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Contribution from the Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

# Transmetalation of Tetranuclear Copper Complexes. 5. Transmetalation of Copper(I) Complexes and Stoichiometry and Kinetics of Oxidation of Neutral Tetranuclear $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4$ Complexes by Dioxygen in Aprotic Solvents

Geoffrey Davies,* Mohamed A. El-Sayed,*† Ahmed El-Toukhy,† Thomas R. Gilbert, and Khadija Nabih

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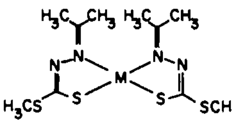
Tetranuclear copper(I) complexes $(\text{DENC})_4\text{Cu}_4\text{X}_4$ (DENC = *N*,*N*-diethylnicotinamide; X = Cl, Br) are quantitatively transmetalated by 1 or 2 equiv of $\text{M(NS)}_2$ complexes (M = Co, Ni, Cu, Zn; NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base) in methylene chloride or nitrobenzene at room temperature to give isolated tetranuclear $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4\cdot\text{DENC}$ or dimeric $(\text{DENC})_4\text{M}_2\text{Cl}_4$ complexes, respectively. The coproduction of 1 or 4 equiv of insoluble Cu(NS), respectively, is the driving force for transmetalation. Tetranuclear $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4$ complexes present in aprotic solvents are stoichiometrically oxidized by dioxygen to give chromatographically isolated tetranuclear $(\text{DENC})_3\text{Cu}_3\text{M(H}_2\text{O)X}_4\text{O}_2$ products. The kinetic data are similar to those for oxidation of $(\text{NCuX})_4$ complexes, indicating insertion of $\text{O}_2$ into the tetranuclear halo core as the rate-determining step for oxidation. Structures containing one $\mu_4$-oxo and one $\mu$-oxo group are suggested for $(\text{DENC})_3\text{Cu}_3\text{M(H}_2\text{O)X}_4\text{O}_2$ complexes.

## Introduction

Direct transmetalation is the exchange of metal centers in a polynuclear complex with retention of its core structure. Previous parts of this series[1-4] discuss synthetic and structural–kinetic aspects of the direct stoichiometric transmetalation of tetranuclear copper(II) complexes $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{X}_6$,[2,4] $[\text{NCuX}]_4\text{X}_4$,[2] and $(\mu\text{-O})_2[\text{NCuX}]_4$[1-3] by $\text{M(NS)}_2$ reagents, where N is *N*,*N*-diethylnicotinamide (DENC) or ethylnicotinate (ENCA), X is Cl or Br, M is Zn[1] or Ni[2-4] and $\text{NS}^-$ is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base in structures I and II. The nickel reagents generally give stable tetranuclear products, examples of which include the series $(\mu_4\text{-O})[\text{N}_4(\text{Cu})_{4-x}(\text{Ni(H}_2\text{O}))_x]\text{X}_6$ ($x$ = 1–4),[2,4] the complexes $[\text{NNi(H}_2\text{O)X}]_4\text{X}_4$,[2] and the two isomeric forms of $(\mu\text{-O})_2[\text{NCuNi(H}_2\text{O)X}_2]_2$.[2,3]



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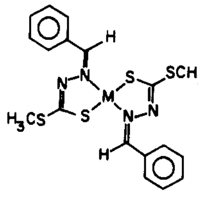

II

The reactions are stoichiometric in all cases because of the high thermodynamic stability of Cu–S bonds in the $\text{Cu(NS)}_2$ coproducts. Kinetic studies of reaction 1 indicate that precursors containing Cu- - -S–Ni- - -X rings are a structural requirement for rapid metal exchange.[4]

$$(\mu_4\text{-O})[\text{NCu}]_4\text{X}_6 + \text{Ni(NS)}_2 \xrightarrow[\text{solvent}]{\text{aprotic}} (\mu_4\text{-O})[\text{N}_4\text{Cu}_3\text{Ni}]\text{X}_6 + \text{Cu(NS)}_2 \quad (1)$$

One of the interesting features of these transmetalation systems is the effect of different tetranuclear core structures on the stoichiometries of the products obtained with large excesses of $\text{Ni(NS)}_2$.[2,3] Specifically, only the isomers $(\mu\text{-O})_2[\text{NCuNi(H}_2\text{O)X}_2]_2$ are obtained with as much as a 10-fold molar excess of $\text{Ni(NS)}_2$:$(\mu\text{-O})_2[\text{NCuX}]_4$, while $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{X}_6$[2,4] and $[\text{NCuX}]_4\text{X}_4$[2] complexes are completely transmetalated by 4 mol of $\text{Ni(NS)}_2$ under the same conditions.

This paper reports the direct transmetalation of tetranuclear copper(I) complexes $[(\text{DENC})\text{CuX}]_4$ (X = Cl, Br) (III) by $\text{M(NS)}_2$ reagents I (M = Co, Ni, Cu, Zn). The isolated solid products are tetranuclear $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4\cdot\text{DENC}$ and dinuclear $(\text{DENC})_4\text{M}_2\text{X}_4$ complexes at 1:1 and 1:2 molar reactant ratios, respectively. The reactions are stoichiometric because of the formation of virtually insoluble Cu(NS) coproducts even with M = Cu. The oxidation of $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4$ with dioxygen in aprotic solvents gives $(\mu\text{-O})_2(\text{DENC})_3\text{Cu}_3\text{M(H}_2\text{O)X}_4$ products, which apparently contain $\mu_4$- and $\mu$-oxo groups on the basis of their transmetalation chemistry and other criteria. The kinetic data for oxidation indicate that rate-determining dioxygen insertion is followed by rapid electron transfer from copper(I) and coordinated $\text{NS}^-$.

## Experimental Section

**Materials and Measurements.** The syntheses of the reactants $[(\text{DENC})\text{CuX}]_4$ (X = Cl, Br) (III)[5] and I (M = Co, Ni, Cu, Zn)[1-4,6-8] have been described previously. Literature procedures[1-5] were followed for solvent purification, elemental analyses, cryoscopic molecular weight and manometric dioxygen uptake measurements, chromatographic product separation, spectral measurements, and kinetic analyses.

