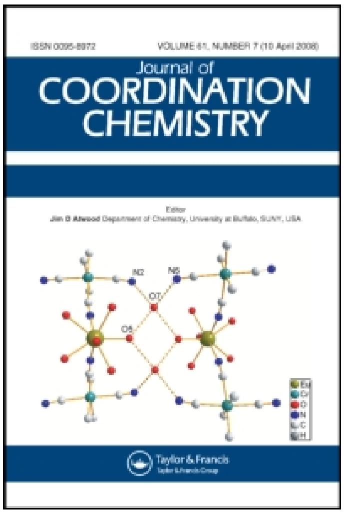

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SYNTHESIS, CHARACTERIZATION, STRUCTURE AND POSSIBLE CATALYTIC PROPERTIES OF *CIS*-OXALATO(1,4,8,11-TETRAAZACYCLOTETRADECANE)COBALT(III) NITRATE

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SYNTHESIS, CHARACTERIZATION, STRUCTURE AND POSSIBLE CATALYTIC PROPERTIES OF *CIS*-OXALATO(1,4,8,11-TETRAAZACYCLOTETRADECANE)COBALT(III) NITRATE

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A new complex of cobalt(III) with 1,4,8,11-tetraazacyclotetradecane (cyclam) and oxalato ion as a bidentate ligand was prepared and characterized by elemental analysis, IR, electronic and ^{1}H NMR spectroscopy and cyclic voltammetry. X-Ray analysis has shown that this compound crystallizes in the orthorhombic system, space group *Pccn*, with $a = 8.583(1)$, $b = 12.854(2)$, $c = 14.944(1)$ Å, $V = 1649.3(4)$ Å^3, $Z = 4$, $R = 0.512$, $R_w = 0.545$, and has a crystallographic two-fold rotation axis. The complex was identified as *cis*-oxalato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) nitrate, $[Co(ox)cyclam]NO_3$ (oxH_2 = oxalic acid), and it can be described in terms of a *cis* octahedral geometry with a folded cyclam configuration around the cobalt atom with the oxalato ion occupying the remaining two sites. Cyclic voltammetric data suggest a large stability for this compound, as well as its possible catalytic effect on electrochemical CO_2 reduction.

KEYWORDS: Cyclam, cobalt(III), oxalate, X-ray structure, catalysis, electrochemistry

INTRODUCTION

Many studies[1–6] of cobalt(II) and cobalt(III) complexes with cyclam and two monodentate ligands have been published. Most of them are described in Lindoy's monograph on macrocyclic ligand complexes.[7] As far as we know, only two cases of cobalt(III) cyclam complexes have been reported containing, besides cyclam, a coordinated bidentate ligand, *i.e.*, ethylenediamine[1] or carbonato ion.[3] With

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monodentate ligands, however, cobalt(III) forms stable complexes with a *trans* configuration.[2] A *trans* disposition allows a planar arrangement of the macrocycle resulting in greater stability of these complexes in comparison with the corresponding *cis* isomers. The *cis* configuration can be favoured by use of a suitable bidentate ligand.[3] Both mononuclear[8] and dinuclear[9] cobalt cyclam complexes have already been observed to act catalytically in some electrochemical processes. We have tried to prepare a cobalt(III) cyclam oxalato complex and to check its catalytic abilities.

EXPERIMENTAL

Cis-[Co(ox)cyclam]NO$_3$

To 1 mmol (184 mg) of potassium oxalate dyhidrate, dissolved in a minimum amount of water, was added an aqueous suspension (50 cm^3) of 1 mmol (200 mg) of cyclam and 1 mmol (291 mg) of cobalt(II) nitrate hexahydrate. The mixture was heated on a water bath at 60°C for 3 hours with continuous stirring and with air-bubbling through the solution. At the end of the reaction, purple crystals were formed. The mixture was allowed to cool to room temperature and the purple crystalline product was filtered off. Yield: 150 mg (59%). *Anal.*: calcd. for $CoC_{12}H_{24}N_5O_7$: C, 35.12; H, 5.91; N, 17.10%. Found: C, 35.43; H, 5.73; N, 17.31%.

Analytical method

Some 2 µl of electrolyte were analysed using a Varian 3700 GC gas chromatograph with FID detector and Varian 4400 integrator by using a 2 m × 2 mm column packed with carbowax 1540 at 25°C. A mixture of hydrogen and nitrogen was used as carrier gas.

Measurements

Electronic spectra were recorded with a GBC UV/VIS 911 A spectrophotometer. Infrared spectra were run on a Perkin Elmer 317 25 × FTIR spectrophotometer, using the KBr disk technique. ^1H nuclear magnetic resonance spectra were run with a Bruker AM 600 Spectrospin spectrometer, in D_2O-D_2SO_4 (20:1) solution. Methanol was used as internal standard with $\sigma = 6.66$. Since *cis*-[Co(ox)cyclam]NO_3^- is only partly soluble in D_2O and thus inconvenient for NMR measurements, the corresponding chloride, being more soluble in D_2O, was used. This was made by passing the nitrate complex through a column filled with Dowex 1 × 4 (200–400 mesh) resin in the chloride form followed by elution with water and evaporation of the coloured eluate to dryness on a vacuum evaporator. The complex was then dried at 105°C. *Anal.*: calcd. for $CoC_{12}H_{26}N_4O_5Cl$: C, 35.97; H, 6.54; N, 13.98%. Found: C, 36.12; H, 6.14; N, 14.08%. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated with Hg[Co(SCN)$_4$]. Molar magnetic susceptibility in the temperature range 77–300 K was $440 \pm 40 \times 10^{-6}$ cm^3 mol^{-1}. Diamagnetic corrections of -204×10^{-6} cm^3 mol^{-1} were used for TIP estimation.

