

NEW COBALT(II)-BASED ELECTROCATALYST FOR REDUCTION OF TRICHLOROACETIC ACID AND BROMATE

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A novel cobalt(II) complex *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂] (C₆H₁₁N₃ = 1-butyl-1*H*-1,2,4-triazole) was synthesized and characterized by X-ray crystallography, IR spectroscopy and elemental analysis. The cobalt center is six-coordinate, Co^{II}N₆, the axial positions being occupied by the isothiocyanate ligands and the equatorial positions by the 1-butyl-1*H*-1,2,4-triazole ligands. A conductive carbon paste electrode (Co-CPE), comprised of the studied complex and a carbon powder, was fabricated by the direct mixing method. The electrochemical behavior and electrocatalytic performance of Co-CPE were studied by cyclic voltammetry. The Co-CPE shows electrocatalytic activities toward the reduction of trichloroacetic acid and bromate. The detection limit and sensitivity are 0.01 μmol dm⁻³ and 76.86 μA μmol⁻¹ dm³ for trichloroacetic acid, and 0.02 μmol dm⁻³ and 96.19 μA μmol⁻¹ dm³ for bromate, respectively. The modified electrode features good reproducibility, high stability, low detection limit, technical simplicity and rapid preparation, which is important for practical applications.

Keywords: Cobalt complexes; Electrocatalysis; Trichloroacetic acid; Bromates; Triazole ligands; Cyclic voltammetry; X-ray diffraction.

The significant contemporary interest in organic-inorganic hybrid materials reflects both the fundamental chemistry of the rational design of complex materials and their practical applications in the fields as diverse as catalysis¹, optical materials²⁻³, membranes⁴⁻⁶ and sorption⁷⁻⁸. One synthetic strategy for the design of inorganic-organic hybrid materials is to select suitable inorganic materials and organic ligands with the structure-directing properties⁹⁻¹¹. 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, charge conductivity and electrocatalysis. Metal complexes have been well recognized for their excellent electrocatalytic properties toward the detection of

hydrogen peroxide^{12–14}, nitrite^{12–15}, bromate^{13–15} and trichloroacetic acid¹⁶, just to name a few. The electrochemistry and electrocatalysis of copper complexes with a variety of ligands have been investigated by several groups^{14,15,17–19}.

Currently, triazole ligands and their derivatives have been considered for constructing novel coordination complexes^{20–22}. These compounds are known for their rich coordination modes and wide applications as multi-dentate bridges in coordination chemistry^{20–22}. Huang et al.²³ reported the syntheses, structures and characterization of Co(II) mono- and bis(triazole) complexes. Zhu et al.²⁴ studied the crystal structures and magnetic properties of Co(II) and Ni(II) complexes with 4-(*p*-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole. Li et al.²⁵ investigated the magnetic behavior of two cobalt coordination polymers with dicyanamide and 1,2-bis(1,2,4-triazol-1-yl)ethane. Couceiro et al.²⁶ studied the structural and magnetic characterization of one-dimensional oxalato-bridged Co(II) complex with 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole ligand. To our best knowledge, however, studies of electrochemistry and electrocatalysis of cobalt complexes containing triazole are scarcely reported^{25,26}.

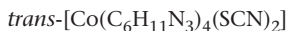
Our group has investigated the electrocatalytic activity of two Co(II) complexes *trans*-[Co(C₄H₉-bim)₂Cl₂] and *trans*-[Co(C₄H₉-bim)₂(SCN)₂] (bim = benzimidazole) towards the reduction of trichloroacetic acid. The detection limit and the sensitivity are 0.21 μmol dm⁻³ and 12.77 μA μmol⁻¹ dm³, respectively²⁷. The significance of this work is to use a new cobalt(II) complex *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂] (C₆H₁₁N₃ = 1-butyl-1*H*-1,2,4-triazole) as a bulk-modifier to fabricate a chemically modified carbon paste electrode by direct mixing. The modified electrode shows good electrocatalytic activities toward the reduction of trichloroacetic acid (TCA) and bromate. The possible mechanisms for these processes are proposed.