**Synthesis of Solid $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4\cdot\text{DENC}$ Complexes (M = Co, Ni, Cu, Zn; X = Cl, Br).** The title complexes were obtained by reaction of III (X = Cl, Br) with 1 equiv of I in methylene chloride or nitrobenzene. A typical example follows. A stirred, clear solution of III (X = Cl; 5.00 mmol) in anhydrous methylene chloride (30 mL) was treated dropwise with I (M = Zn; 5.00 mmol) in anhydrous methylene chloride (40 mL) under dinitrogen to give a yellow product solution. The mixture was then stirred for 6 h under dinitrogen at room temperature, at which point no further spectrophotometric changes were evident. The product mixture was filtered to remove precipitated Cu(NS), which was washed with anhydrous hexane, dried at 100 °C and weighed. Anal. Calcd for 5.00 mmol Cu(NS): 1.225 g; Cu, 28.3%. Found: 1.220 g; Cu, 27.9; strong absorption at 1000 $\text{cm}^{-1}$. The tetranuclear product $(\text{DENC})_3\text{Cu}_3\text{Zn(NS)Cl}_4\cdot\text{DENC}$ (see below), was obtained as a dry, very air-sensitive, yellow solid by vacuum evaporation of the filtrate. Anal. Calcd for $(\text{DENC})_3\text{Cu}_3\text{Zn(NS)Cl}_4\cdot(\text{DENC})$: Cu, 14.98; Zn, 5.14; Cl, 11.1. Found: Cu, 15.54; Zn, 5.25; Cl, 11.7; strong absorption at 1000 $\text{cm}^{-1}$.[6-8]

**Cryoscopy.** Cryoscopic molecular weight measurements on the products $(\text{DENC})_3\text{Cu}_3\text{M(NS)X}_4\cdot\text{DENC}$ in nitrobenzene under dinitrogen showed the presence of equimolar amounts of $(\text{DENC})_3\text{CuM}$-

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† On leave of absence from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

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**Table I.** Analytical and Cryoscopic Data[a]

| symbol | complex | anal., % C | H | N | X | Cu | Ni | Co | Zn | mol wt[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| IV | $N_3Cu_3Ni(H_2O)Cl_4O_2$ | 36.6<br>(36.9) | 4.6<br>(4.5) | 8.35<br>(8.6) | 15.2<br>(14.5) | 20.2<br>(19.5) | 6.63<br>(6.01) | | | 1000 ± 30<br>(976) |
| | $N_2Ni_3(H_2O)_3Cl_4O$ | | | | 14.4<br>(14.4) | | 24.7<br>(23.7) | | | *c* |
| V | $N_3Cu_3Co(H_2O)Cl_4O_2$ | 35.8<br>(36.9) | 4.7<br>(4.5) | 8.5<br>(8.6) | 13.9<br>(14.5) | 18.3<br>(20.1) | | 7.3<br>(6.03) | | 1020 ± 30<br>(976) |
| VI | $N_3Cu_3Zn(H_2O)Cl_4O_2$ | 36.5<br>(36.6) | 4.6<br>(4.5) | 8.7<br>(8.55) | 14.7<br>(14.4) | 18.4<br>(19.4) | | | 6.27<br>(6.65) | 1010 ± 30<br>(983) |
| VII | $N_3Cu_4(H_2O)Cl_4O_2$ | 35.8<br>(36.7) | 4.1<br>(4.5) | 8.6<br>(8.6) | 14.9<br>(14.5) | 26.9<br>(26.0) | | | | 950 ± 20<br>(980) |
| VIII | $N_3Cu_3Ni(H_2O)Br_4O_2$ | 30.8<br>(31.25) | 3.9<br>(3.8) | 7.1<br>(7.3) | 27.9<br>(27.7) | 16.5<br>(16.5) | 5.86<br>(5.03) | | | 1000 ± 40<br>(1153) |
| IX | $N_3Cu_3Co(H_2O)Br_4O_2$ | 30.8<br>(31.25) | 3.7<br>(3.8) | 7.4<br>(7.3) | 27.4<br>(27.7) | 17.9<br>(16.5) | | 4.14<br>(5.03) | | 1020 ± 40<br>(1154) |
| X | $N_3Cu_3Zn(H_2O)Br_4O_2$ | 30.0<br>(31.0) | 3.7<br>(3.8) | 7.5<br>(7.2) | 28.0<br>(27.5) | 15.1<br>(16.4) | | | 5.03<br>(5.6) | 1120 ± 20<br>(1161) |
| XI | $N_4Ni_2Cl_4(H_2O)_2$ | 49.0<br>(49.4) | 6.4<br>(6.2) | 11.4<br>(11.5) | 16.5<br>(14.6) | | 13.4<br>(12.1) | | | 880 ± 35<br>(972) |
| XII | $N_4Co_2Cl_4$ | | | | 16.7<br>(14.6) | | | 13.1<br>(12.1) | | 890 ± 30<br>(972) |
| XIII | $N_4Zn_2Cl_4$ | | | | 14.3<br>(14.4) | | | | 12.8<br>(13.2) | 910 ± 30<br>(984) |
| XIV[d] | $N_4Cu_2Cl_4$ | 48.8<br>(48.9) | 5.6<br>(5.75) | 11.2<br>(11.4) | 14.5<br>(14.5) | 12.4<br>(13.0) | | | | 1000 ± 40<br>(981) |

[a] N = DENC; calculated values in parentheses. [b] Determined cryoscopically in nitrobenzene in the range (1–5) × $10^{-2}$ *m*.[5] [c] Isolated product is too insoluble to give cryoscopic data in nitrobenzene. [d] See ref 12.

(NS)$X_4$ and free DENC, e.g. for M = Zn, X = Cl: found 1080 ± 30; calcd 1112. The former are the species oxidized in eq 2. Conductance measurements indicated the presence of neutral solute species in all cases.

**Synthesis of $(DENC)_4M_2X_4$ Complexes (M = Co, Ni, Cu, Zn; X = Cl, Br).** The title complexes were obtained by the same procedure as in the previous section except with 2 equiv of I. Gravimetric measurements showed the precipitation of 4 mol of Cu(NS)/mol of III for each M. The spectrum of the filtrate was unaffected by treatment with dioxygen. Analytical and cryoscopic data for solid dimeric products of transmetalation are collected in Table I.

