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Transmetalation of tetranuclear copper complexes with tin transmetalators. Molecular structure of *cis*-dichloro-bis(*trans*-*S*-methyl isopropylidenehydrazinecarbodithioato)tin(IV) and consideration of transmetalation mechanisms

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Abstract

Tin complexes $Sn(NS)_2Cl_2$ (**D**) and $Sn(NS)_4$ (**E**) (NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) are very good transmetalators of tetranuclear copper(I) target $[NCuCl]_4$ (**I**: N is *N,N*-diethylnicotinamide). An X-ray crystallographic study shows that **D** is *cis*-dichloro-bis(*trans*-*S*-methyl isopropylidenehydrazinecarbodithioato)tin(IV). Evidence that **I** reacts with 1 or 2 mol of **D** via strong precursors **D**·**I** and $\mathbf{D}_2\cdot\mathbf{I}$ that contain NS ligands bridging tin to copper is used to discuss the transmetalation sequence. The tin-containing transmetalation products include the remarkable air-stable copper(I)–tin(IV) complex $N_3Cu_2Sn(NS)_2Cl_4$ obtained from the reaction of **I** with equimolar **E**.

Introduction

Transmetalation is the stepwise, stoichiometric replacement of the metals in a polymetallic target with other metals from reagents called transmetalators. It is the source of many heteropolymetallic complexes that cannot be obtained by other means [1–6].

Equations (1)–(4) summarize the transmetalation of copper(I) targets $[NCuX]_4$ (**I**) with metal(II) (M = Co, Ni, Cu, Zn) [2] and cobalt(III) [3, 4] transmetalators.

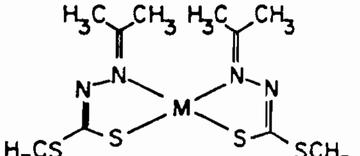
$$\underset{\mathbf{I}}{[NCuX]_4} + \underset{\mathbf{A}}{M(NS)_2} \longrightarrow \underset{\mathbf{II}}{N_3Cu_3M(NS)X_4} + N + Cu(NS)(s) \quad (1)$$

$$\mathbf{II} + N + \mathbf{A} \longrightarrow N_4M_2X_4 + 3Cu(NS)(s) \quad (2)$$

$$\mathbf{I} + \underset{\mathbf{B}}{Co(NS)_3} \longrightarrow N_3Cu_3Co(NS)_2X_4 + N + Cu(NS)(s) \quad (3)$$

$$N + N_3Cu_3Co(NS)_2X_4 + \mathbf{B} \longrightarrow N_4Co_2X_4 + Cu(NS)(s) + 2Cu(NS)_2 \quad (4)$$

Here, N is monodentate *N,N*-diethylnicotinamide, X is Cl or Br and NS is monanionic *S*-methyl isopropylidenehydrazinecarbodithioate. Although reactions (1) [2] and (3) [3, 4] both result in replacement of one copper(I) center in **I** with another metal,



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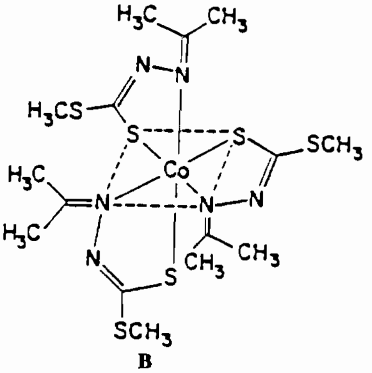

B

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$N_3Cu_3Co(NS)_2X_4$ products from eqn. (3) are mixed valence species that contain one formal copper(II) center as a result of (i) prior electron transfer from **I** to **B** and (ii) preferential formation of insoluble co-product Cu(NS)(s) instead of alternative co-product $Cu(NS)_2$, eqn. (5).

$$\mathbf{I}+\mathbf{B} \longrightarrow N_3Cu_3Co(NS)X_4+Cu(NS)_2 \qquad (5)$$

The different product nuclearities in eqns. (1) and (2) and (3) and (4) are due to intramolecular NS ligand transfer (INLT) from $M(NS)_{1,2}$ centers to target copper on progressive transmelatation with $M(NS)_n$ [1–4, 6]. This transfer is not prevented by excesses of **A** in eqn. (2) [2] or **B** in eqn. (4) [3, 4]. Reactions (4) also occur in the presence of $Ni(NS)_2$, but with equimolar $Co(NS)_2$ or $Zn(NS)_2$ present we observe eqn. (6) [4]. This result and eqns. (7) and (8) show that INLT can be intercepted by faster intermolecular transmetalation in particularly labile systems [4].

$$N_3Cu_3Co(NS)_2X_4+\mathbf{B}+(Co, Zn)(NS)_2 \longrightarrow$$

$$N_3(Co, Zn)Co(NS)_2X_4+2Cu(NS)_2+Cu(NS)(s) \qquad (6)$$

$$N_3Cu_3Co(NS)_2X_4+M(NS)_2+N \longrightarrow$$

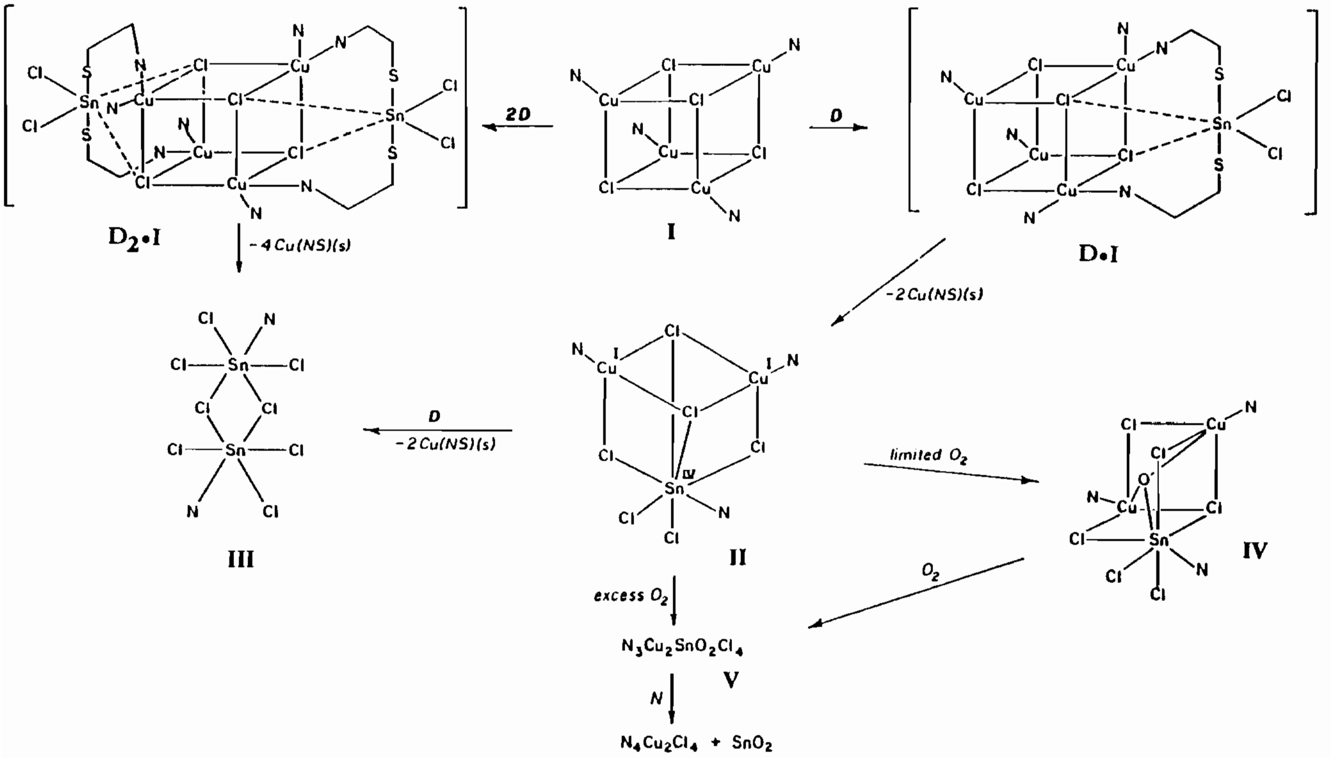
$$N_2CoMX_4+Cu(NS)_2+2Cu(NS)(s) \qquad (7)$$

