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THE THERMAL PROPERTIES OF SOME METAL COMPLEXES OF DIETHYLDITHIOCARBAMIC ACID

NEW VOLATILE METAL CHELATES

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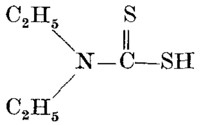
The cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) complexes of diethyldithiocarbamic acid were prepared and their thermal properties determined by TG, DTA, and high temperature reflectance spectroscopy. It was found that the copper(II), nickel(II), and zinc(II) chelates were completely volatile and thus represent a new class of volatile metal chelates. Vapor pressure measurements were made on four of the metal complexes; heats of vaporization ranged from 9.3 ± 0.2 kcal/mole for $Na[Co(DDC)_3]$ to 24.2 ± 0.6 kcal/mole for $Zn(DDC)_2$.

Diethyldithiocarbamic acid (DDC), readily forms complexes with



monovalent, divalent, and trivalent metal ions, having the general formula, $M(DDC)_n$, where n is the positive charge of the metal ion. A preliminary investigation by D'Ascenzo and Wendlandt [1] revealed that several of the metal diethyldithiocarbamates were completely volatile in an inert gas atmosphere. Since the thermal properties of these complexes have not been previously reported, the compounds of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and mercury(II) were prepared and studied by TG, DTA, high temperature reflectance spectroscopy, and by vapor pressure measurements.

Experimental

Instruments

The TG curves were obtained on a Du Pont Model 950 Thermobalance using dynamic air, oxygen, or nitrogen furnace atmospheres. Sample sizes ranged in mass from 10 to 12 mg; a furnace heating rate of 10° per min. was employed.

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A DuPont Model 920 Thermograph and/or a Deltatherm III DTA instrument were used to obtain the DTA curves in dynamic air, oxygen, or nitrogen atmospheres. Sample sizes ranged in mass from 5 to 10 mg; a furnace heating rate of 10° per min was employed.

The reflectance studies were carried out using the heated sample holder previously described by Wendlandt [2—4] and a Beckman Model DK-2A spectroreflectometer. White glass fiber cloth covered with a thin cover glass was used as the reflectance standard. A heating rate of 5 to 10° per min was employed for the DRS mode.

Vapor pressure studies

A conventional isoteniscope and associated vacuum system were used to measure the vapor pressure of the anhydrous compounds in the pressure range from 1 to 260 Torr at temperatures from 25° to 220°. The sample chamber was flushed repeatedly with nitrogen and evacuated a number of times before the pressure measurements were taken in order to remove traces of water and oxygen. "U" tube mercury was changed after each run. The ΔH of sublimation was calculated by conventional methods with the sublimation temperature being obtained by an extrapolation procedure. The Ag(I) and Hg(II) complexes did not give satisfactory results due to their low melting points while the results obtained for the Cd(II) complex were erratic and non-reproducible.

Preparation of compounds

The metal complexes were prepared by adding a 0.1 M solution of the metal chloride to a 0.1 M solution of the sodium diethyldithiocarbamate so that a metal-to-ligand ratio of 1 : 4 was obtained. A precipitate formed immediately, and after stirring and heating the mixture for about one hour, it was filtered off, washed with hot water until free of the carbamic acid salt and dried for 48 hours in a vacuum desiccator at room temperature.

Table 1

Metal and water analyses of metal complexes

Compound	Metal, %		H_2O, %	
	Found	Theor.	Found	Theor.
$Na[Co(DDC)_3] \cdot H_2O$	11.3	11.2	4.9	4.8
$Ni(DDC)_2 \cdot 6\,H_2O$	16.7	16.5	23.0	23.4
$Cu(DDC)_2 \cdot 1.5\,H_2O$	17.6	17.7	7.0	7.0
$Zn(DDC)_2$	18.1	18.1	—	—
$Cd(DDC)_2 \cdot 16\,H_2O$	27.3	27.5	48.2	48.1
Ag(DDC)	42.3	42.1	—	—
$Hg(DDC)_2$	40.7	40.3	—	—

