Stoichiometry and Products of Transmetalation of Dimeric Copper(I) Complexes $L_2Cu_2X_2$ (L is an *N,N,N',N'*-Tetraalkylethylenediamine; X = Cl or Br) by $M(NS)_2$ Reagents in Aprotic Solvents*

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Abstract

Dimeric copper(I) complexes $L_2Cu_2X_2$ react with 1 and 2 mol of $M(NS)_2$ reagents in aprotic solvents to give quantitative yields of products LMX_2 and (NS)M(X,X)M(NS), respectively. Here, L = *N,N,N',N'*-tetraethylethylenediamine, X = Cl or Br, M = Co, Ni, Cu and NS = *S*-methylisopropylidenehydrazinecarbodithioate. Dimers (NS)Cu(X,X)Cu(NS) are oxidatively unstable. $LCoCl_2$ crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5): $a = 7.345(1)$, $b = 11.801(1)$, $c = 17.478(2)$ Å, $\beta = 104.98(1)°$, $Z = 4$. The electronic spectra of LMX_2 and (NS)M(X,X)-M(NS) complexes are discussed.

Introduction

Stoichiometric transmetalation of polymetallic complexes with $M(NS)_n$ reagents, where M is Fe, Co, Ni, Cu or Zn, NS is a monoanionic *S*-methylhydrazinecarbodithioate Schiff base ligand and *n* is 2 or 3 (M = Fe or Co) is a quantitative source of new polymetallic molecules [2–15]††. This remarkable chemistry even applies to copper(II) centers strongly coordinated by bidentate amines [14] or bridged by a monoanionic oxopyridine ligand [6, 8].

Our previous work establishes the stoichiometries and products of transmetalation of different types of tetranuclear copper(I) and copper(II) reactants [2–13, 15, 16]. Tetranuclear copper(II) complexes are most often progressively transmetalated to give polymetallic products containing the same number of metal centers as, for example, in reactions (1), where **A** is a μ_4-oxocopper(II) complex (Fig. 1), N is *N,N*-diethylnicotinamide, DENC, X is Cl or Br

$$\mathbf{A} + x(\mathbf{B}\text{ or }\mathbf{C}) \longrightarrow (\mu_4\text{-oxo})N_4Cu_{4-x}(M(H_2O))_xX_6 + x(\mathbf{B}\text{ or }\mathbf{C}, M = Cu) \quad (1)$$

and *x* is 1, 2, 3 or 4 [2–4, 7, 10]. Such direct [2, 3] transmetalation reactions occur because reactants **B** and **C** and the respective highly stable [11] coproducts $Cu(NS)_2$ have the same stoichiometry. As a result, the final polynuclear products contain no coordinated NS ligands and are stable. However, some primary transmetalation products are unstable, for example eqn. (2) [5, 9, 11, 15].

$$(\mu_4\text{-O}, \mu\text{-O})N_3Cu_3NiX_4 + 2Ni(NS)_2 \xrightarrow{H_2O} (\mu_3\text{-O})N_3(Ni(H_2O))_3X_4 + 2Cu(NS)_2 + CuO \quad (2)$$

Different transmetalation patterns with a given transmetalator serve to distinguish between tetra-

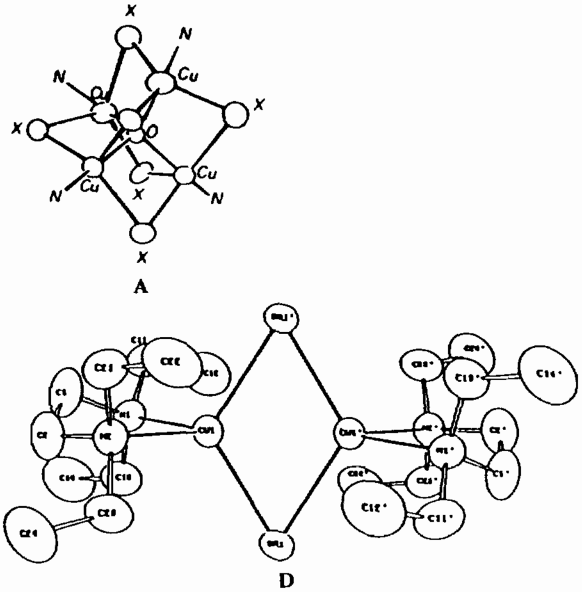

Fig. 1. Molecular structures of $(\mu_4\text{-O})[(DENC)Cu]_4X_6$ (**A**) [2] and (TEED)Cu(Br,Br)Cu(TEED) (**D**) viewed normal to the Cu(Br,Br)Cu plane [17].

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*Taken in part from ref. 1.

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††Some aspects of $Fe(NS)_3$ transmetalation chemistry are substantially different from those in refs. 9 and 11 for $Co(NS)_3$ [16].

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nuclear oxocopper(II) complexes with different core structures [12].

The primary products of monotransmetalation of tetranuclear copper(I) complexes contain coordinated NS ligands because the stoichiometries of **B** [5] and neutral tris-ligand cobalt(III) [9, 11] and -iron(III) [16] transmetalators differ from that of the highly stable, insoluble coproduct Cu(NS)(s). Gravimetric measurements of the Cu(NS)(s) coproduct establish the stoichiometries of eqns. (3)–(6). It is evident that while monotransmetalation of $[NCuX]_4$ is direct, eqns. (3) [5] and (4) [9, 11, 16], further transmetalation causes fragmentation as a

$$[NCuX]_4 + M(NS)_2 \longrightarrow N_3Cu_3M(NS)X_4 + N + Cu(NS)(s) \qquad (3)$$

$$[NCuX]_4 + Co(NS)_3 \longrightarrow N_3Cu_3Co(NS)_2X_4 + N + Cu(NS)(s) \qquad (4)$$

$$N_3Cu_3M(NS)X_4 + M(NS)_2 \xrightarrow{N} N_4M_2X_4 + 3Cu(NS)(s) \qquad (5)$$

$$N_3Cu_3Co(NS)_2X_4 + Co(NS)_3 \xrightarrow{N} N_4Co_2X_4 + Cu(NS)(s) + 2Cu(NS)_2 \qquad (6)$$

