

Spectroscopic identification of 2,5-dimercapto-1,3,4-thiadiazole and its lithium salt and dimer forms

John M. Pope^a, Toshitada Sato^a, Eiichi Shoji^a, Daniel A. Buttry^b, Tadashi Sotomura^c,
Noboru Oyama^{a,*}

^a Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

^b Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838, USA

^c Corporate Research Division, Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka 570, Japan

Accepted 3 October 1996

Abstract

In this contribution we report initial results of our solid phase vibrational spectroscopic study of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and derivatives representing its protonation and oxidation states. We have succeeded in assigning observed bands to modes which are diagnostically useful for studies concerning the electrochemical character of DMcT when used with polyaniline (PAn) as a composite cathode material in a secondary lithium-ion cell. We discuss the implications of the current study for our further investigations of the DMcT/PAn cathode. © 1997 Elsevier Science S.A.

Keywords: Organosulfur compounds; Lithium-ion batteries; Cathode materials

1. Introduction

Previously, we reported the use of a composite material consisting of an organosulfur compound (2,5-dimercapto-1,3,4-thiadiazole, or 'DMcT') in concert with a molecular wire (polyaniline, or 'PAn') as the cathode of an Li-ion secondary battery [1–3].

Recent results indicate that the redox processes of DMcT are accelerated in the presence of a weak base [4–7]. We have attributed this acceleration to a moderation of the local proton activity by the weak base. Elucidation of this effect represents a conceptual breakthrough and has allowed efforts to be focussed on a careful consideration of the proton transfer processes which occur in the cathode material. Toward this end, we have become interested in using infrared (IR) spectroscopy to investigate the oxidation and protonation states of DMcT and PAn during the charging and discharging processes of the cell. While the vibrational assignments for PAn have been studied in great detail [8], a survey of structural assignments based on the vibrational band data in reports available for DMcT reveals many inconsistencies [9–13]. Therefore, this study has been concentrated on providing reliable assignments of the vibrational modes of DMcT in its

various protonation and oxidation states. However, we have limited our assignments to those bands which are useful as diagnostic indicators of the various states of DMcT. Furthermore, due to the complexity of the spectra, we have initially investigated the compounds in the solid state only.

2. Experimental

Spectroscopy was performed using a Bio-Rad 60 FTS/896 FT-IR instrument equipped with a Raman attachment and a mercury–cadmium–telluride (MCT) detector (IR measurements) or a Ge detector (Raman measurements). Raman spectra represent 1024 co-added scans taken at 4 cm⁻¹ resolution. IR spectra represent 512 co-added scans taken at 2 cm⁻¹ resolution.

The mono- and di-lithium salts of DMcT were formed by addition of the proper amount of lithium hydroxide (in a water solution) to nitrogen-purged aqueous solutions of DMcT (Tokyo Kasei) while monitoring the pH of the solution. The water was removed by rotary evaporation and a pale yellow solid dried over P₂O₅ at 50 °C.

The dimer was formed by dropwise addition of one half an equivalent of iodine (Kanto Chemical) to a nitrogen-purged methanol solution of DMcT. The product was precip-

* Corresponding author.

itated by addition of water and recrystallized from methanol. Anal. Calc. for $C_4H_2S_6N_4$: C, 16.10; H, 0.68; N, 18.77; S, 64.45. Found: C, 16.08; H, 0.67; N, 18.75; S, 64.5%.

3. Results

3.1. Tautomeric structure of DMcT and derivatives

The results of crystallographic studies indicate that (in the solid state) DMcT exists predominantly in the thiol/thione form [14] (Scheme 1) and di-DMcT exists primarily in the thione/thione form [15] (Scheme 1). These structures are reflected in the vibrational spectra reported below. In the absence of other reports on the structure of LiDMcT, we have assigned its predominant tautomer form as the thione form using the vibrational bands signature of the thioamide group, *v.i.*

3.2. Vibrational spectra

IR and Raman spectra were obtained for DMcT and three derivatives (shown in Scheme 1). These spectra are presented in Figs. 1 and 2, in order of increasing spectral complexity. The objective of this study was to allow for the unambiguous determination of the oxidation state and the state of protonation of DMcT in the context of its use in battery systems. Thus, the assignments of these spectra are not complete. Rather, we have concentrated on identifying those modes that are diagnostic of the redox and acid/base chemistry of these compounds.

