the hydration phenomena of chloride in nature and have importance in biochemistry, supramolecular chemistry, and design of crystalline materials [9].

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Considerable effort is devoted to the investigation of transition metal complexes of Schiff bases due to their unusual configuration, structural lability, and sensitivity to molecular environments [10]. Schiff-base complexes represent a class of compounds increasingly important as biochemical, analytical, and antimicrobial reagents [11]. Particularly, Schiff-base ligands derived from *N*-(8-quinolyl)salicylaldimine have previously been incorporated into a number of metal complexes. To the best of our knowledge, among the reported complexes dealing with *N*-(8-quinolyl)salicylaldimine and its derivatives as ligands it includes the Cu(II) complexes [12], Tc(V) complex [13], V(V) complex [14], Cr(III) complex [15], Fe(III) complexes [16], and Ni(II) complex [17], but no Co(III) complex has been published.

In continuation of our work on the synthesis and structural studies of transition metal complexes of Schiff bases [18], herein, we report the synthesis and crystal structure of a tridentate Schiff-base complex $[CoL_2]\cdot(Cl)(EtOH)(H_2O)_2$ (**1**) [HL = 5-bromo-*N*-(8-quinolyl)salicylaldimine], in which lattice water, ethanol, and chlorides form octameric water–chloride–ethanol cluster $[(H_2O)_4(Cl)_2(EtOH)_2]^{2-}$ consisting of a cyclic chair-like hexamer and two dangling water molecules. The octameric water–chloride–ethanol clusters are self-assembled in the form of an infinite hybrid water chain through the interactions between the two dangling water molecules. Such a hybrid water–chloride–ethanol chain is relatively rare and is further stabilized by hydrogen bonds to the host molecules. In addition, the spectroscopic and electrochemical properties of complex have also been studied.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals used during the course of this work were reagent grade and used as received from the commercial sources. Elemental analyses were carried out with a Varian EL elemental analyzer. The IR spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer as KBr pellets. Thermogravimetric analyses were performed on SDT 2960 instrument in air with a heating rate of 10°C min^{-1}. The UV spectra were recorded on a Shimadzu UV-2501PC spectrometer and the fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. Cyclic voltammetry measurements were performed on an LK98 Microcomputer-based electrochemical analyzer with a glassy carbon working electrode, a platinum wire as counter electrode, and Ag–AgCl as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAHFP) ($0.2\,mol\,dm^{-3}$) was employed as the supporting electrolyte.

2.2. *Synthesis of 1*

To an absolute ethanol solution (15 mL) of 8-aminoquinoline (0.29 g, 2 mmol) 5-bromo-salicylaldehyde (0.25 g, 2 mmol) was added at 60°C and with constant stirring. The yellow reaction mixture was refluxed for 2 h and allowed to stand at room temperature. Then, an ethanol solution (10 mL) of $CoCl_2\cdot H_2O$ (0.24 g, 1 mmol) was added gradually with stirring. A red precipitate formed immediately. The mixture was stirred for 1 h, after which the solid was filtered and the filtrate was allowed to stand at room

Table 1. Crystal data and refinement details for **1**.

Empirical formula	$C_{34}H_{30}Br_2ClCoN_4O_5$
Formula weight	828.82
Crystal size (mm^3)	0.41 × 0.39 × 0.24
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions (Å, °)	
a	11.7775(12)°
b	12.5793(14)°
c	13.2761(17)°
α	116.580(3)
β	90.880(2)
γ	108.078(3)
Volume (Å^3), *Z*	1644.4(3), 2
Calculated density ($g\,cm^{-3}$)	1.674
Absorption coefficient (mm^{-1})	3.082
F(000)	832
θ range for data collection (°)	1.74–25.01
Reflections collected	8428
Independent reflections	5667 [$R_{int} = 0.0353$)
Observed reflections	3406 [$I > 2\sigma(I)$]
Goodness-of-fit on F^2	0.992
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1260$
R indices (all data)	$R_1 = 0.1083$, $wR_2 = 0.1542$

temperature for 10 days, giving crystals suitable for X-ray diffraction. Yield: 60%. Anal. Calcd for $C_{34}H_{30}Br_2ClCoN_4O_5$ (%): C, 49.32; H, 3.66; N, 6.77. Found (%): C, 49.21; H, 3.46; N, 6.86. IR (KBr) (cm^{-1}): 3374w, 3035w, 1606s, 1580m, 1505s, 1444m, 1415w, 1371w, 1320m, 1302m, 1198m, 1162m, 1139w, 1086w, 828w, 782w, and 653w.

