Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Metal Complexes as Ligands. 8.[1a] Synthesis and Characterization of Polynuclear Dithiooxalate Copper(I)-Tin(IV) Complexes of the General Type $M[(O_2C_2S_2)CuL_2]_n$

M. LEITHEISER and D. COUCOUVANIS*

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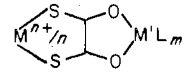
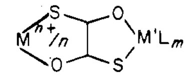
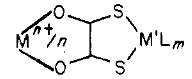
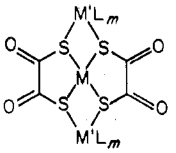
Reactions of the $Sn(S_2C_2O_2)_3^{2-}$ complex with the bis(triphenylphosphine) copper(I) cation, CuL_2^+, the $Zn[(O_2C_2S_2)CuL_2]_2$ complex with stannic halides, and the $O_2C_2S_2CuL_2^-$ complex anion with stannic halides are described. The polynuclear complexes which were obtained and characterized are of the general formula $M[(O_2C_2S_2)CuL_2]_n^m$, where M = Cl_4Sn^{IV}, $CH_3Cl_3Sn^{IV}$, $(CH_3)_2Cl_2Sn^{IV}$, $n = 1$, $m = 1-$; M = Cl_2Sn^{IV}, CH_3ClSn^{IV}, $(CH_3)_2Sn^{IV}$, $n = 2$, $m = 0$; and M = CH_3Sn^{IV}, $ClSn^{IV}$, $BrSn^{IV}$, $n = 3$, $m = 0$. The S,S-chelated $K_2Sn(S_2C_2O_2)_3$ complex reacted with CuL_2^+ to afford the novel dinuclear $KSn(S_2C_2O_2)_3CuL_2$ complex, in which two dithiooxalate ligands are S,S-chelated to the tin while the third is O,O-chelated to the tin and S,S-chelated to the copper atom. The infrared and electronic spectra of the polynuclear complexes show systematic changes which indicate that the extent of Cu-S π back-bonding varies linearly with the acidity of the $SnCl_nR_{4-n}$ Lewis acids.

Introduction

The chemistry of the dithiooxalate ligand, $(C_2S_2O_2)^{2-}$, has been a subject of recent interest because of its multifunctional nature.[1-5] The versatility of this ligand is demonstrated by the existence of O,O-bonded, S,S-bonded, and O,S-bonded complexes. The mode of coordination adopted by a given metal ion depends on the relative affinity of the ion for "hard" vs. "soft" ligands. Substitution of the inert counterions (K^+) by interacting $M(PPh_3)_2^+$ cations in the $K_nM(S_2C_2O_2)_n$ complexes results in adducts whose structures depend on (a) the kinetic characteristics of the parent complexes and (b) the intrinsic affinity of the metal ions involved for "hard" vs. "soft" ligands (Table I). In this paper we report on the coordination chemistry of stannic halides and stannic alkyl halides with the free ligand and subsequent reactions of the resulting complexes with the $Cu(PPh_3)_2^+$ cation.

Table I. Bonding in the Polynuclear Complexes of the Dithiooxalate Ligand

Complex	M	$M'L_m$	Ref
	Ni(II)	SnX_4 (X = Cl, Br, I)	1
	Ni(II)	$Cu(PPh_3)_2$	2
	Co(III)	$Ag(PPh_3)_2$	2
		$Cu(PPh_3)_2$	2
	Cr(III)	$Cu(PPh_3)_2$	2
	Pd(II)	SnX_4 (X = Cl, Br, I)	1
	Pt(II)	SnX_4 (X = Cl, Br, I)	1
	Cu(II)	SnX_4 (X = Cl, Br, I)	3
	$Cu(PPh_3)_2$	$Cu(PPh_3)_2$	2
	$Cu(PPh_3)_2$	$Ag(PPh_3)_2$	2
	$Ag(PPh_3)_2$	$Ag(PPh_3)_2$	2
	Cr(III)	$Ag(PPh_3)_2$	2
	Al(III)	$Cu(PPh_3)_2$	2,4
		$Ag(PPh_3)_2$	2,4
	Fe(III)	$Cu(PPh_3)_2$	2,4
		$Ag(PPh_3)_2$	2,4
	Cr(III)	$Cu(PPh_3)_2$	2
		$Ag(PPh_3)_2$	2
	Rh(III)	$Cu(PPh_3)_2$	2
		$Ag(PPh_3)_2$	2
	Zn(II)	$Cu(PPh_3)_2$	2
	Ni(II)	$Ag(PPh_3)_2$	2,5

