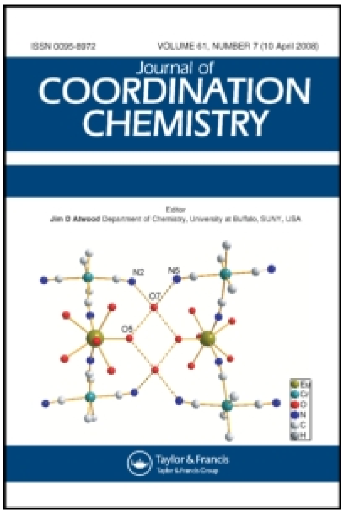
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A ^{1}H AND ^{13}C MAGNETIC RESONANCE AND INFRARED SPECTROSCOPIC STUDY OF COORDINATED 2-AMINOCYCLOPENTENE-1-DITHIOCARBOXYLIC ACID AND ITS S-METHYL ESTER

S. Burman[ab]; D. N. Sathyanarayana[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India [b] Dept. of Chemistry, University of Virginia, Charlottesville, VA, USA

To cite this Article Burman, S. and Sathyanarayana, D. N.(1983) 'A ^{1}H AND ^{13}C MAGNETIC RESONANCE AND INFRARED SPECTROSCOPIC STUDY OF COORDINATED 2-AMINOCYCLOPENTENE-1-DITHIOCARBOXYLIC ACID AND ITS S-METHYL ESTER', Journal of Coordination Chemistry, 13: 1, 51 — 55

To link to this Article: DOI: 10.1080/00958978308079753

URL: http://dx.doi.org/10.1080/00958978308079753

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1983, Vol. 13, pp. 51-55
0095-8972/83/1301-0051 $18.50/0

A ^{1}H AND ^{13}C MAGNETIC RESONANCE AND INFRARED SPECTROSCOPIC STUDY OF COORDINATED 2-AMINOCYCLOPENTENE-1-DITHIOCARBOXYLIC ACID AND ITS S-METHYL ESTER

S. BURMAN† and D.N. SATHYANARAYANA
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

(Received October 10, 1982; in final form February 9, 1983)

The ligating properties of 2-aminocyclopentene-1-dithiocarboxylic acid and its S-methyl esters were investigated. Complexes with Zn(II), Cd(II) and Hg(II) halides were synthesized and characterized by infrared and proton and carbon-13 NMR studies. The results are concordant with a bidentate coordination of the $-CS_2$ group to the metal ions.

INTRODUCTION

In recent years considerable interest has been expressed in 2-aminocyclopentene-1-dithiocarboxylic acid (Acdtc) and its *N*- and *S*-substituted derivatives as ligands.[1-4] However, there appears to be some controversy concerning the mode of coordination of the parent Acdtc itself. This has been summarized neatly by Wasson *et al.*[3] Besides bidentate bonding *via S, S*- or *S, N*-, another type with sulfur insertion in S, S-chelation has also been proposed. A study of the complexes of Acdtc and its *S*-methyl ester (Acdtcme) with Zn(II), Cd(II) and Hg(II) halides described herein is intended to describe the nature of bonding of Acdtc and Acdtcme to metal ions by the use of ^{1}H and ^{13}C NMR and infrared spectroscopic data. The complexes of Acdtcme are new, while those of Acdtc are known.[1,3]

EXPERIMENTAL

Materials

All the commercially available chemicals were of reagent grades. Acdtc and its *S*-methyl ester were prepared and purified by the literature methods.[1,5]

Preparation of the Complexes

The complexes of Acdtcme were prepared by reacting a solution of the metal salt (1 mmol in 10 cm^3 ethanol) with a solution of the ligand (2 mmol in 30 cm^3 ethanol). The solid complexes separate out almost immediately for mercury, and for the other two metal ions when the solution was made slightly alkaline with ethanolic sodium hydroxide. The products were filtered, washed well with ethanol and ether, and dried *in vacuo.* The metal complexes of Acdtc were obtained by known procedures.[1]

---

† Authors for correspondence. Present Address: Dept. of Chemistry, University of Virginia, Charlottesville, VA 22901, USA.