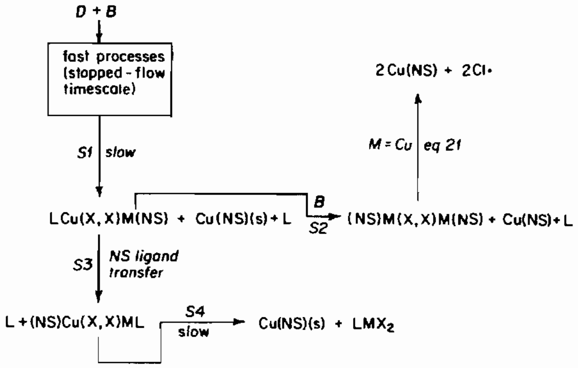
result of intramolecular NS ligand transfer to copper [5, 9, 11] and direct transmetalation is not observed. We have reported data illustrating the results of competition between intramolecular NS ligand transfer and intermolecular transmetalation which demonstrate that, because of the former phenomenon, direct transmetalation is not a general feature of the progressive replacement of tetranuclear copper(I) centers with M from $M(NS)_n$ [5, 8, 9, 11].

In this paper we report gravimetric measurements of rates of slow Cu(NS)(s) precipitation from reactions (3) and (5) (M = Ni) in nitrobenzene under dinitrogen at 21 °C. The results confirm that the rate of intramolecular NS ligand transfer increases on transmetalation of $N_3Cu_3Ni(NS)Cl_4$ obtained from eqn. (3). The data are compared with those for reactions of LCu(X,X)CuL [17–19], (**D**, L = *N,N,N',N'*-tetraethylethylenediamine, TEED) with **B** (M = Co, Ni, Cu) [20] under the same experimental conditions and are used as a guide for isolation of new transmetalation products from Scheme 1. The crystal and molecular structure of $(TEED)CoCl_2$, an ultimate product of transmetalation, is reported. The gravimetric rate measurements demonstrate that formation of discrete Cu(NS) coproducts occurs on the hour timescale at room temperature.

Experimental

Materials

Ligands ethylnicotinate (ENCA), TEED and *N,N,N',N'*-tetrapropylethylenediamine (TPED) (Aldrich or Alfa) were freshly distilled under vacuum before use. The reactants $(ENCA)_4Cu_2Cl_2$ and $L_2Cu_2X_2$ were obtained by dissolving 1 mol of CuX in solutions of 2 mol of ENCA in methylene chloride [21] or 1 mol of **L** in methylene chloride [19] or nitrobenzene [19]. All preparations were conducted under dinitrogen. Previous cryoscopic and kinetic measurements establish the formation of dimeric copper(I) complexes in methylene chloride [17, 19, 21] and nitrobenzene [17, 19]. The same experiments with ligands **L** give monomeric species in acetonitrile [18].



Scheme 1.

Methods of $M(NS)_2$ synthesis, solvent purification, product separation, characterization and other physical measurements have been described elsewhere [2–15, 20].

Transmetalation Products

All synthetic transmetalation experiments were run at room temperature in the above three solvents under dinitrogen. The production of yellowish-white Cu(NS)(s)* [8, 9, 11] from transmetalation of **D** with **B** was measured gravimetrically as a function of the molar reactant ratio $R = \mathbf{B}/\mathbf{D}$, solvent and time. Nitrobenzene was the solvent of choice for detailed time-dependence studies because of its low volatility. The system with **B** (M = Co) that shows clear evidence of two-stage Cu(NS)(s) precipitation at $R = 1$ (see below) was used to obtain monotransmetalated products as follows. When 1 mol of Cu(NS)(s) had been precipitated the product mixture was filtered under dinitrogen. The filtrate was used for cryoscopic molecular weight measurements under dinitrogen, then oxidized with excess dioxygen [17, 19] and the measurements repeated. The system was also characterized cryoscopically after treatment with excess O_2/CO_2. Alternatively, the filtrate either was added to a large excess of deoxygenated hexane in attempts to precipitate the monotransmetalated product LCu(X,X)Co(NS)

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*Crystalline Cu(NS), NS = *S*-methylisopropylidenehydrazinecarbodithioate, is yellow, and the color of the precipitate varies from white to yellow depending on its crystal content.

[5, 9] or oxidized [17, 19] with dioxygen in the absence (to give LCu(X,O,X)CoL) or presence (LCuCl(CO_3)CoClL) of excess CO_2 [19] and then added to excess hexane.

We found that the rates of Cu(NS)(s) precipitation with $R = 1$ and fixed **B** were similar in methylene chloride and nitrobenzene at room temperature (*vide infra*) but were much faster in acetonitrile, evidently because it contains monomeric copper(I) species [18]. In all cases 2 mol of Cu(NS)(s) per mol **D** ultimately were precipitated, leaving 1 mol each of LMX_2 and L in the filtrate. The preferred method of LMX_2 synthesis was to run the respective reaction at $R = 1$ in acetonitrile at room temperature, filter the solution after 2 mol of Cu(NS)(s) had precipitated (2–3 h), treat the filtrate with excess dioxygen to oxidize trace Cu(NS) [5, 8, 9], vacuum evaporate the solvent and finally isolate LMX_2 from the first of two, well-separated colored bands by gel permeation chromatography (methylene chloride eluant) [2, 3].

Experiments with $R \geqslant 2$ were carried out in the manner described above. Analytical data for isolated transmetalation products are given in Table I. Crystallization of (TEED)$CoCl_2$ from methylene chloride by ether diffusion gave blue crystals of dimensions suitable for structural characterization. We were unsuccessful in obtaining single crystals of other transmetalation products.

