J. Am. Chem. Soc. 1984, 106, 4596–4605

Transmetalation Reactions of Tetranuclear Copper(II) Complexes. 2. Stoichiometry and Products of Reaction of $[(DENC)CuCl]_4O_2$, $[(DENC)CuCl]_4(CO_3)_2$, $[(DENC)CuCl]_4Cl_4$, and $(DENC)_4Cu_4Cl_6O$ Complexes (DENC = *N*,*N*-Diethylnicotinamide) with $Ni(NS)_2$ Complexes (NS Is an *S*-Methyl Hydrazinecarbodithioate Schiff Base), the Kinetics of Product Isomerization in Aprotic Solvents, and Inhibition of Copper-Catalyzed Phenolic Oxidative Coupling by Dioxygen through Transmetalation

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Abstract: Attempted crystallization of the tetrameric complexes $[(DENC)CuCl]_4O_2$, I, $[(DENC)CuCl]_4(CO_3)_2$, IV, and $[(DENC)CuCl]_4Cl_4$, IX (DENC = *N*,*N*-diethylnicotinamide), from methylene chloride/methanol/ether gives the complex $(DENC)_4Cu_4Cl_6O$, X, whose molecular structure has been determined in an X-ray structural study. X crystalizes in the tetragonal space group $I4_1$ with $a = b = 15.213$ (3) Å, $c = 22.864$ (4) Å, $V = 5292$ (2) Å^3, and $Z = 4$. Structure solution and refinement with 2461 reflections was complete at $R = 0.069$ and $R_w = 0.079$. The complex consists of a μ_4-oxo group coordinated to four copper atoms, each of which coordinates a monodentate DENC ligand through its pyridine nitrogen atom. Each pair of copper atoms is bridged by a single chlorine atom. The coordination about each copper center is trigonal bipyramidal, with chlorine atoms in the equatorial plane and the copper atom displaced ca. 0.2 Å toward the DENC ligand. The stoichiometries and products of transmetalation of I, IV, IX, and X with $Ni(NS)_2$ complexes, where NS is *S*-methyl isopropylidenehydrazinecarbodithioate in IIIa and *S*-methyl (*p*-methylbenzylidene)hydrazinecarbodithioate in IIIb, have been investigated in methylene chloride. The neutral ligand HNS stoichiometrically demetalates I, showing that a major driving force for transmetalation is the formation of stable $Cu(NS)_2$ coproducts. I reacts stoichiometrically with IIIa or IIIb to give two isomeric forms of $[(DENC)CuNi(H_2O)Cl_2]_2O_2$, V and VI, respectively, after gel permeation chromatographic separation from III (M = Cu and excess Ni). Product V irreversibly isomerizes to VI in aprotic solvents. Isomers V and VI react with CO_2 to give the corresponding dicarbonato derivatives VII and VIII. Derivative VII is also obtained from the reaction of IV with IIIa or IIIb in methylene chloride and irreversibly isomerizes to VIII in aprotic solvents. Such reactions with CO_2 indicate the presence of μ-oxo groups in I, V, and VI. Complexes IX and X are completely transmetalated by IIIa to give $[(DENC)Ni(H_2O)Cl]_4Cl_4$, XI, and $(DENC)_4Ni_4(H_2O)_4Cl_6O$, XII, respectively. Cryoscopic measurements in nitrobenzene indicate that I, IV, and VII–XII are all tetranuclear in solution whereas V and VI are associated as an average of three tetrameric units at ca. 5 °C and $(1–5) \times 10^{-2}$ m. This association is ascribed to intermolecular hydrogen bonding between $Ni(H_2O)$ units and μ-oxo groups. Comparisons of the spectra of I with VI and IV with VIII indicate the presence of the $(DENC)Cu(\mu\text{-}O)Cu(DENC)$ unit in all these complexes. Each such unit in I and VI reacts stoichiometrically with 1 mol of *N*,*N*,*N′*,*N′*-tetraethylethylenediamine, TEED, to give the unit $(DENC)Cu(\mu\text{-}O)Cu(TEED)$ and the $(H_2O)Ni(\mu\text{-}O)Ni(H_2O)$ unit in VI is not substituted. By contrast, complexes IX–XII all react stoichiometrically with 4 mol of TEED. The results in these systems indicate that μ-oxo and μ-carbonato groups (1) limit the coordination numbers of the metal centers of I, IV, V, and VI to 5 (this results in the loss of DENC ligands from the new nickel centers in V, VI, VII, and VIII, (2) control the extent of substitution of Ni for Cu in I and IV, (3) control the extent of substitution of TEED for DENC on copper in I, IV, V, and VI, and (4) prevent the substitution of TEED for water coordinated to nickel in complexes V and VI. The large negative entropies of activation, −(42–63) cal deg^{-1} mol^{-1}, for isomerization of unassociated V in methylene chloride and nitrobenzene and of VII (also in acetonitrile) indicate that these reactions proceed through polar activated complexes with no loss of coordinated ligands. The kinetic parameters for isomerization of V vary much less with solvent than do those for VII, with acetonitrile giving the highest rates possibly because acetonitrile is coordinated by the activated complex. Comparison of activation enthalpies in methylene chloride and nitrobenzene and the apparent stability of Cu–O bonds in I, IV, X, and $(py_mCuO)_n$, (py = pyridine), suggest that the breaking of such bonds is a major enthalpic requirement for isomerization. Nickel(II) complexes $Ni(NS)_2$ effectively inhibit the oxidation of 2,6-dimethylphenol by dioxygen catalyzed by $py_nCu_4Cl_4O_2$ species (n = 3, 4).

Part 1[1] of this series reported that the reaction of 1 mol of $[(DENC)CuCl]_4O_2$,[2] I (Scheme I, N = *N*,*N*-diethylnicotinamide, DENC) with 2 mol of II[3] or 4 mol of III[4] (M = Zn) in aprotic solvents results in complete substitution of Zn for Cu. The primary product $Zn(N_2S_2)\cdot DENC$, eq 1, was isolated shortly after mixing I with II and was structurally characterized. Evidence was presented for steps 1–3 leading to ultimate reaction 4. The last product in eq 4 was isolated and structurally chareceritzed.

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

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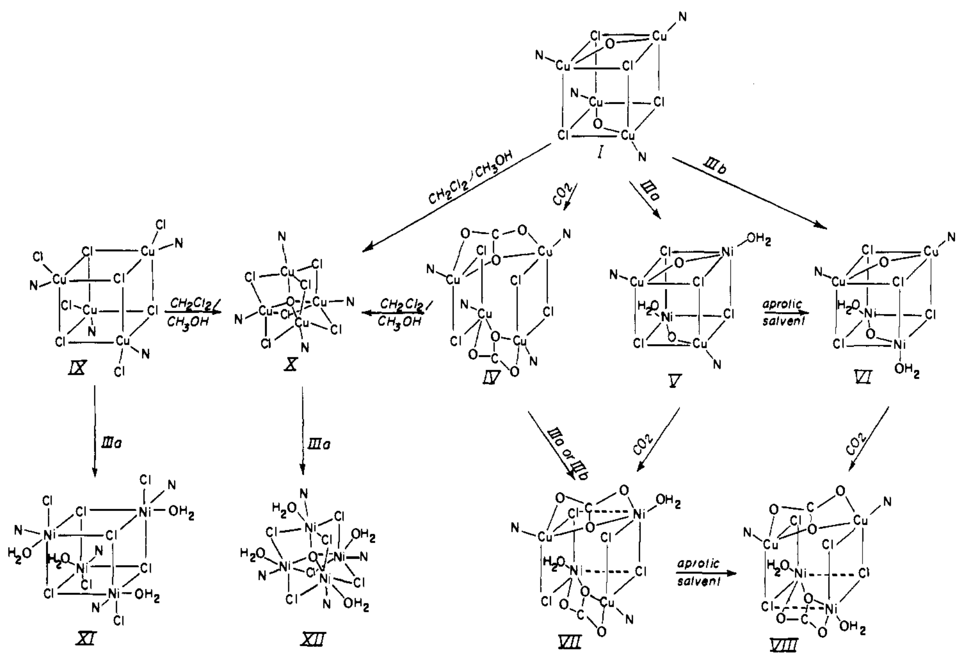
0002-7863/84/1506-4596$01.50/0

Scheme I



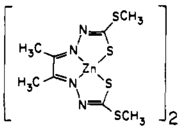
$$\mathrm{I} + 2\mathrm{II} \rightarrow [\mathrm{Cu(N_2S_2)}]_2 + 2\mathrm{Zn(N_2S_2)\cdot DENC} + [\mathrm{(DENC)ZnCuCl_2}]_2\mathrm{O_2} \quad (1)$$

$$[\mathrm{(DENC)ZnCuCl_2}]_2\mathrm{O_2} + 2\mathrm{Zn(N_2S_2)\cdot DENC} \rightarrow [\mathrm{Cu(N_2S_2)}]_2 + [\mathrm{(DENC)Zn_2Cl_2}]_2\mathrm{O_2} + 2\mathrm{DENC} \quad (2)$$

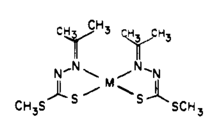
$$[\mathrm{(DENC)Zn_2Cl_2}]_2\mathrm{O_2} \rightarrow 2\mathrm{ZnO(s)} + \mathrm{Cl_2Zn(DENC)_2ZnCl_2} \quad (3)$$

$$\text{net} \quad \mathrm{I} + 2\mathrm{II} \rightarrow 2[\mathrm{Cu(N_2S_2)}]_2 + 2\mathrm{ZnO(s)} + 2\mathrm{DENC} + \mathrm{Cl_2Zn(DENC)_2ZnCl_2} \quad (4)$$