Physical Measurements

Infrared spectra were run on a Perkin-Elmer 599 spectrophotometer in Nujol and fluorocarbon mulls. ^1H NMR spectra were obtained with a Varian T 60 spectrometer using TMS as the internal standard; the spectra of the complexes were measured in DMSO-d_6 while the spectrum of the ligand was run in $CDCl_3$. The ^{13}C NMR spectra have been obtained using a Bruker WH 270 spectrometer operating at 67.89 MHz in the Fourier transform mode at 20° under conditions of off-resonance and complete proton-noise decoupling. Microanalyses were carried out by the microanalytical section of the Department.

RESULTS AND DISCUSSION

The complexes are stable in air and insoluble in most of the common organic solvents. The analytical results are shown in Table I. The main structural features of interest in these complexes center on the question of the coordination sites as to whether both the sulfur atoms, or both sulfur and nitrogen atoms or a single sulfur or nitrogen atom are involved.

Infrared Spectra

The infrared band assignments for Acdtc and Acdtcme could be proposed by analogy with the infrared spectra of dithioacetate,[6] dithiocarbamate[7] and the cyclopentene ring.[8]

We may exclude coordination through $-NH_2$ group of Acdtc since the stretching and bending frequencies of the $-NH_2$ group in the complexes either remain the same or increase slightly (Table II). This is consistent with the idea that coordination would produce a change in geometry of the $-NH_2$ group from a planar to a tetrahedral arrangement and lead to considerable loss of delocalization energy in the complex. The asymmetric dithiocarboxylate ($-CS_2$) stretching frequency is shifted to lower energies in the metal complexes while the less sensitive symmetric one remains nearly the same. This

TABLE I
Analytical data for the metal complexes.

Compound	Color	Carbon %		Hydrogen %		Metal %	
		Found	Calcd	Found	Calcd	Found	Calcd
$Zn(Acdtc)_2$	shining yellow	44.6	45.37	4.9	5.04	20.1	20.60
$Cd(Acdtc)_2$	shining yellow	39.1	39.52	4.6	4.39	30.4	30.84
$Hg(Acdtc)_2$	shining yellow	31.4	31.86	3.8	3.54	44.8	44.25
$Zn(Acdtcme)Cl_2$	pale yellow	27.7	27.13	3.9	3.84	21.6	21.14
$Zn(Acdtcme)Br_2$	pale yellow	21.4	21.14	2.9	2.81	16.0	16.46
$Cd(Acdtcme)Cl_2$	yellowish green	22.9	23.61	2.9	3.10	30.9	31.51
$Cd(Acdtcme)Br_2$	yellow	19.0	18.96	2.8	2.51	25.0	25.32
$Hg(Acdtcme)_2Cl_2$	yellow	26.9	27.22	3.3	3.56	33.4	32.51
$Hg(Acdtcme)_2Br_2$	yellow	23.5	23.86	2.9	3.12	27.9	28.43

TABLE II

Important infrared bands† (cm^{-1}) for the complexes of Acdtc and Acdtcme.

Compound	ν_{NH_2}		$\nu_{C=C}$	δ_{NH_2}	ν_{C-N}	$\nu_a CS_2$	$\nu_s CS_2$	ν M–S + ring deformation
Acdtc (= L)	3310mb	3100wb	1648s	1620s	1485vs	890s	620mb	
ZnL_2	3300s	3180mw	1625s	1610s	1475vs	850ms	610s	550m
CdL_2	3310s	3170s	1630s		1465vs	805ms	610m	
HgL_2	3290mb	3120w	1610s		1460vs	800m	625m	575m
Acdtcme (= L′)	3320wb	3100m	1620sb		1515s	950m	565s	
$ZnL'Cl_2$	3320m	3130sh	1580m		1470sb	865m	575m	500w
$ZnL'Br_2$	3285mb	3150sb	1590sb		1480sb	850m	575w	500w
$CdL'Cl_2$	3285m	3120sb	1605sh		1500m	850mb	550s	495w
$CdL'Br_2$	3280mb	3155sb	1650s	1600sh	1495sh	790m	510w	470w
HgL'_2Cl_2	3280s	3105mb	1670s	1595sh	1495sh	790s	530w	475w
HgL'_2Br_2	3280	3105mb	1670s	1610sh	1495m	790m		

