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Synthesis, Structure, Reactivity and Electrochemistry of a New Molybdenum(0) Dithiocarbamato Complex, $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$

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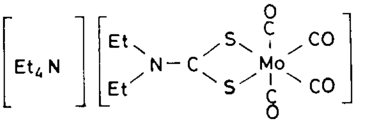
Abstract

A new molybdenum(0) dithiocarbamato complex $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ (**1**) has been synthesized by the reaction of $Mo(CO)_6$, NaS_2CNEt_2 and Et_4NCl in MeCN and characterized by routine elemental analysis, spectroscopy methods. The crystal and molecular structure of **1** was determined from X-ray three dimension data. **1** crystallizes in the orthorhombic, space group $Pbc2_1$ with $a = 8.148(2)$, $b = 19.618(2)$, $c = 14.354(2)$ Å; $V = 2294$ Å^3; $Z = 4$; $R_1 = 0.052$, $R_2 = 0.058$ for 1308 independent reflections with $I \geqslant 3\sigma(I)$. The geometry around Mo(0) atom in the anion $[Mo(CO)_4(S_2CNEt_2)]^-$ of **1** is distorted octahedral with a small SMoS of 67.70° and a small angle of 3.6° between plane MoSS and MoC(1)C(2). Two groups of Mo–CO bond distances and the longer Mo–S bond distance observed in **1** are similar to that in the dinuclear Mo(0) complexes containing SR bridges but very different from those observed in the dithiocarbamato complexes of Mo in higher oxidation states. Different oxidizing products containing Mo in II–V oxidation states $Mo(CO)_2(S_2CNEt_2)_2$, $MoO(S_2CNEt_2)_2$, $Mo_2O_3(S_2CNEt_2)_4$ and $Mo_2O_4(S_2CNEt_2)_2$ were isolated from the oxidation of **1** with I_2 (or in the presence of traces of air). The electrochemical behavior of **1** in MeCN was investigated by cyclic voltammetry at Pt and C electrodes. The anodic peaks observed at 0.04, 0.14, 0.26 and 0.44 V *versus* SCE implied that **1** probably underwent oxidation in company with dissociation of dithiocarbamate and substitution of carbonyls resulting in several complexes of Mo in different oxidation states. The relationship between reactivity and structure is also discussed.

Introduction

The biological significance of molybdenum [1], in particular, the occurrence of Mo–S bonding in molybdenum-containing enzymes [2], has generated current interest in investigation of molybdenum complexes with sulfur-containing ligands. In order to understand the active site of molybdenum in enzymes and the functioning to activate substrate molecules, a great many of the sulfur-containing complexes, especially dithiocarbamato complexes [3–10] of molybdenum in middle or high oxidation states, have been prepared and studied as modelling compounds. Only a few sulfur-containing complexes of molybdenum in the lower oxidation state have been reported [11, 12] and no study on dithiocarbamato complexes of Mo(0) has been found in the literature so far. However, the variety of reactivity and interesting electrochemistry of the complexes of molybdenum in low oxidation states [12] undoubtedly benefit the investigation on the structure and functioning of enzymes and the synthesis of modelling compounds of the Mo site in enzymes. This led us to carry out studies on a dithiocarbamato molybdenum(0) complex following on from our previous research on dinuclear molybdenum(0) complexes with SR bridges [12–15]. Herein we report the synthesis, structure, reactivity and electrochemistry of a new dithiocarbamato Mo(0) complex, $[Et_4N][Mo(CO)_4(S_2CNEt_2)]$ (**1**).



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Experimental

Materials

Acetonitrile and toluene were dried by distillation with CaH_2. $Mo(CO)_6$ and Et_4NCl were purchased from Fluka Company. Iodine and $NaS_2CNEt_2 \cdot 3H_2O$ are products of Shanghai Chemical Reagent Factory. All reactants and solvents were degassed before use and all experiments were carried out under a nitrogen atmosphere.

Instrumentation

Perkin-Elmer 577 Infrared Spectrometer; Enraf Nonius CAD-4 Diffractomater; CV-1B potentiostat

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from BAS (Bioanalytical Systems); CARLO ERBA Strumentazion Elemental Analyzer-MOD 1106.

