

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 074-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY		2. REPORT DATE 6/29/98		3. REPORT TYPE AND DATES COVERED Technical Report, Oct 1996 - June 1998
4. TITLE AND SUBTITLE Vibrational Spectroscopic Identification of Protonation and Oxidation States of DMcT			5. FUNDING NUMBERS N00014-96-1-0673 96PR0-3839	
6. AUTHOR(S) J. M. Pope, T. Sato, E. Shouji, D. A. Buttry, T. Sotomura and N. Oyama				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Wyoming Laramie, Wyoming 82071-3838			8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report 34	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, ONR 331 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared for publication in <i>Journal of Power Sources</i>				
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been prepared for public release and sale; its distribution is unlimited.				12b. DISTRIBU TION CODE
13. ABSTRACT (<i>Maximum 200 Words</i>) In this contribution we report some 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 that 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 also discuss the implications of the current study for our further investigations of the DMcT/Pan cathode.				
14. SUBJECT TERMS lithium secondary battery, electrochemistry, vibrational spectroscopy				15. NUMBER OF PAGES 4
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified		20. LIMITATION OF ABSTRACT
NSN 7540-01-280-5500			Standard Form 298 (Rev. 2-89) Prescribed by ANSI Std. Z39-18 298-102	

OFFICE OF NAVAL RESEARCH

GRANT # N00014-91-J-0201

R&T CODE: 4133032

Technical Report No. 34

Vibrational Spectroscopic Identification of Protonation and Oxidation States of DMcT

J. M. Pope, T. Sato, E. Shouji, D. A. Buttry, T. Sotomura and N. Oyama

Prepared for publication

in

Journal of Power Sources

Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071-3838

June 29, 1998

Reproduction in whole, or in part, is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

REPORT DOCUMENTATION PAGE

2. June 29, 1998
3. Technical Report
4. "Vibrational Spectroscopic Identification of Protonation and Oxidation States of DMcT"
5. GRANT: N00014-96-1-0673, PR # 96PRO-3839
6. J. M. Pope, T. Sato, E. Shouji, D. A. Buttry, T. Sotomura and N. Oyama
7. Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838
8. Org. Report # - none
9. Office of Naval Research, Chemistry Division, 800 N. Quincy Street, Arlington, VA 22217-5660
10. Technical Report NO. 34
11. Submitted to: *Journal of Power Sources*
12. Unlimited distribution
13. Abstract: In this contribution we report some 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 that 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 also discuss the implications of the current study for our further investigations of the DMcT/Pan cathode.
14. Subject terms: lithium secondary battery, electrochemistry, vibrational spectroscopy
15. Number of Pages:4
16. Price Code: UL
17. 18. 19. Unclassified
20. Limitations: UL

Vibrational Spectroscopic Identification of Protonation and Oxidation States of DMcT

John M. Pope, Toshitada Sato, Eiichi Shouji, Daniel A. Buttry,^a Tadashi Sotomura,^b and Noboru Oyama*

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

^aDepartment of Chemistry, University of Wyoming,
Laramie, Wyoming 82071-3838

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

* Author to whom correspondence should be addressed.

Abstract: In this contribution we report some 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 also discuss the implications of the current study for our further investigations of the DMcT/PAn cathode.

Introduction

Previously, we have 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 a Li ion secondary battery.¹⁻³

Our 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 for us and has allowed us to focus our efforts to 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, we have concentrated on providing conclusive 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.

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.

Details of the chemical synthesis of the protonation and oxidation forms of DMcT will be reported in a future communication.

Results

Tautomeric Structure of DMcT and derivatives

The results of crystallographic studies indicate that (in the solid state) DMcT exists predominantly in the thiol/thione form¹⁴ (Scheme 1) and di-DMcT exists primarily in the thione/thione form¹⁵ (Scheme 1). These structures are reflected in the vibrational spectra reported below. In the absence of other reports on the structure of LDMcT, we have assigned its predominant tautomer form as the thione form using the vibrational bands signature of the thioamide group (*vide infra*).

