overall charge of 2+. Furthermore, these values are in excellent agreement with those reported for solvolysis (solvent exchange) of $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$, in which case we are also dealing with a neutral leaving group and an overall charge of 2+. These values suggest that there must be an additional negative contribution toward ΔV^* when the leaving group is a 1– or a 2– species. This negative component most probably originates from changes in dipole interaction when the square-bipyramidal transition state, in which the dien ligand most probably occupies the trigonal plane. This component will depend on the size and nature (especially charge) of the leaving group X. In addition, such volume differences may be more significant in the trigonal-bipyramidal transition state than in the square-planar ground state. It then follows that a ΔV^* of -3 cm^3 mol^{-1} could present the intrinsic component for the limiting associative attack of a water molecule on a 2+-charged square-planar complex with neutral ligands. The additional -9 cm^3 mol^{-1} usually observed for solvolysis reactions of 1+ and neutral Pd(II) complexes must then be due to solvational effects resulting from the described dipole interactions. The intrinsic component of -3 cm^3 mol^{-1} is significantly smaller than that observed and expected for associative solvolysis of octahedral complexes.[19,20] This is quite understandable since the geometry of the square-planar complex is such that the entering solvent molecule may be close to the vacant coordination site (i.e. above or below the plane in the second coordination sphere), such that relatively small volume changes are observed. Futhermore, structural changes from tetragonal pyramidal to trigonal bipyramidal are expected to cause an increase in volume that will counterbalance the intrinsic volume decrease due to bond formation.

We conclude that a limiting associative mechanism can accommodate all the data in Table I, and a ΔV^* value of -3 cm^3 mol^{-1} could represent the intrinsic component for the associative attack of a water molecule on a square-planar complex with neutral ligands. If deviations do occur, we expect these to result from a changeover from limiting A to A, rather than from limiting A to I_a as suggested before.[1] Further investigations to clarify this point are presently under way in our laboratories.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and a gift of $PdCl_2$ from Heraeus GmbH, Hanau.

Registry No. $Pd(MeEt_4dien)NH_3^{2+}$, 103904-37-6; $Pd(MeEt_4dien)C_2O_4$, 103932-99-6; $Pd(MeEt_4dien)Cl^+$, 46848-25-3; $Pd(MeEt_4dien)I^+$, 58619-25-3; $Pd(MeEt_4dien)Br^+$, 58619-24-2; $Pd(MeEt_4dien)py^{2+}$, 91606-31-4; $Pd(Et_5dien)Cl^+$, 70472-44-5.

Supplementary Material Available: Table A, k_{obsd} as a function of X, Y, ionic strength, temperature, and pressure for the reaction $Pd(R_5dien)X^{n+} + Y \rightarrow Pd(R_5dien)Y^{n+} + X$ (4 pages). Ordering information is given on any current masthead page.

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Transmetalation of Tetranuclear Copper Complexes. 9. Stoichiometry and Kinetics of Transmetalation of $(\mu_4\text{-}O)[NCu]_4X_6$ Complexes by $M(NS)_2$ Reagents in Aprotic Solvents

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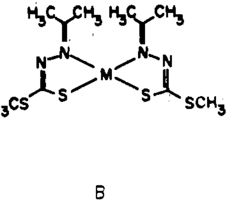
Tetranuclear copper(II) complexes $(\mu_4\text{-}O)[(DENC)Cu]_4X_6$ (A; DENC = *N,N*-diethylnicotinamide; X = Cl, Br) are stoichiometrically transmetalated by 1 mol of structurally characterized $M(NS)_2$ reagents (NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base; M = Co, Ni, Zn) in aprotic solvents. The chromatographically isolated products are equimolar tetranuclear $(\mu_4\text{-}O)[(DENC)_4Cu_3M(H_2O)]X_6$ and $Cu(NS)_2$. Reactants A and products $(\mu_4\text{-}O)[(DENC)_4Cu_3M(H_2O)]X_6$ have electronic spectral features at 775 and 850 nm. The rate laws for reactions of excess A with $M(NS)_2$ in methylene chloride and nitrobenzene depend on X, M, and the structure of the NS ligand. The proposed mechanisms contain common $\overline{Cu\text{–}X\text{–}M\text{–}S}$ rings that facilitate metal replacement in A; however, metal replacement apparently is not rate-determining in the majority of the 18 systems investigated.

Introduction

Our previous work demonstrates that one can make polynuclear copper complexes from commonly available materials and then replace their copper centers with different metals derived from (hydrazinecarbodithioato)metal reagents $M(NS)_n$.[2-9] Attractive features of these transmetalation reactions are that they proceed under mild conditions in aprotic solvents and that they are stoichiometric, stepwise processes because of the high thermodynamic stability of easily separated Cu(NS) and $Cu(NS)_2$ coproducts.

