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A water-soluble derivative of tetrathiafulvalene exhibiting pH sensitive redox properties

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The properties of a water-soluble TTF dicarboxyl salt, $Na_2[C_{10}H_6O_4S_6]\cdot 3H_2O$, have been explored. The cyclic voltammogram of the salt shows two quasi-reversible redox waves at $E_{1/2}(1) = 0.280$ V and $E_{1/2}(2) = 0.556$ V with ΔE ($E^{ox} - E^{re}$) = 78 and 68 mV, respectively, in H_2O–CH_3CN (1 : 1 v/v). The redox potential of this compound is strongly dependent on the proton concentration. An ECEC square reaction, a redox-coupled association/dissociation of proton, was found for the second redox cycle. The redox active salt forms a mono-protonated anion in the pH range of 2–5. The calculated pK_b constant of the salt is 5.93, corresponding to $pK_a^{(2)} = 8.07$ of the original binary acid. A single crystal structure of $Bu_4N[C_{10}H_7O_4S_6]$ was also obtained, which confirms that the mono-protonated compound has a stable conjugated structure.

Introduction

Tetrathiafulvalene (TTF) and its derivatives have been intensively investigated for several decades, due to the spectacular discoveries of their high conductivity and unusual magnetic and optical properties.[1] During the past decade, moreover, great efforts have revealed that the tetrathiafulvalene derivatives are useful beyond the field of material science and substantial progress has been reported in the field of supramolecular chemistry.[2] The host–guest chemistry of TTF-crown ethers first received attention in the context of ion recognition.[3] Recently, a new macrocyclic pyrrolo-TTF system was explored and used for applications in cation and anion sensors and supramolecular devices.[4] Among all of these systems, the most widely studied guest ions are Li^+, Na^+, K^+ [5] and Ba^{2+} ions.[6] The main group ion Pb^{2+} [6,7] and the transition metal ion Ag^+ [8] were also found to elicit a good response from these macrocyclic TTFs. Anion-sensitive TTF compounds have also been studied. For example, mono-TTF-calix[4]pyrrole was used as a probe to monitor the Br^- concentration.[9] However, to the best of our knowledge, TTF derivatives that are sensitive to the concentration of protons have not been explored yet, although a pH-dependent TTF compound with tetracarboxyl has been documented as a charge transfer compound.[10] pH-dependent redox reactions are very important for the elaboration of pH sensors and for research into biosystems, since numerous biological processes are known to involve proton-coupled redox reactions.[11] Some progress has been made in the cases of ferrocenyl and multiferrocenyl systems.[12] In this paper, we report a TTF salt, $Na_2[C_{10}H_6O_4S_6]\cdot 3H_2O$ {hydrated 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4,5-dicarboxylate disodium salt}, and its novel pH-sensitive redox properties.

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Experimental

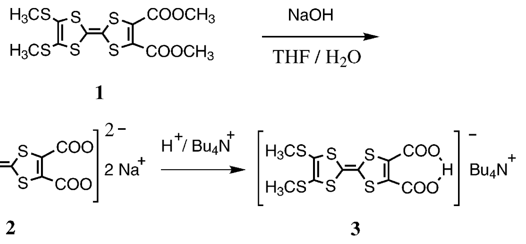
General

Solvents were dried and distilled by standard methods before use. Elemental analysis of C, H and N were performed using an EA1110 elemental analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Magma 550 FT-IR spectrometer. ^1H NMR spectra were measured in $CDCl_3$ or D_2O on a Unity Nova-400 spectrophotometer. UV-Vis spectra were recorded using a Shimadzu UV-240 spectrometer. Cyclic voltammetry (CV) was performed on a CHI600 electrochemistry workstation in a three-electrode system, a single-compartment cell equipped with a platinum working electrode (*ca.* 0.25 cm^2), a platinum wire counter electrode and a saturated calomel electrode (SCE, reference). HPLC grade acetonitrile and ultra purified water were used as solvents and tetrabutylammonium perchlorate was used as electrolyte. Analytically pure hydrochloric acid was used for the potentiometric titration and adjustment of the pH of the solutions for CV measurements. The concentration of HCl used in the CV measurement was sufficiently large so that the added volume of HCl can be ignored.