Rotating ring-disc electrodes with Pt ring and GC disc (Tacusel) were prepared as follows: the Pt ring was cleaned by immersion in 10% H_2SO_4 for 2 minutes. The glassy carbon electrode, serving as a test electrode, was mechanically cleaned by fine emery paper of decreasing grain size, followed by polishing with alumina. The electrode was cleaned in 18 MΩ water in an ultrasonic bath. The polished electrode, with a hydrophobic and mirror like surface, was immediately immersed in 10% H_2SO_4 for 2 minutes, then washed with 18 mΩ water and placed in a cell. The electrode obtained was checked by cyclic voltammetry in 0.5 mol dm^{-3} $NaHCO_3$ solution. The GC electrode was then immersed in a 10^{-4} mol dm^{-3} solution of $[Co(ox)cyclam]NO_3$ for 30 minutes. Cyclic voltammetry was performed with a sweep rate of 50 mV/s, and the potential ranged from −1.4 V to 0.4 V *vs* SCE (saturated calomel electrode). The electronic equipment consisted of a PAR potentiostat/galvanostat (model 273) and a Hewlett Packard X–Y recorder (model PM 8033). The experiments were carried out at 20 ± 2°C. The electrolyte had been deoxygenated by nitrogen gas bubbling before the experiment started.

X-ray crystal structure analysis

Single crystals suitable for X-ray structure determination were grown by slow evaporation of the reaction mixture solution to which ether was added. Diffraction data were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromated MoKα radiation at room temperature. Unit cell parameters were determined from 25 high angle reflections. Pertinent crystallographic parameters are given in Table 1. Reflection data were corrected for Lorentz-polarization effects, but not for absorption. The structure was solved by the heavy atom method. Refinement was carried out by block-diagonal least-squares methods, with anisotropic thermal parameters; hydrogen atoms, located from ΔF map, were isotropically introduced into the last refinement cycle. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$. Calculations were carried out on a FACOM-M 780 computer using the UNICS III[10] program system. Positional parameters of non-hydrogen atoms are given in Table 2. Atomic scattering factors were taken from the literature.[11]

Table 1 Crystal data and data collection details[a] for $[Co(ox)cyclam]NO_3$.

Formula	$C_{12}H_{24}N_5O_7Co$	cryst size/mm	0.2 × 0.4 × 0.3	
M	409.29	μ (Mo Kα)/cm^{-1}	10.8	
Crystal system	orthorhombic	scan mode	$\theta - 2\theta$	
Space group	*Pccn* (No. 56)	2θ range(°)	2.5 - 52	
a/Å	8.583(1)	data collcd.	2407	
b/Å	12.859(2)	No unique data with		
c/Å	14.944(1)	$[Fo] > 3\sigma([Fo])$		1350
V/Å^3	1649.3(4)	R^b		0.512
Z	4	R_w ^{b}		0.545
Dx/g m^{-3}	1.65	λ (Å)		0.71073

[a] Common data: scan speed 4° min^{-1}; weighting scheme $1/[\sigma(F)]^2$. [b] $R = \Sigma|(\Delta F)|/\Sigma|F_o|$; $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{1/2}$.

Table 2 Fractional positional parameters (× 10^5) and thermal parameters of Non-hydrogen Atoms for [Co(ox)cyclam]NO_3*.

atom	*x/a*	*y/b*	*z/c*	$B_{eq}/\text{Å}^2$**
Co	25000 (0)	25000 (0)	17527 (6)	1.46 (2)
NN	25000 (0)	- 25000 (0)	16556 (46)	3.59 (19)
ON1	25000 (0)	- 25000 (0)	24358 (40)	7.43 (26)
ON2	13350 (80)	- 21339 (43)	13227 (38)	10.06 (23)
O1	32512 (43)	33723 (26)	26947 (20)	2.05 (9)
O2	30562 (49)	35288 (31)	41638 (23)	3.51 (12)
N1	34271 (52)	34529 (31)	8646 (25)	1.73 (10)
N2	5007 (50)	32542 (33)	17210 (29)	2.04 (10)
C1	51202 (68)	32469 (44)	8439 (37)	2.58 (14)
C2	31590 (71)	45931 (41)	10354 (34)	2.46 (14)
C3	14779 (79)	48958 (41)	10304 (36)	2.74 (16)
C4	5317 (70)	44179 (42)	17827 (40)	2.80 (15)
C5	- 3540 (67)	29002 (41)	9046 (34)	2.32 (14)
C6	28726 (66)	30495 (41)	34646 (31)	2.32 (15)

* Values in parentheses are estimated standard deviations.