Synthesis of [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (1)

A mixture of solid $NaS_2CNEt_2 \cdot 3H_2O$ (1.3 g, 0.005 mol) and Et_4NCl (0.83 g, 0.005 mol) in 50 ml of acetonitrile was stirred at 55 °C for 4 h. The resulting slurry was filtered onto solid $Mo(CO)_6$ (1.32 g, 0.005 mol) and the mixture was stirred at 45–50 °C overnight resulting in a deep orange solution. After cooling and filtration, the filtrate was evaporated under vacuum to 25 ml, and 40 ml of isopropanol was added. 1.85 g of a microcrystalline yellow product were collected by filtration, washed with i-PrOH and hexane and dried *in vacuo*. Yield, 76%. *Anal.* Calc. for $C_{11}H_{30}N_2O_4S_2Mo$: C, 41.97; H, 6.22; N, 5.76; S, 13.18; Mo, 19.72. Found: C, 42.01; H, 6.48; N, 6.13; S, 13.18; Mo, 19.44%. The IR spectrum of this product contains 4 strong absorption bands (1993, 1868, 1828 and 1783 cm^{-1}) in the range of 1600–2000 cm^{-1}, which indicate the existence of an $Mo(CO)_4$ unit in **1**, and all the characteristic absorption peaks of an Et_2NCS_2 ligand and Et_4N^+ cation. This is well consistent with the formula of **1**.

Oxidation Reaction of [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (1)

(a) To a mixture of **1** (0.55 g) and I_2 (0.17 g) was added 40 ml toluene. The reaction mixture was stirred at room temperature overnight. 0.15 g of red–purple solid product (**2**) was obtained after filtration and evaporation of the filtrate to dryness. *Anal.* Calc. for $MoS_4C_{12}H_{20}N_2O_2$: C, 32.14; H, 4.48; N, 6.25. Found: C, 31.54; H, 4.40; N, 5.70%. Two strong absorption peaks at 1840 and 1920 cm^{-1} appear in the IR spectrum of **2**. Referring to the complex $Mo(CO)_2(S_2CN\text{-}i\text{-}Pr_2)_2$ [4] which possesses two characteristic strong IR absorptions at 1934(s) and 1842(s) cm^{-1} attributable to *cis*-carbonyl ligands and taking account of the analysis data of **2** it is certain that **2** is the Mo(II) complex, $Mo(CO)_2(S_2CNEt_2)_2$.

(b) To a suspension of **1** (1.0 g) in 45 ml of toluene was added 0.25 g of iodine and the resulting mixture was stirred at room temperature overnight. After filtration the filtrate was cooled at 4 °C for 2 weeks resulting in the precipitation of a dark green microcrystalline product. 0.3 g of the microcrystalline product (**3**) was obtained by filtration, washed with toluene and dried *in vacuo*. *Anal.* Calc. for $Mo_2C_{20}H_{40}S_8N_4O_3$: C, 27.78; H, 4.63; N, 6.48. Found: C, 27.57; H, 4.55; N, 6.72%. No absorption in the range of 1600–2500 cm^{-1} but a strong band at 935 cm^{-1} in the IR spectrum of **3** indicated the absence of carbonyl and the presence of Mo=O in **3**. Obviously, **3** is a dinuclear Mo(V) complex containing an oxygen bridge, $Mo_2O_3(S_2CNEt_2)_4$, according to its analysis data. In fact, the IR spectrum of **3** is well consistent with the one of $Mo_2O_3(S_2CNEt_2)_4$ [10] which was prepared by $MoCl_5$. The introduction of oxygen atoms is probably due to exposure of the reaction solution to air during the procedure of filtration.

(c) A mixture of 0.2 g of **1** and 0.05 g of I_2 in 15 ml of toluene was stirred at room temperature for 24 h. After filtration the resulting brown filtrate was cooled at 4 °C for two weeks. Unexpectedly, some yellow crystalline products (**4**) was deposited. The IR spectrum of **4** is consistent with that of the molybdenum(V) complex, $Mo_2O_4(S_2CNEt_2)_2$ [10], prepared by the reaction of $MoCl_5$ with dithiocarbamate. The single-crystal X-ray study of **4** (**4** crystallizes in the triclinic, space group $P\bar{1}$ with $a = 8.095(3)$, $b = 9.250(1)$, $c = 13.935(2)$ Å; $\alpha = 107.66(1)^\circ$, $\beta = 101.41(2)^\circ$, $\gamma = 94.40(2)^\circ$; $Z = 2$; $V = 9642$ Å^3; $R_1 = 0.052$, $R_2 = 0.059$; Mo–Mo, 2.58(1) Å, Mo–O_t, 1.655 Å) confirmed that **4** is μ-oxo-bis[oxo-bis(*N,N*-diethylthiocarbamato)molybdenum(V)], $Mo_2O_4(S_2CNEt_2)_2$.