Synthesis of the compounds (Scheme 1)

$C_{12}H_{12}O_4S_6$ (1). 2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4,5-dimethyl dicarboxylate. The compound was synthesized by a coupling reaction using a method similar to that reported[13] and was characterized by elemental analysis, melting point, IR and ^1H NMR.

$Na_2[C_{10}H_6O_4S_6]\cdot 3H_2O$ (2). Hydrated 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4,5-dicarboxylate diso-



Scheme 1

dium salt. To a THF solution (4.0 ml) of **1** (165 mg, 0.4 mmol) was added an aqueous solution of NaOH (1 mol dm^{-3}, 1 ml) dropwise. The mixture was stirred for 2 h. To the solution excess THF (40 ml) was added and a yellow salt precipitated. The salt was washed with ethyl ether and dried *in vacuo* (yield 80%). Anal. found: C, 25.18; H, 2.37; calcd for $C_{10}H_{12}O_7S_6Na_2$: C, 24.89; H, 2.51%. IR (cm^{-1}): 3425 (vs), 2923 (s), 2853 (w), 1608 (vs), 1371 (vs), 1168 (m), 1094 (m), 759 (m). ^{1}H NMR (ppm) in D_2O: 2.33 (s, CH_3S–).

$(Bu_4N)[C_{10}H_7O_4S_6]$ (3). Tetrabutylammonium salt of 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiol-4,5-dicarboxylate. Crystals of **3** were obtained by evaporating an acidified solution of **2** in water–acetonitrile to which was added excess Bu_4NClO_4 and used for the single-crystal structure determination.

X-Ray crystallography

X-Ray crystallographic data for **3** (0.24 × 0.19 × 0.10 mm^3) was obtained using a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα (λ = 0.71070 Å) radiation, at 193 K. The structure was solved by direct methods using the program SHELXS-97 and refined using SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated using mixed models. H(1) was located from the map and the others were theoretically added. Crystallographic data for compound **3**: $C_{26}H_{43}NO_4S_6$, MW 625.97 g mol^{-1}, triclinic, $P\bar{1}$; a = 11.239(2), b = 12.380(3), c = 13.299(3) Å, α = 74.38(3)°, β = 77.53(3)°, γ = 66.052°, Z = 2, T = 193 K, U = 1616.7(6) Å^3, D_{calc} = 1.286 g cm^{-3}, μ = 0.454 cm^{-1}, F000 = 668, 15617 reflections collected, 5611 unique, 4390 observed [$I > 2\sigma(I)$], 344 variables, R [$I > 2\sigma(I)$] = 0.1083, wR [$I > 2\sigma(I)$] = 0.1787; S = 1.239.†

Results and discussion

Salt **2** is a new compound, which was obtained by alkali hydrolysis of precursor **1** (the dimethyl ester of **2**). The salt **2** is stable for months as a dry powder at room temperature and can easily dissolve in water, but does not dissolve in non-aqueous solvents except for those having a high dipole, such as DMF. The IR spectrum of **2** showed the stretching bands of carboxylate groups at 1607 and 1371 cm^{-1}. The ^{1}H NMR spectrum of the salt in D_2O was determined and, except for the peak of water, only a single signal appeared at 2.33 ppm for the methylthio group. The cyclic voltammogram (CV) of **2** showed two pairs of quasi-reversible redox waves, $E_{1/2}(1)$ = 0.280 V and $E_{1/2}(2)$ = 0.556 V, with ΔE ($E^{ox} - E^{re}$) = 78 and 68 mV, respectively in H_2O–CH_3CN (1 : 1 v/v). Since the redox properties of TTF derivatives have been well-characterized, the two-step one-electron oxidations are doubtless TTF$^+$/TTF and TTF^{2+}/TTF$^+$. However, an unusual small wave at approximately 0.433 V appeared due to protonation of the dicarboxylate in H_2O–CH_3CN (1 : 1 v/v). The CV results show that **2** is more easily oxidized than the precursor **1**, because the two-step half potentials of **1** in the same mixed solvent are 0.504 and 0.710 V, respectively.