** The equivalent isotropic thermal parameter is taken as $B_{eq} = 4/3\ (\Sigma_i \Sigma_j \beta_{ij} a_i a_j)$.

RESULTS AND DISCUSSION

Synthesis

Cis-[Co(ox)cyclam]NO_3 was obtained by direct synthesis with Co(II) to Co(III) oxidation by air. The same complex was obtained by substitution of two oxalato ligands in $K_3[Co(ox)_3]$[12] by cyclam but in about half the yield of the former synthesis. No other Co(III) cyclam complex with oxalato ligand under the described conditions was obtained. This was verified by passing the reaction mixture through a column filled with cation exchange resin (Sephadex C 25). Only one purple zone was eluated by KNO_3, the microanalysis of which was consistent with the mononuclear complex [Co(ox)cyclam]NO_3.

Structure of cis-[Co(ox)cyclam]NO_3

The unit cell consists of complex cations, $[Co(ox)cyclam]^+$, and NO_3^- ions. Figure 1 is an ORTEP diagram of the complex cation. The compound has a two-fold crystallographic rotation axis running through the cobalt atom and nitrate ion (nitrogen and one oxygen atom). Selected interatomic distances and angles are given in Table 3. The cobalt atom is coordinated to the four nitrogens of cyclam and to two oxygens from different carbons of the oxalato ion. The cyclam ring configuration is folded, as predicted on the basis of minimum strain arguments[2] and by analogy with the known structure of *cis*-[Cocyclam(en)]$Cl_3 \cdot 3H_2O$.[1]

Five-membered chelate rings adopt a *gauche*, and six-membered rings a *chair* conformation. The Co-N (cyclam) bonds, average 1.974 ± 0.004 Å, are slightly shorter then the corresponding ones in the ethylenediamine complex, which average 1.996 ± 0.002 Å. The N-Co-N angle of the five-membered ring (86.5(2)°) is, as expected, smaller than that of the six membered one (91.7(2)°). Within the six-membered rings the Co-N-C angles of 115.4(3)° and 118.3(3)° are also smaller than the corresponding ones found in the ethylenediamine analogue of close to 120.6°. These differences suggest that the bidentate oxalato ligand has a less

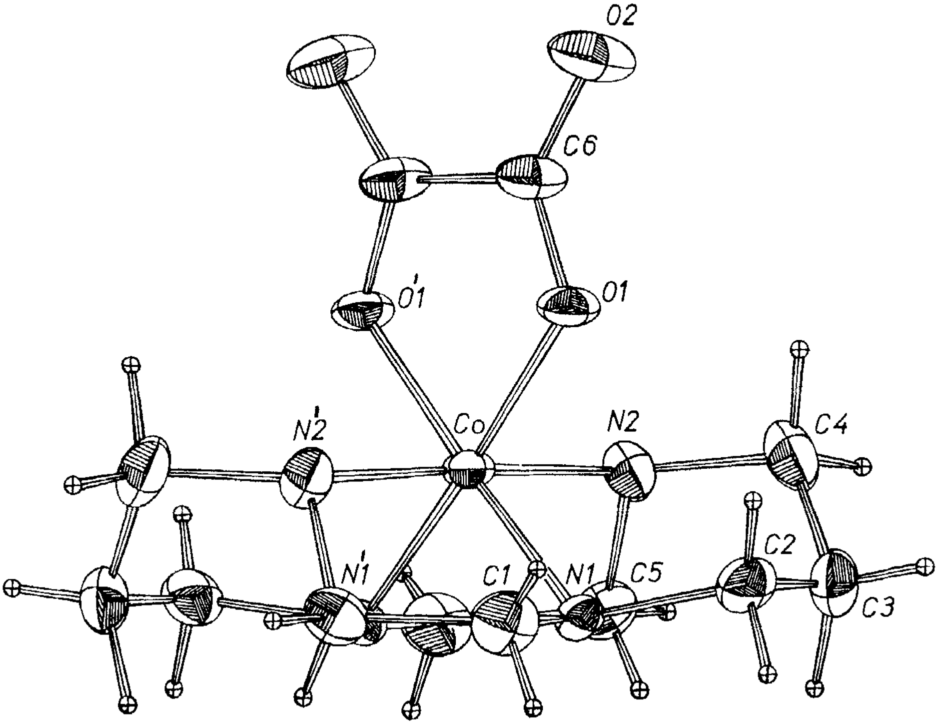

Figure 1 ORTEP diagram of the [Co(ox)cyclam]$^+$ cation.

strained structure and the coordination around the central cobalt ion is consequently a less distorted octahedron. Hydrogen atoms bonded to carbons were located in their calculated positions. Difference Fourier syntheses did not show peaks corresponding to H-N clearly and these were not included in structure factor calculations.

This structure is rather different from the structure of the previously published dinuclear $[Ni_2ox(cyclam)_2](NO_3)_2$[13] complex in which the oxalate anion acts as a bridging *bis*-bidentate ligand.