Experimental Section

The common reagents were used as purchased from Eastman Organic Chemicals or Matheson Coleman and Bell. The tin-116 and -124 isotopes, with assayed purity of 95.74 and 94.74%, respectively, were purchased from Oak Ridge National Laboratory as stannic oxide and were converted to stannic chloride by published methods.[6,7] The chloro- and bromotris(triphenylphosphine)copper(I) and -silver(I) complexes[8-10] and the bis[bis(triphenylphosphine)copper(I)] bis(dithiooxalato-*O,O'*)zincate(II)[2] were prepared by published methods.

Physical Measurements. The near-infrared spectra were recorded as potassium bromide wafers or Nujol mulls between sodium chloride plates on a Perkin-Elmer 21 infrared spectrometer, while the far-infrared spectra (640–140 cm^{-1}) were recorded as Nujol mulls between polyethylene films on a Beckman 11 infrared spectrometer. The electronic spectra were recorded on a Cary 14 recording spectrophotometer with 1-cm quartz cells in dichloromethane or acetonitrile solutions. Molecular weights were determined on a Mehrolab Model 301A vapor pressure osmometer in 1,2-dichloroethane calibrated with benzil. The NMR spectra were determined in chloroform on a Varian HA 100 NMR spectrometer locked on the chloroform signal. The carbon and hydrogen analyses were determined by the microanalytical services laboratory at the University of Iowa. Tin and chloride were determined gravimetrically as stannic oxide and silver chloride, while potassium and copper were determined by atomic absorption spectroscopy.

Preparation of the Complexes. (I) Dipotassium Tris(dithiooxalato-*S,S'*)stannate(IV), $K_2Sn(S_2C_2O_2)_3$. $SnCl_4{\cdot}5H_2O$, 1.0 g (2.9 mmol), and $K_2S_2C_2O_2$, 2.0 g (10.0 mmol), were each dissolved in 15 mL of water. The stannic chloride solution was added with stirring to the ligand solution and 0.8 g of pale yellow solid formed immediately. The yellow solid was isolated by filtration, dried with ether, and recrystallized from acetone–ether.

(II) Potassium Bis(triphenylphosphine)copper(I) Bis(dithiooxalato-*S,S'*)dithiooxalato-*O,O'*-stannate(IV), $KSn(S_2C_2O_2)_2[(O_2C_2S_2)Cu(PPh_3)_2]$. A 1.3-g (2.4-mmol) amount of $K_2Sn(S_2C_2O_2)_3$, complex I, was dissolved in 25 mL of acetone to which 3.0 g (3.3 mmol) of solid chlorotris(triphenylphosphine)copper(I), $(Ph_3P)_3CuCl$, had been added. The suspension was stirred for 5 min and the excess phosphine was then removed by filtration. Ether–pentane (1:4) was added to the filtrate and the orange crystals (2.6 g) were isolated and recrystallized from acetonitrile–ether.