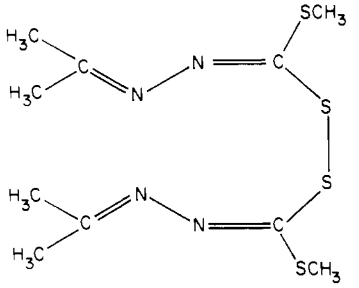
**Stoichiometry and Products of Oxidation of $(DENC)_3Cu_3M(NS)X_4$ Complexes (M = Co, Ni, Cu, Zn; X = Cl, Br) by Dioxygen in Aprotic Solvents.** An immediate color change was observed on exposure of solutions of the title complexes to dioxygen in methylene chloride or nitrobenzene. Manometric measurements in nitrobenzene established the stoichiometry of eq 2, where $N_2S_2$ is the neutral disulfide product of oxidation of coordinated, monoanionic $NS^-$ (eq 3), identified as follows.

$$(DENC)_3Cu_3M(NS)X_4 + O_2 \rightarrow (DENC)_3Cu_3MX_4O_2 + {}^1/_2N_2S_2 \quad (2)$$

$$NS^- \rightarrow {}^1/_2N_2S_2 + e^- \quad (3)$$

Solutions of $(DENC)_3Cu_3M(NS)X_4$ in methylene chloride that had reacted stoichiometrically with dioxygen (eq 2) were subjected to gel permeation chromatographic separation (Biobeads SX-12 resin, methylene chloride eluant).[2-4] In each case the respective solid tetranuclear complex $(DENC)_3Cu_3M(H_2O)X_4O_2$ was obtained by solvent evaporation from the first, well-separated colored fraction. Analytical and cryoscopic data are given in Table I. Eluant collection was continued to give a second chromatographic fraction with a volume 6 times that of the first. This fraction included a minor, black chromatographic band containing the products of oxidation of traces of dissolved Cu(NS) from the syntheses of solutions of $(DENC)_3Cu_3M(NS)X_4$ (see Results and Discussion). The solvent was evaporated under vacuum from this fraction to give a brown-black solid, which was subjected to thin-layer chromatography on silica gel plates with hexane eluant to give three components, $R_f$ 0.0, 0.08, and 0.21, respectively. These $R_f$ values were identical with those of authentic samples of trace-oxidized Cu(NS), DENC, and $N_2S_2$, respectively. The authentic sample of $N_2S_2$ was obtained as a white solid on treatment of a solution of HNS (the neutral form of the ligand from which I is obtained)[2] with the stoichiometric amount of $H_2O_2$ in acetone at 0 °C (eq 4). Anal. Calcd for $C_{10}H_{18}N_4S_2$: C, 37.24; H, 5.63; N, 17.37; S, 39.77%. Found: C, 37.10; H, 5.48; N, 17.15; S, 39.65. Formation of $N_2S_2$ was confirmed by $^1H$ NMR (60 Mz): $\delta$ = 2.17 (12 H, s) and 2.53 (6 H, s) vs. $Me_4Si$, consistent with the neutral structure

$$2HNS + H_2O_2 \rightarrow N_2S_2 + 2H_2O \quad (4)$$



**Synthesis of $(DENC)_2(Ni(H_2O))_3Cl_4O$.** The title complex was obtained as follows. $(DENC)_4Cu_4Cl_4$ (5.00 mmol) was transmetalated with I (M = Ni; 5.00 mmol) in methylene chloride under dinitrogen (see above). Precipitated Cu(NS) (5.00 mmol) was filtered off under dinitrogen, and the filtrate was then oxidized with excess dioxygen. The oxidized solution was transmetalated with 2 or 3 equiv (10.0 or 15.00 mmol) of I (M = Ni). The products were separated by gel permeation chromatography, and the title complex was obtained by solvent evaporation from the first, green, eluted band. Analytical data are given in Table I.

## Results and Discussion

Addition of 1 mol of transmetalating agents I (M = Co, Ni, Cu, Zn) to solutions of 1 mol of III (X = Cl, Br) in methylene chloride or nitrobenzene under dinitrogen at room temperature caused immediate color changes to blue, green, black, or dark yellow, respectively. Gravimetric analyses of the pale yellow precipitate of Cu(NS) that subsequently formed were consistent with the stoichiometry of eq 5, which is also consistent with

$$(DENC)_4Cu_4X_4 + M(NS)_2 \xrightarrow[\text{solvent}]{\text{aprotic}} (DENC)_3Cu_3M(NS)X_4 + Cu(NS)(s) + DENC \quad (5)$$

cryoscopic measurements. The driving force for this stoichiometric direct transmetalation is the quantitative formation of Cu(NS), which is virtually insoluble in the reaction solvents.[9] This in-

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[9] The low solubilities of Cu(NS) in methylene chloride (2 × $10^{-4}$ M) and nitrobenzene (1 × $10^{-4}$ M) at 25 °C lead to quantitative Cu(NS)(s) recovery on transmetalation. Traces of dissolved Cu(NS) do not interfere with cryoscopic measurements or affect rate law 9.

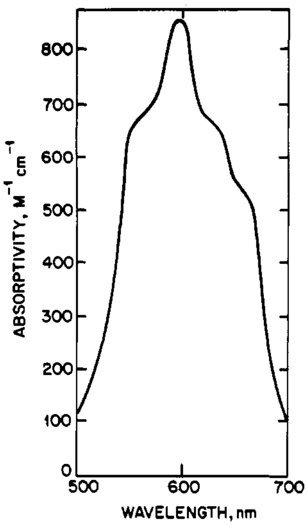

**Figure 1.** Electronic spectrum of $(DENC)_3Cu_3Co(NS)Cl_4$ in nitrobenzene at 25 °C.

solubility provided an excellent means of stoichiometry measurement. Equation 5 is observed even when M = Cu because Cu(NS)(s) is more thermodynamically stable than dissolved $Cu(NS)_2$.

The desired tetranuclear products of transmetalation were obtained as very air-sensitive, dry solids by vacuum evaporation of methylene chloride product filtrates or by addition of these filtrates to excess deoxygenated anhydrous hexane. Attempted recrystallization of solid products always resulted in oxidation by trace dioxygen and disproportionation, but analyses of solids isolated by simple solvent evaporation or hexane precipitation both indicated the presence of 4 mol of coordinated DENC.[10] However, cryoscopic measurements in nitrobenzene in the range (1–5) × $10^{-2}$ *m* under dinitrogen showed the presence of 1 mol of $(DENC)_3Cu_3M(NS)X_4$ and 1 mol of free DENC. We designate solid products as $(DENC)_3Cu_3M(NS)X_4{\cdot}DENC$ since III does not dissociate DENC under the same conditions.[5] Equation 5 thus represents the stoichiometry of transmetalation in solution and identifies $(DENC)_3Cu_3M(NS)X_4$ as the species oxidized by dioxygen in solution (eq 2) (see below).