Among the wide variety of new, polynuclear products is the series $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xX_6$, obtained as discrete tetranuclear products by stoichiometric transmetalation of $(\mu_4\text{-}O)[NCu]_4X_6$ complexes A with x mol of reagents B and C (M = Ni), eq 1. Here, N is monodentate pyridine (py), *N,N*-diethylnicotinamide (DENC), or ethyl nicotinate (ENCA), x is 1–4, and X is Cl or Br. One water molecule is incorporated with each new nickel center during product isolation.[3-5,8]



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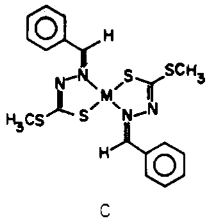

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$$(\mu_4\text{-}O)[NCu]X_6 + x(\text{B or C, M = Ni}) \rightarrow (\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xX_6 + x(\text{B or C, M = Cu}) \quad (1)$$

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(1) (a) Northeastern University. (b) Alexandria University.

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Table I. Analytical, Cryoscopic, and Spectral Data for $(\mu_4\text{-O})N_4Cu_3M(H_2O)X_6$ Products of Transmetalation[a]

product	% C	% H	% N	% Cu	M[b]	M_r[c]	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[d]	ν_{M-O}, cm^{-1}
$N_4Cu_3Ni(H_2O)Cl_6O$[e]	40.0 (39.7)	4.9 (4.8)	8.9 (9.3)	16.3 (15.9)	4.6 (5.0)	1240 ± 20 (1208)	850 (1160), 775 (1030)	495
$N_4Cu_3Ni(H_2O)Br_6O$[e]	32.5 (32.5)	4.0 (3.9)	7.7 (7.6)	14.1 (12.9)	3.9 (4.0)	1500 ± 20 (1475)	850 (1700), 775 (1590)	420
$N_4Cu_3Co(H_2O)Cl_6O$	39.3 (39.7)	4.5 (4.8)	9.8 (9.4)	16.3 (15.8)	4.6 (4.9)	1230 ± 20 (1208)	850 (1110), 775 (1000)	510
$N_4Cu_3Co(H_2O)Br_6O$	33.0 (32.6)	4.0 (4.0)	7.7 (7.6)	13.5 (12.9)	3.1 (3.9)	1500 ± 20 (1475)	850 (1945), 775 (1750)	415
$N_4Cu_3Zn(H_2O)Cl_6O$	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)	500
$N_4Cu_3Zn(H_2O)Br_6O$	32.4 (32.4)	3.9 (3.9)	7.7 (7.6)	12.6 (12.8)	3.4 (4.4)	1510 ± 20 (1482)	850 (1460), 775 (1340)	410

[a] N = DENC; calculated values in parentheses. [b] M = Co, Ni, or Zn. [c] In nitrobenzene at (3–5) × 10^{-2} *m*. [d] In nitrobenzene. [e] Data from ref 5.

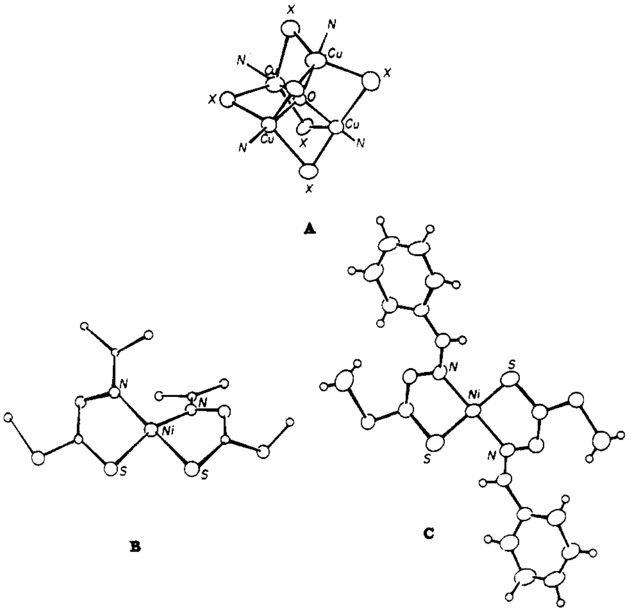

Figure 1. Core structure of reactants A[3] and molecular structures of B[10] and C[11] (M = Ni).

Our previous paper[5] reported that stoichiometric transmetalation reactions 2 occur when complexes A react with 1 mol of reagents

$$A + B \text{ or } C\ (M = Ni) \rightarrow (\mu_4\text{-O})[(DENC)_4Cu_3M(H_2O)]X_6\ (M = Ni) + \underset{D}{} \quad B \text{ or } C\ (M = Cu) \qquad (2)$$

B or C (M = Ni) in aprotic solvents. We studied the kinetics with excess A to ensure that only one copper center of A is replaced. Although D was obtained with either B or C (M = Ni) as transmetalator, the rate laws were third and second order, respectively. Known molecular structures for A,[2-4] B (M = Ni),[10] and C (M = Ni)[11] (Figure 1) were used to account for the different rate laws and to suggest likely rate-determining steps.[5]

