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Synthesis and Characterization of Lead(II), Bismuth (III), Titanium(IV), Selenium(IV), Thorium(IV), Dioxomolybdenum(VI) and Dioxouranium(VI) Hexamethyleniminecarbodithioate and their Biological Activities

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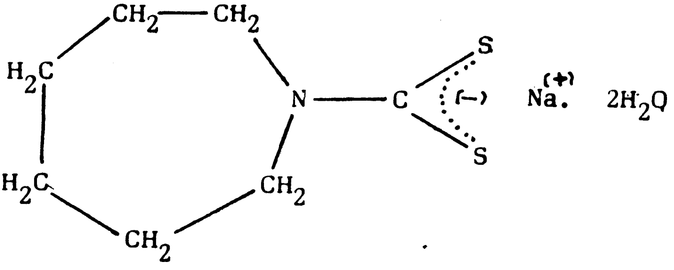
The lead(II), bismuth(III), titanium(IV), selenium(IV), thorium(IV), dioxomolybdenum(VI) and dioxouranium(VI) hexamethyleniminecarbodithioate complexes of the type $M(HMICdt)_2$, $M(HMICdt)_3$, $M(HMICdt)_4$, $MO_2(HMICdt)_2$ (where M = Metal and HMICdt = Hexamethyleniminecarbodithioate) have been synthesized and characterized by elemental analysis, molar conductance, magnetic measurements, electronic, IR, ^1H NMR spectroscopy. The dithio ligand exhibits univalent bidentate character and coordinates with metal symmetrically through bisulfur fork. All these complexes have been tested for their activity against bacteria and fungi and found to possess both antibacterial and antifungal activities.

INTRODUCTION

Many research workers' attention was drawn by the chemistry of dithiocarbamates of various metals because of their striking structural features and their applications[1-4] in diverse areas. A survey of earlier work[5-7] shows that no systematic study was reported on the hexamethyleniminecarbodithioate (HMICdt) complexes of dioxouranium, dioxomolybdenum and metals with high coordination number. Present paper describes the preparation and characterization of seven membered hexamethyleniminecarbodithioate complexes of dioxouranium(VI), dioxomolybdenum(VI) and metals with high coordination number along with usual other metals.



Sodium hexamethyleniminecarbodithioate $NaHMICdt \cdot 2H_2O$

Fig. 1

EXPERIMENTAL

The ligand (sodium hexamethyleniminecarbodithioate $NaHMICdt \cdot 2H_2O$) (Fig. 1) was prepared by a known method[8]. The recrystallized ligand showed satisfactory elemental analysis, IR and ^1H NMR spectra. Thermogravimetric analysis showed two moles of water of crystallization.

Bis(Hexamethyleniminecarbodithioate) Lead(II), $Pb(HMICdt)_2$

To the 100 ml aqueous solution (pH 3–3.35) of $Pb(NO_3)_2$ (2 mmol) was slowly added aqueous solution of ligand (in the ratio of 1 : 2 metal to ligand). The precipitate formed was filtered, washed with distilled water and finally with ethanol and dried over P_2O_5 in vacuum (yield 80%).

Tris(Hexamethyleniminecarbodithioate) Bismuth(III), $Bi(HMICdt)_3$

To the aqueous solution of $Bi(NO_3)_3$, (2 mmol) aqueous solution of ligand was added in the 1 : 3 (M : L) proportion with constant stirring. The resulting intense yellow coloured precipitate was filtered, washed with distilled water and finally with ethanol and dried over P_2O_5 in vacuum (yield 85%).

Bis(Hexamethyleniminecarbodithioate) dioxomolybdenum(VI) and dioxouranium(VI), $MoO_2(HMICdt)_2$ and $UO_2(HMICdt)_2$

Aqueous alcoholic solutions of ammonium molybdate and uranyl nitrate were mixed separately with aqueous solution of ligand (1 : 2 ratio) with constant stirring. The molybdate reaction mixture was chilled and acidified with 1 N HNO_3 till pH was 5.5 and molybdenal complex was obtained. Both the complexes were filtered, washed with water and finally with ethanol and dried over P_2O_5 in vacuum (yield 75%.)