(d) After collecting the product from the preparative reaction of **1** the mother liquid was left in the refrigerator for a few days resulting in the precipitation of yellow crystals, which were recognized as **1** by the IR spectrum, and a small amount of red crystals (**5**). Interestingly, the yellow crystals (**1**) decreased and the red ones (**5**) increased when a trace of air was introduced by opening the flask for a short time. Single-crystal X-ray determination of **5** indicated that **5** is the molybdenum(IV) complex $MoO(S_2CNEt_2)_2$ [13]. Red crystalline **5** will change color and decompose immediately if it is exposed to air.

X-ray Determination of Crystal Structure

A single crystal of **1** with dimensions of 0.08 × 0.3 × 0.35 mm was grown from MeCN. The intensities were collected on an Enraf-Nonius CAD-4 diffractometer by using graphite monochromator Mo Kα radiation ($\lambda = 0.71073$ Å) in the range of $2^\circ \leqslant 2\theta \leqslant 5^\circ$ with scan mode θ–2θ. After LP and absorption correction the intensity data were used in the structure analysis. The structure was solved by direct method and refined by full-matrix least-squares and Fourier synthesis method to $R_1 = 0.052$ and $R_2 = 0.058$ for 1308 independent reflections with $I \geqslant 3\sigma(I)$. **1** crystallizes in the orthorhombic, space group $Pbc2_1$ (standard space group is $Pca2_1$, No. 29) with $a = 8.148(2)$, $b = 19.618(2)$, $c = 14.354(2)$ Å; $V = 2294$ Å^3; $Z = 4$. The final positional and thermal parameters with estimated standard deviations are listed in Table I.

Electrochemical Measurements

Cyclic voltammetry (CV) experiments were carried out with a three electrode cell using 0.1 M

TABLE I. Positional and Thermal Parameters of [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (1)[a]

Atom	x	y	z	B (Å^2)
Mo	0.1135(1)	0.16156(5)	0.890	3.43(2)
S(1)	−0.0600(4)	0.0499(2)	0.8897(4)	3.87(7)
S(2)	0.1373(5)	0.0960(2)	0.7349(3)	3.97(8)
C(1)	0.264(2)	0.2339(6)	0.8663(9)	3.9(4)
C(2)	0.071(2)	0.1983(8)	1.013(1)	5.1(4)
C(3)	0.300(2)	0.1068(7)	0.946(1)	4.4(4)
C(4)	−0.059(2)	0.2236(7)	0.842(1)	4.5(4)
O(1)	0.358(1)	0.2794(5)	0.8535(8)	6.3(3)
O(2)	0.042(2)	0.2221(6)	1.0860(8)	7.4(3)
O(3)	0.409(2)	0.0816(6)	0.979(1)	7.9(3)
O(4)	−0.149(1)	0.2656(6)	0.8156(8)	6.8(3)
C	0.015(2)	0.0336(6)	0.7820(9)	3.0(3)
N	−0.017(1)	−0.0231(5)	0.7346(8)	3.6(3)
C(11)	0.053(2)	−0.0370(7)	0.641(1)	4.6(4)
C(21)	−0.131(2)	−0.0761(7)	0.771(1)	4.0(3)
C(12)	0.216(2)	−0.0766(8)	0.649(1)	6.1(5)
C(22)	−0.307(2)	−0.0683(8)	0.735(1)	5.6(4)
N(1)	−0.410(1)	0.1453(5)	0.5840(8)	3.7(3)
C(01)	−0.300(2)	0.1386(7)	0.672(1)	4.1(3)
C(02)	−0.402(2)	0.1343(9)	0.763(1)	5.8(4)
C(03)	0.456(2)	0.2959(6)	0.095(1)	4.3(4)
C(04)	−0.534(2)	−0.2268(7)	0.615(1)	5.8(5)
C(05)	−0.305(2)	0.1616(8)	0.501(1)	5.2(4)
C(06)	0.825(2)	0.3958(9)	0.982(2)	8.5(6)
C(07)	−0.503(2)	0.0761(6)	0.575(1)	4.5(4)
C(08)	−0.613(2)	0.0746(9)	0.483(1)	7.6(5)

[a] e.s.d.s given in parentheses.

