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Transmetalation of Tetranuclear Copper Complexes. 3. Effects of Ligands (L = *N*,*N*-Diethylnicotinamide or Ethyl Nicotinate; X = Cl or Br) on the Properties of $[LNi(H_2O)X]_4X_4$, $(\mu_4\text{-}O)[LNi(H_2O)]_4X_4$, and $[LCuNi(H_2O)X_2]_2Y_2$ (Y = O or CO_3) Complexes in Aprotic Solvents

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Tetranuclear copper(II) complexes $[LCuX]_4X_4$ (IX, L = *N*,*N*-diethylnicotinamide, DENC; X = Cl or Br), $(\mu_4\text{-}O)[LCu]_4X_6$ (X, L = DENC or ethyl nicotinate, ENCA; X = Cl or Br), and $[LCuX]_4Y_2$ (L = DENC or ENCA; X = Cl or Br; Y = O (I) or CO_3 (IV)), all react with 4 mol of $Ni(NS)_2$ reagents II and III (NS is a methyl hydrazinecarbodithioato Schiff base) in methylene chloride to give the homotetranuclear transmetalated products $[LNi(H_2O)X]_4X_4$ and $(\mu_4\text{-}O)[LNi(H_2O)]_4X_6$ and two heterotetranuclear isomers of $[LCuNi(H_2O)X_2]_2Y_2$, respectively. Spectral comparisons indicate that IX and X contain trigonal-bipyramidal copper(II) centers while those in I and IV are approximately square pyramidal. The water coordinated to each nickel(II) center in the transmetalated products during gel-permeation chromatographic isolation makes some 6-coordinate. As in part 2, it was found that different $Ni(NS)_2$ reagents produce one or the other of the two isomeric forms of $[LCuNi(H_2O)X_2]_2O_2$, V or VI. A coproduct of transmetalation, III (M = Cu), catalyzes the isomerization of V to VI, indicating that V is the primary transmetalation product with different $Ni(NS)_2$ reagents and supporting the previously suggested metal-exchange mechanism of isomerization of V and its dicarbonato derivative, VII. The kinetic activation parameters for isomerization with 12 ligand/solvent systems indicate that this mechanism is general for isomerization of V and VII. The parameters are much less sensitive to change of L (DENC or ENCA) than to changes of X, Y, or solvent. Solvent coordination in the activation process for isomerizations of V and VII in nitrobenzene is suggested to account for the kinetic data.

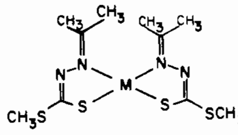
Introduction

New transmetalation products have been obtained by following earlier reported methods (eq 1-3)[1] using reagents II and III. The

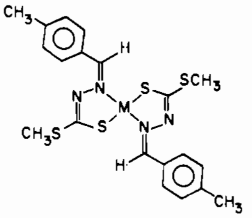
$$[LCuCl]_4Cl_4 + 4Ni(NS)_2 \xrightarrow{H_2O} [LNi(H_2O)Cl]_4Cl_4 + 4Cu(NS)_2 \quad (1)$$

$$(\mu_4\text{-}O)[LCu]_4Cl_6 + 4Ni(NS)_2 \xrightarrow{H_2O} (\mu_4\text{-}O)[LNi(H_2O)]_4Cl_6 + 4Cu(NS)_2 \quad (2)$$

$$[LCuCl]_4Y_2 + 4Ni(NS)_2 \xrightarrow{H_2O} [LCuNi(H_2O)Cl_2]_2Y_2 + 2Cu(NS)_2 + 2Ni(NS)_2L \quad (3)$$



II



III

new reactions and the products isolated are summarized in Scheme I.

Although attempts to obtain single crystals of the new reactants and transmetalation products for structural characterization have been unsuccessful, all their analytical, chemical, and spectral properties[1-4] are consistent with maintenance of the transmetalation patterns of part 2.[1] The kinetics of interconversion of the respective isomers from reaction 3 also have been measured to allow comparison with the results in part 2.[1] Evidence from "capping" experiments supports the general isomerization mechanism shown in Figure 1 and provides an explanation for the production of the particular isomers V, VI, and VII in transmetalation reactions with different $Ni(NS)_2$ reagents. Commonalities and differences between *N*,*N*-diethylnicotinamide (DENC) and ethyl nicotinate (ENCA) as ligands for copper have been discussed.[5,6]

