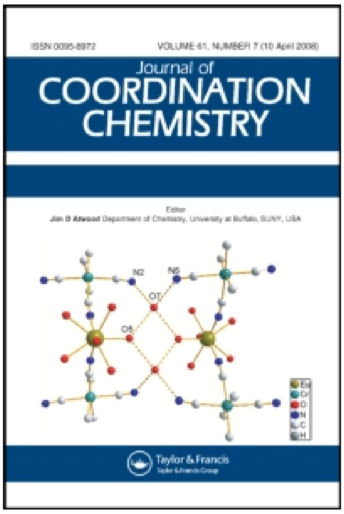

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Synthesis, characterization, and electrocatalysis of a dinuclear cobalt(III) thioxanthate complex

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Synthesis, characterization, and electrocatalysis of a dinuclear cobalt(III) thioxanthate complex

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This study reports on the synthesis, characterization, and performance of a new dinuclear cobalt(III) thioxanthate complex of $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$ as an electrocatalyst for trichloroacetic acid (TCA) and bromate reduction. Its structure was characterized by X-ray crystallography and elemental analysis. The structure contains two different anions of 2-sulfanylethanol thioxanthate and 2-sulfanylethanol. The electrochemical behavior and the electrocatalysis of the cobalt complex bulk-modified carbon paste electrode have been studied by cyclic voltammetry. It shows good electrocatalytic activities toward the reduction of TCA and bromate. The values for the detection limit and the sensitivity are $0.06\,\mu mol\,L^{-1}$ and $19.40\,\mu A\,\mu mol\,L^{-1}$ for TCA detection and $0.01\,\mu mol\,L^{-1}$ and $177.6\,\mu A\,\mu mol\,L^{-1}$ for bromate detection, respectively. This modified electrode exhibits good reproducibility, high stability, low detection limit and technical simplicity, and allows a possibility for rapid preparation, which is important for practical applications.

Keywords: Cobalt thioxanthate complex; Crystal structure; Electrochemistry; Electrocatalysis

1. Introduction

Significant contemporary interest in organic–inorganic hybrid materials reflects both the fundamental chemistry of the rational design of complex materials and practical applications to fields as diverse as catalysis [1], optical materials [2, 3], membranes [4–6], and sorption [7, 8]. One strategy for the design of inorganic–organic hybrid materials is to select suitable inorganic materials and organic ligands with structure-directing properties [9–11]. In these hybrid materials, metal complexes with diverse structural arrangements not only serve as charge-compensating units but also modify the wide-ranging properties, such as magnetic and optical properties, electronic conductivities, and electrocatalysis [9–12].

Metal complexes are well recognized for their excellent electrocatalytic properties toward the detection of hydrogen peroxide [13–15], nitrite [13–16], bromate [14–16], trichloroacetic acid (TCA) [17], and so on. The electrochemistry and electrocatalysis of copper complexes with various different ligands have been investigated by several groups [15, 16, 18–21]. Tas *et al.* [22] reported on the synthesis, spectral

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characterization, and electrochemical studies of copper(II) and cobalt(II) complexes with tetradentate salicylaldimines. Fuenzalida *et al.* [23] reported the electrochemical reduction of sulfite on a glassy carbon electrode modified with a conducting film formed by Co(II) tetra-3-aminophenyl porphyrin. Most of those studies were focused on immobilized metal complexes using various techniques, such as adsorption and fabrication of multilayer ultra-thin films [21, 23, 24]. A serious drawback in the application of these thin film-modified electrodes was their poor long-term stability; moreover, electrode surfaces cannot be renewed. To our best knowledge, the study of the electrochemistry and electrocatalysis of cobalt complex bulk-modified carbon paste electrode (CPE) is less reported [25–27].