$$N_3Cu_3Co(NS)_2X_4+2M(NS)_2 \longrightarrow$$

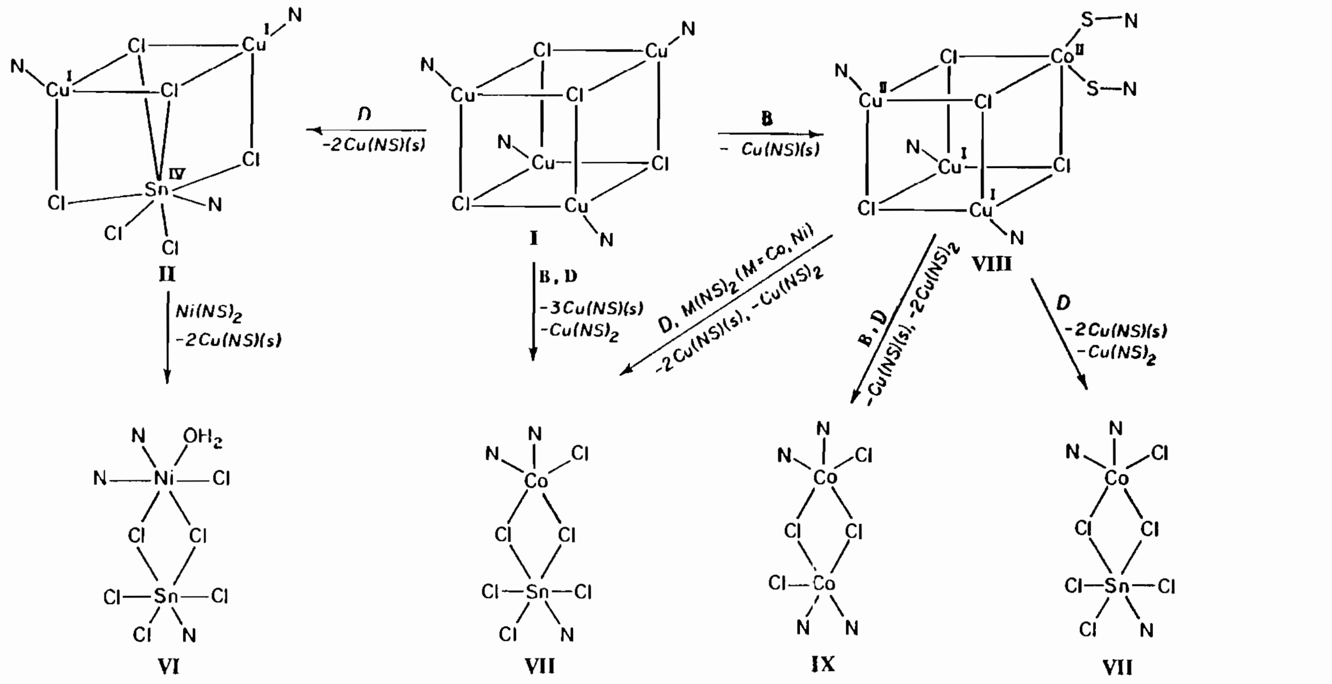
$$N_3M_2Co(NS)_2X_4+Cu(NS)_2+2Cu(NS)(s) \qquad (8)$$

INLT is possible in the transmetalation of polynuclear copper targets because reactants $M(NS)_2$, $Co(NS)_3$ and preferred highly stable co-product Cu(NS)(s) have different NS:metal stoichiometries. INLT is an undesirable phenomenon because it reduces the number of possible transmetalated target derivatives. The factors involved in INLT are the identities of M and NS and the extent of transmetalation [4, 6].

This is the first report of the direct substitution of a main group element for copper in polymetallic targets. It complements other studies of the effects of different transmetalator metal oxidation states on transmetalation patterns [3, 4]. We describe the syntheses and characterization of $Sn(NS)_2$ (**C**), $Sn(NS)_2Cl_2$ (**D**) and $Sn(NS)_4$ (**E**). A single crystal X-ray study shows **D** to be *cis*-dichloro-bis(*trans*-*S*-methyl isopropylidenehydrazinecarbodithioato)tin(IV). Although **C** does not transmetalate **I** at significant rates, **D** and **E** are very good transmetalators of copper(I). As in previous work [2–4, 7], we have established reaction stoichiometries by gravimetric determination of insoluble co-product Cu(NS)(s). It is shown that reactions of target **I** with **D** proceed via strong complexes **D**·**I** and $\mathbf{D}_2$·**I** that apparently contain opened NS chelate rings. Among the variety of new tin-containing transmetalation products is the remarkable air-stable complex $N_3Cu^I{}_2Sn^{IV}(NS)_2Cl_4$ (**V**). Our results are summarized in Schemes 1 and 2.



Scheme 1.



Scheme 2.

Experimental

Materials

Anhydrous tin(II) chloride, tin(IV) acetate and tin(IV) chloride were used as received from Alfa. The syntheses of $[NCuCl]_4$, (**I** [8]) and transmetalators $M(NS)_2$ (M = Co and Ni) [2] and **B** [3, 4, 9] have been described previously. Literature procedures were followed for solvent purification, chromatographic product separation, cryoscopic molecular weight determinations, manometric dioxygen uptake measurements, spectrophotometric titrations and spectral measurements [2–4, 8].

Synthesis of $Sn(NS)_2$ *(C)*

A clear solution of HNS (20 mmol) in ethanol (50 ml) was treated with a hot solution of anhydrous tin(II) chloride (10 mmol) in ethanol (50 ml). The reaction mixture was refluxed for 30 min, then left to cool to room temperature. The yellowish $Sn(NS)_2$ which precipitated (70% yield) was filtered and washed with ethanol and diethyl ether.

Synthesis of $Sn(NS)_2Cl_2$ *(D)*

The title complex was prepared by treating a clear solution of HNS (20 mmol) in absolute ethanol (40 ml) with 10 mmol of anhydrous tin(IV) chloride at room temperature under N_2. The neutral $Sn(NS)_2Cl_2$ that immediately precipitated was filtered and washed with ethanol and diethyl ether. Crystallization from methylene chloride–diethyl ether gave colorless crystals of dimensions suitable for structural characterization.

Synthesis of $Sn(NS)_4$ *(E)*

The title complex was prepared by adding a clear solution of anhydrous tin(IV) acetate (10 mmol) in absolute ethanol (50 ml) to a solution of HNS (40 mmol) in ethanol (30 ml). The reaction mixture was refluxed for 1 h. Yellow product **E** which precipitated on cooling was filtered and washed with ethanol and diethyl ether.

Synthesis of $N_3Cu_2SnCl_6O$ *(IV)*

Complex $N_3Cu_2SnCl_6$ (**II**) was prepared by treatment of **I** in methylene chloride or nitrobenzene with equimolar **D** at room temperature under N_2. A sequence of distinct color changes was observed (see 'Results and discussion'). After 8 h the mixture was filtered to remove co-product Cu(NS)(s), which was dried at 100 °C and weighed [2–4, 7]. The filtrate was provided with a limited supply of O_2 and then added to a large excess of hexane to precipitate product **IV**.

Synthesis of $N_3Cu_2SnCl_4O_2$ *(V)*

This complex was obtained by flushing a solution of **IV** in methylene chloride with O_2 for 30 min. The solvent was then removed in a vacuum rotary evaporator to give solid product **V**.

Synthesis of binuclear complexes $N_2Sn_2Cl_8$ (III), $N_3SnNi(H_2O)Cl_6$ (VI) and $N_3SnCoCl_6$ (VII)

The title complexes were obtained from simultaneous reactions of **I** with 2 mol of **D**, 1 mol each of $Ni(NS)_2$ [2] and **D**, and with 1 mol each of **B** and **D**, respectively, in methylene chloride under N_2 at room temperature. After 8 h the insoluble co-product Cu(NS)(s) was filtered off, dried and weighed. The title products were easily separated from trace oxidized Cu(NS)(s) [2–4, 7] by gel permeation chromatography (methylene chloride eluent [10]). Solid products **III, VI** and **VII** were isolated by vacuum solvent evaporation from the first eluted band in each system.

Synthesis of $N_3Cu_2Sn(NS)_2Cl_4$ (XI)

Orange product **XI** was prepared by reacting **I** with 1 mol of **E** in methylene chloride under N_2 at room temperature. After 8 h, reaction co-product Cu(NS)(s) was removed by filtration, dried and weighed. Vacuum solvent evaporation of the filtrate gave pure solid samples of **XI**.

Analytical and cryoscopic data for transmetalators **C**–**E** and transmetalation products are given in Table 1.

Physical measurements

Electronic spectra were recorded with a Perkin-Elmer Lambda 4B spectrophotometer at 25 °C. IR spectra were obtained with a Perkin-Elmer model 567 spectrophotometer. ^1H NMR spectra were measured with a Varian XL300 spectrometer at 25 °C with tetramethylsilane as internal reference.