EXPERIMENTAL

Chemicals and Experimental Setup

All chemicals used were of analytical reagent grade and were used without further purification. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. Infrared spectra were recorded on a Nicolet 170SX spectrometer using KBr pellets. Single crystal X-ray diffraction was performed on a Bruker-Nonius diffractometer with Kappa geometry, equipped with a Bruker APEX-CCD detector. Electrochemical measurements were carried out with an Autolab PGSTAT-30 digital potentiostat/galvanostat (EcoChemie). A three-electrode cell was used in the experiments: the working electrode was a modified CPE, the counter electrode a platinum wire, and the reference electrode an Ag|AgCl, 1 M KCl. All electrode potentials reported in this work are given relative to this electrode (236.3 mV/SHE at 25 °C).

A 0.1 M Britton–Robinson (BR) buffer at pH 6.1 was used as the supporting electrolyte. The solutions were deaerated with pure nitrogen for 30 min and kept under a nitrogen atmosphere during the experiments. All the measurements were performed at room temperature (25 ± 2 °C).



Cobalt thiocyanate (175 mg, 1 mmol) and 1-butyl-1*H*-1,2,4-triazole (500 mg, 4 mmol) were dissolved in ethanol (50 ml). After stirring for 2 h, a pink precipitate formed was filtered and recrystallized from acetonitrile. Yield 76%. For $\text{C}_{26}\text{H}_{44}\text{CoN}_{14}\text{S}_2$ (675.80) calculated: 46.21% C, 6.56% H, 29.02% N; found: 46.19% C, 6.57% H, 29.05% N.

In the IR spectrum, the band at 3125 cm^{-1} was assigned to the C–H (triazole ring) stretching vibration. The bands at 1611 and 1523 cm^{-1} belong to vibrations of the triazole ring skeleton. The bands at 2958, 2932, 2873, 1465 and 1395 cm^{-1} are due to the C–H stretching and bending vibrations of the alkyl group. The band at 1258 cm^{-1} has been attributed to the C–N stretching vibration of the triazole ring.

The X-ray data collection was carried out by CCD at 20 °C, using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The structure of the title complex was solved by direct methods and refined by least squares on F_{obs}^2 using the SHELXTL software package²⁸. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed to calculated positions and allowed to ride on their parent atoms. The molecular graphics was plotted using the SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography²⁹.

CCDC 702327 contains 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, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Preparation of Co-CPE

The common carbon paste electrode (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 title complex was employed to fabricate the modified CPE due to its insolubility in water and the BR buffer solution (pH 6.1). The procedure was as follows: graphite powder (0.3 g) and the title complex (0.03 g) 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 i.d.) to a depth of 0.8 cm. Electrical contact was established with a copper rod. The surface of the Co-CPE was carefully polished on a piece of weighing paper.

The different quality ratios of the graphite powder and the title complex were investigated to determine the optimum preparation condition. The investigated graphite powder to the title complex ratios were 20:1, 14:1, 10:1, 8:1 and 5:1 (w/w). The optimum value was 10:1. When the amount of the title complex was too low, the electrochemical signal was weak. Conversely, when the amount of the title complex was high, the conductivity of the modified carbon paste electrode was low.

RESULTS AND DISCUSSION

Crystal Structure of the Title Complex

The molecular structure of *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂] is shown in Fig. 1a and the crystal structure with the atomic numbering scheme in Fig. 1b. Crystal data and structure refinement are listed in Table I. The cobalt atom is six-coordinate, with two isothiocyanate-nitrogen atoms in *trans* positions and the four 1-butyl-1*H*-1,2,4-triazole ligands in the equatorial plane. The Co–N bond lengths (Co(1)–N(7) 2.096(5) Å, Co(1)–N(7)^{#1} 2.096(5) Å, Co(1)–N(4)^{#1} 2.140(5) Å, Co(1)–N(4) 2.140(5) Å, Co(1)–N(3) 2.158(4) Å and Co(1)–N(3)^{#1} 2.158(4) Å) are comparable with those found in the similar structures reported earlier^{23,30}. The bond angles around the Co center N–Co(1)–N (N(7)–Co(1)–N(4)^{#1} 89.9(2)°, N(7)–Co(1)–N(4) 90.1(2)°, N(7)–Co(1)–N(3) 91.3(2)°, N(4)–Co(1)–N(3) 88.2(2)°, N(7)–Co(1)–N(3)^{#1} 88.7(2)° and N(4)–Co(1)–N(3)^{#1} 91.8(2)°) are also consistent with the literature data^{23,30}. The 1-butyl-1*H*-1,2,4-triazole skeleton is planar, as expected, and the dihedral angle between the adjacent triazole planes is 76.31°. The thiocyanate ligand is almost linear (178.1(3)° for N(7)–C(13)–S(1)). There is a potential weak hydrogen bond intermolecular interaction, with the donor–acceptor distance of 3.6651 Å for C(7)⋯S(1). Finally, five types of π – π stacking interactions are documented. In the solid state, all the above intermolecular interactions stabilize the crystal structure.

