

Transmetalation of Tetranuclear Copper Complexes. 8. Transmetalation of Tetranuclear Copper(I) Complexes with a $\text{Co}(\text{NS})_3$ Reagent¹

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Stoichiometric transmetalation of the tetranuclear copper(I) complexes $(\text{DENC})_4\text{Cu}_4\text{X}_4$ (I: $\text{DENC} = N,N$ -diethylnicotinamide; $\text{X} = \text{Cl}$ or Br) by tris(*S*-methyl isopropylidenehydrazinecarbodithioato)cobalt(III) ($\text{Co}(\text{NS})_3$, II) in aprotic solvents under dinitrogen is preceded by electron transfer from copper(I) to cobalt(III) and gives cobalt(II)-containing products. The stoichiometries $\text{I} + \text{II} \rightarrow (\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ (III) + $\text{Cu}(\text{NS})(\text{s})$ and $\text{I} + 2\text{II} \rightarrow (\text{DENC})_4\text{Co}_2\text{X}_4$ (VI) + $2\text{Cu}(\text{NS})(\text{s})$ + $2\text{Cu}(\text{NS})_2$ were established by gravimetric determination of insoluble $\text{Cu}(\text{NS})(\text{s})$ and other techniques. Product III reacts stoichiometrically with dioxygen to give tetranuclear $(\text{DENC})_3\text{Cu}_3\text{CoX}_4\text{O}_2$ (IV). Electron transfer from copper(I) and coordinated NS^- rapidly follows rate-determining O_2 insertion into the halo cores of III. Product III is stoichiometrically transmetalated by 1 mol of $\text{M}(\text{NS})_2$ reagents to give heterometallic dimers $(\text{DENC})_4\text{CoMX}_4$ (VIII) or by 2 mol of $\text{M}(\text{NS})_2$ to give heterometallic trimers $(\text{DENC})_4\text{Co}(\text{NS})_2\text{M}_2\text{X}_4$ (IX). Stoichiometric aprotic oxidation of IX with dioxygen gives trimeric products $(\text{DENC})_3\text{CoM}_2\text{X}_4\text{O}$ (X). Product IV is transmetalated by 1 mol of $\text{M}(\text{NS})_2$ to give the less stable trimeric $(\text{DENC})_3\text{CoCuMX}_4\text{O}$ (XI) and by 2 mol of $\text{M}(\text{NS})_2$ to give the trimeric product X. The spectral and other properties of these transmetalation products are compared and discussed.

Introduction

Direct transmetalation of tetranuclear copper complexes by $\text{M}(\text{NS})_2$ reagents in aprotic solvents leads to a wide variety of new polymetallic products.¹⁻⁷ Here, NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base, and a major driving force for transmetalation is the formation of very stable $\text{Cu}(\text{NS})_6$ and $\text{Cu}(\text{NS})_2$ ^{1-5,7} coproducts. The reactions described in previous parts of this series are stepwise, stoichiometric processes. Evidence has been presented for structurally required Cu-X-M-S rings ($\text{X} = \text{Cl}$ or Br ; $\text{S} =$ carbothioate sulfur) that facilitate metal exchange.⁵ Aside from providing metal complexes that have not been obtained by other means, transmetalation is also useful in assigning the spectra of $(\mu\text{-O})_2[\text{LCu}]_4$ ⁷ and $(\mu_4\text{-O})[\text{NCu}]_4\text{X}_6$ ¹ complexes.

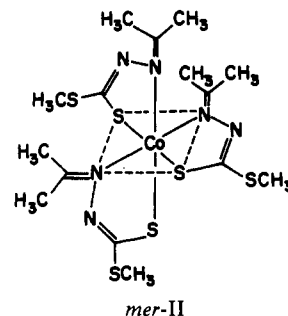
Part 5⁶ described the transmetalation of tetranuclear copper(I) complexes $[(\text{DENC})\text{CuX}]_4$ (I: $\text{DENC} =$ monodentate *N,N*-diethylnicotinamide)⁸ by $\text{M}(\text{NS})_2$ reagents ($\text{M} = \text{Co}, \text{Ni}, \text{Cu},$ or Zn). The products $(\text{DENC})_3\text{CuM}(\text{NS})_2\text{X}_4$ and $(\text{DENC})_4\text{M}_2\text{X}_4$ were obtained with 1 and 2 equiv of $\text{M}(\text{NS})_2$ reagents, respectively, as verified by gravimetric determination of 1 and 4 equiv of the insoluble coproduct $\text{Cu}(\text{NS})_2$.⁶ The oxidation of $(\text{DENC})_3\text{Cu}_3\text{M}(\text{NS})_2\text{X}_4$ complexes by dioxygen in aprotic solvents proceeds by rate-determining dioxygen insertion into the X_4 reactant core followed by rapid 4-electron transfer (from copper(I) and coordinated NS),⁶ analogous to the behavior of the parent $[(\text{DENC})\text{CuX}]_4$ complexes.⁸ The products $(\text{DENC})_3\text{Cu}_3\text{CoX}_4\text{O}_2$ apparently contain μ -oxo and μ_4 -oxo groups that lead to distinctive patterns of transmetalation.⁶

This is the first report of the transmetalation of $[(\text{DENC})\text{CuX}]_4$ complexes by a $\text{M}(\text{NS})_3$ reagent, II.⁹ We have used gravimetric determinations of the $\text{Cu}(\text{NS})_2$ coproduct and other techniques to establish the formation of cobalt(II)-containing products $(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ and $(\text{DENC})_4\text{Co}_2\text{X}_4$ with 1 and 2 equiv of $\text{Co}(\text{NS})_3$, respectively. Electron transfer from copper(I) to cobalt(III) precedes transmetalation. Dioxygen insertion is the rate-determining step in the aprotic oxidation of $(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ complexes by dioxygen. Consecutive transmetalation of $[(\text{DENC})\text{CuX}]_4$ with $\text{Co}(\text{NS})_3$ and $\text{M}(\text{NS})_2$ reagents gives a variety of heterometallic trimer and dimer products. All the systems investigated are shown in Scheme I.