The increasing commercial value of transition metal xanthate complexes has aroused considerable interest in organic thiochemistry. Most previous studies were mainly focused on xanthates as flotation agents for thiophilic minerals of copper, zinc, cobalt, nickel, and gold [28]. Lewis *et al.* [29] reported on the syntheses and structures of monomeric and sulfur-bridged dimeric cobalt(III) thioxanthate complexes. Winograd *et al.* [30] reported the crystal structure of $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]$. But electrochemical properties of the metal thioxanthate complexes are less reported. The significance of this work is to use a new cobalt complex, $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$, as a bulk-modifier to fabricate a chemically modified CPE (Co-CPE) by direct mixing. This modified electrode shows excellent electrocatalytic activities toward the reduction of TCA and bromate, and possible mechanisms are proposed.

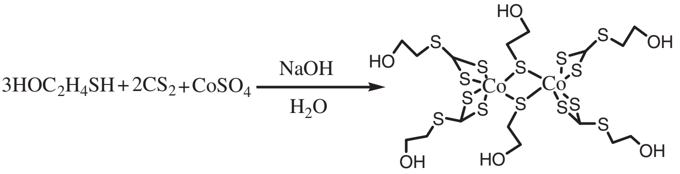
2. Experimental

2.1. *Chemicals and measurement*

All chemicals were of analytical reagent grade and used without purification. Elemental analysis was measured with a Perkin Elmer 1400C analyzer (USA). Crystal structure determination by X-ray diffraction was performed on a Bruker–Nonius diffractometer with Kappa geometry attached with an APEXII-CCD detector (Bruker, Germany). Electrochemical measurements were using an Autolab PGSTAT-30 digital potentiostat/galvanostat (Eco-Chemie BV, Utrecht, the Netherlands). A three-electrode cell was used in the experiments. The working electrode was a modified CPE. The counter electrode was a platinum wire. The reference electrode was a Ag|AgCl, KCl ($1\,mol\,L^{-1}$)‖, and all the potentials reported in this study were measured relative to this electrode (236.3 mV/SHE at 25°C). Britton–Robinson (B–R) buffer solution ($0.1\,mol\,L^{-1}$, pH 6.1) was used as the supporting electrolyte. All solutions were deaerated with pure nitrogen for 30 min and kept under nitrogen during the experiments. All the measurements were performed at room temperature ($25 \pm 2°C$).

2.2. *Preparation and physical measurement of the cobalt complex*

The synthetic route for $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$ is shown in scheme 1. The mixture of 2-sulfanylethanol (2.72 mL, $6.0\,mmol\,L^{-1}$) and carbon disulfide (2.41 mL, $40.0\,mmol\,L^{-1}$) was added to sodium hydroxide saturated solution (40 mL) under vigorous stirring. After refluxing for 5 h, cobaltous sulfate (5.62 g, $20\,mmol\,L^{-1}$)



Scheme 1. Synthesis of $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$.

was added to the solution. Black precipitate was obtained (3.71 g, yield, 42%) upon collection by filtration and washed with ethanol and dried in air. The cobalt complex showed good solubility in nonpolar solvents, but not in polar solvents or water. Single crystals suitable for X-ray analysis were obtained by slow evaporation of Tetrahydrofuran (THF) solution at room temperature (m.p. 291°C). The C, H, and S contents were determined by elemental analysis (Calcd for $C_8H_{15}CoO_3S_7$ (%): C, 21.7; H, 3.4; and S, 50.6. Found: C, 21.8; H, 3.4; and S, 50.7).

X-ray diffraction was measured at 20°C using Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The structure of the cobalt complex was solved by direct methods and refined by least-squares on F^2_{obs}, using the SHELXTL software package [31]. All nonhydrogen atoms were refined anisotropically, and hydrogens were placed in calculated positions and allowed to ride on their parent atoms. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray crystallography [32].