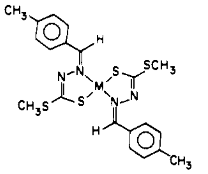
Thus, although complete transmetalation of I takes place, it appears that tetranuclear zinc(II) analogues of I are not isolatable as such from aprotic solvents, presumably because they contain 20-electron metal centers.[1]



II



IIIa



IIIb

Since a major driving force for transmetalation is the high thermodynamic stability of the $\mathrm{Cu(N_2S_2)}$ products from II or III in these systems (see ref 5 and Results and Discussion), it ought to be possible to substitute other metals for copper in I and its homologues.[6] Two likely benefits of transmetalation would be (a) direct structural information on tetranuclear analogues of I and related complexes[2,6] which have not been obtained by other means and (b) the possibility of altering the efficiency and specificity of such oxocopper(II) species as catalysts for oxidative reactions of phenols with dioxygen[7] by partial substitution of other metals for copper. An ongoing effort in this laboratory is inhibition of metal-catalyzed phenolic oxidation by dioxygen which is believed to be responsible for the storage instability of liquefied coals.[8,9]

The following questions arise from our earlier work:[1] (1) Is aprotic transmetalation of tetranuclear copper(II) complexes by other $\mathrm{M(NS)_2}$ reagents[4,10] possible? (2) Does complete transmetalation always take place or are intermediate tetranuclear species containing $(4 - x)$ copper centers and x other metal centers stable? (3) Do the products contain fewer DENC ligands than are initially present in I and if not, why not? (4) How does the constitution of I affect the extent of transmetalation and, in particular, are the two original μ-oxo groups in I[2,6] present in the product?

This paper reports the stoichiometries and products of reaction of I[2] and its dicarbonato derivative $[\mathrm{(DENC)CuCl}]_4\mathrm{(CO_3)_2}$, IV,[11] with III (M = Ni) in methylene chloride. Attempted crystallization of I, IV, and $[\mathrm{(DENC)CuCl}]_4\mathrm{Cl_4}$, IX, from methylene chloride/methanol/ether produces crystalline $\mathrm{(DENC)_4Cu_4Cl_6O}$, X, which has been structurally characterized for use as a reactant for transmetalation. The stoichiometries of reaction of IX and X with III (M = Ni) differ from those with I and IV. Proposed core structures for all reactants and products are given in Scheme I.

We chose to study nickel(II) transmetalation because tetranuclear $\mathrm{M_4Cl_4}$ and $\mathrm{Cu_2M_2Cl_4}$ units should be more stable with M = Ni(II) (d^8) than with M = Zn(II) (d^{10}) (see above) and the nickel(II) products should also be stable to reaction with dioxygen. We have found that the identity of the copper(II) reactant determines whether $\mathrm{Ni_2Cu_2Cl_4}$ or $\mathrm{Ni_4Cl_4}$ core structures are formed and whether or not each metal center of the product coordinates DENC. It will be shown that two structural isomers of

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Table I

Crystallographic Data for $(DENC)_4Cu_4Cl_6O$	
mol formula	$Cu_4C_{40}H_{56}N_8Cl_6O_5$
fw	1195.8
space group	$I4_1$
cell dimens	
$a = b$, Å	15.213 (3)
c, Å	22.864 (4)
V, Å^3	5292 (2)
ρ_{calcd}, g/cm^3	1.501
Z	4
Collection and Refinement Parameters	
linear abs coeff, cm^{-1}	49.7
scan type	$\theta/2\theta$
bkgnd time/scan time	0.5
quadrant collected	$+h,\pm k,+l$
no. of unique data	3769
no. of data with $I \geq 2\sigma(I)$	2461
R	0.069
R_w	0.079
no. of parameters	286

$[(DENC)CuNi(H_2O)Cl_2]_2O_2$, which we propose are V and VI, can be obtained from I with different $Ni(NS)_2$ reagents III. These products react with CO_2 to give different dicarbonato derivatives, VII and VIII, respectively. The kinetics of isomerization of V to VI and of VII to VIII have been measured in aprotic solvents. The oxidation of 2,6-dimethylphenol by dioxygen initiated by $py_nCu_4Cl_4O_2$ (py = pyridine; n = 3 or 4)[6] was found to be inhibited by addition of IIIa (M = Ni).

Experimental Section

Materials and Reagents. The copper reactants I[2] and IV[11] and the $Ni(NS)_2$ complexes III[4] were prepared as previously described. The preparation and purification of copper(I) chloride, methylene chloride (Aldrich or Burdick and Jackson), *N,N,N',N'*-tetraethylethylenediamine, (TEED, Aldrich), nitrobenzene (Aldrich), and diethyl ether (Fisher) followed literature procedures.[1] Acetonitrile (Baker) was treated with CaH_2 overnight, distilled from P_4O_{10} (Alfa), and stored over 4 Å molecular sieves. Anhydrous copper(II) chloride was obtained from the hydrate (Alfa) by heating overnight at 120 °C under vacuum. Nickel(II) acetate tetrahydrate (Aldrich) and methanol (Burdick and Jackson) were used as received. High purity dinitrogen was deoxygenated with a freshly activated column of DE-OX (Alfa) before use.

The complex $[(DENC)CuCl]_4Cl_4$, IX, was prepared by treating a large excess of anhydrous copper(II) chloride (30 mmol) with DENC (10 mmol) in methylene chloride (60 mL). The mixture was stirred vigorously at room temperature for 12 h, after which the dark brown product solution was filtered into hexane (200 mL). The precipitated yellowish brown complex was filtered off and dried in a vacuum desiccator.

The complex $(DENC)_4Cu_4Cl_6O$, X, was obtained by attempted crystallization of I, IV, and IX from methylene chloride in the presence of methanol/diethyl ether. In a typical experiment, a freshly prepared sample of IX (1 mmol) was dissolved in 50% v/v methanol/methylene chloride (20 mL) followed by addition of diethyl ether (5 mL). Evaporation of the solvent over a 2–3-day period at room temperature gave a green solution and a brown-green precipitate. Brown crystals of the desired product were mechanically separated from the precipitate and washed with methanol. Since X is a characteristic disproportionation product in these systems, we have determined its X-ray crystal structure and have used it as a reactant for transmetalation.

Collection of Diffraction Data for Crystalline X. The opaque, reddish-brown crystal chosen for data collection had the shape of a truncated square pyramid and dimensions of approximately 0.17 × 0.17 × 0.16 mm. The crystals available were not of excellent quality. The systematic absences ($h + k + l \neq 2n$ for hkl and $l \neq 4n$ for $00l$) and the observation of $4/m$ Laue symmetry defined the tetragonal space group $I4_1$. Crystal data are summarized in Table I.

Intensity data, $4 < 2\theta < 115°$, were collected on a Syntex $P2_1$ automated diffractometer with Ni-filtered, Cu Kα radiation (1.5418 Å). Accurate cell constants and an orientation matrix were obtained from a least-squares refinement of 15 reflections with $46 < 2\theta < 72°$ and were well separated in reciprocal space. Two standard reflections were measured every 100 reflections; their intensities showed no diminution in intensity over the duration of the data collection. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction, obtained via a ψ scan, was applied. A total of 2461 reflections with $I \geq 2\sigma(I)$ were used in the structure solution and refinement.

Solution and Refinement of the Structure. The complex is constrained to lie on a crystallographic twofold axis (Wycoff position a). The unique copper atoms were determined by the solution of a three-dimensional Patterson map and subsequent Fourier summations resulted in the location of all non-hydrogen atoms. These atoms were refined by anisotropic full-matrix least-squares treatment.[12] The refinement was complete at $R = 0.069$ and $R_w = 0.079$.[13] Scattering factors for Cu, Cl, O, N, and C were taken from ref 14 and scattering factors for H, from ref 15. Real and imaginary terms for anomalous scattering were taken from ref 16. The function minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were assigned in the following manner: $(w)^{1/2} = 1$ for $|F_o| \leq 40.0$ and $(w)^{1/2} = 40.0/|F_o|$ for $F_o| > 40.0$.

The positional parameters are listed in Table II; selected bond lengths and angles with estimated standard deviations are given in Table III.

Synthesis of $[(DENC)CuNi(H_2O)Cl_2]_2O_2$. Isomers V and VI. A clear, greenish brown solution of I (1 mmol) in methylene chloride (30 mL) was stirred with IIIa (M = Ni, 4 mmol) in methylene chloride (50 mL) at room temperature under dry dinitrogen. The reaction was monitored spectrophotometrically. No further absorbance change was evident after 6 h. Gel permeation chromatography (Biobeads SX-12 resin, 150 cm × 2.5 cm diameter column, methylene chloride eluant)[17] separated the black product solution into a brownish green band subsequently identified (Table IV) as a solution of V followed by black IIIa (M = Cu).[10,18] Solid V was isolated by vacuum solvent evaporation of the green band. Experiments with molar reactant ratios IIIa/I = 3–10 gave the same product V after chromatographic separation from IIIa (M = Ni and Cu).

The second isomeric form of $[(DENC)CuNi(H_2O)Cl_2]_2O_2$, VI, was obtained in exactly the same manner as for V except that the nickel reactant was IIIb (M = Ni).[4] The coproduct IIIb (M = Cu) is much less soluble than IIIa (M = Cu)[10] and can be filtered off prior to chromatography. Isomer VI can also be obtained by evaporating the solvent from a solution of V in methylene chloride after 1 week at room temperature.

