Stoichiometry, Products and Kinetics of Monotransmetalation and Complexation of Dimeric Complexes $[N_2CuCl_2]_2$ and $[N_2NiCl_2]_2$ (N is *N,N*-diethylnicotinamide) with $M(NS)_2$ Reagents in Nitrobenzene

MOHAMED A. EL-SAYED*
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria (Egypt)
and GEOFFREY DAVIES*
Department of Chemistry, Northeastern University, Boston, MA 02115 (U.S.A.)

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Abstract

This study reports the stoichiometry, products and kinetics of rapid monotransmetalation of the dimeric $(\mu,\mu$-dichloro)dichlorotetrakis-(*N,N*-diethylnicotinamide)dicopper(II) complex $N_2ClCu(Cl,Cl)CuClN_2$ (I) with $M(NS)_2$ reagents, where M is Co, Ni and Zn and NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base ligand in transmetalators A and B. The isolated transmetalation products are the heterometallic dimers $N_2ClCu(Cl,Cl)MClN(H_2O)\cdot H_2O$. The stoichiometry and kinetics of complexation of I by A (M = Cu) and of the reaction of the corresponding nickel(II) dimer $N_2ClNi(Cl,Cl)NiClN_2$ (II) with transmetalator A (M = Co) are also described. The results are compared with those for monotransmetalation of other halocopper targets with $M(NS)_2$ transmetalators.

Introduction

Copper(I) and copper(II) halides form a wide variety of mononuclear and polynuclear complexes with amines in aprotic solvents [1–4]. Examples for copper(I) include py_3CuCl [5], $[py_2CuCl]_2$ [6], $[pyCuCl]_4$ [7] and $[py_2CuCl]_4$ [6], where py is pyridine. The proportions of these pyridine–copper(I) species critically depend on the molar ratio [py]/[CuCl] and the total pyridine and copper(I) concentrations [2, 5–7]. By contrast, for copper(II) we only observe mononuclear py_2CuCl_2 [8].

Changing the pyridine ligand to N = *N,N*-diethylnicotinamide(N) has three major effects. First, the solubilities of halocopper(I)– and halocopper(II)–N complexes in aprotic solvents are generally higher than those with pyridine, which benefits their use in synthesis. Second, copper(I) chemistry is now restricted to $[NCuCl]_4$, which has very low affinity for additional N [6]. Third, copper(II) halides CuX_2 are now able to form tetranuclear $[NCuX_2]_4$ [3] in addition to the corresponding mono-, di- and trinuclear complexes N_3CuX_2 [9], $[N_2CuX_2]_2$ [9] and $[N_2CuCl_2]_3$ [10], respectively.

A recent study [9] demonstrates the very interesting behavior of CuX_2–N systems and the relationship between the various molecular forms. One observation was that dinuclear $[N_2CuCl_2]_2$ (I) is bridged by the O,(ring)N system of N in the solid state but by chloride in solution, while the corresponding bromocomplex is always bridged by bromide. EPR and other measurements led to assignment of the structures of Scheme 1 to this system. Another finding was that very high N concentrations are required to shift equilibria (1) and (2) [9]. This means that CuX_2 solutions at molar ratio $[N]/[CuX_2] = 2$ do not disproportionate in eqns. such as (3), a property we will take advantage of in this study.

$$\underset{\text{I}}{[N_2CuCl_2]_2} + 2N \rightleftarrows \underset{\text{I}_m}{2N_3CuCl_2} \qquad (1)$$

$$[N_2CuBr_2]_2 + 2N \rightleftarrows 2N_3CuBr_2 \qquad (2)$$

$$4[N_2CuX_2]_2 \rightleftarrows [NCuX_2]_4 + 4N_3CuX_2 \qquad (3)$$

Transmetalation is the replacement of the metals in a polynuclear target with other metals from reagents called transmetalators. It is a simple means of systematic synthesis of large families of related heteropolymetallic molecules [3, 11, 12]**. Equation (4) is an example of a series of transmetalation reactions, where M is Co, Ni or Zn, NS is mono-

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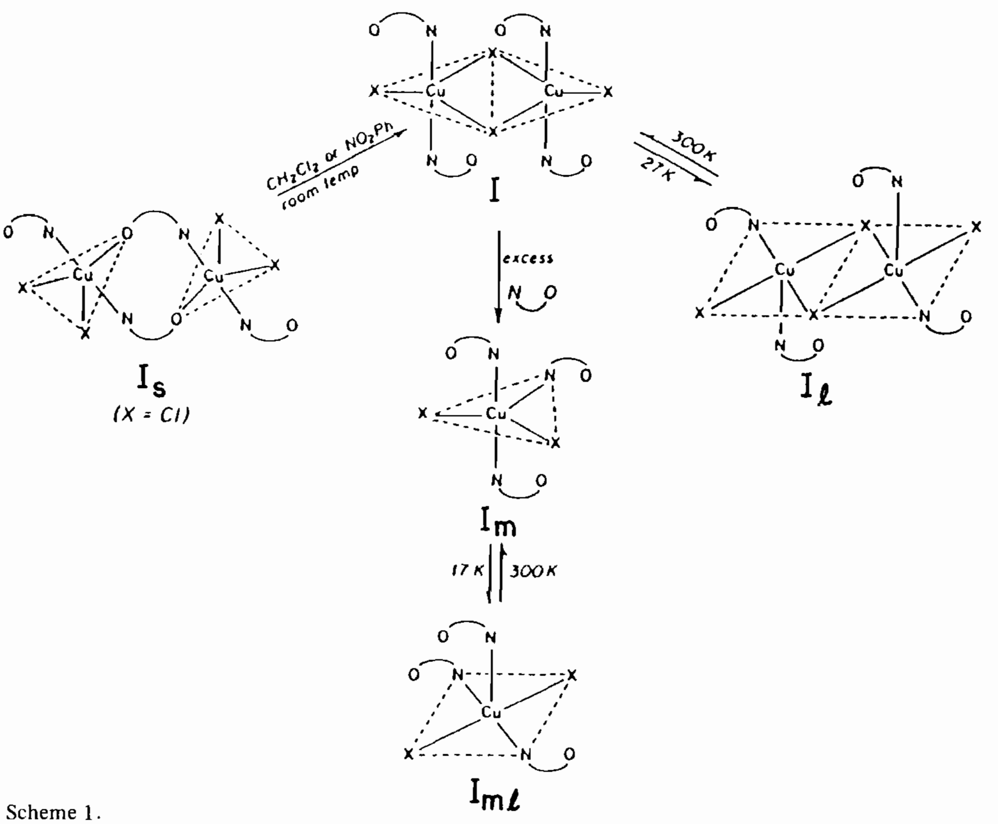
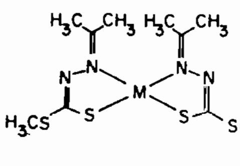
*Authors to whom correspondence should be addressed.