Bu_4NBF_4 as the supporting electrolyte and MeCN as solvent. The working electrodes were C and Pt. The reference electrode was an aqueous SCE separated from the sample solution by a salt bridge. Solutions were deoxygenated and blanketed with argon.

Results and Discussion

Synthesis of [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (1)

Molybdenum(0) dithiocarbamato complex [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (**1**) was prepared in high yield by the reaction of molybdenum hexacarbonyl with tetraethylammonium dithiocarbamate, which was obtained from the reaction of NaS_2CNEt_2 and Et_4NCl, in acetonitrile at 45–50 °C. The preparative reaction seemed to be a simple substitution of carbonyls by the dithiocarbamate (dtc^-) ligand, however, employment of an anaerobic technique is very important in order to obtain the product in high yield and good quality because of the sensitivity of **1** to air. **1**, even in the crystal state, was oxidized immediately in the presence of a trace of air.

Structure of [Et_4N][$Mo(CO)_4(S_2CNEt_2)$] (1)

The bond distances and bond angles of the anion of **1** are given in Tables II and III, respectively. The molecular structure of the anion of **1** is depicted in Fig. 1. **1** consists of two structural fragments, cation Et_4N^+ and anion [$Mo(CO)_4(S_2CNEt_2)$]$^-$. As shown in Fig. 1 and Table I, the geometry around the Mo atom in the anion of **1**, [$Mo(CO)_4(S_2CNEt_2)$]$^-$, is a distorted octahedral with a small SMoS angle of 67.70° and a small dihedral angle of 3.6° between plane MoS(1)S(2) and plane MoC(1)C(2). The dihedral angles between plane MoC(3)C(4) and plane MoS(1)S(2) and between plane MoC(3)C(4) and MoC(1)C(2) are 91.9° and 93.1° respectively. Thus, the structure of the anion of **1** which possesses only a C_2 axis through Mo, C, and N atoms is pseudo-C_{2v} symmetry. Being similar to dinuclear Mo(0)–SR complexes (Table IV), **1** possesses two groups of Mo–CO bond distances of 1.924 and 2.006 Å (average) due to the *trans*-effect resulting in the fact that two carbonyls of **1** could be substituted to form $Mo(CO)_2(S_2CNEt_2)_2$ (**2**). Compared with dinuclear Mo(0)–SR complexes and Mo(II,IV)–dtc complexes, the Mo–S bond distance of **1** is nearly the same as that of dinuclear Mo(0)–SR complexes, [$Mo_2(CO)_8(SCH_2CO_2Et)_2$]$^{2-}$ (2.593 and 2.587 Å) and is longer than that observed in the dithiocarbamato complexes of molybdenum in higher oxidation

TABLE II. Bond Distances (Å) of [$Mo(CO)_4(S_2CNEt_2)$]$^-$

Mo–S(1)	2.607(3)	C(4)–O(4)	1.169(15)
Mo–S(2)	2.578(4)	S(1)–C	1.692(12)
Mo–C(1)	1.905(13)	S(2)–C	1.719(13)
Mo–C(2)	1.943(16)	C–N	1.329(13)
Mo–C(3)	2.031(15)	N–C(11)	1.49(2)
Mo–C(4)	1.981(15)	N–C(21)	1.48(2)
C(1)–O(1)	1.195(13)	C(11)–C(12)	1.54(2)
C(2)–O(2)	1.168(16)	C(21)–C(22)	1.53(3)
C(3)–O(3)	1.113(15)		

TABLE III. Bond Angles (°) of [$Mo(CO)_4(S_2CNEt_2)$]$^-$

S(1)–Mo–S(2)	67.7(2)	Mo–C(1)–O(1)	179(1)
S(1)–Mo–C(1)	167.0(4)	Mo–C(2)–O(2)	177(1)
S(1)–Mo–C(2)	102.5(5)	Mo–C(3)–O(3)	174(1)
S(1)–Mo–C(3)	87.9(4)	Mo–C(4)–O(4)	173(1)
S(1)–Mo–C(4)	97.6(4)	S(1)–C–S(2)	115.7(7)
S(2)–Mo–C(1)	99.8(4)	S(1)–C–N	123.8(9)
S(2)–Mo–C(2)	170.2(5)	S(2)–C–N	120.6(9)
S(2)–Mo–C(3)	91.4(4)	C–N–C(11)	123(1)
S(2)–Mo–C(4)	93.4(5)	C–N–C(21)	122(1)
C(1)–Mo–C(2)	90.0(6)	C(11)–N–C(21)	115(1)
C(1)–Mo–C(3)	89.0(5)	N–C(11)–C(12)	111(1)
C(1)–Mo–C(4)	86.3(5)	N–C(21)–C(22)	113(1)
C(2)–Mo–C(3)	88.0(6)	Mo–S(1)–C	88.0(5)
C(2)–Mo–C(4)	88.0(6)	Mo–S(2)–C	88.0(4)
C(3)–Mo–C(4)	173.8(6)		