(III) Tris[bis(triphenylphosphine)copper(I)] Bromotris(dithiooxalato-*O,O'*)stannate(IV), $BrSn[(O_2C_2S_2)Cu(PPh_3)_2]_3$. A 1.3-g (1.2-mmol) of $KSn(S_2C_2O_2)_2[(O_2C_2S_2)Cu(PPh_3)_2]$, complex II, was suspended in 75 mL of dichloromethane and 2.2 g (2.4 mmol) of bromotris(triphenylphosphine)copper(I), $(Ph_3P)_3CuBr$, was added. The resulting solution was filtered and pentane was added to cloudiness to give the brown crystalline complex.

The corresponding chloro complex IV was prepared in a similar manner using the $(Ph_3P)_3CuCl$ complex.

(IV–VIII) $X_2Sn[(O_2C_2S_2)Cu(PPh_3)_2]_2$ Complexes. These complexes (Figure 1) were synthesized by the use of either of the following two procedures. The molar ratios were found to be important in the syntheses.

Method I. One milliequivalent of the metal halide was added to 1 mequiv of potassium dithiooxalate in 40 mL of tetrahydrofuran,

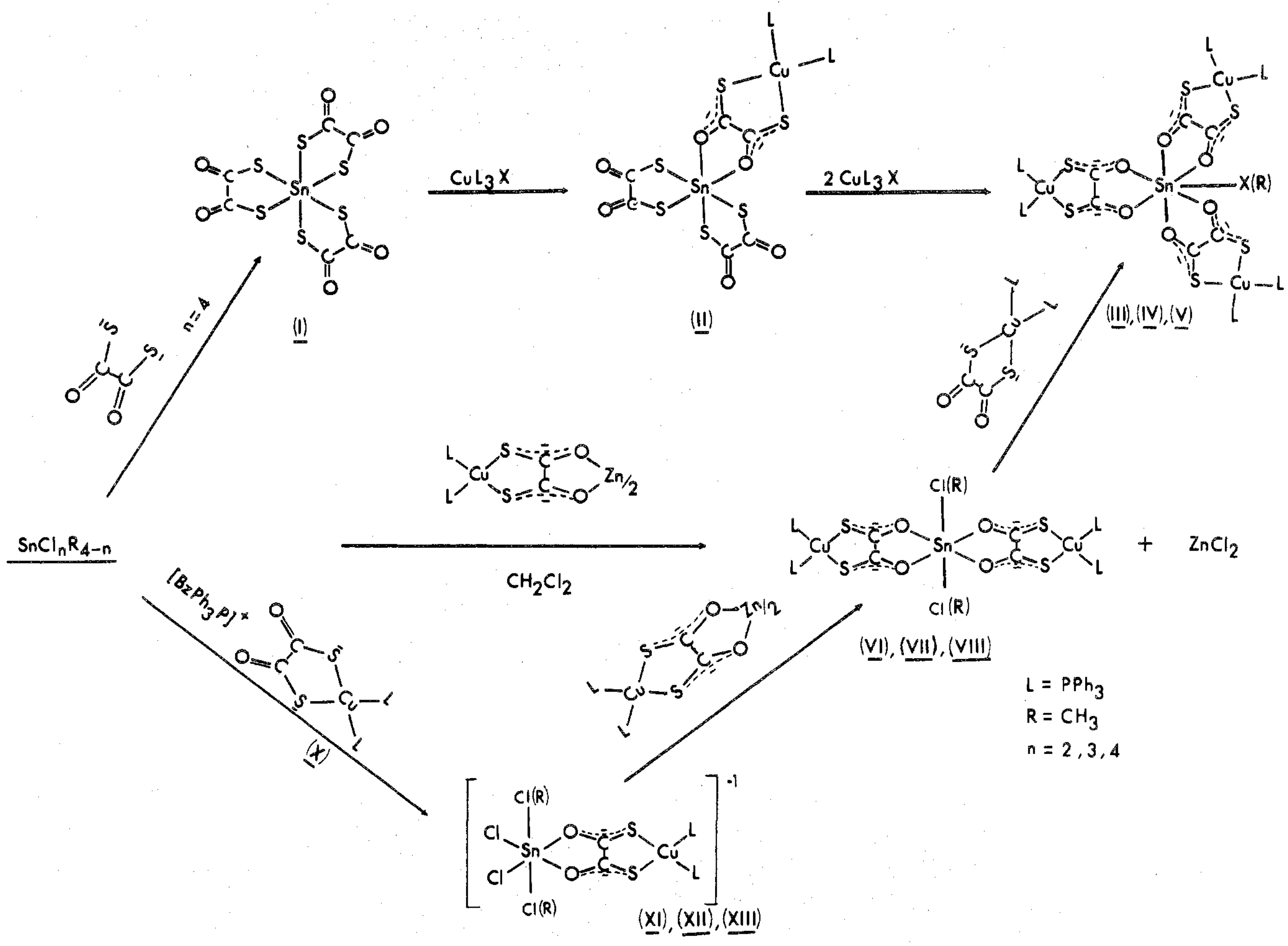


Figure 1. Syntheses and reactions of the stannic dithiooxalate complexes.

THF. Enough water (approximately 1 mL) was added until these salts dissolved. The resulting solution was then extracted with a 100-mL dichloromethane solution of 1 mequiv of the $(Ph_3P)_3CuCl$ complex.

The extracted dichloromethane layer was collected and passed through phase separating paper. Ether–pentane (1:4) was added to the filtrate until first permanent cloudiness to yield the crystalline product.

