The kinetics of adduct formation between heteropolymetallic targets $(\mu_4\text{-O})N_4Cu_{4-x}M_xX_6$ and $Cu(NS)_2$ reagent in nitrobenzene

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Abstract

The rate laws for the earliest events in the specific stoichiometric monotransmetalation of heteropolymetallic targets $(\mu_4\text{-O})(\text{amine})_4Cu_{4-x}M_xX_6$, where the amine ligand is pyridine (py) or monodentate N,N,-diethylnicotinamide (N), x is 1–3, M is Co or Ni(H₂O), X is Cl or Br, by transmetalators $M'(NS)_2$ and their solution adduct formation by reagent $Cu(NS)_2$ in nitrobenzene, where M′ is Co, Ni or Zn and NS is monoanionic S-methylisopropylidinehydrazine-carbodithioate, depends on the amine, M, M′, x and X. The observed event can be the formation of reaction precursors P₁, P₂ or P₃, metal exchange within the precursors, rearrangement of successors S₁, S₂ or S₃ complexes or their dissociation to separate products. The kinetic and thermodynamic data are compared with those of a neutral monomeric target $Cu(ac.ac.)_2$ containing only oxygen donor atoms. The structural-mechanistic origins of monotransmetalation specificity and adduct formation in these systems are discussed.
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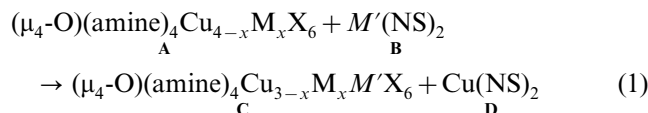*Keywords:* Kinetics; Adduct; Transmetalation; Heteropolymetallic; Target; Formation

1. Introduction

This paper discusses kinetic and mechanistic relationship between the irreversible transmetalation of hetero-polymetallic targets $(\mu_4\text{-O})(\text{amine})_4Cu_{4-x}M_xX_6$ (**A**) by transmetalators $M'(NS)_2$ (**B**) and their solution adduct formation by reagent $Cu(NS)_2$ (**D**), where the amine ligand is pyridine (py) or monodentate N,N,-diethyl-nicotinamide (N), x is 1–3, M is Co or Ni(H₂O), X is Cl or Br, M′ is Co, Ni or Zn in transmetallator **B** and NS is monoanionic S-methylisopropylidenehydrazinecarbo-dithioate in reactants **B** and **D** [1–11].[1]

Transmetalation is the stoichiometric replacement of the metals in a polymetallic molecules that cannot be made by other means [1].

Demetalation and transmetalation of a heteropoly-metallic target can be specific in the sense that one of the different target metals is preferentially removed or replaced [2–5]. The origins of specificity are best explored by study of direct [1] reactions in which the target and product have the same molecularity [2,4,5].

Eq. (1) is an examples of rapid [4–11] direct, specific [4,5] monotransmetalations (Fig. 1).

$$(\mu_4\text{-O})(\text{amine})_4\underset{\mathbf{A}}{Cu_{4-x}M_x}X_6 + \underset{\mathbf{B}}{M'(NS)_2}$$
$$\rightarrow (\mu_4\text{-O})(\text{amine})_4\underset{\mathbf{C}}{Cu_{3-x}M_xM'}X_6 + \underset{\mathbf{D}}{Cu(NS)_2} \qquad (1)$$

Identification of quantitative products **C** in Eq. (1) constitutes proof of the specific replacement of the copper(II) in targets **A** [4,5].

One factor favoring specific reaction (1) is the high relative thermodynamic stability of copper(II) co-product **D** in the known order $\mathbf{D} > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$ [2].

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[1] (a) Example of abbreviation for targets A and C mentioned in this paper are as follows: NCu₄Cl is complex $(\mu_4\text{-O})N_4Cu_4Cl_6$ [9]; NNiCl is the complex $(\mu_4\text{-O})N_4Ni_4Cl_6$ [10]; NNi₃ZnCl represents the complex $(\mu_4\text{-O})N_4(Ni(H_2O))_3 ZnCl_6$. (b) We have observed that the nickel centers of these complexes generally carry one water molecule which is coordinated during gel permeation chromatographic isolation [1,3–7,9,10].
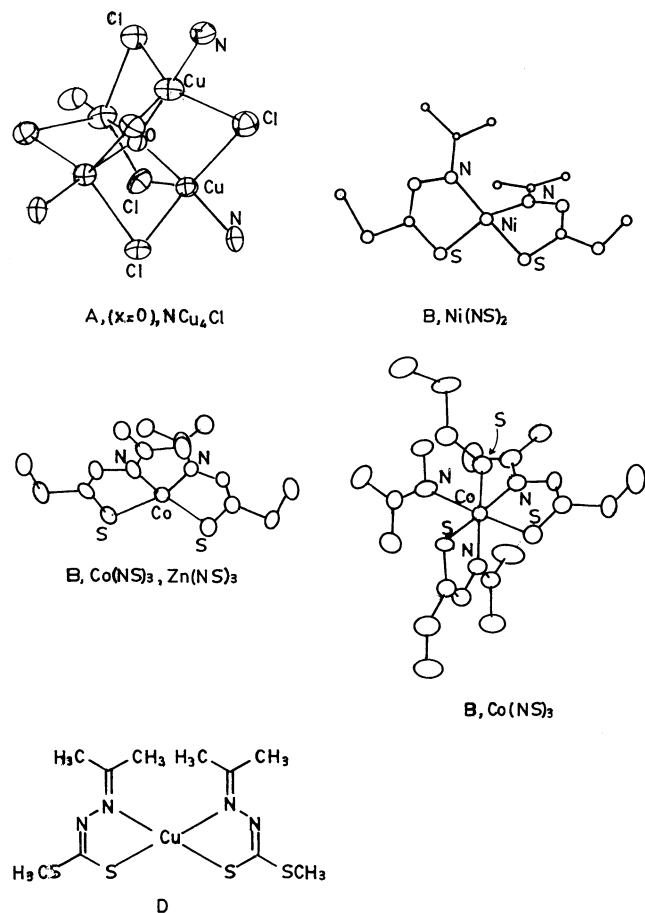
Fig. 1. The core structure of A ($x = 0$), bis(S-methylisopropylidene-hydrazinecarbodithioate) metal(II); M(NS)$_2$, B, where (M = Ni [17]; M = Co or Zn [14], Zn(NS)$_2$ is isomorphous with Co(NS)$_2$, tris(S-methylisopropylidene-hydrazinecarbodithioate) cobalt (III), Co(NS)$_3$ [18], and the Cu(NS)$_2$, D.

Another is the apparent involvement of reaction precursors with equilibrium constant β_n in Eq. (2).

$$\mathbf{B} + n\mathbf{A} \rightleftharpoons \mathbf{B} \cdot \mathbf{A}_n \qquad \beta_n \qquad (2)$$

We also report that $\mathbf{A} \cdot \mathbf{D}$ adduct formation Eq. (3) proceeds with rate law 4 or 5, depending on reactants $\mathbf{A}$.

$$\mathbf{A} + \mathbf{D} \rightleftharpoons \mathbf{A} \cdot \mathbf{D} \qquad k_3, \ k_{-3}, \ K_3 \qquad (3)$$
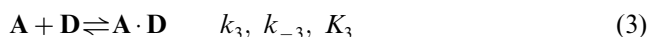
$$\text{Rate} = k_3[\mathbf{B} \text{ or } \mathbf{D}] \qquad (4)$$

$$\text{Rate} = k_3[\mathbf{A}][\mathbf{D}] + k_{-3} \qquad (5)$$

Analogous behavior is observed in reactions of Zn(NS)$_2$ and $\mathbf{D}$ with targets (μ_4-O)N$_4$Cu$_{4-x}$ (Ni(H$_2$O))$_x$Cl$_6$. Rate law 5 is used to obtain equilibrium constants for $\mathbf{A} \cdot \mathbf{D}$ complex formation that are compared with β_1 for transmetalation precursor formation [4,5]. A classification of the precursors involved in second-order transmetalation and adduct formation systems is suggested. One particular system exhibit spectral and kinetic evidence for the transfer of Ni(NS)$_2$ from primary transmetalation product NNi$_3$ZnCl·Ni(NS)$_2$ to excess target NNi$_4$Cl.

