Reactions of the *cis*-1,2-Dicyanoethylenedithiolate Ion with Disubstituted Group IVb Organometallic Compounds[1]

EDWARD S. BRETSCHNEIDER and CHRISTOPHER W. ALLEN*

The reactions between disodium dicyanoethylene-1,2-dithiolate (Na$_2$mnt) and various group IVb dialkyl and diaryl halides in the presence of tetraalkylammonium, tetraphenylphosphonium, and tetraphenylarsonium ions have been investigated. Complexes exhibiting the following stoichiometries have been prepared and characterized: $[(C_6H_5)_4E][M(mnt)R_2X]$ (E = P, As; M = Sn, R = CH$_3$, X = Cl, Br, I; R = C$_6$H$_5$, X = Cl; M = Pb, R = C$_6$H$_5$, X = Cl) and $[R'_4N]_2[M(mnt)_2R_2]$ (M = Sn, R = CH$_3$, C$_6$H$_5$; M = Pb, R = C$_6$H$_5$). The coordination number of the anionic complexes is dependent on the cation employed. Neutral complexes, R$_2$M(mnt) (M = Sn, R = CH$_3$, C$_6$H$_5$; M = Pb, R = C$_6$H$_5$), have also been prepared and characterized. Facile lead–carbon cleavage was noted in reactions of organometallic lead compounds. Nmr, ir, and mass spectra, X-ray powder patterns, and conductivity data are reported and discussed.

Introduction

Despite the large volume of information available on transition metal complexes with dithiolate ligands,[2,3] detailed studies of main-group element complexes derived from such ligands have only recently appeared, *e.g.*, group IIIb,[4] IVb,[5a] and Vb[5b] complexes employing the *cis*-dicyanoethylene-1,2-dithiolate (mnt[6]) or toluene-3,4-dithiolate ligands. There have been some investigations of the organometallic chemistry of the main-group element complexes with bidentate sulfur donor ligands.[7–9] The interaction of the mnt ion with disubstituted organotin compounds is reported to yield neutral four-coordinate compounds.[8] We have recently observed that the reaction of Na$_2$mnt with monosubstituted group IVb organometallic compounds leads to metal–carbon bond cleavage while analogous reactions with the trisubstituted species lead to pentacoordinate complexes of the type R$_3$M(mnt)$^-$.[10] As part of our continuing interest in the coordination chemistry of the main-group elements with bidentate sulfur donor ligands, we now report the interaction of the mnt ion with disubstituted group IVb organometallic compounds.

Experimental Section

Materials. Disodium dicyanoethylene-1,2-dithiolate (Na$_2$mnt)[11] and diphenyltin dichloride[12] were prepared by previously reported procedures. Dimethyltin dichloride was provided through the courtesy of M & T chemicals. Dimethyltin diiodide was obtained from Chemical Procurement Laboratories. All other group IVb organometallic compounds were obtained from Alfa Inorganics. Tetraphenylarsonium nitrate was prepared by the reaction of tetraphenylarsonium chloride hydrochloride with silver nitrate. The product was recrystallized from an ethanol–water solution. Spectral grade solvents were used for nmr spectra measurements. All other reagents and solvents were used without further purification.

Measurements. X-Ray powder patterns were determined using film methods (Cu Kα). Conductivity measurements were obtained at 25° using an Industrial Instruments Model RC 1682 bridge with a cell calibrated with 0.01 m KCl solution. Infrared spectra were obtained with a Beckman IR 5A spectrophotometer (CsBr) using KBr disks and solution cells. Nmr measurements were recorded on a Varian A-60 spectrophotometer. Mass spectra were provided through the courtesy of JEOL Corp. Measurements were made at 75 eV and 100°.

Syntheses. The preparation of a neutral and an anionic complex will be described. The preparations of all other complexes were similar to those described below and are summarized in Table I.

Preparation of (CH$_3$)$_2$Sn(mnt). Dimethyltin dichloride (2.20 g, *ca.* 0.01 mol) was added to a solution of 2.00 g (*ca.* 0.01 mol) of Na$_2$mnt in 10 ml of methanol and stirred for several minutes. The resulting precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue remaining after evaporation was treated with acetone and the mixture was filtered. Ethanol was added to the filtrate and the solution was reduced in volume until precipitation occurred. The solid, white precipitate was collected by filtration and dried. The product was shown to be (CH$_3$)$_2$Sn(mnt) by elemental analyses and conductivity data.