Experimental Section

Materials and Reagents. Procedures for the preparation, purification, and analysis of most of the solvents, reactants, and products have been described previously.[1-4] Attempts to prepare $[LCuX]_4X_4$ (L = ENCA; X = Cl or Br) complexes (IX) by reaction of large excesses of the respective copper(II) halides with ENCA in methylene chloride instead gave insoluble, pale blue dihalobis(ethyl nicotinate)copper(II) products. (Anal. Found: C, 43.62; H, 4.15; N, 6.27; Cu 14.41; Cl, 16.40. Calcd for $(ENCA)_2CuCl_2$: C, 43.30; H, 4.06; N, 6.29; Cu, 14.54; Cl, 16.25. Found: Cu, 12.32, Br, 30.17. Calcd for $(ENCA)_2CuBr_2$: Cu, 12.09; Br, 30.44.) Reaction of anhydrous $CuBr_2$ (30 mmol) with DENC (10 mmol) in methylene chloride (60 mL) for 12 h at room temperature gave a brown solution after filtration from excess $CuBr_2$. Gel-permeation chromatography (methylene chloride eluant)[1] gave first a brown band (identified as IX (L = DENC; X = Br), Scheme I; 85% isolated yield) and then a minor black band, which analyzed as $(DENC)_2Cu_2Br_4$. (Anal. Found: Cu, 15.67; Br 39.52; mol wt, 800 ± 20. Calcd: Cu, 15.82; Br 39.84; mol wt, 803.) By contrast, gel-permeation chromatography of the product solution from the corresponding reaction of excess $CuCl_2$ with DENC[1] indicated that IX (L = DENC; X = Cl) is the sole product. The reactants $(\mu_4\text{-}O)[LCu]_4X_6$ (L = DENC or ENCA; X = Cl or Br) were obtained by the method of Dickinson.[7] The molecular weights of reactants and products were determined cryoscopically in nitrobenzene.[1] These and other analytical data[8] are collected in Table I.

Physical Measurements. Electronic and IR spectral data were obtained as before.[1,2] ESR spectra were measured for microcrystalline samples and methylene chloride solutions of the tetranuclear reactants and products with a Bruker ER-200 spectrometer at room temperature. Procedures for monitoring the isomerization of products from reaction 3 and kinetic data analysis have been described.[1]

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† A.E.-T. was on leave from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

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Table I. Analytical and Cryoscopic Data for Reactants and Transmetalation Products[a]

no.	complex	% C	% H	% N	% X	% Cu	% Ni	mol wt
V	$[(DENC)CuNi(H_2O)Br_2]_2O_2$	24.73	3.53	5.70	32.89	12.53	11.62	4030 ± 200
		(24.31)	(3.26)	(5.67)	(32.35)	(12.86)	(11.89)	(987.6)
	$[(ENCA)CuNi(H_2O)Cl_2]_2O_2$	25.27	2.95	3.62	18.45	15.85	14.91	2290 ± 200
		(25.39)	(2.93)	(3.70)	(18.74)	(16.35)	(15.40)	(757)
VI	$[(DENC)CuNi(H_2O)Br_2]_2O_2$	24.72	2.81	5.58	32.06	13.10	10.95	4030 ± 200
		(24.31)	(3.26)	(5.67)	(32.35)	(12.86)	(11.89)	(987.6)
	$[(ENCA)CuNi(H_2O)Cl_2]_2O_2$	26.66	3.28	4.05	18.20	15.89	15.80	2290 ± 200
		(25.39)	(2.93)	(3.70)	(18.74)	(16.35)	(15.40)	(757)
VII	$[(DENC)CuNi(H_2O)Br_2]_2(CO_3)_2$	23.73	3.25	5.33	29.20	11.40	10.65	1155 ± 50
		(23.45)	(3.00)	(5.21)	(29.67)	(11.81)	(10.91)	(1075.6)
	$[(ENCA)CuNi(H_2O)Cl_2]_2(CO_3)_2$	29.27	3.25	5.14	17.30	14.39	13.46	820 ± 50
		(25.58)	(2.62)	(3.32)	(16.79)	(15.04)	(13.90)	(845)
VIII	$[(DENC)CuNi(H_2O)Br_2]_2(CO_3)_2$	23.66	3.14	5.30	29.38	12.10	10.42	1155 ± 50
		(23.45)	(3.00)	(5.21)	(29.67)	(11.81)	(10.91)	(1075.6)
	$[(ENCA)CuNi(H_2O)Cl_2]_2(CO_3)_2$	26.60	3.14	3.52	17.12	15.15	14.14	820 ± 50
		(25.58)	(2.62)	(3.32)	(16.79)	(15.04)	(13.90)	(845)
IX	$[(DENC)CuBr]_4Br_4$	30.82	3.75	7.42	40.36	15.67		1550 ± 50
		(29.93)	(3.52)	(6.98)	(39.82)	(15.80)		(1605)
X	$[(DENC)Cu]_4Br_6O$	32.77	3.69	7.51	32.71	17.56		1420 ± 50
		(32.85)	(3.86)	(7.66)	(32.82)	(17.47)		(1462)
	$[(ENCA)Cu]_4Cl_6O$	35.24	3.31	5.12	20.10	23.7		1055 ± 50
		(35.32)	(3.34)	(5.15)	(19.56)	(23.4)		(1088)
	$[(ENCA)Cu]_4Br_6O$	27.00	2.50	3.97	36.06	19.20		1290 ± 50
		(28.38)	(2.90)	(4.14)	(35.41)	(18.80)		(1354)
XI	$[(DENC)Ni(H_2O)Br]_4Br_4$	29.72	4.18	7.18	38.45		14.33	1680 ± 50
		(28.96)	(3.89)	(6.76)	(38.54)		(14.16)	(1659)
XII	$[(ENCA)Ni(H_2O)]_4Cl_6O$	33.55	3.45	5.15	18.60		19.94	1120 ± 50
		(33.71)	(3.18)	(4.92)	(18.70)		(20.59)	(1140)
	$[(ENCA)Ni(H_2O)]_4Br_6O$	27.40	3.00	3.64	33.50		18.06	1380 ± 50
		(27.30)	(3.13)	(3.98)	(34.12)		(16.69)	(1407)