Electrochemical Behavior of the Co-CPE

The electrochemical behavior of the Co-CPE was investigated by cyclic voltammetry in the aqueous solution. We chose a 0.1 M aq. KCl, 0.1 M Britton–Robinson buffer (pH 7) and 0.1 M phosphate buffer (pH 7) as supporting electrolytes. The modified electrode in the BR buffer solution showed a strong current response and a symmetric peak shape. Then, we investigated the electrochemical behavior of the modified CPE in the BR buffer at pH 4–8 and found that the electrochemical signal was relatively stable at pH 6.1. Therefore, we studied the electrochemical behavior and electrocatalytic properties of the modified CPE in 0.1 M BR buffer solution at the latter pH value.

The cyclic voltammogram (CV) of the Co-CPE is presented in Fig. 2. In the potential range from 0 to –1.6 V, there was no redox response at the bare CPE. The CV scan with the modified Co-CPE, however, showed a well-defined redox couple at $E^0 = -0.793$ V assigned as Co(II)/Co(I). The

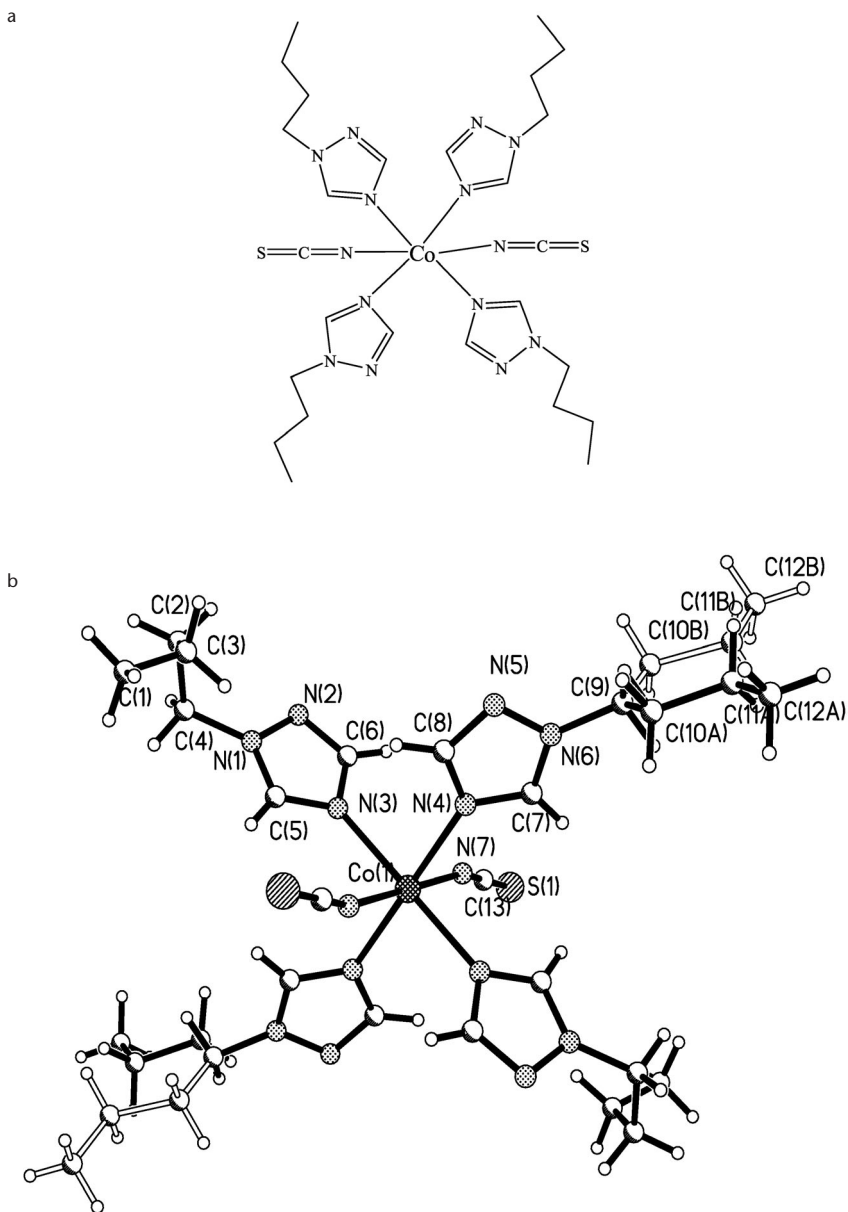


FIG. 1
a The schematic structure of *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂]. b The molecular structure of *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂] showing the atom numbering scheme

cathodic to anodic peak separation, $\Delta E = 0.112$ V and the peak-current ratio $i_{pc}/i_{pa} = 1.08$ indicate that the electrochemical behavior of the title complex on the CPE electrode is quasireversible.

The scan rate dependence of the electrochemical behavior of the Co-CPE is presented in Fig. 2. Varying the scan rate from 0.03 to 0.30 V s⁻¹, the

TABLE I
Crystal data and structure refinement for *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂]

Empirical formula	C ₂₆ H ₄₄ CoN ₁₄ S ₂
M_r	675.80
T , K	293(2)
λ , Å	0.71073
Crystal system, space group	triclinic, $P\bar{1}$
a , Å	8.730(2)
b , Å	8.994(2)
c , Å	12.823(2)