2. Experimental

2.1. Materials and methods

Procedures for syntheses of $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{D}$ have been described [1–5,9–11]. Analytical cryoscopic and electronic spectral data for the reactants of this study are collected in Table 1. Many attempts to obtain single crystals of adducts $\mathbf{A} \cdot \mathbf{D}$ by variety of diffusion, evaporation and mixed solvent methods were unsuccessful.

2.2. Kinetic measurements

All kinetic measurements were conducted in anhydrous nitrobenzene under nitrogen with a sufficient stoichiometric excess of targets $\mathbf{A}$ to ensure monotransmetalation under pseudo-first-order conditions, as described previously [6]. Initial concentrations of $\mathbf{A}$ and $\mathbf{D}$ were varied in the ranges $10^4[\mathbf{A}]_o = 2.5$–25.0 M and $10^5[\mathbf{D}]_o = 2.5$–5.0 M, respectively. Temperature was varied from 8 to 40 °C. These experimental parameters are typical of previous kinetic work on transmetalation systems [4–11]. Monitoring wavelengths in the thermostated (± 0.05 °C) Hi-Tech SFL40 stopped-flow spectrophotometer were in the range 575–650 nm, where $\mathbf{D}$ exhibits strong absorption [10]. All reaction were monitored for at least ten half-lives. On-line computer-generated [12] plots of $\ln|A_\infty - A_t|$ where A_t is the absorbance at time t versus time gave the pseudo-first-order rate constant, k_{obsd}, for each set of fixed experimental conditions. Each run was repeated at least five times and each k_{obsd} was reproducible to $+4\%$ or better. There were no significant kinetic effects of using different samples of $\mathbf{A}$, $\mathbf{B}$ or $\mathbf{D}$. Raw kinetic data for each system are available.[2]

3. Results and discussion

3.1. The kinetics of transmetalation and solution adduct formation reactions general observation

Monotransmetalation (the replacement of just one metal center in a target) [1] is ensured by maintaining a large excess of targets $\mathbf{A}$ [4,5]. Identification of quantitative products $\mathbf{C}$ in Eq. (1) demonstrates the specific replacement of a copper(II) center in targets $\mathbf{A}$ with M′ from reagent $\mathbf{B}$ [4,5,7,9]

Precursors with moderate or large β_1 apparently contain the reactants linked as in P$_2$ and P$_3$. Primary linkages involve the X atoms in an edge of target $\mathbf{A}$ and the thiocarbote S atoms of $\mathbf{B}$ [4–7]. Such interactions

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[2] Kinetic data for monotransmetalation of $\mathbf{A}$ (2 pages) is available from the author on request.

Table 1
Analytical, cryoscopic molecular weight and electronic spectral data for transmetalation targets and products (calculated values in parentheses)

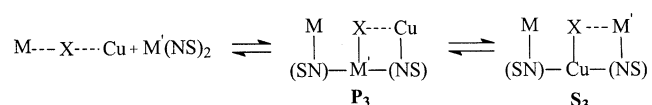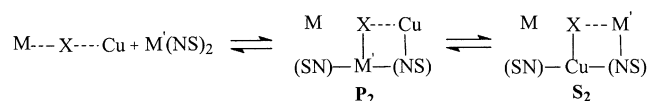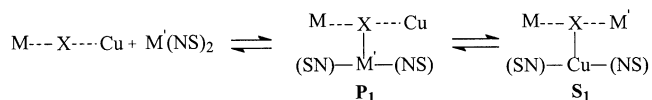| Complex	Anal. (%)									λ_{max}, nm (ε_λ, M^{-1} cm^{-1})[d]
	C	H	N	Cl	Cu	Ni	Zn	Co	Mr	
A. Targets										
$N_4Cu_4Cl_6O$ [a]	40.0 (40.0)	4.7 (4.7)	9.2 (9.4)		21.0 (21.2)				1180±20 (1196)	850(1630), 775(1400)
$N_4Cu_3NiCl_6O \cdot H_2O$ [a]	40.0 (39.7)	4.9 (4.8)	8.9 (9.3)		16.3 (15.8)	4.6 (5.0)			1240±20 (1208)	850(1160), 775(1030)
$N_4Cu_2Ni_2Cl_6O \cdot 2H_2O$ [a]	36.6 (36.4)	4.6 (4.9)	8.7 (9.2)		11.0 (10.4)	10.2 (9.6)			1250±20 (1223)	850(840), 775(760)
$N_4CuNi_3Cl_6O \cdot 3H_2O$ [a]	36.5 (36.9)	4.7 (5.1)	8.7 (9.1)		5.5 (5.1)	15.1 (14.3)			1200±20 (1236)	850(360), 775(340)
$N_4CuNi_3Br_6O \cdot 3H_2O$ [a]	32.0 (31.9)	4.07 (4.13)	7.56 (7.46)		4.17 (4.23)	11.93 (11.73)			1500±20 (1502)	850(355), 775(330)
$N_4Ni_4Cl_6O \cdot 4H_2O$ [a]	37.8 (38.5)	5.1 (5.2)	8.7 (9.0)			18.5 (18.8)			1270±20 (1249)	[e]
$py_4Cu_2Ni_2Cl_6O \cdot 2H_2O$	29.6 (29.7)	2.6 (2.9)	6.8 (6.9)	25.4 (26.0)	15.3 (15.7)	14.3 (14.6)			815±20 (823)	860(650), 775(850)
$N_4CuCo_3Cl_6O$ [b]	38.2 (40.6)	4.2 (4.7)	8.9 (9.5)	16.1 (17.9)	4.8 (5.3)			12.9 (14.9)	1180±20 (1181)	875(450), 675(1000), 650(1200), 600(1390), 575(1380)
B. Products										
$N_4Cu_3ZnCl_6O \cdot H_2O$ [c]	38.9 (39.6)	4.4 (4.7)	9.2 (9.2)		16.2 (15.7)		4.1 (5.4)		1240±20 (1215)	850(1130), 775(1020)
$N_4Cu_2NiZnCl_6O \cdot H_2O$	39.1 (39.8)	4.3 (4.8)	9.1 (9.3)	17.0 (17.4)	10.1 (10.5)	4.1 (4.9)	4.9 (5.4)		1220±20 (1207)	850(820), 775(720)
$N_4CuNi_2ZnCl_6O \cdot 2H_2O$	38.8 (39.3)	4.7 (4.9)	8.9 (9.2)	17.0 (17.2)	5.0 (5.2)	8.9 (9.6)	4.9 (5.2)		1240±20 (1220)	850(400), 775(310)
$N_4Ni_3ZnCl_6O \cdot 3H_2O$	37.6 (38.9)	4.8 (5.0)	8.8 (9.1)	16.5 (17.0)		13.9 (14.3)	4.8 (5.3)		1250±20 (1234)	[e]
$N_4Ni_3ZnBr_6O \cdot 3H_2O$	30.9 (31.9)	3.8 (4.1)	7.2 (7.4)			9.2 (11.8)	3.9 (4.3)		1515±20 (1504)	850(80), 775(83)
$N_4Ni_3CoCl_6O \cdot 3H_2O$ [a]	37.9 (39.0)	4.7 (5.0)	8.7 (9.1)	16.7 (17.1)		13.8 (14.4		4.2 (4.8)	1240±20 (1228)	630(350), 610(420), 575(370)
$py_4Cu_2Ni_2Cl_6O \cdot 2H_2O$	29.5 (29.6)	2.6 (2.7)	6.7 (6.9)	25.4 (25.9)	15.1 (15.6)	6.2 (7.3)	7.6 (8.1)		825±20 (811)	850(230), 775(240)
$N_4Co_3ZnCl_6O$	40.1 (40.7)	4.3 (4.7)	9.4 (9.5)	17.0 (17.8)			5.0 (5.5)	14.2 (15.0)	1170±20 (1180)	630(1050), 610(1340), 575(1150)