Tetrakis (Hexamethyleniminecarbodithioate) Titanium(IV), Selenium(IV) and Thorium(IV), $Ti(HMICdt)_4$, $Se(HMICdt)_4$ and $Th(HMICdt)_4$

All these complexes were prepared by mixing titanium terachloride, selenium dioxide and thorium nitrate in aqueous solution of ethanol and the stoichiometric (1 : 4 molar) quantity of the ligand in aqueous ethanol with constant stirring. When the reaction was complete, the alcohol was removed under vacuum at room temperature. The complexes were washed with distilled water and finally with ethanol and dried over P_2O_5 in vacuum (yield 70%).

RESULTS AND DISCUSSION

Results of elemental analysis recorded in Table 1 authenticate the assigned stoichiometries. The molar conductance values of all the complexes in $PhNO_2$ fall in 0.19–0.46 $\Omega\ cm^{-1}\ mol^{-1}$ range suggesting the non-electrolytic nature of these complexes. All the complexes are diamagnetic in nature.

$Pb(HMICdt)_2$

In the IR spectrum of the diamagnetic $Pb(HMICdt)_2$ complex the $\nu(C \overset{\cdots}{-} N)$, $\nu_{asym}(C \overset{\cdots}{-} S)$, $\nu_{sym}(C \overset{\cdots}{-} S)$, and $\nu(Pb–S)$ bands appear at $1505\ cm^{-1}$, $985\ cm^{-1}$, $620\ cm^{-1}$ and $380\ cm^{-1}$ respectively. The nature and extent of shift observed in $\nu(C \overset{\cdots}{-} N)$, $\nu_{sym}(C \overset{\cdots}{-} S)$, $\nu_{asym}(C \overset{\cdots}{-} S)$ and (M–S) bands on complexation were of the same order (Table 3) of magnitude as reported in the literature[9] for square planar complex indicating symmetric bonding of the dithiocarbamate (CSS) group. To understand further about the bonding of bisulfur form of HMICdt$^{(-)}$ with the lead (Pb(II)) the ^{1}H NMR of the ligand and Pb(II) complex were studied (Table 2). The α-CH_2 proton appearing at δ 3.32(t) ppm showed no change in the fine structure of the triplet. This suggests that on complexation, CSS$^{(-)}$ group coordinates symmetrically as univalent bidentate ligand. Moreover the β- and γ-CH_2 protons appearing at 1.81(m) and 1.51(m) ppm respectively further supported the inference that the bisulfur fork is symmetrically bonded to metal.

TABLE 1

CHARACTERIZATION DATA OF COMPLEXES

Complex and colour	Calc. (Found)%					m.pt. (°C)
	M	C	H	N	S	
Pb(HMICdt)$_2$ (White)	37.29	30.27	4.32	5.04	23.06	175
(m.wt. 555)	(37.30)	(30.30)	(4.25)	(5.12)	(23.00)	(dec)
Bi(HMICdt)$_3$ (Intense yellow)	28.59	34.47	4.92	5.74	26.26	170–172
(m.wt. 731)	(28.64)	(34.55)	(4.95)	(5.64)	(26.16)	
Ti(HMICdt)$_4$ (Reddish orange)	6.45	45.16	6.45	7.52	34.40	116–118
(m.wt. 744)	(6.37)	(45.26)	(6.36)	(7.40)	(34.20)	
Se(HMICdt)$_4$ (Orange red)	10.19	43.35	6.19	7.22	33.03	126–128
(m.wt. 775)	(10.26)	(43.10)	(6.00)	(7.05)	(33.00)	
Th(HMICdt)$_4$ (White)	25.00	36.20	5.17	6.03	27.58	168
(m.wt. 928)	(24.92)	(36.35)	(5.28)	(6.15)	(27.30)	(dec)
UO_2(HMICdt)$_2$ (Yellow)	38.51	27.18	3.88	4.53	20.71	178–180
(m.wt. 618)	(38.46)	(27.05)	(3.98)	(4.49)	(20.68)	(dec)
MoO_2(HMICdt)$_2$ (Greenish yellow)	20.16	35.29	5.04	5.88	26.29	193–198
(m.wt. 476)	(20.20)	(35.18)	(5.00)	(5.67)	(26.06)	(dec)

dec = melts with decomposition

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ ppm) OF THE COMPLEXES IN d_6 DMSO USING TMS AS AN INTERNAL STANDARD