The presence of coordinated $NS^-$ was confirmed by a strong band in the isolated solid and methylene chloride solution IR spectra at 1000 $cm^{-1}$.[6-8] Conductance measurements in nitrobenzene under dinitrogen corresponded to those of neutral species, ruling out formulations such as $[(DENC)_4Cu_3MX_4]^+(NS)^-$. It thus appears that one NS ligand remains coordinated to M on transmetalation of one copper(I) center of III by $M(NS)_2$. Since III very probably are "cubanes"[5] and only one copper(I) center has been replaced by M(NS), we suggest cubane core structures for tetranuclear $(DENC)_3Cu_3M(NS)X_4$ products. Bidentate NS coordination to M would give 5-coordinate M in such structures (see below). Unfortunately, many attempts to crystallize pure $(DENC)_3Cu_3M(NS)X_4$ complexes were unsuccessful (see above).

**Electronic Spectra of $(DENC)_3Cu_3M(NS)X_4$ Complexes.** No absorption maxima were detected in the region 500–1000 nm in solution spectra of the title complexes with M = Ni or Zn and X = Cl or Br. A prominent split band between 550 and 675 nm for M = Co (Figure 1) is characteristic of 5-coordinate cobalt(II)[11] (see previous section).

**Dimeric Products of Transmetalation.** Reaction 6 takes place when 1 mol of $(DENC)_4Cu_4Cl_4$ is treated with 2 mol of $M(NS)_2$ in methylene chloride or nitrobenzene under dinitrogen. This stoichiometry was confirmed in every case by gravimetric determination of 4 mol of precipitated Cu(NS).[9]

**Table II.** Spectral Data

| complex | band maxima,[a] nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) | $\nu_{M-O}$,[b] $cm^{-1}$ |
|---|---|---|
| $N_4Cu_4Cl_4O_2$[c] | 770 (710); 850 (715) | 510 |
| $N_4Cu_4Br_4O_2$[c] | 759 (910); 825 (910) | 505 |
| IV | 750 (660); 850 (710) | 550 |
| $N_2Ni_3(H_2O)_3Cl_4O$ | 725 (50) | 500 |
| V | 750 (680); 850 (760) | 550 |
| VI | 750 (630); 860 (650) | 550 |
| VII | 725 (700); 850 (770) | 515 |
| VIII | 750 (1110); 835 (1030) | 530 |
| IX | 850 (1190); 900 (1030) | 530 |
| X | 750 (1210); 830 (1270) | 530 |
| XI | 670 (58); 780 (45) | 510 |
| XII | 575 (720); 600 (910); 630 (720) | 510 |
| XIV[d] | 720 (330); 850 (330) | |

[a] In methylene chloride solution. [b] In methylene chloride solution or KBr disk. [c] Data from ref 5. [d] See ref 12.

$$(DENC)_4Cu_4Cl_4 + 2M(NS)_2 \rightarrow (DENC)_4M_2Cl_4 + 4Cu(NS)(s) \quad (6)$$

It is evident that tetranuclear structures $(DENC)_nCu_2(M(NS))_2Cl_4$ do not survive under the experimental conditions.

Complexes XIII and XIV (Table I) were isolated as anhydrous colorless and blue solids, respectively. The IR spectrum of solid XIII exhibits a single $\nu_{C=O}$ band at 1630 $cm^{-1}$ (terminal DENC),[5,12] whereas $\nu_{C=O}$ for solid XIV is split into two components at 1635 and 1610 $cm^{-1}$, indicating the known DENC-bridged, dimeric structure.[12] The two absorption maxima in the electronic spectrum of XIV (Table II) are those of the 5-coordinate, bis($\mu$-halo)-bridged dimer formed in solution.[12]

Isolated solid complex XI and particularly XII are very water-sensitive. Their IR spectra exhibit a strong, broad band at 3400 $cm^{-1}$ ($\nu_{O-H}$ for water), a single $\nu_{C=O}$ band at 1630–1635 $cm^{-1}$ (terminal DENC),[5,12] and a weak band at 500–510 $cm^{-1}$ ($\nu_{M-OH_2}$). The electronic spectra of methylene chloride solutions of solids XI (Table II) are characteristic[11] of 6-coordinate nickel(II) centers in dimers $Cl(DENC)_2(H_2O)Ni(Cl,Cl)Ni(H_2O)(DENC)_2Cl$ (Table I). The electronic spectrum of the anhydrous, blue filtrate containing XII from reaction 6 (Table II) is consistent with 5-coordinate cobalt(II) centers in the analogous dimeric structure without coordinate water.[11] This complex was isolated in anhydrous form under rigorously anhydrous conditions (Table I).

**Stoichiometry and Products of Oxidation of $(DENC)_3Cu_3M(NS)X_4$ Complexes (M = Co, Ni, Cu, Zn; X = Cl, Br) by Dioxygen. General Observations.** Manometric dioxygen uptake measurements in nitrobenzene indicated that the tetrameric product filtrates from transmetalation of $(DENC)_4Cu_4X_4$ by 1 equiv of $M(NS)_2$ reagents I (eq 5) all react with dioxygen with the stoichiometry of eq 2. Four products were obtained by gel permeation chromatography of the oxidized solutions with a given M. The first is a discrete, heterotetranuclear complex $(DENC)_3Cu_3M(H_2O)X_4O_2$,[13] identified by analysis and cryoscopy (Table I). The second is a minor black, unidentified band resulting from the oxidation of traces of dissolved Cu(NS) remaining from transmetalation (eq 5).[9] Third is the disulfide product $N_2S_2$ from oxidation of coordinated $NS^-$ in $(DENC)_3Cu_3M(NS)X_4$, identified by TLC and $^1H$ NMR measurements (Experimental Section). The fourth is free DENC remaining from reaction 5.[14]

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(10) Because of their marked air sensitivity, $(DENC)_3Cu_3M(NS)X_4{\cdot}DENC$ solids often gave irreproducible elemental analyses.[5] For this reason, transmetalation product filtrates from eq 5 were most often used directly for measurement of the stoichiometry and kinetics of oxidation by dioxygen. The presence of $(DENC)_3Cu_3M(NS)X_4$ was confirmed cryoscopically for all M and X in nitrobenzene.