[a] Data from Ref. [9].
[b] Data from Ref. [12].
[c] Data from Ref. [16].
[d] In nitrobenzene.
[e] Negligible molar absorptions in the region 775–860 nm.

associate M′ in the transmetalation with Cu rather than M in the target. The observed event can be the formation of reaction precursors P_1, P_2 or P_3, metal exchange within the precursors, rearrangement of successors S_1, S_2, or S_3 complexes or their dissociation to separate products.

$$M\text{---}X\text{----}Cu + M'(NS)_2 \rightleftharpoons \begin{array}{c} M\text{---}X\text{----}Cu \\ | \\ (SN)\text{---}M'\text{---}(NS) \\ \mathbf{P_1} \end{array} \rightleftharpoons \begin{array}{c} M\text{---}X\text{---}M' \\ | \\ (SN)\text{---}Cu\text{---}(NS) \\ \mathbf{S_1} \end{array}$$

$$M\text{---}X\text{----}Cu + M'(NS)_2 \rightleftharpoons \begin{array}{c} M \quad X\text{----}Cu \\ | \quad | \\ (SN)\text{---}M'\text{---}(NS) \\ \mathbf{P_2} \end{array} \rightleftharpoons \begin{array}{c} M \quad X\text{---}M' \\ | \quad | \\ (SN)\text{---}Cu\text{---}(NS) \\ \mathbf{S_2} \end{array}$$

$$M\text{---}X\text{----}Cu + M'(NS)_2 \rightleftharpoons \begin{array}{c} M \quad X\text{----}Cu \\ | \quad | \\ (SN)\text{---}M'\text{---}(NS) \\ \mathbf{P_3} \end{array} \rightleftharpoons \begin{array}{c} M \quad X\text{---}M' \\ | \quad | \\ (SN)\text{---}Cu\text{---}(NS) \\ \mathbf{S_3} \end{array}$$

Their stabilities and specific structures are thought to be responsible for observed rate laws 6–8 as x, M, X, M′ and NS are varied [5–7,11].

$$\text{Rate} = k_6[\mathbf{B}][\mathbf{A}]^2 \tag{6}$$
$$\text{Rate} = \beta_1 k_5[\mathbf{B}][\mathbf{A}] \tag{7}$$
$$\text{Rate} = \beta_1 k_4[\mathbf{B}][\mathbf{A}]/(1 + \beta_1[\mathbf{A}]) \tag{8}$$

Rate law 6 suggests involvement of $\mathbf{B}\cdots(\mathbf{A})_2$ precursors with small β_1 in Eq. (3) [6,7]. Increasing the strength of interaction as P_1 becomes P_2 with particular reactants leads to second-order rate law 7 (with small β_1) and ultimately to first-order rate law 4 (with very large β_1) when structures P_3 can form [7,11]. Rate law 8 is the special case of rate laws 4 and 7 where β_1 is moderately large and measurable [4,5].

Targets containing X = Br tend to react with first-order rate law 4, which obscures variations of β_1 in reactions of a target family $\mathbf{A}$ with M′(NS)$_2$ reagents. However, a study of rate law variations in monotransmetalation reaction (1) with M = Ni(H$_2$O) and X = Cl indicates that β_1 is especially large at $x = 2$ and 3 with transmetalators Co(NS)$_2$, Zn(NS)$_2$ and Co(NS)$_3$ [4,5]. This suggests the involvement of target Ni–Cl–Cu edges in the formation of especially stable 1:1 precursors P_2 or P_3. Such interaction can direct specific replacement of copper(II) in targets $(\mu_4\text{-O})(\text{amine})_4\text{Cu}_{4-x}(\text{Ni(H}_2\text{O}))_x X_6$ with M′ [4,5].

Use of reactants $\mathbf{A}$ and $\mathbf{D}$ in Eq. (3) could lead to complexes $\mathbf{A}\cdot\mathbf{D}$ that cannot undergo metal exchange because the M′(NS)$_n$ stability order is $\mathbf{D} > \text{Ni(NS)}_2 > \text{Co(NS)}_2 > \text{Co(NS)}_3 > \text{Zn(NS)}_2$ [2]. These complexes are analogues of primary transmetalation products $\mathbf{C}\cdot\mathbf{D}$ and perhaps of precursors $\mathbf{B}\cdots\mathbf{A}$. Knowledge of their stability would improve our understanding of specific transmetalation. Stability of $\mathbf{C}\cdot\mathbf{D}$ determines whether the products of transmetalation reaction (1) are adduct $\mathbf{C}\cdot\mathbf{D}$ or separate entities.

Suppose the primary products of transmetalation reaction (1) are complexes $\mathbf{C}\cdot\mathbf{D}$ with different electronic spectra than those of discrete $\mathbf{C}$ and $\mathbf{D}$. We should observe reaction (9), where k_{-9} is the dissociation rate constant and $1/k_9$ is the instability constant of $\mathbf{C}\cdot\mathbf{D}$.

$$\mathbf{CD} \rightleftharpoons \mathbf{C} + \mathbf{D} \qquad k_{-9}, \; k_9 \tag{9}$$

No absorbance change will be seen if (a) equilibrium (9) lies well to the left; (b) dissociation of primary transmetalation product $\mathbf{C}\cdot\mathbf{D}$ with first-order rate constant k_{-9} is much faster than pseudo first-order transmetalation reaction (1); or (c) there is no difference between the absorption spectra of $\mathbf{C}\cdot\mathbf{D}$ and unassociated $\mathbf{D}$.

A single, exponential absorbance increase in reaction (1) [4–7], therefore, does not necessarily mean that separate entities $\mathbf{C}$ and $\mathbf{D}$ result from copper(II) transmetalation. This is an important point for the following reasons:

1) The existence of very stable complexes $\mathbf{C}\cdot\mathbf{D}$ will complicate isolation of desired pure products $\mathbf{C}$ [11].[3]
2) Some transmetalation systems proceed with first-order rate law 4, which indicates large β_1 in Eq. (3) [4–7] strong transmetalation precursors imply that there should be some strong product complexes $\mathbf{C}\cdot\mathbf{D}$ or $\mathbf{A}\cdot\mathbf{D}$.
3) Complexes $\mathbf{A}\cdot\mathbf{D}$ are reasonable analogues of precursors $\mathbf{A}\cdots\mathbf{B}$ that are frozen in time because they cannot undergo metal exchange. Comparison of the stabilities of $\mathbf{A}\cdots\mathbf{B}$ and $\mathbf{A}\cdot\mathbf{D}$ might give a better understanding of the origins of specific transmetalation.