Ligand/Complex	^{1}H		
	α-CH_2	β-CH_2	γ-CH_2
(NaHMICdt)·$2H_2O$	4.13(t)	1.68(m)	1.43(m)
Pb(HMICdt)$_2$	3.32(t)	1.81(m)	1.51(m)
Bi(HMICdt)$_3$	3.32(t)	1.77(m)	1.57(m)
Ti(HMICdt)$_4$	3.36(t)	1.74(m)	1.56(m)
Se(HMICdt)$_4$	3.33(t)	1.79(m)	1.53(m)
Th(HMICdt)$_4$	3.34(t)	1.69(m)	1.59(m)
UO_2(HMICdt)$_2$	3.34(t)	1.77(m)	1.56(m)
MoO_2(HMICdt)$_2$	3.32(t)	1.82(m)	1.51(m)

m = multiplet, t = triplet

$Bi(HMICdt)_3$

The electronic spectrum of the diamagnetic $Bi(HMICdt)_3$ in chloroform exhibits bands at 23.80 kK, 27.39 kK, 30.76 kK and 38.10 kK as expected for an octahedral bismuth(III) where band at 38.10 kK is assigned to metal-ligand charge transfer ($^1A_{1g} \rightarrow {}^1T_{1g}$) and band at 30.76 kK is attributed to a second charge transfer ($^1A_{1g} \rightarrow {}^1T_{2g}$). The low intensity bands at 27.39 kK and 23.80 kK are assigned to intraligand transitions. This low intensity band arises from the moving of non-bonding electron in (C=S) group to an antibonding π molecular orbital[10, 11]. Then the (Bi–S) in the IR spectrum was observed at 380 cm^{-1}. The nature and extent of shift in the IR spectra (Table 3) of $Bi(HMICdt)_3$ are in agreement with symmetric chelation of $CSS^{(-)}$ group which is further supported by the ^{1}NMR of $Bi(HMICdt)_3$ (Table 2).

$UO_2(HMICdt)_2$ and $MoO_2(HMICdt)_2$

Both $UO_2(HMICdt)_2$ and $MoO_2(HMICdt)_2$ complexes behaved as non-electrolytes in nitrobenzene and were sparingly soluble in methanol and acetonitrile. The electronic spectra of the diamagnetic $UO_2(HMICdt)_2$ and $MoO_2(HMICdt)_2$ in chloroform displayed bands at 27.71 kK, 35.66 kK and 40.95 kK and 29.41 kK, 31.25 kK and 38.64 kK respectively. Absorptions at 27.71 kK and 29.41 kK may be assigned to metal ligand charge transfer while absorption bands at 35.66 kK and 31.25 kK may be assigned to intraligand transition. Bands at 40.95 and 38.64 kK are assigned to typical UO_2^{+2} and MoO_2^{+2} species. All these observations suggest the octahedral structure for both $UO_2(HMICdt)_2$ and $MoO_2(HMICdt)_2$ complexes.

In the IR spectra (Table 3) of $UO_2(HMICdt)_2$ and $MoO_2(HMICdt)_2$ the ν(U–S) and ν(Mo–S) bands were observed at 380 cm^{-1} and 390 cm^{-1} respectively. The O=Mo=O and and O=U=O bands were observed at 925 cm^{-1} and 928 cm^{-1} respectively due to terminal[12-14] (M=O) bond ruling out the presence of M–O–M–O chain. The nature and the extent of shifts of $\nu(C \overset{\cdots}{=} N)$, $\nu_{sym}(C \overset{\cdots}{=} S)$ and $\nu_{asym}(C \overset{\cdots}{=} S)$ bands suggested that the chelation in these two complexes is symmetrical through the bisulfur fork of $CSS^{(-)}$ group. This is further supported by ^{1}H NMR spectra (Table 2) where the α-CH_2 proton appear at δ 3.32(t) and δ 3.34(t) ppm for $MoO_2(HMICdt)_2$, $UO_2(HMICdt)_2$ respectively, showed no change in the fine structure of the triplet. This suggests that on complexation $CSS^{(-)}$ group coordinates symmetrically as univalent bidentate ligand. Moreover the β- and γ-CH_2 protons appeared at 1.83(m), 1.77(m) and 1.51(m), 1.56(m) ppm for $MoO_2(HMICdt)_2$ and $UO_2(HMICdt)_2$ respectively. This further supported the inference that the bisulfur fork is symmetrically bonded to metal.

$Ti(HMICdt)_4$, $Se(HMICdt)_4$ and $Th(HMICdt)_4$

The electronic spectra of the diamagnetic $Ti(HMICdt)_4$, $Se(HMICdt)_4$ and $Th(HMICdt)_4$ in chloroform exhibited absorption bands approximately in the region of 27 kK--33 kK and 36 kK–40kK.