Results and discussion

Tin transmetalators

Tin(II) transmetalator $Sn(NS)_2$ (**C**) is easily obtained by reaction of tin(II) chloride with 2 mol of HNS in refluxing anhydrous ethanol [11]. Colorless solid **C** is fairly soluble in methylene chloride and nitrobenzene and has good storage stability. Two new tin(IV) transmetalators with different NS:Sn ratios have been obtained. They are the first examples of metal(IV) transmetalators. *cis*-Dichloro-bis(*trans*-*S*-methyl isopropylidenehydrazinecarbodithioato)tin(IV) (**D**) is obtained by reaction of anhydrous $SnCl_4$ with 2–6 mol of HNS in anhydrous ethanol at 25 °C or at reflux. By contrast, treatment of tin(IV) acetate with just 4 mol of HNS in refluxing ethanol readily gives tetrakis(*S*-methyl

TABLE 1. Analytical, cryoscopic and electronic spectral data for tin transmetalators and transmetalation products

Symbol[b]	Complex	Anal.[a] (%)								M_r[c]	λ_{max}[d] (ϵ_λ (M^{-1} cm^{-1}))
		C	H	N	S	Cl	Sn	Cu	Co		
C	$Sn(NS)_2$	27.5 (27.2)	3.7 (4.1)	12.2 (12.7)	28.2 (29.0)		26.2 (27.0)			[e]	
D	$Sn(NS)_2Cl_2$	23.2 (23.4)	3.4 (3.5)	10.6 (10.9)	24.6 (25.0)	14.4 (13.9)	23.5 (23.2)			530±30 (512)	
E	$Sn(NS)_4$	31.1 (31.5)	4.2 (4.7)	14.3 (14.7)	33.8 (33.6)		16.1 (15.6)			735±25 (736)	
III	$N_2Sn_2Cl_8$	28.0 (27.3)	4.1 (3.2)	7.3 (6.4)		32.1 (32.0)	26.5 (27.1)	0.0 (0.0)		[e]	
IV	$N_3Cu_2SnCl_6O$	36.2 (35.7)	4.5 (4.2)	8.8 (8.3)		21.3 (21.1)	12.2 (11.8)	12.0 (12.6)		990±20 (1009)	850(540), 775(525)
V	$N_3Cu_2SnO_2Cl_4$	38.4 (37.7)	5.0 (4.4)	8.1 (8.8)		15.7 (14.9)	12.2 (12.4)	13.2 (13.3)		1000±30 (954)	850(580), 775(570)
VI[f]	$N_3SnNi(H_2O)Cl_6$	38.9 (38.1)	4.8 (4.7)	9.1 (8.9)		23.1 (22.6)	12.2 (12.6)			920±30 (943)	
VII	$N_3SnCoCl_6$	38.5 (38.2)	4.8 (4.8)	8.9 (9.0)		22.9 (22.6)	12.1 (12.6)		6.7 (6.3)	940±20 (926)	650(350), 630(420), 575(350)
IX	$N_4Co_2Cl_4$	46.0 (46.5)	6.1 (6.0)	10.8 (11.1)		14.6 (14.1)			11.9 (11.7)	990±20 (1009)	[g]
X	$N_3Cu_2Sn(NS)_2Cl_4$	38.4 (38.5)	4.1 (4.7)	10.8 (11.2)	9.9 (10.2)	12.0 (11.4)	10.1 (9.6)	10.6 (10.3)		1200±30 (1244)	[h]

[a] Calculated values in parentheses. [b] In Schemes 1 and 2. [c] Measured in nitrobenzene at $3–5\times10^{-2}$ m. [d] In methylene chloride. [e] Solubility too low for cryoscopy in nitrobenzene. [f] Ni: 6.5% (found), 6.3% (calc.). [g] See ref. 2. [h] See Fig. 6.

isopropylidenehydrazinecarbodithioato)tin(IV) (**E**). Product **E** and tin(IV) acetate are very water- and air-sensitive so that rigorously anhydrous conditions were required for reproducible syntheses.

Single crystals of $Sn(NS)_2Cl_2$ (**D**) are easily obtained and considerably more stable than the powdered solid, but all attempts to store and crystallize **E** were unsuccessful and all transmetalations with **E** were therefore conducted with freshly prepared samples. Attempts to prepare examples of the series $Sn(OAc)_{4-x}(NS)_x$ ($x = 1$–3) by reaction of tin(IV) acetate with x mol of HNS in ethanol led to extremely water-sensitive, impure products that are not recommended as transmetalators.

Analytical and cryoscopic data (Table 1) show that transmetalators **C**–**E** are pure products and that **D** and **E** exist as discrete molecules in nitrobenzene.

X-ray crystallographic study of $Sn(NS)_2Cl_2$ (D)

The details of the crystal data, data collection methods and refinement procedures are given in Table 2. See also 'Supplementary material'. Crystal data: orthorhombic space group *Pbna*, $a = 8.819(4)$, $b = 13.858(6)$, $c = 15.994(4)$ Å, $V = 1954.7(9)$ Å^3, $Z = 4$, structure solution and refinement based on 1135 reflections ($F_o \geqslant 6\sigma(F_o)$) converged at $R = 0.063$. Full details of the crystallographic methodologies are given elsewhere [15].

Description of the structure

Atomic positional parameters for $Sn(NS)_2Cl_2$ are given in Table 3 and bond lengths and angles are listed in Tables 4 and 5.

As illustrated in Fig. 1, the coordination geometry about tin is pseudo-octahedral with a crystallographic two-fold axis passing through tin and bisecting the Cl–Sn–Cl angle. The Sn coordination consists of nitrogen and sulfur donors from the two $(C_5H_9N_2S_2)^-$ ligands and the two chlorine atoms. The major angular distortion from octahedral limits is the S(1)–Sn–S(1a) angle of 159.7(2)°, which appears to be a consequence of nonbonding interactions between the S donors and the Cl ligands. The ligand bite angle of 88.7(3)° is comparable to values of 85.6–88.7° observed for other examples of complexes of this ligand and which depend on the ionic radii of metals and the coordination number [9, 16, 17]. The Sn–Cl, Sn–S(1) and Sn–N(1) bond distances of 2.400(5), 2.457(4) and 2.313(11) Å, respectively, are similar to values reported for other examples of tin(IV) complexes [18]. The tin atom is displaced 0.16 Å from the N(1)–N(1a)–Cl(1)–Cl(1a) plane toward S(1). The chelate ring C–N and N–N bond distances, 1.30(1) and 1.42(2) Å, respectively, are intermediate between the usual values for single and double bonds reported earlier [9, 16, 17, 19, 20]. One bond distance in the chelate ring, S(1)–C(1) = 1.780(14) Å, is somewhat longer than the usual range of 1.69 to 1.74 Å previously reported.

TABLE 2. Summary of experimental details for the X-ray diffraction studies of $Sn(C_5H_9N_2S_2)_2Cl_2$

Crystal parameters at 296 K[a]	
a (Å)	8.819(4)
b (Å)	13.858(6)
c (Å)	15.994(4)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å^3)	1954.690(096)
Space group	*Pbna*
Z	4
ρ_{calc} (g cm^{-3})	1.74
Measurement of intensity data	
Crystal shape and color	oblong box, colorless
Crystal dimensions (mm)	0.30×0.48×0.43
Instrument	Nicolet R3m diffractometer
Radiation	Mo Kα ($\gamma = 0.71073$ Å)
Scan mode	coupled θ (crystal)–2θ (counter)
Scan rate (°/min)	7–30
Scan range (°)	$0.0 < 2\theta \leqslant 50$
Scan length	from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
Background measurement	stationary crystal, stationary counter, at the beginning and end of each 2θ scan, each for the time taken for the scan
Standards	3 collected every 197
No. reflections collected: ($+h$ $+k$, $+l$)	2031
No. reflections used in solution: $F_o \geqslant 6\sigma(F_o)$	1135
Reduction of intensity data and summary of structure solution and refinement[b]	
Data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion	
Absorption coefficient (cm^{-1})	19.92
Absorption corrections	not applied
T_{max}/T_{min}	1.011
Structure solution	Patterson synthesis yielded the Sn position; all remaining non-hydrogen atoms were located via standard Fourier techniques
Atom scattering factors[c]	neutral atomic scattering factors were used throughout the analysis
Anomalous dispersion[d]	applied to all non-hydrogen atoms
Final discrepancy factor[e]:	
$R=$	0.0632
$R_w=$	0.0742
Goodness of fit[f]	1.898

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32 K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in ref. 12. [c] Ref. 13. [d] Ref. 14. [e] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o) + g^*(F_o), g = 0.002$. [f] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o is the number of observations and N_v is the number of variables.

TABLE 3. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) of $Sn(C_5H_9N_2S_2)_2Cl_2$

Atom	x	y	z	U_{iso}[a]
Sn	1158(1)	2500	0	34(1)*
Cl	3023(5)	3465(4)	703(3)	74(2)*
S(1)	667(4)	3582(3)	−1187(3)	55(1)*
S(2)	−2421(5)	3763(4)	−1845(3)	68(2)*
N(1)	−855(12)	3445(8)	435(7)	35(3)*
N(2)	−1920(12)	3584(8)	−221(7)	38(4)*
C(1)	−1302(15)	3657(10)	−953(9)	40(5)*
C(2)	−4264(18)	3821(14)	−1370(11)	64(6)*
C(3)	−1325(18)	3788(14)	1161(11)	66(6)*
C(4)	−2872(17)	4216(14)	1273(12)	74(7)*
C(5)	−384(20)	3689(14)	1922(9)	69(7)*

[a]Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{iso} tensor.