Crystal Data

$C_{10}H_{24}Cl_2CoN_2$, molecular weight = 302.2; monoclinic, $a = 7.345(1)$, $b = 11.801(1)$, $c = 17.478(2)$ Å, $\beta = 104.98(1)°$, $U = 1463.4(2)$ Å^3; $D_{calc} = 1.371$ g cm^{-3}, $Z = 4$, F(000) = 636. Cu Kα radiation, $\lambda = 1.5418$ Å, μ(Cu Kα) = 126.0 cm^{-1}; space group $P2_1/c$ (C^5_{2h}) by systematic absences $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

Crystallographic Measurements

A crystal of approximate dimensions $0.08 \times 0.20 \times 0.50$ mm was oriented on the Syntex $P2_1$ automated four-circle diffractometer and accurate cell parameters were derived by least-squares treatment of 15 reflections with $61° < 2\theta < 70°$ and widely separated in reciprocal space. Intensities to $2\theta = 130°$ were measured by the $\theta/2\theta$ scanning technique using variable scan speeds, the lowest being 3.0° min^{-1}. Periodic remeasurement of the 315 and 152 reflections showed no significant variation in intensities. Of the 2393 unique reflections measured, the 1758 with $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization effects and used in structure solution and refinement. An empirical absorption correction, determined from a ψ scan, was applied to the data.

Structure Analysis

The Patterson map revealed the cobalt atom: subsequent Fourier maps allowed placement of all

TABLE I. Analytical and Spectral Data for Transmetalation Products

Complex	Elemental analyses[a] (%)					M_r[b]	Band maxima[c] (nm) (ϵ (M^{-1} cm^{-1}))
	C	H	N	X	M		
$(NS)_2Ni_2Cl_2$[d]	23.2 (23.5)	3.4 (3.5)	10.8 (11.0)	13.6 (13.9)	23.1 (22.9)	280 ± 20 (285)	390(1250), 560(165)
(TEED)$NiCl_2$	39.7 (39.8)	7.7 (7.9)	9.1 (9.3)	23.6 (23.8)	19.2 (19.45)	295 ± 20 (302)	510(167), 540sh(118), 615sh(31), 857sh(33), 980(71)
(TEED)$NiBr_2$	30.4 (30.7)	6.2 (6.1)	7.2 (7.2)	40.6 (40.9)	14.1 (15.0)	395 ± 20 (391)	520(180), 620sh(65), 860sh(46), 1050(84)
(TPED)$NiCl_2$[e]	46.7 (46.9)	8.8 (8.9)	7.7 (7.8)	19.6 (19.8)	16.3 (16.4)	345 ± 20 (358)	515(176), 550sh(123), 620sh(60), 850sh(37), 900sh(43), 975(62)
(TEED)$CoCl_2$	39.6 (39.8)	7.8 (7.9)	9.1 (9.3)	24.1 (23.8)	19.2 (19.5)	290 ± 20 (302)	570(227), 640(428), 1000[f](13)
(TEED)$CoBr_2$	30.6 (30.7)	6.2 (6.1)	7.1 (7.2)	41.6 (40.9)	14.9 (15.1)	385 ± 20 (391)	570(180), 590(365), 650(592), 1015[f](65)
(TEED)$CuCl_2$	38.9 (39.1)	7.6 (7.8)	9.2 (9.1)	23.3 (23.2)	20.6 (20.7)	300 ± 20 (307)	690(204)
(TEED)$CuBr_2$	30.2 (30.3)	5.9 (6.1)	7.1 (7.1)	40.5 (40.4)	15.9 (16.1)	380 ± 20 (396)	725(217)

[a] Calculated values are given in parentheses. [b] Molecular weight measured in nitrobenzene at $(3–5) \times 10^{-2}$ m. [c] Spectra measured in CH_2Cl_2. [d] NS = *S*-methylisopropylidenehydrazinecarbodithioate (see text). [e] L = *N,N,N′,N′*-tetrapropylethylenediamine. [f] Broad band.

other non-hydrogen atoms. Refinement of positional and thermal parameters (anisotropic for non-hydrogen atoms, isotropic for hydrogen atoms) led to convergence at $R = 0.069$, $R_w = 0.078$. All crystallographic calculations were carried out on a VAX 11/780 computer. The principal programs used are given in ref. 22.

Neutral atom scattering factors were those of Cromer and Waber [23] for non-hydrogen atoms and those of Stewart *et al.* [24] for hydrogen; anomalous dispersion corrections were made [25]. In the least-squares calculations $\Sigma w\Delta^2$ $(\Delta = |F_o| - |F_c|)$ was minimized with weights w assigned $w^{1/2} = 1$ for $|F_o| \leqslant 27$ and $w^{1/2} = 27/|F_o|$ for $|F_o| > 27$. A final difference Fourier map revealed no unexpected parameters.

Results and Discussion

Stoichiometry and Products. General Observations

The monoanionic *S*-methylisopropylidenehydrazinecarbodithioate ligand NS^- in $M(NS)_2$ complexes **B** [2] and $Co(NS)_3$ [9, 11] gives insoluble coproduct Cu(NS)(s) on transmetalation of tetranuclear $[NCuX]_4$ complexes with these reagents, eqns. (3)–(6). This insolubility makes the reactions quantitative and is an excellent means of gravimetric determination of transmetalation stoichiometries [5, 9, 11].

The other final products of $[NCuX]_4$ transmetalation depend on the molar reactant ratio $R = (\mathbf{B}$ or $Co(NS)_3)/[NCuX]_4$. Reactions (3) [5] and (4) [9, 11, 16] occur when $R = 1$; products $N_3Cu_3Co(NS)_2X_4$ (eqn. (4)) are mixed-valence species because of prior electron transfer from copper(I) to cobalt(III) [9, 11]. The transmetalated products are isolatable, tetranuclear molecules that are oxidized by dioxygen, eqns. (7) and (8), respectively, to give tetranuclear oxocopper(II) products and the disulfide N_2S_2 [5, 9, 11].