Dicarbonato Derivatives of V and VI. Reaction of IV[11] with excess IIIa or IIIb (M = Ni) in CO_2-saturated methylene chloride in a CO_2 atmosphere followed by gel permeation chromatography (see above) gave the dicarbonato derivative of V, labeled VII in Scheme I. A solution of VII in methylene chloride gives the dicarbonate derivative of VI, labeled VIII, after 1 week at room temperature and evaporation of the solvent. The dicarbonates VII and VIII can also be obtained by treatment of methylene chloride solutions of V and VI, respectively, with dry CO_2.

Synthesis of Tetranickel(II) Complexes. A clear brown solution of the octachloro complex IX (Table IV, 1 mmol) in methylene chloride (30 mL) was treated with a reddish violet solution of IIIa (M = Ni, 4.5 mmol) in methylene chloride (50 mL). The mixture was stirred at room temperature under dinitrogen for 6 h. Gel permeation chromatography[17] of the black product solution gave well-separated bands of $[(DENC)Ni(H_2O)Cl]_4Cl_4$, XI (olive green), followed by IIIa (M = Cu, Ni, black). The nickel(II) complex was isolated by vacuum evaporation of the solvent from the olive green fractions.

The complex $(DENC)_4Ni_4(H_2O)_4Cl_6O$, XII, was isolated in exactly the same manner except that the copper(II) reactant was $(DENC)_4Cu_4Cl_6O$, X.

Analytical Procedures. The elemental copper and nickel contents of reactants and products were determined with a Leeman Labs Plasma Spec inductively coupled plasma emission spectrometer equipped with a computer-controlled scanning echelle grating monochromator. The in-

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(13) All crystallographic calculations were carried out on a VAX 11/780 computer. The principal programs used were: The X-RAY system-version of 1976, J. M. Stewart, editor, Technical Report TE-446 of the Computer Science Center, University of Maryland, College Park, Maryland; FMLS, anisotropic full-matrix least-squares refinement, Ganzel, P.L., Sparks, R.A. and Trueblood, K.N., UCLA; modified by McPhail, A.T., Duke University; ORTEP, crystallographic illustration programs, Johnson, C.K., Oak Ridge, ORNL-3794.

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Table II. Fractional Atomic Coordinates (×10^4) for the Non-Hydrogen Atoms in $(DENC)_4Cu_4Cl_6O$, with Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*
Cu(1)	856 (1)	4440 (1)	−7 (1)
Cu(2)	569 (2)	5857 (1)	−958 (1)
Cl(1)	67 (2)	3085 (2)	−338 (1)
Cl(2)	1887 (2)	5049 (3)	−646 (2)
Cl(3)	0 (-)	5000 (-)	−1745 (2)
Cl(4)	0 (-)	5000 (-)	811 (2)
O(1)	0 (-)	5000 (-)	−506 (8)
N(1)	1678 (6)	3805 (6)	511 (5)
C(2)	1422 (8)	3265 (10)	883 (7)
C(3)	1928 (9)	2779 (7)	1241 (5)
C(4)	2834 (10)	3014 (10)	1244 (6)
C(5)	3226 (12)	3516 (10)	858 (7)
C(6)	2538 (9)	3978 (7)	486 (6)
C(7)	1462 (14)	1961 (13)	1686 (7)
N(8)	1222 (8)	2194 (6)	2173 (5)
C(9)	1267 (15)	3030 (16)	2408 (9)
C(10)	480 (17)	3551 (24)	2352 (11)
C(11)	708 (11)	1627 (11)	2539 (8)
C(12)	1378 (12)	933 (12)	2895 (7)
O(2)	1460 (10)	1288 (7)	1376 (6)
N(13)	1185 (8)	6705 (8)	−1457 (5)
C(14)	1817 (9)	6307 (8)	−1841 (5)
C(15)	2266 (9)	6816 (9)	−2283 (4)
C(16)	2111 (8)	7734 (9)	−2271 (6)
C(17)	1448 (9)	8072 (7)	−1870 (6)
C(18)	1067 (9)	7579 (8)	−1499 (5)
C(19)	2947 (7)	6504 (8)	−2557 (5)
N(20)	2791 (12)	6091 (9)	−3085 (6)
C(21)	1905 (13)	6117 (11)	−3388 (6)
C(22)	1529 (9)	5191 (12)	−3283 (8)
C(23)	3639 (9)	5771 (9)	−3378 (6)
C(24)	3928 (15)	6366 (14)	−3785 (8)
O(3)	3659 (7)	6564 (10)	−2417 (5)

Table III. Interatomic Distances (Å) and Valency Angles (deg) in the Coordination Spheres of $(DENC)_4Cu_4Cl_6O$, with Estimated Standard Deviations in Parentheses[a]

(a) Bond Lengths			
Cu(1)–O(1)	1.930 (-)	Cu(2)–O(1)	1.875 (-)
Cu(1)-Cl(1)	2.504 (3)	Cu(2)–Cl(1)′	2.352 (4)
Cu(1)–Cl(2)	2.336 (4)	Cu(2)–Cl(2)	2.458 (4)
Cu(1)–Cl(4)	2.433 (-)	Cu(2)–Cl(3)	2.385 (-)
Cu(1)–N(1)	1.975 (10)	Cu(2)-N(13)	1.930 (12)
(b) Valency Angles			
O(1)–Cu(1)–Cl(1)	82.0 (-)	O(1)–Cu(2)–N(13)	177.0 (-)
O(1)–Cu(1)–Cl(2)	84.7 (-)	Cl(1)′–Cu(2)–Cl(2)	120.2 (1)
O(1)–Cu(1)–Cl(4)	86.5 (-)	Cl(1)′–Cu(2)–Cl(3)	132.8 (1)
O(1)–Cu(1)–N(1)	176.4 (-)	Cl(1)′–Cu(2)–N(13)	95.6 (4)
Cl(1)–Cu(1)–Cl(2)	117.3 (1)	Cl(2)–Cu(2)–Cl(3)	104.0 (1)
Cl(1)–Cu(1)–Cl(4)	105.3 (-)	Cl(2)–Cu(2)–N(13)	96.2 (4)
Cl(1)–Cu(1)–N(1)	94.7 (3)	Cl(3)–Cu(2)–N(13)	95.4 (3)
Cl(2)–Cu(1)–Cl(4)	134.6 (-)	Cu(1)–O(1)–Cu(2)	108.7 (-)
Cl(2)–Cu(1)–N(1)	98.3 (3)	Cu(1)–O(1)–Cu(2)′	109.3 (-)
Cl(2)–Cu(1)–N(1)	92.8 (3)	Cu(1)–Cl(1)–Cu(2)′	79.4 (1)
O(1)–Cu(2)–Cl(1)′	87.4 (-)	Cu(1)–Cl(2)–Cu(2)	80.3 (1)
O(1)–Cu(2)–Cl(2)	82.5 (-)	Cu(2)–Cl(3)–Cu(2)′	82.0 (-)
O(1)–Cu(2)–Cl(3)	82.4 (-)	Cu(1)–Cl(4)–Cu(1)′	79.5 (-)

[a] Primes indicate coordinates from Table II translated about the twofold axis at $x = 0$ and $y = {}^1/_2$.

strument was programmed to monitor emission intensity at each analytical wavelength for three 3-s intervals. The analytical wavelengths were 324.7 nm for copper and either 231.6 or 352.4 nm for nickel. The instrument was calibrated with commercial standard solutions of these elements (Spex) that were stabilized after dilution with concentrated nitric acid (1 mL/100 mL solution). Detection limits for analytical determinations were established to be 3 and 7 ng/mL for copper and nickel, respectively.

All other elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

The water contents of nickel-containing products were determined with a Perkin-Elmer TGS-2 thermogravimetric system and a heating rate of 2.5 °C/min in flowing dry air (50 mL/min). Data were acquired with a Bascom-Turner M8110 intelligent recorder, stored on disk, and subsequently replotted in 8.5 × 11 in. format for interpretation.

Cryoscopic molecular weight measurements of freshly-prepared tetranuclear reactants and products were made in nitrobenzene, as described previously.[6]

Analytical data are collected in Table IV.

Physical Measurements. Solution electronic spectral measurements were made with Cary 14 and Beckman DK-1A spectrophotometers in matched quartz cells at room temperature. Infrared spectra (KBr disks) were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with the 906.5 or 3026.3 cm^{-1} absorption of polystyrene. Spectrophotometric determinations of reaction stoichiometries were carried out by standard techniques at 25 °C in the thermostated cell compartment of a Beckman DK-1A spectrophotometer using matched quartz cells. The solvent (methylene chloride) was used as reference.

Kinetic measurements of isomerization of V to VI and of VII to VIII were monitored spectrophotometrically at 850 nm in the Beckman DK-1A spectrophotometer at temperatures controlled to within ±0.1 °C of the desired value. First-order rate constants for isomerization, k_{obsd}, were derived from linear least-squares plots of ln $(A_\infty - A_t)$ vs. time, where A_t is the absorbance at time t.