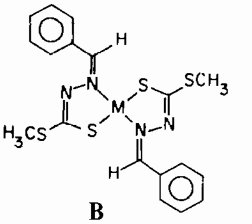
**The transmetalation phenomenon is not restricted to copper targets [11].



Scheme 1.



A



B

$$N_4Cu_4Cl_6O + xM(NS)_2 \longrightarrow N_4Cu_{4-x}M_xCl_6O + xCu(NS)_2 \quad (4)$$

anionic isopropylidenehydrazinecarbodithioate in transmetalators **A** and x is 1–4 [12]*. Such stoichiometric transmetalations depend on a large driving force (provided in this case by formation of highly stable coproduct $Cu(NS)_2$ [3]), which makes each copper(II) replacement step discrete [12, 13]. Other desirable features are the involvement of only one target form (that is, the occurrence of no equilibria like (1)–(3)) and the formation of discrete heterotetranuclear products rather than equilibrium mixtures. Reactions (4) also proceed with reasonable rates under mild conditions [14]. Lastly, we benefit from easy product separation [3, 11–14]. Most of these requirements are met by a range of polynuclear copper(I) and copper(II) targets in reactions with a number of $M(NS)_n$ transmetalators [11].

Having established the major patterns of transmetalation of common polynuclear copper targets [11], we have turned our attention to establishing the detailed structural-mechanistic features of practical transmetalation systems through direct kinetic measurements.

Our studies to date have been of monotransmetalation systems (for example, $x = 1$ in eqn. (4)) [14–19]. The targets all have at least one kind of nucleophilic site (most often halide, X) to which M of $M(NS)_2$ in **A** or **B** may attach in an acid–base interaction to form precursors **P**. This interaction and an additional one with carbothioate S of $M(NS)_2$ is sometimes strong enough to result in simple first-order transmetalation rate laws [14b, 17–19]. Weaker precursor interaction in precursors P_n is signalled by third- and second-order rate laws that are most often associated with transmetalation **A** (M = Ni) and **B**, respectively [14–19]. The existence of particular precursor interactions is necessary to explain selective replacement of particular elements in heteropolymetallic targets [18, 19].

We have developed an analytical procedure to account for precursor formation that reduces every

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*Equation (4) only gives tetranuclear transmetalation products with transmetalators **A** (M = Co or Zn) when $x \leq 2$.

higher-order rate law to first-order so that the rate-determining transmetalation step can be assigned [14b, 16, 17]. The primary assignment criteria are the measured (for experimental first-order) and derived (for higher-order system) entropies of activation. On this basis we concluded that formation of discrete transmetalation products is the most common rate-determining step in the replacement of copper(II) centers but that the actual rates and rate laws depend on the target and transmetalator structures and stabilities [14–17]. This conclusion has recently been verified by the discovery of selective transmetalation systems for which thermodynamic data for precursor formation can be obtained directly from the rate law [18, 19].

The impetus for the present study was that dimer I (Scheme 1) contains only Cl as a potential nucleophilic site for precursor construction. Actually, our previous work shows that this Cl in other targets could be a bridging [14, 16–19] or terminal [17] atom. Target **I** contains both kinds of atom, Scheme 1 [9]. Our objective was to characterize the products **III** of eqn. (5) and to compare its kinetics with those for reactions of other polynuclear copper targets reacting with the same $M(NS)_2$ transmetalators. Particular attention was paid to comparison with the results for copper(II) targets $[LCuX]_2Y$ (L is an *N,N,N′,N′*-tetraalkyldiamine and Y is O or CO_3), whose bridging atoms O and CO_3 differ from those in **I** but which also contain terminal halogen atoms X [17, 20].

$$\mathbf{I} + \mathrm{A\ or\ B} \longrightarrow \underset{\mathbf{III}}{N_2CuCl(Cl,Cl)ClMN_2} + \mathrm{A\ or\ B}\ (M = Cu) \qquad (5)$$

Experimental

Materials

Anhydrous copper(II) and nickel(II) chlorides were obtained by heating the respective hydrates (Alfa) under vacuum at 120 °C overnight. *N,N*-Diethylnicotinamide (N, Aldrich) was distilled under reduced pressure immediately before use. Nitrobenzene was distilled under reduced pressure from P_2O_5 and stored over 4 Å molecular sieves.

Target $[N_2CuCl]_2$ (**I**) was obtained by treating a solution of N (0.1 mol) in 50% vol./vol. methylene chloride/ethanol (30 ml) with a solution of anhydrous copper(II) chloride (0.05 mol) in absolute ethanol (25 ml). The mixture was refluxed for 1 h and solid **I** was obtained by vacuum solvent evaporation. Target $[N_2NiCl]_2$ (**II**) was obtained in a similar manner from anhydrous nickel(II) chloride.

Transmetalators $M(NS)_2$ (NS = monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate in **A** and monoanionic *S*-methyl benzylidenehydrazinecarbodithioate in **B**) were obtained by literature procedures [3].