Table 2

Procedural TG decomposition temperature for metal diethyldithiocarbamates

Complex	Atm.	Decomposition step, °C					
		I	II	III	IV	V	VI
$Na[Co(DDC)_3] \cdot \cdot H_2O$	N_2	35[a] 30—45[b]	310 250—340				
	air	40 30—50	300 250—315	460 435—560	820 710—870		
	O_2	35 30—45	260 240—270				
$Ni(DDC)_2 \cdot 6\,H_2O$	N_2	45 30—60	305 250—320				
	air	50 30—75	305 245—350	560 440—665	765 725—875		
	O_2	45 30—60	290 220—315				
$Cu(DDC)_2 \cdot 1.5\,H_2O$	N_2	40 30—45	260 170—330				
	air	45 30—50	260 170—310	470 325—500	665 590—750		
	O_2	40 30—50	230 170—265	415 365—485	660 515—760		
$Zn(DDC)_2$	N_2		265 165—320				
	air		265 165—320	535 500—590	825 685—850		
	O_2		230 165—310	470 410—500	760 700—800		
$Cd(DDC)_2 \cdot 16\,H_2O$	N_2	50 30—70	290 225—350				
	air	70 30—95	285 235—330	630 490—700	915 760—930		
	O_2	55 30—80	280 235—325	625 480—700	910 760—930		
AgDDC	N_2		250 150—320				
	air		250 155—300	480 420—520	580 520—610	770 610—830	890 830—920
	O_2		230 150—290	450 375—480	500 480—520	550 520—600	890 830—920
$Hg(DDC)_2$	N_2		235 165—280	360 280—425			
	air		220 150—245	335 245—420			
	O_2		205 150—230	305 230—415			

[a] Refers to temperature at maximum rate of mass-loss.
[b] Temperature range of mass-loss.

Table 3

DTA procedural peak temperatures in various atmospheres

Complex	Atm.	Peak temperatures, °C						
		I	II	III	IV	V	VI	VII
Na[Co(DDC)$_3$] · H_2O	N_2	65^a 30—105^b	265 255—280	310 300—330	345 330—355			
	air	70 30—105	265 250—270	305 270—330↑	460 400—520↑	860 800—910		
	O_2	65 30—105	265 245—285					
Ni(DDC)$_2$ · 6 H_2O	N_2	60 30—100	230 225—280	320 280—355				
	air	70 30—100	230 225—280	335 300—340	345 340—355↑	560 450—625↑	865 725—885	
	O_2	60 30—100	210 205—220	285 220—300↑				
Cu(DDC)$_2$ · 1.5 H_2O	N_2	60 30— 80	200 190—220	310 280—340				
	air	70 30—100	200 190—220	280 220—315↑	490 335—530↑	575 540—615		
	O_2	60 30— 80	200 190—215	265 215—300↑	415 300—500↑	600 515—675		
Zn(DDC)$_2$	N_2	80 30—100	175 160—190	305 280—325				
	air	80 30—100	175 160—190	305 280—310	320 310—350↑	540 500—600↑	825 700—850	
	O_2	80 30—100	175 160—185	280 200—295↑	310 295—360↑	460 405—500↑	760 695—790	

$Cd(DDC)_2 \cdot 16\,H_2O$	N_2	85	240	295				
		30—150	220—250	275—330				
	air	90	240	310	640	840		
		30—150	220—250	290—325↑	510—710↑	750—920		
	O_2	90	240	290	340	505	900	
		30—150	230—250	270—300↑	325—400↑	400—540↑	760—910	
AgDDC	N_2	55	165	280				
		30— 85	150—180	250—330				
	air	60	165	270	450	580	780	880
		30— 90	150—185	240—300↑	425—510↑	510—610	710—830↑	830—915
	O_2	55	165	260	445	495	545	855
		30— 85	150—185	230—280↑	420—480↑	480—510	510—600↑	810—910
$Hg(DDC)_2$	N_2	60	115	245	345	415		
		30— 90	105—130	130—310	310—375	375—450		
	air	60	115	225	240	390	420	
		30— 90	105—130	210—230	230—350↑	350—410↑	410—430	
	O_2	60	115	225	240	420	480	
		30— 90	105—130	205—230	230—260↑	350—440↑	440—500	

[a] Peak maximum temperature

[b] Temperature range of peak.

Note: All endothermic peaks except those indicated (↑).