$$N_3Cu_3M(NS)X_4 + O_2 \longrightarrow N_3Cu_3MX_4O_2 + \tfrac{1}{2}N_2S_2 \qquad (7)$$

$$N_3Cu_3Co(NS)_2X_4 + O_2 \longrightarrow N_3Cu_3CoX_4O_2 + N_2S_2 \qquad (8)$$

However, when $R \geqslant 2$ we obtained dioxygen-stable, dimeric products $N_4M_2X_4$ with either **B** or $Co(NS)_3$ as transmetalators, eqns. (5) and (6), respectively. Dimeric $N_4M_2X_4$ also were obtained when the first products of eqns. (3) and (4) were reacted with excesses of **B** or of $Co(NS)_3$, respectively. We concluded that the copper centers of the products from eqns. (3) and (4) are transmetalated by 1 mol of **B** or $Co(NS)_3$, but that NS ligand transfer from M(NS) to copper(I), eqn. (9) [5], or from $Co(NS)_2$ to copper(II), eqn. (10) [9, 11], is faster than the transmetalation of remaining copper by **B** or $Co(NS)_3$ and much more rapid than in the monotransmetalated products of eqns. (3) and (4) [5, 9, 11]. Because of this unfavorable competition, product

$$N_3Cu_3M(NS)X_4 + \mathbf{B} \longrightarrow N_2Cu_2(M(NS))_2X_4 + Cu(NS)(s) \xrightarrow{N} N_4M_2X_4 + 2Cu(NS)(s) \qquad (9)$$

$$N_3Cu_3Co(NS)_2X_4 + Co(NS)_3 \longrightarrow N_2Cu_2(Co(NS)_2)_2X_4 + Cu(NS)(s) \xrightarrow{N} N_4Co_2X_4 + 2Cu(NS)_2 \qquad (10)$$

fragmentation on progressive transmetalation is a common feature of tetranuclear copper(I) systems [5, 8, 9, 11]*.

Copper(I) dimers **D** are prevented from forming tetramers by their N-alkyl substituents and by a preference for four-coordinate copper(I) [17–19]**. As such, **D** may formally be regarded as halves of tetramers $[NCuX]_4$. Equation (11) is the analog of eqn. (3) and eqns. (12) and (13) are, in principle, competitive processes

$$\mathbf{D} + \mathbf{B} \longrightarrow LCuM(NS)X_2 + Cu(NS)(s) + L \qquad (11)$$

$$LCuM(NS)X_2 \longrightarrow LMX_2 + Cu(NS)(s) \qquad (12)$$

$$LCuM(NS)X_2 + \mathbf{B} \longrightarrow (M(NS))_2X_2 + Cu(NS)(s) + L \qquad (13)$$

which both produce 1 additional mol of Cu(NS)(s) but which can be distinguished by measuring the rate of Cu(NS) formation and by the identity of the other products. In particular, $(M(NS))_2X_2$, if formed, might react with dioxygen to give dimeric products $L_2M_2X_2O$, eqn. (14) [5, 9, 11].

$$(M(NS))_2X_2 + \tfrac{1}{2}O_2 \xrightarrow{L} L_2M_2X_2O + N_2S_2 \qquad (14)$$

The reactions of polynuclear copper(I) complexes with $M(NS)_n$ reagents are multistep processes, Scheme 1. In this paper we establish that discrete Cu(NS) coproduct formation is a very slow process.

Gravimetric Measurements

The time-dependence of Cu(NS)(s) precipitation as a result of transmetalation of $[NCuCl]_4$ (N = DENC) and **D** (L = TEED; X = Cl or Br), all 2.1 X 10^{-2} M, by **B** were made at $R = \mathbf{B}/([NCuCl]_4$ or $\mathbf{D}) = 1$ or 3 in nitrobenzene at 21 °C under dinitrogen.

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*Intramolecular NS ligand transfer after monotransmetalation of L_4Cu_4 with $M(NS)_2$ seems particularly favored by bridging of pairs of copper(I) centers by L = 6-methyl-2-oxo-pyridinate: see eqns. (4) and (5) of ref. 8.

**ENCA forms tetranuclear complexes $[(ENCA)CuX]_4$ and $[(ENCA)_2CuX]_4$ with copper(I) halides CuX if the solvent is nitrobenzene under comparable experimental conditions [21].

Rates of Cu(NS)(s) Precipitation from Reactions (3) and (5) (M = Ni)

Figure 2 shows the time-dependence of Cu(NS)(s) precipitation resulting from transmetalation of $[NCuCl]_4$ (N = DENC) by **B** (M = Ni). The data indicate that only 1 mol of Cu(NS)(s) is precipitated with $R = 1$ and confirm that product $N_3Cu_3Ni(NS)Cl_4$, eqn. (3), has no significant tendency to transfer its coordinated NS from nickel to copper(I) to give additional Cu(NS)(s) and trimeric products $N_nCu_2NiCl_4$. At $R = 2$ [5] and 3 we find that 4 mol of Cu(NS)(s) are produced on reaction of $[NCuCl]_4$ with **B** (M = Ni) [5] at a higher rate than at $R = 1$. The processes that lead to production of additional Cu(NS)(s) are (i) exchange of Ni for Cu in $N_3Cu_3Ni(NS)Cl_4$; (ii) NS ligand transfer from Ni(NS) to copper(I); and (iii) fragmentation resulting in 2 mol of Cu(NS)(s) and one mol of $N_4Ni_2Cl_4$, eqn. (9). The initial rates at $R = 1$ (0.18 mol h^{-1}), 3 (1.8 mol h^{-1}) and 5 (4.3 mol h^{-1}) are approximated by rate laws (15) (at $R = 1$) and (16), respectively, where

$$d[Cu(NS)(s)]/dt = k_3[N_4Cu_4Cl_4]\,[\mathbf{B}] \qquad (15)$$

$$d[Cu(NS)(s)]/dt = 4k_3[N_4Cu_4Cl_4]\,[\mathbf{B}] \qquad (16)$$

$k_3 = 1.4 \times 10^{-2}$ M^{-1} s^{-1} is the rate constant for rate-determining Cu(NS)(s) production in reaction (3). This indicates that 1 mol of **B** reacts much more rapidly with $N_3Cu_3Ni(NS)Cl_4$ than with $N_4Cu_4Cl_4$ and that NS ligand transfer and concomitant Cu(NS)(s) production are much faster in $N_nCu_2(Ni(NS))_2Cl_4$ than in $N_3Cu_3Ni(NS)Cl_4$. Gross core structural differences between the latter two species were suggested previously from qualitative rate comparisons and product analyses [5].