Method II. One milliequivalent of the bis[bis(triphenylphosphine)copper(I)] bis(dithiooxalato-*O,O′*)zincate(II),[2] $Zn[(O_2C_2S_2)Cu(PPh_3)_2]_2$, was added to a 25-mL acetone solution containing 1 mequiv of the stannic halide. After standing for 6 h at 10 °C, the crystalline product was isolated by filtration, washed with ether, and dried in vacuo. The complexes were then routinely recrystallized from dichloromethane–pentane–ether (see above).

(IX) Hydrogen Dithiooxalato-*S,S′*-bis(triphenylphosphine)cuprate(I), $(Ph_3P)_2Cu(S_2C_2O_2H)$. A 1.5-g (7.5-mmol) amount of $K_2S_2C_2O_2$ was dissolved in 100 mL of water. This solution was then extracted with a 100-mL solution composed of 0.4 g (2.3 mmol) of $CuCl_2 \cdot 2H_2O$ in 20 mL of ethanol and 2.0 g (7.6 mmol) of triphenylphosphine in 80 mL of dichloromethane. The resulting orange-red dichloromethane layer was passed through phase-separating paper and nitrogen was bubbled through the filtrate. Pentane was added until first permanent cloudiness and 1.9 g of crystalline product resulted. The crude product was dissolved in dichloromethane, and after filtration pentane was again added under nitrogen to give the crystalline product.

(X) Benzyltriphenylphosphonium Dithiooxalato-*S,S′*-bis(triphenylphosphine)cuprate(I), $[BzlPh_3P]Cu(S_2C_2O_2)(PPh_3)_2$. This complex was prepared by the replacement of the proton in IX by $BzlPh_3P^+$ as follows. A 2.0-g (2.8-mmol) sample of IX (see above) was dissolved in 100 mL of dichloromethane in a separatory funnel. A 1.0-g (2.6-mmol) sample of $BzlPh_3PCl$ and 5 mL of water were added. The solution was agitated vigorously for 5 min while the solution changed from orange to pale yellow. The water was removed with phase-separating paper and an additional 0.5 g of PPh_3 was added to the filtrate. Addition of *n*-pentane gave the yellow crystalline product.