Table 1 details our assignment of the observed bands to the various modes in the molecules. In particular, we have assigned the C=N stretch (split when the ring includes two C=N bonds) to bands at ~ 1400 to ~ 1450 cm^{-1} (based on

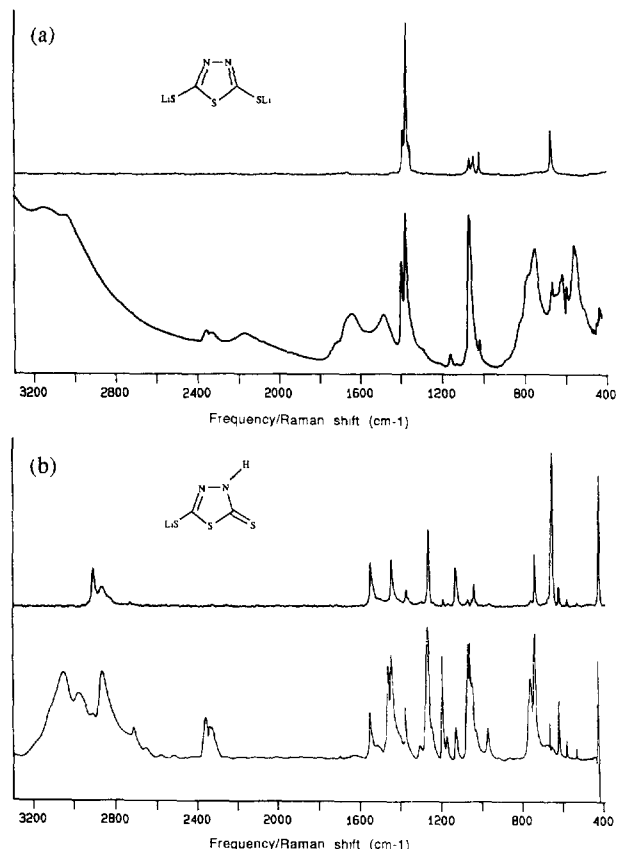
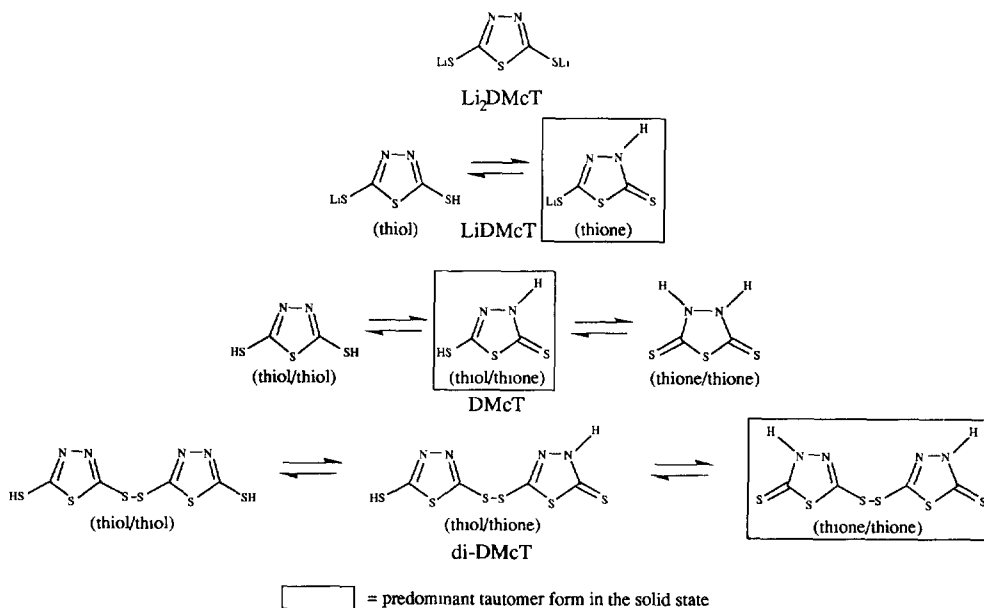


Fig. 1. Vibrational spectra of the lithium salts of DMcT: (a) (top) Raman and (bottom) IR spectra of Li_2DMcT , and (b) (top) Raman and (bottom) IR spectra of $LiDMcT$.

the skeletal vibrations for pyrrole and furan [16,17]), the N–N stretch to a band near ~ 1025 cm^{-1} , and C–S–C asymmetric and symmetric stretches to bands at ~ 720 and ~ 660 cm^{-1} , respectively [18,19]. Also, a strong band near 1280 cm^{-1} is assigned to an A_1 mode that is predominantly due to