Recently, we succeeded in crystallizing B (M = Co and Zn) and C (M = Zn) and found them to be tetrahedral.[12] Since B (M = Ni) is a flattened tetrahedron with *cis*-carbothioate sulfur[10] while C is a trans square-planar molecule,[11] we have investigated reaction 2 with B (M = Co or Zn) and C (M = Zn) in methylene chloride and nitrobenzene to see if geometrical effects are important in determining transmetalation products, kinetics, and mechanisms. We have isolated products D (M = Co or Zn) and B or C (M = Cu) and find that the transmetalation rate laws depend on X, M, and the structure of the NS ligand. Our proposed mechanisms are based on common $\overline{\mathrm{Cu{-}X{-}M{-}S}}$ rings that facilitate copper replacement in A.[5] However, consideration of the observed activation parameters indicates that copper replacement is not rate-determining in the majority of the 18 systems investigated.

Experimental Section

Materials and Measurements. Our previous work[2-9,12] details all the materials, procedures, analyses, and measurements used here. The glass-quartz stopped-flow spectrophotometer[5] was updated by interfacing to a Digital Equipment PRO-350 computer with advanced acquisition, processing, graphics, and storage capabilities.[13] All kinetic measurements were conducted with A in sufficient excess to ensure pseudo-first-order conditions: $10^4[A]_0 = 5.0\text{–}30.0$ M (upper limit set by solubility); $[B]_0$ or $[C]_0 = (2\text{–}5) \times 10^{-5}$ M (lower limit set by the signal/noise ratio of reaction traces). Product formation was monitored between 550 and 610 nm, and temperature was controlled to ±0.05 °C in the range 4.8–47.9 °C.

Results and Discussion

Product Identification. Analytical and cryoscopic data in Table I refer to the products of equimolar reactions 2 in methylene chloride, which were isolated by gel permeation chromatography (methylene chloride eluant).[2] All the reactions are quantitative, as expected for copper(II) reactants containing μ_4-oxo groups.[2-5,8] Each product is molecular $(\mu_4\text{-O})[(DENC)_4Cu_3M(H_2O)]X_6$ in nitrobenzene, which corresponds to 5-coordinate copper(II) and 6-coordinate M centers.[4-8]

Electronic spectra are summarized in Table I. Each near-infrared spectrum contains a maximum at 850 nm and a shoulder at 775 nm. These spectra are characteristic of trigonal-bipyramidal copper(II) centers with three equatorial halogen atoms.[14] The presence of a central μ_4-oxo group in all these complexes stabilizes the same copper(II) geometries when one copper is replaced by M.[8] Since none of the M centers absorb appreciably between 775 and 850 nm, any effect of M on the molar absorptivities of copper(II) must be predominantly electronic.

Molar absorptivities of $(\mu_4\text{-O})(DENC)_4Cu_3M(H_2O)Cl_6$ are invariant with M and about 75% of those for $(\mu_4\text{-O})(DENC)_4Cu_4Cl_6$. By contrast, the molar absorptivities of $(\mu_4\text{-O})[(DENC)Cu_3M(H_2O)]Br_6$ complexes at 850 nm are 90, 80, and 70% of those for $(\mu_4\text{-O})[(DENC)Cu]_4Br_6$ for M = Co, Ni, and Zn, respectively, and decrease with the number of electrons in M.[15]

Kinetics of Reactions 2. Plots of ln $(A_\infty - A_t)$ vs. time, where A_t is the absorbance at time *t*, were linear to at least 4 half-lives in all systems where $[A]_0 >> [B]_0$ or $[C]_0$ (Figure 2), indicating a first-order dependence of transmetalation rates on [B] and [C] and no detectable reaction intermediates.[5] Checks of absorbances immediately after reactant mixing gave no spectrophotometric evidence for reaction precursors at 550–610 nm. The pseudo-first-order rate constants, k_{obsd}, were measured as a function of N and X in A at fixed temperature, monitoring wavelength, M

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[15] One interpretation of the spectral data is that cobalt(II) and zinc(II), respectively, promote and quench electronic coupling, through μ_2-Br groups, between copper(II) centers in $(\mu_4\text{-O})[(DENC)_4Cu_3M(H_2O)]Br_6$ complexes.

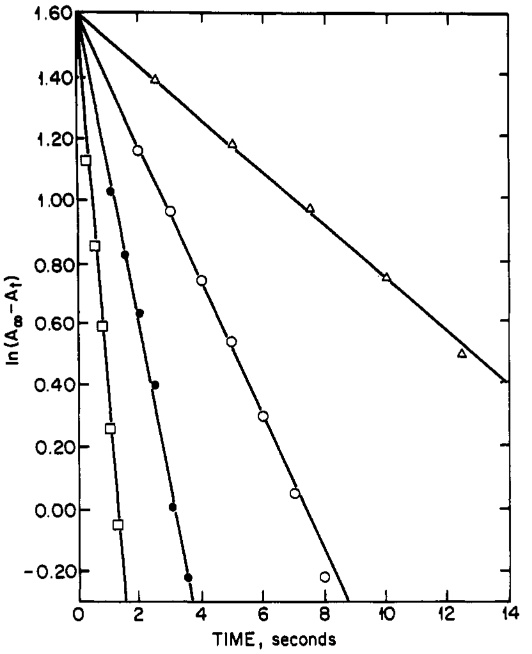

Figure 2. First-order plots in the reactions of A (X = Cl) with B (M = Ni) in methylene chloride at the following temperatures (°C): 7.3, △; 13.8, ○; 22.3, ●; 32.9, □.