Spectroscopic and Magnetic Properties

Electronic absorption spectra of *cis*-$[Co(ox)cyclam]NO_3$ are typical for d-d transitions in Co(III) complexes with a CoN_4O_2[14] chromophore with two absorption maxima in the visible region at 512 nm (ε = 19.23 m^2 mol^{-1}) and 364 nm (ε = 25.18 m^2 mol^{-1}). These maxima, in comparison with those of $[Co(ox)(en)_2]Cl$ H_2O[15] [maxima of which are at 500 nm (ε = 10.3 m^2 mol^{-1}) and 360 nm (ε = 15.0 m^2 mol^{-1})], as expected, are shifted to longer wavelengths and have greater molar absorption coefficients.[3] The similarity between the absorption spectra of the

Table 3 Selected Bond distances and angles for [Co(ox)cyclam]NO_3.

	Bond distances (Å)		
a) Part of bidentate ligand			
Co—O1	1.912(3)	O1—C6	1.266(6)
C6—O2	1.223(6)	C6—C6′	1.551(8)
b) Macrocycle			
Co—N1	1.974(4)	Co—N2	1.972(4)
N1—C1	1.477(7)	N1—C2	1.506(7)
N2—C4	1.499(7)	N2—C5	1.495(7)
C1—C5′	1.491(8)	C2—C3	1.494(9)
C3—C4	1.517(8)		
c) Nitrate ion			
ON1—NN	1.166(9)	ON2—NN	1.212(7)
	Bond Angles (°)		
a) Coordination sphere of Co			
O1—Co—N1	89.7(2)	O1—Co—N2	91.3(2)
O1—Co—N1′	174.4(2)	O1—Co—N2′	90.7(2)
N1—Co—N2	91.7(2)	N1—Co—N1′	95.5(2)
N1—Co—N2′	86.5(2)	N2—Co—N2′	177.3(2)
O1—Co—O1′	85.2(1)		
b) Macrocycle			
Co—N1—C1	107.4(3)	Co—N1—C2	115.4(3)
C1—N1—C2	109.2(4)	Co—N2—C4	118.3(3)
Co—N2—C5	107.3(3)	C4—N2—C5	111.3(4)
N1—C1—C5′	108.0(5)	N1—C2—C3	113.6(5)
C2—C3—C4	114.1(5)	C3—C4—N2	111.6(5)
N2—C5—C1′	106.6(4)		
c) Part of bidentate ligand			
Co—O1—C6	113.0(3)	O2—C6—O1	125.3(5)
O1—C6—C6′	113.9(4)	O2—C6—C6′	120.8(4)
c) Nitrate ion			
ON1—NN—ON2	114.2(4)		

complex at the time of preparation and after 2 months indicated its high stability. The infrared spectrum of [Co(ox)cyclam]NO_3 complex displays bands characteristic of the oxalato ion as a bidentate ligand[16]: ν_{asym}(O-C-O) at 1677 s, 1705 m; ν_{sym}(O-C-O) at 1420 s, 1407 m, and δ(O-C-O) at 1264 w cm^{-1}, where s, m, and w refer to strong, medium and weak intensities, respectively. The use of infrared spectroscopy as a diagnostic method for *cis* or *trans* coordination suggests that vibrational modes of both secondary amine and methylene groups appearing in the 800–900 cm^{-1} region may be used. Being less symmetrical than *trans* isomers, *cis* isomers exhibit at least five bands spread between 800 and 910 cm^{-1}, whereas no *trans* complex shows more than three bands[17] in that region. The appearance of bands at 800, 828, 854, 880, and 894 cm^{-1} in the infrared spectrum of the newly synthesized complex indicates *cis* configuration. The N-H stretching region displays two peaks of medium intensity at 3234 and 3113 cm^{-1} which is consistent with the proposed structure, whereas bands of ionic nitrate[18] are located at 2415 w, 1386 s, and 816 m cm^{-1}. Although X-ray analysis did not show peaks for the amine protons clearly, there are resonance bands indicating two non-equvalent pairs of protons[3] in the amine proton region of the well-resolved ^{1}H NMR spectrum. The resonance at 5.78 ppm arising from the two amine protons adjacent to the oxalato ligand is assigned to *cis* configuration. The resonance at 4.61 ppm can be related to the *cis*-configuration of two amine protons in the environment of the methylene groups and *trans* related to the oxalato ligand. These conclusions undoubtedly confirm the actual *cis* configuration as a result of minimum strain arguments[2] for cyclam as a cyclic ligand. These observations could be explained as being due to the anisotropy of Co(III).[19] In the region of aliphatic protons, the resonances at 1.27 ppm (2H, *d*, J ~ 16 Hz) and at 1.39 ppm (2H, *q*, J ~ 16 Hz) could be assigned, according to the chemical shifts, to the methylene groups remote from the nitrogens (*i.e.*, C_3 and C_3' hydrogens). The remaining, rather tentative, partial assignments, mostly based on characteristic coupling patterns are as follows: the resonances at 2.21 ppm (2H, *fd*, J ~ 13 Hz) and at 2.05 ppm (2H, *fd*, J ~ 13 Hz) could be assigned to one of the -N-$(CH_2)_2$-N- groups and those at 1.90 ppm (4H, m) to the remaining -N-$(CH_2)_2$-N- group; the resonances at 2.14 ppm (2H, *t*, J = 13.5 Hz), 2.32 ppm (2H, *fd*, J~13 Hz), 1.76 ppm (2H, *d*, J = 13.5 Hz) and 1.68 ppm (2H, *d*, J = 13 Hz) could be assigned to the protons of the -N-$(CH_2)_3$-N- moiety α to the nitrogens.