2.3. *Crystal structure determination*

The intensity data for a single crystal of **1** were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. An empirical absorption correction using SADABS was applied for the data. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. The H-atoms attached to O2 and O5 were located in a difference density map and the other hydrogens were located geometrically and refined isotropically. The data collection and refinement details are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of 1*

The molecular structure of **1** is illustrated in figure 1 with the atom numbering scheme. Bond parameters associated with the metal ion are listed in table 2. The asymmetric unit contains $[CoL_2]^+$ with chloride counterion, ethanol, and two lattice waters. The Co(III)

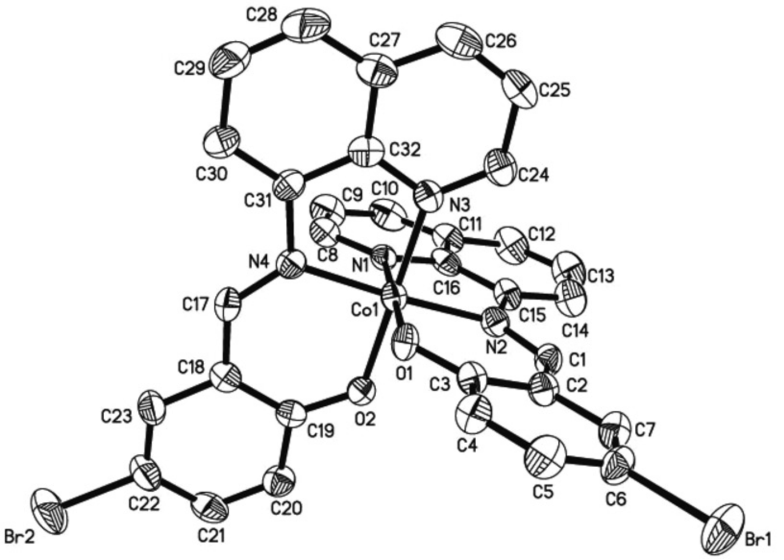

Figure 1. ORTEP drawing of the cation in $[CoL_2]\cdot(Cl)(EtOH)(H_2O)_2$ (**1**) with hydrogen atoms omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Co(1)–O(1)	1.882(4)	Co(1)–N(2)	1.918(4)
Co(1)–O(2)	1.891(4)	Co(1)–N(1)	1.924(4)
Co(1)–N(4)	1.912(4)	Co(1)–N(3)	1.930(4)
O(1)–Co(1)–O(2)	90.67(16)	N(4)–Co(1)–N(1)	93.84(18)
O(1)–Co(1)–N(4)	86.70(16)	N(2)–Co(1)–N(1)	84.29(18)
O(2)–Co(1)–N(4)	94.77(17)	O(1)–Co(1)–N(3)	88.77(17)
O(1)–Co(1)–N(2)	95.25(16)	O(2)–Co(1)–N(3)	179.37(19)
O(2)–Co(1)–N(2)	88.29(17)	N(4)–Co(1)–N(3)	84.89(19)
N(4)–Co(1)–N(2)	176.36(19)	N(2)–Co(1)–N(3)	92.07(19)
O(1)–Co(1)–N(1)	178.59(17)	N(1)–Co(1)–N(3)	92.57(18)
O(2)–Co(1)–N(1)	87.98(16)		

is octahedrally coordinated by four nitrogens and two phenolic oxygens of two tridentate Schiff-base ligands. As shown in table 2, the Co–O distances are slightly shorter than the Co–N distances, which lead to a slight distortion of the CoN_4O_2 from idealized octahedral geometry. The Co–O and Co–N distances are comparable to the distances observed in other Co(III) complex having the same coordinating atoms [19].