TABLE 4. Bond lengths (Å)

Sn–Cl	2.400(5)	Sn–S(1)	2.457(4)
Sn–N(1)	2.313(11)	Sn–Cl(a)	2.400(5)
Sn–S(1a)	2.457(4)	Sn–N(1a)	2.313(11)
S(1)–C(1)	1.780(14)	S(2)–C(1)	1.741(15)
S(2)–C(2)	1.796(17)	N(1)–N(2)	1.422(15)
N(1)–C(3)	1.322(21)	N(2)–C(1)	1.295(18)
C(1a)–S(1a)	1.780(14)	C(1a)–S(2a)	1.741(15)
C(2a)–S(2a)	1.796(17)	C(3)–C(4)	1.498(23)
C(3)–C(5)	1.480(24)		

TABLE 5. Bond angles (°)

Cl–Sn–S(1)	98.2(2)	Cl–Sn–N(1a)	169.3(3)
S(1)–Sn–N(1)	88.7(3)	Cl–Sn–Cl(a)	93.5(2)
S(1)–Sn–Cl(a)	95.7(2)	N(1)–Sn–Cl	94.0(3)
Cl–Sn–S(1a)	95.7(2)	S(1)–Sn–S(1a)	159.7(2)
N(1)–Sn–S(1a)	75.6(3)	Cl(a)–Sn–S(1a)	98.2(2)
Cl–Sn–N(1)	94.0(3)	S(1)–Sn–N(1a)	75.6(3)
N(1)–Sn–N(1a)	79.8(5)	Cl(a)–Sn–N(1)	169.3(3)
S(1a)–Sn–N(1a)	88.7(3)	Sn–S(1)–C(1)	92.6(5)
C(1)–S(2)–C(2)	99.8(8)	Sn–N(1)–N(2)	111.2(7)
Sn–N(1)–C(3)	135.2(10)	N(2)–N(1)–C(3)	113.1(11)
N(1)–N(2)–C(1)	113.6(11)	N(2)–C(1)–S(1)	126.6(11)
N(2)–C(1)–S(2)	120.6(10)	S(1)–C(1)–S(2)	112.7(8)
N(1)–C(3)–C(4)	122.2(15)	N(1)–C(3)–C(5)	120.9
C(4)–C(3)–C(5)	116.7(15)		

The Sn–S(1) (2.457(4) Å) and Sn–N(1) distances (2.313(11) Å) are longer than those reported for **B** (mean values 2.207 and 2.045 Å [9]), $Co(NS)_2$ (mean values 2.226 and 2.03 Å [17]) and $Ni(NS)_2$ (mean values 2.153 and 1.934 Å [19]) despite the fact that tin has a higher formal oxidation state (IV) than in cobalt(III), cobalt(II) and nickel(II). Sn–S(1) bond lengthening is ascribed to the *trans*-effect of two sulfur atoms in the axial plane. The observed Sn–(N) lengthening is due to Cl---N interactions across the central tin atom.

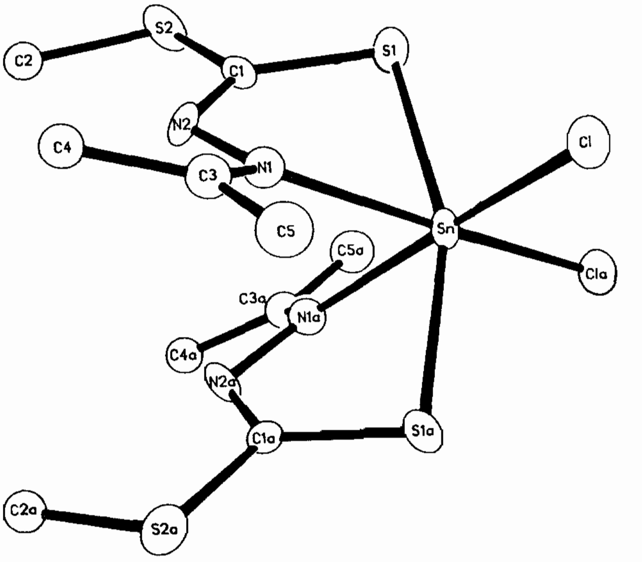


Fig. 1. Molecular structure of *cis*-dichloro-bis(*S*-methyl isopropylidenehydrazinecarbodithioato)tin(IV).

TABLE 6. ^1H NMR spectra of HNS and $M(NS)_n$ complexes in $CDCl_3$ at 25 °C

Complex	δ (ppm)			
	$S–CH_3$	CH_3(*syn*)	CH_3(*anti*)	N–H
HNS	2.57	1.96	2.04	10.05
$Zn(NS)_2$	2.50	2.18	2.35	
$Ni(NS)_2$	2.50	2.55	2.93	
$Sn(NS)_2Cl_2$	2.47	2.26	2.72	
$Sn(NS)_4$	2.60	1.95	2.06	

Competition experiments (see below) indicate that $Sn(NS)_2Cl_2$ is more reactive as a transmetalator of copper(I) than are $Co(NS)_2$ and $Ni(NS)_2$. However, it is less labile than $Co(NS)_3$ because $Co(NS)_3$ reactions proceed via complete electron transfer while the $Sn(NS)_2Cl_2$ reactions apparently proceed via limited electron transfer (see below).

NMR spectra of tin transmetalators

The ^1H NMR spectra of ligand HNS and its diamagnetic complexes $Zn(NS)_2$, $Ni(NS)_2$, $Sn(NS)_2Cl_2$ and $Sn(NS)_4$ were obtained in $CDCl_3$ at 25 °C. The characteristic resonances are listed in Table 6 and illustrated in Fig. 2. The spectra all exhibit an $S–CH_3$ signal at $\delta = 2.52 \pm 0.03$ ppm that is essentially constant and independent of the rest of the molecule [21, 22].

The HNS ligand exhibits a downfield signal at $\delta = 10.05$ ppm due to its N–H proton. This signal disappears either on deuteration or on metal complex formation.

Because of restricted rotation around the C=N double bond, the HNS ligand and its neutral metal complexes $M(NS)_2$ exhibit separate signals for the $(CH_3)_2C=N$

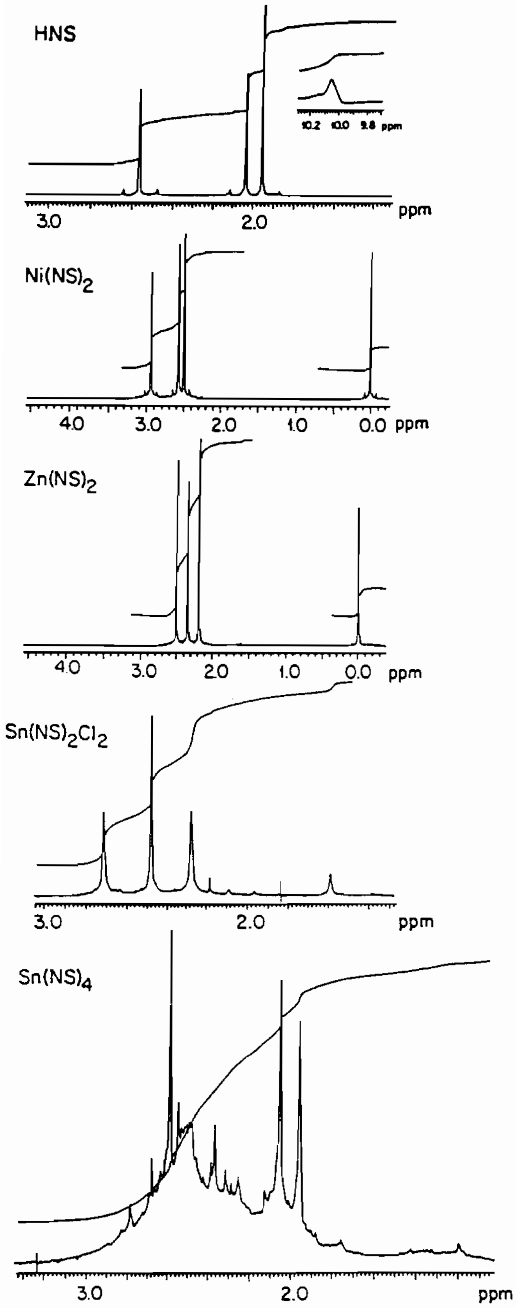


Fig. 2. ^{1}H NMR spectra of HNS, $Ni(NS)_2$, $Zn(NS)_2$, $Sn(NS)_2Cl_2$ and $Sn(SN)_4$ in $CDCl_3$ at 25 °C with tetramethylsilane as internal reference.

group (Fig. 2). The signal for the methyl groups *syn* to the C=N bond resonates at higher field than the *anti* CH_3 group [23].

Figure 2 shows that the chemical shift of methyl groups of the isopropylidene moiety is very sensitive to the metal present in these complexes. Downfield shifts occur on complexation of NS^-. This can be attributed to the quasiaromatic character of the chelate ring. The two signals for methyl groups of HNS and $Zn(NS)_2$ are located to the right of the S–CH_3 signal, with $\Delta\delta = 0.08$ and 0.17 ppm, respectively, while the *syn* and *anti* methyl signals of the $Ni(NS)_2$ complex appear to the left of the S–CH_3 signal, with $\Delta\delta = 0.38$ ppm due to the aromatic character in the chelate ring. The resulting ring current causes deshielding of groups attached to the chelate ring [23–26].