Vibrational Spectra

IR and Raman spectra were obtained for DMcT and three derivatives (shown in Scheme 1). These spectra are presented in Figure 1. 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 ca. 1400 to 1450 cm⁻¹ (based on the skeletal

vibrations for pyrrole and furan^{16,17}, the N-N stretch to a band near ca. 1025 cm⁻¹, and C-S-C asymmetric and symmetric stretches to bands at ca. 720 and 660 cm⁻¹, respectively.^{18,19} Also, a strong band near 1280 cm⁻¹ is assigned to an A1 mode that is predominantly due to 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 although this band has not been assigned for the DMcT family of compounds previously to this work.

The predominant tautomer forms of the compounds is established to be the thione forms (boxed in Scheme 1) by the presence of several bands in the spectra which are characteristic of this 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.^{12d,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 here we assign this mode predominantly C-N stretch character. Also for the thioamide group, the bands from ca. 3200 to 2600 cm⁻¹ have been assigned by Suzuki²¹ 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 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 of these compounds provide a relatively comprehensive basis from which to unambiguously determine both the oxidation state and the degree of protonation of DMcT and its derivatives. 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.

Acknowledgments

The work at TUAT has been supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (Nos. 07555267, 07241218, and 07242224) and the work at UW has been fully supported by the Office of Naval Research.

References

1. Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T. *Nature*, 1995, 373, 598.
2. Tatsuma, T.; Sotomura, T.; Sato, T.; Butry, D. A.; Oyama, N. *J. Electrochem. Soc.*, 1995, 142, L182-L184.
3. Sotomura, T.; Tatsuma, T.; Oyama, N. *J. Electrochem. Soc.*, in press.
4. Shouji, E.; Matsui, H.; Oyama, N. *J. Electroanal. Chem.*, in press.
5. Pope, J. M.; Shouji, E.; Oyama, N. *J. Chem. Soc. Faraday Trans.*, in preparation.
6. Pope, J. M.; Christensen, P. A.; Oyama, N. *in preparation*.
7. Shouji, E.; Yokoyama, Y.; Pope, J. M.; Butry, D. A.; Oyama, N. *in preparation*.
8. Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules*, 1988, 21, 1297-1305.
9. a.) Lawson, E. E.; Edwards, H. G. M.; Johnson, A. F. *J. Raman Spectr.*, 1995, 26, 617-22. b.) Edwards, H. G. M.; Johnson, A. F.; Lawson, E. E. *J. Mol. Struct.*, 1995, 351, 51-63.
10. a.) Fabretti, A. C.; Franchini, G. C.; Peyronel, G. *Trans. Met. Chem.*, 1982, 7, 105-8. b.) Fabretti, A. C.; Franchini, G. C.; Peyronel, G. *Spectrochim. Acta*, 1981, 37A, 587-90. c.) Fabretti, A. C.; Franchini, G. C.; Peyronel, G. *Spectrochim. Acta*, 1980, 36A, 517-20.
11. a.) Siddiqi, K. S.; Islam, V.; Khan, P.; Zaidi, F. R.; Siddiqi, Z. A.; Zaidi, S. A. A. *Synth. React. Inorg. Met.-Org. Chem.*, 1980, 10, 41-51. b.) *Chim. Acad. Sci. Hung.*, 1977, 95, 383-388. c.) Zaidi, S. A. A.; Farooqi, A. S.; Varshney, D. K.; Islam, V.; Siddiqi, K. S. *J. Inorg. Nucl. Chem.*, 1977, 39, 581-583. d.) Zaidi, S. A. A.; Varshney, D. K. *J. Inorg. Nucl. Chem.*, 1975, 37, 1806-8.
12. a.) Gajendragad, M. R.; Agarwala, U. *J. Inorg. Nucl. Chem.*, 1975, 37, 2429-34. b.) Gajendragad, M. R.; Agarwala, U. *Aust. J. Chem.*, 1975, 28, 763-71. c.) Gajendragad, M. R.; Agarwala, U. *Z. Anorg. Allg. Chem.*, 1975, 415, 84-96. d.) Gajendragad, M. R.; Agarwala, U. *Indian J. Chem.*, 1975, 13, 697-701.
13. Thom, G. D. *Can. J. Chem.*, 1960, 38, 1439-44.
14. Bats, J. W. *Acta Cryst.*, 1976, B32, 2866-70.
15. Ferrari, M. B.; Fava, G. G.; Pelizzi, C. *Inorg. Chim. Acta*, 1981, 55, 167.
16. Reference 17, pages 286-88.
17. Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, Academic Press: San Diego, California, 1990.
18. Reference 19, page 228-230.
19. Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press: San Diego, California, 1991.
20. Reference 19, pages 166 and 236.
21. Suzuki, I. *Bull. Chem. Soc. Japan*, 1962, 35, 1456-64.