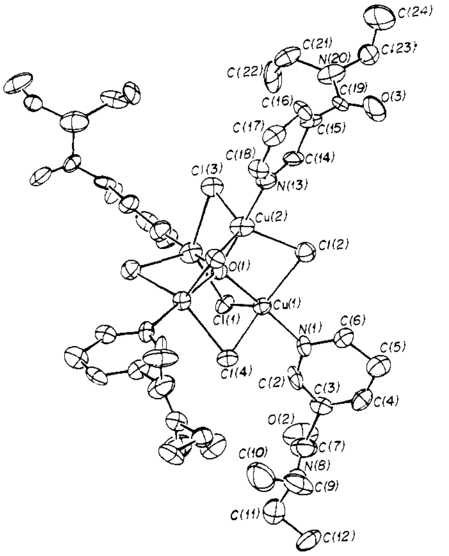

Figure 1. View of $(DENC)_4Cu_4Cl_6O$. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted.

Results and Discussion

One major goal of this study has been to demonstrate that substitution of nickel for copper in tetranuclear (pyridine)chlorocopper(II) complexes, via transmetalation, gives tetranuclear products. Another has been to examine how the presence of oxo groups affects the properties of copper(II) complexes and their transmetalated forms.

Copper(II) Reactants. We have had to rely on analytical and cryoscopic data (Table IV) to establish the tetranuclear constitutions of the neutral copper(II) reactants I, IV, and IX because we have not succeeded in growing single crystals of these complexes from aprotic solvent systems. Complexes I and IV characteristically disproportionate on attempted crystallization.[2,6] Addition of excess methanol to such systems gives $(DENC)_4Cu_4Cl_6O$, X, as a crystalline product. Formaldehyde was detected[19] in the supernatant solutions from which X was grown, showing that methanol acts as a protic reductant for the copper(II)[18,20,21] centers

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

symbol[b]	complex	% C	% H	% N	% Cl	% Cu	% Ni	% H_2O[c]	mol wt[d]
I	$[(DENC)CuCl]_4O_2$[e]	41.50	5.10	9.80	12.91	22.10			1140 ± 20
		(42.11)	(4.95)	(9.82)	(12.43)	(22.28)			(1141)
IV	$[(DENC)CuCl]_4(CO_3)_2$[e]	39.43	4.48	8.93	11.32	20.24			1120 ± 20
		(41.05)	(4.59)	(9.12)	(11.56)	(20.68)			(1229)
V	$[(DENC)CuNi(H_2O)Cl_2]_2O_2$	30.67	4.20	6.88	17.26	15.29[f]	14.22[f]	4.55	2500 ± 200[g]
		(29.63)	(3.98)	(6.91)	(17.49)	(15.67)	(14.48)	(4.44)	(811)
VI	$[(DENC)CuNi(H_2O)Cl_2]_2O_2$	29.78	4.12	6.85	17.10	15.15[h]	13.99[h]	4.49	2500 ± 200[g]
		(29.63)	(3.98)	(6.91)	(17.49)	(15.67)	(14.48)	(4.44)	(811)
VII	$[(DENC)CuNi(H_2O)Cl_2]_2(CO_3)_2$	29.90	4.20	6.80	15.57	13.20	13.20	[i]	850 ± 20
		(29.40)	(3.59)	(6.23)	(15.78)	(14.14)	(13.06)	(4.01)	(899)
VIII	$[(DENC)CuNi(H_2O)Cl_2]_2(CO_3)_2$	29.62	4.08	6.64	15.62	13.37	13.13	[i]	920 ± 20
		(29.40)	(3.59)	(6.23)	(15.78)	(14.14)	(13.06)	(4.01)	(899)
IX	$[(DENC)CuCl]_4Cl_4$	38.25	4.62	8.77	21.54	20.50			1250 ± 20
		(38.41)	(4.51)	(8.96)	(22.68)	(20.32)			(1251)
X	$(DENC)_4Cu_4Cl_6O$	40.05	4.68	9.15	17.66	20.98			1180 ± 20
		(40.18)	(4.72)	(9.37)	(17.79)	(21.25)			(1196)
XI	$[(DENC)Ni(H_2O)Cl]_4Cl_4$	35.80	5.00	8.40	21.58		18.00	5.50	1280 ± 20
		(36.86)	(4.95)	(8.60)	(21.76)		(18.02)	(5.53)	(1303)
XII	$(DENC)_4Ni_4(H_2O)_4Cl_6O$	37.69	5.10	8.67	16.84		18.50	5.54	1270 ± 20
		(38.48)	(5.17)	(8.98)	(17.04)		(18.81)	(5.77)	(1249)

[a] Analytical methods are described in the text; calculated values given in parentheses. [b] Symbols used in Scheme I. [c] Determined by thermogravimetric analysis (see footnote i). [d] In nitrobenzene: typical molal concentration 2 × 10^{-2}. [e] Data from ref 6. [f] Average of results for eight independently prepared samples of V. Respective standard deviations are Ni, ±0.37%, and Cu, ±0.69%. [g] Average of three measurements in the range (1–5) × 10^{-2} m. No variation of molecular weight can be discerned within experimental error. [h] Average of five independently prepared samples of VI. Respective standard deviations are Ni, ±0.06%, and Cu, ±0.71%. [i] Water loss in these complexes is coupled with decarboxylation and cannot be distinguished clearly (see Table VI, footnote *e*).

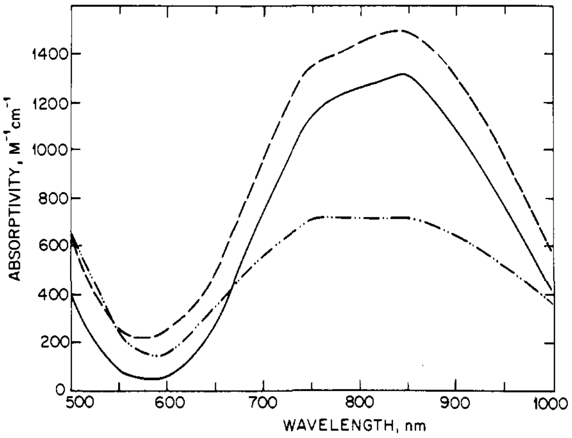

Figure 2. Electronic spectra of copper reactants I (–··–), IX (---) and X (—) in methylene chloride at 25 °C.

in I, IV, and IX. The stable structure X evidently results from reoxidation of copper(I) by dioxygen and disproportionation in an unknown sequence of reactions. We have determined the X-ray crystal structure of X and have used it with I, IV, and IX as reactants for transmetalation by $Ni(NS)_2$ complexes.

The Molecular Structure of $(DENC)_4Cu_4Cl_6O$, X. The molecular structure of $(DENC)_4Cu_4Cl_6O$, X (Figure 1), consists of a μ_4-oxo group tetrahedrally coordinated to four copper(II) centers. Each pair of copper(II) centers is bridged by a single chlorine atom. The coordination sphere about each copper(II) is trigonal bipyramidal, with three chlorine atoms in the equatorial plane. Each copper atom is displaced ca. 0.2 Å from this plane toward the pyridine nitrogen of DENC, which acts as a monodentate ligand. Because the complex possesses crystallographic twofold symmetry, the μ_4-oxo group and two of the chlorine atoms lie on a twofold axis.

Although atomic parameters (Table III) exhibit rather large estimated standard deviations, the mean values of the bond lengths and angles within the coordination sphere agree very well with those observed previously for molecules possessing a μ_4-oxo, μ-chloro Cu_4Cl_6O core structure.[22-27] The pertinent mean bond lengths in X are Cu–O 1.903 Å, Cu–N 1.968 Å, and Cu–Cl 2.411 Å. The mean bond angles are as follows: Cu–O–Cu 109.0°, Cu–Cl–Cu 80.3°, O–Cu–N 176.7°, O–Cu–Cl 84.3°, N–Cu–Cl 95.5°, and Cl–Cu–Cl 119.0°. The range for the Cl–Cu–Cl angles, while large (104.0–134.6°), is not surprising in light of previously studied structures.[22,26]

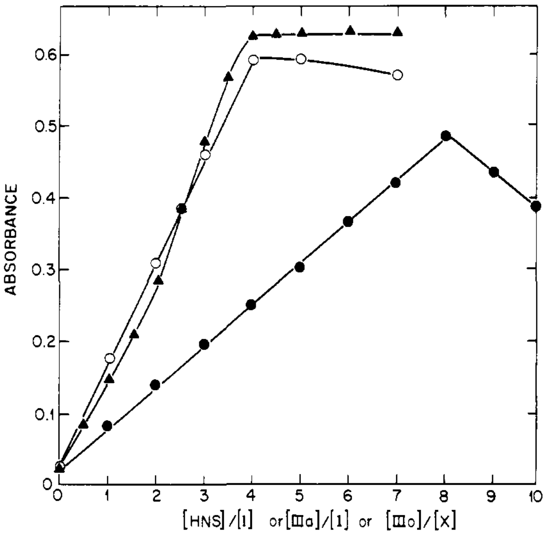

Figure 3. Spectrophotometric titrations of 1.0 × 10^{-4} M methylene chloride solutions of I with HNS (●) and with IIIa (▲) and of X with IIIa (○) at 575 nm.