The molar magnetic susceptibility of the complex shows the absence of any paramagnetic species. The sample exibits a TIP characteristic for diamagnetic Co(III) compounds.

Electrochemical Behaviour

The effect of $[Ni(cyclam)]^{2+}$ on CO_2 reduction had been reported[20] and it was noticed that CO_2 reduction was catalysed by $[Ni(cyclam)]^{2+}$ complex in aqueous solution. In order to investigate the possible catalytic properties of $[Co(ox)cyclam]^+$, $[Ni(cyclam)]^{2+}$ was used as a reference substance. Figure 2 represents CV of a stationary GC electrode in the absence and in the presence of $[Ni(cyclam)]^{2+}$ (Figure 2a) and $[Co(ox)cyclam]^+$ (Figure 2b). In neither case was electron exchange between the complex and electrode surface observed. It is also clear from the same Figure that hydrogen evolution was decreased in the presence of CO_2 and apparently decreased in the presence of CO_2 and each of the complexes. These observations can be attributed to CO_2 reduction being favoured in the presence of the complexes. Under the same experimental conditions we can conclude from Figure 2 that $[Ni(cyclam)]^{2+}$ and $[Co(ox)cyclam]^+$ exhibit the same electrochemical behaviour. The potential of the reaction is slightly shifted to negative values. Gas chromatographic analysis of the liquid phase after long term electrolysis shows that methanol is the main product of CO_2 reduction for both complexes under the described experimental conditions. The concentration of complexes was 10^{-5} mol dm^{-3}. After four hours of electrolysis at a potential of −1.2V, the obtained concentration of CH_3OH for both complexes was about 3 10^{-6} mol dm^{-3}. In reference 20 it was reported that the main product of CO_2 reduction in the presence of $[Ni(cyclam)]^{2+}$ is CO, which presence was not confirmed under our experimental conditions. The disk ring measurements were used to verify the amount of evolved hydrogen in the absence and in the presence of CO_2 and complexes. The rotating GC disk electrode was used under the experimental conditions described in Figure 2 and the potential of the Pt-ring was selected at −0.35V in order to obtain conditions for the diffusion control of the hydrogen oxidation. The results for both of the complexes are presented in Figure 3. The cathodic directions are presented only, to avoid confusion of anodic curves not essential for CO_2 reduction. It is clear for $[Ni(cyclam)]^{2+}$ (Figure 3a) and $[Co(ox)cyclam]^+$ (Figure 3b) that at the rotating