The obvious way to investigate those possibilities is to mix excess $\mathbf{A}$ or $\mathbf{C}$ with $\mathbf{D}$ and monitor absorbance changes at fixed wavelength as a function of time. This already has been done with targets $L_2Cu_2X_2$ and reactants M′(NS)$_2$ [14]. Three systems were found to be governed by rate law 5, which indicates reversible adduct formation. The experimental values of k_4, k_5 and k_6 are collected in Tables 2–4, respectively.

In this work we have mixed various excess $\mathbf{A}$ with $\mathbf{D}$ and monitored absorbance changes near 600nm by stopped-flow spectrophotometry. We observed small (5–10%) absorbance decreases[4] in every system except one, which will be described separately. Complexes $\mathbf{A}\cdot\mathbf{D}$

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[3] Very poor behavior is observed in the separation of the products of $(\mu\text{-CO}_3)L_2Cu_2X_2$ transmetalation reactions by gel permeation chromatography. The targets are well-known to contain terminal halide [11]. This feature of $(\mu\text{-CO}_3)L_2Cu_2MX_2$ products LCuMX should stabilize LCuMX·D complexes. In the limit it would result in a single eluted band of LCuMX·D on attempted chromatographic separation.

[4] The absorbance changes were too small to allow the determination of accurate independent values of K_3.

Table 2
Kinetic data for first-order transmetalation systems

	Target	B	Solvent [a]	K_4 [b]	$\Delta H_4^{\ddagger}$ [c]	$\Delta S_4^{\ddagger}$ [d]	Ref., note
A. Kinetic data for transmetalation							
1	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Zn(NS)_2$ [e]	NB	27.5	29.0 ± 0.4	46 ± 3	[4], k_8
2	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Zn(NS)_2$	NB	8.0	17.0 ± 0.3	4 ± 3	[4], k_8
3	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Co(NS)_2$	NB	3.3	8.5 ± 0.3	-28 ± 3	[4], k_8
4	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Co(NS)_2$	NB	0.18	9.5 ± 0.3	-25 ± 3	[4], k_4
5	$N_4Cu(Ni(H_2O))_3Br_6O$	$Zn(NS)_2$	NB	7.3	14.7 ± 0.4	-5 ± 3	[4], k_4
6	$N_4Cu_2(Ni(H_2O))_2Cl_6O$	$Zn(NS)_2$	NB	4.2	21.1 ± 0.4	16 ± 3	[4], k_4
7	$py_4Cu_2(Ni(H_2O))_2Cl_6O$	$Zn(NS)_2$	NB	1.2	21.8 ± 0.4	18 ± 3	[4], k_4
8	$N_4Cu_4Br_6O$	$Zn(NS)_2$	NB	2.8	12.8 ± 0.4	-13 ± 3	[7], k_4
9	$N_4Cu_4Br_6O$	$Zn(NS)_2$	NB	0.85	17.0 ± 0.4	-1 ± 2	[7], k_4
10	$N_4Cu_4Br_6O$	$Co(NS)_2$	MC	0.52	18.0 ± 0.4	1 ± 2	[7], k_4
11	$N_4Cu_4Br_6O$	$Co(NS)_2$	MC	1.1	15.8 ± 0.4	-5 ± 2	[7], k_4
12	$(TEED)_2Cu_2Cl_2O$ [f]	$Co(NS)_2$	NB	0.027	20.0 ± 0.4	3 ± 3	[11], k_4
13	$(TEED)_2Cu_2Br_2O$	$Co(NS)_2$	NB	0.16	10.6 ± 0.4	-26 ± 4	[11], k_4
14	$(TEED)_2Cu_2Cl_2CO_3$	$Co(NS)_2$	NB	0.00039	25.6 ± 0.4	-17 ± 3	[11], k_4
15	$(TEED)_2Cu_2Cl_2CO_3$	$Zn(NS)_2$	NB	0.023	12.7 ± 0.3	-6 ± 3	[11], k_4
16	$(TEED)_2Cu_2Cl_2CO_3$	$Co(NS)_2$	NB	0.0046	17.1 ± 0.4	-11 ± 3	[11], k_4
17	$(TEED)_2Cu_2Br_2CO_3$	$Co(NS)_2$	NB	0.0040	9.4 ± 0.3	-38 ± 4	[11], k_4
B. Kinetic data for adduct formation							
1	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Cu(NS)_2$	NB	3.16	14.0 ± 0.3	-9 ± 3	this work, k_3
2	$N_4Cu_2(Ni(H_2O))_2Cl_6O$	$Cu(NS)_2$	NB	3.8	16.0 ± 0.4	1 ± 2	this work, k_3
C. Kinetic data for dissociation of adduct							
1	$N_4Cu_4Cl_6O$	$Cu(NS)_2$	NB	0.045	19.7 ± 0.4	1.3 ± 1	this work, k_{-3}
2	$N_4(Ni(H_2O))_4Cl_6O$	$Cu(NS)_2$	NB	0.056	19.4 ± 0.3	0.7 ± 1	this work, k_{-3}
3	$(TEED)_2Cu_2Cl_2O$	$Cu(NS)_2$	NB	0.93	13.3 ± 0.3	-14 ± 1	[12], k_{-3}
4	$(TEED)_2Cu_2Cl_2O$	$Cu(NS)_2$	NB	5.0	11.9 ± 0.4	-15 ± 2	[12], k_{-3}
1	$N_4Cu(Ni(H_2O))_3Cl_6O$	$Cu(NS)_2$	NB	3.16	14.0 ± 0.3	-9 ± 3	this work, k_3
2	$N_4Cu_2(Ni(H_2O))_2Cl_6O$	$Cu(NS)_2$	NB	3.8	16.0 ± 0.4	1 ± 2	this work, k_3

[a] NB, nitrobenzene; MC, methylene chloride.
[b] Units are s^{-1} at 23 °C (typical error $\pm 5\%$).
[c] Units are $kcal^{-1} mol^{-1}$.
[d] Units are $cal\ deg^{-1} mol^{-1}$ at 25 °C.
[e] NS, *S*-methyl benzylidenehydrazinecarbodithioate.
[f] TEED, *N,N,N′,N′*-tetraethylethylenediamine.

have electronic spectra that differ from that of D because of a change of copper(II) ligand environment on adduct formation.

The observed exponential absorbance decreases on adduct formation were accounted for by rate laws 4 or 5, depending on the reactants.

3.2. Adduct formation with rate law 5

The reactions of NCuCl and NNiCl with D are governed by rate law 5, which indicates reversible complex formation. Kinetic and equilibrium data are collected in Tables 2–4 and illustrated in Figs. 2 and 3. Linear plots like Fig. 3 indicates that rate law 5 governs these adduct formation reactions over the temperature range 14.0–33.0 °C in nitrobenzene.

3.3. First-order adduct formation reaction

The reactions NCu$_2$Ni$_2$Cl and NCuNi$_3$Cl with **D** are governed by first-order rate law 4. This is the first time

that adduct formation of polymetallic copper-containing targets has been found to have a first-order rate law. Kinetic data are collected in Table 3 and illustrated in Figs. 4 and 5. Linear plots like Fig. 5 indicate that rate law 4 governs these adduct formation reactions over the temperature range 12.0–40.0 °C in nitrobenzene.