[a] Calculated values are given in parentheses.

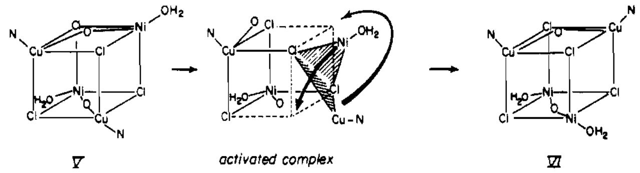

Figure 1. Model for isomerization via metal exchange between tetrahedral holes in an X_4 core structure.[1]

Results and Discussion

General Observations. The analytical data in Table I indicate that Scheme I is valid for different combinations of L (=DENC or ENCA) and X (=Cl or Br) in tetranuclear copper(II) complexes with $Ni(NS)_2$ reagents II and III except for IX (L = ENCA; X = Cl or Br), which are not stable tetranuclear species in methylene chloride (Experimental Section). Tetranuclear copper(II) complexes give quantitative yields of tetranuclear nickel(II)-containing products in every transmetalation system that we have investigated.

Electronic and Infrared Spectra. Electronic and IR spectral data for copper(II) reactants and transmetalated products are collected in Table II. All these complexes are highly soluble in methylene chloride and nitrobenzene and can be precipitated unchanged from these solvents.

At room temperature, the Nujol mull and solution electronic spectra of copper(II) reactants, I, IV, IX, and X are similar and exhibit two intense, broad maxima between 730 and 860 nm. All of these complexes contain 5-coordinate copper(II) centers in which the coordinated halide:copper(II) ratio is at least 3.[9] Characterized 5-coordinate copper(II) complexes with zero,[10a] one,[10b,c] or two[6] halides per copper(II) center exhibit only a single absorption maximum near 700 nm, sometimes with a discernible shoulder near 900 nm.[6,10] The ion $CuBr_5^{3-}$ has an unresolved band in its electronic spectrum at 1150 nm.[11] Available evidence thus indicates that a minum 3:1 halide:copper(II) ratio in 5-coordinate centers is a requirement for the characteristic spectra

Table II. Spectral Data for Tetranuclear Copper Reactants and Transmetalated Products

complex	L	X	band maxima, nm (ϵ, M^{-1} cm^{-1})	ν_{M-O}, cm^{-1}	ref
I	DENC	Cl	770 (710), 850 (715)	510	3
		Br	750 (910), 825 (910)	490	3
	ENCA	Cl	730 (750), 825 (760)	505	3
IV	DENC	Cl	775 (830), 850 (880)	500	3
		Br	775 (1250), 850 (1260)	490	3
	ENCA	Cl	740 (700), 840 (730)	505	3
V	DENC	Cl	750 (149)	490	1
		Br	770 (286)	485	a
	ENCA	Cl	700 (209)	500	a
VI	DENC	Cl	750 (334), 850 (350)	490	1
		Br	770 (413), 850 (438)	485	a
	ENCA	Cl	770 (375), 850 (386)	500	a
VII	DENC	Cl	750 (143)	485	1
		Br	750 (348)	490	a
	ENCA	Cl	725 (120)	495 w	a
VIII	DENC	Cl	750 (284), 850 (293)	485	1
		Br	783 (616), 850 (660)	490	a
	ENCA	Cl	740 (205), 840 (212)	500	a
IX	DENC	Cl	740 (1380), 850 (1500)		1
		Br	765 (1970), 850 (2180)		a
X	DENC	Cl	750 (1210), 850 (1320)	530	1
		Br	765 (2900), 850 (3200)	525	a
	ENCA	Cl	770 sh (1015), 860 (1165)	520	a
		Br	780 sh (2000), 860 (2145)	510	a
XI	DENC	Cl	720 (34), 1250 (18)	495[b]	1
		Br	720 (73), 1250 (29)	490[b]	a
XII	DENC	Cl	720 (28), 1245 (16)	505	1
		Br	775 (75), 840 sh (71), 1275 vbr (20)	495	a
	ENCA	Cl	725 (84), 835 sh (69), 1240 vbr (29)	505	1
		Br	775 (105), 850 (145), 1220 vbr (34)	460	a