In contrast to the chemical shift behavior of the $(CH_3)_2C{=}N$ group in $M(NS)_2$ complexes, the resonance of the S–CH_3 group in $Sn(NS)_2Cl_2$ (**D**) lies between the *syn* and *anti* signals, with the largest $\Delta\delta = 0.46$ ppm yet observed. This behavior is attributed to the inductive effects of the chlorine atoms in **D**, which create a relatively positive charge on the tin atom. This charge is transmitted to the *anti* methyl group that lies in the same plane of the chelate ring (Fig. 1) and causes the observed downfield shift.

Although we could not crystallize $Sn(NS)_4$ (**E**) its NMR spectrum resembles that of $Zn(NS)_2$, with the *syn* and *anti* methyl resonances to the right of the S–CH_3 signal. The integrated signals for **E** (1:1:1) indicate that **E** has four chelated NS ligands in an eight-coordinate geometry.

Tetranuclear copper(I) complexes

Copper(I) halides react quantitatively with equimolar *N,N*-diethylnicotinamide (N) in dioxygen-free, weakly coordinating aprotic solvents like methylene chloride and nitrobenzene to form tetranuclear complexes $[NCuX]_4$, eqn. (9) [8].

$$4N + 4CuX(s) \longrightarrow [NCuX]_4(I) \qquad (9)$$

The chloro complex is the most soluble in all solvents investigated, with $[NCuI]_4$ virtually insoluble [27]. Cryoscopic and analytical data [2–4, 8] establish the formation of discrete tetranuclear molecules $[NCuX]_4$ in eqn. (9).

Transmetalation of polynuclear copper targets with tin transmetalators $Sn(NS)_2$ (C), $Sn(NS)_2Cl_2$ (D) and $Sn(NS)_4$ (E); general observations

Transmetalation of copper(II) targets by $M(NS)_2$ complexes (M = Co, Ni and Zn) rapidly gives $Cu(NS)_2$ co-products [10, 28], whereas Cu(NS)(s) is formed much more slowly on transmetalation of copper(I) targets with these same $M(NS)_2$ reagents [7]. From kinetic studies [7, 28–30] it has been proposed that complete $\overline{Cu–X–M–S}$ rings are required for metal exchange leading to transmetalation, but that slow Cu(NS)(s) formation also requires breaking of strong X–Cu^I bonds in the primary products [7].

The availability of tin reagents **C**, **D** and **E** containing different oxidation states of the same element and different NS:Sn ratios enables us to provide answers to the following questions.

1. Do **C**, **D** and **E** react with representative polynuclear copper(I) and copper(II) targets under mild conditions? If so, what are the products?

2. What are the effects of different tin oxidation states and NS:Sn ratios on these reactions? Are reaction precursors and intermediates identifiable? Are redox reactions or INLT involved?

Transmetalation of tetranuclear oxocopper(II) targets with tin(II) transmetalator $Sn(NS)_2$ *(C)*

Transmetalation of target $(\mu_4\text{-O})N_4Cu_4Cl_6$ [10, 28] with equimolar **C** results in quantitative formation of trimer $(\mu_3\text{-O})N_3Cu_3Cl_4$, eqn. (10) [11].

$$(\mu_4\text{-O})N_4Cu_4Cl_6 + \mathbf{C} \longrightarrow (\mu_3\text{-O})N_3Cu_3Cl_4 + NSnCl_2 \cdot Cu(NS)_2 \quad (10)$$

We now report that transmetalation of dioxocopper(II) target $(\mu\text{-O})_2N_4Cu_4Cl_4$ [8, 10] with 1 mol of **C** in methylene chloride at room temperature gives the same trimeric product, eqn. (11), as shown by comparison with an authentic sample [11]. Reaction (11) involves replacement of one copper(II) center with tin followed by fragmentation of SnO(s) and oxo group rearrangement.

$$(\mu\text{-O})_2N_4Cu_4Cl_4 + \mathbf{C} \longrightarrow (\mu_3\text{-O})N_3Cu_3Cl_4 + SnO(s) + Cu(NS)_2 \quad (11)$$

Reactions (10) and (11) indicate that tin(II) is too large to be accommodated by available sites in targets $(\mu_4\text{-O})N_4Cu_4Cl_6$ and $(\mu\text{-O})_2N_4Cu_4Cl_4$, a situation remedied by fragmentation of $SnCl_2$ (eqn. (10)) and SnO (eqn. (11)). Fragmentation to give products of lower nuclearity than the target appears to be a general feature of the transmetalation of tetranuclear oxocopper(II) targets with equimolar **C**.

Attempted transmetalation of tetranuclear copper(I) target ***I*** *with* ***C***

Transmetalation of tetranuclear copper(I) complex **I** with equimolar or excess **C** is insignificant in methylene chloride at room temperature, as indicated by negligible precipitation of Cu(NS)(s) in periods up to 30 h. Reagent **C** thus appears to be specific for copper(II) transmetalation, although all reactions with oxocopper(II) targets are likely to result in SnX_2 and SnO fragmentation (see above).

$Sn(NS)_2$ is not as desirable a transmetalator as other $M(NS)_2$ complexes because it is less soluble in appropriate aprotic solvents. Solubility is higher in the presence of **I**, but any adducts formed are evidently stable to metal exchange and Cu(NS)(s) production.

Transmetalation of tetranuclear copper(II) targets with tin(IV) reagent ***D***

Transmetalations of the copper(II) targets of eqns. (10) and (11) with equimolar **D** are very much slower than those with $M(NS)_2$ reagents **A** (M = Co, Ni, Zn) in methylene chloride at room temperature, although all result in the co-production of $Cu(NS)_2$. Attempted separation of $Cu(NS)_2$ from the desired transmetalation products by gel permeation chromatography gave very diffuse, single bands which indicate that anticipated products $(\mu_4\text{-O})N_mCu_3SnCl_6$ and $(\mu\text{-O})_2N_nCu_3SnCl_8$ disproportionate. This conclusion is supported by isolation of variable amounts of dimer $N_4Cu_2Cl_4$ and trimer $(\mu_3\text{-O})N_3Cu_3Cl_4$ products (identified by comparison with authentic samples [11, 31]) from many careful attempts at fractional chromatography. We might expect higher stability for $Cu^{II}Sn^{IV}$ combinations than for $Cu^{II}Sn^{II}$, but the systems are too slow and too irreproducible to warrant further study. Such behavior is expected of any inert metal(IV) transmetalator.

Transmetalation of tetranuclear copper(I) complex ***I*** *with* $Sn(NS)_2Cl_2$ *(D)*

Under typical conditions (see 'Experimental'), the title reactions proceed in two distinct stages via precursor complex formation between transmetalator **D** and target **I** (Scheme 1), as indicated by the following evidence.

(i) Spectral changes

Addition of 1 or 2 mol of colorless **D** to pale yellow **I** in methylene chloride or nitrobenzene at room temperature under N_2 results in the development, over a period of 15–30 min, of a brown-green color due to appearance of a new spectral feature at 340 nm (Fig. 3). At fixed concentration of **I**, the absorptivity of this feature increases with [**D**] until the molar ratio $R = [\mathbf{D}]/[\mathbf{I}]$ reaches 2.0.

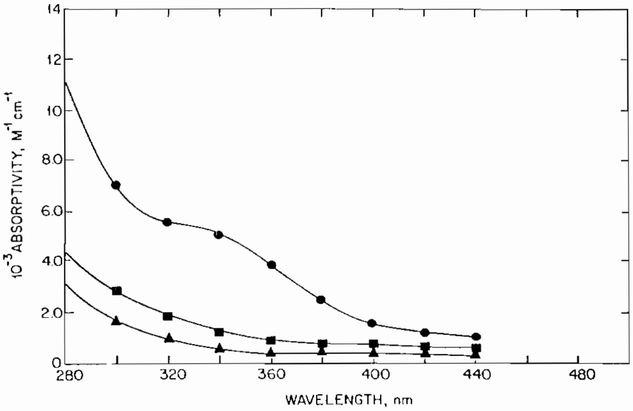


Fig. 3. Electronic spectra of $[NCuCl]_4$ (**I**, ■), $Sn(NS)_2Cl_2$ (**D**, ▲) and precursor **D**·**I** (●) in methylene chloride at 25 °C.

(ii) Cryoscopic data

At $R = 1.0$, subsequent precipitation of co-product Cu(NS)(s) (Fig. 4) to give colorless trimer **II** (Scheme 1) was sufficiently slow to allow cryoscopic molecular weight determination of the precursor **D**·**I** (calculated 1570; observed 1620±30 g/mol). However, at $R = 2.0$ the rate of Cu(NS)(s) precipitation to give dimer **III** (Scheme 1) was too high to permit cryoscopic determination of the molecular weight of adduct $\mathbf{D}_2 \cdot \mathbf{I}$.