2.3. *Preparation of Co-CPE*

Traditional CPE was prepared by hand mixing of graphite powder with paraffin oil at a ratio of 70 : 30 (w/w) in an agate mortar. The cobalt complex was employed to fabricate modified CPEs due to its insolubility. The modified Co-CPE was fabricated as follows: 0.3 g of graphite powder and 0.03 g of the cobalt complex were mixed and ground together using agate mortar and pestle for about 30 min to achieve an even, dry mixture. Paraffin oil (0.1 mL) was added to the mixture and stirred with a glass rod. Then, the homogenized mixture was used to fill a glass tube (3 mm inner diameter) to a depth of 0.8 cm. Electrical contact was established with a copper rod and the surface of Co-CPE was polished on a piece of weighing paper until it had a shiny surface.

Different ratios of graphite powder and cobalt complex were investigated to determine the optimum preparation condition, 20 : 1, 14 : 1, 10 : 1, 8 : 1, and 5 : 1 (w/w), and it was found that the optimum preparation condition was 10 : 1. When the amount of the complex was too low, the electrochemical signal was weak. Conversely, when the amount of the complex was high, the conductivity of the modified CPE was low.

3. Results and discussion

3.1. *Crystal structure of the cobalt complex*

The molecular structure of the cobalt complex with atomic numbering scheme is shown in figure 1. Crystal data and structure refinement for the cobalt complex are

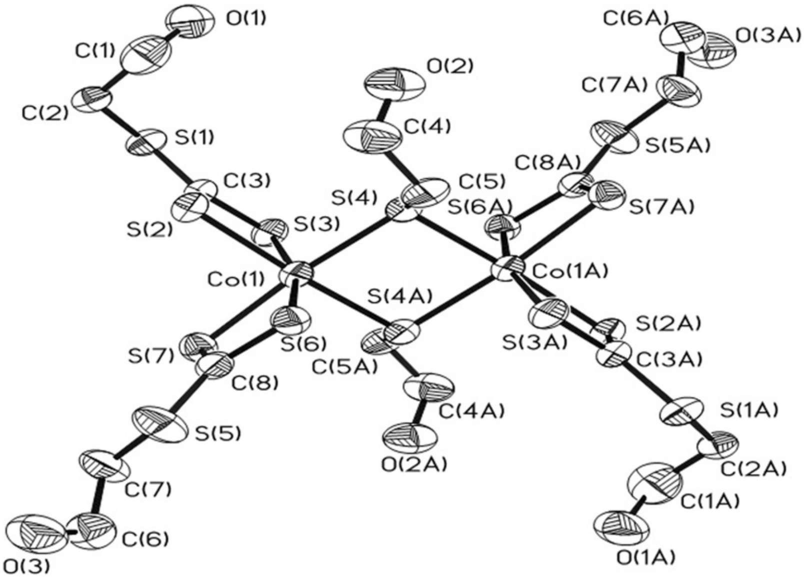


Figure 1. The molecular structure of $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$ with the atomic numbering scheme.

listed in table 1. The cobalt is six-coordinate with a distorted octahedral geometry of four sulfurs from different 2-sulfanylethanol xanthates and two sulfurs from two 2-sulfanylethanol molecules, respectively. The two cobalts are linked by two sulfurs from two 2-sulfanylethanols as dibridging ligands, arranged in a four-membered ring. The nonbonded Co–Co distance is 3.331 Å, which is similar to previous reports [29, 30]. The six Co–S bond lengths [2.235(2)–2.287(3) Å] are consistent with those reported earlier [29, 30, 33]. The bond angles around the Co center S(4)–Co(1)–S(6) [99.89(9)°], S(4)–Co(1)–S(3) [89.47(9)°], S(6)–Co(1)–S(2) [94.12(9)°], C(3)–S(2)–Co(1) [85.1(3)°], and C(5)–S(4)–Co(1) [111.1(3)°] are comparable to the corresponding values in similar complexes [29, 30, 33]. There are three C–H $\cdots$ S intramolecular hydrogen bonds; the donor–acceptor distances are 3.187(1) Å for C(2) $\cdots$ S(2), 3.407(1) Å for C(5) $\cdots$ S(6), and 3.229(1) Å for C(7) $\cdots$ S(7), respectively. There is an intermolecular O–H $\cdots$ O hydrogen bond at 2.715(1) Å for O(3) $\cdots$ O(2), which is shorter than that of ice (2.76 Å) [34]. In the solid state, intermolecular interaction stabilizes the crystal structure.