Rates of Cu(NS)(s) Precipitation from Reactions (11)–(13) of D (L = TEED, X = Cl or Br) with B (M = Co, Ni, Cu)

Results for the title reactions at $R = \mathbf{B}/\mathbf{D} = 1$ or 3 at fixed $[\mathbf{D}] = 2.1 \times 10^{-2}$ M (Figs. 3 and 4, respectively) and product analysis (see below) are consistent with the reactions shown in Scheme 1. At $R = 1$, Fig. 3, we observe that the initial rate of Cu(NS)(s) precipitation in slow step S1 of Scheme 1 decreases for M = Co > Cu > Ni in **B**. The occurrence of Cu(NS)(s) precipitation as a result of intramolecular NS ligand transfer reaction S3 is clear for M = Co but much less well-defined for M = Cu

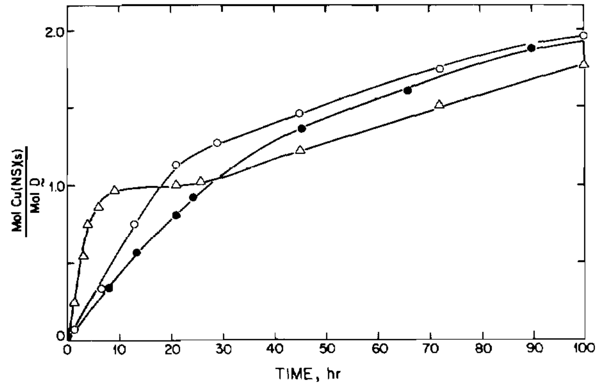

Fig. 3. Time-dependence of Cu(NS)(s) precipitation in the reaction of **D** (L = TEED, X = Cl), 2.1×10^{-2} M, with **B**, M = Ni, ●; M = Cu, ○; M = Co, △ (all 2.1×10^{-2} M) in nitrobenzene under dinitrogen at 21 °C.

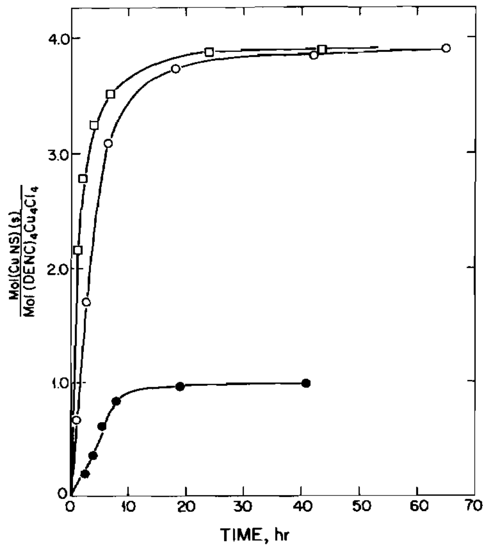

Fig. 2. Time-dependence of Cu(NS)(s) precipitation in the reaction of $[(DENC)CuCl]_4$, 2.1×10^{-2} M, with **B** (M = Ni) in nitrobenzene at 21 °C under dinitrogen with $R = [\mathbf{B}]/[(DENC)CuCl]_4 = 1.0$, ●; 3.0, ○; 5.0, □.

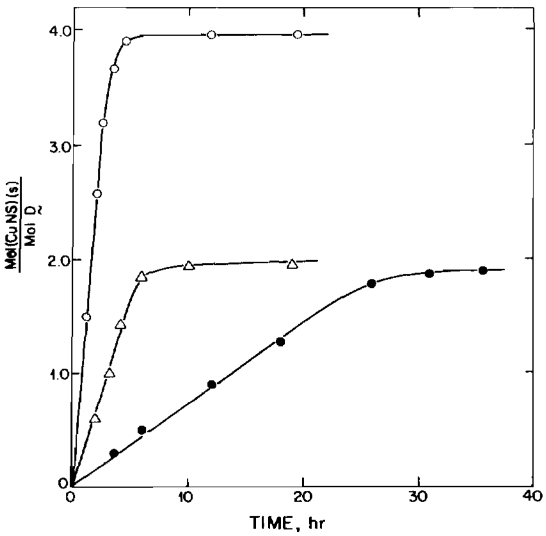

Fig. 4. Time-dependence of Cu(NS)(s) precipitation in the reaction of **D** (L = TEED, X = Cl), 2.1×10^{-3} M, with **B**, M = Ni, ●; M = Co, △; M = Cu, ○ (all 6.3×10^{-2} M) in nitrobenzene under dinitrogen at 21 °C.

and Ni. The results indicate that pure products of monotransmetalation reaction (11) are best isolated with M = Co at $R = 1$ after 10–15 h reaction (see below). Plots of $\log(\mathrm{Cu}_\infty - \mathrm{Cu}_t)$ *versus* time, where Cu_t is the weight of Cu(NS)(s) precipitated at time t, were linear for the second reaction stages and gave first-order rate constants 2.5, 4.8, 9.8×10^{-2} h^{-1} for M = Co, Cu, Ni in reaction (12), respectively, in nitrobenzene at 21 °C.

Interpretation

We know that the stability of transmetalators **B** decreases in the order M = Cu ≫ Ni ≫ Co [11] and would anticipate the same stability order for the M(NS) centers in the products of steps S1, Scheme 1. A narrow range of rate constants in an unexpected order suggests that step S3 is considerably faster than step S4 in Scheme 1. Step S4 requires breaking Cu–X bonds in (NS)Cu(X,X)ML from step S3 and should be affected by changing X. Confirming the assignment of rate-determining step S4, we found that changing X from Cl to Br in $(\mathrm{TEED})_2\mathrm{Cu}_2\mathrm{X}_2$ greatly reduced the rate of Cu(NS)(s) precipitation (Fig. 5): only 1 mol of Cu(NS)(s) was precipitated at 210 h at R = **B** (M = Ni)/$(\mathrm{TEED})_2\mathrm{Cu}_2\mathrm{Br}_2$ = 1 and there was no indication of a second reaction stage (*cf.* Fig. 3). This result also indicates that breaking of Cu–X bonds is required in step S1.

An important point is that rates of Cu(NS)(s) production due to NS ligand transfer are measurable in LCu(Cl,Cl)M(NS) but not in $\mathrm{N_3Cu_3M(NS)X_4}$ [5]. We feel that the cubane structures of the latter are responsible for very low rates. In our view the M centers in $\mathrm{N_3Cu_3M(NS)X_4}$ complexes are more firmly and deeply located in the tetrahedral holes of the $\mathrm{X_4}$ core [3,21] than are copper(I) because of their higher nuclear charge. As a result, the X atoms obstruct NS ligand transfer to copper(I) and the transfer distance is relatively large. By contrast, NS transfer step S3 in LCu(Cl,Cl)M(NS) is much faster, despite the need to displace bidentate L to maintain four-coordinate copper(I). The simplest explanation is geometrical: the Cu(Cl,Cl)M system is planar [17, 18] and so the NS ligand transfer distance is shorter than in $\mathrm{N_3Cu_3M(NS)Cl_4}$ complexes.