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(12) Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chem. Acta* **1985**, *98*, 85.

(13) The analytical data (Table I) are consistent with a molar ratio of $H_2O$:M = 1 in products IV–X. See ref 2–4.

(14) Sticky residues are obtained on vacuum evaporation of methylene chloride solvent from oxidized transmetalation filtrate solutions (eq 5), indicating the presence of free DENC (bp 296 °C): $(DENC)_3Cu_3M(H_2O)X_4O_2$ and $N_2S_2$ (eq 3) are solids at room temperature.

The stoichiometry of eq 2 and the analytical and spectral data[15] indicate that the three copper(I) centers and the coordinated $NS^-$ of $(DENC)_3Cu_3M(NS)X_4$ are oxidized by dioxygen; DENC, M, and X are not oxidized even when M = Co.[16] Thus, $(DENC)_3Cu_3M(NS)X_4$ complexes, like $(DENC)_4Cu_4X_4$,[5] are tetranuclear, four-electron-reducing agents that are oxidized by dioxygen to tetranuclear dioxometal species (eq 2).

Copper(II) has a high affinity for DENC;[2-4] the fixed molar ratio DENC:Cu = 1 in all the products $(DENC)_3Cu_3M(H_2O)X_4O_2$ strongly suggests that DENC is not coordinated to M.

Attempted crystallization of all the $(DENC)_3Cu_3M(H_2O)X_4O_2$ complexes in Table I gave crystalline $(\mu_4\text{-}O)[(DENC)Cu]_4X_6$ (crystallographically isomorphous with authentic samples[2-4]) and other unidentified, amorphous products of disproportionation. The formation of ($\mu_4$-oxo)copper(II) crystals is often observed on attempted crystallization of neutral, tetranuclear dioxocopper(II) complexes.[2-4]

**Infrared and Electronic Spectra of $(DENC)_3Cu_3M(H_2O)X_4O_2$ Complexes.** Infrared and electronic spectra of $(DENC)_3Cu_3M(H_2O)X_4O_2$ complexes are summarized in Table II.

A single, sharp band, $\nu_{C=O}$, at 1630–1635 $cm^{-1}$ indicates that DENC is coordinated only through its pyridinic nitrogen atom.[5,12] A split, medium-intensity band in the 490–550-$cm^{-1}$ region is ascribed in $\nu_{M-O}$ (O = oxo or $OH_2$).[2-5,12]

The near-infrared electronic spectra of tetrameric $(DENC)_3Cu_3M(H_2O)X_4O_2$ complexes consist of two broad maxima in the region 725–900 nm (Table II). With fixed X there is little variation of the maximum molar absorptivities with M, except for M = Zn and X = Cl, with absorptivity 70–80% of those with other metals M. The complexes with X = Br have spectral maxima at slightly longer wavelengths (except with M = Zn) with maximum molar absorptivities that average 1.5 times those with X = Cl.

We observed a prominent, split band in the 550–675-nm region for $(DENC)_3Cu_3Co(NS)X_4$ (Figure 1) and dimeric $(DENC)_4Co_2Cl_4$ (Table II). These bands are absent in the spectra of $(DENC)_3Cu_3Co(H_2O)X_4O_2$ complexes (Table II) despite clear evidence for the presence of cobalt(II) in a discrete tetranuclear structure (Table I).

This lack of spectral sensitivity to the presence and identity of M is very surprising, particularly since (a) the molar absorptivities of $(\mu_4\text{-}O)[(DENC)_4Cu_{4-x}Ni_x(H_2O)_x]Cl_6$ complexes are proportional to their copper contents[4,17] and (b) the maximum molar absorptivities of $[(NCuNi(H_2O)X_2)_2]Y_2$ complexes (isomer structures VI and VIII of ref 2 and 3; Y = O, $CO_3$) are close to half those of the respective $[NCuX]_4Y_2$ complexes.[2,3]

**Attempted Synthesis of Carbonato Derivatives.** We have previously used reaction 7 to establish the presence of $\mu$-oxo groups in oxocopper(II) complexes.[2-4,18] However, analytical and spectral

$$[NCuX]_4O_2 + 2CO_2 \rightarrow [NCuX]_4(CO_3)_2 \qquad (7)$$

data for the products of reaction 2 with fixed M and X were indistinguishable in the presence or absence of excess $CO_2$, even with M = Cu. In no case were carbonato derivatives of products IV–X (Table I) obtained. This indicates that the products of reactions 2 and 8 have different tetranuclear oxocopper(II) core structures (see below).

$$[NCuX]_4 + O_2 \rightarrow [NCuX]_4O_2 \qquad (8)$$

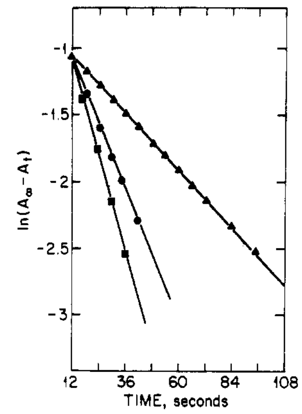

**Figure 2.** First-order product formation in the oxidation of excess $(DENC)_3Cu_3Co(NS)Cl_4$ by dioxygen (4.4 × $10^{-4}$ M) in nitrobenzene at 25 °C. Initial reductant concentrations (mM): (▲) 3.33; (●) 7.24; (■) 9.98.

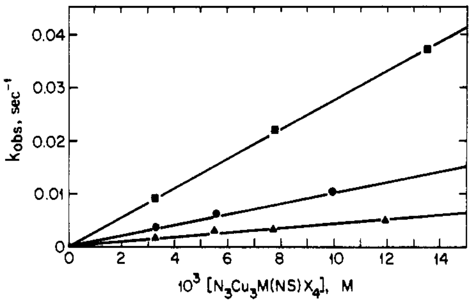

**Figure 3.** Plots of $k_{obsd}$ vs. $[(DENC)_3Cu_3M(NS)X_4]$ for the oxidation of excesses of the following complexes at 25 °C: (■) $(DENC)_3Cu_3Ni(NS)Cl_4$ in nitrobenzene; (▲) $(DENC)_3Cu_3Ni(NS)Br_4$ in nitrobenzene; (●) $(DENC)_3Cu_3Ni(NS)Cl_4$ in methylene chloride.