(XI) Benzyltriphenylphosphonium Dithiooxalato-*S,S′*-bis(triphenylphosphine)cuprate(I) Stannic Chloride, $[BzlPh_3P](Ph_3P)_2Cu(S_2C_2O_2)SnCl_4$. A 5.0-g (0.5-mmol) sample of $[BzlPh_3P](Ph_3P)_2Cu(S_2C_2O_2)$ was dissolved in 50 mL of dichloromethane and 1.0 mL of a 0.5 M solution of anhydrous stannic chloride solution in dichloromethane was added. Addition of ether–pentane (1:4) caused an oil to form which later crystallized. This material can be recrystallized from dichloromethane–pentane–ether.

The corresponding adducts of CH_3SnCl_3 (XII) and $(CH_3)_2SnCl_2$ (XIII) were prepared in a similar fashion.

Results and Discussion

The data characterizing the diamagnetic complexes are available as supplementary material. The numbering of the new complexes established in the synthesis part is maintained in all tables as well as Figure 1.

The reaction of stannic chloride with potassium dithiooxalate results in the formation of sparingly soluble $K_2Sn(S_2C_2O_2)_3$ (I). On the basis of criteria established previously,[2] the presence of a carbonyl stretching frequency at 1598 cm^{-1} and the absence of absorptions around 1400 cm^{-1} indicate S,S chelation of the ligand in this complex. Six-coordinate Sn(IV) chelates with sulfur chelates have been reported previously.[11] The reaction of I with tris(triphenylphosphine)copper(I) chloride in acetone results in a crystalline complex (II) which, in addition to a high-energy C=O band, shows a new, strong absorption at 1371 cm^{-1}. In the polynuclear dithiooxalate complexes C–O vibrational frequencies around 1350 cm^{-1} are characteristic of $M[OO{-}C_2{-}SS{-}M'(PPh_3)_2]_n$ (M′ = Ag(I), Cu(I)) chelation.[2,4] The infrared spectra suggest then either

Table II. Tin-116 and -124 Far-Infrared Isotope Study[a]

$(CH_3)Sn[(O_2C_2S_2)Cu(PPh_3)_2]_3$ (V)	$BrSn[(O_2C_2S_2)Cu(PPh_3)_2]_3$ (III)	$ClSn[(O_2C_2S_2)Cu(PPh_3)_2]_3$ (IV)	$KSn[(C_2S_2O_2)_3Cu(PPh_3)_2]$ (II)
660 m	656 m	655 m	
638 m	643 m	646 m	642 s
618 m	615 m	614 m	615 m
597 m	599 m	600 m	
575 w	584 w	584 w	578 s
540–470 vs[b]	540–470 vs[b]	540–470 vs[b]	540–470 vs[b]
434 m	434 m	434 m	439 m
410 m	410 m	411 m	
		348 (6) s[d,e]	332 (6) s[d,f]
			323 (6) sh[d,f]
292 w	280 (6) s[c,d]	291 w	268 sh

[a] Frequencies in cm^{-1}. Key: m, medium; s, strong; w, weak; sh, shoulder. [b] Triphenylphosphine absorptions. [c] Sn–Br stretch. [d] The number in parentheses is the hypsochromic shift in cm^{-1} found for the ^{116}Sn isotope; the preceding frequency is that of the ^{124}Sn isotope. [e] Sn–Cl stretch. [f] Sn–S vibrations.