The most interesting feature for **1** is the hydrogen-bonding interactions of two lattice waters, one ethanol, and one chloride, providing the formation of octameric water–chloride–ethanol cluster $[(H_2O)_4(Cl)_2(EtOH)_2]^{2-}$ (figure 2a). The geometrical parameters of the hydrogen bonds are given in table 3. Hence, two symmetry-equivalent water molecules of crystallization O4, ethanol molecules O3 and chloride ions Cl1 are doubly interconnected through O4–H4A $\cdots$ Cl1, O3–H3 $\cdots$ Cl1, and O4–H4B $\cdots$ O3 hydrogen bonds generating the cyclic water–chloride–ethanol hexamer. The cyclic hexamer adopts chair-like conformation with O3 $\cdots$ Cl1 $\cdots$ O4, Cl1 $\cdots$ O3 $\cdots$ O4, and

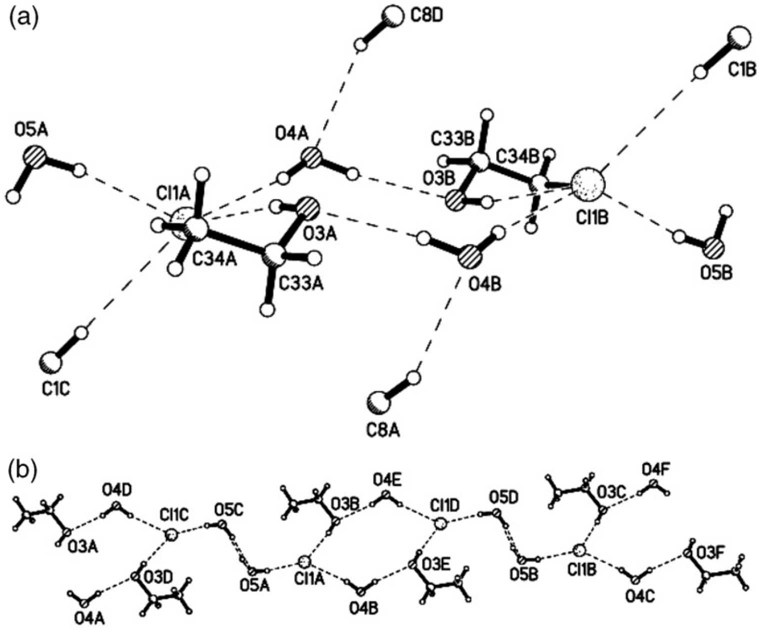

Figure 2. (a) A hybrid water–chloride–ethanol octamer and the surrounding environment. C1 and C8 atoms are from metal complexes. (b) An infinite hybrid water chain formed by the self-assembly of water–chloride–ethanol octamers.

Table 3. Hydrogen bonds for **1**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
O3–H3···Cl1	0.820	2.426	3.237	169.79
O4–H4A···Cl1	0.850	2.303	3.142	169.51
O4–H4B···O3^a	0.850	2.041	2.880	169.14
O5–H5A···Cl1^b	0.850	2.270	3.111	170.17
O5–H5B···O5^c	0.850	2.197	3.038	170.11
C1–H1···Cl1	0.930	2.828	3.727	163.0
C8–H8···O4	0.930	2.410	3.248	149.9

Symmetry operator: $^a-x+1, -y+1, -z+1$; $^b x, y+1, z$; $^c-x+1, -y+2, -z$.

Cl1 ··· O4 ··· O3 of 83.3°, 130.9°, and 124.0°, respectively. The cyclic hexamer is further connected through the O5–H5A ··· Cl1 interactions to give the octameric association (figure 2a). Within the hybrid octamer the O ··· O separation of 2.880 Å (table 2) is nearly identical to the contact of 2.885 Å in the mixed water–methanol cluster $(H_2O)_{15}(CH_3OH)_3$ [2d], but is slightly longer than those in other water octamers [5]. The O ··· Cl separations (3.142, 3.237 Å) within the hexameric core are longer than that of 3.111 Å connecting dangling water molecules, but lie in the range found in other previously identified water–chloride assemblies [8, 9].