*Synthesis and Isolation of Monotransmetalation Products **IIIa–d***

Target **I** (0.1 mol) in methylene chloride (30 ml) was treated with the respective $M(NS)_2$ transmetalator (0.1 mol) in methylene chloride (25 ml) at room temperature under dinitrogen. The transmetalator was added dropwise over a period of 1 h to ensure monotransmetalation of **I**. Each mixture was stirred under dinitrogen at room temperature for 2 h to ensure complete reaction, filtered when necessary to remove precipitated co-product **B** (M = Cu [3]) and then separated by gel permeation chromatography on Biobeads SX-12 resin* under a positive dinitrogen pressure with methylene chloride as the eluent [3]. Two well separated colored bands were eluted. The first band contained the respective product $N_3CuMCl_4{\cdot}2H_2O$ (**IIIa–c**) [20], which was obtained as a solid by vacuum solvent evaporation. The second band contained co-product **A** or **B** (M = Cu) of eqn. (5). A similar procedure was used to isolate $N_3NiCoCl_4{\cdot}2H_2O$ (**IIId**), the product of monotransmetalation of $[N_2NiCl_2]_2$ (**II**) by **A** (M = Co). Analytical, cryoscopic and electronic spectral data for **I–IIId** are given in Table 1.

Analytical Measurements

Metal analyses were performed with a Leeman Labs PlasmaSpec inductively coupled plasma emission spectrometer equipped with a computer-controlled scanning Echelle grating monochromator. The instrument was programmed to monitor emission intensity at each analytical wavelength for three, 3-second intervals. The analytical wavelengths (nm) and detection limits (ng/ml) were Co (228.62, 8); Ni (231.60, 20); Cu (324.75, 3) and Zn (213.62, 7).

Chloride was determined by a literature method calibrated with sodium chloride [21]. Carbon, hydrogen and nitrogen analyses were performed by Desert Analytical Laboratories, Tucson, AZ.

Physical Measurements

The electronic spectra of **I–IIId** in methylene chloride were measured with Beckman DK-1A and DB-G spectrophotometers in matched quartz cells at room temperature. EPR spectra of these solutions were recorded at 100 kHz and 6.28 G modulation

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*Biobeads SX-12 resin extracts and accumulates traces of water from eluting solvents. This water is often stoichiometrically coordinated by nickel, cobalt and zinc centers during the chromatographic isolation of transmetalation products. A good example is isolation of the family $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xX_6$ on chromatographic separation of the products of $(\mu_4\text{-}O)N_4Cu_4X_6/Ni(NS)_2$ reactions in eqn. (4) [13].

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

Label	Complex	Anal. (%)[a]				M_r [b]	λ_{max} (nm)[c] (E_λ (M^{-1} cm^{-1}))
		C	H	N	Cl		
I	$[N_2CuCl_2]_2$ [d]	48.9 (48.8)	5.8 (5.6)	11.4 (11.2)	14.5 (14.5)	1000 ± 30 (981)	770(350); 850(385)
II	$[N_2NiCl_2]_2$	49.4 (49.0)	6.2 (6.2)	11.5 (11.4)		880 ± 35 (972)	670(58); 780(45)[e]
IIIa	$N_3CuCo(H_2O)Cl_4 \cdot H_2O$	42.8 (43.1)	5.5 (5.5)	10.0 (10.1)	16.9 (17.0)	900 ± 40 (834)	570(500); 600(770); 660(520); 770(155); 850(170)
IIIb	$N_3CuNi(H_2O)Cl_4 \cdot H_2O$	43.1 (39.3)	5.5 (5.2)	10.1 (9.1)	17.0 (16.6)	900 ± 40 (836)	770(230); 850(240)
IIIc	$N_3CuZn(H_2O)Cl_4 \cdot H_2O$	42.8 (42.0)	5.5 (5.3)	10.0 (10.1)	16.9 (16.3)	900 ± 40 (842)	770(325); 850(360)
IIId	$N_3NiCo(H_2O)Cl_4 \cdot H_2O$	43.1 (43.4)	5.5 (5.5)	10.0 (10.1)	16.9 (17.1)	900 ± 40 (830)	570(375); 600(470); 650(330) 650(330)

[a]Calculated values in parentheses. [b]Measured in nitrobenzene at the 3–5 × 10^{-2} molal level (ref. 6). [c]In methylene chloride. [d]Data from ref. 9. [e]The spectrum of II has no pronounced absorption maxima in the region of interest: data are given for comparative purposes only.

amplitude on a Bruker Electrospin Model ESP 300 spectrometer. Incident power was 100 mW. Resonance conditions were found at *c.* 9.39 GHz (X-band) at room temperature and 130 K. Infrared measurements of **II** and **IIIa–d** in KBr disks or methylene chloride solution were made with a Perkin-Elmer model 567 spectrometer at room temperature. Cryoscopic measurements of products **IIIa–d** in nitrobenzene [6] were consistent with the presence of equimolar $N_3CuM(H_2O)Cl_4$ and H_2O.

Kinetic measurements of transmetalation and complex formation reactions of **I** and **II** with **A** and **B** were conducted in anhydrous nitrobenzene with a sufficient stoichiometric excess of target **I** or **II** to ensure monotransmetalation under pseudo-first-order conditions [14–19]. In all systems the concentration ranges were [target] = 8.3–20.8 × 10^{-4} M and [transmetalator] = 1.0 × 10^{-4} M. Temperature was varied in the range 17.8–42.2 °C. Monitoring wavelengths in the thermostated (±0.05 °C) Hi-Tech SFL-41 stopped-flow spectrophotometer were in the range 550–650 nm, where co-products **A** and **B** (M = Cu) are the principal absorbers [3]. All reactions were monitored for at least 10 half-lives under each set of fixed experimental conditions. The stopped-flow apparatus is interfaced to a Digital Equipment PRO-380 computer with advanced acquisition, processing and graphics capabilities [15]. The slopes of on-line plots of $\ln|(A_\infty - A_t)|$ versus time, where A_t is the absorbance at time t, were used to calculate each observed pseudo-first-order rate constant k_{obs} under fixed experimental conditions. Each run was repeated as least five times and each k_{obs} was reproducible to ±5% or better except where noted.