3.4. Relationship between rate laws 4, 5 and 6–8 for transmetalation and adduct formation

Suppose adduct formation reaction (3) proceeds via the mechanism shown in Eq. (10). Here $\mathbf{A}\cdots\mathbf{D}$ is a 1:1 precursors with equilibrium constant β_1 and $\mathbf{A}\cdot\mathbf{D}$ is the adduct, Table 5. We will assume with considerable precedent that $\mathbf{A}\cdots\mathbf{D}$ equilibration is very rapid [4–7] compared to $\mathbf{A}\cdots\mathbf{D}\rightleftharpoons\mathbf{A}\cdot\mathbf{D}$ interconversion with k_3 and k_{-3}. The rate law predicted by this mechanism is Eq. (11). The overall equilibrium constant in reaction (10) is $K_4 = \beta_1 k_4/k_{-4}$, where $\mathbf{A}$ replaces $\mathbf{C}$ in equilibrium system 9.
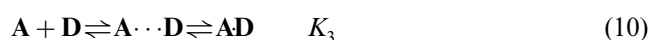
$$\mathbf{A} + \mathbf{D} \rightleftharpoons \mathbf{A}\cdots\mathbf{D} \rightleftharpoons \mathbf{AD} \qquad K_3 \qquad (10)$$

Table 3
Kinetic data for second-order transmatalation systems

	Target	B	Solvent [a]	K_5 [b]	$\Delta H_5^{\ddagger}$ [c]	$\Delta S_5^{\ddagger}$ [d]	Ref., note
1	$N_4Cu_3(Ni(H_2O))Cl_6O$	$Zn(NS)_2$	NB	10.0	12.2 ± 0.3	13 ± 3	[4]
2	$N_4(Ni(H_2O))_4Cl_6O$	$Zn(NS)_2$	NB	22.4	10.2 ± 0.4	-18 ± 3	[4]
3	$N_4Co_3CuCl_6O$	$Zn(NS)_2$	NB	5.5	12.5 ± 0.4	-13 ± 4	[4]
4	$N_4(Ni(H_2O))_4Cl_6O$	$Cu(NS)_2$	NB	47.7	13.0 ± 0.4	-7 ± 3	this work, $-k_f$
5	$N_4Cu_4Cl_6O$	$Cu(NS)_2$	NB	67.6	-0.3 ± 0.2	-51 ± 4	this work, $-k_f$
6	$(TEED)_2Cu_2Cl_2$ [e]	$Ni(NS)_2$	NB	17.8	20.4 ± 0.4	16 ± 3	[14]
7	$(TEED)_2Cu_2Br_2$	$Ni(NS)_2$	MC	55.0	20.2 ± 0.4	18 ± 3	[14]
8	$(TEED)_2Cu_2Br_2$	$Ni(NS)_2$	NB	6.0	26.2 ± 0.4	34 ± 3	[14]
9	$(TEED)_2Cu_2Br_2$	$Co(NS)_2$	NB	251	9.6 ± 0.4	-15 ± 3	[14]
10	$(TEED)_2Cu_2Cl_2$	$Co(NS)_2$	MC	530	9.5 ± 0.4	-14 ± 3	[14]
11	$(TEED)_2Cu_2Cl_2$	$Co(NS)_2$	NB	370	10.6 ± 0.123	-11 ± 3	[14]
12	$(TEED)_2Cu_2Br_2O$	$Ni(NS)_2$	NB	5.2	9.2 ± 0.3	-24 ± 4	[11]
13	$(TMPD)_2Cu_2Cl_2O$ [f]	$Ni(NS)_2$	NB	1.1	15.0 ± 0.3	-8 ± 3	[11]
14	$(TMPD)_2Cu_2Cl_2O$	$Co(NS)_2$	NB	18.0	12.7 ± 0.3	-10 ± 3	[11]
15	$(TEED)_2Cu_2Br_2CO_3$	$Co(NS)_2$	NB	4.5	8.8 ± 0.3	-26 ± 3	[11]
16	$(TMPD)_2Cu_2Br_2CO_3$	$Ni(NS)_2$	NB	0.63	13.2 ± 0.4	-15 ± 4	[11]
17	$(TMED)_2Cu_2Cl_2CO_3$ [g]	$Ni(NS)_2$	NB	2.4	15.3 ± 0.4	-5 ± 3	[11]

[a] NB, nitrobenzene; MC, methylene chloride.
[b] Units for k_5 or k_f are $M^{-1} s^{-1}$ at 21 °C (typical error $\pm 5\%$).
[c] Units are $kcal^{-1} mol^{-1}$.
[d] Units are $cal \ deg^{-1} \ mol^{-1}$ at 25 °C.
[e] TEED, N,N,N',N'-tetraethylethylenediamine.
[f] TMPED, N,N,N',N'-tetramethylpropanediamine.
[g] TMPED, N,N,N',N'-tetrapropylethylenediamine.

$$\text{Rate} = \beta_1 k_3[\mathbf{A}][\mathbf{D}]/(1 + \beta_1[\mathbf{A}]) + k_{-3} \quad (11)$$

Eq. (11) is Eq. (8) with the additional term k_{-3}. It is the desired relationship between rate laws 4–8 for irrever-

sible transmetalation (k_{-3} formally zero) and reversible adduct formation illustrated graphically in Fig. 6. Experimental rate laws 4 and 5 thus arise from large and small β_1 in system 10, respectively.

Table 4
Kinetic data for third-order systems

	Target	B	Solvent [a]	K_6 [b]	$\Delta H_6^{\ddagger}$ [c]	$\Delta S_6^{\ddagger}$ [d]	Ref., note
1	$(_4\text{-}O)N_4Cu_4Cl_6$	$Ni(NS)_2$	NB	16 200	20.0 ± 0.3	29 ± 3	[7]
2	$(_4\text{-}O)N_4Cu_4Br_6$	$Ni(NS)_2$	NB	250	24.0 ± 0.4	35 ± 3	[7]
3	$(_4\text{-}O)py_4Cu_4Cl_6$	$Ni(NS)_2$	NB	18 900	20.0 ± 0.4	30 ± 4	[7]
4	$(_4\text{-}O)N_4Cu_4Cl_6$	$Ni(NS)_2$	MC	97 000	16.5 ± 0.4	20 ± 3	[7]
5	$(_4\text{-}O)N_4Cu_4Cl_6$	$Co(NS)_2$	NB	860 000	20.0 ± 0.4	36 ± 4	[7]
6	$(_4\text{-}O)N_4Cu_4Cl_6$	$Co(NS)_2$	MC	340 000	19.0 ± 0.3	33 ± 3	[7]
7	$(_4\text{-}O)N_4Cu_4Cl_6$	$Zn(NS)_2$	NB	164 000	20.0 ± 0.3	33 ± 3	[7]
8	$(_4\text{-}O)N_4Cu_4Cl_6$	$Zn(NS)_2$	MC	475 000	14.0 ± 0.4	15 ± 3	[7]
9	$(_4\text{-}O)N_4Cu_4Cl_6$	$Hg(NS)_2$	NB	980 000	12.2 ± 0.3	11 ± 3	[8]
10	$(TEED)_2Cu_2Cl_2O$ [e]	$Co(NS)_2$	NB	85	14.5 ± 0.4	0.0 ± 3	[11]
11	$(TEED)_2Cu_2Cl_2CO_3$	$Co(NS)_2$	NB	1100	11.1 ± 0.4	-7 ± 3	[11]
12	$(TEED)_2Cu_2Br_2CO_3$	$Ni(NS)_2$	NB	1400	11.8 ± 0.4	-4 ± 4	[11]
13	$(TEED)_2Cu_2Cl_2O$ [f]	$Ni(NS)_2$	MC	46 000	8.4 ± 0.3	-9 ± 3	[12]
14	$(TEED)_2Cu_2Cl_2O$	$Ni(NS)_2$	NB	4000	8.9 ± 0.3	-6 ± 3	[12]
15	$(TEED)_2Cu_2Br_2$	$Ni(NS)_2$	MC	830	20.0 ± 0.3	23 ± 3	[12]
16	$(TPED)_2Cu_2Cl_2$ [f]	$Ni(NS)_2$	NB	23 000	13.4 ± 0.4	7 ± 4	[12]
17	$(_4-O)Cu(Ni(H_2O))_3Cl_6$	$Ni(NS)_2$	NB	355 0000	13.2 ± 0.4	17 ± 3	This work