Preparation of [(C$_2$H$_5$)$_4$N]$_2$Sn(mnt)$_2$(CH$_3$)$_2$. Dimethyltin dichloride (1.10 g, *ca.* 0.005 mol) was added to a solution of 2.00 g (*ca.* 0.01 mol) of Na$_2$mnt and 1.65 g (*ca.* 0.01 mol) of tetraethylammonium chloride in 100 ml of ethanol. After several minutes of continued stirring, the resulting precipitate was removed by filtration. The filtrate was reduced in volume until precipitation occurred. The solid was collected and washed with acetone. Ethanol was added to the filtrate and the solution was reduced in volume until precipitation occurred. The yellow, solid product was isolated by filtration and shown to be [(C$_2$H$_5$)$_4$N]$_2$Sn(mnt)$_2$(CH$_3$)$_2$ by elemental analyses and conductivity data.

Addition of [(C$_6$H$_5$)$_4$As]Cl·HCl to an ethanolic solution of [(C$_4$H$_9$)$_4$N]$_2$Sn(mnt)$_2$(C$_6$H$_5$)$_2$ results in the precipitation of [(C$_6$H$_5$)$_4$As]Sn(mnt)(C$_6$H$_5$)$_2$Cl.

Upon interaction with Na$_2$mnt, disubstituted organometallic silicon and germanium chlorides yielded complex reaction mixtures which appear to result from ligand degradation.

Analytical data and physical properties for the products are reported in Tables II and III.

Results and Discussion

The reaction of Na$_2$mnt with disubstituted organometallic tin(IV) and lead(IV) halides gives rise to a variety of complexes the constitution of which is a function of the mole ratio of the reactants and the cation employed. The corresponding reaction with silicon(IV) and germanium(IV) species results in ligand degradation. A possible explanation for this observation could be rapid solvolysis of any silicon–sulfur or germanium–sulfur bonds formed.[13,14]

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(6) mnt is an abbreviation of the trivial name maleonitriledithiolate for the dicyanoethylene-1,2-dithiolate ion, S$_2$C$_2$(CN)$_2$$^{2-}$.

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Table I. Syntheses

Organometallic species	Ligand:metal ratio	Cation	Product
$(CH_3)_2SnCl_2$	1:1		$(CH_3)_2Sn(mnt)$
$(C_6H_5)_2SnCl_2$	1:1		$(C_6H_5)_2Sn(mnt)$
$(C_6H_5)_2PbCl_2$	1:1		$(C_6H_5)_2Pb(mnt)$
$(CH_3)_2SnCl_2$	2:1	$[(C_2H_5)_4N]Cl$	$[(C_2H_5)_4N]_2Sn(mnt)_2(CH_3)_2$
$(C_6H_5)_2SnCl_2$	2:1	$[(C_2H_5)_4N]Cl$	$[(C_2H_5)_4N]_2Sn(mnt)_2(C_6H_5)_2$
$(C_2H_5)_2PbCl_2$	2:1	$[(C_2H_5)_4N]Cl$	$[(C_2H_5)_4N]_2Pb(mnt)_2$ [a]
$(C_6H_5)_2PbCl_2$	2:1	$[(C_4H_9)_4N]Cl$	$[(C_4H_9)_4N]_2Pb(mnt)_2(C_6H_5)_2$ [b]
$(C_6H_5)_2SnCl_2$	2:1	$[(C_4H_9)_4N]Cl$	$[(C_4H_9)_4N]_2Sn(mnt)_2(C_6H_5)_2$
$(CH_3)_2SnCl_2$	2:1	$[(C_6H_5)_4As]Cl \cdot HCl$	$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$
$(CH_3)_2SnCl_2$	3:1	$[(C_6H_5)_4As]Cl \cdot HCl$	$[(C_6H_5)_4As]_2Sn(mnt)_2(CH_3)_2$
$(C_6H_5)_2SnCl_2$	2:1	$[(C_6H_5)_4As]Cl \cdot HCl$	$[(C_6H_5)_4As]Sn(mnt)(C_6H_5)_2Cl$
$(C_6H_5)_2PbCl_2$	2:1	$[(C_6H_5)_4As]Cl \cdot HCl$	$[(C_6H_5)_4As]Pb(mnt)_2(C_6H_5)_2Cl$
$(C_2H_5)_2PbCl_2$	2:1	$[(C_6H_5)_4As]Cl \cdot HCl$	$[(C_6H_5)_4As]_2Pb(mnt)_2$
$(CH_3)_2SnBr_2$	2:1	$[(C_6H_5)_4As]NO_3$	$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$
$(CH_3)_2SnI_2$	2:1	$[(C_6H_5)_4As]NO_3$	$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$
$(CH_3)_2SnCl_2$	2:1	$[(C_6H_5)_4P]Cl$	$[(C_6H_5)_4P]Sn(mnt)(CH_3)_2Cl$