Results and Discussion

Targets I and II: General Observations

The dimeric target $[N_2CuCl_2]_2$ (**I**) forms spontaneously at room temperature on mixing anhydrous copper(II) chloride with N at molar ratio [N]/[$CuCl_2$] = 2.0 in methylene chloride or nitrobenzene. We have concluded from detailed EPR, infrared and kinetic measurements on these solutions that **I** behaves as shown in Scheme 1 [9]. **I** and its bromo analogue exist in methylene chloride as halo-bridged dimers with a trigonal pyramidal (tbp) geometry about each copper(II) center. These dimers react fairly rapidly with large excesses of N at ambient temperatures to give monomers $\mathbf{I_m}$ which also contain tbp copper(II). The third-order rate law for $\mathbf{I_m}$ formation indicates that **I** has a very low affinity for 2 mol of N. Cooling methylene chloride solutions of **I** or $\mathbf{I_m}$ to 17–27 K results in species $\mathbf{I_l}$ and $\mathbf{I_{ml}}$, respectively, which contain square pyramidal (sp) copper(II). From this and the fact that **I** crystallizes from methylene chloride as the O,(ring N)-bridged dimer $\mathbf{I_s}$, we learn (i) that the halo bridges of **I** are easily broken and (ii) that the coordination geometry about copper(II) is easily changed [9].

We did not succeed in crystallizing the analogous nickel dimer $[N_2Cu_2Cl_2]_2$ (**II**, Table 1). However, we examined its infrared spectrum as a solid in a KBr disk and in methylene chloride solution. There was no indication of a split ν(C=O) band at 1640 cm^{-1} that is characteristic of dimer $\mathbf{I_s}$ [9]. We thus conclude that the core structures of dimeric targets **I** and **II** are formed with bridging chloride in aprotic solvents. This means that **I** and **II** also contain terminal chloride (Scheme 1; see below).

Stoichiometry and Products of Transmetalation of I and II with A and B

Spectrophotometric titrations of **I** and **II** (0.1 mM) with **A** and **B** (M = Co, Ni, Zn) at 600 nm indicated the stoichiometry Δ[**A** or **B**]/Δ[**I** or **II**] = 2.0 in cases where metal exchange is thermodynamically favored (see below and ref. 22). Thus, the copper(II) and nickel(II) centers of **I** and **II** are completely replaceable with M from **A** and **B**. We attempted to separate the primary products of monotransmetalation of **I** and **II** by **A** and **B** (eqn. (5)) with gel permeation chromatography employing methylene chloride as the eluent [3]. However, the isolated solid products are aquodimers **IIIa–d** (Table 1) and not the Cu–M and Ni–M analogues of **I** and **II**, respectively.

Gel permeation chromatographic separation of the products of reactions (5) results in the incorporation of 1 mol of water and the loss of 1 mol of N per mol of primary heterodimer product. Coordination of water is often observed in such separations [21]. Substitution of water for N indicates a strong preference for maintenance of five coordination at new metal centers M (see below).

The infrared spectra of products **IIIa–d** exhibited no evidence of a split ν(C=O) band at 1640 cm^{-1} either in KBr disks or in methylene chloride solution. These dimers are thus always bridged by chloride [9].

No reaction was observed on mixing **I** with equimolar **II** in methylene chloride at room temperature. This is another indication that transmetalation is the only route to heterometallic complexes that do not form spontaneously from their constituents [11].

Electronic Spectra of IIIa–d

The visible electronic spectra of targets **I** and **II** and monotransmetalation products **IIIa–d** are summarized in Table 1 and illustrated in Fig. 1. Like **I**, products **IIIa–c** exhibit broad, intense maxima at 770 and 850 nm. These features indicate that the single copper(II) centers of **IIIa–c** are five coordinate (two N, three coordinated chloro ligands) [9, 13]. However, the molar absorptivities of **IIIa–c** are not half those of **I**, as might be expected if their single copper(II) centers were electronically isolated and solely responsible for absorbance from 700–900 nm. The nickel and zinc centers of **IIIb** and **IIIc** significantly enhance the atomic absorptivity of the copper(II) center that shares the chloro bridging system*, while the cobalt(II) center of **IIIa** attenuates it. Similar effects have been noted in other transmetalation products, especially as a result of bridged electronic interactions between cobalt(II) and copper(II) [12, 23].

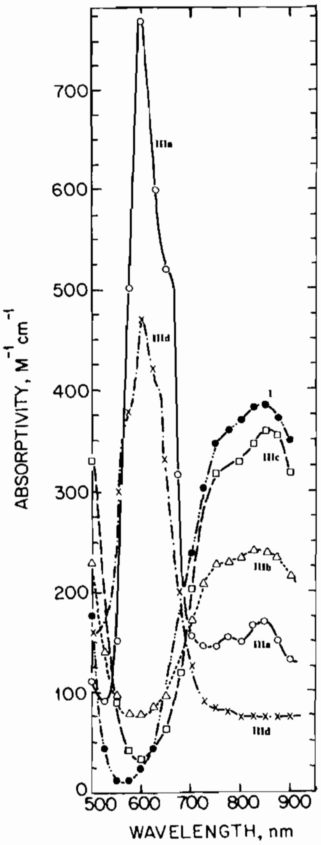

Fig. 1. Electronic spectra of **I** and **IIIa–d** in methylene chloride at 25 °C.

The spectra of molecules **IIIa** and **IIId** exhibit structured bands centered at 600 nm that are very characteristic of five-coordinate cobalt(II) [12, 22, 23]. This indicates that the cobalt(II) center of the primary product of the **I**/**A** (M = Co) reaction has maintained five coordination by replacing one of its N ligands with an aquo ligand. There are many examples of a preference for aquo ligands by M in heteropolymetallic transmetalation products [3, 11]. We note that the molar absorptivities of cobalt(II)-containing molecules **IIIa** and **IIId** are very sensitive to the identity of M.

EPR Spectra of IIIc

In view of the interesting temperature dependence of the EPR spectrum of **I** and the evidence given above for Cu–Cl–M and Co–Cl–M interactions in products **IIIa–d**, we examined the EPR spectra of copper–zinc product **IIIc** in methylene chloride solution as a function of temperature. The results are summarized in Table 2 and illustrated in Fig. 2.