(iii) Time dependence of Cu(NS)(s) precipitation

The time dependence of Cu(NS)(s) precipitation in nitrobenzene at 21 °C with $R = 1.0$ and 2.0 was studied by established methods [7] (Fig. 4). The observed induction period is inversely proportional to the concentration of **D** and the initial rate doubled between $R = 1.0$ and 2.0. These results are expected if respective precursors **D**·**I** and $\mathbf{D}_2 \cdot \mathbf{I}$ are prerequisites for Cu(NS)(s) production. Initial rates that are proportional to [**D**] indicate that the two halves of $\mathbf{D}_2 \cdot \mathbf{I}$ are very similar to the active face of precursor **D**·**I** (Scheme 1) and that conversion of these precursors to products has the same rate-determining step [7].

(iv) NMR spectra

The ^{1}H NMR spectra of **I**, **D** and the precursor **D**·**I** solution formed in $CDCl_3$ at 25 °C are shown in Fig. 5. The broadening of the signals assigned to the methyl groups of the NS ligand and the change in position of the *anti* methyl signal (see Fig. 2) indicate opening of a chelate ring around tin and the formation of a Cu–N–S–Sn bridge. Copper(II) character in **D**·**I** causes loss and broadening of the aromatic protons of ligand N that is not observed in $[NCuX]_4$ (Fig. 5). Electron transfer from copper(I) to tin(IV) is responsible for formation of the brown–green color on mixing **D** with **I** under N_2. The disappearance of the color that accompanies formation of Cu(NS)(s) indicates that NS stabilizes copper(I). We could not obtain ^{1}H NMR data for the precursor $\mathbf{D}_2 \cdot \mathbf{I}$ formed at $R = 2.0$ because Cu(NS)(s) formation is too rapid at room temperature.

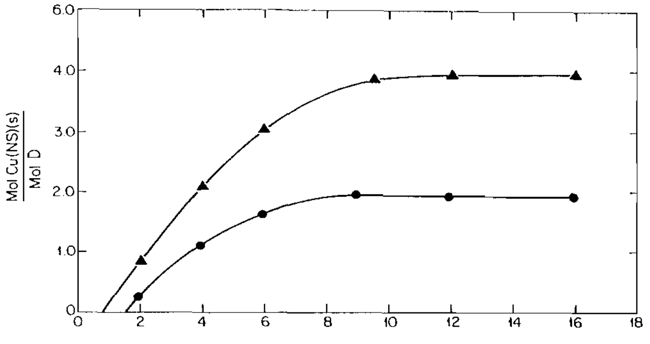


Fig. 4. Time-dependence of Cu(NS)(s) precipitation in the reaction of $[NCuCl]_4$ (**I**, 21 mM) with $Sn(NS)_2Cl_2$ (**D**) in nitrobenzene at 21 °C under N_2 with $R = [\mathbf{D}]/[\mathbf{I}] = 1.0$ (●) and 2.0 (▲).

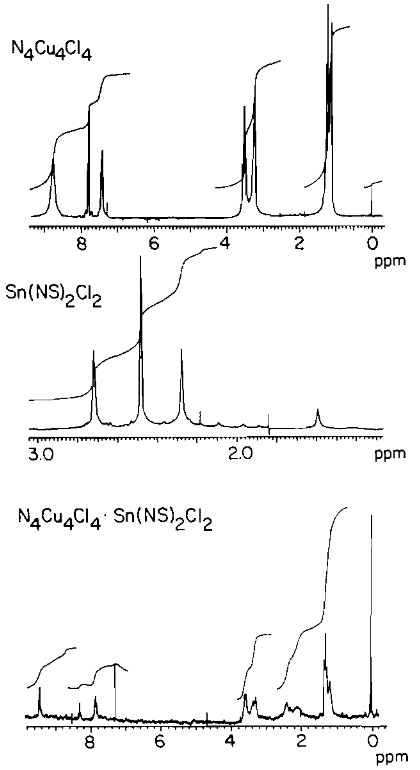


Fig. 5. ^{1}H NMR spectra of $[NCuCl]_4$ (**I**), $Sn(NS)_2Cl_2$ (**D**) and precursor **D**·**I** in $CDCl_3$ at 25 °C with tetramethylsilane as internal reference.

Implications for transmetalation mechanisms

Because **D** contains chelated NS ligands (Fig. 1), is kinetically inert (previous sections) and is a weak oxidant for **I**, we have obtained unprecedented detail of the transmetalation mechanism proposed in Scheme 1. The following questions pertain to this mechanism.

1. Is electron transfer from copper(I) to tin(IV) involved? If so, to what extent does it occur and is it reversible?
2. Does electron transfer accompany or cause ring opening in **D**? If so, are Sn–N or Sn–S bonds the first to be broken? Are *both* chelate rings of **D** open in precursor **D**·**I**?
3. Does transfer of the NS ligand(s) from tin to copper result in immediate Cu(NS)(s) formation?

Electron transfer

We envision that **D** first loosely attaches itself to one or both of the chlorine atoms in one face of **I** (Scheme 1). This would increase the coordination number of Sn from 6 to 7 or 8, respectively, and is reasonable because of the existence of eight-coordinate complex **E** (see below). Such attachment would provide a loose bridge for inner-sphere electron transfer from copper(I) to tin(IV). Any electron transfer to tin would be expected to increase its lability and provide an opportunity for a reduction of coordination number by NS chelate ring opening, which would increase the strength of existing **D**---**I** interactions through chlorine bridges. By the time the cryoscopic experiment is conducted, formation of the brown-green color is complete (15–30 min). Electron transfer is the most obvious reason for ring opening in **D** to form strong reaction precursors. It is very probably faster than ring opening in **D** itself and amounts to electron transfer-catalyzed precursor formation. Catalysis by prior electron transfer is an obvious possibility in reactions (3), but the spectral changes are much faster there because **B** is a stronger oxidant and is inherently more labile than **D** [4].

Sn–N or Sn–S bond breaking in D

The M–S bond of $M(NS)_n$ complexes is derived from the enol form of HNS [9, 32]. It is thus expected to be stronger than the Sn–N bond and less likely to be broken than Sn–N in the formation of any NS-bridged precursors like **D**·**I**. Support for this idea comes from the relative high affinity of tin for sulfur [33, 34]. There are changes in the ^{1}H NMR spectrum of **D** on precursor formation (Fig. 5). The $S\text{–}CH_3$ signal is unchanged ($\delta \simeq 2.5$ ppm) though broadened. Broadening suggests coordination of the N atom of bridging NS to copper(II) in **D**·**I** and that *both* NS ligands are opened on precursor formation.

The situation at copper

When the brown-green color is fully formed, the copper centers in the active face of the precursor have copper(II) character and they retain their coordinated ligands N, as indicated by no evidence for free N in the NMR experiment (Fig. 5). Precursor formation thus results in an increase in copper coordination number from 4 to 5. The situation in the active precursor face is now formally $Cl_3NCu^{II}\text{–N–S–}Sn^{II}(Cl, Cl)\text{–S–N–}Cu^{II}NCl_3$.

NS ligand transfer from tin to copper

Fading of the brown-green color with time is due to formation of the following structure in each active face: $Cl_3N(NS)Cu^{I}ClSn^{IV}ClCu^{I}(NS)NCl_3$. Reinstatement of colorless copper(I) by electron transfer from tin(II) to copper(II) is due to stabilization of the copper(I) state by NS chelation. This process is slow because the Sn–S bond is strong. Nevertheless, the change to colorless products is faster than discrete Cu(NS)(s) production because of the need to break Cu–Cl bonds in the successor complex.

Completion of metal exchange

Loss of two Cu(NS) units and one N ligand from the active face of precursor **D**·**I** leaves tin(IV) bonded to two Cl atoms and N in **II** (Scheme 1). Metal exchange and transmetalation are now complete.

Properties of heterotrinuclear complex $N_3Cu_2SnCl_6$ (II) and its reactions with O_2

The very air-sensitive trinuclear product **II** of the previous section is obtained by removing co-product Cu(NS)(s) under N_2 (Schlenk). Cryoscopic molecular weight measurements under N_2 showed that **II** contains three ligands N. The absence of spectral features in the 700–900 nm region indicates [8, 10, 31] that **II** contains two copper(I) and one tin(IV) centers.

We suggest structure **II** (Scheme 1) based on attachment of **D** to **I** through the two chlorine atoms in one face of **I** and the ultimate product stoichiometry. Cryoscopic measurements showed one free N in the product filtrate. The two remaining copper(I) centers of **II** each carry one N ligand, which means that tin(IV) in **II** has a coordinated N ligand and is thus seven coordinate. Because one $Cu^{I}(Cl, Cl)Cu^{I}$ face of **I** remains after its monotransmetalation with equimolar **D**, **II** is oxidizable with O_2 to give very interesting chemistry.