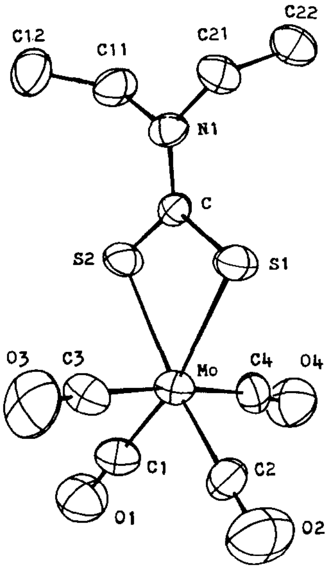

Fig. 1. Structure of the anion of 1, $Mo(CO)_4(S_2CNEt_2)^-$.

TABLE IV. Mo–S and Mo–CO Bond Distances of Several SR and dtc Complexes of Molybdenum in Different Oxidation States

Complexes	Mo–CO (Å)	Mo–S (Å)	Reference
$[Mo(CO)_4(S_2CNEt_2)]^-$	1.924 2.006	2.593	this work
$[Mo_2(CO)_8(SCH_2CO_2Et)]^{2-}$	1.945 2.026	2.587	14, 15
$Mo(CO)_2(S_2CN\text{-}i\text{-}Pr_2)_2$	1.911	2.458	4
$MoO(S_2CNEt_2)_2$		2.409	13

states. It seems that the higher the Mo oxidation state is, the shorter the Mo–S bond distance becomes. Thus, it is easy to understand the dissociation of dtc^- shown in the cyclic voltammogram of **1** (see below) and less stability for **1**.

Oxidation of [Et₄N][Mo(CO)₄(S₂CNEt₂)] (1)

1 is very sensitive to air. On exposure to air **1** is oxidized, resulting in a red Mo(IV) complex, $MoO(S_2CNEt_2)_2$ (**5**) immediately. **5** could be obtained in good quality on condition that an appropriate amount of air was introduced because 5 could be further converted to $MoO_2(S_2CNEt_2)_2$ [2a] by absorbing another oxygen. In anaerobic conditions, **1** reacted with I_2 resulting in the formation of an Mo(II) product, $Mo(CO)_2(S_2CNEt_2)_2$ (**2**) with occurrence of partial substitution of carbonyls. The fact that no additional dtc^- was added to the reaction system but the $(dtc)_2$-containing product **2** was obtained indicated that the reaction itself involved a dissociation of dtc^- from **1** and substitution of carbonyls in **1** by dtc^-. As a matter of fact, an oxidation peak at 0.004 V *versus* SCE shown in the cyclic voltammogram of **1** in acetonitrile indicated the presence of the free dtc^- in the solution (see below). **1** reacted with I_2 in the presence of traces of air (or traces of moisture in the reaction solvent) leading to the formation of oxo-bridged dinuclear Mo(V) complexes, $Mo_2O_3(S_2CNEt_2)_4$ (**3**) and $Mo_2O_4(S_2CNEt_2)_2$ (**4**). It is obvious that the reactivity of **1** is relevant to its structure mentioned above.

Electrochemical behavior of [Et₄N][Mo(CO)₄(S₂CNEt₂)] (1)