Scheme 1

Table 1
Vibrational band assignments for DMcT and derivatives^a

Li ₂ DMcT		LiDMcT		DMcT		di-DMcT		Primary contributing mode or modes
Raman	IR	Raman	IR	Raman	IR	Raman	IR	
		3200–2700		3200–2700		3250–2700		ν (N–H), overtones, and Fermi resonances
				2483	2480	2486vw	2491vw	ν (S–H)
		1501vw	1503	1508	1506	1506	1501	δ_{ip} (C–N–H)
		1402	1405	1448	1452	1473	1474	ν (C=N)
						1446	1449	
	1393							ν_{as} (C=N)
1375	1372							ν_s (C=N)
		1307	1290	1279	1265	1274	1271	thioamide II mode
1024	1021	1026	1030	1038		1107		ν (N–N)
1072	1068		1038					A1 ring mode
				941	938			ν (C=S)
					750			τ (N–H)
	751	722	720	712	715	717	718	ν_{as} (C–S–C endocyclic)
671	669	668		656	659	650	655	ν_s (C–S–C endocyclic)
						532		ν (S–S)

^a ν = stretch, δ = deformation, τ = torsion. ip = in-plane, as = asymmetric, s = symmetric

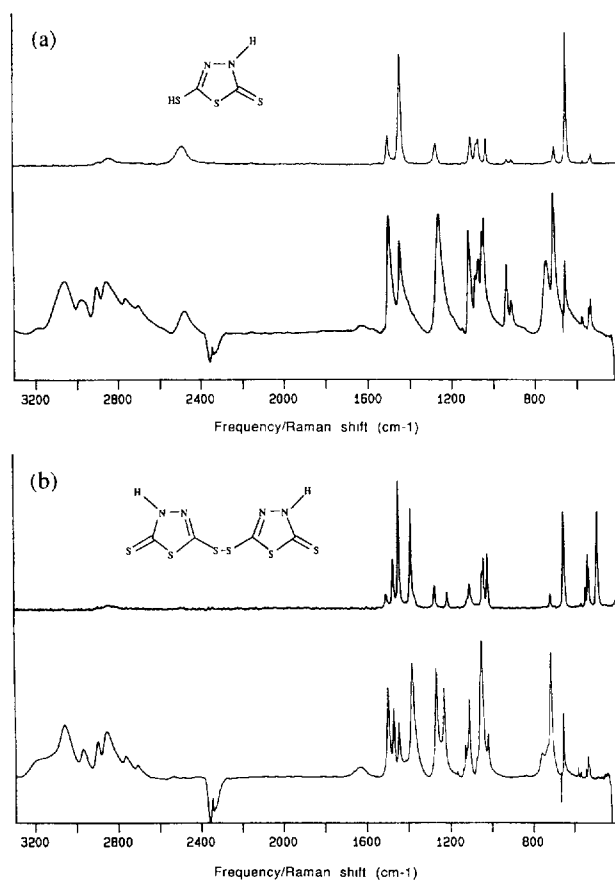


Fig. 2 Vibrational spectra of the monomer and dimer forms of DMcT (a) (top) Raman and (bottom) IR spectra of DMcT, and (b) (top) Raman and (bottom) IR spectra of di-DMcT.

an out-of-phase combination of the N–N and symmetric C–S–C stretches. Modes of this type are frequently observed in the IR spectra of diene-like five membered rings, with pyrrole and furan being the parent examples [16].

The predominant tautomer forms of the compounds are established to be the thione forms (boxed in Scheme 1) by the presence of several bands in the spectra which are characteristic for that tautomer [20]. These bands include the N–H bend near 1505 cm^{-1} in the IR, the single C=N stretch, and the band near 1280 cm^{-1} which can be assigned to the thioamide II mode [12]d[21]. The latter mode is generally assumed to be a combination of C–N and C=S stretching and N–H bending for acyclic thioamides, but here we assign this mode predominantly C–N stretch character. Also for the thioamide group, the bands from ~ 3200 to $\sim 2600\text{ cm}^{-1}$ have been assigned by Suzuki [21] to overtones of the thioamide group, stretching of the N–H bond, and Fermi resonances between those two modes. We have not assigned these peaks because they are not diagnostically useful. (Note that the C=N stretching frequencies in both this compound (1405 cm^{-1}) and the dianion of DMcT ($1393, 1372\text{ cm}^{-1}$) are quite low due to the electron donating character of the thiolate group.)