It seems to be agreed[15] that the bands near 27 kK and 30 kK are due to metal-ligand charge transfer and the bands near 36 kK and 40 kK are due to ligand transitions (π–π^*). These observations suggest the dodecahedral structure[16, 17] as expected for $Ti(HMICdt)_4$, $Se(HMICdt)_4$ and $Th(HMICdt)_4$ complexes.

In the IR spectra (Table 3) all the three complexes showed strong band in the range of 980–985 cm^{-1} authenticating[15, 18] the fact that all the three complexes contain eight coordinated metal complexes. All these complexes were non-conductors in nitrobenzene and thus ruled out the electrolytic structures such as $[M(HMICdt]_3^{(+)}[HMICdt]^{(-)}$. The metal sulfur stretching frequencies of all the three complexes were found in the region of 380–400 cm^{-1}. These values are relatively higher than the M–S frequencies for the NN–dialkyldithiocarbamates of Ti(IV)[15] and Th(IV)[18, 19]. Therefore it is reasonable to expect the higher M–S frequencies because two alkyl groups are replaced by saturated aromatic ring system. The nature and the extent of shifts of $\nu(C \cdots N)$, $\nu_{sym}(C \cdots S)$ and $\nu_{asym}(C \cdots N)$ modes in the IR spectra (Table 3) of these three complexes suggest that the bisulfur fork is symmetrically chelated to metal. The ^1H NMR spectra (Table 2) of these three complexes were alomost identical to those of remaining complexes and thus further supported the symmetrical chelation by the bisulfur fork.

TABLE 3
CHARACTERISTIC IR BANDS (cm^{-1})

Complex	ν(C–N)	ν_{asym}(CSS)	ν_{sym}(CSS)	ν(M–S)	O=U=O	O=Mo=O
NaHMICdt	1490(vs)	958(vs) 978(vs)	625(sm)	—	—	—
$Pb(HMICdt)_2$	1505(s)	985(vs)	620(sm)	380(sm)	—	—
$Bi(HMICdt)_3$	1505(vs)	985(m)	630(sm)	380(sm)	—	—
$Ti(HMICdt)_4$	1520(s)	1005(m) 985(sm)	625(sm)	385(sm)		
$Se(HMICdt)_4$	1510(vs)	1010(m) 980(sm)	625(s)	400(sm)	—	—
$Th(HMICdt)_4$	1500(s)	985(s)	635(sm)	385(sm)	—	—
$UO_2(HMICdt)_2$	1510(vs)	980(sm)	635(sm)	380(sm)	925(vs)	—
$MoO_2(HMICdt)_2$	1550(vs)	965(vs)	640(sm)	390(sm)	—	928(s)

s = strong; vs = very strong; m = medium; sm = small.

Antimicrobial Screening

Antimicrobial activities of the ligand (NaHMICdt) and some of its complexes have already been reported[6]. In continuation of these studies, 5% solution of above complexes were tested for antibacterial activities by using the Agar-Ditch-Plate method. Antifungal activities were determined in sabourand's broth. The results are summarized below (Table 4).

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TABLE 4
ANTIMICROBIAL RESULTS

Complex	S.a.	K.p.	Pr. v	P.a.	C.a	E.c.	T.m.
$Pb(HMICdt)_2$	(++)	(+)	(+)	(+)	(+)	(±)	(+)
$Bi(HMICdt)_3$	(–)	(–)	(–)	(±)	(–)	(–)	(+)
$Ti(HMICdt)_4$	(–)	(–)	(±)	(–)	(–)	(–)	(+)
$Se(HMICdt)_4$	(–)	(–)	(±)	(–)	(–)	(–)	(+)
$Th(HMICdt)_4$	(+++)	(–)	(+)	(++)	(+)	(++)	(+)
$UO_2(HMICdt)_2$	(+++)	(–)	(+)	(++)	(+)	(++)	(+)
$MoO_2(HMICdt)_2$	(–)	(–)	(–)	(–)	(–)	(–)	(–)

S.a = *Staphylococcus aureus,* C.a. = *Candida albicans* K.p. = *Klebsiella pneumoniae* E.c. = *Escherichia coli* Pr.v. = *Proteus vulgaris,* T.m. = *Trichophyton mentagrophytes* P.a. = *Pseudomonas aeruginosa,* (–) = No inhibition; (±) = Partial inhibition; (+) = Total inhibition; (++) = Marked inhibition; (+++) = Very much marked inhibition

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