[a] This work. [b] These IR bands are assigned to ν_{M-OH_2}.

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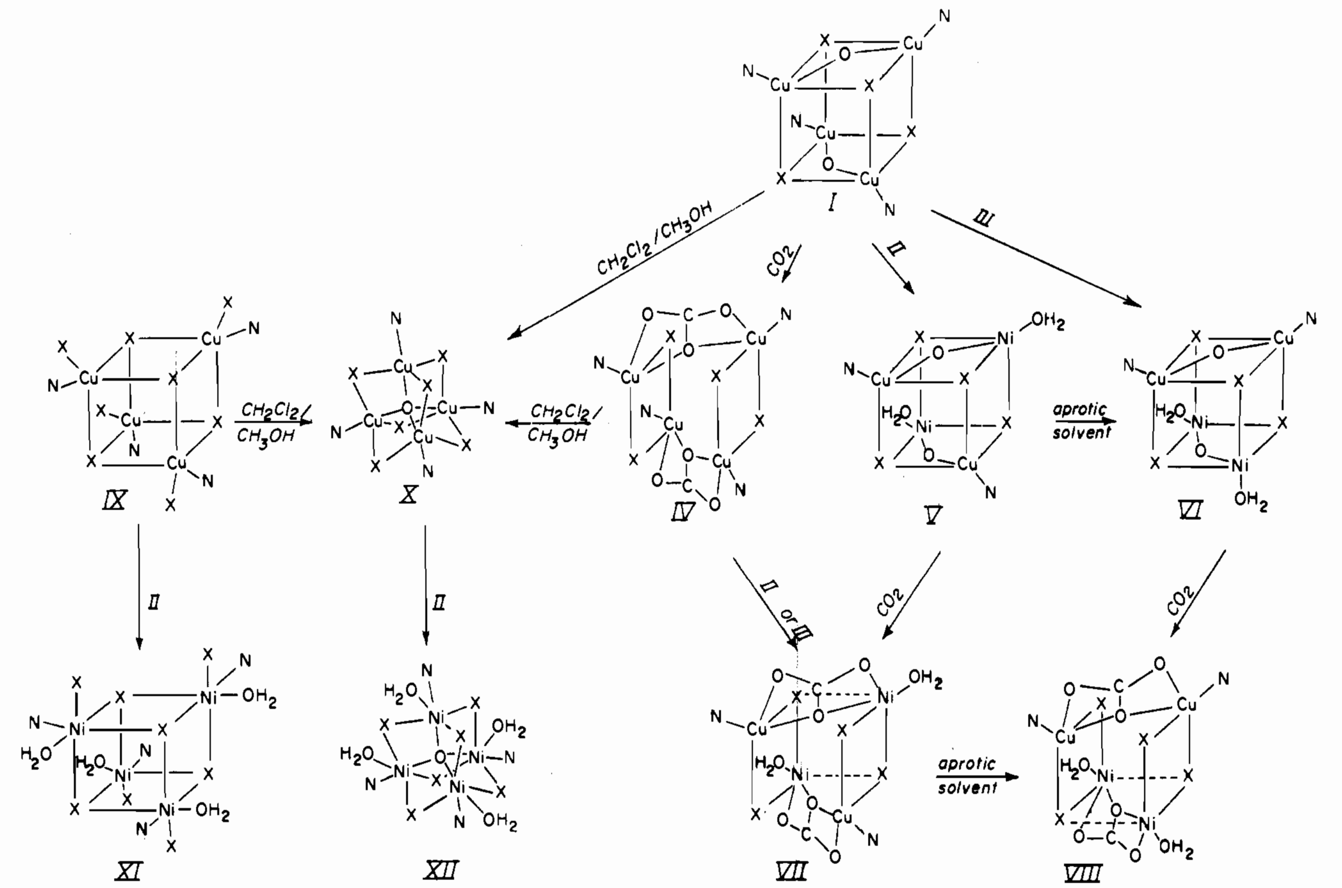
Scheme I



of the reactant and particular product structures in Table II. Replacement of DENC with ENCA moves both maxima to higher energy in complexes I and IV, while the opposite effect is observed in X. For all reactants and products the maximum molar absorptivities are larger for X = Br than for X = Cl.