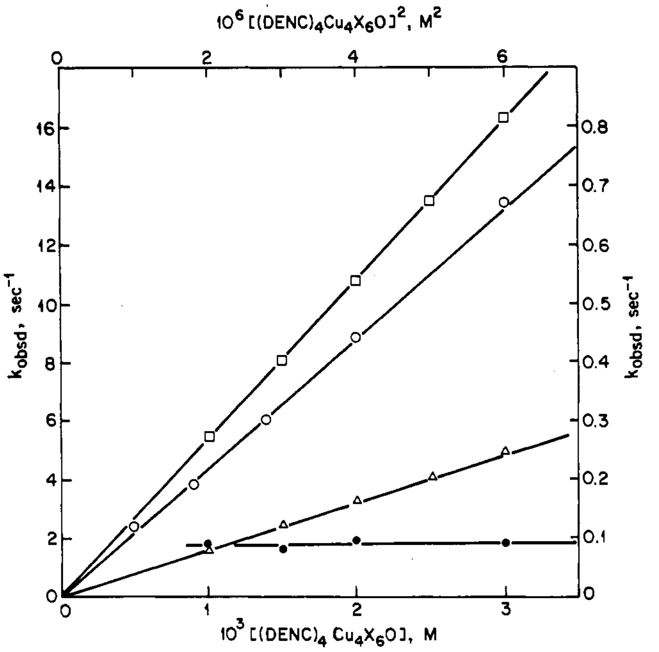

Figure 3. Plots of k_{obsd} vs. $[A]_0^n$ in the following systems in nitrobenzene. Left and bottom scales: A (X = Br) with B (M = Zn) (rate law 4) at 13.9 °C, ●; A (X = Cl) with C (M = Zn) (rate law 5) at 14.5 °C, □; A (X = Br) with C (M = Zn) (rate law 5) at 14.5 °C, △. Right and top scales: A (X = Cl) with B (M = Zn) (rate law 3) at 17.8 °C, ○.

Table III. Kinetic Data for Rate Laws 3–5

(a) Rate Law 3

X in A	reagent, M	solvent[a]	k_3[b]	$\Delta H_3^{\ddagger}$[c]	$\Delta S_3^{\ddagger}$[d]
Cl[e]	B, Ni	N	16200	20.0 ± 0.3	29 ± 3
Br[e]	B, Ni	N	250	24.0 ± 0.4	35 ± 3
Cl[e,f]	B, Ni	N	18900	20.4 ± 0.4	30 ± 3
Cl	B, Ni	M	97000	16.5 ± 0.4	20 ± 3
Cl	B, Co	N	860000	20.0 ± 0.4	36 ± 3
Cl	B, Co	M	340000	19.5 ± 0.4	33 ± 3
Cl	B, Zn	N	164000	20.0 ± 0.3	33 ± 3
Cl	B, Zn	M	475000	14.0 ± 0.4	15 ± 3

(b) Rate Law 4

X in A	reagent, M	solvent[a]	k_4[g]	$\Delta H_4^{\ddagger}$[c]	$\Delta S_4^{\ddagger}$[d]
Br	B, Zn	N	2.8	12.8 ± 0.4	−(13 ± 2)
Br	B, Zn	M	0.85	17.0 ± 0.4	−(1 ± 2)
Br	B, Co	M	0.52	18.0 ± 0.4	1 ± 2
Br	B, Co	M	1.1	15.8 ± 0.4	−(5 ± 2)

(c) Rate Law 5

X in A	reagent, M	solvent[a]	k_5[h]	$\Delta H_5^{\ddagger}$[c]	$\Delta S_5^{\ddagger}$[d]
Cl[e]	C, Ni	N	12.6	4.2 ± 0.3	−(38 ± 4)
Cl	C, Ni	M	3.8	4.8 ± 0.3	−(39 ± 3)
Cl	C, Zn	N	8700	8.5 ± 0.3	−(12 ± 2)
Br	C, Zn	N	3900	21.2 ± 0.4	33 ± 3
Cl	C, Zn	M	2100	9.7 ± 0.3	−(11 ± 2)
Br	C, Zn	M	4000	17.7 ± 0.3	18 ± 3

[a] N = nitrobenzene; M = methylene chloride. [b] Units are M^{-2} s^{-1} at 21 °C. [c] Units are kcal mol^{-1}; error shown is one standard deviation. [d] Units are cal deg^{-1} mol^{-1} at 25 °C; error shown is one standard deviation. [e] Data are from ref 5. [f] Ligand in A is py; all others have DENC as ligand. [g] Units are s^{-1} at 21 °C. [h] Units are M^{-1} s^{-1} at 21 °C.