that one of the dithiooxalate ligands in I assumed the O,O chelation mode to the tin following the formation of the $Cu(PPh_3)_2^+$ adduct or that II is a mixture of $Cu(PPh_3)_2^+$ adducts of $Sn(SS)_3$ and $Sn(OO)_3$ chelated complexes. The ligand isomerization (S,S to O,O) suggested above has been observed previously in the Lewis acid adducts of the tris(dithiooxalato)iron(III) and -aluminum(III) complexes.[2,4] A crystal structure determination[12] conclusively has shown $Sn(SS)_2(OO)Cu(SS)$ chelation in II. The reaction of II with additional $Cu(PPh_3)_3Cl$ in dichloromethane solution results in a new crystalline complex (IV) which is characterized by only one frequency that can be associated with the C–O bond at 1368 cm^{-1}. This complex has been characterized by elemental analysis as the seven-coordinated tris[bis(triphenylphosphine)copper(I)] tris(dithiooxalato-*O,O*)monochlorostannate(IV), $ClSn[(O_2C_2S_2)Cu(PPh_3)_2]_3$ (Figure 1—IV). Monohalo, seven-coordinate complexes of tin(IV) with oxygen chelates are known and a well-characterized series are the tris(tropolonatohalo)stannate(IV) complexes.[13] The Sn–Cl and Sn–Br stretching vibrations found at 350 and 284 cm^{-1}, respectively, for IV and III are in agreement with similar frequencies observed in the tropolonate complexes. Furthermore the halogen atoms in III and IV are inert to substitution. The absence of any absorptions in the far-infrared spectra that may be attributed to Sn–S vibrations are compatible with the near-infrared results (ν(C–O) at 1368 cm^{-1}) and indicate that all three dithiooxalate ligands are O,O chelated to the tin(IV) ion. Attempts to isolate six-coordinate complexes analogous to II by substitution of both potassium ions in I by $(PPh_3)_2Cu^+$ failed and mixtures of III and II were obtained.

An attempt was made to locate the Sn–O vibration(s) with a tin-116 and -124 isotope substitution study in II–V (Table II). The only isotope-sensitive vibrations observed in III and IV were those assigned previously to the Sn–Br and Sn–Cl stretching frequencies.

Two isotope-sensitive absorptions were found in II at 332 and 323 cm^{-1} and were assigned[14] to Sn–S vibrations because of the absence of similar absorptions in any of the other polynuclear tin dithiooxalato complexes (Table II). The Sn–O vibrations for various delocalized-ligand complexes of tin have been observed[16,17] between 400 and 700 cm^{-1}. Our inability to detect the Sn–O vibrations undoubtedly is due to the presence of intense PPh_3 absorptions in the 470–530-cm^{-1} region of the spectra.

The $X_2Sn[(O_2C_2S_2)Cu(PPh_3)_2]_2$ complexes VI–VIII (Figure 1) were prepared by (a) the metathesis reaction between bis[bis(triphenylphosphine)copper(I)] bis(dithiooxalato-*O,O'*)zincate(II) and the appropriate tin halide in acetone (eq 1) and (b) the extraction of aqueous solutions of mixed halo-dithiooxalate complexes, $Sn(S_2C_2O_2)_2X_2$, with dichloromethane solutions of $Cu(PPh_3)_3Cl$. In the latter method $Cu(PPh_3)_2^+$ is generated in situ and the cation exchange (eq 2) occurs across the $H_2O–CH_2Cl_2$ interphase. The water-soluble alkali metal salts are thus separated from the CH_2Cl_2 solutions of the products. The complexes VI and VIII react further (Figure 1) with an excess of the $Zn(O_2C_2S_2)_2(Cu(PPh_3)_2)_2$ complex to give the seven-coordinate complex IV and the monomethyl analogue V. The presence of the methyl group in V is evident in the NMR spectrum by a single resonance at δ 0.8.[16,17]

$$Zn[O_2C_2S_2Cu(PPh_3)_2]_2 + SnCl_nCH_{3(4-n)} \rightarrow Cl_{n-2}CH_{3(4-n)}Sn[O_2C_2S_2Cu(PPh_3)_2]_2 \quad (n = 2\text{–}4) \qquad (1)$$

$$K_2Sn(S_2C_2O_2)_2X_2(aq) + Cu(PPh_3)_2^+ \xrightarrow{CH_2Cl_2} X_2Sn[O_2C_2S_2Cu(PPh_3)_2]_2 + 2KX(aq) \qquad (2)$$

To ascertain the disposition of the methyl and chloro ligands (cis vs trans) in VII and VIII the NMR spectrum of the former and the IR and Raman spectrum of the latter were examined. The tin–proton coupling constants for the dimethyl complex VII of 87 and 92 Hz for the two tin isotopes, respectively, are in agreement with the coupling constants of known trans or distorted *trans*-dimethyltin complexes.[17,18] The presence of only one Sn–Cl band in the infrared spectrum of the dichloro complex at 350 cm^{-1} and only one absorption in the Raman spectrum (362 cm^{-1}) are consistent with a trans arrangement for the chlorine atoms in a centrosymmetric molecule. A trans arrangement also is presumed for the chloromethyl complex VI.