The data in Table II show that the maximum molar absorptivities of copper reactants I and IV are considerably lower than those of IX and X. The copper centers in complexes with structure X and monodentate pyridine ligands are trigonal bipyramids (tbp).[1,9] Although we have not succeeded in obtaining single crystals of complexes IX that are suitable for X-ray crystallography, the similarity of the electronic spectra of IX and X suggests tbp geometry for both. The metal centers in I, IV, and V–VIII are depicted as approximate square pyramids (sp, axial L or H_2O) in Scheme I. ESR spectroscopy is the method of choice in distinguishing copper(II) tbp or sp geometries,[12] but complexes I, IV, and V–VIII are all ESR silent and so our assignment of approximate sp geometry is based on structural intuition and the spectral evidence in Table II.

The spectra of the pairs V, VII and VI, VIII are similar, consistent with their proposed respective isomeric structures.[1] Our earlier observation that the molar absorptivities of VI and VIII are about half those of the corresponding complexes I and IV is also apparent for the new products in Table II, indicating that VI and VIII contain single LCu–O–CuL and $LCu(CO_3)CuL$ structural units, respectively. These units result from irreversible isomerization of V and VII, respectively.

The totally transmetalated products XI and XII have spectra characteristic of 6-coordinate nickel(II) complexes.[13] Splitting of the low-energy bands in three samples of XII suggests strong tetragonal distortion in these cases.[13]

The ν_{M-O} observed in the IR spectra of oxometal complexes tends to be exhibited at slightly lower frequency when X = Br.

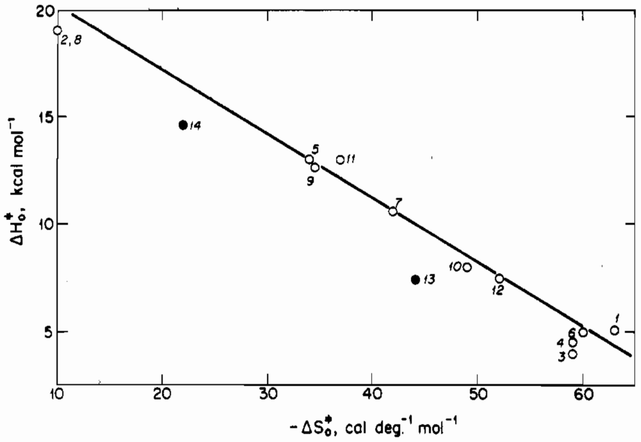


Figure 2. Plot of ΔH_0^* vs. ΔS_0^* for isomerization of complexes V and VII in methylene chloride and nitrobenzene. Data are taken from Table IV and numbered consecutively. Also included are activation parameters from Table V for two catalyzed isomerizations of V, L = DENC: X = Cl (**13**) and X = Br (**14**).

Kinetics and Mechanism of Isomerization of Complexes V and VII. General Observations. The spontaneous isomerizations of complexes V and VII are strictly first-order processes in aprotic solvents. The analytical data in Table I indicate that complexes V associate in nitrobenzene. We have previously ascribed this observation and increases of the observed first-order rate constants (k_{obsd}) with increasing analytical concentration of V, $[V]_0$ (ref 1, Table V), to intermolecular hydrogen bonding Ni(OH_2)---O-(Cu, Ni) between reactant tetramers. The data in Table III[14] indicate that this phenomenon only affects some rates of isomerization of complexes V; where observed, it has the same general effect on k_{obsd} over similar ranges of $[V]_0$ as observed previously.[1]

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(14) Supplementary data.

Table IV. Rate Parameters for Isomerization of Unassociated Complexes V and VII in Aprotic Solvents