[a] Same product obtained at 0°.   [b] Lead–carbon bond cleavage occurs in refluxing ethanol resulting in the isolation of $[(C_4H_9)_4N]_2Pb(mnt)_2$.

Table II. Analytical Results for Dicyanoethylene-1,2-dithiolato Complexes[a]

Complex	Calcd						Obsd					
	% C	% H	% N	% S	% halogen	Mol wt	% C	% H	% N	% S	% halogen	Mol wt [b]
$(CH_3)_2Sn(mnt)$	24.94	2.10	9.71			289	24.68	2.13	9.61			309
$(C_6H_5)_2Sn(mnt)$	46.46	2.44				413	46.18	2.38				419
$(C_6H_5)_2Pb(mnt)$	38.31	2.01				501	38.38	2.13				443
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$	50.46	3.99	3.96	9.06	5.08		50.91	3.69	3.87	8.42	5.66	
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$	47.91	3.49			10.62		48.46	3.91			10.44	
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$	45.08	3.29					44.81	3.38				
$[(C_6H_5)_4As]Sn(mnt)(C_6H_5)_2Cl$	58.16	3.67					58.03	3.75				
$[(C_6H_5)_4P]Sn(mnt)(CH_3)_2Cl$	54.27	3.96					54.37	4.11				
$[(C_6H_5)_4As]Pb(mnt)(C_6H_5)_2Cl$	52.18	3.29					52.11	3.37				
$[(C_2H_5)_4N]_2Sn(mnt)_2(CH_3)_2$	45.28	6.72	12.33	18.59			45.59	6.74	11.83	18.90		
$[(C_6H_5)_4As]_2Sn(mnt)_2(CH_3)_2$	58.33	3.89	4.69				58.82	3.87	4.39			
$[(C_2H_5)_4N]_2Sn(mnt)_2(C_6H_5)_2$	53.13	6.19	10.33	15.75			52.83	6.13	10.46	14.96		
$[(C_4H_9)_4N]_2Sn(mnt)_2(C_6H_5)_2$	60.13	7.98					60.22	8.02				
$[(C_4H_9)_4N]_2Pb(mnt)_2(C_6H_5)_2$	55.42	7.34		11.37			55.34	7.25		10.98		
$[(C_2H_5)_4N]_2Pb(mnt)_2$	38.53	5.40					38.60	5.51				
$[(C_6H_5)_4As]_2Pb(mnt)_2$	53.28	3.48					54.37	4.11				

[a] Analyses by Robertson and Galbraith Laboratories.   [b] Determined by Dornis & Kolbe Laboratory; osmometrically in acetone.

Table III. Physical Properties of Dicyanoethylene-1,2-dithiolato Complexes

Complex	Mp,[a] °C	Color	Conductivity[b]
$(CH_3)_2Sn(mnt)$	>300	White	Nonelectrolyte
$(C_6H_5)_2Sn(mnt)$	>200	White	Nonelectrolyte
$(C_6H_5)_2Pb(mnt)$	>200	Yellow	Nonelectrolyte
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$	134–135	Yellow	129
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$	134–135	Yellow	124
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$	136–137	Yellow	128
$[(C_6H_5)_4As]Sn(mnt)(C_6H_5)_2Cl$	166–167	Yellow	117
$[(C_6H_5)_4As]Pb(mnt)(C_6H_5)_2Cl$	164–165	Yellow	113
$[(C_2H_5)_4N]_2Sn(mnt)_2(CH_3)_2$	124–125	Yellow	318
$[(C_2H_5)_4N]_2Sn(mnt)_2(C_6H_5)_2$	158–159	Pale yellow	296
$[(C_4H_9)_4N]_2Pb(mnt)_2(C_6H_5)_2$	109–110	Red	253

[a] Uncorrected.   [b] In cm^2/ohm mol; 10^{-3} M solution in acetonitrile.