3.2. *Electrochemical behavior of the Co-CPE*

The electrochemical behavior of Co-CPE was investigated by cyclic voltammetry in aqueous solution. We chose a 0.1 mol L^{-1} KCl aqueous solution, a 0.1 mol L^{-1}, pH 7.0, Britton–Robinson (B–R) buffer solution and a 0.1 mol L^{-1}, pH 7.0, phosphate buffer solution as the supporting electrolyte solutions. The modified electrode in B–R buffer solution showed strong current response and symmetric peak shape. Then, we investigated the electrochemical behavior of modified CPE in the pH range from

Table 1. Crystal data and structure refinement for $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$.

Empirical formula	$C_8H_{15}CoO_3S_7$
Formula weight	442.55
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	11.890(2)
b	12.090(2)
c	13.360(6)
β	119.94(2)
Volume (Å^3), Z	1664.2(8), 4
Calculated density ($g\,cm^{-3}$)	1.766
Absorption coefficient (mm^{-1})	1.907
$F(000)$	904
θ range for data collection (°)	1.98–27.49
Limiting indices	$-14 \leq h \leq 15$; $-14 \leq k \leq 14$; $-17 \leq l \leq 16$
Reflections collected	12823
Unique reflection	3493 [$R(\text{int}) = 0.1188$]
Completeness to $\theta = 27.49$ (%)	91.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3493/0/173
Goodness-of-fit on F^2	0.930
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0633$, $wR_2 = 0.1320$
R indices (all data)	$R_1 = 0.1853$, $wR_2 = 0.1765$
Largest difference peak and hole (e Å^{-3})	0.659 and −0.445

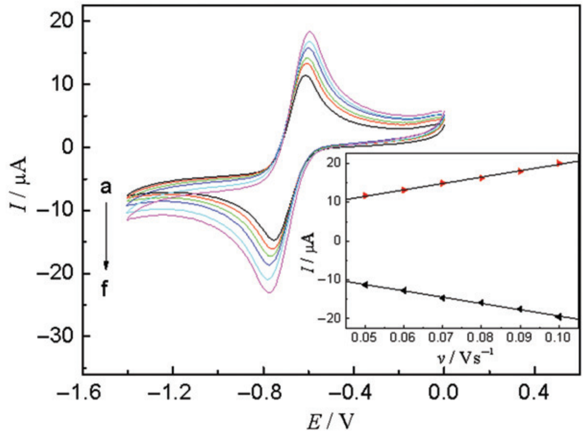


Figure 2. CVs of Co-CPE in 0.1 mol L^{-1}, pH 6.1, B–R buffer solution. Curves (**a**–**f**) correspond to the scan rates 0.05, 0.06, 0.07, 0.08, 0.90, and 0.10 V s^{-1}. Inset: the peak current *vs.* the scan rate.

4.0 to 8.0 B–R buffer solution and found that the electrochemical signal was relatively stable at pH 6.1. Therefore, we studied the electrochemical behavior and electrocatalytic properties in 0.1 mol L^{-1}, pH 6.1, B–R buffer solution.

The cyclic voltammograms (CVs) of Co-CPE are shown in figure 2. In the potential range from 0 to −1.5 V, when the scan rate was 0.05 V s^{-1}, curve **a** had a couple of well-defined redox peaks at −0.757 V and −0.605 V, with the formal potential ($E^{0'}$)

at −0.681 V, corresponding to the electrochemical process of Co(III)/Co(II). The separation of the cathodic and anodic peak potential, $\Delta E = 0.152$ V, $i_{\mathrm{pa}}/i_{\mathrm{pc}} = 1.05$, indicated that the electrochemical behavior of the cobalt complex on the electrode was quasireversible.