in B or C, and solvent to establish rate laws 3–5, respectively. These rate laws are illustrated in Figure 3 and data are collected in Tables II[16] and III.

$$d[Cu(NS)_2]/dt = k_3[B][A]^2 \tag{3}$$

$$d[Cu(NS)_2]/dt = k_4[B] \tag{4}$$

$$d[Cu(NS)_2]/dt = k_5[C][A] \tag{5}$$

Features of the Kinetic Data. Rate Law 3. Third-order rate law 3 was observed previously in reactions 2 of A (N = py or DENC, X = Cl or Br) with B (M = Ni).[5] Table III and Figure 3 show that this rate law also is obeyed with B (M = Co or Zn) and X = Cl, but not Br (see below). The third-order concentration dependence strongly suggests that k_3 is composite (see below). Observed entropies of activation, $\Delta S_3^{\ddagger}$, are all distinctly positive (Table III). A linear plot of $\Delta H_3^{\ddagger}$ vs. $\Delta S_3^{\ddagger}$ for all the data indicates compensated changes in activation parameters that suggest a common transmetalation mechanism in methylene chloride or nitrobenzene.

Rate Law 4. Changing X in A from Cl to Br results in first-order rate law 4 for monotransmetalation of A by B (M = Co or Zn, but not Ni). The entropies of activation, $\Delta S_4^{\ddagger}$, range from moderately negative for the lowest $\Delta H_4^{\ddagger}$ to near zero for the highest $\Delta H_4^{\ddagger}$. No systematic solvent dependences are apparent in the data for rate law 4.

Rate Law 5. Second-order rate law 5 is observed for transmetalation of excess A (X = Cl or Br) with C (M = Ni or Zn) and appears to be characteristic of C. The enthalpies of activation, $\Delta H_5^{\ddagger}$, are lowest for M = Ni, and the corresponding $\Delta S_5^{\ddagger}$ are very negative. Changing from X = Cl to X = Br in A causes sharp, compensated increases in $\Delta H_5^{\ddagger}$ and $\Delta S_5^{\ddagger}$ in either methylene chloride or nitrobenzene.

Interpretation of the Kinetic Data. We found previously that monotransmetalation of A (N = py or DENC; X = Cl or Br) by B and C (M = Ni) obeys rate laws 3 and 5, respectively. Structural mechanisms in eq 6 and 7 were proposed to account for these distinct rate law differences and are based on the known cis[10] and trans[11] geometries of B and C (M = Ni), respectively (Figure 1). The new data for M = Co or Zn in Table III indicate that rate laws 3 and 5 are associated with the ligands present in B and C, respectively, rather than the geometries of $M(NS)_2$.[10-12]

The essential features of eq 6 and 7 are four-membered Cu–X–Ni–S rings containing X from A and carbothioate S from B or C as bridging atoms.[5] They are analogues of the Cu–X–Ni–X rings in $[NCuNi(H_2O)X_2]_2Y_2$ complexes (N = monodentate DENC or ethyl nicotinate, X = Cl or Br, and Y = O or CO_3, respectively) in which the X atoms provide surfaces for metal exchange resulting in isomerization.[3,4] Metal exchange over X and S atom surfaces in Cu–X–Ni–S rings results in trans-

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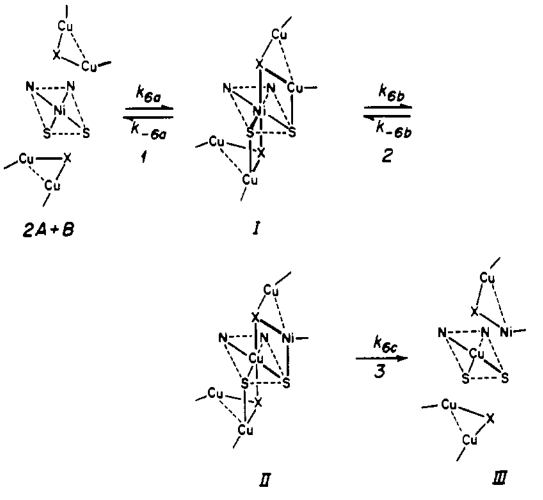
[16] Table II is available as supplementary material.