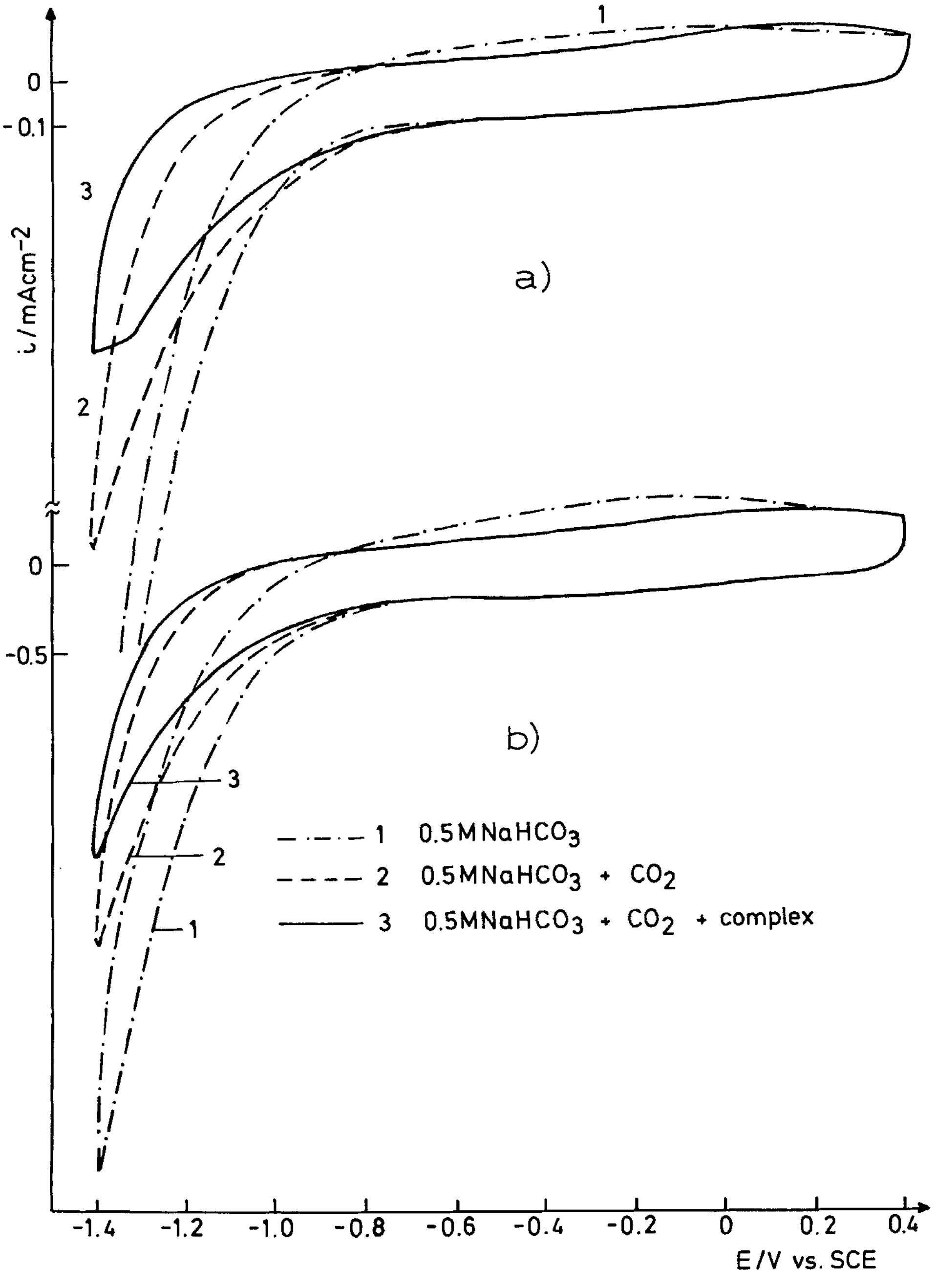

Figure 2 (a) Cyclic voltammograms of a GC electrode in 0.5 mol dm^{-3} NaHCO$_3$ solution (– · – · –) in the presence of CO$_2$ (------) and in the presence of [Ni(cyclam)]$^{2+}$ (———); (b) the same as above in the presence of [Co(ox)cyclam]$^{+}$ (———). Sweep rate = 100 mV/s.

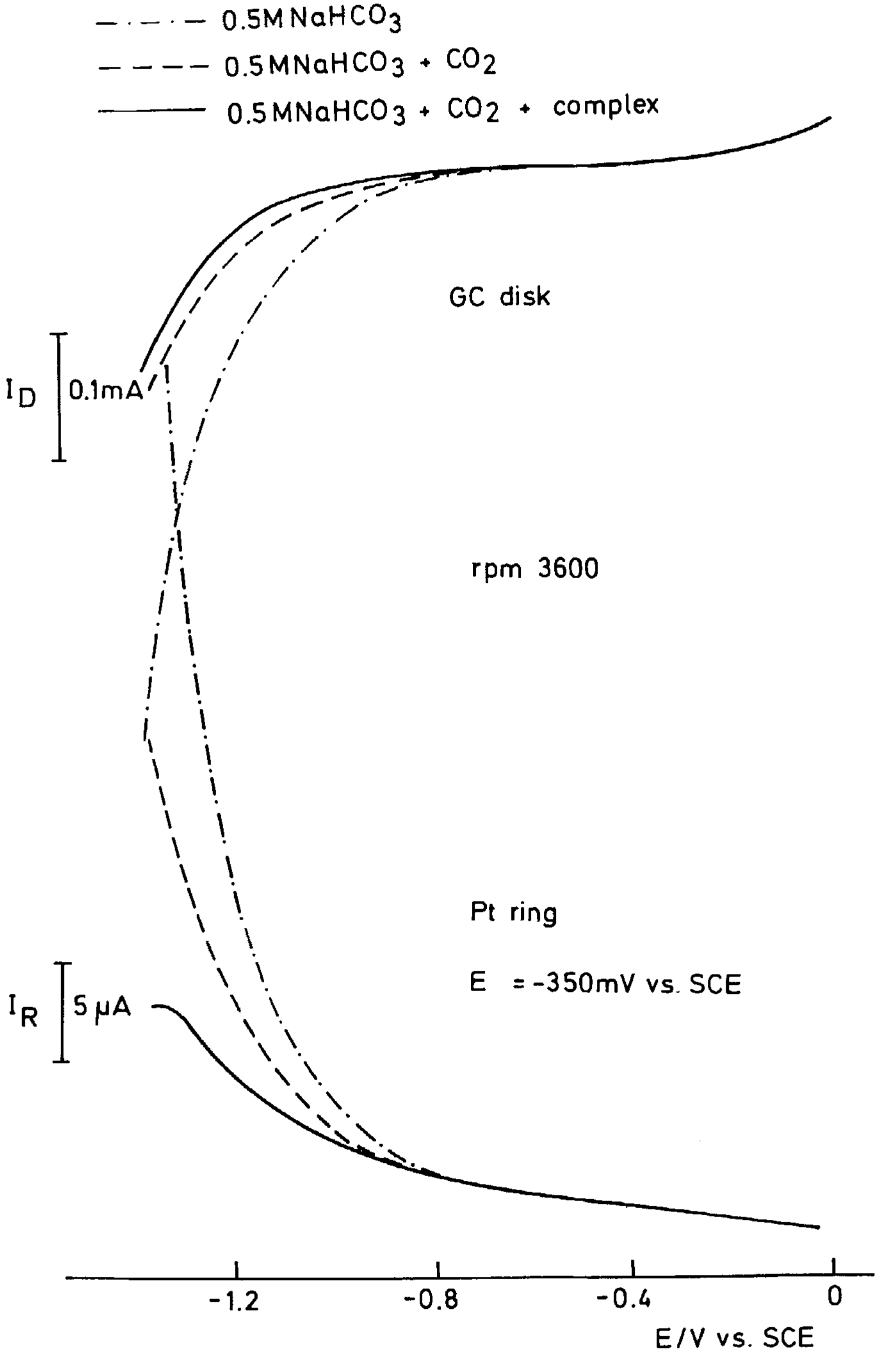

Figure 3 (a) Cyclic voltammograms of a rotating GC electrode in 0.5 mol dm^{-3} $NaHCO_3$ solution (– · – · –) in the presence of CO_2 (------) and in the presence of $[Ni(cyclam)]^{2+}$ (———);