Cyclic voltammograms of **1** in acetonitrile for Pt and C electrodes are depicted in Figs. 2 and 3 respectively. As shown in Figs. 2 and 3, there are four oxidation peaks at 0.04, 0.14, 0.26 and 0.44 V *versus* SCE and two correspondent reduction waves at 0.2 and 0.4 V *versus* SCE. In terms of the electrochemical data of Mo–dtc complexes reported by De Hayes *et al.* [3], the oxidation peak at 0.04 V *versus* SCE was derived from the reaction: $2\ dtc^- \rightarrow (dtc)_2 + 2e^-$. In fact, as shown in Fig. 4, which is the cyclic voltammogram of **1** with a small amount of additional NaS_2CNEt_2 in acetonitrile, addition of NaS_2CNEt_2 enhanced the oxidation peak at 0.04 V *versus* SCE. The oxidation peak at 0.14 V *versus* SCE probably derived from the oxidation of **1** as suggested for the oxidation of $Mo(CO)_5(SPh)^-$ at 0.17 V *versus* SCE [11]. Two oxidation peaks at 0.44 and 0.26 V *versus* SCE and correspondent reduction waves at 0.4 and 0.2 V *versus* SCE seemed to be two redox couples. This implied that **1** probably underwent oxidation in company with dissociation of dithiocarbamate and substitution of carbonyls resulting in several complexes of molybdenum in different oxidation states.

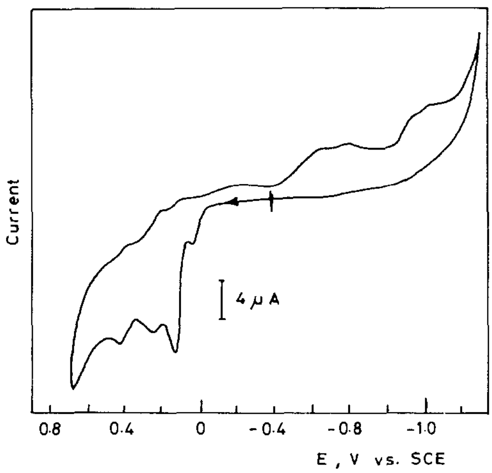

Fig. 2. Cyclic voltammogram of **1** in MeCN: sample concentration, 0.002 M; scan rate, 50 mV/s; working electrode, Pt.

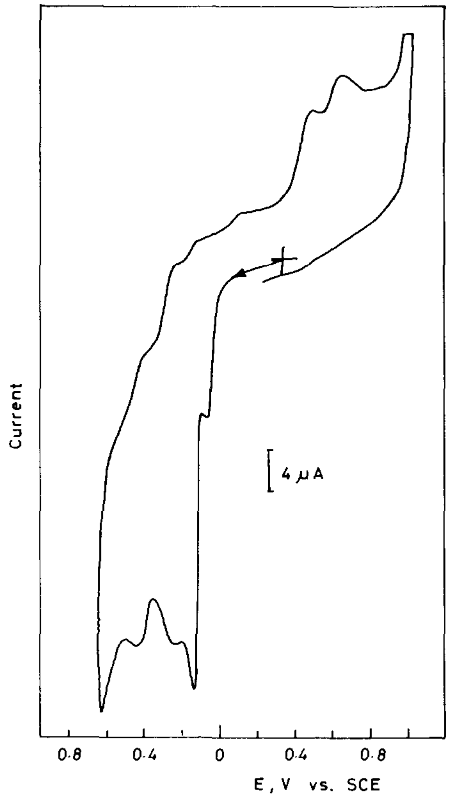

Fig. 3. Cyclic voltammogram of 1 in MeCN: scan rate 50 mV/s; working electrode, C.

Acknowledgements

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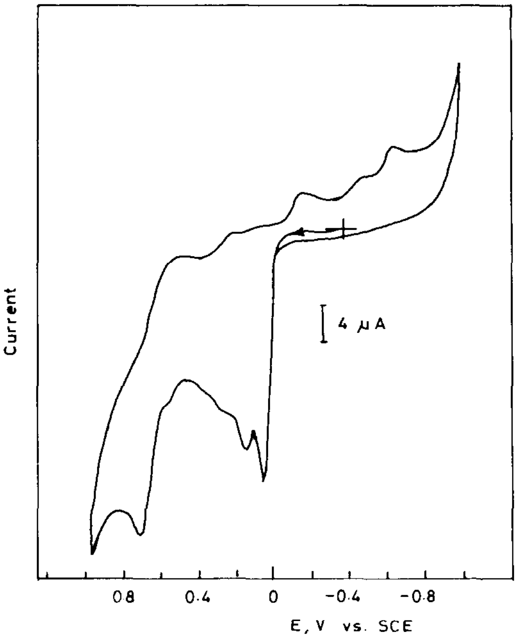

Fig. 4. Cyclic voltammogram of 1 with a small amount of additional NaS_2CNEt_2 in MeCN: scan rate, 50 mV/s; working electrode, Pt.

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