In both unique DENC ligands the diethylamido side chain is approximately perpendicular to the pyridine ring. This conformation also has been observed in $[(DENC)_2CuCl_2]_3$[28] and in $Zn(N_2S_2)(DENC)$.[1]

Spectra of the Copper Reactants. The complexes I, IV, IX, and X are all freely soluble nonelectrolytes in methylene chloride and

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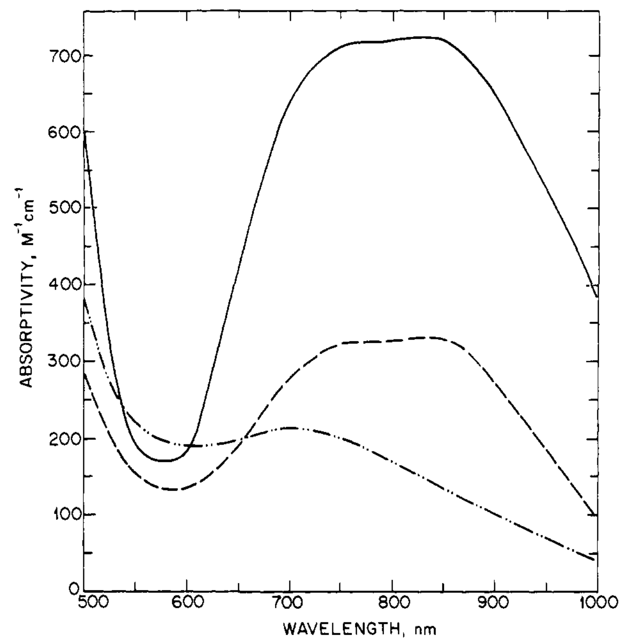

Figure 4. Electronic spectra of I (—), V (–··–) and VI (2.3×10^{-3} M, - - -) in methylene chloride at 25 °C.

nitrobenzene. Their similar electronic spectra (Figures 2 and 5) support a common "cubane" structure, Scheme I. The KBr disk IR spectra of I, IV, and X exhibit broad, medium intensity bands at 510, 500, and 530 cm^{-1}, respectively, which are ascribed to $\nu_{\text{Cu-O}}$ since they are not observed in the otherwise closely similar spectrum of IX. The close correspondence of $\nu_{\text{C=O}}$ for coordinated DENC indicates that this ligand is coordinated only through its pyridine nitrogen atom.[2,6,11]

Demetalation of I by HNS. Figure 3 illustrates the result of a spectrophotometric titration of I with HNS, the neutral form of the ligand from which the complexes IIIa are obtained, in methylene chloride. The titration shows a primary stoichiometry $\Delta(\text{HNS})/\Delta(\text{I}) = 8$, consistent with eq 5.[29] This result supports

$$[(\text{DENC})\text{CuCl}]_4\text{O}_2 + 8\text{HNS} \rightarrow 4\text{Cu(NS)}_2 + 4\text{HCl} + 4\text{DENC} + 2\text{H}_2\text{O} \quad (5)$$

the contention that a major driving force for transmetalation of copper(II) complexes by M(NS)_2 reagents III is the high thermodynamic stability of the Cu(NS)_2 coproducts.[1,5]

Transmetalation by Ni(NS)_2 Reagents. General Observations. All the anhydrous copper(II) and nickel(II) reactants of this study are soluble in methylene chloride. When such solutions are mixed, one observes the formation of a dark greenish black color with IIIa or a brown, microcrystalline precipitate with IIIb; these results are due to transmetalation to produce the corresponding Cu(NS)_2 complexes. In either case the complete separation of the desired nickel-containing product from Cu(NS)_2 and any excess Ni(NS)_2 is best accomplished by aprotic gel permeation chromatography. The total isolation procedure results in the incorporation of water that is responsible for strong, broad absorption centered at 3400 cm^{-1} in the IR spectra of the nickel-containing products.[30] However, the analytical and TGA data (Table IV) demonstrate that the molar ratio of water/nickel(II) is always 1. We interpret this result as indicating that each nickel(II) center coordinates one water molecule.[31] The water in these complexes must remain coordinated in solution otherwise anomalously low cryoscopic molecular weights would be observed.

Stoichiometry and Products of Transmetalation of $[(\text{DENC})\text{CuCl}]_4\text{O}_2$, I and $[(\text{DENC})\text{CuCl}]_4(\text{CO}_3)_2$, IV, by Ni(NS)_2 Reagents. Spectrophotometric titrations of I with IIIa in methylene chloride at 575 nm (Figure 3) show that complete reaction requires 4 equiv of IIIa. However, the same product $[(\text{DENC})\text{CuNi}(\text{H}_2\text{O})\text{Cl}_2]_2\text{O}_2$, V, was isolated with molar ratios of IIIa/I = 3–10. The slight change of slope at IIIa/I = 2 in Figure 3 is due to the formation of $\text{Ni(NS)}_2\cdot\text{DENC}$ as the titration proceeds to the end point and is reflected by the stoichiometry of reaction (eq 6a).

$$\text{I} = 4\text{IIIa} \xrightarrow[\text{H}_2\text{O}]{} \text{V} + 2\text{Ni(NS)}_2\cdot\text{DENC} + 2\text{Cu(NS)}_2 \quad (6a)$$

$$\text{I} + 3\text{IIIb} \xrightarrow[\text{H}_2\text{O}]{} \text{VI} + \text{Ni(NS)}_2\cdot2\text{DENC} + 2\text{Cu(NS)}_2 \quad (6b)$$

It is important to note that the combined transmetalation reaction and isolation procedure represented by eq 6a always gives the same spectrum, that of V (Figure 4), irrespective of the reaction ratio IIIa/I = 3–10 and the time taken for the transmetalation reaction and subsequent chromatographic isolation (ca. 10 min)[17] of V. This indicates that isomerization of the primary transmetalation product, which is V without its coordinated water, to VI (see below) occurs only when this water is incorporated. The anhydrous precursor of V would contain 4-coordinate nickel(II) centers that evidently can isomerize only very slowly, if at all, to the anhydrous precursor of VI. Also important is the fact that V, once isolated, will react with 2 more mol of Ni(NS)_2 to give fully transmetalated products that we shall describe in a subsequent paper.

The corresponding reaction of I with IIIb follows the stoichiometry of eq 6b; the product VI has an electronic spectrum that differs from that of V (Figure 4). However, the analytical data for V and VI are the same within experimental error (Table IV), showing them to be isomers. The spectrum of an aprotic solution of V changes to that of VI on standing, and the kinetics of this process have been measured (see below). Figure 4 shows that the spectrum of VI is similar in form to that of tetranuclear I but that VI has about half the maximum molar absorptivity of I. Since I contains two $(\text{DENC})\text{Cu}(\mu\text{-O})\text{Cu}(\text{DENC})$ units,[2,6,11] we propose that VI has one such unit, leading to the core structure of VI shown in Scheme I. The assumption that the contribution of the $(\text{H}_2\text{O})\text{Ni}(\mu\text{-O})\text{Ni}(\text{H}_2\text{O})$ unit to the maximum absorption is negligible is supported by the very low molar absorptivities of completly transmetalated products (see below).

Freshly prepared products V and VI react with 2 mol of CO_2[11] in methylene chloride to give the respective *tetranuclear* dicarbonato derivatives VII and VIII (Table IV), whose electronic spectra are shown in Figure 5. The formation of these derivatives shows that the two μ-oxo groups of I are retained in V and VI.[11] The fact that the maximum molar absorptivity of VIII is about half of that of IV is further strong support for the existence of one $(\text{DENC})\text{Cu}(\mu\text{-O})\text{Cu}(\text{DENC})$ unit in VI. We propose the core structure of Scheme I for V to be consistent with the similarity of spectra for V and tetranuclear VII, which isomerize in solution to give VI and VIII, respectively. The latter also have similar spectra.

All the reactants and products in Table IV except V and VI behave as neutral tetranuclear species in nitrobenzene near its freezing point (ca. 5 °C), despite the fact that complexes V–VIII, XI, and XII all contain one coordinated water molecule per nickel center. The measured cryoscopic molecular weights for isomers V and VI roughly correspond to an average of three associated tetrameric units (M_r = 811 g/mol) per solute species at the (1–5) $\times 10^{-2}$ m level in nitrobenzene. Since none of the anhydrous copper reactants and, particularly, neither of the aquo carbonato

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[29] The decrease in absorbance at $\Delta(\text{HNS})/\Delta(\text{I}) > 8$ in Figure 3 is due to destruction of the azomethine bonds in Cu(NS)_2 by HCl, produced in eq 5, to give $[\text{Cu}(\text{NH}_2\text{NHCSSCH}_3)_2]\text{Cl}_2$ which is a well-characterized reaction product: El-Toukhy, A. M.S. Thesis, Alexandria University, 1973. Similar observations in other related systems are discussed in: Ali, M. A.; Livingston, S. E.; Phillips, D. J. *Inorg. Chim. Acta* **1971**, *5*, 493. El-Sayed, L.; El-Toukhy, A.; El-Kady, N.; Iskander, M. F. *Transition Met. Chem. (Weinheim, Ger.)*, **1980**, *5*, 293.

[30] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd Ed., Wiley, New York (1978), p. 226; The presence of aquo ligands in all the transmetallated products V-VIII, XI and XII makes the assignment of $\nu_{\text{M-O}}$ uncertain.

[31] There are examples of copper–nickel complexes in which water is exclusively coordinated to nickel: Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.