$(BzlPh_3P)((Ph_3P)_2Cu)(S_2C_2O_2)SnCl_nR_{4-n}$ Complexes. The $Cu^I(S_2C_2O_2H)(PPh_3)_2$ complex, IX, was obtained in an unsuccessful attempt at the synthesis of $Cu^{II}(S_2C_2O_2)(PPh_3)_2$ (see Experimental Section). This diamagnetic complex is acidic in water and titration with standard base confirms the presence of *one* proton. This proton, presumably bound to the α-diketone end of the dithiooxalate ligand, accounts for the low C–O vibration in the complex (1536 cm^{-1}). Cation exchange occurs readily in water between IX and $BzlPh_3PCl$ to give X. The anion $Cu(S_2C_2O_2)(PPh_3)_2^-$ generated, as noted previously, from the zinc(II) complex (eq 1) reacts with Sn(IV) halides to form complexes such as VI–VIII. The reaction of the same anion, as the $BzlPh_3P^+$ "salt" X, with tin(IV) halides and alkyl halides results in the adducts XI–XIII (Figure 1). The C–O vibrational frequency in these compounds, 1402, 1421, and 1447 cm^{-1}, respectively, shows a bathochromic shift whose magnitude is proportional to the Lewis acidity of the tin compounds.

Stannous Complexes. The reaction of anhydrous stannous chloride with the $Zn(O_2C_2S_2)_2(Cu(PPh_3)_2)_2$ complex produces a neutral complex (XIV) which appears to be monomeric in solution by a molecular weight study and four-coordinate by the presence of only a low-energy carbonyl band in the infrared

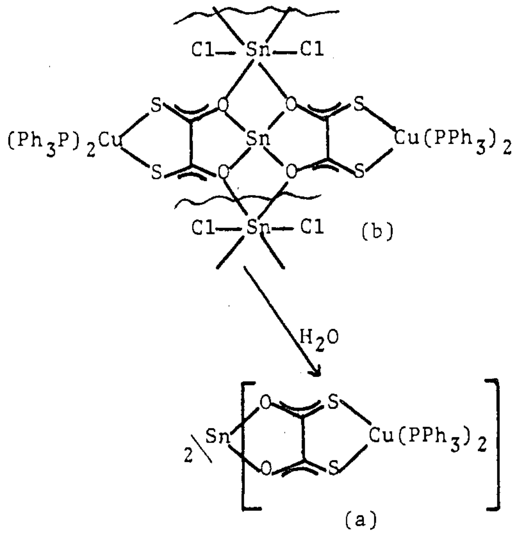


Figure 2. Reactions of stannous chloride with the $(Ph_3P)_2Cu(S_2C_2O_2)^-$ ligand.