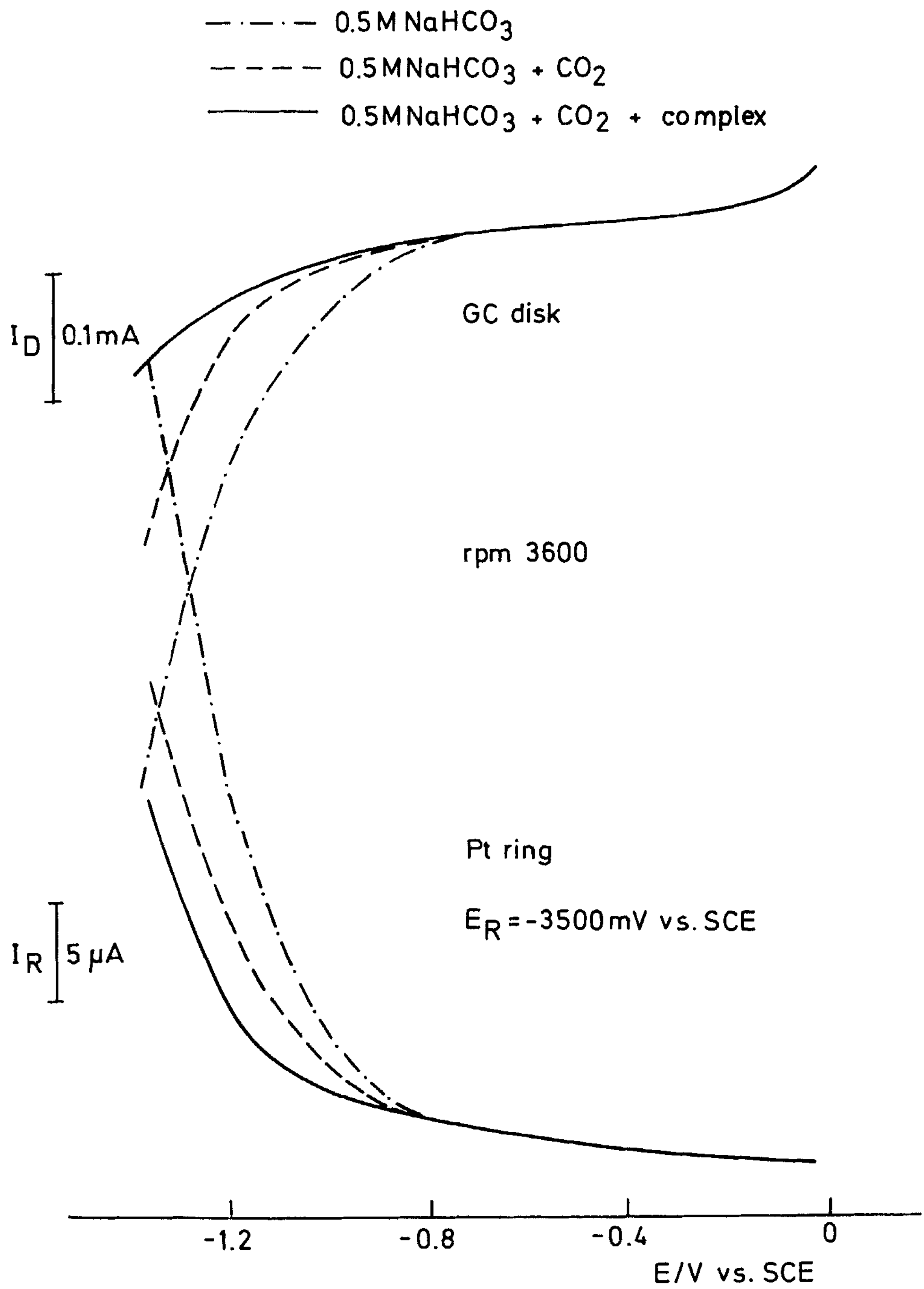

Figure 3 (b) the same as above in the presence of [Co(ox)cyclam]$^+$ (———). Sweep rate = 50 mV/s, E_r = -0.35V, collection efficiency N = 0.19, rpm: 2500.