	$10^6 k_0$[a]					
	CH_2Cl_2			$PhNO_2$		
temp[b]	DENC, Cl[f]	DENC, Br	ENCA, Cl	DENC, Cl[f]	DENC, Br	ENCA, Cl
			(a) Data for V			
0.0	2.8	6.8	13.0			
15.0	3.8		20.7		8.1	
20.0	5.6	29.8	25.4			
25.0	5.9	57.4			26.3	
30.0	8.1	113.0	37.2	11.0		
50.0				70.0	101	55.5
65.0				206	264	82.7
80.0				545		120
95.0				1220		168
$\Delta H_0^{\ddagger}$[c]	5.1 ± 0.5	19.0 ± 0.5	4.5 ± 0.5	3.9 ± 0.5	13.0 ± 0.5	4.9 ± 0.5
$\Delta S_0^{\ddagger}$[d]	−63 ± 2	−10 ± 2	−59 ± 2	−59 ± 2	−34 ± 2	−60 ± 2
			(b) Data for VII			
0.0	5.2[f]	8.4				
15.0	16.0	19.3	12.5	45.8	5.2	
20.0	21.3	26.3	18.8	57.9		32.6
25.0	32.0		28.4		9.1	
30.0	83.5	102	41.5	83.2	13.6	63.8
40.0				103	28.5	74.9
50.0				291[e]	47.6	101
$\Delta H_0^{\ddagger}$[c]	10.6 ± 0.5	19.0 ± 0.5	12.7 ± 0.5	7.9 ± 0.5	13.0 ± 0.5	7.4 ± 0.5
$\Delta S_0^{\ddagger}$[d]	−42 ± 2	−10 ± 2	−34 ± 2	−49 ± 2	−37 ± 2	−52 ± 2

[a] Units are s^{-1}. [b] Given in °C. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25 °C. [e] Isomerization of VII cannot be investigated at higher temperatures in $PhNO_2$ because of rapid decarboxylation to give V; the data at 50 °C agree with those for isomerization of V under the same conditions. [f] Data from ref 1.

As before, we have factored out this intractable kinetic complication (ref 1, eq 7) by extrapolating k_{obsd} to $[V]_0 = 0$.

Kinetic data for isomerization of the discrete tetranuclear complexes V and VII are collected in Table IV. At 30 °C the lowest value of k_0 is found for V (L = DENC; X = Cl) in methylene chloride. Figure 2 shows that ΔH_0^{*} increases smoothly with ΔS_0^{*} for all 12 reactant/solvent systems investigated. We take this interrelationship of activation parameters to indicate that isomerizations of V and VII proceed by a common mechanism.[15]

Figure 1 illustrates metal exchange that leads to isomerization via a polar activated complex. There is an alternative mechanism for isomerization that should be considered.[16]

Consider the general "cubane" structure for V in Scheme I. Breaking Cu–O and Ni–O bonds in the top and bottom faces, respectively, and re-forming Ni–O and Cu–O bonds in the back and front faces, respectively, lead to isomerization with all metal centers stationary. The following results indicate that this mechanism is not likely to account for isomerization of V in the present systems.

Planar complex III (M = Cu) is a coproduct of the synthesis of VI. Complex III (M = Cu) is a Lewis acid[17] and, as such, might be expected to form an acid–base adduct with each μ-oxo group of I, V, or VI.[5,18] When aprotic solutions of 2–4 mol of III (M = Cu) for each 1 mol of V (L = DENC; X = Cl or Br) are mixed with V, two subsequent first-order reactions can be monitored spectrophotometrically. The first reaction (rate constant k_1 (s^{-1}); absorbance increase at 850 nm) gives a product spectrum identical with that of a mixture of solutions of VI and III (M = Cu) at the same concentrations, showing it to be due to V → VI isomerization. Rate constant k_1 is independent of $[V]_0$ (Table V). The second, slower process (absorbance decrease at 850 nm) is governed by identical values of k_2 (s^{-1}) for reaction of III with isomerized V, VI, or I; however, the total absorbance decrease ΔA_2 for I + III is about 2 times that for VI + III. Rate constant k_2 is independent of reactant concentrations provided $[III]_0/[I]_0$, $[V]_0$, or $[VI]_0 \geq 2$.

Table V. Rate Parameters for Catalyzed Isomerization of V by $Cu(NS)_2$ (III) in Nitrobenzene

	$10^6 k_1$, s^{-1}	
temp[a]	L = DENC; X = Cl	L = DENC; X = Br
25	170	606
35	300	1200
50	610	3580
$\Delta H^{\ddagger}$[b]	7.3 ± 0.5	14.7 ± 0.5
$\Delta S^{\ddagger}$[c]	−44 ± 2	−22 ± 2

[a] Given in °C. [b] Units are kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C.

The simplest explanation for these results is that one acidic $Cu(NS)_2$ complex rapidly forms a singly bonded Cu–O adduct with each μ-oxo unit in V, breaking intermolecular hydrogen bonding and making the complex $[(DENC)CuNi(H_2O)X_2]_2O_2{\cdot}2Cu(NS)_2$ (V·2III), which isomerizes to VI·2III with rate constant k_1. The latter is 40–90 times greater than k_0 for isomerization of V (L = DENC; X = Cl or Br (Table IV)) in nitrobenzene at 50 °C, and the observed activation parameters (Table V) deviate significantly from the relationship of Figure 2. On the basis of two points only, we observe that ΔH_0^{*} is lower for catalyzed reactions at fixed ΔS_0^{*}, which suggests that M–O and M–X bonds that have to be broken for isomerization[1] are weakened by adduct formation and that no translation of oxo groups accompanies isomerization.