A series of hexacoordinate dianionic complexes of the type $M(mnt)_2R_2{}^{2-}$ was prepared by the reaction of Na_2mnt with the appropriate organometallic halide in a 2:1 molar ratio in the presence of a tetraalkylammonium halide as shown in Table I. Surprisingly however, if the tetraphenylarsonium or tetraphenylphosphonium cations were employed as the counterions, pentacoordinate complexes of the type $[M(mnt)R_2X]^-$ were isolated. If the ligand:metal ratio was increased, the hexacoordinate $R_2M(mnt)_2{}^{2-}$ complexes were isolated. Furthermore, the reaction of $[(C_4H_9)_4N]_2Sn(mnt)_2$-$(C_6H_5)_2$ with tetraphenylarsonium chloride hydrochloride yields the pentacoordinate species $[(C_6H_5)_4As]Sn(mnt)$-$(C_6H_5)_2Cl$. Thus, it appears that the choice between penta- and hexacoordinate tin in these systems is a function of the

counterion and presumably the packing forces in the solid. Preferential stabilization of certain complexes by the use of specific counterions has been observed in other systems.[15,16]

When diethyllead dichloride was used as the starting material with any of the aforementioned cations, lead–carbon cleavage occurred resulting in the formation of the previously characterized[5] $[(C_2H_5)_4N]_2Pb(mnt)_2$ moiety. A similar cleavage occurred when the $Pb(mnt)_2(C_6H_5)_2{}^{2-}$ ion was heated in refluxing ethanol.

Neutral complexes, $R_2M(mnt)$, were prepared by the reaction of Na_2mnt with the organometallic halide in a 1:1

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molar ratio. This type of complex has previously been reported.[8,9] The stoichiometries of all the complexes prepared were established by the analytical and conductivity data reported in Tables II and III.

The X-ray powder patterns (Table IV) show that the neutral complexes $(C_6H_5)_2Sn(mnt)$ and $(C_6H_5)_2Pb(mnt)$ are isomorphous. The experimental molecular weights in acetone (Table II) are close to monomer values. On the other hand, the high decomposition temperatures and poor solubility in noncoordinating solvents suggest that the tendency of the tin atom to have a coordination number greater than 4 can be achieved by intermolecular association in the solid state or *via* solvation by donor solvents in solution. The tin–methyl (Table V) coupling constants for $(CH_3)_2Sn(mnt)$ in acetone are in the range normally associated with penta-[17–19] and cis[20] hexacoordinated dimethyltin(IV) complexes.

The infrared spectra (Table VI) of the neutral complexes do not have cation absorptions in the 1400–1600-cm^{-1} region, so $\nu_{C=C}$ can be assigned in these species. [In previous papers in this series,[5,10] the complexity of the spectra in this region prevents assignment of $\nu_{C=C}$ and leads to the incorrect assumption that there was virtually no change from the spectrum of the free ligand.] The values of $\nu_{C=C}$ for the tin complexes are in the range of those observed for transition metal[21] and other posttransition metal[4,6] mnt complexes. There has been considerable discussion of the relationship of $\nu_{C=C}$ in dithiolato complexes to the electronic structure of the complex.[2] Based on this[2] work, one could propose a shift toward dithioketone character in the main-group mnt complexes. However, extensive perturbation of the ligand electronic structure is not commonly observed in complexes of the heavy main-group elements; hence reduction of the anionic nature of the ligand may be responsible for the observed shifts.[21] The lower values of $\nu_{C=C}$ for the lead complex reflect the expected poorer acceptor nature of the lead atoms.