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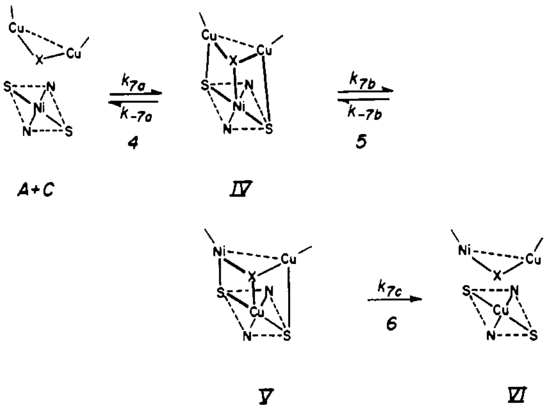

(7)

metalation.[5]

Equations 6 and 7 are appealing for four reasons. First, they are consistent with the Lewis acid character of $Ni(NS)_2$ complexes, which readily coordinate pyridine Lewis bases.[17] Second, they employ the accessible X atoms of Cu–X–Cu units in A (Figure 1) as reactant bridges. Third, the Cu–X–Ni–S rings include carbothioate sulfur atoms that are expected to be nucleophilic because they are derived from the enol form of the NS ligand (see below).[12,17] Finally, the involvement of S atoms in the activated complexes for transmetalation is expected because strong Cu–S bond formation is responsible for quantitative copper replacement on transmetalation.[2-9]

We therefore adopt eq 6 and 7 as structural mechanisms for transmetalation. Our main proposal is the involvement of Cu–X–M–S transmetalation rings irrespective of the planar (M = Ni) or tetrahedral (M = Co, Zn) geometries of B or C.

The involvement of species B·2A (I) in eq 6 accounts for the highest observed reaction order (eq 3) and can be used to consider alternative rate-determining steps 1, 2, or 3 in eq 6.

We feel that step 1 cannot be rate-determining for two reasons. First, Iskander and co-workers found that the formations of bisadducts of type B·2py, where py is a monodentate pyridine and M is Ni, were too rapid to measure on the stopped-flow time scale.[17] Second, the absorbance increases monitored at 550–610 nm in reaction 2 are due to formation of coproduct B (M = Cu), which strongly suggests step 2 as the earliest possible rate-determining step.

Assumption of a steady state in species I and II in eq 6, with III representing the reaction products on the stopped-flow time scale, leads to eq 8, which has the same form as eq 3. If $k_{6b} << k_{-6a} >> k_{-6b} << k_{6c}$, we obtain eq 9, which corresponds to rate-determining step 2 (eq 6) with step 1 (eq 6) ($K_{6a} = k_{6a}/k_{-6a}$) as a rapid preequilibrium. These conditions predict that $k_3 = K_{6a}k_{6b}$, $\Delta H_3^{\ddagger} = \Delta H_{6a} + \Delta H_{6b}^{\ddagger}$, and $\Delta S_3^{\ddagger} = \Delta S_{6a} + \Delta S_{6b}^{\ddagger}$ in eq 3. If I is present at stoichiometrically significant concentrations, we obtain eq 10, which reduces to eq 11 if $K_{6a}[A]^2 >> 1$. Equation 11 is of the same form as eq 4, with $k_4 = k_{6b}$, $\Delta H_4^{\ddagger} = \Delta H_{6b}^{\ddagger}$, and $\Delta S_4^{\ddagger} = \Delta S_{6b}^{\ddagger}$.

$$\text{rate} = \frac{k_{6a}k_{6b}k_{6c}[B][A]^2}{k_{-6a}k_{-6b} + k_{-6a}k_{6c} + k_{6b}k_{6c}} \tag{8}$$

$$\text{rate} = K_{6a}k_{6b}[B][A]^2 \tag{9}$$

$$\text{rate} = \frac{K_{6a}k_{6b}[B][A]^2}{1 + K_{6a}[A]^2} \tag{10}$$

$$\text{rate} = k_{6b}[B] \tag{11}$$

Rate-determining step 3 in eq 6 arises if $k_{6c} << k_{-6b}$ and $k_{-6a} >> k_{6b}$ in eq 8. The result of these conditions is eq 12, which is of the same form as eq 3, with $k_3 = K_{6a}K_{6b}k_{6c}$, $\Delta H_3^{\ddagger} = \Delta H_{6a} + \Delta H_{6b} + \Delta H_{6c}^{\ddagger}$, and $\Delta S_3^{\ddagger} = \Delta S_{6a} + \Delta S_{6b} + \Delta S_{6c}^{\ddagger}$. If II is present at significant concentrations, we obtain eq 13, which reduces to eq 14 if $K_{6a}K_{6b}[A]^2 >> 1$. Equation 14 is of the same form as eq 4, with $k_4 = k_{6c}$, $\Delta H_4^{\ddagger} = \Delta H_{6c}^{\ddagger}$, and $\Delta S_4^{\ddagger} = \Delta S_{6c}^{\ddagger}$.

$$\text{rate} = K_{6a}K_{6b}k_{6c}[B][A]^2 \tag{12}$$

$$\text{rate} = \frac{K_{6a}K_{6b}k_{6c}[B][A]^2}{1 + K_{6a}K_{6b}[A]^2} \tag{13}$$

$$\text{rate} = k_{6c}[B] \tag{14}$$

The same analysis of limiting conditions in eq 7 gives eq 8–14 with C replacing B, a first-order dependence of eq 8–10, 12, and 13 on [A], and k_{7a} instead of k_{6a}, etc., throughout.

Our task is now to attempt to assign steps 2 or 3 in eq 6 and steps 5 or 6 in eq 7 as rate-determining processes.