Analysis of compounds

The metal contents of the dried complexes, except silver, were all determined by titration with EDTA. Silver in the metal complexes was determined by the Volhard method. Water contents were determined by TG. The metal and water analyses are given in Table 1.

Results and discussion

The metal complexes were all studied by TG and DTA in air, oxygen, and nitrogen atmospheres. However, only the curves obtained in nitrogen will be discussed (except for $Na[Co(DDC)_3] \cdot H_2O$), the other data will be included in Tables 2 and 3. All temperatures referred to in the TG and DTA data are procedural decomposition temperatures at the heating rate of 10° per min. High temperature reflectance spectroscopy (HTRS) and dynamic reflectance spectroscopy (DRS) data were obtained on all of the complexes, but only $Na[Co(DDC)_3] \cdot H_2O$ will be reported here.

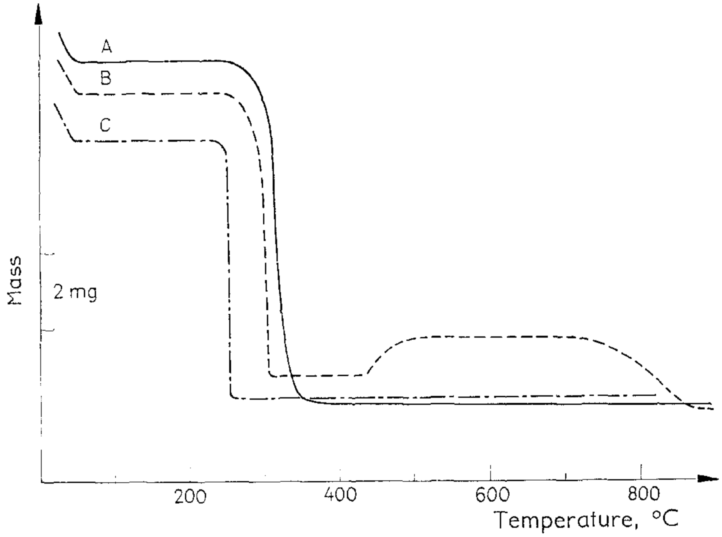

Fig. 1. Mass-loss curves of $Na[Co(DDC)_3] \cdot H_2O$ under various conditions; heating rate of 10° per min. A: nitrogen, B: air, C: oxygen

$Na[Co(DDC)_3] \cdot H_2O$

This compound precipitates from solution as the 1-hydrate; water of hydration is evolved in a single step in all of the gaseous atmospheres studied, as was expected. In a nitrogen atmosphere, the mass-loss curve (Fig. 1) shows a large mass-loss beginning at about 250°C which is caused by volatilization and partial decomposition of the complex. Some of the vaporized material was collected and analyzed and found to be anhydrous Na[Co(DDC)$_3$]. A small amount of residue (Co_3O_4) in the sample container (11.3%) indicated that some decomposition of the complex had also taken place. In an air atmosphere, the anhydrous compound decomposes in a single step at about the same temperature, but the decomposition residue is a mixture of Co_3O_4 and CoS; the latter is then oxidized to $CoSO_4$ which accounts for the mass gain starting at about 430°. The $CoSO_4$ then dissociates to the oxide beginning at about 700°. The decomposition behavior is somewhat different in oxygen; the anhydrous compound begins to decompose at about 225° but apparently goes directly to the oxide. The absence of CoS is shown by the fact that oxidation to $CoSO_4$ does not take place at higher temperatures. Also, the stoichiometry of the reaction indicates only cobalt oxide formed (21.0% found, 21.1% theor.).