The metal–sulfur stretching modes are higher for the neutral complexes than for the anionic complexes presumably reflecting the greater effective charge on the metal atom in the neutral species. The higher tin–sulfur stretching frequency observed for the phenyl-substituted complexes compared to those for methyl-substituted complexes for the neutral and many anionic complexes reflects the greater group electronegativity of the phenyl group[22] and hence the greater effective positive charge on the tin center. We have observed this effect in other Sn–mnt complexes.[10]

Mass spectra of the neutral complexes were obtained in order to investigate further the possibility of intramolecular association in these compounds. Although overlapping lines and complex patterns prevented complete assignment, several interesting features do appear in the spectra (see Table VII). Parent dimers were not observed; however in both tin complexes several fragments containing two tin atoms were observed. [Assignment of fragments containing two tin atoms was verified by calculation of the isotope distribution for a

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Table IV. X-Ray Powder Patterns^a

Complex	Interplanar (*d*) spacings of the prominent peaks, Å
Ph$_2$Sn(mnt)	7.98 s, 6.40 m, 5.93, 4.80 m, 4.48 m, 3.88 w, 3.55 m, 3.33 w, 3.15 w, 2.97 w, 2.82 w, 2.39 w
Ph$_2$Pb(mnt)	8.04 s, 6.01 m, 5.88 m, 4.91 m, 4.50 m, 3.88 w, 3.70 m, 3.41 w, 3.04 w, 2.93 w, 2.76 w, 2.48 w
(Bu$_4$N)$_2$Sn(mnt)$_2$Ph$_2$	11.53 w, 9.99 s, 8.91 w, 7.51 m, 6.73 w, 6.63 w, 5.98 s, 5.50 s, 4.53 m, 4.43 w, 4.09 m, 3.79 m, 3.47 m, 3.31 m
(Bu$_4$N)$_2$Pb(mnt)$_2$Ph$_2$	11.93 w, 10.62 s, 9.06 w, 7.73 m, 7.02 w, 6.51 w, 5.83 s, 5.25 s, 4.63 m, 4.46 w, 4.05 m, 3.81 m, 3.50 m, 3.36 m

^{a} The powder patterns of the complexes containing the tetraphenylarsonium cation are not reported due to the fact that the large number of closely spaced lines makes any comparisons futile.

ditin fragment.] A similar phenomenon was observed in the mass spectrum of cyclohexanone *O*-trimethylstannyloxime.[23] A reasonable proposal for the decomposition of the ditin fragments involves the process

$$R_2SnS_2SnR_2{}^+ \xrightarrow{-R\cdot} R_2SnS_2SnR^+ \xrightarrow{-S\cdot} R_2SnSSnR^+$$

Low-intensity fragments with *m/e* values greater than that of the parent ion are observed in the spectrum of the lead complex but the isotope distribution does not correspond to a dilead fragment. No reasonable assignment of the peaks can be made so it must be assumed that they arise from impurities. The stability of the dimeric lead fragments in the gas phase thus appears to be lower than those of the corresponding tin complexes.

Two major fragmentation processes appear to occur in the mass spectra of the neutral complexes. The first process is successive elimination of the organic group as a radical until Sn(mnt)$^+$ is formed; then ligand fragmentation occurs. Radical elimination of organic substituents has been previously observed in the mass spectra of organometallic tin compounds.[24,25] The relative abundance of the resulting ions suggests that in the first step of this process alkyl cleavage is more favorable than aryl cleavage. The low abundance of the parent ion for the lead complex compared to the corresponding tin complexes parallels the ease of lead–carbon cleavage observed in the synthetic aspects of this investigation. A second fragmentation process involves ligand fragmentation leading to species such as RMS$^+$ and RM$^+$.

In both tin complexes, fragments such as SnCN$^+$ and SnS$_2$C$_2$(CN)$^+$ occur. These fragments arise from a rearrangement resulting in transfer of a cyano group from the ligand to the metal. A related process was observed in the mass spectrum of $[(CF_3)_2C_2S_2Co(CO)_3]_3$ in which CoF$_2$ was eliminated in the decomposition process.[26] Intramolecular migrations have been observed in the mass spectra of organotin compounds.[25,27]

The pentacoordinate complexes R$_2$M(mnt)X$^-$ may be compared to the analogous *N,N*-dimethyldithiocarbamato

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Table V. Selected Nmr Data for Methyl-Substituted Dicyanoethylene-1,2-dithiolato Complexes