Figure caption: Vibrational spectra of the compounds studied. (a) shows the Raman (top) and IR (bottom) spectra of Li₂DMcT. (b) shows the Raman (top) and IR (bottom) spectra of LiDMcT. (c) shows the Raman (top) and IR (bottom) spectra of DMcT. (d) shows the Raman (top) and IR (bottom) spectra of di-DMcT.

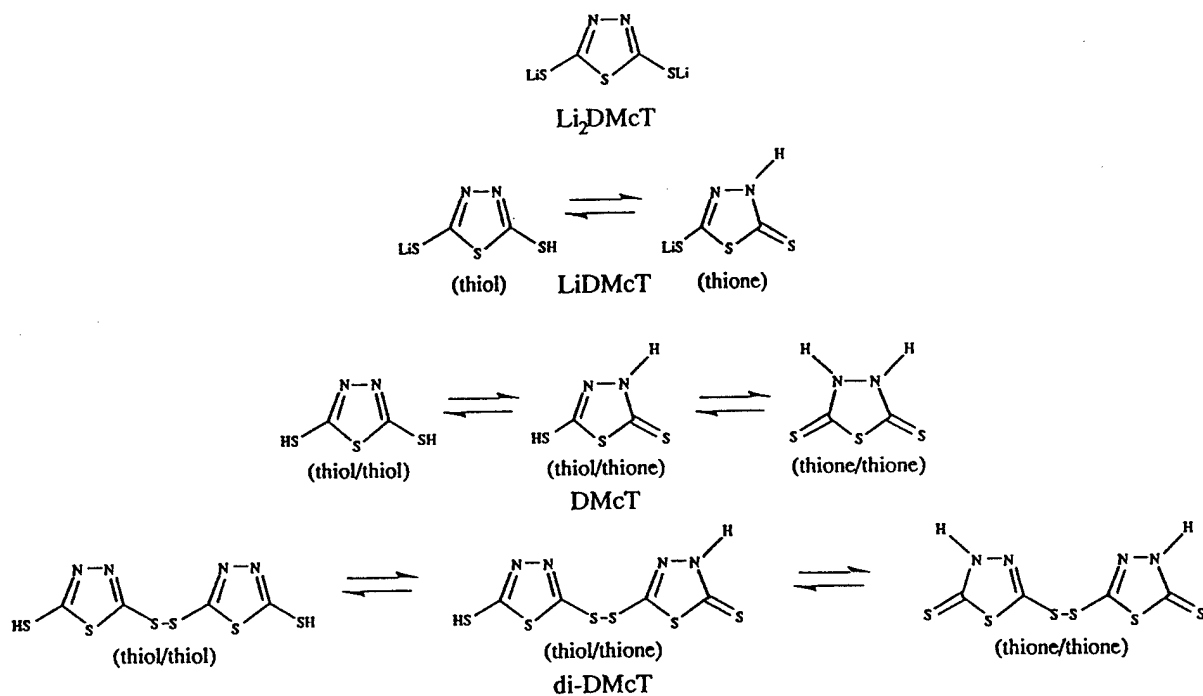
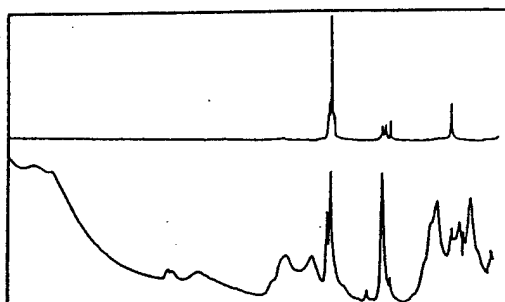