**Table III.** Kinetic Parameters for Oxidation of $N_4Cu_4X_4$ and $N_3Cu_3M(NS)X_4$ Complexes (N = DENC; X = Cl, Br; M = Ni, Co, Zn) by Dioxygen in Aprotic Solvents

| reactant | solvent | $k_T$,[a] $M^{-1}$ $s^{-1}$ | $\Delta H_T^\ddagger$, kcal $mol^{-1}$ | $\Delta S_T^\ddagger$, cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|
| $N_4Cu_4Cl_4$[b] | $CH_2Cl_2$ | 5.4 | 2.1 ± 0.3 | −48 ± 3 |
| $N_4Cu_4Cl_4$[b] | $PhNO_2$ | 16.2 | 3.9 ± 0.3 | −40 ± 3 |
| $N_4Cu_4Br_4$[d] | $PhNO_2$ | 0.66 | 5.9 ± 0.4 | −40 ± 3 |
| $N_3Cu_3Ni(NS)Cl_4$ | $CH_2Cl_2$ | 1.4 | 6.2 ± 0.3 | −38 ± 3 |
| $N_3Cu_3Ni(NS)Cl_4$ | $PhNO_2$ | 5.1 | 4.7 ± 0.3 | −40 ± 3 |
| $N_3Cu_3Ni(NS)Br_4$ | $PhNO_2$ | 0.99 | 8.3 ± 0.3 | −31 ± 3 |
| $N_3Cu_3Co(NS)Cl_4$ | $PhNO_2$ | 5.4 | 4.3 ± 0.3 | −41 ± 3 |
| $N_3Cu_3Zn(NS)Cl_4$ | $PhNO_2$ | 3.7 | 8.4 ± 0.4 | −26 ± 3 |

[a] Given at 25 °C. [b] Data from ref 5.

**Kinetics of Oxidation of $(DENC)_3Cu_3M(NS)X_4$ Complexes (M = Co, Ni, Zn; X = Cl, Br) by Dioxygen in Aprotic Solvents.** Reactions of pseudo-first-order excesses of $(DENC)_3Cu_3M(NS)X_4$ complexes with dioxygen in methylene chloride and nitrobenzene were easily monitored by conventional spectrophotometry in the wavelength range 500–850 nm. In each system plots of ln ($A_\infty - A_t$) vs. time, where $A_t$ is the absorbance of $(DENC)_3Cu_3MX_4O_2$ at time *t* under fixed experimental conditions, were linear to at least 4 half-lives (Figure 2), indicating that reaction 2 is first order in $[O_2]$.

Absorbances extrapolated to zero time corresponded to those expected for the $(DENC)_3Cu_3M(NS)X_4$ reactant at monitoring wavelengths from 500 to 850 nm, thus providing no evidence for reactant preequilibria. The simple first-order rate dependence indicates either that significant concentrations of reaction intermediates are not formed or that they do not absorb appreciably in the wavelength range 500–850 nm.

The derived pseudo-first-order rate constants $k_{obsd}$ were accurately proportional to $[(DENC)_3Cu_3M(NS)X_4]$, giving straight lines passing through the origin (Figure 3). Reaction 2 is thus a second-order process (eq 9) when $(DENC)_3Cu_3M(NS)X_4$ is in excess.

$$d[(DENC)_3Cu_3MX_4O_2]/dt = k_T[(DENC)_3Cu_3M(NS)X_4][O_2] \qquad (9)$$

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(15) The IR spectra of products IV–XIV (Table II) contain no bands at 1000 $cm^{-1}$, indicating the absence of coordinated $NS^-$.[6-8]

(16) The stoichiometry of eq 2 would not be observed if $Co^{II}$ were oxidized by $O_2$.

(17) Davies, G.; El-Sayed, M. A.; El-Toukhy, A., submitted for publication in *Inorg. Chem.*

(18) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Fournier, J. A.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chem.* **1984**, *23*, 783 and references cited therein.

Second-order rate constants $k_T$ and their associated activation parameters in two solvents are listed in Table III together with those for $(DENC)_4Cu_4X_4$.[5]

**Interpretation of the Kinetic Data.** The second-order rate constants $k_T$ for oxidation of $(DENC)_3Cu_3M(NS)Cl_4$ are 4–12 times lower than those for oxidation of $(DENC)_4Cu_4Cl_4$ at 25 °C in nitrobenzene. The rate constant for oxidation of $N_3Cu_3Ni(NS)Cl_4$ at 25 °C increases by only a factor of 3.6 on changing the solvent from low-polarity methylene chloride to highly polar nitrobenzene. A much larger solvent effect would be expected if charge development were important in the rate-determining step,[5] strongly suggesting that electron transfer from copper(I) or coordinated $NS^-$ to dioxygen, which would produce a polar transition state, is not the rate-determining step. The low activation enthalpies found in these two solvents indicate a low probability of major structural rearrangements or solvation changes on activation of the reactants.[5]

The rate of oxidation of $N_3Cu_3Ni(NS)Br_4$ by dioxygen is about 5.5 times slower at 25 °C than that of the chloro complex in nitrobenzene. This decrease is largely due to a higher activation enthalpy when X = Br (Table III).

It has previously been concluded that the rate-determining step in the aprotic oxidation of $N_4Cu_4X_4$ complexes (X = Cl or Br) by dioxygen is insertion of $O_2$ into the halo core of the copper(I) reactant.[5] This conclusion is based on simple second-order oxidation kinetics, no detectable precursors or intermediates, negligible solvent effects, low activation enthalpies (increasing as X is changed from Cl to Br), and very negative activation entropies.[5]

These same features are observed in the corresponding reactions of $N_3Cu_3M(NS)X_4$ (Table III). It seems certain that insertion of $O_2$ into the core of $N_3Cu_3M(NS)X_4$ is rate-determining.