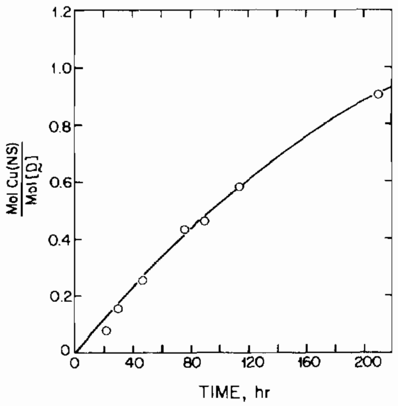

Fig. 5. Time-dependence of Cu(NS)(s) precipitation in the reaction of **D** (L = TEED, X = Br), 2.1×10^{-2} M, with **B** (M = Ni), 4.2×10^{-2} M, in nitrobenzene under dinitrogen at 21 °C.

Rates of Cu(NS)(s) Precipitation with Excess B

The results in Fig. 4 were obtained at $R = 3$ and $[\mathbf{B}] = 6.3 \times 10^{-2}$ M. The data for M = Ni show that 2 mol of Cu(NS)(s) are produced at one characteristic rate and that step S4 is complete in 25 h in nitrobenzene at 21 °C. Since step S1 consumes 1 mol of **B**, this must mean (i) that step S2, transmetalation of LCu(Cl,Cl)M(NS) from step S1 by **B**, is much faster than competitive reaction S3 and (ii) that step S1 is the rate-determining step for Cu(NS)(s) precipitation. Reactions S1 and S2 lead to the isolation of pure products at $R = 2$ (see below).

The initial rates in Figs. 3 and 4 are consistent with rate laws (17) and (18) for M = Co and Ni at

$$d[\mathrm{Cu(NS)(s)}]/dt = k_{11}[\mathbf{D}]^m \tag{17}$$

$$d[\mathrm{Cu(NS)(s)}]/dt = 2k_{11}[\mathbf{D}]^m \tag{18}$$

$R = 1$, respectively. Although [**D**] was not varied in these experiments we anticipate that $m = 1$ from detailed kinetic studies with excess **B** (M = Ni) [26]. The significant point is that eqns. (17) and (18) are independent of [**B**] (M = Co or Ni), which indicates marked reactant preassociation at $[\mathbf{D}] = 2.1 \times 10^{-2}$ M and $[\mathbf{B}] = 2.1–6.3 \times 10^{-2}$ M in nitrobenzene at 21 °C (see below).

Reaction of D with B (M = Cu)

Reaction of **D** with **B** (M = Cu) is remarkably different in that it produces 4 mol Cu(NS)(s)/mol **D** at $R = 2$ and 3 (Fig. 4).

Comparison of the initial rates and Cu(NS)(s) yields for **B** (M = Cu) in Figs. 3 and 4 suggests rate laws (19) and (20) at $R = 1$ and $R = 3$, respectively.

$$d[\mathrm{Cu(NS)(s)}]/dt = k_{11}[\mathbf{D}]^m[\mathbf{B}]^n \tag{19}$$

$$d[\mathrm{Cu(NS)(s)}]/dt = 4k_{11}[\mathbf{D}]^m[\mathbf{B}]^n \tag{20}$$

If we assume that step S1 is rate-determining then $n \approx 1.25$* from the data shown. The dependence on [**B**] suggests that **B** (M = Cu) forms weaker complexes with **D** than do **B** (M = Co and Ni), *cf.* eqns. (17) and (18), under the same experimental conditions.

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*Although the apparent rate law order $n \approx 1.25$ is approximate, it does suggest that **D** is capable of associating with more than one mol of **B** (M = Cu) under the conditions of these experiments ($[\mathrm{D}] = 2.1 \times 10^{-2}$ M, $[\mathrm{B}] = 2.1–6.3 \times 10^{-2}$ M).

The product of step S2, Scheme 1, must decompose via eqn. (21) since NS^- is not oxidized to the

$$(NS)Cu^{II}(Cl,Cl)Cu^{II}(NS) \longrightarrow 2Cu(NS)(s) + 2Cl^{\cdot} \quad (21)$$

disulfide N_2S_2 and thus Cl^- is the only source of electrons in this system. An extremely large driving force must exist for formation of Cu(NS)(s) from the reactant of eqn. (21), since Cl^- is not a strong reductant. We passed the effluent N_2 through aqueous potassium iodide to identify Cl_2 from chlorine atom combination but none was found. We presume that chlorine atoms react with TEED to give unidentified chlorinated products.

Comparison of the data in Figs. 3 and 4 indicates that electron-transfer reaction (21) occurs only in the product of step S2 (M = Cu) and not in the corresponding monotransmetalated product from reaction (11); it also does not occur in eqn. (9) with up to a four-fold excess of **B** (M = Cu) [5].

Our summary of the results to this point refers to Scheme 1 and is as follows: (i) the rate-determining step for slow production of discrete Cu(NS)(s) from the reactions of **D** with **B** is step S1 and the relative rates of the processes shown are $S1 < S2 > S3 > S4$; (ii) step S2 with M = Cu and X = Cl gives (NS)Cu(Cl,Cl)Cu(NS) which spontaneously decomposes to give 2 mol of Cu(NS)(s) and chlorine atoms; and (iii) Cu(NS)(s) production in these systems is much too slow to be involved in events observed on the stopped-flow timescale [26].