[a] NB, nitrobenzene; MC, methylene chloride.
[b] Units are $M^{-1} s^{-1}$ at 21 °C.
[c] Units are $kcal^{-1} mol^{-1}$.
[d] Units are $cal \ deg^{-1} \ mol^{-1}$ at 25 °C.
[e] TEED, N,N,N',N'-tetraethylethylenediamine.
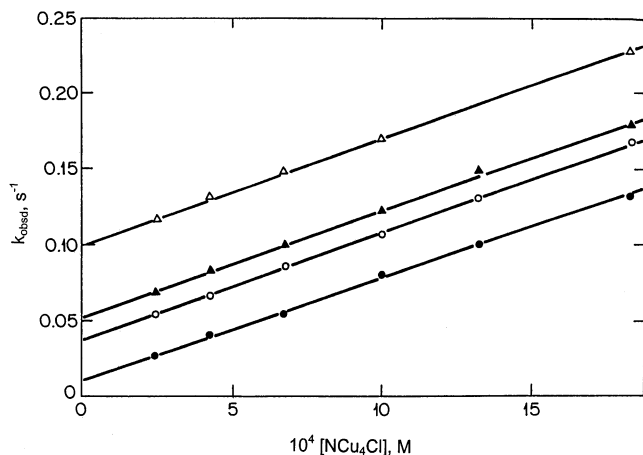[f] TPED, N,N,N',N'-tetrapropylethylenediamine.

Fig. 2. Plots of k_{obsd} (s^{-1}) vs. [NCu$_4$Cl] (M) for the reversible reaction of excess A ($x = 0$) with D in nitrobenzene at the following temperatures. ●, 14.0 °C; ○, 20.0 °C; ▲, 27.0 °C; △, 33.0 °C.
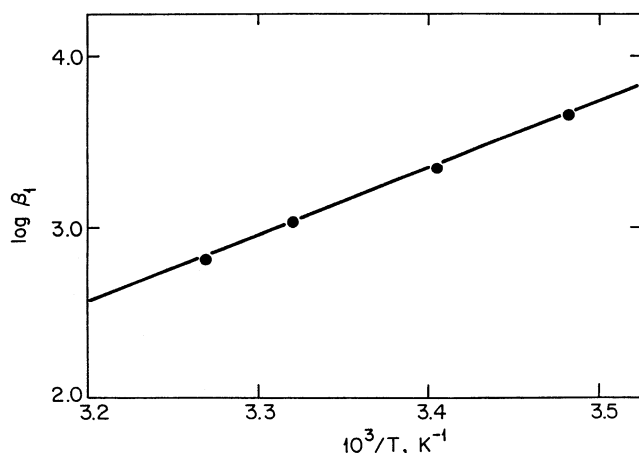

Fig. 3. Plot of log β_1 (M^{-1}) vs. $1/T$ (K^{-1}) for the reversible reaction of excess A ($x = 0$) with D in nitrobenzene.
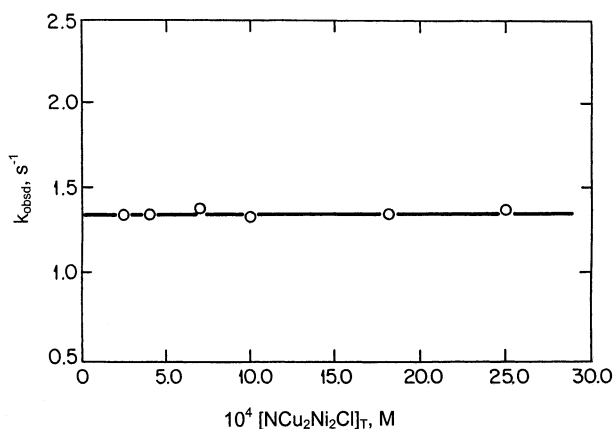

Fig. 4. Plot of k_{obsd} (s^{-1}) vs. [NCu$_2$Ni$_2$Cl] (M) for the reaction of excess A ($x = 2$) with D in nitrobenzene.

We interpret rate law 3 to indicate large β_1 and K_3 in mechanism 10.[5] Transmetalation and adduct formation reactions with rate law 4 involve especially 'sticky' interactions between particular targets A and Co(NS)$_2$, Zn(NS)$_2$ and D (see below).

We interpret rate law 5 to indicate small β_1 in equilibrium reaction (10). The targets of this section thus form weaker precursors A···D and adduct A·D than do those that form complexes A·D with rate law 4.

3.5. The nature of target stickiness

Recently, Davies and coworkers [4–7] reported on rate law 8 for the monotransmetalation of NCuNi$_3$Cl by reagents Co(NS)$_2$ and Zn(NS)$_2$ and rate law 4 or 5 for the corresponding reactions of other (μ_4-O)(amine)$_4$Cu$_{4-x}$M$_x$Cl$_6$ targets. We concluded from these rate law differences that NCuCo$_3$Cl and NCu$_{4-a}$Ni$_x$Cl Cl are 'stickier' than copper(II) target NCuCl, which reacts with Co(NS)$_2$ and Zn(NS)$_2$ with third-order rate law 6. Stickiness generally increases on replacing X = Cl with Br in these targets [4–7]. The stickiness order NCu$_{4-x}$Ni$_x$Cl > NCuCo$_3$Cl > NCuCl was interpreted to indicate bond strength decreases in the order Cu–Cl > Co–Cl > Ni–Cl in targets A. Targets NCu$_{4-x}$-Ni$_x$Cl are stickiest when $x = 2$ and 3, apparently because this maximizes the number of Ni–Cl edges that are site of precursor formation [5].

The steps leading to proposed structures P$_1$–P$_3$ involve M–X bond breaking, M′–X bond formation and S–Cu bonding. The strength of resulting interactions is expected to be a sensitive function of M, X, M′ and NS. This is demonstrated by correlation of activation parameters for first-order transmetalation, complexation and isomerization of polynuclear copper-containing complexes [4]. However, progressively closer interaction between the reactants should lead to the most negative entropy of formation for precursors with structures like P$_3$ (see below).

Use of reagent D is a good test for the origins of stickiness because this reagent is much less likely to open its NS chelate rings on precursors formation than is thermodynamically weaker [2] complex Zn(NS)$_2$. However, Table 6 shows that Zn(NS)$_2$ and D both form the stickiest precursors at $x = 2$ when the target is (amine)$_4$Cu$_{4-x}$Ni$_x$Cl. The opening of M′(NS) chelate rings