Changing from M = Ni to M = Co has a negligible effect on the kinetic parameters, but changing to M = Zn causes $\Delta H_T^*$ and $\Delta S_T^*$ to increase. However, within experimental error, all five data pairs with X = Cl from Table III fit a straight line plot of $\Delta H_T^*$ vs. $\Delta S_T^*$ at 25 °C, further supporting dioxygen insertion as the common rat-determining step.[19]

**Factors Controlling Rates of Insertion.** The tetranuclear halo(pyridine)copper(I) complexes $[N_nCuX]_4$ (N = DENC, ENCA, pyridine; $n$ = 1, 2; X = Cl, Br, I) all consist of a tetrahedral core of halogen atoms with copper(I) in each tetrahedral hole.[5,20] Two effects are anticipated on substituting one $(DENC)Cu^I$ with M(NS). First, the $X_4$ core would "stiffen", causing $\Delta H_T^*$ for insertion to increase because of the higher effective nuclear charge of M. This is particularly noticeable with M = Zn, which is isoelectronic with copper(I). Second, dioxygen insertion into three of the six distorted "cubane" faces of $(DENC)_3Cu_3M(NS)X_4$ would be relatively obstructed by the large $NS^-$ ligand system. Both effects would cause comparatively low rates of insertion, as observed (Table III).

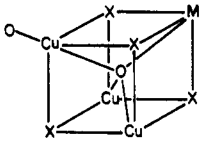
We assume that dioxygen preferentially inserts through one of the three unobstructed faces in the rate-determining step. It was previously concluded that dioxygen insertion through $X_4$ of $N_4Cu_4X_4$ (N = DENC, ENCA) proceeds almost entirely before the three electrons necessary to break the O–O bond are transferred from copper(I).[5,22] As a result, bis($\mu$-oxo)copper(II) products, which react with $CO_2$ to form dicarbonato derivatives, (eq 7), are formed.[5,22]

**Core Structures of $(DENC)_3Cu_3M(H_2O)X_4O_2$ Products.** The title complexes disproportionate on attempted crystallization (see above). However, we can suggest core structures from their properties as follows.

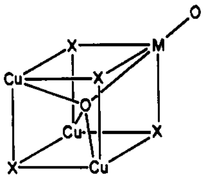
1. Stoichiometric (eq 2), analytical, and spectral data (Tables I and II) establish that they are neutral, tetrameric dioxometal complexes.

2. They do not react with $CO_2$ (eq 7); thus, any $\mu$-oxo groups present are incapable of reacting with $CO_2$.[2-5]

3. They do not initiate the oxidative coupling of phenols by dioxygen.[23] Core structure XV (M = Cu) has been proposed previously for the initiators $(py)_mCu_4X_4O_2$ ($m$ = 3, 4), which contain a particularly basic terminal oxo group.[5,24] Because complexes IV–X, and particularly VII (Table I), are not phenolic oxidative-coupling initiators, we neglect core structures XV and XVI.[25]



XV



XVI

4. The anhydrous product $(DENC)_3Cu_3NiCl_4O_2$ (IVa), prepared in situ in methylene chloride through reaction 5, removal of Cu(NS), and then reaction 2, is transmetalated by 2 or more equiv of I (M = Ni) to give trimeric $(DENC)_2(Ni(H_2O))_3Cl_4O$ as the first product of chromatographic separation (eq 10) (see Experimental Section and Table I).[26]

$$(DENC)_3Cu_3NiCl_4O_2 + 2I \xrightarrow{H_2O} (DENC)_2(Ni(H_2O))_3Cl_4O + 2Cu(NS)_2 + (DENC)CuO \quad (10)$$

This distinctive transmetalation chemistry[27] can be interpreted as follows.

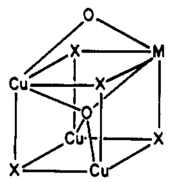
(a) If IV contained two $\mu$-oxo groups we would expect reaction 11,[2,3] where the first product shown is isomer V of ref 2 and 3.

$$(DENC)_3Cu_3NiCl_4O_2 + 2I \xrightarrow{H_2O} [(DENC)CuNi(H_2O)Cl_2]_2O_2 + I{\cdot}DENC + Cu(NS)_2 \quad (11)$$

Here, the incorporation of only one additional nickel center is due to an apparent trans effect across the two $\mu$-oxo groups.[2,3]

(b) Transmetalation beyond the $Cu_2Ni_2$ stage (eq 10) is characteristic of copper(II) complexes containing $\mu_4$-oxo groups. Thus, complexes $(\mu_4\text{-}O)[NCu]_4X_6$ are completely transmetalated by $Ni(NS)_2$ reagents in stoichiometric steps to give stable tetrameric products like $(\mu_4\text{-}O)(DENC)_4Cu(Ni(H_2O))_3X_6$.[2,4,17]

(c) The appearance of a trimeric product containing no copper in reaction 10 (Table I) suggests reactant structure XVII, which



XVII

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(19) $\Delta G_T^*$ for oxidation at 25 °C covers only a small range for the systems investigated, so $\Delta H_T^*$ should be a linear function of $\Delta S_T^*$. However, correlation of all the activation parameter data for X = Cl in Table III suggests that all the reactions are subject to the same basic activation requirements. See: Wells, P. R. *Linear Free Energy Relationships*; Academic: London, 1968; p 21.

(20) See Figure 2 of ref 21 for a view of a distorted $Cu_4X_4$ core structure.

(21) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1982**, *21*, 995.

(22) Comparable rate-determining insertion data for $L_4Cu_4$ (L = 6-methyl-2-hydroxypyridinate) oxidation by dioxygen are $\Delta H_T^*$ = 6.7 kcal mol$^{-1}$ and $\Delta S_T^*$(25 °C) = −39 cal deg$^{-1}$ mol$^{-1}$. See: Cai, G.-Z.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine: Guilderland, NY, 1986; Volume 2, p 115.

(23) Equation 1 of ref 18.

(24) Davies, G.; El-Sayed, M. A. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine: Guilderland, NY, 1983; p 281.

(25) Cu–O (in structure XV) and M–O (XVI) groups should be sufficiently basic to deprotonate phenols; the resulting phenolate anions would be oxidized by copper(II) in either structure.[24]

(26) We have not succeeded in separating the third product of eq 10 by chromatography in the absence of decomposition.