Brief exposure of the filtrate containing equimolar **II** and N to O_2 or air results in a green coloration. Analytical and cryoscopic data (Table 1) and the spectrum of the product isolated by addition of the partially oxidized product filtrate to a three-fold excess of hexane (Fig. 6) indicate that the two copper(I) centers of **II** are oxidized to copper(II) in **IV**. The spectrum of **IV** in Fig. 6 is typical of complexes that contain Cl_3Cu^{II} chromophores [8, 10, 31], which suggests the formulation

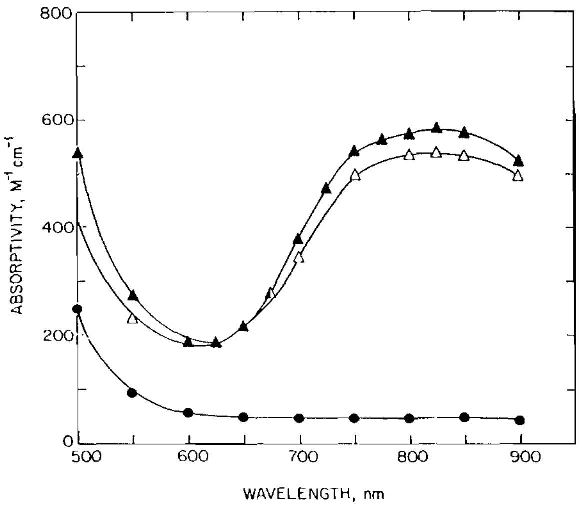


Fig. 6. Electronic spectra of trinuclear complexes $N_3Cu_2SnCl_6O$ (**IV**, ▲), $N_3Cu_2SnO_2Cl_4$, (**V**, △) and $N_3Cu_2Sn(NS)_2Cl_4$ (**X**, ●) in methylene chloride at 25 °C.

of **IV** in Scheme 1. This proposed structure contains seven-coordinate tin(IV).

Manometric measurements in nitrobenzene showed that **II** is completely oxidized by 1 mol of O_2. The isolated product $N_3Cu_2SnO_2Cl_4$ (**V**, Table 1) contains two copper(II) centers (Fig. 6) and two fewer Cl atoms than **II** and **IV**. Dioxygen is thus reduced by **II** in eqn. (12). No evidence for elemental Cl_2 could be obtained.

$$N_3Cu_2SnCl_6\ (\mathbf{II}) + O_2 \longrightarrow N_3Cu_2SnO_2Cl_4\ (\mathbf{V}) + 2Cl^{\bullet} \quad (12)$$

We conclude that $Cl^{\bullet}$ reacts preferentially with N or the nitrobenzene solvent.

Product **V** disproportionates slowly via eqn. (13), especially in aprotic solvents, as verified by gravimetric determination and identification of $SnO_2(s)$.

$$N + \mathbf{V} \longrightarrow N_4Cu_2Cl_4 + SnO_2(s) \quad (13)$$

This further indicates the incompatibility of tin and copper(II) in polynuclear oxo(halo)amine ligand environments because of a preference of tin for a high coordination number with oxo ligands.

*Sequential and simultaneous transmetalation of **I** with $Co(NS)_2$, $Ni(NS)_2$, **B** and **D***

In previous work we have reacted $[NCuX]_4$ targets with mixtures of **B**, $M(NS)_2$ and $M'(NS)_2$ reagents, where M and M′ are different metals [4]. This work showed that $[NCuX]_4$ targets react selectively with a particular reagent when there are alternatives. It led to a reaction selectivity order that is related to the thermodynamic stability of $M(NS)_n$ complexes and their different reaction rate laws [29, 30].

In this section we report the results of ambient sequential and simultaneous transmetalation of copper(I) target **I** with the title transmetalators under N_2 as practical approaches to obtaining specific products and to establishing relative transmetalator reactivities. All the reactions were conducted in methylene chloride under N_2. Scheme 2 summarizes our results.

Target **I** reacts with equimolar **D** and $Ni(NS)_2$ to give the heterobinuclear complex $N_3SnNiCl_6$ (**VI**, Table 1) together with 4 mol of Cu(NS)(s) and 1 mol of N. The reaction can be run sequentially by adding 1 mol of $Ni(NS)_2$ to **II**. The homologues of **VI** (Table 1) all contain three N ligands, which appears to be characteristic of binuclear products containing tin(IV) in this ligand system.

Target **I** reacts simultaneously with equimolar **B** and **D** to give $N_3SnCoCl_6$, **VII** (Table 1), 3 mol of Cu(NS)(s) and 1 mol of $Cu(NS)_2$. Dimer **VII** also is obtained by treatment of complex **VIII** (from reaction (3)) with equimolar **D** (Scheme 2). Figure 7 shows the electronic spectra of dimers **VII** and **IX** that contain cobalt. Multiple absorption maxima in the region 575–650 nm are characteristic of five-coordinate cobalt(II) [3].

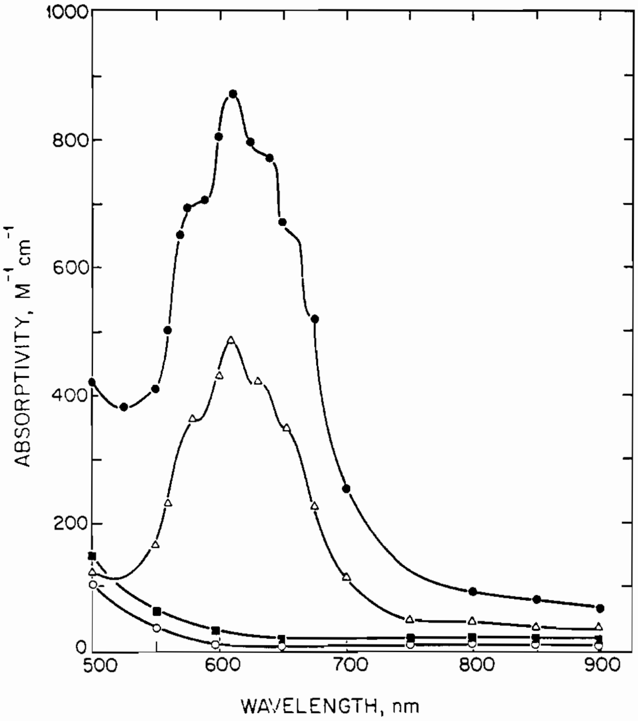


Fig. 7. Electronic spectra of binuclear complexes $N_4Co_2Cl_4$ (**IX**, ●), $N_3SnCoCl_6$ (**VII**, △), $N_3SnNi(H_2O)Cl_6$ (**VI**, ■) and $N_2Sn_2Cl_8$ (**III**, ○) in methylene chloride at 25 °C.

Higher reactivity of **B** than **D** for **VIII** is indicated by formation of product $N_4Co_2Cl_4$ (**IX**) on simultaneous transmetalation of **VIII** with equimolar **B** and **D** (Scheme 2).

To establish the relative reactivities of $Ni(NS)_2$, $Co(NS)_2$ and **D**, complex **VIII** was reacted with (i) equimolar $Co(NS)_2$ and **D**; and (ii) equimolar $Ni(NS)_2$ and **D**. The formation of the same binuclear product $N_3SnCoCl_6$ (**VII**) and the previous result indicate the reactivity order $\mathbf{B} > \mathbf{D} > Co(NS)_2 > Ni(NS)_2$ for transmetalation of **I**. High reactivity of **B** is due to electron transfer from copper(I) to cobalt(III) [3]. The high relative reactivity of **D** is due, at least in part, to strong complex formation with the copper(I) centers of **I** (Scheme 1), which evidently excludes reaction with $Co(NS)_2$ and $Ni(NS)_2$. In line with the above reactivity order, we found that **I** reacts with a mixture of 2 mol of **D** and 1 mol of $Co(NS)_2$ to give tin(IV) dimer **III**, eqn. (14) and not tin–cobalt dimer **VII**, eqn. (15).

$$\mathbf{I} + 2\mathbf{D} + Co(NS)_2 \longrightarrow \mathbf{III} + Co(NS)_2 + 4Cu(NS)(s) \quad (14)$$

$$\mathbf{I} + 2\mathbf{D} + Co(NS)_2 \longrightarrow \mathbf{VII} + \mathbf{D} + 4Cu(NS)(s) \quad (15)$$

*Transmetalation of copper(I) target **I** with $Sn(NS)_4$ (**E**)*

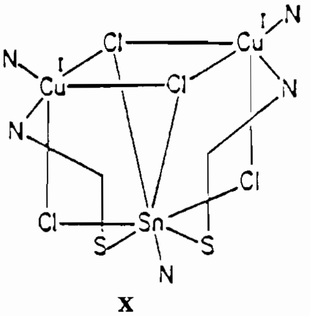
Treatment of target **I** with equimolar **E** in methylene chloride under N_2 results in an immediate color change to red. Precipitation of 2 mol of Cu(NS)(s), eqn. (16), in 1 h at room temperature is accompanied by slight diminution of the red color. Product $N_3Cu_2Sn(NS)_2Cl_4$ (**X**, Table 1) is easily obtained by filtration of Cu(NS)(s) and evaporation of the filtrate.