Table 1: Vibrational Band Assignments for DMcT and Derivatives

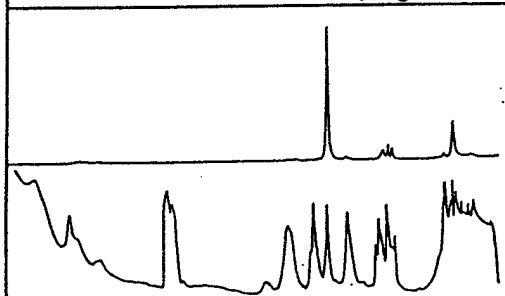
Li ₂ DMcT	LiDMcT		DMcT		di-DMcT		Primary Contributing Mode or Modes
	Raman IR	IR	Raman IR	IR	Raman IR	IR	
	ca. 3200-2700	ca. 3200-2700	ca. 3200-2700	ca. 3250-2700			$\nu(\text{N-H})$, overtones, and Fermi resonances
			2483	2480	2486vw	2491vw	$\nu(\text{S-H})$
	1501vw	1503	1508	1506	1506	1501	$\delta_{\text{ip}}(\text{C-N-H})$
	1402	1405	1448	1452	1473	1474	$\nu(\text{C=N})$
					1446	1449	$\nu_{\text{as}}(\text{C=N})$
1393							$\nu_{\text{s}}(\text{C=N})$
1375			1279	1265	1274	1271	thioamide II mode
1024	1307	1290	1038		1107		$\nu(\text{N-N})$
1072	1026	1030	941	938			A1 ring mode
		1388		750			$\nu(\text{C=S})$
	722	720	712	715	717	718	$\tau(\text{N-H})$
671	668		636	659	650	655	$\nu_{\text{as}}(\text{C-S-C endocyclic})$
					532		$\nu_{\text{s}}(\text{C-S-C endocyclic})$
							$\nu(\text{S-S})$

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

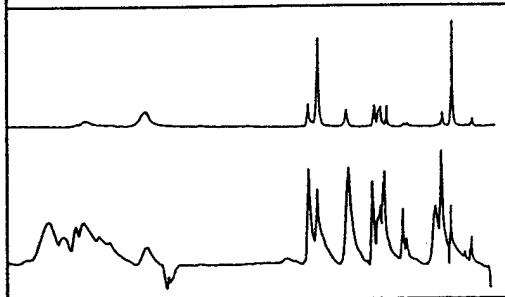
a. Li_2DMcT



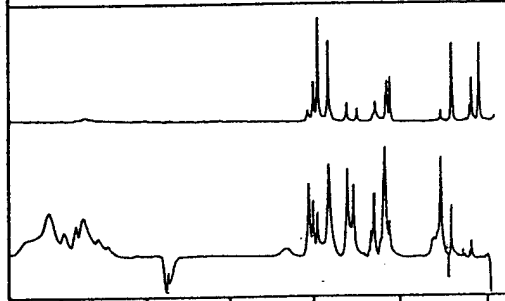
b. LiDMcT



c. DMcT



d. di- DMcT



3000 2000 1000
Wavenumbers (cm^{-1})