(27) Products IV–X show none of the time-dependent properties that plague isolation of the products of transmetalation of $(py)_4Cu_4Cl_4O_2$ (structure XV),[2] which also supports neglect of structure XV.

contains $\mu$-oxo and $\mu_4$-oxo units.[27] Fragmentation of a soluble form of CuO[26,28] after transmetalation appears to be characteristic of such complexes.[29] Reaction 10 with 3 mol of I (M = Ni) gives the same trimeric product, $(DENC)_2(Ni(H_2O))_3Cl_4O$, showing that (DENC)CuO fragmentation from $(DENC)_3CuNi_3X_4O_2$ is faster than its transmetalation by I.

**Absence of Carbonato Derivatives.** Coordination of all four metals to a central $\mu_4$-oxo group in XVII presumably draws Cu and M centers into the tetrahedral holes of the $X_4$ core so that the Cu-$\mu$-O-M angle is smaller and "stiffer" than those in $(\mu\text{-}O)_2[(DENC)CuNi(H_2O)X_2]_2$ isomers and $(\mu\text{-}O)_2[NCuX]_4$ complexes.[2,3] The latter, which contain no strongly coordinating central $\mu_4$-oxo units, readily undergo reaction 7, evidently because their Cu–O–M angles can open to accommodate the linear Cu–O–M arrangement in known ($\mu$-carbonato)dicopper complexes.[18,30]

**Electron Transfer to Dioxygen.** Equation 2 shows that $(DENC)_3Cu_3M(NS)X_4$ complexes transfer 4 electrons to dioxygen. The tetranuclear products do not contain coordinated $NS^-$ (Table II). Now $M(NS)_2$ complexes do not suffer coordinated $NS^-$ ligand oxidation by dioxygen at appreciable rates in methylene chloride or nitrobenzene at room temperature.[6-8] We therefore conclude that the oxidation of coordinated $NS^-$ in $(DENC)_3Cu_3M(NS)X_4$ complexes requires prior reduction of dioxygen by copper(I). $NS^-$ oxidation must occur rapidly after rate-determining dioxygen insertion to explain the first-order rate dependence on $[O_2]$ (eq 9).

Our view is that the $\mu$-oxo group of product structure XVII is the leading oxygen atom of the original dioxygen molecule inserted through the equivalent left, front, or bottom faces of the $Cu_3MX_4$ core in $(DENC)_3Cu_3M(NS)X_4$. We cannot distinguish whether $NS^-$ is oxidized by $O_2^{2-}$ or $O^-$ because in no case is electron transfer to dioxygen rate-determining and thus no information on the role of M in electron transfer is available. However, the NS· radical produced by rapid $NS^-$ oxidation (eq 3) must rapidly dissociate from M and dimerize to form the neutral, uncoordinated disulfide product (eq 12).

$$2NS\cdot \rightarrow N_2S_2 \qquad (12)$$

$(\mu\text{-}O)_2[NCuX]_4$ complexes are stoichiometrically demetalated by HNS[2] but complexes IV–X do not coordinate $N_2S_2$, consistent with the low affinity of copper(II) for neutral disulfide ligands.[31]

Intuitively, we would expect electron transfer to oxygen in the core from $NS^-$ outside the core to be mediated by M. This is one reason for suggesting that O remains coordinated (as an oxo group) to M in the products. However, the distinction between alternative products XVI and XVII must remain tentative in the absence of detailed structural information, which appears difficult to obtain in these systems.

**Conclusions.** Copper(I) complexes $[(DENC)CuX]_4$ are transmetalated by $M(NS)_2$ complexes in aprotic solvents to give $(DENC)_3Cu_3M(NS)X_4$. The apparent instability of more highly transmetalated tetrameric copper(I) complexes is unfortunate because study of the stoichiometry and kinetics of oxidation of the series $(DENC)_nCu_{4-x}(M(NS))_xX_4$ might indicate the minimum state of reduction of $O_2$ necessary to effect the oxidation of coordinated $NS^-$ in such complexes. On the basis of our interpretation of the data in Table III, we would expect that increase of $x$ would decrease rates of oxidation if dioxygen insertion were always rate-determining.

**Acknowledgment.** Financial support for this work by the Department of Health and Human Services (Grant RR07143) is gratefully acknowledged. M.A.E.-S. and A.E.-T. thank Alexandria University for study leave and the Egyptian Government for financial support. H. El-Wakil, M. Henary, and K. D. Onan are thanked for experimental assistance and valuable discussions.

**Registry No.** I (M = Co), 54166-06-2; I (M = Ni), 34214-73-8; I (M = Cu), 34156-34-8; I (M = Zn), 72871-59-1; III (X = Cl), 80105-82-4; III (X = Br), 80105-83-5; IV, 102109-35-3; V, 102109-36-4; VI, 102109-37-5; VII, 102109-38-6; VIII, 102109-39-7; IX, 102109-40-0; X, 102109-41-1; HNS, 27268-57-1; $N_2S_2$, 102109-43-3; $N_3Cu_3Ni(NS)Cl_4$, 102132-57-0; $N_3Cu_3Ni(NS)Br_4$, 102132-58-1; $N_3Cu_3Co(NS)Cl_4$, 102132-59-2; $N_3Cu_3Zn(NS)Cl_4$, 102132-60-5; Cu(NS), 102109-42-2; $O_2$, 7782-44-7.

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(28) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814. Davies, G.; El-Sayed, M. A.; Fasano, R. E. *Inorg. Chlm. Acta.* **1983**, *71*, 95.

(29) The behavior of $(DENC)_2(Ni(H_2O))_3Cl_4O$ on gel permeation chromatographic separation (methylene chloride eluant)[2,3] is similar to those of analogous known trimers obtained in other transmetalation systems: Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M., to be submitted for publication.

(30) The molar absorptivities of $(\mu_4\text{-}O)[(DENC)_4Cu_{4-x}(Ni(H_2O)_x]Cl_6$ are proportional to their molar copper(II) contents.[4,17] The presence of $\mu_4$-oxo *and* $\mu$-oxo groups in preferred structure XVII for $(DENC)_3Cu_3Ni(H_2O)X_4O_2$ complexes may be responsible for $\epsilon_{IV-IX} > 0.75\epsilon_{(DENC)_4Cu_4X_4O_2}$ (Table II); each $M(H_2O)$ unit is expected to be a weak chromophore in the 750–850-nm region.[1-4,17]

(31) Freeman, H. C. In *Inorganic Biochemistry*; Eichorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Chapter 4, p 158.