The process governed by rate constant k_2 (Table V) only occurs after V has isomerized to VI or when I is reacted with III (M = Cu). The reaction probably involves the formation of Cu–S bonds between the NS ligands of $Cu(NS)_2$ and the metal centers

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(15) ΔG_0^{*} for isomerization at 25 °C covers only a small range for the systems investigated, so ΔH_0^{*} should be a linear function of ΔS_0^{*}. However, Figure 2 shows that changing X, L, Y and solvent for the V and VII isomerizations gives a linear relationship, suggesting that all the reactions are subject to the same activation requirements. See: Wells, P. R. "Linear Free Energy Relationships"; Academic Press: London, 1968; p 21.

(16) We are indebted to Dr. M. A. El-Sayed for suggesting this alternative mechanism of isomerization.

(17) El-Toukhy, A. M.S. Thesis, Alexandria University, Egypt, 1973.

(18) Acid–base interactions of μ-oxo groups (H bonding (ref 1 and Tables I and III)), adduct formation with III (Table V), and coordination of exogenous ligands by copper(II) (*N,N,N',N'*-tetraethylenediamine in the isomerization of V[1] or acetonitrile in the isomerization of VII[1]) all catalyze isomerization.

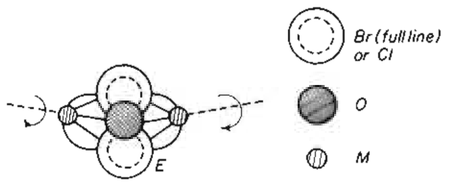

Figure 3. View down an S_4 axis of an $L_4Cu_4X_4O_2$ complex. Pyridine ligands are omitted, and the μ-oxo group is nearest to the viewer. Metal atoms are shown lying along the visible C_3 axes at a distance that determines the M–O–M bridging geometry. Consult ref 2a, Figure 2, for a similar view of $[(DENC)CuI]_4$, where Cu^I_4 is smaller than I_4. Dotted circles predict longer M–X bonds for X = Cl than for X = Br with fixed M–O–M geometry (see text). E is an "active" edge for isomerization via metal exchange in $[LCuNi(H_2O)X_2]Y_2$ complexes (cf. Figure 1).

of Cu–O–Cu units. Since I contains two such units while VI contains just one, the absorbance change ΔA_2 for I·2III $\xrightarrow{k_2}$ products is about 2 times that for VI·2III $\xrightarrow{k_2}$ products. The rate constants k_2 for reactions of VI and I (L = DENC; X = Br) with III (M = Cu) are 8×10^{-4} and 30×10^{-4} s^{-1}, respectively, in nitrobenzene at 50 °C.

The ultimate products of these $Cu(NS)_2$ reactions have not been identified because they dissociate on attempted isolation by gel-permeation chromatography, which is, of course, also the case in the synthesis of VI (coproduct III (M = Cu)) from the reaction of I with III (M = Ni), Scheme I. Attempted crystallization of adduct solutions regenerates the reactants.

Complex II (M = Cu) is a much weaker Lewis acid than complex III.[19] The catalysis of isomerization of V to VI by III (M = Cu) thus explains how reaction of I with II or III (M = Ni) gives V or VI, respectively: primary product V is formed in both cases. This conclusion is supported by the fact that isomerization of VII to VIII is not catalyzed by III (M = Cu), and hence reaction of IV with II or III (M = Ni) gives the same product, VII.

Structural Implications of Kinetic Results. Having concluded that metal exchange occurs in the isomerization of V and VII (Figure 1), we now consider structural aspects of the isomerization mechanism.

Although we do not have detailed structures for any of the tetranuclear reactants and transmetalated products except X (L = DENC; X = Cl),[1,20] all but X and XII contain an M_4X_4 core. On the basis of examination of space-filling models for each reactant, we can envisage the core structure as a cube of interpenetrating X_4 and M_4 tetrahedra. In the absence of other information we have shown tetrahedra of the same size in Scheme I, but there is reason to believe that M_4 is larger than X_4 in complexes I, IV, and V–VIII for the following reasons.