†ν = stretching, δ = in-plane bending, s = symmetric, a = asymmetric.

indicates bidentate coordination through the $-CS_2$ group, a suggestion which is supported by the appearance of a new band near 550-500 cm^{-1} due to a ring deformation mode coupled with M-S stretching.[6]

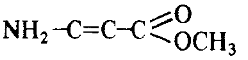
Analogous to the 890 cm^{-1} band of Acdtc, the spectrum of Acdtcme has a strong band at 950 cm^{-1} which shifts to lower energies in the metal complexes. Other assignments similar to those for Acdtc may be proposed for Acdtcme (Table II). Chelation of Acdtcme through the two sulfur atoms as in Acdtc seems therefore likely. The coordination *via* the *S*-methyl group is favored due to the inductive effect of the methyl group.[9]

The infrared spectra of the mercury(II) complexes of the ester reveal some differences from the pattern noted for the Zn(II) and Cd(II) complexes. For example, the 1620 cm^{-1} band of the free ligand displays a shift to higher energy. The spectra seem to suggest strong bonding through the terminal C=S group and a weak interaction through the *S*-methyl group.

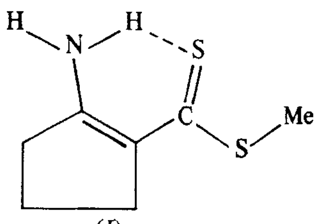
Proton NMR Spectra

The signal derived from NH_2 protons of the free Acdtc is found at 8.9 ppm as a broad band. In the Zn(II) and Cd(II) complexes, the NH_2 resonance is split into a doublet while for the Hg(II) complex only a broad singlet is observed with a large downfield shift. The splitting of the NH_2 resonance in the Zn(II) and Cd(II) complexes of Acdtc is due to the weak metal-sulfur bond and consequent hydrogen bond formation resulting in magnetically anisotropic NH_2 protons. In the Hg(II) complex, the coordinate bond is strong and the hydrogen bonding seems to be absent and hence magnetically isotropic NH_2 protons result whose signals are shifted downfield. These observations are in agreement with those of Wasson *et al.*[3]

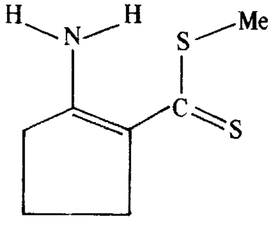
The *S*-methylation of Acdtc causes disappearance of the singlet arising from the $-NH_2$ protons and new signals are recorded at 5.8 and 11.0 ppm; the peak due to the *S*-CH_3 protons is found at 2.50 ppm (Table III). We recorded the variable temperature ^1H NMR spectra of Acdtcme in $CDCl_3$ between 233 and 313 K. The spectra showed considerably decreased line widths at sub-ambient temperatures. The two signals do not coalesce even at 313 K, the highest temperature that could be reached with $CDCl_3$ as solvent. Extensive studies have established that the carboxylic acid esters exist in a stable *cis*



$NH_2{-}C{=}C{-}C{\overset{\displaystyle O}{\underset{\displaystyle OCH_3}{\lessgtr}}}$ conformation. Recent investigations have demonstrated that the preferred conformation for mono- and dithio-carboxylic acid esters is also the *cis* form. Accordingly, two planar structures (*I*, *II*) could be written for Acdtcme. The NMR results favour conformation (*I*). The other structure (II) could also be discounted on the basis of steric repulsions between the $-NH_2$ and $-SCH_3$ groups.



(*I*)



(*II*)

Important changes are noticed for the $-NH_2$ signal in the spectra of the complexes of Acdtcme. While for the Zn(II) complex, the $-NH_2$ protons still appear as a broad singlet, the spectra of the Cd and Hg complexes display doublets with large separations. Stronger metal-sulfur covalent bonding in Cd and Hg complexes with consequent greater delocalization of the nitrogen lone-pair is suggested. The appearance of a single peak for the Zn(II) complex at a resonance position almost unaffected in comparison to Acdtc or the mean position of Acdtcme indicates weak metal-sulfur bonding. This result is in agreement with the HSAB principle. The peak arising from S-CH_3 does not exhibit any detectable change in the spectra of metal complexes (Table III), and metal to ligand π back-bonding might partially counteract the expected small shift.