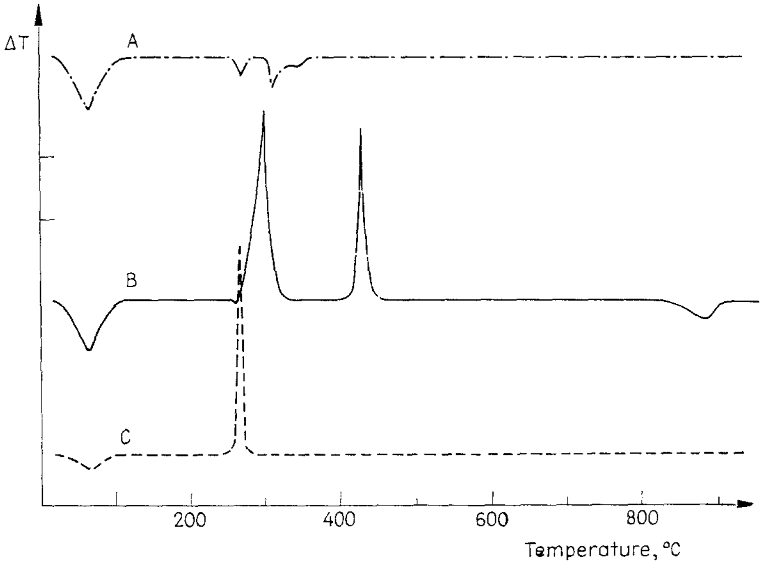

Fig. 2. DTA curves of Na[Co(DDC)$_3$] · H_2O in various atmospheres; heating rate: 10° per min. A: nitrogen, 1°, B: air 1°, C: oxygen 10° in ΔT

The DTA curves of this compound in the various atmospheres are shown in Fig. 2. In nitrogen, three endothermic peaks and a shoulder peak are present. The first peak is due to the dehydration reactions, the second to the fusion of the anhydrous compound, and the other to the volatilization and decomposition of the fused compound. In air, two endothermic and two exothermic peaks were found in the DTA curve. The first endothermic peak is due to the fusion, decomposition, and oxidation of the fused complex to give a mixture of Co_3O_4 and CoS.

The CoS is then oxidized to $CoSO_4$ as indicated by the next exothermic peak. The last endothermic peak in the 800—900° temperature range is due to the decomposition of the $CoSO_4$. In oxygen, as was expected from the TG curve, only dehydration (first endothermic peak) followed by fusion, decomposition, and oxidation of the anhydrous compound (the exothermic peak) took place.

The HTRS curve at 25° (Fig. 3) contains a single maximum at 540 nm which decreases in intensity as the temperature increases. At 250° the curve is essentially

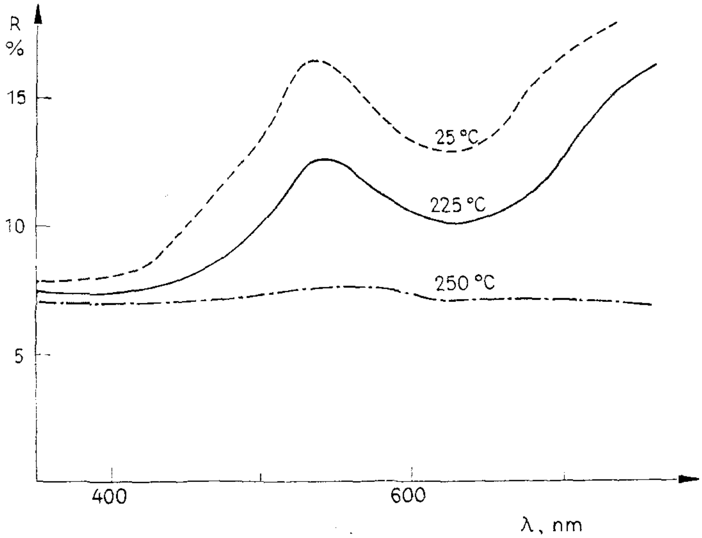

Fig. 3. HTRS curve of Na[Co(DDC)$_3$] · H_2O at various temperatures

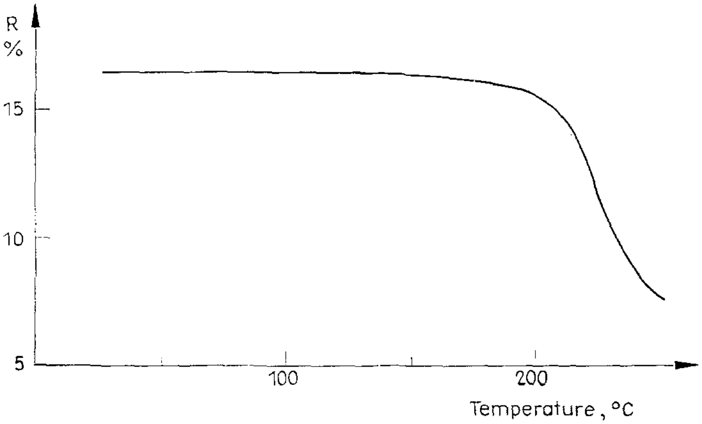

Fig. 4. DRS curve of Na[Co(DDC)$_3$] · H_2O at 540 nm, heating rate: 5° per minute