The rhombic X-band EPR spectrum of **I** (1.6 mM) at 300 K (Fig. 2(a)) is characteristic of a d_{z^2} ground

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*This must be so because nickel dimer **II** has very low absorptivity in the 500–900 nm region and no absorption maxima are evident at 770 or 850 nm. The zinc center (d^{10}) of **III** is expected to absorb weakly, if at all, in this wavelength range [12].

TABLE 2. EPR data for transmetalation target I and product IIIc in methylene chloride

Complex C	[C] ^{a}	Temperature^b	EPR parameters							
			g_1	g_2	g_3	$g_\parallel$	$A_\parallel$ ^{c}	$g_\perp$	g_i	A_i ^{c}
I^d	1.6	300	2.21	2.12	2.07					
		130				2.26	140	2.04		
IIIc	3.2	300	2.21	2.12	2.07					
		130							2.07	40

^{a}Concentration, mM. ^{b}Given in degrees K. ^{c}Units are 10^4 cm^{-1}. ^{d}Data from ref. 9.

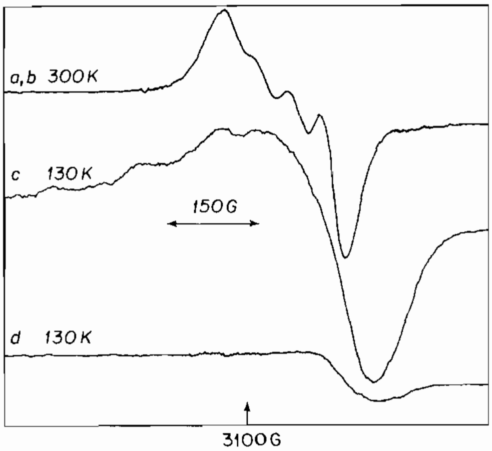

Fig. 2. EPR spectra in methylene chloride as follows: a, I (1.6 mM) at 300 K (gain 3.2×10^5); b, IIIc (3.2 mM) at 300 K (gain 3.2×10^5); c, I (1.6 mM) at 130 K (gain 8.0×10^4); d, IIIc (3.2 mM) at 130 K (gain 8.0×10^4).

state and tbp geometry for copper(II). Cooling the solution to 130 K results in an axial spectrum (Fig. 2(c)) that indicates a $d_{x^2-y^2}$ ground state and sp geometry [9, 24].

The X-band EPR spectrum of IIIc (3.2 mM) in methylene chloride at 300 K (Fig. 2(b)) is superimposable on that of I at half the molar concentration. Product IIIc thus contains tpb copper(II) in an environment that resembles that in I. This indicates that the enhancement of copper(II) absorptivity in IIIc (Fig. 1) is an electronic effect. Cooling this same solution to 130 K gave an isotropic spectrum (Fig. 2(d)) with greatly decreased intensity. This result indicates that the EPR activity of the single copper(II) center in IIIc is quenched by the presence of zinc that shares the chloro bridging system. Similar effects have been observed in other polynuclear transmetalation products [12, 23].

Kinetics of Transmetalation of Excess I and II by A and B: General Observations

Targets I and II react rapidly with reagents A and B in nitrobenzene at ambient temperatures, as found with targets $[LCuX]_2$ [16], $[LCuX]_2Y$ ($Y = O$ or CO_3) [17] and $(\mu_4\text{-}O)N_4Cu_{4-x}M_xX_6$ (x = 1–4) [14, 18, 19]. The reactions are accompanied by absorbance changes in the 550–700 nm region that are consistent with (i) exchange of M from A or B for copper(II) in I and nickel(II) in II in cases where this is expected from the known stability order $Cu(NS)_2 \gg Ni(NS)_2 \gg Co(NS)_2 \gg Zn(NS)_2$ [22]; and (ii) complexation of I by A (M = Cu) in reactions where no net metal exchange can occur.

We first studied the reaction of excess I with A (M = Ni) with the expectation that it would be a single-step process with a simple rate law [14–19]. This reaction actually proceeds in two separable steps with characteristics that are very useful in explaining the kinetic behavior of the other systems.

Kinetics of the reaction of I with A (M = Ni) in nitrobenzene

Figure 3 shows the absorbance changes that occur at 575 nm in the stopped-flow spectrophotometer on mixing excess I with A (M = Ni) in nitrobenzene at 22.6 °C. Events that cause an absorbance increase and decrease, respectively, are clearly observed. Monophasic absorbance increases associated with the formation of co-products $Cu(NS)_2$ of transmetalation of copper(II) centers have been reported in many systems [14, 17–19].

The absorbance changes associated with these two events were easily resolved and gave excellent linear plots of $\ln|(A_\infty - A_t)|$ versus time, indicating that they are both pseudo-first-order. The respective pseudo-first-order rate constants $k_{obs}(1)$ and $k_{obs}(2)$ obtained from the slopes of such plots under a

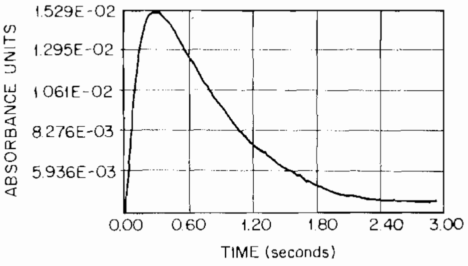

Fig. 3. Absorbance–time data for the reaction of I (0.83 mM) with A (M = Ni) (0.10 mM) in nitrobenzene at 22.6 °C. The monitoring wavelength is 575 nm.

TABLE 3. Experimental kinetic data for the reaction of target I with A (M = Ni) in nitrobenzene

$10^4 \times$ [I] [a]	Temperature[b]	$k_{obs}(1)$ [c]	$k_{obs}(2)$ [c, d]
8.3	17.8	9.3	0.70
12.5		10.5	0.52
16.6		11.2	0.50
20.8		12.2	0.60
			av. 0.58 ± 0.07
8.3	22.6	13.2	1.05
12.5		15.0	0.95
16.6		16.8	0.78
20.8		19.0	0.80
			av. 0.90 ± 0.10
8.3	30.6	21.0	1.37
12.5		25.6	1.15
16.6		29.7	1.00
20.8		34.0	1.20
			av. 1.18 ± 0.10

[a] Units are M. [b] Given in °C. [c] Units are s^{-1}. [d] The data in this column give $\Delta H_2^{\ddagger}$ = 9.0 ± 1.0 kcal mol^{-1} and $\Delta S_2^{\ddagger}$ = −30 ± 6 cal deg^{-1} mol^{-1} at 25 °C in eqn. (9); see text.

variety of experimental conditions are listed in Table 3.