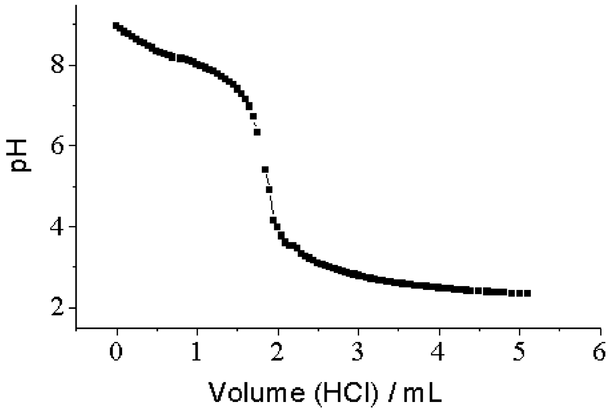


Fig. 1 Potentiometric titration of **2** (2.00 × 10^{-3} mol dm^{-3}, 10 ml) by HCl (1.00 × 10^{-2} mol dm^{-3}) in mixed solvent (H_2O–CH_3CN 1 : 1 v/v) at 18 °C.

The protonation tendency of the salt **2** was evaluated by potentiometric titration at 18 °C in the mixed solvent. The result and the experiment details are shown in Fig. 1. The data confirms that the salt is only singly protonated and gives the equivalent point at pH = 5.42. The calculated pK_b constant of the salt is 5.93, corresponding to the p$K_a^{(2)}$ 8.07 of the original binary acid.

Cyclic voltammetry of **2** was also studied in the case of titration by HCl (0.10 mol dm^{-3}) in the mixed solvent H_2O–CH_3CN (1 : 1 v/v). Table 1 gives a summary of the results. Fig. 2 shows representative CV curves at different stages and an explanation of the CV results is described in Scheme 2. Due to the hydrolysis of salt **2**, the pH of the solution was about 9.0 before being adjusted by hydrochloric acid. In the pH range from 9.00 to 2.00, the CV behavior of **2** changes remarkably and it can be divided into three types. (a) At higher pH (pH = 9), there are two steps of redox reaction at $E_{1/2}(1_L)$ = 0.280 V (L^-/L^{2-}) and $E_{1/2}(2_L)$ = 0.556 V (L/L^-) (Fig. 2, solid thick line), except for a very weak peak that appears around 0.40 V. The anion of **2** is represented here as L^{2-} (similarly, HL^- for the protonated anion of **2**) and the subscript L represents all the redox species of **2** (similarly, subscript HL for all the redox species of protonated **2**). (b) At moderate pH (pH = 6), the weak peaks develop into a new pair of redox waves at *ca.* $E_{1/2}(1_{HL})$ = 0.38 V (Fig. 2, dotted line), which is assigned to the redox reaction of the mono-protonated **2** (HL/HL^-). The large shift of $E_{1/2}(1_{HL})$ of the new redox wave from $E_{1/2}(1_L)$ of the original one (L^-/L^{2-}) is about 100 mV, which indicates that there is a strong interaction between the proton and the salt (O–H bonds, see structural discussion). It is noteworthy that at the present pH the second redox wave has basically the character of the unprotonated one (L/L^-), and only $E^{ox}(2_L)$ shows some shift. This is evidence that the protonation tendency of the anion decreases when it is sequentially oxidized. (c) At lower pH (pH = 4), the salt is completely mono-protonated (HL^-), so that the lowest pair of redox peaks disappears (Fig. 2, solid thin line). In this case $E^{ox}(2_L)$ shifts to $E^{ox}(2_{HL})$, but $E^{re}(2_L)$ is not changed due to proton expulsion from the cation ($HL^+ \rightarrow L + H^+$). As soon as L is one-electron reduced again, mono-protonated HL is recovered predominantly. Thus, in acidic conditions, an ECEC square reaction for the second step redox is completed (Scheme 2). However, there is a very small shoulder at 0.63 V for the reduction of undissociated HL^+.

