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Preparative and Spectral Studies on Some Metal Hexamethyleniminecarbodithioates

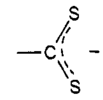
R. K. Rawlley, B. K. Puri, and A. K. Singh*

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

Hexamethyleniminecarbodithioate complexes of VO(II), Cr(III), Cu(II), Ni(II), Zn(II), Cd(II), and Hg(II) have been synthesized and subjected to elemental analysis, magnetic and conductivity measurements, IR, electronic, NMR (^{1}H and ^{13}C), and EPR spectral studies, and X-ray powder diffraction studies to find their molecular structure. All the chelates are stable at room temperature except that of vanadyl which is prone to aerial decomposition. The Zn(II), Cd(II), and Hg(II) complexes being isomorphous with the Cu(II) chelate appear to possess a pentacoordinate dimeric structure. The IR spectral recordings down to 200 cm^{-1} reveal that the ligand bite to the metal ions is through the bisulfur fork.

Introduction

Metal complexes of *N*,*N*-dialkyldithiocarbamates have been extensively studies (*1*, *2*). Recently the complexes of heterocyclic dithiocarbamates have also been made the subject of several publications (*3*). Influence of different heterocyclic groups on the C⋯N and C⋯S bonds of such ligands has been recently analyzed (*3*), but all the studies made so far are limited to six-membered ring systems (or its fused ring systems) attached to the group A



A

through N which is also part of the ring. Complexation of heterocyclic carbodithioates is different from that of the simple dialkyl derivatives in several respects. The behavior of such a ligand having a seven-membered nonplanar saturated heterocyclic ring system linked to group A is expected to be different from that of other heterocyclic dithiocarbamates and has not been attended so far. The seven-membered saturated ring system may cause more steric hindrance and thus can give metal complexes of unusual geometries. It is, therefore, thought worthwhile to examine the metal hexamethyleniminecarbodithioates. In the course of such studies it is observed that this ligand (Figure 1) can form Co(II) as well as Co(III) complexes (*4*). The complexes of both Fe(II) and Fe(III) can be prepared which are found to exhibit entirely different magnetic behaviors while their variable-temperature magnetic susceptibilities are measured (*4*). Such novel behavior has been rarely reported for other heterocyclic carbodithioates. X-ray powder diffraction data give an indication that the zinc(II), cadmium(II), and mercury(II) complexes are isomorphous with the copper(II) chelate, the diethyl analogue of which is known to possess a five-coordinate arrangement of sulfurs about the metal through dimerization (*5*). In the present paper, preparation of the complexes of divalent oxovanadium(IV), copper, nickel, zinc, cadmium, mercury, and trivalent chromium with this ligand and their spectral and magnetic properties along with *d* spacings obtained from X-ray powder patterns are reported for the first time.

Table I. Physical Properties of Metal Hexamethyleniminecarbodithioates[a]

complex	color	mp, °C	Λ_M, Ω^{-1} cm^2 mol^{-1}	μ_{eff}, μB
$VO(HMICdt)_2$	yellow	81–83	0.90	1.65
$Cr(HMICdt)_3$	bluish grey	>250	0.70	3.80
$Ni(HMICdt)_2$	yellowish green	212–13	0.85	dia
$Cu(HMICdt)_2$	chocolate	189–91	1.24	1.81
$Zn(HMICdt)_2$	white	176–77	1.02	dia
$Cd(HMICdt)_2$	white	223–24	1.14	dia
$Hg(HMICdt)_2$	light yellow	146–47	0.70	dia

[a] Elemental analyses were submitted for review.

Experimental Section

Synthesis of the Ligand. To prepare sodium hexamethyleniminecarbodithioate dihydrate ($NaHMICdt{\cdot}2H_2O$), sodium hydroxide pellets (2.0 g) were dissolved in a minimum amount of a mixture of ethanol and distilled water (4:1). Hexamethylenimine (5.0 g) in distilled diethyl ether was stirred with the NaOH slurry for 5 min and carbon disulfide (4.0 g) in 100 mL distilled diethyl ether was slowly added to the mixture under vigorous stirring during 1.5 h. The contents were further stirred for another 1.5 h and the precipitate was filtered, washed thoroughly with small portions of distilled ether, and dried over anhydrous calcium chloride in vacuo. The crude product (yield, 91%) was recrystallized from acetone–petroleum ether mixture, mp 188–89 °C. The recrystallized product yielded satisfactory elemental analysis, IR, NMR and mass spectra authenticating the purity of the compound. Presence of 2 mol of water as water of crystallization was confirmed by thermogravimetric analysis.