First event. Plots of rate constants $k_{obs}(1)$ versus [I] at fixed temperature were found to be linear with finite intercepts (Fig. 4). This indicates a reversible first step, eqn. (6) with rate law (7), as observed in the reactions of some dimeric copper(I) targets $[LCuX]_2$ with particular A (see Fig. 5 of ref. 16). The equilibrium constant for formation of complex C′ in reaction (6) is $K_6 = k_6/k_{-6}$. Values for k_6, k_{-6}, K_6 and their associated thermodynamic parameters are collected in Table 4.

$$\mathrm{I + A\ (M = Ni)} \overset{k_{-6}}{\underset{k_6}{\leftrightarrows}} \mathrm{C'} \qquad K_6 \qquad (6)$$

$$\text{rate} = k_6[\mathrm{I}] + k_{-6} \qquad (7)$$

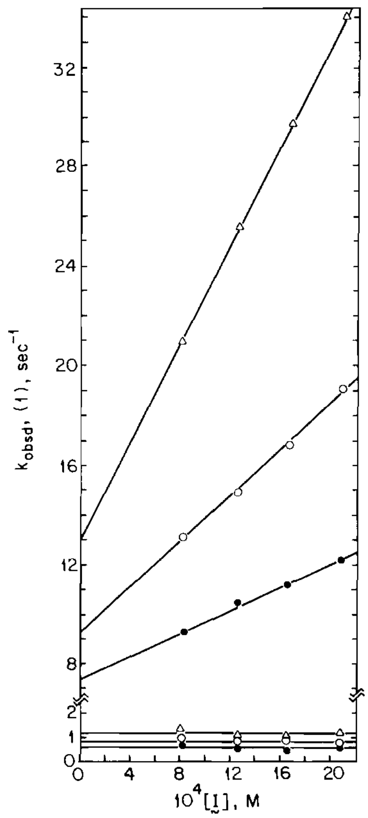

Fig. 4. Upper section: plots of $k_{obs}(1)$ vs. [I] for the reaction of I with A (M = Ni) in nitrobenzene at 17.8 (●), 22.6 (○) and 30.6 (△) °C. Lower section: plots of $k_{obs}(2)$ vs. [I] or [II] for the reactions of I with A (M = Co) (○); I with A (M = Zn) (●); II with A (M = Co) (△) in nitrobenzene at 21.0 °C. The monitoring wavelength is 600–610 nm.

Other systems with rate law (7) involve copper(I) targets $[LCuX]_2$ with μ-μ-dihalo bridges and no terminal halide [16]. None of the earlier systems involve A (M = Ni). Their equilibrium constants K_6 are 400–560 M^{-1} in nitrobenzene at 21 °C [16]. Despite the presence of terminal chloride in I (Scheme 1), K_6 = 460 M^{-1} for the I/A (M = Ni) reaction at 22.6 °C (Table 4) is remarkably similar. A plot of ΔH_6 versus ΔS_6 generated from the data in Table IV of ref. 16 is linear, which suggests a common interaction in the analogues of C′ that maintain

TABLE 4. Derived kinetic parameters for the reaction of target I with A (M = Ni) in nitrobenzene (Scheme 2)

T [a]	k_6 [b]	$\Delta H_6^{\ddagger}$ [c]	$\Delta S_6^{\ddagger}$ [d]	k_{-6} [e]	$\Delta H_{-6}^{\ddagger}$ [c]	$\Delta S_{-6}^{\ddagger}$ [d]	K_6 [f]	ΔH_6 [c]	ΔS_6 [d]
17.8	2.9			7.4			400		
22.6	4.3			9.3			460		
30.6	10.0	17.0	0	13.0	7.4	−29	770	10.3	−28

[a] Temperature in °C. [b] Units are 10^3 M^{-1} s^{-1}. [c] Units are kcal mol^{-1} (typical error is ±0.5 kcal mol^{-1}). [d] Units are cal deg^{-1} mol^{-1} at 25 °C (typical error is ±4 cal deg^{-1} mol^{-1}). [e] Units are s^{-1}. [f] Units are M^{-1}.

bridging halide in the $[LCuX]_2$ target*. The effect of changing the ligand from L to N, copper(I) to copper(II) and presenting terminal chloride in **I** to **A** (M = Ni) is to make ΔS_6 at least 70 cal deg^{-1} mol^{-1} more negative than expected on the basis of the other data [16].

The second-order rate constant k_6 at 21 °C is 2–10 times greater for the reaction of **I** with **A** (M = Ni) than for the earlier $[LCuX]_2$/**A**,**B** systems [16]. This is because $\Delta S_6^{\ddagger}$ for the **I**/**A** (M = Ni) reaction is about 20 cal deg^{-1} mol^{-1} more negative than expected from the data for the other systems [16]. The rate constant for dissociation of C′ in eqn. (6) is 2–10 times greater than for dissociation of $[LCuX]_2$/**A**,**B** complexes [16]. A straight line plot of $\Delta H_{-6}^{\ddagger}$ versus $\Delta S_{-6}^{\ddagger}$ accommodates the data from Table IV of ref. 16 and Table 4 of this work. This indicates that such comparisons are not always a reliable guide to differences of complexation product structures in systems with different targets.