Isolation and Characterization of LCu(Cl,Cl)Co(NS) from Reaction (11)

On the basis of the data in Fig. 3, we attempted to isolate the blue–green title product from reaction of **D** with **B** (M = Co) at $R = 1$ (reaction (11)) under dinitrogen in nitrobenzene at 21 °C after 12 h. Although we succeeded in isolating and characterizing air-sensitive complexes $N_3Cu_3Co(NS)X_4$ (eqn. (3)) [5], $N_3Cu_3Co(NS)_2X_4$ (eqn. (4)) [9, 11] and $N_mM_2Co(NS)_2X_4$ [9, 11] and their oxidized products in previous work, we found that solid (TEED)Cu(Cl,Cl)Co(NS) is exceedingly air sensitive and that the solid products of its oxidation by dioxygen are extremely hygroscopic even if reaction (14) is run in the presence of excess CO_2 [19]. We were not satisfied with analytical data from many careful attempts to characterize and crystallize solid products. However, cryoscopic measurements on product filtrates in nitrobenzene are consistent with the presence of the products in eqns. (11), (22) and (23): M_r found (calc.): 330 ± 20 (350); 380 ± 20 (366); 420 ± 20 (410), respectively.

$$(NS)Co(Cl,Cl)CuL + \tfrac{1}{2}O_2 \xrightarrow{L} L_2CoCuCl_2O + \tfrac{1}{2}N_2S_2 \quad (22)$$

$$(NS)Co(Cl,Cl)CuL + \tfrac{1}{2}O_2 + CO_2 \xrightarrow{L} L_2CoCuCl_2(CO_3) + \tfrac{1}{2}N_2S_2 \quad (23)$$

Attempted crystallization of the first product of eqn. (22) from methylene chloride/diethyl ether gave crystalline $(TEED)CuCl(OH)_2ClCu(TEED)$ as one of the disproportionation products, which shows clear evidence for bridging OH (3180 cm^{-1}) in its IR spectrum. Examination of the electronic spectrum of (TEED)Cu(Cl,Cl)Co(NS) before and after treatment with O_2 in nitrobenzene showed that absorption maxima at 1000, 640 and 570 nm due to four- or five-coordinate cobalt(II) [27] were still present; cobalt(II) also is not oxidized in eqns. (7) [5] or (8) [9, 11]. Increased absorption centered near 700 nm is due to oxidation of copper(I) to copper(II) [19]. Species LCu(X,X)Co(NS) are thus 2-electron reducing agents; the products of eqns. (22) and (23) are brown, dimeric but extremely water-sensitive species.

Isolation and Characterization of (NS)Ni(Cl,Cl)-Ni(NS) from Reaction (13)

To demonstrate that step S2 is faster than step S3 (Scheme 1) we isolated the brown title product from reaction of **D** (L = TEED; X = Cl) with **B** (M = Ni) at $R = 2$ in nitrobenzene under dinitrogen. Analytical and spectral data are given in Table I. Cryoscopic measurements on the filtrate after Schlenk removal of 2 mol of Cu(NS)(s) indicated the presence of 2 mol of L and one mol of dimeric (NS)Ni(Cl,Cl)Ni(NS): M_r found 280 ± 20; calc. 285. This product was isolated by addition of the filtrate to excess hexane. We found that the title complex is not oxidized at a significant rate by dioxygen, in sharp contrast to the results of the previous section; this is presumably because of the unavailability of the Ni(III) state in this ligand system, which might otherwise result from Ni(II) oxidation by O_2 [9, 11].

Brown dimeric species (NS)Ni(Cl,Cl)Ni(NS) is the first reported example of a potential mono-NS-metal transmetalating agent to be obtained by transmetalation. Its electronic spectrum lacks absorption beyond 700 nm and contains maxima at 390 (ϵ 1250) and 560 nm (165), consistent with *cis*-square-planar geometry at nickel [27]. Square-planar geometry evidently is favored in $Ni(NS)_mX_n$ complexes ($m = 2$ [20] or 1; $n = 0$ or 1).

The results of the previous sections indicate that it would be difficult and futile to attempt isolation of the corresponding products of step S2, Scheme 1, with M = Co and Cu, respectively.

Properties of LMX_2 Products

Monomeric complexes $(TEED)CuX_2$ were first obtained by Wasson *et al.* [28] as the earliest products of the reaction of CuX_2 with L in ethanol or methanol. Belford *et al.* [29] confirmed that distorted square-planar $LCuX_2$ have little affinity for L and the structural work of Hodgson *et al.* [30] shows that steric interactions allow the formation of only weak, asymmetrically-bridged dimers even with L = *N,N,N',N'*-tetramethylethylenediamine. Reactions of CuX_2 with L in hydroxylic solvents always give LMX_2 as one of many different products [28–30].

By contrast, transmetalation of **D** with **B** at *R* = 1 is an excellent means of obtaining just LMX_2, especially in acetonitrile. We obtained quantitative yields of LMX_2 (Table I) and confirmed that the cobalt and nickel complexes cannot be obtained from reaction of MX_2 with L in methylene chloride or nitrobenzene.

Crystal and Molecular Structure of (TEED)CoCl$_2$

Crystalline (TEED)$CoCl_2$ consists of discrete monomeric, four-coordinate, well-separated molecules. A view of the molecular structure is shown in Fig. 6, together with the atom numbering scheme. Fractional atomic coordinates for the non-hydrogen atoms and intramolecular distances and angles are given in Tables II and III.

The coordination about cobalt is nearly tetrahedral, with the angle between the Cl–Co–Cl and the N–Co–N planes being 86.6°. The distortion is due to the 86.7(2)° bite of the bidentate TEED ligand. The Co–N distances in (TEED)$CoCl_2$, mean 2.123 Å, are very similar to Co–N lengths in $[Co(NCS)(Me_2NCH_2CH(Me)N(CH_2CH_2NMe_2)_2)]ClO_4$, mean 2.12 Å [31]. However, the Co–Cl distances (2.233(2) and 2.182(2) Å) are significantly different, though both refer to terminal chlorine atoms. The longer bond is very similar to the terminal Cu–Cl unit in dimeric ((tetramethylethylenediamine)$CuCl_2)_2$ [30a, c]. There is no obvious steric or electronic factor to explain the difference in the two Co–Cl lengths since neither chlorine atom suffers from close contacts. The smallest intracomplex Cl...C and Cl...H separations are 3.54 and 2.83 Å, respectively, approximately the sum of van der Waals radii; the smallest Cl...H intercomplex separation is 3.08 Å.