Although octameric water clusters exhibiting conformation of cubane, opened cube, cyclic ring, and extended array of cyclic octamers have been observed in organic or organic–inorganic host [5], the present mode of hybrid water–chloride–ethanol octamer

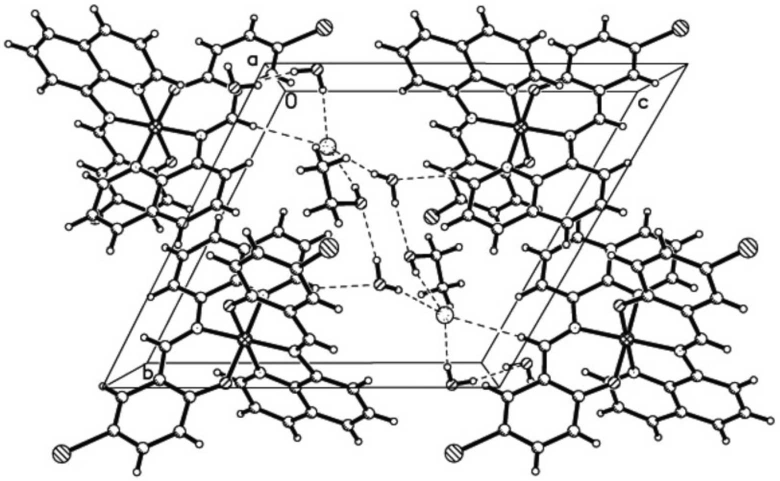

Figure 3. Representation of the hydrogen-bonding associations between hybrid water chain and metal complexes in $[CoL_2] \cdot (Cl)(EtOH)(H_2O)_2$ (**1**).

with chair-like hybrid hexamer core and two dangling water molecules in **1** is rare. To the best of our knowledge, the only other examples of octameric water cluster consisting of chair-like water hexamer and two dangling water molecules are observed in $Ce(dipic)_2(H_2O)_3 \cdot 4H_2O$ [5g] and $[Pd(HL)] \cdot 4[0.85(H_2O)]$ [5f]. As shown by calculation, such octameric cluster is highly unstable with respect to other conformers of the octamer [5g].

Hybrid water–chloride–ethanol octamers are self-assembled in **1** in the form of an infinite hybrid water chain through the interactions between two dangling water molecules (figure 2b). This unique self-assembly is not observed in $Ce(dipic)_2(H_2O)_3 \cdot 4H_2O$ and $[Pd(HL)] \cdot 4[0.85(H_2O)]$, in which the water octamers are not connected directly to one another but to host molecules [5g, 5f]. Also, we believe that this motif of association of water molecules has not been previously speculated.

The hybrid $[(H_2O)_4(Cl)_2(EtOH)_2]^{2-}$ clusters occupy voids in the crystal cell of **1** and extensively interact through multiple C–H $\cdots$ Cl and C–H $\cdots$ O hydrogen bonds with the host metal matrix (table 3), resulting in the 3-D structure (figure 3).

3.2. *Thermogravimetric analysis and IR spectra*

To estimate the stability of the hybrid water chain, thermogravimetric analysis (TGA) was carried out. The TGA curve shows a weight loss of 10.88% between the room temperature and 120°C, consistent with the theoretical value of 9.92% for the loss of two waters and one ethanol, confirming that the hybrid water–chloride–ethanol clusters have weak interactions with metal complexes [2d]. The presence of the water chain is also confirmed by a broad absorption at $3374\,cm^{-1}$ in IR spectra of **1**, very close to the value reported for the cyclic water hexamer with four dangling water molecules in $[Cu_2(SIP–O)(bpy)_2(H_2O)_2] \cdot 7H_2O$ ($3357\,cm^{-1}$) [5h]. A characteristic strong band corresponding to $\nu(C{=}N)$ at $1606\,cm^{-1}$ indicates the coordination of the