Second event. The rate of the second observed event in the **I**/**A** (M = Ni) system (Fig. 3) was found, within an experimental error of 8–10%, to be independent of the target concentration [**I**] (Table 3), indicating rate law (8). Detailed discussion of the $k_{obs}(2)$ data in Table 3 will be deferred until our other rate information has been presented.

$$k_{obs}(2) = k_8 \qquad (8)$$

Reaction of excess I with B (M = Ni) in nitrobenzene

The reaction of excess **I** with **B** (M = Ni) in nitrobenzene resulted in a monophasic absorbance increase at 550 nm that is expected for formation of transmetalation co-product **B** (M = Cu) [3, 16]. Excellent linear plots of $\ln(A_\infty - A_t)$ versus time under fixed experimental conditions demonstrate that the title reaction is first-order in [**B**]. Plots of k_{obs} (s^{-1}) versus [**I**] at fixed temperature were linear and passed through the origin, indicating that the title reaction is an irreversible second-order process, eqn. (9). The second-order rate constants k_9 and its associated activation parameters are collected in Table 5.

$$\text{rate} = k_9[\mathbf{I}][\mathbf{B}] \qquad (9)$$

In previous work, we found that **B** (M = Ni) nearly always reacts with copper(I) [16] and copper(II) [14, 17–19] targets with second-order rate law (9) (eqn. (10) of ref. 17). This is accounted for by the weak nucleophilic character of the carbodithioate S atom in **B** relative to that in **A** with the same metal M and to geometrical differences between these transmetalators [14–19]. The data for the title reaction fit the lowest line of the activation parameter correlation in Fig. 6 of ref. 17, which refers to reactions of targets $(\mu_4\text{-O})N_4Cu_4X_6$ (**D**) with **B** (M = Ni or Zn). Each pair of copper(II) centers in **D** is bridged by two-coordinate halide [3, 13]. The correlation of data with **I** or **D** as targets suggests the involvement of terminal halide in all such systems, since **I** definitely contains terminal chloride [9].

TABLE 5. Kinetic data for reactions of **I** and **II** with **A** and **B** in nitrobenzene

Target	TM[a]	Temperature[b]	k_9 [c]	$\Delta H_9^{\ddagger}$ [d]	$\Delta S_9^{\ddagger}$ [e]
(a) Second-order system					
I	**B** (M = Ni)	21.0	0.92		
		31.5	2.2		
		36.3	2.8		
		39.2	3.6		
		42.1	4.3	13.6	−4
			k_8 [f]	$\Delta H_8^{\ddagger}$ [d]	$\Delta S_8^{\ddagger}$ [e]
(b) First-order systems					
I	**A** (M = Co)	21.0	0.095		
		30.8	0.14		
		35.9	0.16		
		42.9	0.19		
		47.0	0.21	5.9	−43
	A (M = Cu)	21.0	1.0		
		28.2	1.7		
		36.0	3.0		
		41.0	4.3	12.7	−15
	A (M = Zn)	21.0	0.60		
		23.4	0.73		
		30.0	1.2		
		38.0	2.1		
		42.0	2.9	13.4	−18
II	**A** (M = Co)	21.0	1.3		
		29.8	3.0		
		34.2	4.0		
		42.2	6.0	16.0	−4

[a] TM = transmetalator. [b] Temperature in °C. [c] Units are M^{-1} s^{-1}. [d] Units are kcal mol^{-1} (typical error is ±0.5 kcal mol^{-1}). [e] Units are cal deg^{-1} mol^{-1} at 25 °C (typical error is ±5 cal deg^{-1} mol^{-1}). [f] Units are s^{-1}.

First-order Reactions

Kinetic data for other reactions of targets **I** and **II** investigated in this work are collected in Table 5 and illustrated in the lower section of Fig. 4. All these reactions result in an absorbance increase at 525–610 nm which is too rapid to follow by the stopped-flow technique at ambient temperatures. This means that **I** is much more labile than the other copper(I) and copper(II) targets we have investigated [14–19], to the extent that we can only collect $k_{obs}(1)$ data for the **I**/**A** (M = Ni) system.

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*We have speculated from activation parameter correlations that reactions of copper targets containing only bridging halide can proceed via breaking of such bridges for interaction with $M(NS)_2$ in transmetalation precursors [16].

The very rapid absorbance increases preceded absorbance decreases that were easily monitored in the range 525–610 nm (Fig. 5). The rates of these first-order reactions (eqn. (8)) were independent of [**I**] (Fig. 4, lower section) and similar in magnitude (Table 5) to those for the second step of the reaction between **I** and **A** (M = Ni: $k_{obs}(2)$ of Table 3). All these reactions result in an absorption decrease over the same wavelength range, which is another indication that they refer to a process whose rate largely depends on the properties of the target. This is almost certainly true because similar rates are observed for reactions of **I** with **A** (M = Zn) and **A** (M = Cu), despite the fact that the latter complex is by far the more thermodynamically stable $M(NS)_2$ complex [22] and does not exchange its copper with **I**. Consistent with the idea of target dominance, we note that dimeric nickel target **II** reacts 20–30 times faster than **I** with the same transmetalator **A** (M = Co) (Table 5).

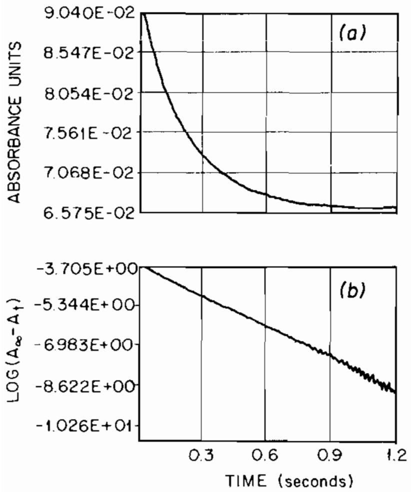
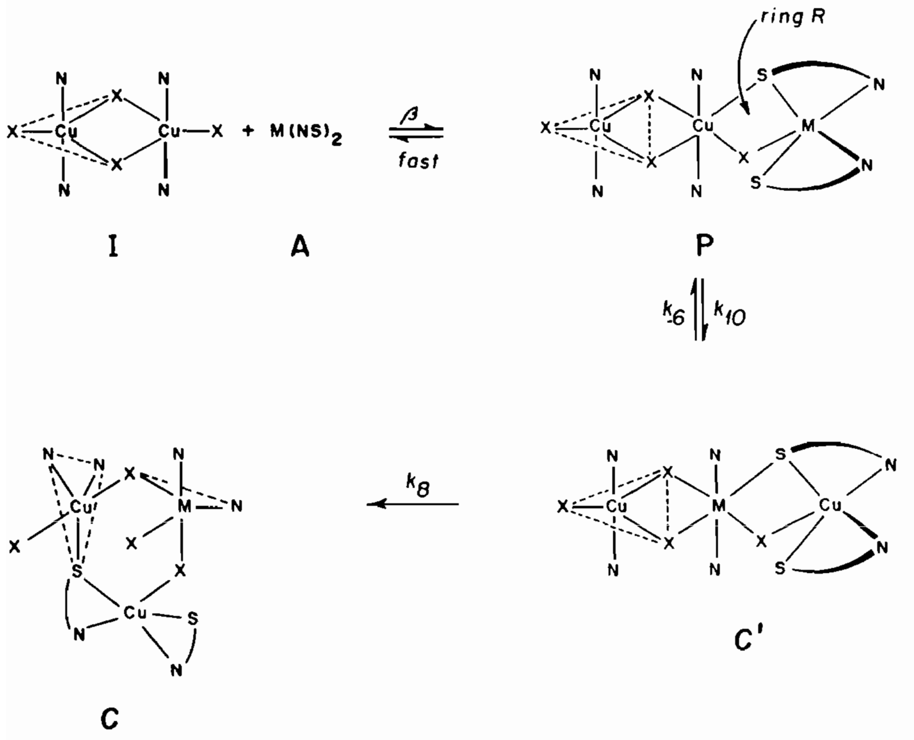