Synthesis of the Complexes. All the metal complexes except that of chromium(III) were obtained by reaction of the corresponding metal salt (0.25 g) and the ligand in 1:2 molar ratio in aqueous medium. The compounds which precipitated almost instantaneously were digested, washed repeatedly with distilled water, and dried over anhydrous calcium chloride followed by P_2O_5 under vacuum.

For the synthesis of the chromium(III) chelate the ligand in absolute ethanol was slowly added to a solution of $CrCl_3{\cdot}6H_2O$ in absolute ethanol in a 3:1 mole ratio. The resulting mixture was stirred vigorously and the precipitate so obtained was filtered, washed with absolute ethanol, and dried over anhydrous calcium chloride followed by P_2O_5 under vacuum.

Elemental Analysis. Analyses of the complexes were submitted for review. All the compounds were analyzed for C and H on Coleman C, H. analyzer, Model 33. Perkin Elmer-240B elemental analyzer was used for nitrogen content. Metal analyses were carried out, after destroying the organic moiety with concentrated nitric and hydrochloric acids, on a Pye Unicam SP 191 atomic absorption spectrophotometer using Pye Unicam hollow cathode lamps, for the respective elements.

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Table II. Electronic Absorption Spectral Bands and Their Assignments

complex	band positions, 10^3 cm^{-1} ($10^2\epsilon$, L mol^{-1} cm^{-1}) I	II	III	IV	V	ref
VO(HMICdt)$_2$[a]	16.45 [$b_2 \rightarrow b_1{}^b$]	18.38 [$b_2 \rightarrow e^b$]	21.01 [$b_2 \rightarrow a_1{}^b$]	26.04[b]	30.77[b]	*6*
Cr(HMICdt)$_3$	15.25 (3.770) [$^4A_{2g} \rightarrow {}^4T_{2g}(F)$]	20.00 (4.185) [$^4A_{2g} \rightarrow {}^4T_{1g}(F)$]	31.00[b] (248.8)	33.50[b] (267.67)		*7, 8*
Ni(HMICdt)$_2$	15.87 (0.887) [$^1A_{1g} \rightarrow {}^1B_{1g}$]	21.05 (2.341) [$^1A_{1g} \rightarrow {}^1B_{3g}$]	23.26[b] (13.889)	25.84[b] (63.333)	30.30[b] (35.139)	*7*
Cu(HMICdt)$_2$	16.39 (10.625) [$^2B_{1g} \rightarrow {}^2A_{1g}$]	22.99 (127.659) [$^2B_{1g} \rightarrow {}^2E_g$]	34.48[b] (199.148)	36.36[b] (334.468)		*9–11*

[a] Spectrum recorded in Nujol mull. [b] Bands are charge transfer in origin.

Table III. ESR Parameters of VO(II) and Cu(II) Chelate Complexes

	solution						polycryst (room temp)	
	room temp		liq nitrogen temp					
complex	A_0	g_0	$A_\parallel$	$A_\perp$	$g_\parallel$	$g_\perp$	$g_\parallel$	$g_\perp$
VO(HMICdt)$_2$	94.28	1.9847	105.71	88.56	1.9004	2.0268		
Cu(HMICdt)$_2$	96.67	2.0171	173.33	58.33	2.0638	1.9937	2.1292	1.9654

Table IV. Major Infrared Frequencies (cm^{-1}) in the Ligand and the Metal Complexes[a]

compound	ν(C–N)	$\nu(CSS)_{asym}$	$\nu(CSS)_{sym}$	ν(MS)
NaHMICdt·2H$_2$O	1490 vs	1013 sm, 978 vs, 958 vs	625 m	
VO(HMICdt)$_2$	1510 s	992 m	623 sm	408 m, 375 sm
Cr(HMICdt)$_3$	1510 vs	1010 sm, 990 m	628 sm	378 s, 352 sm
Ni(HMICdt)$_2$	1508 vs	1004 sm, 996 sm, 980 m	622 sm	394 s, 300 sm
Cu(HMICdt)$_2$	1508 vs	1010 m, 995 sm, 982 m	630 sm	368 s, 328 sm
Zn(HMICdt)$_2$	1510 vs	1010 sm, 985 s, 960 m	623 s	395 s, 302 s
Cd(HMICdt)$_2$	1508 s	1010 m, 985 s, 962 s	623 m	390 m, 380 m, 302 m
Hg(HMICdt)$_2$	1500 s	1005 sm, 995 sm, 980 m, 958 m	620 m	385 m, 303 m

[a] s = strong; v = very; m = medium; sm = small.