The μ-oxo and μ-carbonato bridges are responsible for the existence of isomeric pairs V, VI and VII, VIII, respectively. Space-filling models with reasonable ionic radii[21] indicate that if the metals penetrated the tetrahedral holes of X_4, then the M–O–M angles of V and VI would be very acute. This situation seems even less likely in derivatives VII and VIII, since the Cu–O–Cu vector in known (μ-carbonato)dicopper(II) derivatives is close to linear.[10b,22] This suggests that the angular requirements of the bridges in V–VIII could cause the metals to lie out of the tetrahedral holes of X_4 along its C_3 axes, which would mean that, on average, M_4 is larger than X_4 (Figure 3). This would explain why $\Delta H_0^{\ddagger}$ for isomerization is always less when X = Cl than when X = Br (Table IV) since M–Cl is longer than M–Br because the Cl_4 core is smaller than the Br_4 core.[20]

Changes from L = DENC to L = ENCA with X = Cl have very minor effects on the activation parameters for isomerization of V in methylene chloride and nitrobenzene. However, the solvent dependence is very marked when X = Br, with $\Delta H_0^{\ddagger}$ smaller and $\Delta S_0^{\ddagger}$ more negative in nitrobenzene.

On the basis of the fact that the isomerizations of V and VII are irreversible processes, we have concluded that when L = DENC and X = Cl the major contributor to $\Delta H_0^{\ddagger}$ is Cu–O bond breaking.[1] This also appears to be the case when L = ENCA, with $\Delta H_0^{\ddagger}{}_{VII} \approx 2\Delta H_0^{\ddagger}{}_{V}$. This relationship does not hold for X = Br, since $\Delta H_0^{\ddagger}{}_{VII} \approx \Delta H_0^{\ddagger}{}_{V}$ in both solvents, consistent with much stronger Cu–Br (vis-à-vis Cu–Cl) bonds to be broken for isomerization of V^1 (see above).

The lower $\Delta H_0^{\ddagger}$ and more negative $\Delta S_0^{\ddagger}$ for isomerization of VII in nitrobenzene suggest some coordination of nitrobenzene by the metal centers in the activated complexes. Such coordination would weaken M–O and M–X bonds (lowering $\Delta H_0^{\ddagger}$) and give more ordered activated complexes (more negative $\Delta S_0^{\ddagger}$). This effect has been noted previously, particularly for isomerization of VII (L = DENC; X = Cl) in acetonitrile.[1] It is also presumed to be responsible for the lower $\Delta H_0^{\ddagger}$ and more negative $\Delta S_0^{\ddagger}$ for isomerization of V (L = DENC, X = Br) in nitrobenzene in comparison to the corresponding parameters in methylene chloride.

We are investigating the stepwise transmetalation of tetranuclear copper(I) and copper(II) complexes with $M^{II}(NS)_2$ and $M^{III}(NS)_3$ reagents (M = Co, Fe, Mn, etc.) and are measuring the kinetics of isomerization of $[CuMX_2]_2Y_2$ species to test the generality of the proposed metal-exchange mechanism.

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Registry No. I (L = DENC, X = Cl), 80105-85-7; I (L = DENC, X = Br), 80105-86-8; I (L = ENCA, X = Cl), 85049-03-2; II (M = Ni), 66514-12-3; III (M = Cu), 95785-52-7; III (M = Ni), 95785-53-8; IV (L = DENC, X = Cl), 95785-49-2; IV (L = DENC, X = Br), 95785-50-5; IV (L = ENCA, X = Cl), 95785-51-6; V (L = DENC, X = Br), 95785-37-8; V (L = ENCA, X = Cl), 95785-38-9; VI (L = DENC, X = Br), 95785-39-0; VI (L = ENCA, X = Cl), 95785-40-3; VII (L = DENC, X = Br), 95798-77-9; VII (L = ENCA, X = Cl), 95785-41-4; VIII (L = DENC, X = Br), 95785-42-5; VIII (L = ENCA, X = Cl), 95785-43-6; IX (L = DENC, X = Br), 95798-78-0; IX (L = DENC, X = Cl), 90762-75-7; X (L = DENC, X = Br), 95785-44-7; X (L = ENCA, X = Cl), 95785-45-8; X (L = ENCA, X = Br), 95798-79-1; X (L = DENC, X = Cl), 90741-95-0; XI (L = DENC, X = Br), 95798-80-4; XII (L = ENCA, X = Cl), 95785-46-9; XII (L = ENCA, X = Br), 95785-47-0; $(ENCA)_2CuCl_2$, 32491-98-8; $(ENCA)_2CuBr_2$, 32491-99-9; $(DENC)_2Cu_2Br_4$, 95785-48-1.

Supplementary Material Available: Table III (variation of the observed first-order rate constant for isomerization of V as a function of the analytical concentration, $[V]_0$) (1 page). Ordering information is given on any current masthead page.

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[20] We hope to derive the unknown core structures of reactants and transmetalated products from EXAFS data in the near future.

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