α , °	77.858(3)
β , °	76.728(3)
γ , °	70.515(3)
Volume, Å ³	914.0(2)
Z	1
d_{calc} , g cm ⁻³	1.228
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.621
$F(000)$	357
θ range for data collection, °	1.65–28.28
Limiting indices	$-11 \leq h \leq 10$, $-11 \leq k \leq 9$, $-16 \leq l \leq 17$
Reflections collected/unique	5865/4168 ($R_{\text{int}} = 0.0375$)
Completeness to $\theta = 28.28$, %	91.9
Data/restraints/parameters	4168/0/192
Goodness-of-fit on F^2	0.941
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0793$, $wR_2 = 0.2007$
R indices (all data)	$R_1 = 0.1837$, $wR_2 = 0.2624$
Largest diff. peak and hole, e Å ⁻³	0.410 and -0.324

cathodic peak potentials shifted gradually in the negative direction and the anodic counter peak shifted in the positive direction. The peak current dependence on the scan rate is shown in the inset of Fig. 2. The anodic and cathodic currents are proportional to the scan rate, suggesting that the redox process is confined to the electrode surface.

Electrocatalytic Reduction of Trichloroacetic Acid on the Co-CPE

Organohalides are serious environmental pollutants. Trichloroacetic acid is formed in the course of water chlorination. Electrochemical oxidation or reduction is an effective way to handle pollutants of environment¹⁶. Some insoluble metal complexes containing redox mediators can be used for electrocatalysis. The electrocatalytic activity of the Co-CPE towards TCA is shown in Fig. 3. On the addition of TCA into the electrolyte solution (curves *a–e*), the anodic and cathodic peak potentials remained unchanged, while there was a dramatic enhancement of the cathodic peak current accompanied by decreasing anodic peak current. For the TCA concentration of $0.20 \mu\text{mol dm}^{-3}$, the reduction peak current reached its maximum value,

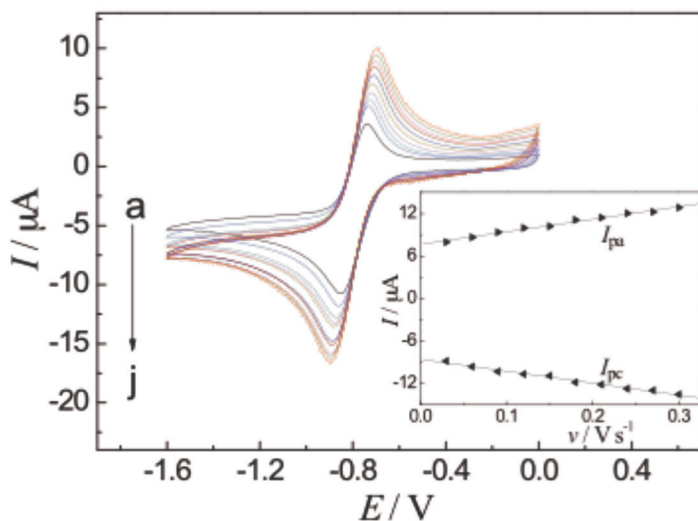
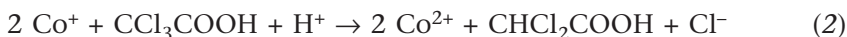