Rate Law 4. We first consider the assignment of the simplest rate law, eq 4. The alternative predicted forms are eq 11 and 14. If step 3 is rate-determining we have $\Delta S_4^{\ddagger} = \Delta S_{6c}^{\ddagger}$. Step 3 is the fragmentation of discrete products D and B and would be expected to have positive entropies of activation. However, none of the measured entropies of activation, $\Delta S_4^{\ddagger}$, in Table III are markedly positive. This leads us to propose step 2 as rate-determining when A (X = Br) is transmetalated by B (M = Co or Zn) because we would not expect very negative or very positive entropies of activation for exchange of metals between A and B in the relatively stable Cu–Br–M–S rings indicated by the independence of rate law 4 on [A]. Activation entropies near zero strongly suggest slow metal exchange when A (X = Br) reacts with B (M = Co or Zn).

Rate Law 3. We next consider the assignment of rate law 3. The alternative predicted forms are eq 10 and 12.

Iskander and co-workers[17] have investigated the thermodynamics of formation of $Ni(NS)_2 \cdot 2P$ adducts in benzene. Here, NS is one of four monoanionic *S*-methyl *N*-arylidenehydrazinecarbodithioate ligands and P is py, 3-methylpyridine, or 4-methylpyridine. The measured average enthalpies and entropies of formation for $Ni(NS)_2 \cdot 2P$ are 14 ± 2 kcal mol^{-1} and −44 ± 4 cal deg^{-1} mol^{-1} at 25 °C, respectively.[17,18] We feel that the latter average value, −44 cal deg^{-1} mol^{-1}, is a good approximation for the entropy of formation of I, ΔS_{6a}, in step 1 of eq 6 and that the measured average entropy of formation of the monoadduct $Ni(NS)_2 \cdot bpy$ (bpy = 2,2′-bipyridyl), −25 ± 3 cal deg^{-1} mol^{-1} at 25 °C,[17,18] reasonably approximates ΔS_{7a} for step 4 of eq 7 (see below).

If step 2 of eq 6 is rate-determining, we have $\Delta S_{6b}^{\ddagger} = \Delta S_3^{\ddagger} - \Delta S_{6a}$. Since $\Delta S_3^{\ddagger}$ is positive (Table III), this would mean that $\Delta S_{6b}^{\ddagger}$ is very markedly positive, which is inconsistent with near-zero $\Delta S_{6b}^{\ddagger}$ in our assignment of rate-determining step 2 to rate law 4 (see above).

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(17) Iskander, M. F.; El-Sayed, L.; Labib, L.; El-Toukhy, A. *Inorg. Chim. Acta* **1984**, *86*, 197.

(18) We give the average and average deviation for the data in ref 17.

If step 3 of eq 6 is rate-determining, then $\Delta S_3^\ddagger = \Delta S_{6a} + \Delta S_{6b} + \Delta S_{6c}^\ddagger$. The assignment of near-zero ΔS_{6b} to the rapid equilibrium between I and II in eq 6 is reasonable because II has the same molecularity and both are neutral species. Thus, $\Delta S_{6c}^\ddagger \approx \Delta S_3^\ddagger + 44$, which supports the assignment of rate-determining product fragmentation, step 3 of eq 6, to rate law 3.

Our analysis thus suggests that metal exchange is faster than rate-determining product fragmentation in the monotransmetalation of A (X = Cl) with B (M = Co, Ni or Zn). Rate law 3 obtains if $K_{6a}K_{6b}[A]^2 \lesssim 0.1$ in eq 13 at the highest [A] investigated (3.0×10^{-3} M). Thus, $K_{6a}K_{6b} \lesssim 10^4$ M^{-2} at the lowest experimental temperature (7.7 °C, Table II).[16] We are inclined to believe that low $K_{6a}K_{6b}$ is due to small K_{6a}[19] rather than to small K_{6b} because $Cu(NS)_2$ formation is the driving force for transmetalation.[2-9] In any event, weak precursors and rapid metal exchange are apparent with X = Cl in A.

Origin of Rate Law 4. Changing X from Cl to Br in A and M from Ni to Co or Zn in B leads to rate law 4, which is independent of [A] and indicates that there is no free B under the experimental conditions. Rate law 4 is interpreted through eq 10, with $K_{6a}[A]^2 \gtrsim 10$ at the lowest [A] investigated (1.0×10^{-3} M). This corresponds to $K_{6a} \gtrsim 10^7$ M^{-2} at the highest experimental temperature (42.2 °C, Table II).[16] Longer M–S bonds in B (average 2.275 (5) Å with M = Co and Zn)[12] than in B (2.153 (3) Å with M = Ni)[10] indicate more nucleophilic carbothioate atoms for M = Co and Zn; this and a higher nucleophilicity of A with X = Br evidently give rise to especially stable species I. However, the latter have not been detected spectrophotometrically at the monitoring wavelengths. Metal exchange evidently is necessary for significant absorbance changes.