A major outcome of this study is that the spectral characteristics for these compounds provide a relatively comprehensive basis from which both the oxidation state and the degree of protonation of DMcT and its derivatives can be unambiguously determined. The fact that vibrational spectroscopy can be employed for this purpose is particularly attractive because of its ease of use as an in situ tool in electrochemical studies. Thus, the present work serves as a prelude to a thorough in situ vibrational spectroscopic study of the redox and acid/base behavior of the DMcT/poly(aniline) lithium secondary cathode system.

Acknowledgements

The work at the Tokyo University of Agriculture and Technology has been supported in part by a Grant-in-Aid for

Scientific Research from the Ministry of Education, Science, and Culture of Japan (Nos. 07 555 267, 07 241 218, and 07 242 224) and the work at University of Wyoming has been fully supported by the US Office of Naval Research.

References

- [1] N. Oyama, T. Tatsuma, T. Sato and T. Sotomura, *Nature*, **373** (1995) 598
- [2] T. Tatsuma, T. Sotomura, T. Sato, D.A. Buttry and N. Oyama, *J. Electrochem. Soc.*, **142** (1995) L182–L184.
- [3] T. Sotomura, T. Tatsuma and N. Oyama, *J. Electrochem. Soc.*, in press
- [4] E. Shouji, H. Matsui and N. Oyama, *J. Electroanal. Chem.*, in press.
- [5] J.M. Pope, E. Shouji and N. Oyama, in preparation.
- [6] J.M. Pope and N. Oyama, in preparation.
- [7] E. Shouji, Y. Yokoyama, J.M. Pope, N. Oyama and D.A. Buttry, *J. Phys. Chem.*, in press.
- [8] Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima and T. Kawagoe, *Macromolecules*, **21** (1988) 1297–1305.
- [9] (a) E.E. Lawson, H.G.M. Edwards and A.F. Johnson, *J. Raman Spectr.*, **26** (1995) 617–622; (b) H.G.M. Edwards, A.F. Johnson and E.E. Lawson, *J. Mol. Struct.*, **351** (1995) 51–63.
- [10] (a) A.C. Fabretti, G.C. Franchini and G. Peyronel, *Trans. Met. Chem.*, **7** (1982) 105–108; (b) A.C. Fabretti, G.C. Franchini and G. Peyronel, *Spectrochim. Acta*, **37A** (1981) 587–590; (c) A.C. Fabretti, G.C. Franchini and G. Peyronel, *Spectrochim. Acta*, **36A** (1980) 517–520.
- [11] (a) K.S. Siddiqi, V. Islam, P. Khan, F.R. Zaidi, Z.A. Siddiqi and S.A.A. Zaidi, *Synth. React. Inorg. Met.-Org. Chem.*, **10** (1980) 41–51; (b) S.A.A. Zaidi, D.K. Varshney, K.S. Siddiqi, Z.A. Siddiqi and V. Islam, *Acta Chim. Acad. Sci. Hung.*, **95** (1977) 383–388; (c) S.A.A. Zaidi, A.S. Farooqi, D.K. Varshney, V. Islam and K.S. Siddiqi, *J. Inorg. Nucl. Chem.*, **39** (1977) 581–583; (d) S.A. Zaidi and D.K. Varshney, *J. Inorg. Nucl. Chem.*, **37** (1975) 1806–1808.
- [12] (a) M.R. Gajendragad and U. Agarwala, *J. Inorg. Nucl. Chem.*, **37** (1975) 2429–2434; (b) M.R. Gajendragad and U. Agarwala, *Aust. J. Chem.*, **28** (1975) 763–771; (c) M.R. Gajendragad and U. Agarwala, *Z. Anorg. Allg. Chem.*, **415** (1975) 84–96; (d) M.R. Gajendragad and U. Agarwala, *Indian J. Chem.*, **13** (1975) 697–701.
- [13] G.D. Thorn, *Can. J. Chem.*, **38** (1960) 1439–1444.
- [14] J.W. Bats, *Acta Cryst.*, **B32** (1976) 2866–2870
- [15] M.B. Ferrari, G.G. Fava and C. Pelizzi, *Inorg. Chim. Acta*, **55** (1981) 167.
- [16] N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego 1990, pp 286–288.
- [17] N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego, 1990.
- [18] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991, pp 228–230.
- [19] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991.
- [20] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, 1991, p 166; p. 236.
- [21] I. Suzuki, *Bull. Chem. Soc. Japan*, **35** (1962) 1456–1464.