Fig. 5. (a) Absorbance–time data for the reaction of **I** (0.83 mM) with **A** (M = Cu) (0.10 mM) in nitrobenzene at 41.0 °C. Monitoring wavelength is 525 nm; (b) computer-generated plot of $\ln(A_t - A_\infty)$ vs. time for the data in the upper panel.

Reaction Mechanism

The proposed mechanism for the reactions of this study is given in Scheme 2.

Precursor **P** is very rapidly formed in reaction (10) from **A** or **B** and **I** or **II** with equilibrium constant β. Terminal Cl from the target and carbothioate S are used to construct four-membered ring R that we feel is necessary for metal exchange reaction (11) [14–19]. The observed rate constants for the formation of **C**′ in the **I**/**A** (M = Ni) reaction and the irreversible second-order reaction of **I** with **B** (M = Ni) are then given by $k_6 = \beta k_{10}$ and $k_9 = \beta k_{10}$ in the respective systems. Differences between k_6 and k_9 could be due to differences of β, k_{10} or both. Linear plots in Fig. 4 (upper section) indicate very low concentra-



(10)

(11)

(12)

Scheme 2.

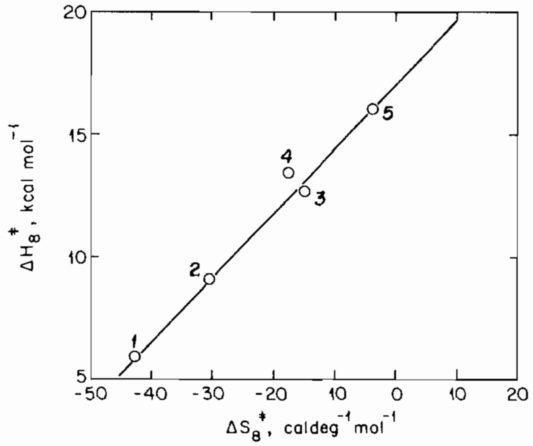


Fig. 6. Plot of $\Delta H_8^{\ddagger}$ vs. $\Delta S_8^{\ddagger}$ for the following reactions in nitrobenzene with first-order rate law (8): 1, I with A (M = Co); 2, I with A (M = Ni); 3, I with A (M = Cu); 4, I with A (M = Zn); 5, II with A (M = Co). The data are taken from Tables 3 and 5.

tions of **P** and very small β in equilibrium (10) [18, 19].

As noted earlier, we were not able to collect data for metal exchange step (11) when M = Co or Zn in **A**. This and the fact that step (11) is reversible with M = Ni are indications that the thermodynamic stability order $Cu(NS)_2 \gg Ni(NS)_2 \gg Co(NS)_2 \gg Zn(NS)_2$ [22] is responsible for what is observed. We would expect the smallest difference of $M(NS)_2$ stability to give the lowest k_{10} and the greatest likelihood of reversibility, as observed.

Step 12 of Scheme 2 is not apparent in the reactions of copper(II) targets $[LCuX]_2Y$ ($Y = O$ or CO_3) with these same transmetalators. Targets $[LCuX]_2Y$ contain very strong oxo and carbonato bridging systems [17, 20]. That is why we feel that the products of slow, first-order reactions (12) are complexes **C** that contain a single chloro bridge.

Reaction of **I** with **A** (M = Cu) consists of rapid formation of **C'** and its rate-determining conversion to **C**. We observe a decrease in absorbance in reaction (12) because of changes in the atoms coordinated by copper. A plot of $\Delta H_8^{\ddagger}$ versus $\Delta S_8^{\ddagger}$ is linear (Fig. 6), which strongly suggests that reactions (12) have a common rate-determining step or steps. Our suggestion is that these steps involve Cu–S or Ni–S (for **II**) bond formation and Cu–Cl(bridge) or Ni–Cl(bridge) rupture.

Implications for Product Separation

Products **IIIa–d** are easily separated from coproducts $Cu(NS)_2$ and $Ni(NS)_2$ in reactions (5) by gel permeation chromatography. This method depends on differences in molar volumes of discrete products. It would not work if the product complexes **C** of Scheme 2 were very stable (i.e. they dissociated very slowly), as implied by irreversible rate law (8). The incorporation of water in **IIIa–d** suggests a role for water in catalyzing the dissociation of **C** on the gel permeation column, which will then retain monomeric $Cu(NS)_2$ in preference to dimeric **IIIa–c**.

Conclusions

Targets **I** and **II** are much more labile than any other targets we have investigated because they have much weaker bridging systems. The primary products of their transmetalation with **A** (M = Co, Ni, Cu or Zn) are complexes of the form $[N_2CuCl_2]_2 \cdot Cu(NS)_2$ and $N_4NiCoCl_4 \cdot Ni(NS)_2$. They are not separate products as implied in eqn. (5).

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