In order to further confirm the existence of the ECEC square reaction of the second redox cycle, CV measurements were carried out at pH = 4.0 with different scan rates and the results

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† CCDC reference number 230828. See http://www.rsc.org/suppdata/nj/b4/b411380b/ for crystallographic data in .cif or other electronic format.

Table 1 Oxidation and reduction peak data (E/mV) from CV measurements of **2** in H_2O–CH_3CN (1 : 1 v/v)

	L^-/L^{2-}		HL/HL^-		L/L^-		HL^+/HL	
pH	$E^{ox}(1_L)$	$E^{re}(1_L)$	$E^{ox}(1_{HL})$	$E^{re}(1_{HL})$	$E^{ox}(2_L)$	$E^{re}(2_L)$	$E^{ox}(2_{HL})$	$E^{re}(2_{HL})$
9.0	320	242	433w	—	590	522	—	—
8.0	323	244	423	356vw	613	530	—	—
7.0	324w	254	433	346w	648	534	—	—
6.0	324vw	274	435	341	—	536	680	—
5.0	—	298w	432	336	—	538	696	625vw
4.0	—	—	432	330	—	538	699	624vw
2.0	—	—	409	325	—	544	687	625vw

are shown in Fig. 3. The peak $E^{re}(2_{HL})$ increases obviously at rapid scan rates, due to the dynamical difference in the reactions of proton dissociation and electrode reduction. At 100 mV s^{-1}, judging from the peaks $E^{re}(2_L)$ and $E^{re}(2_{HL})$, more than half of the HL^+ ions are dissociated to H^+ + L before being reduced, while at 5000 mV s^{-1}, almost all of the HL^+ are reduced before being dissociated. These characteristics are typical of an ECEC square reaction.[14]

Using the $E_{1/2}$ instead of E° as an approximation, the constant values of $pK_L{}^1$ (L^-/L^{2-}), $pK_{HL}{}^1$ (HL/HL^-), $pK_L{}^2$ (L/L^-) and $pK_{HL}{}^2$ (HL^+/HL) (see Scheme 2, $pK = -\log K$) for the redox equilibria were calculated. From these data and the $pK_b{}^1$ (L^{2-}/HL^-) constant of the salt, $pK_b{}^2$ (L^-/HL) and $pK_b{}^3$(L/HL^+) (see Scheme 2) were calculated. All of these constants are listed in Table 2. The K_b constants decrease by about 1.7 orders of magnitude when the salt is one-electron oxidized. Therefore, the higher the oxidation state of the salt, the more difficult it is for the salt to attach a proton.

The protonation tendency of the salt is also correlated to the solvent. Fig. 4 gives the CV results in varied ratios for the mixed solvent. In contrast to that in the 1 : 1 solvent, the salt ions are completely mono-protonated to form HL^- in 6 : 1 CH_3CN–H_2O [$E_{1/2}(1_{HL})$ = 0.38 V, HL/HL^-]. Experiments also revealed that the solubility of the mono-protonated salt in CH_3CN is better than that in water.