TABLE III

Proton and Carbon-13 chemical shifts (δ, in ppm) of the Acdtcme complexes.

Compound[a]	Proton			Carbon-13						
	$-NH_2$		$-SCH_3$	C-1	C-2	C-3	C-4	C-5	$-CS_2$	$-SCH_3$
Acdtcme (= L)	5.6sb	11.0sb	2.50s	117.8	165.1	36.6	20.5	32.9	205.9	16.2
$ZnLCl_2$	8.6sb		2.48s	120.8	164.7	33.9	20.4 20.2	32.4	189.0 191.9	15.4
$ZnLBr_2$	8.7sb		2.48s	120.7	164.7	33.8	20.2		196.3 193.4	15.4
$CdLCl_2$	8.1sb	10.8sb	2.48s			34.0	20.4	32.0	196.3 188.9	15.0
$CdLBr_2$	7.7sb	10.7sb	2.52s	116.8	169.1	35.4	20.2	32.2	193.4 194.8	15.9
HgL_2Cl_2	9.6sb	10.9sb	2.60s	120.5	173.1	35.7	20.2	32.6	196.4 189.0	16.2
HgL_2Br_2	9.3	10.7sb	2.60s							

[a] Acdtcme recorded in $CDCl_3$, the rest in DMSO-d_6 ; s = singlet, b = broad

Carbon-13 NMR Spectra

Carbon-13 NMR offers a unique method for directly observing the effects of bonding of the coordinated group. The individual ^{13}C resonances of Acdtcme have been assigned by means of proton noise decoupled and single frequency off-resonance techniques and relevant literature data.[10]

In the present study, the signals due to *S*-methyl and dithiocarboxylate carbons may be predicted to be most sensitive if coordination of the $-CS_2$ group to metal ions occurs, the C-1 and C-2 ring carbons may be affected to a lesser extent due to the delocalization of the nitrogen lone-pair. The carbon-13 spectra show pronounced upfield shifts for the $-CS_2$ carbon and a small upfield shift for the *S*-CH_3 carbon resonance in all the complexes of Acdtcme. A smaller downfield shift for the C-1 ring carbon is found while the other ring carbon resonances remain nearly unchanged in the metal complexes (Table III). This observation appears diagnostic of the coordination mode of Acdtcme through the $-CS_2$ group. The metal ion-induced upfield shifts can be described as due to the dominance of paramagentic contributions.[11,12]

REFERENCES

1. K. Nag and D.S. Joardar, *Inorg. Chim. Acta,* **14,** 133 (1975); **17,** 111 (1976).
2. D.S. Joardar, S.K. Mandal and K. Nag, *Bull. Chem. Soc. Jpn.,* **50,** 1489 (1977).
3. S.N. Choi and J.R. Wasson, *Inorg. Chem.,* **14,** 1964 (1975).
4. M.F. Mackay, M.J.O. Connor, P.J. Oliver, K.S. Murray and P.J. Newman, *Inorg. Nucl. Chem. Letts.,* **13,** 417 (1977).
5. B. Bordas, P. Sohar, G. Matolcsy and P. Barencsi, *J. Org. Chem.,* **37,** 1727 (1972).
6. K.A. Jensen, H. Mygind, P.H. Nielsen and G. Borch, *Acta Chem. Scand.,* **24,** 1492 (1970).
7. G.D. Prasad, D.N. Sathyanarayana and C.C. Patel, *Can. J. Chem.,* **47,** 631 (1969).
8. J.R. Villarreal, J. Laane, S.F. Bush and W.C. Harris, *Spectrochim. Acta,* **35A,** 331 (1979).
9. H.C. Brinkoff and J.M. Dautzenberg, *Rec. Trav. Chim.,* **91,** 117 (1972).
10. L.F. Johnson and W.C. Jankowski, Carbon-13 NMR spectra, A collection of Assigned, Coded and Indexed Spectra, Wiley-Interscience, New York (1972).
11. A.J. Jones, D.M. Grant, J.G. Russell and G. Frankel, *J. Phys. Chem.,* **73,** 1624 (1969).
12. M. Hughes, R.H. Prince and P. Wyeth, *J. Inorg. Nucl. Chem.,* **40,** 713 (1978).