flat. The DRS curve in Fig. 4 shows that the reflectance decreases slightly with temperature until about 200°. Above this temperature, the reflectance decreases much more rapidly.

$Ni(DDC)_2 \cdot 6\,H_2O$

This compound precipitates from solution as the 6-hydrate. The mass-loss curve in nitrogen shows that all of the water is evolved at 55°, giving anhydrous $Ni(DDC)_2$. The latter begins to vaporize at 220°, giving an empty sample container at 310°. The DTA curve shows a large endothermic peak due to the dehydration reaction followed by two smaller endothermic peaks. The latter peaks are due to the fusion and volatilization of the anhydrous complex, respectively.

$Cu(DDC)_2 \cdot 1.5\,H_2O$

The water of hydration is evolved at temperatures up to 45°, giving anhydrous $Cu(DDC)_2$. The $Cu(DDC)_2$ volatilizes completely in the temperature range from 170° to 330° in nitrogen. The DTA curve reveals the same type of behavior as was observed for $Ni(DDC)_2 \cdot 6\,H_2O$—dehydration, fusion, and then total volatilization.

$Zn(DDC)_2$

The mass-loss curve showed that the anhydrous complex began to volatilize at about 160° giving an empty sample container at 320°. The DTA curve showed only an endothermic peak due to the fusion reaction and another such peak for the volatilization of the fused compound.

$Cd(DDC)_2 \cdot 16\,H_2O$

The large amount of water of hydration in this compound may be due to hydrate-bound water and/or absorbed or occluded water of some type. The water is evolved at relatively low temperatures; room temperature to 60° as indicated by the mass-loss curve. The anhydrous $Cd(DDC)_2$ then volatilizes in the temperature range of 225° to 350°. The DTA curve was similar to those obtained for the copper(II) and nickel(II) compounds.

AgDDC

The mass-loss curve indicates partial volatilization in the temperature range of 150° to 325°. The DTA curve contains endothermic peaks for the fusion and volatilization reactions, respectively.

$Hg(DDC)_2$

The anhydrous compound began to volatilize at 170° giving a break in the curve at about 270°. Further volatilization and/or decomposition took place above this temperature resulting in an empty sample container at 410°. The DTA curve contained three endothermic peaks due to fusion, volatilization, and volatilization and/or decomposition, respectively.

Vapor pressure studies

The vapor pressures of the anhydrous cobalt(II), nickel(II), copper(II), and zinc(II) complexes were obtained by use of the isoteniscope. A typical vapor pressure curve is represented by that for $Na[Co(DDC)_3]$ as shown in Fig. 5. The calculated ΔH of sublimation and the extrapolated sublimation temperatures are given in Table 4.

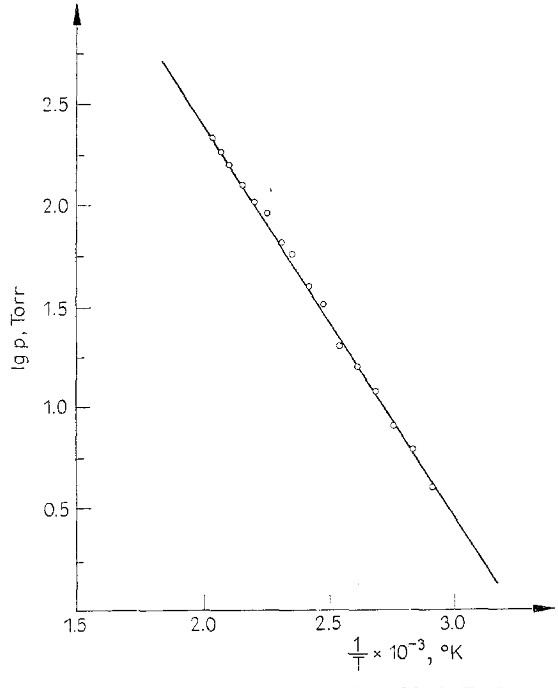

Fig. 5. Vapor pressure curve of $Na[Co(DDC)_3]$

General

From the mass-loss curves and the vapor pressure measurements, it is seen that most of the metal diethyldithiocarbamates are highly volatile. The volatility of these complexes is due, perhaps, to their structural properties as determined by