Compared with other ion-sensitive systems, the advantages of this electrochemical proton probe are the following. (a) Not only the first step, but also the second redox step, is sensitive to the pH change. More importantly, in the low pH range, an ECEC square reaction was found at the second redox step, which might be used as a controllable proton source in molecular devices. (b) Since the salt is water-soluble, water can be introduced into the electrochemical system, which is an important property of this compound for potential applications in biosystems. (c) The shifts of the CV curves are about

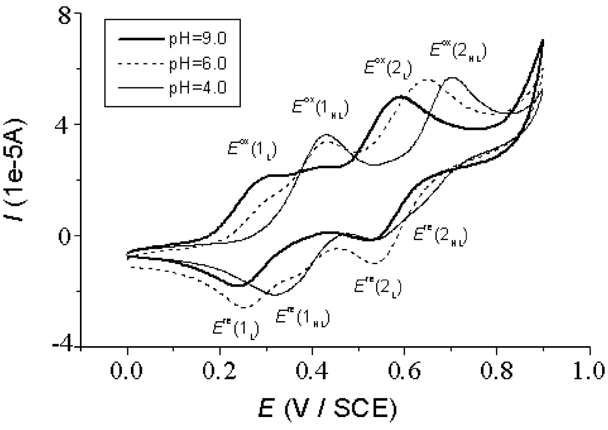
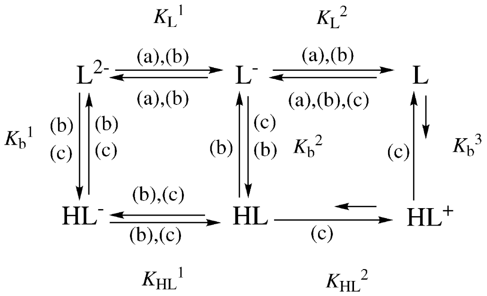


Fig. 2 Representative CV curves of 1 × 10^{-3} M **2** in H_2O–CH_3CN mixed solvent (1 : 1 v/v), with 0.1 M Bu_4NClO_4, for different pH stages: (a) solid thick line, pH = 9.0; (b) dotted line, pH = 6.0; (c) solid thin line, pH = 4.0. Scan rate 0.1 V s^{-1}. $E^{ox}(1_L)/E^{re}(1_L)$ and $E^{ox}(2_L)/E^{re}(2_L)$ are the two redox steps of the unprotonated salt. $E^{ox}(1_{HL})/E^{re}(1_{HL})$ and $E^{ox}(2_{HL})/E^{re}(2_{HL})$ are the two redox steps of the protonated salt.



Scheme 2 The main equilibria or reactions occurring in stages (a), (b) and (c) (see text). The K represent the equilibrium constants.