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[5] Stickiness is a useful qualitative measure of the strength of precursor interactions which may be guaged in any particular transmetalation system from the rate law. Marked stickiness (large β_1) is indicated by rate laws 5 and 6. Reversion of rate law 6 to rate law 5 requires β_1[A] > 10 at the lowest experimental [A], which in our systems is 2.5×10^{-4} M. This gives $\beta_1 > 4 \times 10^{-4}$ M^{-1} at a comparison temperature of 23 °C, which is at least ten times greater than the largest known 3,4] values of β_1 (Table 3). Rate law 5 thus indicates stickier interaction than rate law 6.
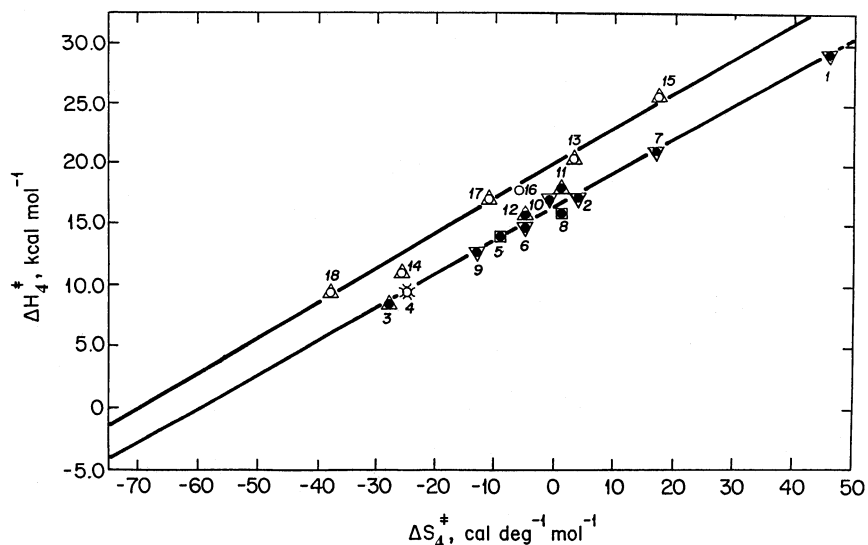
Fig. 5. Plots of $\Delta H_4^{\#}$ (kcal mol^{-1}) vs. $\Delta S_4^{\#}$ (cal deg^{-1} mol^{-1}) for the following first-order rate systems. (i) The numbers from 1 to 6 refer to the reactions of NCuNi$_3$Cl with Zn(NS)$_2$, ▼; Co(NS)$_2$, ▲; Co(NS)$_3$, ○; Cu(NS)$_2$, ■. (ii) The numbers from 7 to 8 refer to the reactions of NCu$_2$Ni$_3$Cl with Zn(NS)$_2$, ▼; Cu(NS)$_2$, ■. (iii) The numbers from 9 to 12 refer to the reactions of NCuBr with Zn(NS)$_2$, ▼; Co(NS)$_2$, ▲ [11]. (iv) The numbers from 13 to 18 refer to the reactions of L$_2$Cu$_2$X$_2$Y with Co(NS)$_2$, ▼; Zn(NS)$_2$, ▼ [11].

is thus not necessary in the formation of sticky precursors A···Zn(NS)$_2$. This identifies the M–X–Cu edges of (amine)Cu$_{4-x}$M$_x$ targets as the primary location of sticky precursors interactions. Nevertheless, the existence of two forms of 1:1 precursors in the NCuNi$_3$Cl/Zn(NS)$_2$ system is an indication that endothermic M′(NS) chelate ring opening can occur at ambient temperatures when M′(NS)$_2$ is a relatively weak adduct [5].

3.6. Relationship between precursors stabilities and second-order rate parameters

The relationships in Fig. 6 indicate that the observed second-order rate constants for transmetalation and adduct formation of A with M′(NS)$_2$ and D, respec-

tively, are given by $k_4 = \beta_1 k_3$. This means that $\Delta H_4^{\ddagger} = \Delta H_{\beta 1} + \Delta H_5^{\ddagger}$ and $\Delta S_4^{\ddagger} = \Delta S_{\beta 1} + \Delta S_5^{\ddagger}$. Previously, Ali and Davies used $\Delta S_5^{\ddagger} = -25$ cal deg^{-1}mol^{-1} for other 1:1 adduct-forming systems [15] in attempts to estimate $\Delta H_5^{\ddagger}$. This assumption will now be examined in detail and an attempt will be made to assign structure types to the precursors and activated complexes for transmetalation and adduct formation.

3.7. Classification of precursor and complex structures

Fig. 7 shows a plot of $\Delta H_{\beta 1}$ versus $\Delta S_{\beta 1}$ for eight transmetalation and adduct forming systems. These data sets are correlated by line A, which suggests the species involved have common features. Species with $\Delta S_{\beta 1} > 5$ cal deg^{-1}mol^{-1} are assigned structure P$_1$

Table 5
Equilibrium data for rate laws 8 and 11

Target	B	Solvent [a]	β_1 [b]	ΔH_1 [c]	ΔS_1 [d]	Ref., note
A. Transmetalation						
N$_4$Cu(Ni(H$_2$O))$_3$Cl$_6$O	Zn(NS)$_2$ [f]	NB	250	-31.0 ± 0.4	-94 ± 4	[4]
N$_4$Cu(Ni(H$_2$O))$_3$Cl$_6$O	Zn(NS)$_2$	NB	1400	-0.81 ± 0.2	-41 ± 4	[4]
N$_4$Cu(Ni(H$_2$O))$_3$Cl$_6$O	Co(NS)$_2$	NB	3300	-2.2 ± 0.3	-50 ± 4	[4]
B. Adduct formation						
N$_4$Cu$_4$Cl$_6$O	Cu(NS)$_2$	NB	1780	-20.0 ± 0.4	-53 ± 3	this work
N$_4$(Ni(H$_2$O))$_4$Cl$_6$O	Cu(NS)$_2$	NB	1260	-6.4 ± 0.2	-8 ± 2	this work
(TEED)$_2$Cu$_2$Cl$_2$ [e]	Co(NS)$_2$	NB	400	-2.7 ± 0.3	-3 ± 2	[12]
(TEED)$_2$Cu$_2$Cl$_2$	Cu(NS$_2$	NB	350	-0.6 ± 0.2	-10 ± 2	[12]

[a] NB, nitrobenzene; MC, methylenechloride.
[b] Units are M^{-1} s^{-1} at 23 °C (typical error ±5%).
[c] Units are cal^{-1} mol^{-1}.
[d] Units are cal deg^{-1} mol^{-1} at 25 °C.
[e] TEED, N,N,N′,N′-tetraethylethylenediamine.
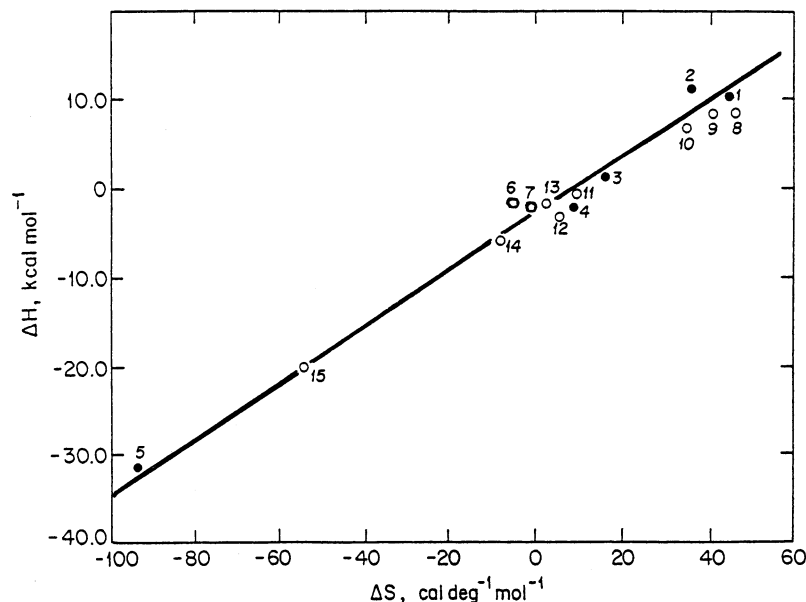[f] NS, S-methyl benzylidenehydrazinecarbodithioate.