FIG. 2

Cyclic voltammograms of the Co-CPE in 0.1 M BR buffer solution at pH 6.1. Curves *a–j* correspond to the scan rates 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27 and 0.30 V s^{-1} , respectively. Inset: the scan rate dependence of the cathodic and anodic peak currents

while the oxidation peak current was reduced almost to zero, pointing to a strong catalytic effect. The likely reaction steps involved could be described by the following equations^{16,31}:



The inset of Fig. 3 shows that the catalytic current increases linearly with the TCA concentration in the range 0.02–0.20 $\mu\text{mol dm}^{-3}$. The linear regression equation is I_{pc} (in μA) = $-76.86 C$ (in $\mu\text{mol dm}^{-3}$) – 10.35, with a correlation coefficient of 0.998. The detection limit (given the signal-to-noise ratio is 3) and the sensitivity are 0.01 $\mu\text{mol dm}^{-3}$ and 76.86 $\mu\text{A } \mu\text{mol}^{-1} \text{dm}^3$, respectively. Comparison with our previous work on the TCA electrocatalytic reduction with a similar 1-butyl-1*H*-benzo[d]imidazole cobalt complex proves that the latter detection limit is significantly lower than the reported value²⁷.

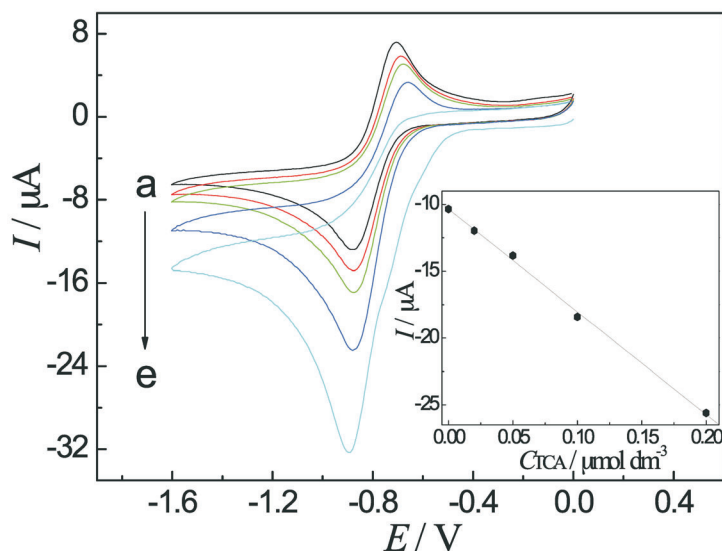


FIG. 3

Cyclic voltammograms of the Co-CPE in 0.1 M BR buffer solution at pH 6.1, containing trichloroacetic acid at concentrations 0, 0.02, 0.05, 0.10 and 0.20 $\mu\text{mol dm}^{-3}$ (a–e). Scan rate 0.15 V s^{-1} . Inset: the dependence of the cathodic peak current on the TCA concentration

Electrocatalytic Reduction of Bromate at the Co-CPE

Bromate is a disinfectant by-product contaminant found in drinking water, being formed during the ozonation of source water containing bromide ions. The overpotential for bromate reduction is high and therefore an efficient electrocatalyst would be beneficial¹⁴. Here we document that the reduction of bromate can in fact readily be catalyzed by the Co-CPE in the 0.1 M BR buffer solution at pH 6.1. As shown in Fig. 4 by curves *a–e* on the addition of bromate, the cathodic and anodic peak potentials do not vary. The cathodic peak current increases, reaching its maximum value for the concentration of bromate 0.15 $\mu\text{mol dm}^{-3}$. The value of the anodic peak current then becomes reduced almost to zero at this bromate concentration, revealing that the Co-CPE features excellent electrocatalytic activity also for this process. The likely reaction steps are as follows^{14,31}:

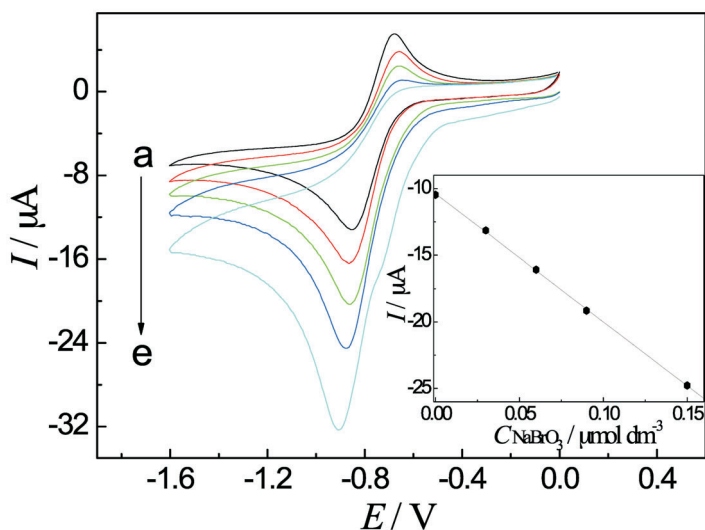
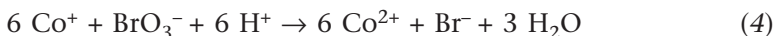


FIG. 4

Cyclic voltammograms of the Co-CPE in 0.1 M BR buffer solution at pH 6.1, containing bromate at concentrations 0, 0.03, 0.06, 0.09 and 0.15 $\mu\text{mol dm}^{-3}$ (*a–e*). Scan rate 0.15 V s^{-1} . Inset: the dependence of the cathodic peak current on the bromate concentration

The inset of Fig. 4 shows that the catalytic current rises linearly with the bromate concentration in the range 0.03–0.15 $\mu\text{mol dm}^{-3}$. The linear regression equation is I_{pc} (in μA) = $-96.19 C$ (in $\mu\text{mol dm}^{-3}$) – 10.37, with a correlation coefficient of 0.999. The detection limit (given the signal-to-noise ratio is 3) and the sensitivity are 0.2 $\mu\text{mol dm}^{-3}$ and 96.19 $\mu\text{A } \mu\text{mol}^{-1} \text{ dm}^3$, respectively. Various other modified electrodes as electrochemical sensors for bromate reported in the literature show higher detection limits, viz. 0.1 (ref.¹⁷), 0.036 (ref.³²) and 0.6 $\mu\text{mol dm}^{-3}$ (ref.³³).

Compared with other modified film electrodes, the studied Co-CPE features high stability. After the electrocatalytic reaction, as described above, the peak potentials and peak currents (Fig. 2) remained unchanged, implying that no new materials developed and the title complex remained stable during the electrocatalytic reactions. When the potential range was maintained the Co-CPE was stable over 100 cycles at a scan rate of 0.15 V s^{-1} and its current response remained unaffected. Storing the Co-CPE at room temperature for at least 2 months caused the current response to decrease only by 2.1%.

CONCLUSIONS

In summary, the new complex *trans*-[Co(C₆H₁₁N₃)₄(SCN)₂] in the modified carbon paste electrode, Co-CPE, shows remarkable electrocatalytic activities toward the reduction of trichloroacetic acid and bromate. The detection limit and sensitivity are 0.01 $\mu\text{mol dm}^{-3}$ and 76.86 $\mu\text{A } \mu\text{mol}^{-1} \text{ dm}^3$ for trichloroacetic acid, and 0.02 $\mu\text{mol dm}^{-3}$ and 96.19 $\mu\text{A } \mu\text{mol}^{-1} \text{ dm}^3$ for bromate, respectively. The results are reproducible, the detection limits being lower than encountered in the literature for similar sensors. This makes the bulk-modified Co-CPE suitable for the quantitative analysis of environmentally hazardous materials. Its advantages are stability, good catalytic activity, low detection limit and simplicity of preparation

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