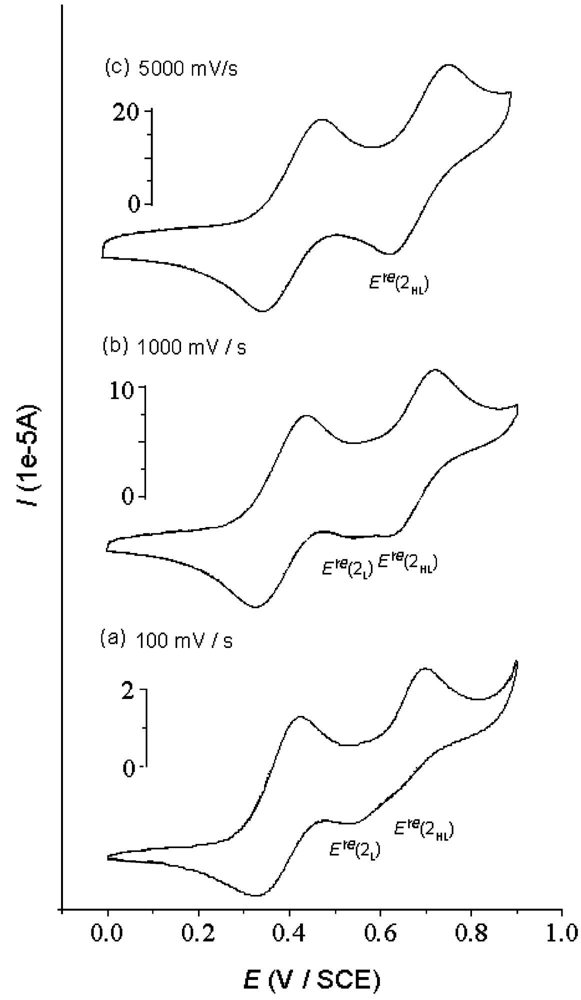


Fig. 3 CV curves of 1 × 10^{-3} M **2** in H_2O–CH_3CN mixed solvent (1 : 1 v/v) with 0.1 M Bu_4NClO_4 at pH = 4.0 for scan rates of (a) 100, (b) 1000 and (c) 5000 mV s^{-1}.

Table 2 Redox potentials ($E_{1/2}$), redox equilibrium constants (pK) and acid–base equilibrium constants (pK_b) of L and HL (L = anion of compound **2**) in H_2O–CH_3CN mixed solvent (1 : 1 v/v)

$E_{1/2}(1_L)$	0.28
$E_{1/2}(1_{HL})$	0.38
$E_{1/2}(2_L)$	0.56
$E_{1/2}(2_{HL})$	0.66
$pK_L{}^1$	4.73
$pK_{HL}{}^1$	6.42
$pK_L{}^2$	9.46
$pK_{HL}{}^2$	11.15
$pK_b{}^1$	5.93
$pK_b{}^2$	7.62
$pK_b{}^3$	9.31

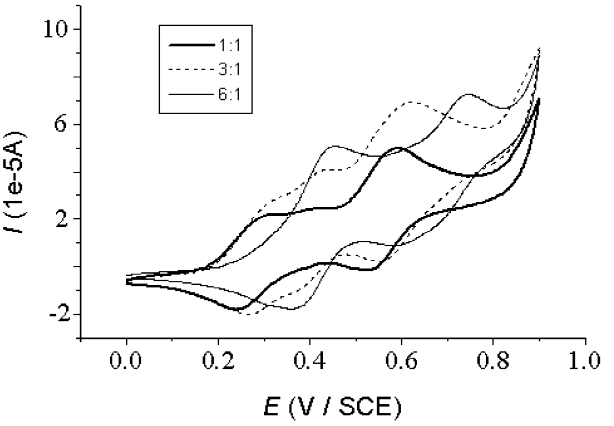
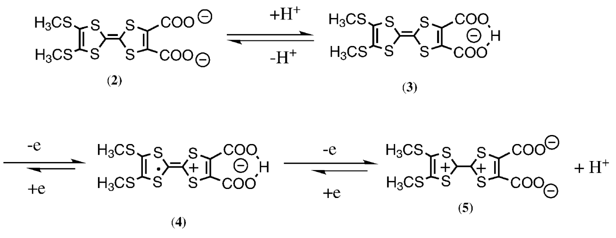


Fig. 4 CV curves of 1 × 10^{-3} M **2** in different mixed solvents (H_2O–CH_3CN) with 0.1 M Bu_4NClO_4: (a) solid thick line, 1 : 1; (b) dotted line, 3:1 and (c) solid thin line, 6 : 1. Scan rate 0.1 V s^{-1}.

100 mV for E^{ox} (1), E^{re}(1) and E^{ox}(2) (Tables 1 and 2), and the response quantity of the proton to the host molecule is in a 1 : 1 mole ratio. These results are more sensitive than those of most alkali metal systems and are similar to those found in Pb(II)/TTF macrocycle systems.[7]

Table 3 Selected bond lengths (Å) and angles (°) for **3**

C(1)–C(2)	1.350(8)	C(3)–C(4)	1.325(8)
C(5)–C(6)	1.333(8)	C(7)–O(1)	1.286(7)
C(7)–O(2)	1.214(7)	C(8)–O(3)	1.226(7)
C(8)–O(4)	1.273(7)	O(1)–H(1)	1.14(13)
O(4)–H(1)	1.29(13)		
C(2)–C(1)–C(7)	131.3(5)	C(1)–C(2)–C(8)	130.4(5)
C(1)–C(7)–O(1)	118.0(6)	C(2)–C(8)–O(4)	118.1(5)
C(7)–O(1)–H(1)	118(6)	C(8)–O(4)–H(1)	118(5)