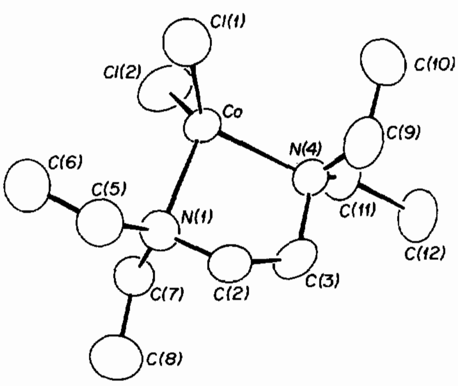

Fig. 6. View of the Co(TEED)Cl_2 monomer with the crystallographic numbering scheme. Hydrogen atoms have been omitted for clarity.

TABLE II. Fractional Atomic Coordinates (×10^4) for the Non-hydrogen Atoms[a]

Atom	*x/a*	*y/b*	*z/c*
Co	3422(1)	220(1)	1949(1)
Cl(1)	6488(3)	284(2)	1998(1)
Cl(2)	2058(3)	−1418(2)	1629(1)
N(1)	2113(8)	1633(4)	1279(3)
C(2)	2304(11)	2487(6)	1916(4)
C(3)	1693(11)	2048(6)	2604(4)
N(4)	2749(8)	999(5)	2938(3)
C(5)	3131(11)	2024(6)	692(4)
C(6)	3148(12)	1187(8)	48(5)
C(7)	101(10)	1346(6)	900(4)
C(8)	−1164(13)	2325(9)	539(6)
C(9)	4430(10)	1302(8)	3558(4)
C(10)	5553(12)	279(10)	3944(5)
C(11)	1443(10)	241(7)	3234(4)
C(12)	787(11)	687(8)	3928(4)

[a] e.s.d.s. given in parentheses.

Bond lengths and angles in the five-membered TEED rings are similar to those found in other ethylenediamine complexes [29, 30]. Because the space group in which the molecule crystallizes has a center of symmetry, half of the rings are λ and half are δ. The magnitude of this helicity is given by the N–C–C–N dihedral angle, 56.6(4)°.

The four ethyl groups adopt conformations which place the methyl groups as far from one another as possible. The steric bulk of these groups prevents the dimerization of this $LMCl_2$ complex as it does with M = Cu [30b].

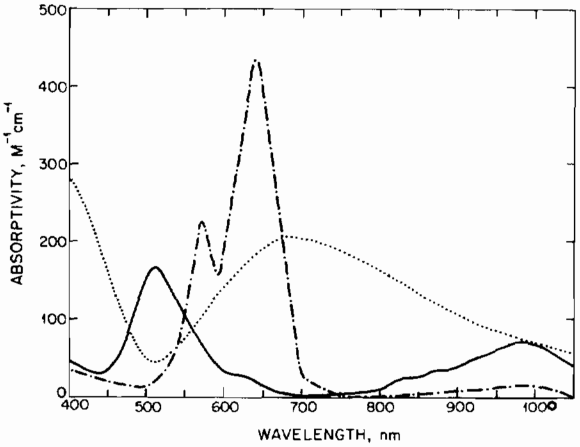

Fig. 7. Electronic spectra of LMX_2 complexes (L = TEED, X = Cl, M = Co, – · –; M = Ni, ——; M = Cu, ······ in methylene chloride at 25 °C.

TABLE III. Interatomic Bond Lengths (A) and Valency Angles (°)[a]

Bond lengths			
Coordination sphere			
Co–Cl(1)	2.233(2)	Co–N(1)	2.121(5)
Co–Cl(2)	2.182(2)	Co–N(4)	2.125(6)
Ligand			
N(1)–C(2)	1.482(9)	N(4)–C(11)	1.497(9)
N(1)–C(5)	1.490(10)	C(5)–C(6)	1.499(12)
N(1)–C(7)	1.494(9)	C(7)–C(8)	1.514(12)
C(2)–C(3)	1.481(11)	C(9)–C(10)	1.519(14)
C(3)–N(4)	1.498(9)	C(11)–C(12)	1.510(10)
N(4)–C(9)	1.460(9)		
Valency angles			
Coordination sphere			
Cl(1)–Co–Cl(2)	115.6(1)	Cl(2)–Co–N(1)	116.2(2)
Cl(1)–Co–N(1)	107.6(2)	Cl(2)–Co–N(4)	113.8(2)
Cl(1)–Co–N(4)	113.5(2)	N(1)–Co–N(4)	86.7(2)
Ligand			
Co–N(1)–C(2)	100.2(4)	Co–N(4)–C(9)	112.3(4)
Co–N(1)–C(5)	112.8(4)	Co–N(4)–C(11)	109.1(4)
Co–N(1)–C(7)	108.8(4)	C(3)–N(4)–C(9)	109.9(6)
C(2)–N(1)–C(5)	109.9(5)	C(3)–N(4)–C(11)	108.3(5)
C(2)–N(1)–C(7)	112.2(6)	C(9)–N(4)–C(11)	112.6(5)
C(5)–N(1)–C(7)	112.3(5)	N(1)–C(5)–C(6)	114.6(6)
N(1)–C(2)–C(3)	112.5(6)	N(1)–C(7)–C(8)	116.2(6)
C(2)–C(3)–N(4)	111.7(6)	N(4)–C(9)–C(10)	113.1(7)
Co–N(4)–C(3)	104.3(4)	N(4)–C(11)–C(12)	115.8(6)

[a] e.s.d.s. given in parentheses.

Electronic Spectra of LMX_2 Complexes

Electronic spectral data for (TEED)MX_2 (M = Co, Ni, Cu; X = Cl or Br) and (TPED)$NiCl_2$ complexes in methylene chloride are collected in Table I and representative data are shown in Fig. 7. Similar Nujol mull and methylene chloride solution spectra indicate retention of configuration in solution and are consistent with the distorted tetrahedral geometries for M = Co and Ni [27] established by our X-ray crystallographic study of (TEED)$CoCl_2$. The spectra in methylene chloride are unaffected by addition of excess L, which confirms the general low stability of L_2MX_2 complexes [28–30].

Earliest Reaction Events

The kinetics of the earliest events of reaction of **D** with **B** are described in the following paper [26].

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom parameters and calculated and observed structure factors for $LCoCl_2$ are available from the authors on request.

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