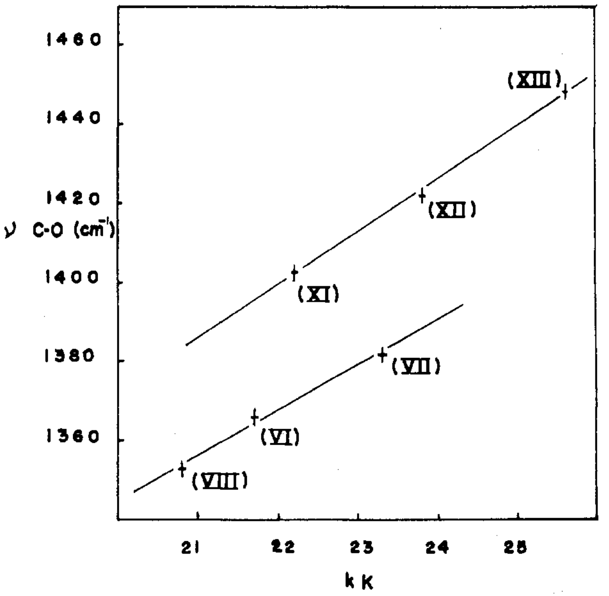


Figure 3. Plot of the C–O stretching frequency (cm^{-1}) vs. the electronic transitions (10^3 cm^{-1}) in polynuclear dithiooxalate complexes of tin. The numbering scheme is identical with the one used in Figure 1.

spectrum. The reaction of this complex with additional stannous chloride results in a slightly soluble complex (XV) in which the carbonyl stretching frequency is lowered to 1331 cm^{-1}. An absorption at 268 cm^{-1} in the far-infrared spectrum of this compound was assigned to the Sn–Cl stretching vibration. The presence of only one carbonyl vibration and the insolubility of the complex indicate that all of the oxygen atoms are involved in coordination in the new complex and that the polymeric structure (Figure 2b) best accounts for the observed data. The polymer can be degraded and the four-coordinate complex (XIV) (Figure 2a) regenerated by hydrolysis in acetone solution.

Electronic Effects. Additions of Lewis acids to the α-diketone portion of the S,S-coordinated ligand in dithiooxalate complexes of Ni(II), Pd(II), Cr(III), and Co(III) have been reported previously.[1,2] A bathochromic shift of a M→S charge-transfer absorption in the "parent" complexes and a concomitant shortening of the M–S bond were interpreted as a consequence of M→S π-back-bonding enhancement brought about by inductive effects of the Lewis acids. In the complexes reported herein the same effects are operative on the $(PPh_3)_2CuS_2C_2O_2^-$ complex, as the α-diketone end of the coordinated $S_2C_2O_2^{2-}$ ligand is bonded to various Sn(IV) complexes.

The predominant feature in the electronic spectra of the polynuclear complexes is a charge-transfer band that varies between 21 000 and 25 000 cm^{-1}. This absorption apparently is associated with the $(PPh_3)_2CuS_2C_2O_2^-$ moiety since no such absorption is found in the spectrum of the $K_2Sn(S_2C_2O_2)_3$ complex. A large bathochromic shift of this absorption, which we assign to a Cu→S charge transfer, is accompanied by a similar shift in the C–O vibrational frequency. This correlation, which is linear for the homologous series VI, VII, VIII and XI, XII, XIII (Figure 3), shows that the magnitudes of the observed perturbations follow the Lewis acidity of the stannic complexes and further supports the proposed model for the changes that occur following adduct formation.

The increase in the Cu–S bond stretching frequency expected to follow adduct formation as a result of increased Cu→S π back-bonding could not be measured. Invariably the bathochromic shift of the Cu–S vibration shifted the absorption band in a region obscured by intense triphenylphosphine absorptions.

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Registry No. I, 62415-55-8; II, 62430-60-8; III, 62430-62-0; IV, 62430-63-1; V, 62430-64-2; VI, 62392-92-1; VII, 62392-91-0; VIII, 62392-90-9; IX, 62392-89-6; X, 62392-88-5; XI, 62476-50-0; XII, 62476-49-7; XIII, 62476-48-6; XIV, 62430-61-9; XV, 62476-46-4; $(Ph_3P)_3CuBr$, 15709-74-7; $Zn[(O_2C_2S_2)Cu(PPh_3)_2]_2$, 42532-00-3; $(Ph_3P)_3CuCl$, 15709-76-9.

Supplementary Material Available: Tables of elemental analyses data, infrared spectra, and electronic spectra (5 Pages). Ordering information is given on any current masthead page.

References and Notes

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