Complex	Solvent	$J(^{119}Sn-H)$, Hz	$J(^{117}Sn-H)$, Hz	τ, ppm
$(CH_3)_2Sn(mnt)$	$(CH_3)_2CO$	74.0	72.0	9.47
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$	CH_2Cl_2	75.5	72.0	9.03
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$	CH_2Cl_2	74.0	71.0	8.92
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$	CH_2Cl_2	73.5	70.0	8.72
$[(C_6H_5)_4As]_2Sn(mnt)_2(CH_3)_2$	CH_2Cl_2	78.0	76.0	9.20

Table VI. Selected Ir Data for Dicyanoethylene-1,2-dithiolato Complexes[a]

Complex	$\nu_{C\equiv N}$	$\nu_{C=C}$	ν_{C-S}	$\nu_{R-C(S)C}$	ν_{M-C}	ν_{M-S}
Na_2mnt	2192 ms	1442 m	1162 m 1123 s	867 s		
$(CH_3)_2Sn(mnt)$	2192 m	1481 m	1200 m 1447 s	862 s	553 ms 509 sh	353 s 291 s
$(C_6H_5)_2Sn(mnt)$	2197 m	1484 s	1192 w 1154 m	867 s		358 s 292 s
$(C_6H_5)_2Pb(mnt)$	2197 m	1460 s	1185 w 1140 m	859 s		324 s
$[(C_2H_5)_4N]_2Sn(mnt)_2(CH_3)_2$ [b]	2197 m				531 sh	318 m
$[(C_4H_9)_4N]_2Sn(mnt)_2(C_6H_5)_2$	2197 m					331 m
$[(C_4H_9)_4N]_2Pb(mnt)_2(C_6H_5)_2$	2189 m					
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$	2197 m				548 m	324 m
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$	2197 m				546 m	324 m
$[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$	2197 m				542 m	324 m
$[(C_6H_5)_4As]Sn(mnt)(C_6H_5)_2Cl$	2197 m					325 m
$[(C_6H_5)_4As]Pb(mnt)(C_6H_5)Cl$	2190 m					303 m

[a] In cm^{-1}; obtained from KBr disks unless otherwise noted.   [b] In CH_2Cl_2 solution.

Table VII. Monoisotopic Mass Spectra

$(CH_3)_2Sn(mnt)$			$(C_6H_5)_2Sn(mnt)$			$(C_6H_5)_2Pb(mnt)$		
m/e^a	Rel abund	Assignment	m/e^a	Rel abund	Assignment	m/e^c	Rel abund	Assignment
15	49.3	CH_3^+	77	100	$C_6H_5^+$	77	27.9	$C_6H_5^+$
120	42.2	Sn^+	120	91	Sn^+	208	100	Pb^+
135	49.3	CH_3Sn^+	152	7.5	SnS^+	243	12.4	
146	2.4	$SnCN^+$	178	9.8	$SnCNS^+$	285	47.5	$C_6H_5Pb^+$
152	1.8	SnS^+	197	74.4	$C_6H_5Sn^+$	317	1.8	$C_6H_5PbS^+$
178	14.1	$SnCNS^+$	229	28.6	$C_6H_5SnS^+$	326	2.5	
184	3.8	SnS_2^+	234	0.6	$SnS_2C_2CN^+$	348	2.5	$Pb(mnt)^+$
197	2.5		254	1.4		361	1.4	
223	5.2		260	12	$Sn(mnt)^+$	397	8.7	
234	2.8	$SnS_2C_2CN^+$	300	2.6		425	0.9	$C_6H_5Pb(mnt)^+$
260	15.5	$Sn(mnt)^+$	337	21.8	$C_6H_5Sn(mnt)^+$	439	49	
275	100	$CH_3Sn(mnt)^+$	351	11.3		471	0.2	
290	37.5	$(CH_3)_2Sn(mnt)^+$	369	1.0	$C_6H_5Sn(mnt)S^+$	502	0.9	$(C_6H_5)_2Pb(mnt)^+$
317^b	1.0		383	2.6	$C_6H_5Sn(mnt)CNS^+$	515	0.9	
347^b	2.8	$(CH_3)_2SnS_2SnCH_3^+$	414	36.1	$(C_6H_5)_2Sn(mnt)^+$	548	0.3	
362^b	0.8	$(CH_3)_2SnS_2Sn(CH_3)_2^+$	501^b	2.9	$(C_6H_5)_2SnSSn(C_6H_5)^+$			
			533^b	4.3	$(C_6H_5)_2SnS_2Sn(C_6H_5)^+$			
			610^b	0.3	$(C_6H_5)_2SnS_2Sn(C_6H_5)_2^+$			

[a] Based on ^{120}Sn.   [b] The most intense line of the ditin isotopic cluster occurs at m/e 2.   [c] Based on ^{208}Pb.