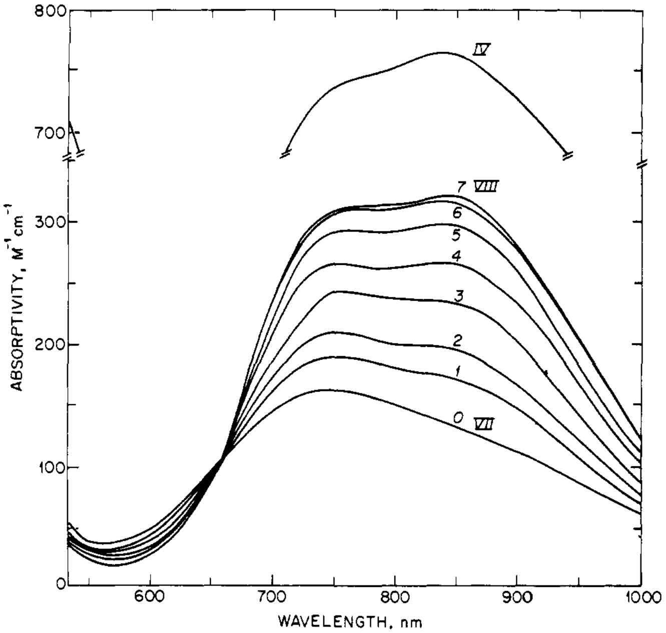

Figure 5. Spectral changes due to isomerization of VII (2.57×10^{-3} M) to VIII in methylene chloride at 25 °C. The spectra were measured at the following intervals (h): 0, zero; 1, 3; 2, 5; 3, 8; 4, 11; 5, 14; 6, 17; 7, 24. An isobestic is observed at 660 nm. Also shown is the relevant part of the spectrum of IV for comparison (see text).

derivatives VII and VIII give anomalous molecular weights under the same conditions, we conclude that association of isomers V and VI arises from intermolecular hydrogen bonding between aquo ligands and the μ-oxo groups of V and VI (see below). This association is not significant when the μ-oxo groups are converted to μ-carbonato groups in the respective derivatives VII and VIII.

As noted above, the incorporation of 1 mol of water/mol of nickel in transmetalation products appears to occur during the preferred chromatographic isolation procedure. A strong affinity of nickel centers for traces of water and a tendency for relatively small displaced DENC molecules to be retained by the gel permeation chromatography column would favor DENC replacement by water, but the water is simply *added* in completely transmetalated products (see below). The high general affinity of the nickel centers in transmetalation products for aquo ligands is indicated by the invariance of the electronic spectra of V and VII in the presence of up to a 100-fold excess of DENC in methylene chloride and by the same analytical data for solid products isolated from such solutions by chromatography or by precipitation with hexane.

Conformation with the Beer–Lambert Law and Solvent Dependence of the Spectra of Complexes V–VIII. We have previously noted significant differences in the spectra of the asymmetrical, polar species (μ_4-oxo)py$_n$Cu$_4$Cl$_4$O (py = pyridine; n = 3 or 4) in methylene chloride and nitrobenzene and have used this as a line of evidence for the fundamental difference between the core structures of (μ_4-oxo)py$_n$Cu$_4$Cl$_4$O and I; the spectra of I are virtually identical in those solvents.[6] The species V, VII and VI, VIII are formulated as symmetrical and asymmetrical pairs, respectively (Scheme I). Cryoscopic molecular weight data (Table IV) indicate that the oxo complexes V and VI are associated in nitrobenzene while the dicarbonato derivatives VII and VIII are not. Despite these differences of association and proposed core structures (Scheme I) the only complex whose spectrum does not conform to the Beer–Lambert law ((1–500) × 10^{-4} M) and whose spectra differe significantly in methylene chloride and nitrobenzene is VI (typical data at 850 nm (molar absorptivity = 54, 70, and 81 (g atom metal)$^{-1}$ cm^{-1} in methylene chloride at [VI]$_{\text{total}}$ = 0.2, 2.0, and 20 × 10^{-3} M, respectively; the corresponding values in nitrobenzene are 50, 60, and 72 (g atom metal)$^{-1}$ cm^{-1}, respectively). Comparison of the spectra and molar absorptivities of I, IV, and V–X, their reaction products with TEED (see below), and the spectra of completely transmetalated products XI and XII (which have low molar absorptivities, see below) indicates that the copper centers in V–VIII are largely responsible for their spectral absorption in the 500–900 nm region. We have to conclude that the proposed (DENC)Cu(μ-O)Cu(DENC) chromophore in VI is sensitive to intermolecular hydrogen bonding with the aquo ligand of another tetrameric unit while the (DENC)-Cu(μ-O)Ni(H_2O) chromophore of V is not. However, despite these differences of spectral behavior V exhibits the effects of intermolecular association in its rates of isomerization (see below).

Table V. Observed First-Order Rate Constants for Isomerization of V in Methylene Chloride and Nitrobenzene

methylene chloride			nitrobenzene		
temp[a]	10^4[V]$_0$[b]	10^5k_{obsd}[c]	temp[a]	10^4[V]$_0$[b]	10^5k_{obsd}[c]
0.0	10.0	0.30	30.0	5.0	1.34
	31.1	0.28		20.0	1.76
	62.2	0.28		40.0	1.89
15.0	10.0	0.39	50.0	1.38	7.04
	31.1	0.44		31.6	17.7
	62.2	0.41		124	44.2
	197	1.66			
20.0	10.0	0.56	65.0	2.21	20.8
	31.1	0.56		18.4	22.5
	62.2	0.56		184	48.0
	193	2.58			
25.0	10.0	0.59	80.0	2.00	54.5
	31.1	0.58		20.0	54.6
	62.2	0.62		200	54.5
	193	3.73			
30.0	10.0	0.84	95.0	19.6	122
	31.1	0.89			
	62.2	0.92			
	172	4.04			

[a] In °C. [b] Units are M and refer to the analytical concentration of tetrameric units of V. [c] Units are s^{-1}.

Reactions with TEED. We have investigated TEED as an example of a hard, bidentate ligand that might be expected to displace the coordinated water in V and VI. The results are not consistent with this expectation and instead point to a very distinctive influence of μ-oxo groups in determining substitution behavior. We include here results for TEED titrations of completely transmetalated products XI and XII that are described in a later section.

Addition of excess TEED to solutions of I, IV–VIII, IX, and X (all of which contain at least two copper(II) centers) in methylene chloride gives green product solutions with single broad absorption maxima near 700 nm and closely similar band shapes.[11,17] Spectrophotometric titrations reveal sharp isosbestic points near 520 (all reactants) and 680 nm (I, IV, IX, X only) that imply the formation of a common product chromophore.

The product of complete reaction of I with 2 mol of TEED has a spectrum with λ_{max} 700 nm (ϵ 105 (g atom Cu)$^{-1}$ cm^{-1}). It was concluded that this product contains two (DENC)Cu(μ-O)Cu-(TEED) chromophores.[11] The common product of complete reaction of V or VI with 1 mol of TEED has a spectrum with λ_{max} 710 nm, but the maximum molar absorptivity, 56 (g atom metal)$^{-1}$ cm^{-1}, is only about half of that of the product of reaction of I with 2 mol of TEED.[11] The simplest explanation for these results is that the product of reaction of V and VI with TEED contains one absorption-dominating (DENC)Cu(μ-O)Cu(TEED) unit because (1) TEED catalyzes the isomerization of V to VI and (2) TEED replaces DENC coordinated to copper (not water coordinated to nickel). Crystalline (TEED)CuCl(OH,OH)-ClCu(TEED)[32] can be isolated as a major product from the reaction of V or VI with a large excess of TEED in methylene chloride, further supporting the existence of the (DENC)Cu(μ-O)Cu(DENC) unit[11] in the structure proposed for VI (Scheme I).

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[32] Data for (TEED)$_2$Cu$_2$Cl$_2$(OH)$_2$: Anal found (calcd)--Cu, 20.92 (22.00); Cl, 12.14 (12.33%); ir: intense sharp band at 3160 cm^{-1} (bridging OH). A crystalline sample is currently being characterized structurally by M.R. Churchill and coworkers at the State University of New York, Buffalo, NY.

The influence of μ-oxo groups in determining the extent of substitution of TEED for DENC coordinated to copper is demonstrated by the results for titration of the complexes IX–XII with TEED. First, the stoichiometry of complete reaction of TEED with copper complexes IX and X is a Δ(TEED)/Δ(IX or X) = 4.00. The respective product spectra have IX, λ_{max} 695 nm (ϵ 150 (g atom Cu)$^{-1}$ cm^{-1}) and X, λ_{max} 690 nm (147).

Second, titration of the tetranickel(II) complexes XI and XII with TEED in methylene chloride gives *pink* products (λ_{max} (nm) (ϵ (g atom Ni)$^{-1}$ cm^{-1}): XI, 520 (91), 550 sh (61), 610 sh (21), 990 (44); XII, 518 (87), 550 sh (59), 610 sh (20), 985 (40)), respectively, with a stoichiometry Δ(TEED)/Δ(XI or XII) = 4.00. These spectra are typical of octahedral nickel(II) complexes.[33] If the Ni(H_2O) centers of V–VIII had been substituted by TEED, we should have expected discernible absorption maxima near 520 nm in the spectra of the new Ni(TEED) centers and a reaction stoichiometry of Δ(TEED)/Δ(V–VIII) = 3.00, neither of which are observed.

Origin of Isomers V and VI. The structures[34] and properties[4,10,35] of IIIa and IIIb are significantly different and evidently responsible for the production of two isomers, V and VI, in their respective reactions with I. By contrast, both IIIa and IIIb give only VII in their reactions with IV. Kinetic measurements of these transmetalation reactions that we have initiated hopefully will provide a mechanistic explanation for these differences.

Kinetics of Isomerization of V to VI and of VII to VIII in Aprotic Solvents. General Observations. The isomerization of V to VI and VII to VIII are slow irreversible processes in aprotic solvents. Product monitoring at 850 nm gives the largest total absorbance change.[36] Plots of ln ($A_\infty - A_t$) vs. time showed excellent linearity for at least 3 half-lives in all cases. The observed first-order rate constants, k_{obsd}, under fixed experimental conditions (Table V) were reproducible to ±5% between different reactant samples and at different monitoring wavelengths.