$$I+E \longrightarrow N_3Cu_2Sn(NS)_2Cl_4+2Cu(NS)(s) \qquad (16)$$

The remarkable features of this reaction are (i) the rapid color change and precipitation of Cu(NS)(s) and (ii) the ambient stability of product **X**, as indicated by no evidence for oxidation of copper(I) to copper(II) by O_2 over long periods of time. We attribute these results to (i) the presence of four bidentate NS ligands in **E** that make it unusually labile as an eight-coordinate complex; (ii) electron transfer-assisted opening of two of the NS chelate rings of **E**, which leads to much faster color changes, precursor formation and Cu(NS)(s) production than with **D**; and (iii) inhibition of copper(I) oxidation by NS ligands. It is very important to point out that INLT, eqn. (17), is insignificant for **X** over long time periods at room temperature in aprotic solvents.

$$X \longrightarrow SnCl_4+2Cu(NS)(s)+3N \qquad (17)$$

The reactions of **I** with **E** are too rapid to be elucidated in detail by NMR spectroscopy at room temperature. In the absence of single crystals, we suggest the following structure for **X**. Whatever its detailed structure, the molecule is somehow protected from air oxidation by coordination of NS by copper(I) but exhibits a negligible INLT rate at room temperature.



X

*Oxidation of **X** by bromine*

Complexes $[L_3Cu^I_2M]L$ (L = 6-methyl-2-oxopyridinate, M = Co, Ni, Zn) are air-sensitive and also are oxidized by bromine [35]. Figure 8 shows that **X** reacts with 2 mol of Br_2 in two distinct stages. Reaction of **X** with 1 mol of Br_2 results in development of no absorption due to copper(II) at 850 nm [8, 31], indicating that it corresponds to reaction (18), where N_2S_2 is the disulfide from oxidation of coordinated NS^- [2]. As expected, the first product of eqn. (18) can react with O_2, eqn. (19), or with one mol of Br_2, eqn. (20), because its copper(I) centers are no longer protected by NS ligands.

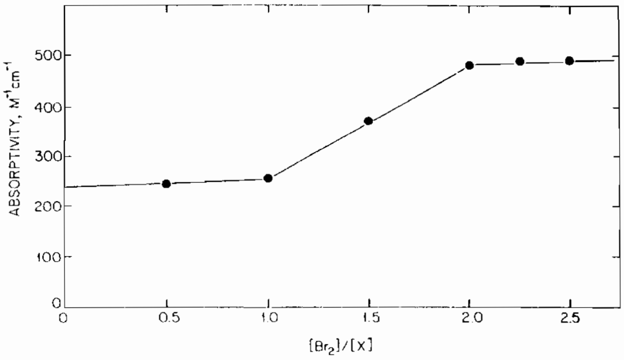


Fig. 8. Spectrophotometric titration of 1.0 mM $N_3Cu_2Sn(NS)_2Cl_4$ with Br_2 in methylene chloride at 25 °C. Absorptivities were measured at 850 nm.

$$X+Br_2 \longrightarrow N_3Cu^I_2SnCl_4Br_2+N_2S_2 \qquad (18)$$

$$N_3Cu^I_2SnCl_4Br_2+\tfrac{1}{2}O_2 \longrightarrow N_3Cu_2SnCl_4Br_2O \qquad (19)$$

$$N_3Cu^I_2SnCl_4Br_2+Br_2 \longrightarrow N_3Cu_2SnCl_4Br_4 \qquad (20)$$

Conclusions

Syntheses of heteropolymetallic products containing tin can be designed to give predictable products on the basis of established transmetalation patterns [6] and the relative reactivities of **B**, **D** and $M(NS)_n$. Among a variety of interesting new tin-containing products is the remarkable air-stable copper(I)–tin(IV) complex $N_3Cu^I_2Sn^{IV}(NS)_2Cl_4$ (**X**).

The successful observation of reaction precursors **D**·**I** and D_2·**I** that contain opened NS chelate rings and evidence for a similar situation in the transmetalation of **I** with **E** is the result of two happy circumstances. First is the use of relatively inert metal(IV) transmetalator **D**, which gives us sufficient time for NMR spectroscopy. Second is limited intramolecular electron transfer from copper(I) to tin(IV), with two other consequences: (i) accelerated NS ligand transfer but (ii) minimal paramagnetic broadening of proton resonances that would otherwise obscure the ^1H spectra of opened NS chelate rings.

Transmetalation is a special kind of ligand exchange. It is special because the ligand exchange is organized and facilitated by the molecular framework of the target and the preference of any given transmetalator for specific target sites [30]. This framework consists of the halogen atoms X of halocopper targets. These ligands provide a foothold for reaction precursor formation, which results in an increase of coordination number of the transmetalator metal and can be weak or strong, depending on the coordinative unsaturation of M and its affinity for X [28–30]. There is no question that the interactions that lead to reaction precursors are specific [30] and cooperative [36].

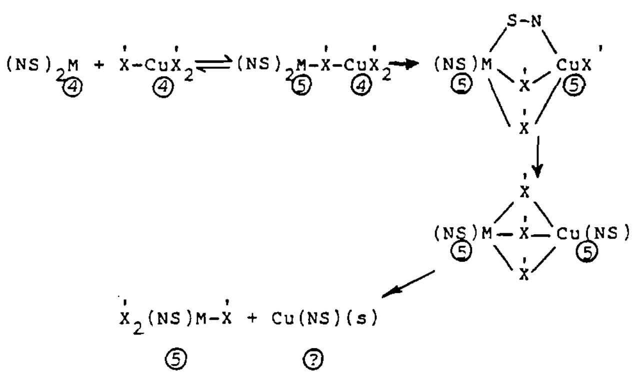
An increase in coordination number of the transmetalator metal on precursor formation leads to weakening of M–N and M–S bonds in transmetalators $M(NS)_n$. Any electron transfer through the foothold ligand(s) to M also weakens these bonds. Transfer of NS ligands to target copper then proceeds in discrete steps. Our work indicates that it is slow in copper(II)–tin(IV) complexes, is faster in copper(I)–tin(IV) systems and that it begins by breaking Sn–N bonds in **D**. Breaking these bonds lowers the coordination number of M. As a result, M forms stronger bonds to foothold ligands X. At the same time, Cu–X bonds are weakened because of an increase in the coordination number of copper on coordination of NS. What is happening is the net replacement of Cu–X bonds with M–X bonds.

The transmetalation act is almost complete when an entire NS ligand has been transferred from $M(NS)_n$ to copper(I) in $[NCuCl]_4$ to give $N_4Cu_3Cu(NS)Cl_4 \cdot M(NS)_{n-1}$. This species contains one five-coordinate copper(I) center, which can be tolerated in an intermediate [29]. Studies of the time dependence of Cu(NS)(s) precipitation [7 and this work] show that fragmentation of an intermediate containing $M(NS)_{n-1}$ is slow because (i) the coordination number of copper(I) is not impossibly high and (ii) strong Cu–X bonds have to be broken [7]. Loss of Cu(NS)(s) is the slowest step of complete transmetalation of halocopper(I) targets with $M(NS)_2$ reagents [6, 29].

The proposed transmetalation sequence is summarized in Scheme 3, where the N ligands on copper have been omitted, X′ are framework atoms and the numbers represent likely coordination numbers of Cu and M.

All of our established copper(II) targets contain five-coordinate metal centers [1, 5, 6]. A similar course of events to Scheme 3 that includes the transfer of one complete NS ligand from equimolar $M(NS)_n$ to target copper(II) would give one seven-coordinate copper(II) center in an active site like (O,N,Cl_2)-$Cu(NS)Cl \cdot M(NS)_{n-1}$. Copper(II) transmetalation is driven by formation of $Cu(NS)_2$ [10], but transfer of just one atom of a second NS ligand would give eight-coordinate copper(II), which is unprecedented. Loss of the copper(II) ligand N would help to relieve the steric congestion at copper, and there is evidence that polynuclear copper(II) complexes containing very strongly held amine ligands are poor transmetalation targets [37]. These considerations help to explain the rapid production of $Cu(NS)_2$ in transmetalations of labile copper(II) targets with labile $M(NS)_2$ reagents [28, 30]: there is a very marked decrease in Cu^{II}–X bond strengths as NS ligands are transferred to copper(II) to increase its coordination number above five.

The remarkable feature of transmetalation systems is, of course, the maintenance of the target molecular framework while Cu–X bonds are being replaced with M–X bonds. The details of Scheme 3 could perhaps be substantiated by time-resolved vibrational spectroscopy of the intermediates, especially in **I**/**D** systems. Scheme 3 is favored over a mechanism involving metal movement (with extant ligands) [28–30] in light of the evidence for open NS ligands in **D**·**I**.



Scheme 3.

Supplementary material

Complete structure factor information is available from author J.Z.

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