(dtc)-tin complexes $(CH_3)_2Sn(dtc)X$ (X = Cl, Br, I).[28]   The molecular structure of $(CH_3)_2Sn(dtc)Cl$ has been determined.[29]   The structure consists of a distorted trigonal bipyramid with equatorial methyl groups, an axial chlorine atom, and the dithiocarbamate group bridging axial and equatorial sites. An analogous structure is a reasonable model for the mnt complexes since the methyl–tin coupling constants are nearly identical in the two systems. The variation in the methyl–tin coupling constant within the mnt series is in the direction which one would expect from isovalent hybridization arguments.[30]   The variation in methyl group chemical shift can be ascribed to the changes in the anisotropic effect of the halogen atom.

The nmr spectrum of a complex formed by the reaction of tetraphenylarsonium chloride hydrochloride with dimethyltin diiodide and Na_2mnt in equimolar quantities exhibits a single methyl–tin chemical shift. This peak is midway between the resonances for the $(CH_3)_2Sn(mnt)Cl^-$ and the $(CH_3)_2Sn(mnt)I^-$ ions. This observation can be taken as being indicative of labile halogen atoms in this series of compounds. Interestingly, one does not observe any halogen exchange in the formation of the $Sn(mnt)_2X_2^{2-}$ (X = Cl, Br, I)[5] or $In(i-mnt)_2X^-$ (X = Cl, Br, I)[4] complexes.

The hexacoordinate complexes $(C_6H_5)_2M(mnt)_2^{2-}$ (M = Sn, Pb) are isomorphous. Mossbauer spectroscopy studies have shown that virtually all $(C_6H_5)_2SnL_2$ (L = bidentate ligand) have cis phenyl groups.[31]   Hence a cis configuration

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for the $(C_6H_5)_2M(mnt)_2{}^{2-}$ complexes is a reasonable proposal.

The tin–carbon asymmetric stretching mode in the $(CH_3)_2\cdot Sn(mnt)_2{}^{2-}$ ion is found at 531 cm^{-1}. The region where the symmetric stretching mode would occur (if present) is masked by ligand absorptions.[10] The value of the methyltin coupling constant is closer to the value for a cis disposition of methyl groups[20] than that observed for a complex exhibiting the trans configuration.[32] Therefore, as a tentative proposal, a distorted cis geometry is preferred for the $(CH_3)_2Sn(mnt)_2{}^{2-}$ moiety. Further investigations on the stereochemistry of these complexes is in progress.

(32) M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, **87**, 1909 (1965).

Hydrolysis Kinetics of the
trans-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) and
-cobalt(III) Cations in Acidic Aqueous Solution