Table V. *d* Spacings from the X-ray Diffraction Powder Patterns[a]

Cu(HMICdt)$_2$	Zn(HMICdt)$_2$	Cd(HMICdt)$_2$	Hg(HMICdt)$_2$
7.698 (s)	7.789 (m)	7.721 (s)	7.721 (m)
6.529 (w)	6.254 (m)	6.435 (w)	6.435 (w)
4.766 (w)	4.805 (vw)	4.754 (vw)	4.799 (m)
4.607 (m)	4.655 (m)	4.631 (m)	4.643 (m)
4.392 (m)	4.318 (w)	4.360 (w)	4.329 (m)
4.187 (w)	4.197 (m)	4.207 (m)	4.227 (m)
4.073 (m)	3.914 (m)	3.914 (m)	4.055 (vw)
3.751 (m)	3.735 (w)	3.630 (w)	3.652 (w)
3.463 (w)	3.437 (m)	3.483 (vw)	3.348 (m)
3.118 (w)	3.167 (m)	3.151 (w)	3.145 (w)
2.919 (w)	2.928 (vw)	2.961 (w)	2.914 (w)
2.752 (m)	2.846 (w)	2.732 (vw)	2.833 (w)

[a] s = strong; m = medium; w = weak; vw = very weak.

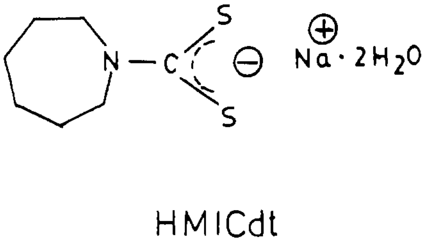

Figure 1.

Physical Measurements. Molar conductance of the metal chelates was determined at room temperature in nitrobenzene at 1 mM concentration on a W.G. Pye conductance bridge. Magnetic susceptibilities of polycrystalline samples were measured on a PARC vibrating sample magnetometer, Model 155, at room temperature, using a $^3/_{32}$ in × $^3/_{32}$ in cylindrical sample of high-purity nickel as calibrant and were corrected for diamagnetism. Electronic spectra of solid samples in Nujol mull and in chloroform were recorded on 554 Perkin Elmer UV–vis spectrophotometer. IR spectra in CsI were recorded in the range 4000–200 cm^{-1} on a Perkin Elmer 580 B IR spectrophotometer. Atmospheric moisture was removed from the spectrophotometric housing by flushing with dry air. ESR spectra of copper complex (polycrystalline sample and chloroform solution) and vanadyl complex (DMF solution), both at room and liquid nitrogen temperatures, were recorded on Varian E-12 EPR spectrometer. Proton and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide solutions on a Jeol JNM-FX 100 Fourier transform NMR spectrometer at 27 °C. The powder

Table VI. Nuclear Magnetic Resonance Chemical Shifts (δ)[a]

		^{13}C			
compound	^{1}H	C_γ	C_β	C_α	$>CS_2$
HMICdt·Na	1.46 (m), 1.68 (m), 4.12 (t)	26.56	27.29	53.52	212.15
Ni(HMICdt)$_2$	1.52 (m), 1.74 (m), 3.67 (t)	26.27		49.27	206.44
Zn(HMICdt)$_2$	1.54 (m), 1.75 (m), 3.96 (t)	26.19	26.49	54.84	203.00
Cd(HMICdt)$_2$	1.52 (m), 1.75 (m), 3.98 (t)	25.24	25.61	55.21	205.55
Hg(HMICdt)$_2$	1.56 (m), 1.78 (m), 3.94 (t)	26.05	26.27	57.48	201.6

[a] Chemical shifts in ppm from Me$_4$Si; m = multiplet, t = triplet.

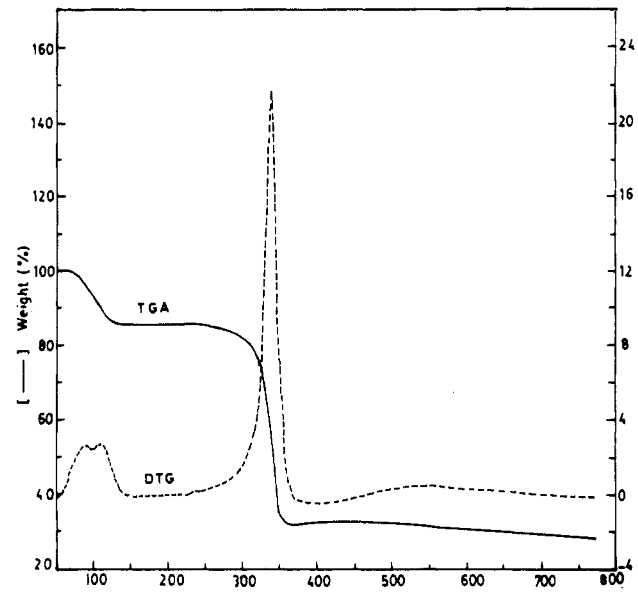

Figure 2. Thermogram of the ligand.