Scheme 3

Since the mother compound of the salt is a binary acid, it needs to be further confirmed that the mono-protonated species is a primary anion in the pH range. Single crystals of the protonated product were obtained in the presence of Bu_4N^+ as a counter-ion. The anion structure of $Bu_4N[C_{10}H_7O_4S_6]$ (**3**) is illustrated in Fig. 5 and selected bond lengths and angles for **3** are listed in Table 3. The anion takes a boat configuration formed by three planes defined as plane 1: S(1), S(2) C(3), C(4), S(3), S(4) (central plane), plane 2: 11 atoms on the right hand side of S(1) and S(2) (see Fig. 5), including the acidic proton, and plane 3: S(5), S(4) C(5), C(6), S(5), S(6). The planes share two common edges, S(1)–S(2) and S(3)–S(4), with a dihedral angle of *ca.* 25° and 20°, respectively. The two ortho-substituted carboxyl groups are essentially equivalent and chelate the proton H(1) to form a 7-membered cycle within plane 2. The O(1)–H(1) and O(4)–H(1) distances are 1.14(13) and 1.29(13) Å, respectively, and both of the C(7)–O(1)–H(1) and C(8)–O(4)–H(1) angles are 117.7°. This conjugated structure ensures that the mono-protonated compound **3** is quite stable, so that a second protonation does not occurred at pH above 2. Namely, the K_a(1) of the corresponding binary acid should be large enough to prevent the addition of a second proton to the dicarboxylate. The 1.336(3) Å length of the C(3)–C(4) bond (central double bond of the TTF moiety) is in accordance with those of unoxidized TTF compounds. For example, the length of the central C–C bond of tetramethylthio-TTF is 1.33–1.35 Å, while that in the one-electron oxidized compound is elongated to 1.38–1.40 Å.[15]

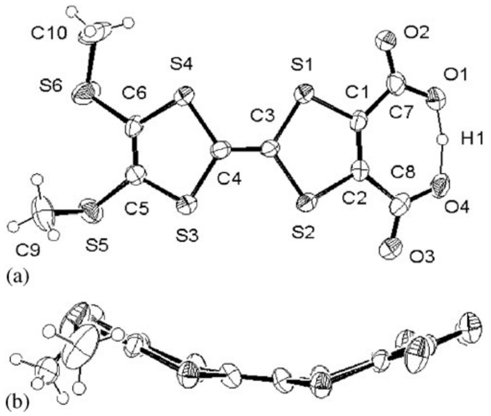


Fig. 5 The structure of the anion of **3** with labelling scheme and ellipsoids at 50% probability: (a) top view and (b) side view. The Bu_4N^+ cation has been omitted for clarity.

In summary, the reactions of proton association/dissociation and oxidation/reduction of the TTF salt are described in Scheme 3. The redox-coupled proton transfer is the most notable difference of this pH sensitive TTF system compared to the pH-sensitive ferrocenyl systems. Most reports concerning the pH-sensitive ferrocenyl systems only show a simple redox shift.[12] On the other hand, unlike most TTF-crown ethers, the conjugated π system of this anion is extended to the oxygen atoms of the carboxyl groups, therefore the response to the guest ion should be more direct and effective, although it is not a cyclic structure. The redox-coupled association/dissociation of the proton is very important in potential applications of electrochemically controllable chemical or physical processes, such as H^+ promoted fluorescent emission.[16] Although the real applications of this TTF system are still limited at the present time, the preliminary experimental results have shown the concept; the prospects of this electrochemical system are very promising and further research work is expected.

Acknowledgements

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