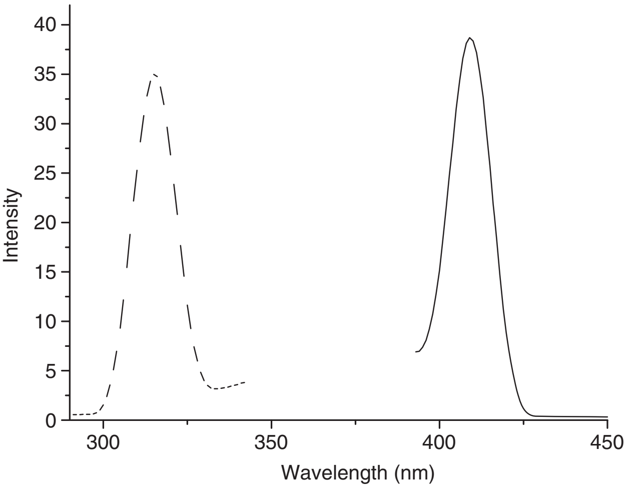

Figure 4. Excitation (– – –) and emission (—) spectra of $[CoL_2] \cdot (Cl)(EtOH)(H_2O)_2$ (**1**). (1×10^{-3} mol L^{-1}) in DMF at room temperature.

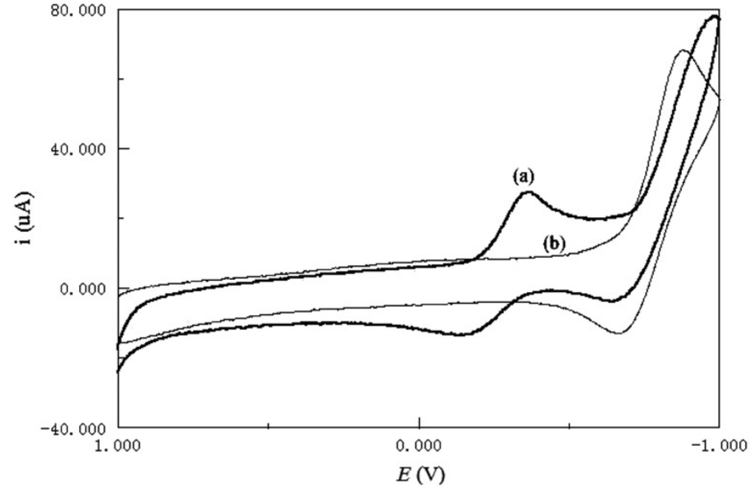

Figure 5. Cyclic voltammogram of sample and blank sample in DMF with 0.2 M Bu_4NPF_6; (a) $[CoL_2] \cdot (Cl)(EtOH)(H_2O)_2$ (**1**) (1×10^{-3} mol L^{-1}), (b) blank sample (scan rate 100 mV s^{-1}).

imine nitrogen. The coordination through oxygen is inferred from a sharp band of ν(ph–O) at 1199 cm^{-1} [20].

3.3. *Electronic and fluorescence spectra*

The electronic spectra of **1** in dimethylformamide (DMF) show bands at 335, 349, and 366 nm, attributed to L^{2-} $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The band at 479 nm may be assigned to ligand to metal charge transfer [21].

The excitation and emission spectra of **1** in DMF at room temperature are shown in figure 4. When excited at 315 nm, this complex undergoes fluorescence emission with the maximum emission peak located at 409 nm. The peaks would be assigned to the intra-ligand $\pi \rightarrow \pi^*$ emission from the ligand [22, 23].

3.4. *Cyclic voltammetry*

Electrochemical behavior of **1** was studied using cyclic voltammetry (CV) in DMF containing 0.2 M TBAHFP (figure 5). The CV of **1** exhibits one irreversible reduction with a peak separation value ($\Delta E = 0.199$ V). The reduction wave could be assigned to the metal-based Co(III)/Co(II) couples in the complex. The cathodic peak potential of complex is located at $E_{pc} = -0.349$ V *versus* Ag/AgCl. This observation is in accord with the results reported for Co(III) Schiff-base complexes [20, 22, 24, 25].

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