diffraction patterns were recorded by a Philips PW 1140/90 X-ray diffractometer using nickel filtered CuKα radiation and setting the goniometer speed at 1°/min. A Du Pont 1090 thermal analyzer having a 951 TGA module was used to study the thermal decomposition pattern of the ligand at a heating rate of 10 °C/min in the nitrogen atmosphere (Figure 2). The results are tabulated in Tables I-VI.

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Registry No. VO(HMICdt)$_2$, 15005-23-9; Cr(HMICdt)$_3$, 60351-87-3; Ni(HMICdt)$_2$, 14434-67-4; Cu(HMICdt)$_2$, 14353-95-8; Zn(HMICdt)$_2$, 35215-07-7; Cd(HMICdt)$_2$, 15308-66-4; Hg(HMICdt)$_2$, 94491-00-6.

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Synthesis of Some New 3-(2'-Benzothiazolyl)-4(3*H*)-quinazolinones as Antifungal Agents

Ram Lakhan* and Babban J. Rai

Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

Five new 2-methyl-3-[(substituted)benzothiazol-2'-yl]-4(3*H*)-quinazolinones have been synthesized. Three of them were tested for their antifungal activity against agricultural fungi by the food poison technique and the activity was compared with that of Dithan M-45.

Certain remarkable pharmacological and antimicrobial activities are known to be associated with the 4(3*H*)-quinazolinone ring system. Typically, quinazolinone derivatives are potent hypertensive (*1*), amoebicidal (*2*), antifungal (*3*), herbicidal (*4*), pesticidal (*5*), and bactericidal agents (*6*).

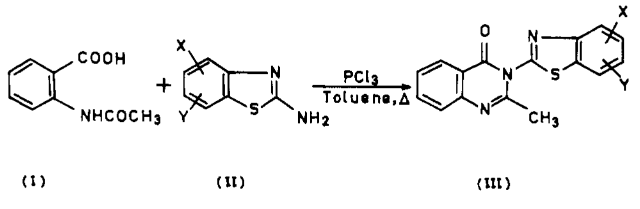
Several 4(3*H*)-quinazolinones have also been synthesized by incorporating other heterocyclic nuclei into the ring system with encouraging results. Kumar et al. (*7*) have synthesized a number of thiadiazolylquinazolinones and correlated their structure with in vitro antitubercular activity against *Mycobacterium smegmatis* and *Mycobacterium tuberculosis* H$_{37}$Rv strain. Furthermore, 6,8-disubstituted 2-methyl- and 2-styryl-3-[(substituted)benzothiazol-2-yl]-4(3*H*)-quinazolinones prepared by Chaurasia and co-workers (*8*) are found to exhibit both central nervous system (CNS) stimulating and depressive activities on mice.

In view of the diverse biological activities of 4(3*H*)-quinazolinones and the benzothiazole ring (*9*, *10*), it was considered worthwhile to synthesize some 4(3*H*)-quinazolinones incorporating the substituted benzothiazolyl moiety. 2-Methyl-3-[(substituted)benzothiazol-2'-yl]-4(3*H*)-quinazolinones (III) were prepared by heating the corresponding 2-aminobenzo-

Table I. 2-Methyl-3-[(mono- or disubstituted)benzothiazol-2'-yl]-4(3*H*)-quinazolinones[a] (III)

no.	substituents X	substituents Y	yield, %	mp, °C
1	5-NO$_2$	H	70	185
2	6-NO$_2$	H	72	200
3	4-CH$_3$O	7-Cl	65	195[b]
4	4-NO$_2$	6-Cl	68	245
5	4-Cl	6-NO$_2$	66	188

[a] All these compounds gave elemental analyses (C, H, N, S) within ±0.4% of the theoretical values. [b] NMR (Me$_2$SO-d_6) δ 2.06 (s, 3 H, CH_3), 2.15 (s, 3 H, OCH_3), 7.06-8.53 (m, 6 H, Ar-H).



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