Table 4

Heats of sublimation of metal chelates

Metal chelate	ΔH, kcal/mole	Subl. temp.,[a] °C
$Na[Co(DDC)_3]$	9.3 ± 0.2	267
$Ni(DDC)_2$	14.6 ± 0.4	286
$Cu(DDC)_2$	20.8 ± 0.4	229
$Zn(DDC)_2$	24.2 ± 0.6	217

[a] Extrapolated from vapor pressure curves.

a number of investigations [5—8]. It is found that the metal ion coordinates to both of the sulfur atoms in the ligand and in the case of copper(II) and zinc(II); a fifth sulfur may be coordinated also in some cases. The remarkable stability of the metal-to-sulfur bond and the particular structure forming four-membered chelate rings probably accounts for the high volatility of these compounds.

The volatility of these compounds is also quite interesting because it perhaps could not have been predicted from the information available at the present time. The volatility of these metal complexes suggests their immediate use for separation processes *via* the gas chromatographic technique.

The ΔH of sublimation of the compounds reported in Table 4 shows that the values range from 9.3 for cobalt(II) to 24.2 kcal per mole for the zinc(II) chelate. The ΔH values increase in the same order as the increase in electronegativity of the metal ion.

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RÉSUMÉ — On a préparé les complexes de cobalt(II), nickel(II), cuivre(II), zinc(II), cadmium(II), argent(I) et mercure(II) avec l'acide diéthyle-dithiocarbaminique et étudié leurs propriétés thermiques par TG, ATD et spectroscopie de reflexion à haute température. On a trouvé que les complexes de cuivre(II), nickel(II) et zinc(II) volatilisent parfaitement; ils représentent une nouvelle sorte de chélates métalliques volatiles. On a fait des mesures de pression de vapeur sur quatre de ces complexes. Les valeurs des chaleurs de vaporisation s'étalent de 9.3 ± 0.2 kcal/mole pour $Na[Co(DDC)_3]$ jusqu'à 24.2 ± 0.6 kcal/mole pour $Zn(DDC)_2$.

ZUSAMMENFASSUNG — Es wurden die Komplexe von Kobalt(II), Nickel(II), Kupfer(II), Zink(II), Cadmium(II), Silber(I) und Quecksilber(II) mit Diäthyldithiokarbaminsäure hergestellt und ihre thermischen Eigenschaften durch Thermogravimetrie, Differentialthermoanalyse und Hochtemperatur Reflexions Spektroskopie untersucht. Man fand, daß die Kupfer(II)-, Nickel(II)- und Zink(II)-Komplexe vollständig verflüchtigen. Sie stellen eine neue Sorte flüchtiger Metallchelate dar. Dampfdruckmessungen wurden an vier der Komplexe unternommen. Die Verdampfungswärmen liegen zwischen den Werten von 9.3 ± 0.2 Kcal/Mol für $Na[Co(DDC)_3]$ bis 24.2 ± 0.6 Kcal/Mol für $Zn(DDC)_2$.

Резюме. — Синтезированы комплексы кобальта [II], никкеля [II], меди [II], цинка [II], кадмия [II], серебра [I] и ртути [II] с диэтилдитиокарбаминовой кислотой и определены их термические свойства методами ТГ, ДТА и спектроскопии отражения при высокой температуре. Найдено, что хелаты меди [II], никеля и цинка [II] являются летучими соединениями — представителями нового класса летучих хелатов металлов. Измерено давление пара для четырёх металл-комплексов; теплота испарения колеблется в интервалах 9,3 ± 0,2 ккал/моль для $Na[Co(DDC)_3]$ и 24,2 ± 0,6 ккал/моль для $Zn[DDC]_2$.