The effect of scan rate on the electrochemical behavior of Co-CPE can be seen in figure 2. When the scan rate was varied from 0.05 to 0.10 V s^{-1}, the peak potentials changed gradually: the cathodic peak potentials shifted to negative direction and the corresponding anodic peak potentials shifted to positive direction with increasing scan rate. The plot of peak current *versus* scan rate is shown in the inset of figure 2. The anodic and cathodic currents are proportional to the scan rates, suggesting that the redox process is confined to the surface.

3.3. *Electrocatalytic activity of Co-CPE*

3.3.1. Electrocatalytic reduction toward TCA. Organohalide is a pollutant; TCA is formed during water chlorination. Electrochemical oxidation or reduction is an effective way to deal with environmental pollutants [17]. Some insoluble metal complexes containing redox mediators can be used for electrocatalysis. The electrocatalytic activity toward TCA of Co-CPE is shown in figure 3. With the addition of TCA in the solution (curves **a**–**f**), the oxidation and reduction peak potentials had no obvious change, but there was a dramatic enhancement of the cathodic peak current, and the anodic peak current decreased. When the concentration of TCA was changed to 1.00 μmol L^{-1}, the maximum value of the reduction peak current was obtained, while the value of the oxidation peak current was almost reduced to zero, which indicated a strong catalytic effect. The possible reaction processes could be described using the following equations [17, 35]:

$$\mathrm{Co(III)} + \mathrm{e}^- \longleftrightarrow \mathrm{Co(II)}$$

$$2\mathrm{Co(II)} + \mathrm{CCl_3COOH} + \mathrm{H}^+ \longleftrightarrow 2\mathrm{Co(III)} + \mathrm{CHCl_2COOH} + \mathrm{Cl}^-.$$

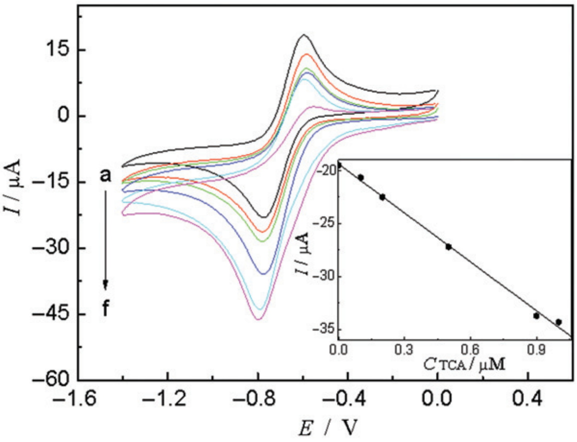


Figure 3. Co-CPE in 0.1 mol L^{-1}, pH 6.1, B–R buffer solution. Curves (**a**–**f**) containing 0, 0.10, 0.20, 0.50, 0.90, and 1.00 μmol L^{-1} TCA with the scan rate as 0.10 V s^{-1}. Inset: the cathodic peak current *vs.* TCA concentration.

The inset of figure 3 shows that the catalytic current is linear *versus* TCA concentration in the range 0.10–1.00 μmol L^{-1}. The linear regression equation is I_{pc} (μA) = − 19.40C (μmol L^{-1}) − 15.39 with a correlation coefficient of 0.998. The detection limit (signal to noise ratio is 3) and the sensitivity are 0.06 μmol L^{-1} and 19.40 μA μmol L^{-1}, respectively.