Fig. 6. Plot of enthalpy vs. entropy changes for precursor (filled circles squares) and overall successor adduct formation (○). The data are taken from Table 5 of this paper and Ref. [4] (targets $NCu_{4-x}Ni_xCl$), Table 2 of Ref. [15] (target, $Cu(ac.ac.)_2$), Table 5 of Ref. [12] (target $L_2Cu_2X_2$) and Table 3 of Ref. [19] (target E). The parameters refer to Eq. (11), the solvent is either methylene chloride or nitrobenzene and the temperature is 25 °C.

Table 6
Sticky interactions in transmetalation and adduct formation reaction

Target	Other reactant	Result/ratio [a]	Basis
NCuCl	$Zn(NS)_2$	w; 1	rate law 3
	$Cu(NS)_2$	ms; 1	rate law 7
NCu_3NiCl	$Zn(NS)_2$	w; 1	rate law 4
NCu_2Ni_2Cl	$Zn(NS)_2$	s; 1	rate law 5
	$Cu(NS)_2$	s; 1	rate law 5
$NCuNi_3Cl$	$Zn(NS)_2$	ms; 1	rate law 6
	$Cu(NS)_2$	s; 1	rate law 5
NNiCl	$Zn(NS)_2$	w; 1	rate law 4
	$Cu(NS)_2$	ms; 1	rate law 7

[a] w, weak; ms, moderately strong; s, strong.

because entries 6–8 of Table 3 involve copper(I) targets $L_2Cu_2X_2$ that do not contain terminal halide [13]. Systems with $-40 < \Delta S_{\beta 1} < 5$ cal deg^{-1}mol^{-1} are assigned structure P_2 because availability halide for precursors construction should lead to lower $\Delta S_{\beta 1}$. The average $\Delta S_{\beta 1} = -23$ cal deg^{-1}mol^{-1} for this segment of line A is similar to measured $\Delta S_{\beta 1}$ for single point adduct formation in $Ni(NS)_2 \cdot py$ systems [16]. Precursors and complexes with $\Delta S_{\beta 1} < -40$ cal deg^{-1}mol^{-1} are assigned structure P_3, which has more than one point of interaction and should, therefore, be more ordered.

3.8. Classification of activated complexes for second–order systems

Line B of Fig. 7 shows that the activation parameters $\Delta H_{\beta 1}^{\ddagger}$ and $\Delta S_{\beta 1}^{\ddagger}$ for all the second-order transmetalation

and adduct formation reactions in Table 3 are strongly correlated. The fact that lines A and B of Fig. 7 are parallel suggests that $\Delta H_4^{\ddagger}$, $\Delta S_4^{\ddagger}$, $\Delta H_{\beta 1}$ and $\Delta S_{\beta 1}$ have common structural origins. The vertical distance between any two points on line A and B represents $\Delta H_5^{\ddagger}$ for conversion of a particular precursors to a particular activated complex for transmetalation or adduct formation. The fact $\beta_1 < 10^3$ M^{-1} in the second-order systems of Table 3 from unfavorable $\Delta H_{\beta 1}$ and $\Delta S_{\beta 1}$ for particular reactant combination.

We have segmented lines A and B of Fig. 7 on the basis of the measured activation entropies. This assignment seems for reactions (12)–(17) of Table 3, all of which involve $L_2Cu_2X_2Y$ targets with terminal chloride [11]. The segmentation suggests that systems 6–8 of Table 3 involve activated complexes like P_1, with no clear examples of activated complexes like P_3. Fig. 7 suggests that systems involving first-order rate-determining steps $P_1 \rightarrow S_1$ and $P_2 \rightarrow S_2$ would have $\Delta H_5^{\ddagger} = 20$ kcal mol^{-1}, which is close to the value for known first-order systems [6]. On the other hand, rate–determining steps $P_1 \rightarrow S_2$ would have $\Delta H_5^{\ddagger}$ averaging about 10 kcalmol^{-1} as observed for entries 8–10 and 12 in Table 3. Finally, we predict that conversion $P_3 \rightarrow S_1$ would have prohibitively large $\Delta H_5^{\ddagger}$ and that conversion $P_1 \rightarrow S_3$ would have $\Delta H_5^{\ddagger}$ zero or negative, which makes no chemical sense.

The upshot of this discussion is that the measured activation enthalpies $\Delta H_5^{\ddagger}$ and $\Delta H_4^{\ddagger}$ for first- and second-order transmetalation and adduct formation reactions are given by $\Delta H_4^{\ddagger} = \Delta H_{\beta 1} + \Delta H_5^{\ddagger}$. The activation enthalpies for second-order systems are accounted for by
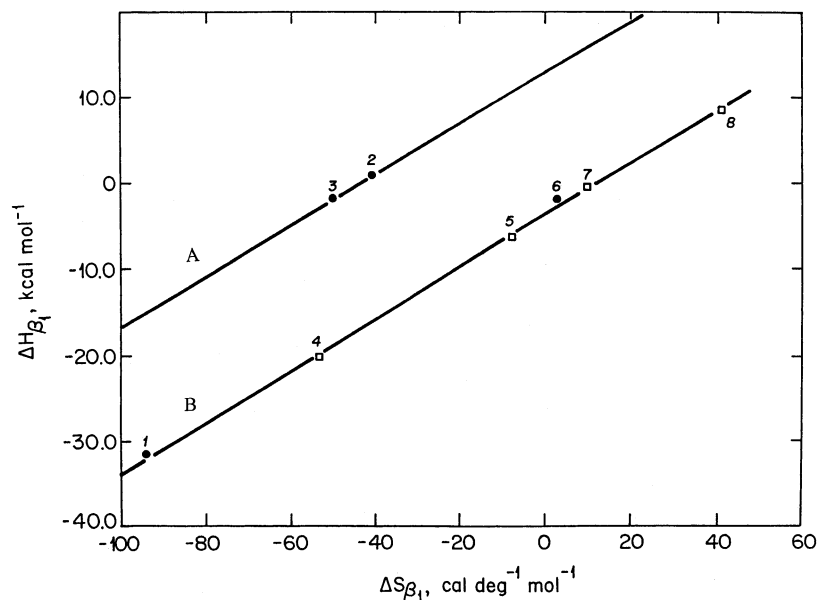
Fig. 7. Plots of $\Delta H_{\beta 1}^{\#}$ (kcal mol^{-1}) vs. $\Delta S_{\beta 1}^{\#}$ (cal deg^{-1} mol^{-1}) for the following system. (1) NCuNi$_3$Cl with Zn(NS)$_2$ in nitrobenzene at low temperature. (2) NCuNi$_3$Cl with Zn(NS)$_2$ in nitrobenzene at high temperature. (3) NCuNi$_3$Cl with Co(NS)$_2$ in nitrobenzene. (4) NCu$_4$Cl with Cu(NS)$_2$ in nitrobenzene. (5) NNi$_4$Cl with Cu(NS)$_2$ in nitrobenzene. (6) (TEED)$_2$Cu$_2$Cl$_2$ with Co(NS)$_2$ in nitrobenzene. (7) (TEED)$_2$Cu$_2$Cl$_2$ with Cu(NS)$_2$ in nitrobenzene; here, NS is S-methylbenzylidenehydrazineacrbodithioate. (8) (TEED)$_2$Cu$_2$Br$_2$ with Cu(NS)$_2$ in nitrobenzene; here, NS is S-methylbenzylidenehydrazineacrbodithioate.

different rate–determining steps $P_m \rightarrow S_n$, where m and n are the same or different. Combinations $m = n = 1$, $m = 1$ with $n = 2$ and $m = n = 2$ appear to reconcile the majority of the data in Table 3.

Acknowledgements

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