M. C. COULDWELL, D. A. HOUSE,* and H. K. J. POWELL

The syntheses of trans-[Cr(en)(tmd)Cl$_2$]ClO$_4$ and trans-[Cr(en)(tmd)(OH)(OH$_2$)](ClO$_4$)$_2$ and a simplified synthesis of trans-[Co(en)(tmd)Cl$_2$]X (X = Cl·H$_2$O, ClO$_4$) are described. From these, the cations trans-Cr(en)(tmd)Cl$_2{}^+$, trans-Cr(en)(tmd)(OH$_2$)Cl^{2+}, trans-Cr(en)(tmd)(OH$_2$)$_2{}^{3+}$, cis-Cr(en)(tmd)(OH$_2$)$_2{}^{3+}$, trans-Co(en)(tmd)Cl$_2{}^+$, cis-Co(en)(tmd)-(OH$_2$)Cl^{2+}, and cis-Co(en)(tmd)(OH$_2$)$_2{}^{3+}$ have been isolated and characterized in solution. At 25.0°, the first-order rate constants and kinetic parameters for the primary hydrolysis of trans-M(en)(tmd)Cl$_2{}^+$ (M = Cr, Co) (corresponding to the formation of trans- and predominantly cis-M(en)(tmd)(OH$_2$)Cl^{2+}, respectively) are $10^5 k$ (sec^{-1}) = 1.93 ± 0.09 (0.4 F HNO$_3$), 39.6 ± 1.2 (0.3 F HNO$_3$); E_a (kcal mol^{-1}) = 23.4 ± 0.3, 24.2 ± 0.3; log [PZ (sec^{-1})] = 12.43, 14.38; $\Delta S^{\ddagger}_{298}$ (cal deg^{-1} mol^{-1}) = −3.6 ± 0.5, +5.1 ± 0.5, respectively. The first-order halide release rate constants and kinetic parameters for trans- and cis-M(en)(tmd)(OH$_2$)Cl^{2+} (M = Cr, Co, respectively) in 1.0 F HNO$_3$ at 25.0° are (units as above) $10^5 k$ = 0.31 ± 0.05, 10.3 ± 0.2; E_a = 21.9 ± 1, 18.8 ± 0.5; log PZ = 10.54, 9.81; $\Delta S^{\ddagger}_{298}$ = −12.3 ± 2, −15.7 ± 1, respectively. The trans-Cr(en)(tmd)(OH$_2$)Cl^{2+} cation also hydrolyzes via Cr–N bond rupture, and Cr(tmd)(OH$_2$)$_4{}^{3+}$ has been isolated as the major decomposition product.

Introduction

As part of a program to investigate the acid hydrolysis of some analogous Cr(III) and Co(III) complexes,[1] we have studied the rate of halide release and mode of decomposition of the *trans*-M(en)(tmd)Cl$_2{}^+$ cations[2] (M = Cr, Co) in acid solution. The rate constants and kinetic parameters allow a comparison with similar data for the *trans*-M(AA)$_2\cdot$Cl$_2{}^+$ (M = Cr, Co; AA = en, pn, tmd) systems.

Experimental Section

1,2-Diaminoethane (ethylenediamine) was obtained from Fluka AG Laboratories and 1,3-diaminopropane (trimethylenediamine) from Aldrich Chemical Co.; both were used without further purification. All other chemicals were of reagent grade quality. The ion-exchange material was Zeo-Karb 225, SRC-6 cation-exchange resin in the Na$^+$ form (52–100 mesh). The dichloro cations were isolated using 6 × 1 cm columns cooled by a jacket of circulating ice water, and all others were isolated using a 10 × 1 cm tap water cooled column. The preparation and analyses of the cationic complexes

(1) M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972), and references cited therein.

(2) Abbreviations used: en, NH$_2$(CH$_2$)$_2$NH$_2$; pn, NH$_2$CH(CH$_3$)-CH$_2$NH$_2$; tmd, NH$_2$(CH$_2$)$_3$NH$_2$; DMSO, dimethyl sulfoxide.

were repeated at least three times to check the reproducibility of the ion-exchange separations and the visible absorption spectral parameters.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these complexes should be treated as potentially explosive and handled with care.

trans-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)-chromium(III) Perchlorate. This salt was obtained using a modification of the preparation used for *trans*-[Cr(tmd)$_2$Cl$_2$]ClO$_4$.[1,3] A solution of green CrCl$_3$·6H$_2$O (16.2 g) in DMSO[2] (75 ml) was boiled for 10 min. An equimolar mixture of the diamines (9.3 ml) in DMSO (45 ml) was added to the hot solution and boiling was continued for a further 2 min. After cooling to 60°, the dull green solution was poured into 900 ml of well-stirred acetone. The purple precipitate that deposited was filtered and washed with acetone (three 50-ml portions), and the still damp solid was suspended in HCl (60 ml, 12 F). This suspension was heated on a steam bath for 10 min, when HClO$_4$ (30 ml, 60%) was added. The solution was cooled slowly and the green crystals that deposited overnight were collected, washed with 2-propanol and then ether, and air-dried. The mother liquors were returned to the steam bath for 15 min. HCl (15 ml, 12 F) was added and the solution was cooled slowly. This procedure was repeated several times to give either green or purple crystals. The

(3) D. A. House, *Inorg. Nucl. Chem. Lett.*, **6**, 741 (1970).