GC electrode these complexes exhibit similar electrochemical behaviour as described for the stationary electrode. The Pt ring also exhibits decreased oxidation of hydrogen in the presence of CO_2 and each of the complexes. From Figures 2 and 3 it is obvious that the decrease of hydrogen evolution could be attributed to favoured CO_2 reduction. The potential shift to negative values at the disc electrode is probably due to the formation of some kind of CO species. Methanol found in the liquid phase indicates that the CO_2 reduction process exists. The most surprising fact was that from Figure 3 there was no evidence for any Faradaic process between the complex and the GC electrode surface. In order to explain the behaviour of $[Co(ox)cyclam]^+$, the current scale was expanded ten times and the CV was recorded at the GC electrode in the presence of $[Co(ox)cyclam]^+$ under nitrogen (Figure 4a). With the expanded scale (with shorter negative limits of potential) a Faradaic process exists to a certain extent between the GC electrode and the complex ion. It is not possible simultaneously to verify hydrogen evolution, CO_2 reduction and the Faradaic process between complex and GC electrode with the same current scale. After 4 hours of electrolysis (CO_2 reduction) in the presence of $[Co(ox)cyclam]^+$ at $-1.2V$, the first CV at the GC electrode was recorded and is presented in Figure 4b. Anodic and cathodic peaks indicate electrochemical processes which can be attributed to the oxidation and reduction of organic species formed during CO_2 reduction and to the Faradaic process between the complex and the GC electrode. After the ninth cycle the CV exhibits the same shape as observed in Figure 4a. At constant potential a layer of the products is formed (Figure 4b) and can be remove by cycling. It can be assumed that the layer makes further CO_2 reduction difficult. All experimental data, and the identical electrochemical behaviour of $[Co(ox)cyclam]^+$ and $[Ni(cyclam)]^{2+}$, strongly suggest a catalytic influence of the cobalt complex on CO_2 reduction. The main problem in the proposition of a mechanism for this catalytic process is that $[(Co(ox)cyclam]^+$, in contrast to $[Ni(cyclam)]^{2+}$, does not have any labile or vacant coordination sites. A final conclusion requires further investigation.

The preparation of complexes with other dicarboxylic acids such as malonic, succinic and glutaric acid, was also attempted. From electronic spectra it was evident that such complexes exist in solution; namely, absorption maxima of a similar shape in the visible region are regularly shifted towards longer wavelengths, as expected in when carboxylic acids of larger chain length are coordinated. These reactions will be further investigated.

Supplementary Material

Tables of bond distances and angles, atomic parameters, anisotropic thermal parameters and structure factors are available upon request from Naohide Matsumoto.

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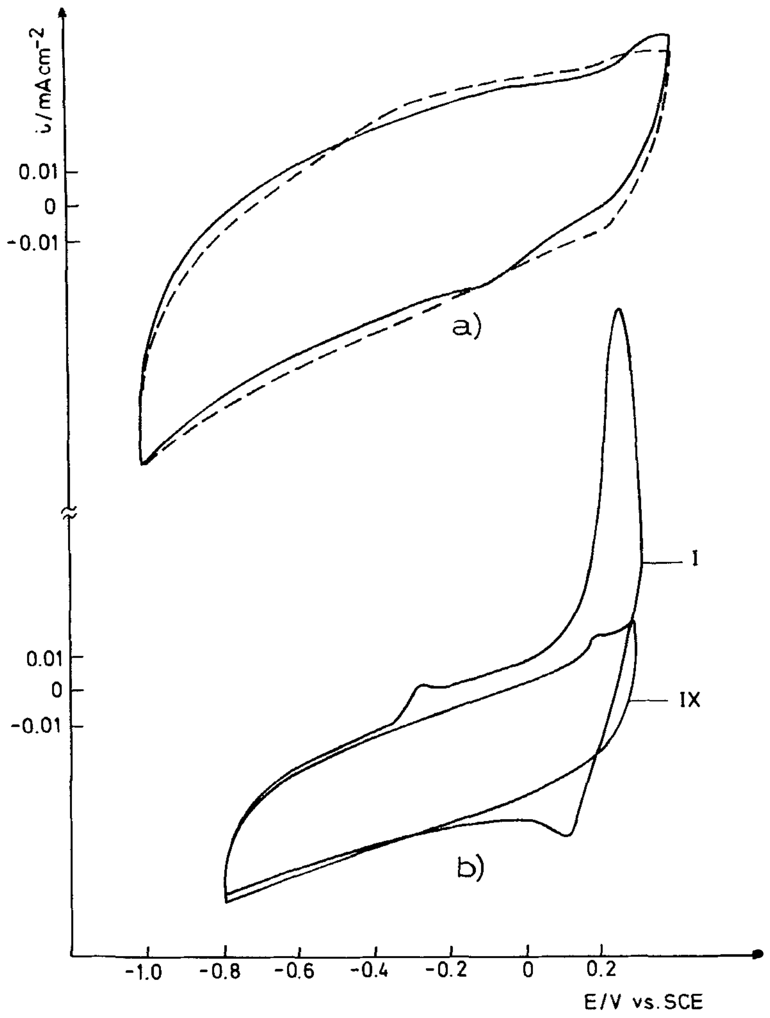

Figure 4 (a) Cyclic voltammograms of a GC electrode in 0.5 mol dm^{-3} $NaHCO_3$ solution under N_2 in the presence of $[Co(ox)cyclam]^+$ (———) and the ninth sweep (------); (b) cyclic voltammograms of a GC electrode modified by $[Co(ox)cyclam]^+$ in 0.5 mol dm^{-3} $NaHCO_3$ after 4 hours of electrolysis in the presence of CO_2 (the first and the ninth sweep). Sweep rate = 100 mV/s.

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