The kinetic data in Table V show that k_{obsd} for isomerization of V increases with increasing initial analytical concentration of V, $[V]_0$. This phenomenon is much more marked in nitrobenzene than it is in methylene chloride. The observed rate constant becomes independent of concentration at 80 °C in nitrobenzene. Since there is separate cryoscopic evidence for association of V at ~5 °C in nitrobenzene (Table IV), we conclude that associated forms $(V)_n$ isomerize more rapidly than the tetrameric unit of Scheme I (that is $k_0 < k_0'$, k_0'' in eq 7).[37] However, since the

$$\begin{tikzcd} V \arrow[r, shift left, "K_1"] \arrow[d, "k_0"] & (V)_2 \arrow[l, shift left] \arrow[r, shift left, "K_2"] \arrow[d, "k'_0"] & (V)_3\cdots \arrow[l, shift left] \arrow[d, "k''_0"] \\ {} & {} & {} \end{tikzcd} \qquad (7)$$

individual values of K_1, K_2, k_0', and k_0'' are unknown, we have extrapolated k_{obsd} to $[V]_0 = 0$ to obtain the values of k_0 for isomerization of V (Scheme I). This procedure gives accurately linear plots of ln k_0 vs. $1/T$ leading to the kinetic parameters in Table VI.

The data in Table V show that V does not associate in methylene chloride below $[V]_0 = 6.22 \times 10^{-3}$ M over the temperature range 0.0–25.0 °C.[38] The averaged values to $k_{obsd} = k_0$ below this limit give a linear plot of ln k_0 vs. $1/T$ and lead to the activation parameters for isomerization of V in Table VI.

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

(a) Data for V

	10^6k_0[b]	
temp[a]	CH_2Cl_2	$PhNO_2$
0.0	2.8	
15.0	3.8	
20.0	5.6	
25.0	5.9	
30.0	8.1	11.0
50.0		70.0
65.0		206
80.0		545
95.0		1220
	$\Delta H^\ddagger_0 = 5.1 \pm 0.5$[c]	$\Delta H^\ddagger_0 = 3.9 \pm 0.5$[c]
	$\Delta S^\ddagger_0 = -63 \pm 2$[d]	$\Delta S^\ddagger_0 = -59 \pm 2$[d]

(b) Data for VII

		10^6k_0[b]	
temp[a]	CH_2Cl_2	$PhNO_2$	CH_3CN
0.0	5.2		
15.0	16.0	45.8	468
20.0	21.3	57.9	
25.0	32.0		
30.0		83.2	522
40.0		103	676
50.0		291[e]	1070
	$\Delta H^\ddagger = 10.6 \pm 0.5$[c]	$\Delta H^\ddagger = 7.9 \pm 0.5$[c]	$\Delta H^\ddagger = 4.8 \pm 0.5$[c]
	$\Delta S^\ddagger = -42 \pm 2$[d]	$\Delta S^\ddagger = -49 \pm 2$[d]	$\Delta S^\ddagger = -56 \pm 2$[d]

[a] In °C. [b] Units are s^{-1}. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25.0 °C. [e] Isomerization of VII to VIII cannot be investigated at higher temperatures in nitrobenzene because of rapid decarboxylation to give V; the data at 80.0 °C agree with those for isomerization of V under the same conditions (see Table IV, footnote *i*).

We are not equipped to measure cryoscopic molecular weights in methylene chloride (fp −100 °C) and so cannot assess the extent of association of V for comparison with the results in nitrobenzene (Table IV). However, it is clear that V associates most readily in nitrobenzene at temperatures below 80.0 °C.

By contrast, the first-order rate constants for isomerization of the dicarbonato derivative VII are independent of $[VII]_0$ in three solvents under concentration conditions comparable to those used for V. This result is consistent with no evidence for intermolecular association of VII in nitrobenzene (Table IV) and leads to the assignment of $k_{obsd} = k_0$ for isomerization of discrete tetrameric units of VII to VIII (Table VI).

The formation of very stable[2,6] (DENC)Cu(μ-O)Cu(DENC) and (DENC)Cu(CO_3)Cu(DENC) units in VI and VIII, respectively, is postulated to be responsible for the irreversible isomerization of V and VII since, to our knowledge, the proposed (H_2O)Ni(μ-O)Ni(H_2O) and (H_2O)Ni(CO_3)Ni(H_2O) units have not been reported in other structures. On the basis of the kinetic data for isomerization we would predict very slow (if any) intramolecular copper exchange in I and IV (see next section).

The most prominent feature of the kinetic data for isomerization of V and VII (Table VI) is large, negative entropies of activation. We interpret this result as indicating that polar activated complexes are involved in the formation of polar products VI and VIII, respectively. It seems clear that no ligands dissociate in the activation process.

The rate constant for isomerization of V at 30 °C is slightly higher in nitrobenzene than in methylene chloride because of a slightly smaller activation enthalpy in nitrobenzene. Otherwise the kinetic data for this reaction exhibit little solvent dependence despite the entropic evidence for a polar activated complex in both solvents.

By contrast, the kinetic parameters for isomerization of VII are highly solvent dependent.

The activation enthalpies for isomerization of VII in methylene chloride and nitrobenzene are about 2 times larger than the

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(33) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; p 333.

(34) Structure IIIa (M = Ni): Glowiak, T.; Ciszewska, T. *Inorg. Chim. Acta* **1978**, *27*, 27. Structure IIIb (M = Ni): Uechi, T.; Oniki, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 971.

(35) Iskander, M. F.; El-Toukhy, A.; Mishrikey, M. M. *J. Inorg. Nucl. Chem.* **1980**, *42*, 361.

(36) The result of an increase in ϵ_{850} for VI with increasing concentration (see text) is that the total absorbance change per mol of V due to isomerization increases with increasing $[V]_0$.

(37) The equilibria in eq 7 would have to be rapid to account for strictly linear first-order plots for isomerization of V at all concentrations.

(38) The rate constant k_0 at 30 °C has been obtained by extrapolation of the k_{obsd} data in methylene chloride (Table V) to $[V]_0 = 0$.

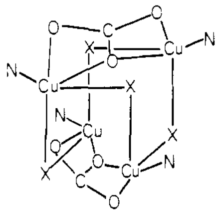
corresponding parameters for V (see next section). The activation enthalpies and entropies for isomerization of VII are lower in more polar solvents, with acetonitrile[39] giving the lowest values in the three solvents investigated. We suspect that acetonitrile is acting as a loosely held ligand in the activated complex in this solvent because $\Delta H^\ddagger$ and $\Delta S^\ddagger$ would both be expected to be lowered by coordination of extra ligands by the exchanging metals (see discussion of results for TEED titrations of V and VI above).

We intend to investigate whether strong solvent dependences of rates of isomerization are a general feature in $[LCuM(H_2O)X_2]_2(CO_3)_2$ (L = DENC, ethylnicotinate;[6] M = Co(II), Mn(II), etc; X = Cl or Br) analogues of VII.

Structural Considerations. Through examination of space-filling models we can envisage a 5-coordinate (μ-oxo)halo- or (μ-carbonato)halocopper(II) complex as consisting of a tetrahedron of halogen atoms with copper atoms in the tetrahedral holes. Two of the six "passes" or "valleys" between the tetrahedral sites are occupied by bridging oxygen atoms. The other four passes are represented by "active" faces in cubane structures that allow unobstructed metal exchange between sites.

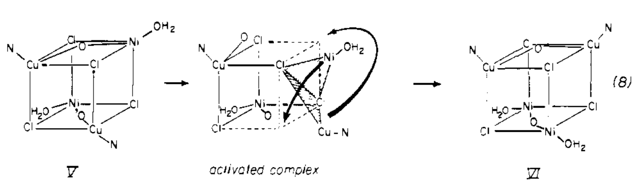
Replacement of two of the coppers in I or IV with two nickels gives rise to the isomeric pairs V, VI and VII, VIII (Scheme I) because of the relative dispositions of the bridging groups and the distinct tetrahedral sites. We wish to develop the idea that isomerization, which involves exchange of metals between tetrahedral sites, occurs in particular "active" faces.

Three distinguishable valence structures that maintain 5-coordination for copper can be drawn for $[(DENC)CuCl]_4(CO_3)_2$.[11] Structure IV (Scheme I) and its mirror image represent two of these structures. Both structures contain two faces in which the copper atoms are all formally bonded to two halogen atoms, two oxygen atoms, and the pyridine nitrogen atom of DENC. By contrast, the third distinguishable valence structure for $[(DENC)CuCl]_4(CO_3)_2$ shown here



contains copper centers that would have to break an additional metal–halide bond in order to exchange across the four idential active faces. We suppose that all three valence structures are of equal stability, although that of the third could be different. It should be noted in this regard that both racemic and enantiomeric products have been isolated from the reaction of $[(DENC)CuCl]_4(CO_3)_2$ with *N,N,N′,N′*-tetramethyl-1,3-propanediamine.[11] The above structural considerations also hold for VII, whose right-hand face (Scheme I) contains 5-coordinate metal centers[40] each of which would only need to break two M–O bonds in order to exchange.

Isomerization of V. Two of the four active faces in V allow exchange of copper and nickel between tetrahedral sites. Exchange across one of these faces results in structure VI, the thermodynamically favored isomer for this combination of metals and ligands. Equation 8 is an attempt to visualize the exchange of metals in one active face via a polar activated complex. In this view, the metals, with their respective coordinated monodentate ligands, are detached from their respective oxo and halo groups and pass each other on contours of spherical core halogen atoms that allow adequate separation between them. We propose that either metal is always in contact with a halogen atom of the active face to reconcile the very negative activation entropies for isomerization (Table VI).