The involvement of especially stable species I leads to a change from product fragmentation, step 3, to metal exchange, step 2, as the slowest process in eq 6. This also is consistent with higher stability of I when X = Br and M = Co or Zn.

Rate Law 5. The wide range of rate constants and activation parameters for monotransmetalation of A by C with second-order rate law 5 suggest different rate-determining steps for different X and M. The predicted rate law with step 5 of eq 7 as the rate-determining step and stoichiometrically insignificant concentrations of IV is eq 15. Under these conditions $k_5 = K_{7a}k_{7b}$,

$$\text{rate} = K_{7a}k_{7b}[C][A] \qquad (15)$$

$\Delta H_5^\ddagger = \Delta H_{7a} + \Delta H_{7b}^\ddagger$, and $\Delta S_5^\ddagger = \Delta S_{7a} + \Delta S_{7b}^\ddagger$. Adopting $\Delta S_{7a} = -25$ cal deg^{-1} mol^{-1} for rapid equilibration of A and C (see above) gives $\Delta S_{7b}^\ddagger = \Delta S_5^\ddagger + 25$ for the data in Table III. This assignment gives predicted $\Delta S_{7b}^\ddagger$ ranging from ca. −14 cal deg^{-1} mol^{-1} for transmetalation of A (X = Cl) with C (M = Ni) to +56 cal deg^{-1} mol^{-1} for the corresponding reaction of A (X = Br) with C (M = Zn). On the basis of our assignment of near-zero $\Delta S_4^\ddagger$ to rate-determining metal exchange, we conclude that step 5 is rate-determining with M = Ni in C but not when X = Br and M = Zn. If product fragmentation, step 6 of eq 7, is the rate-determining step in the latter system and V is stoichiometrically insignificant, then $\Delta S_5^\ddagger = \Delta S_{7a} + \Delta S_{7b} + \Delta S_{7c}^\ddagger$. We predict $\Delta S_{7c}^\ddagger \approx 60$ cal deg^{-1} mol^{-1} with $\Delta S_{7a} = -25$ and $\Delta S_{7b} \approx 0$ cal deg^{-1} mol^{-1}. The assignment of slow product fragmentation is less definite for A (X = Cl) reacting with C (M = Zn), since $\Delta S_{7c}^\ddagger$ is 11–12 cal deg^{-1} mol^{-1} if the same values of ΔS_{7a} and ΔS_{7b} are adopted.

Conclusions

Different rate laws for transmetalation of A by B and C arise from different nucleophilicities of carbothioate sulfur atoms in the transmetalators that affect their capacity to coordinate A. When X = Cl, the transmetalation precursors are weak but product fragmentation is the rate-determining step in the transmetalation of A by B. More nucleophilic carbothioate S in B (M = Co and Zn) together with X = Br leads to especially stable species I and a shift to rate-determining metal exchange. The carbothioate sulfur atoms of C are not sufficiently nucleophilic to give C·2A transmetalation precursors, and C·A precursors are weak even with X = Br. There is evidence for metal-mediated interactions between carbodithioate sulfurs of separate ligands in C but not in B.[20] Precursor I, eq 6, does not form with C because the coordination of 1 mol of A to C reduces the basicity of the second carbodithioate sulfur, irrespective of the preferred conformation of C.[11,12] Thus, only one $\overline{\text{X–Zn–S–Cu}}$ ring may be present in IV (eq 7) for M = Zn. The entropies of activation for transmetalation with C suggest that metal exchange is slowest for M = Ni, consistent with evidence that C (M = Ni) is a more thermodynamically stable complex than C (M = Co or Zn).[21]

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Registry No. B (M = Ni), 66514-12-3; B (M = Co), 54166-06-2; B (M = Zn), 72871-59-1; C (M = Ni), 62303-68-8; C (M = Zn), 72860-38-9; $N_4Cu_3Co(H_2O)Cl_6O$, 104267-54-1; $N_4Cu_3Co(H_2O)Br_6O$, 104267-55-2; $N_4Cu_3Zn(H_2O)Cl_6O$, 104267-56-3; $N_4Cu_3Zn(H_2O)Br_6O$, 104267-57-4; $N_4Cu_3Ni(H_2O)Cl_6O$, 101998-13-4; $N_4Cu_3Ni(H_2O)Br_6O$, 101998-14-5.

Supplementary Material Available: Table II (kinetic data for monotransmetalation of $(\mu_4\text{-O})[(DENC)Cu]_4X_6$ complexes by $M(NS)_2$ in aprotic solvents) (5 pages). Ordering information is given on any current masthead page.

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(19) The largest reported equilibrium constant for formation of $Ni(NS)_2{\cdot}2P$ complexes is 71 ± 4 M^{-2} in benzene at 25 °C with NS = *S*-methyl *p*-chloroarylidenehydrazinecarbodithioate monoanion and P = 4-methylpyridine.[17]

(20) Iskander, M. F.; El-Sayed, L.; Khamis, A., to be submitted for publication.

(21) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M., work in progress.