3.3.2. Electrocatalytic reduction toward bromate. Bromate is a disinfectant by-product contaminant found in drinking water, formed during the ozonation of the source water containing bromide. The overpotential for bromate reduction is high, and therefore an efficient electrocatalyst would be beneficial [15, 36]. However, the reduction of bromate can be readily catalyzed by Co-CPE in 0.1 mol L^{-1}, pH 6.1, B–R buffer solution. As shown by curves **a**–**e** in figure 4, with the addition of bromate, the peak potentials had little change and the reduction peak currents increased while the corresponding oxidation peaks decreased, indicating that Co-CPE showed excellent electrocatalytic activity toward the reduction of bromate. Possible reaction processes could be described in the following equations [15, 35]:

$$\mathrm{Co(III)} + e^- \longleftrightarrow \mathrm{Co(II)}$$

$$6\mathrm{Co(II)} + \mathrm{BrO_3^-} + 6\mathrm{H^+} \longleftrightarrow 6\mathrm{Co(III)} + \mathrm{Br^-} + 3\mathrm{H_2O}.$$

The inset of figure 4 shows that the catalytic current varies linearly with bromate concentration in the range 0.02–0.10 μA μmol L^{-1}. The linear regression equation is I_{pc} (μA) = − 177.6C (μmol L^{-1}) − 17.79 with a correlation coefficient of 0.998. The detection limit (signal to noise is 3) and the sensitivity are 0.01 μmol L^{-1} and 177.6 μA μmol L^{-1}, respectively. Comparing the performances of different electrochemical sensors for bromate, this detection limit is much lower than earlier reports (0.019 μmol L^{-1} [36], 0.1 μmol L^{-1} [18], 0.036 μmol L^{-1} [37], and 0.6 μmol L^{-1} [38]) in which other modified electrodes were used.

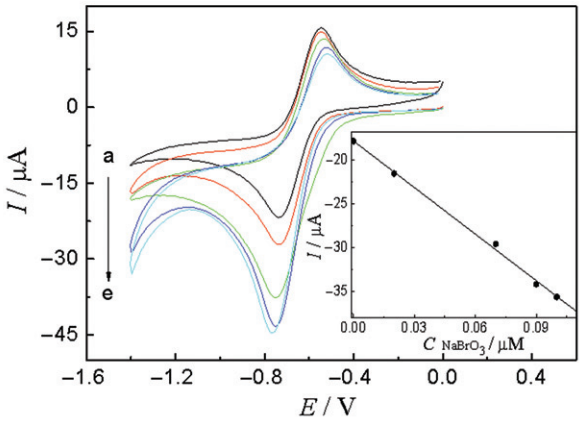


Figure 4. CVs of Co-CPE in 0.1 mol L^{-1}, pH 6.1, B–R buffer solution. Curves (**a**–**e**) containing 0, 0.02, 0.07, 0.09, and 0.10 μmol L^{-1} bromate with the scan rate as 0.10 V s^{-1}. Inset: the cathodic peak current *vs.* bromate concentration.

Compared with other modified film electrodes, the Co-CPE showed high stability. After the electrocatalytic reaction, the Co-CPE was investigated in buffer solution under the same condition as shown in figure 2, and the peak potentials and peak currents showed no obvious change, suggesting that no new materials appeared. This indicated that the cobalt complex was still stable and played a catalytic role during the reactions. When the potential range was maintained at the same range, it was stable over 200 cycles at a scan rate of $0.10\,\mathrm{V\,s^{-1}}$ and the current response remained almost unchanged. When the bulk-modified CPE was stored at room temperature for at least 2 months, the current response decreased only by 2.1%.

4. Conclusions

A new dinuclear cobalt(III) thioxanthate complex, $[Co_2(\mu\text{-}SC_2H_4OH)_2(HOC_2H_4SCS_2)_4]$, was synthesized and the structure was determined. The cobalt complex was employed to fabricate bulk-modified CPEs. This modified electrode showed excellent electrocatalytic activities toward the reduction of TCA and bromate, and the results are reproducible with a low-detection limit, which may be suitable for the quantitative analysis of environmentally hazardous materials. The advantages of the bulk-modified Co-CPE are stability, excellent catalytic activity, low-detection limit, and simplicity of preparation. The preliminary results in this study represent potential applications on electrochemical sensors.

Supplementary material

The crystallographic data of the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference no. 668639. Copies of this information can be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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