Isomerization of VII. Isomerization via exchange of copper and nickel across the right-hand face of structure VII (Scheme I) requires the breaking of two M–O bonds at each metal center via an activated complex analogous to that for isomerization of V in eq 8.

The findings that $\Delta H^\ddagger_0$ for isomerization of V (Cl–M–O units broken for activation, eq 8) are roughly half those for isomerization of VII (O–M–O units broken for activation) in both methylene chloride and nitrobenzene (Table VI) and that (DENC)Cu(μ-O)Cu(DENC) and $(DENC)Cu(CO_3)Cu(DENC)$ units appears to be especially stable[6,41] lead us to suggest that Cu–O bond breaking is a major enthalpic requirement for isomerization of V and VII. This suggestion can be tested by investigating the kinetics of isomerization of other $[LCuM(H_2O)X_2]_2(O,CO_3)_2$ analogues in the same solvents.

Stoichiometry and Products of Transmetalation of $[(DENC)CuCl_4]Cl_4$, IX, and $(DENC)_4Cu_4Cl_6O$, X, by $Ni(NS)_2$ Reagents. We have reacted other tetranuclear copper(II) complexes (Table IV) with the same $Ni(NS)_2$ reagents to discover whether complete transmetalation occurs in the absence of μ-oxo groups to give tetranuclear products.

Spectrophotometric titrations of solutions of X (Figure 3) and IX with IIIa in methylene chloride at 575 nm indicated that the reaction stoichiometry is $\Delta(\text{IIIa})/\Delta(\text{IX or X}) = 4.0$ and gave no evidence for any variation in this stoichiometry, eq 9 and 10. This

$$\text{IX} + 4\text{IIIa} \xrightarrow[H_2O]{} \text{XI} + 4Cu(NS)_2 \qquad (9)$$

$$\text{X} + 4\text{IIIa} \xrightarrow[H_2O]{} \text{XII} + 4Cu(NS)_2 \qquad (10)$$

result is consistent with a high affinity of completely transmetalated products XI and XII (Table IV) for DENC (compare eq 6, 9, and 10). The formulations of isolated XI and XII in Scheme I include the four aquo ligands required by their analytical (Table IV), IR (strong absorptions at 3400 cm^{-1}),[30] and electronic spectral data (XI, λ_{max} 720 nm (ϵ 34 M^{-1} cm^{-1}), 1250 (18); XII, λ_{max} 720 nm (ϵ 28 M^{-1} cm^{-1}), 1245 (16)) that are typical of octahedral nickel(II) complexes.[33]

Both XI and XII are stable tetranuclear nonelectrolytes in anhydrous methylene chloride and nitrobenzene (Table IV). However, precipitated crystals of the transmetalation products VI, VIII, XI, and XII are all very water sensitive and fragile, which is frustrating attempts to obtain single crystals of sufficient stability and quality for X-ray structural determinations.

The effects of the μ-oxo and μ-carbonato groups in copper reactants and transmetalation products can be summarized as follows: (1) they limit the coordination numbers of the metal centers of I, IV, V, and VI to 5[40] (this results in the loss of DENC ligands from the new nickel centers in V, VI, VII, and VIII; water may be preferred as a ligand in these complexes because it can intramolecularly hydrogen bond with bridging μ-oxo and μ-carbonato groups (there is independent evidence for *intermolecular* hydrogen bonding in V and VI, see above)); (2) they clearly control

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[39] We have not been able to study the kinetics of isomerization of V to VI in acetonitrile since V is essentially insoluble in this solvent.

[40] The dotted lines shown in the core structures for VII and VIII in Scheme I allow for the possibility that the nickel centers in these complexes are 6-coordinate; this possibility, which exists in XI and XII,[33] cannot be assessed from the spectra of VII and VIII (which are dominated by copper chromophores) in the absence of detailed structures.

[41] Other indications that (pyridine)Cu–O bonds are particularly thermodynamically stable[6] include (1) the exothermic reactions of copper(I) halide slurries with dioxygen in pyridine to give discrete stoichiometric $(py)_2CuX_2$ and $(py_nCuO)_n$ products,[42] (2) the facile formation of these same products by simple addition of pyridine to $py_nCu_4Cl_4O_2$ (n = 3 or 4)[43] in aprotic solvents, and (3) the characteristic formation of X on attempted crystallization of IX in the presence of methanol (see text).

the extent of substitution of Ni for Cu in I and IV; (3) they control the extent of substitution of TEED for DENC on copper in I,[2,6] IV,[11] V, and VI; (4) they prevent the substitution of TEED for water coordinated to nickel in complexes V and VI.

Transmetalation of $py_nCu_4Cl_4O_2$ Species ($n = 3, 4$) by $Ni(NS)_2$ Reagents. We have concluded that $py_nCu_4Cl_4O_2$ species, which are structural isomers of I,[2,6] have a tetrahedral μ_4-oxo structure with a terminal oxo group on one of the four copper(II) centers. This structural difference gives rise to very complicated results in reactions with $Ni(NS)_2$ reagents. Thus, although the same 4:1 spectrophotometric reaction stoichiometry (like eq 10) is observed in the reaction of IIIa with $py_nCu_4Cl_4O_2$[6,41] in nitrobenzene, we have not yet succeeded in separating the products by a number of procedures, including gel permeation chromatography. In addition, the properties of product solutions are time dependent in a manner that experience[43] suggests is due to disproportionation processes that are not observed in the corresponding reactions of I and IV.

Inhibition of Copper-Catalyzed Phenolic Oxidative Coupling. The species $py_nCu_4Cl_4O_2$ are effective initiators for the oxidation coupling of 2,6-dimethylphenol to the corresponding diphenoquinone by dioxygen (eq 1b of ref 6). Addition of 4 mol of IIIa to 1 mol of $py_4Cu_4Cl_4O_2$ in nitrobenzene gives a solution that no longer initiates phenolic oxidative coupling by dioxygen. Also, 4 mol of $Ni(NS)_2$ abruptly halts dioxygen consumption and diphenoquinone production in an active catalytic system initiated by 1 mol of $py_4Cu_4Cl_4O_2$. These results are consistent with complete transmetalation of oxocopper(II) initiators and copper catalysts to produce catalytically inactive nickel(II) species.

Future Applications. HNS reagents are potentially useful for the demetalation/analysis of transition-metal complexes in aprotic media. $Ni(NS)_2$ reagents convert copper(II) complexes into new but similar nickel(II) structures. We are actively seeking structural information on these systems. The transmetalation reactions proceed in aprotic media and therefore should be valuable for conversion of water-sensitive complexes (e.g., superoxides, peroxides) to similar species with a choice of metal centers. We have already observed transmetalation reactions of copper complexes with other $M(NS)_2$ reagents (M = Mn, Fe, Co) and will describe our results in subsequent papers.[44]

Also significant is $Ni(NS)_2$ inhibition of copper-catalyzed phenolic oxidation by dioxygen, which might be useful for establishing the (unknown) catalytic mechanism.[7] Transmetalation with other $M(NS)_2$ reagents might give $[L_4M_4X_4]X_4$ complexes (analogues of XI) whose metal centers further react with dioxygen to give entirely new species with a variety of catalytic applications.

Acknowledgment. This work was supported financially by Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Faculty Research Grant 7590 (G.D.) from Northeastern University. We also wish to thank Alexandria University for study leave and the Egyptian Government for financial support (A.E.). K.D.O. is grateful to the National Science Foundation (CHE76-06503) for funding toward the purchase of the diffractometer. We also thank Dr. S. E. Wentworth (AMMRC, Watertown, MA) for thermogravimetric analyses, Professor David Forsyth and Ms. Leslie Root for useful discussions and Rudy Montalvo for experimental assistance.

Registry No. I, 80105-85-7; I (TEED derivative), 90742-01-1; IIIa (M = Ni), 34214-73-8; IIIb (M = Ni), 72871-85-3; IV, 80105-81-3; V, 90741-96-1; VI, 90741-97-2; VI (TEED derivative), 90742-02-2; VII, 90762-76-8; VIII, 90741-98-3; IX, 90762-75-7; IX (TEED derivative), 90742-03-3; X, 90741-95-0; X (TEED derivative), 90742-04-4; XI, 90741-99-4; XI (TEED derivative), 90742-05-5; XII, 90742-00-0; XII (TEED derivative), 90742-06-6; $(py)_3Cu_4Cl_4O_2$, 85049-06-5; $(py)_4Cu_4Cl_4O_2$, 85049-07-6; CO_2, 124-38-9; 2,6-dimethylphenol, 576-26-1; *S*-methyl isopropylidinehydrazinecarbodithiol, 27268-57-1; *S*-methyl (*p*-methylbenzylidene)hydrazinecarbodithiol, 26155-36-2.

Supplementary Material Available: Tables of atomic thermal parameters, calculated hydrogen atom fractional coordinates, and interatomic distances and angles for the DENC ligands and a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(42) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814.

(43) Davies, G.; El-Sayed, M. A.; Fasano, R. E. *Inorg. Chim. Acta* **1983**, *71*, 95.

(44) Judicious consecutive additions of different transmetalating agents $M(NS)_2$ conceivably could give complexes with core structures like $[M^1M^2M^3M^4X_4]O_2$, where M^1, M^2, M^3, and M^4 are different metals and X = halide.