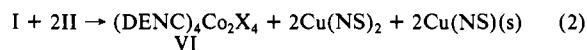
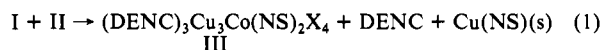
Experimental Section

Most of the procedures and measurement techniques of this work have been described previously.¹⁻⁸ Tris(*S*-methyl isopropylidenehydrazinecarbodithioato)cobalt(III) (II) was synthesized by a literature method.⁹

General Transmetalation Procedure. A clear yellow solution of $(\text{DENC})_4\text{Cu}_4\text{X}_4$ ⁸ (I; 5 mmol) in anhydrous methylene chloride (30 mL) was treated dropwise with 1 or 2 equiv of the brown *mer* isomer of II⁹



in methylene chloride (20 mL) under dinitrogen. The latter solution was allowed to stand so that *fac-mer* isomerization was complete^{9,10} before addition, which resulted in a rapid color change to deep blue, signaling the formation of cobalt(II).^{6,7} This color change was much faster than the subsequent precipitation of virtually insoluble⁵ $\text{Cu}(\text{NS})_2$ (eq 1 and 2) and the formation of black $\text{Cu}(\text{NS})_2$ (eq 2) (see Results and Discussion).



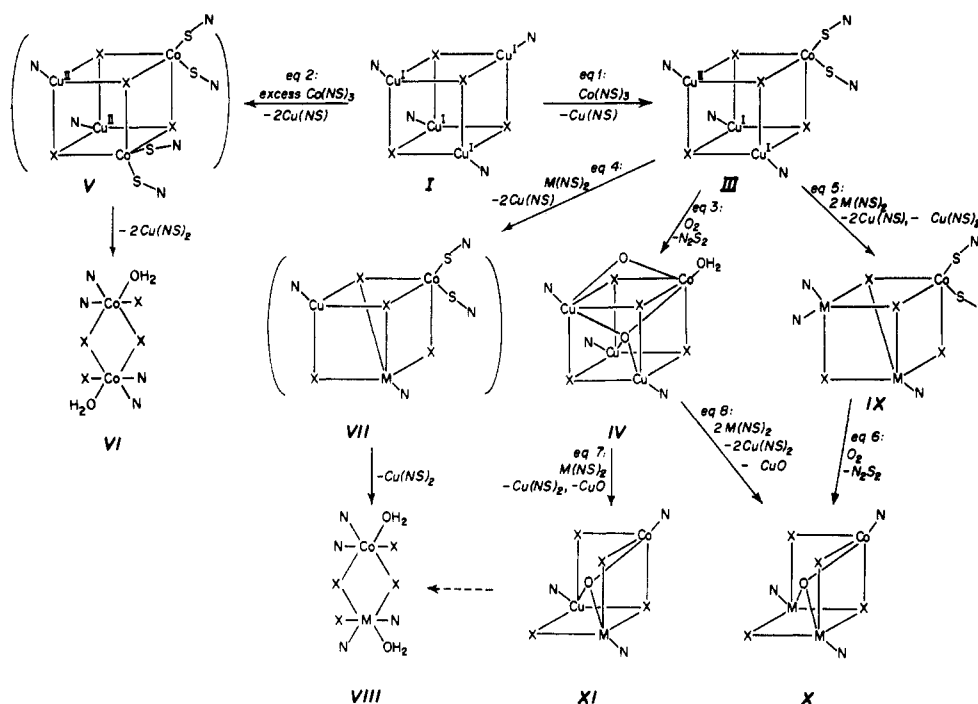
After 12 h of reaction at room temperature under dinitrogen the product mixtures were filtered (Schlenk) to remove $\text{Cu}(\text{NS})(\text{s})$, which was washed with hexane, dried at 100 °C under vacuum, and weighed.⁶

Product Filtrates. The product filtrates from reaction 1 were used for the following purposes. Filtrates from the reaction in nitrobenzene were used to establish the presence of III and free DENC in eq 1 by cryos-

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- (2) Part 1: Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chim. Acta* **1984**, *84*, 41.
- (3) Part 2: El-Toukhy, A.; Cai, G.-Z.; Davies, G.; Gilbert, T. R.; Onan, K. D.; Veidis, M. *J. Am. Chem. Soc.* **1984**, *106*, 4596.
- (4) Part 3: Cai, G.-Z.; Davies, G.; El-Toukhy, A.; Gilbert, T. R.; Henary, M. *Inorg. Chem.* **1985**, *24*, 1701.
- (5) Part 4: Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 1925.
- (6) Part 5: Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Nabih, K. *Inorg. Chem.* **1986**, *25*, 1929.
- (7) Part 6: Cai, G.-Z.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Onan, K. D. *Inorg. Chem.* **1986**, *25*, 1935.
- (8) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, *22*, 1257.
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- (10) We are currently investigating the kinetics of isomerization of II.

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Scheme I



copy.^{6,8} Filtrates in both solvents were either added under dinitrogen to a large excess of hexane to precipitate $(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ (III), which was analyzed (Table I), or aprotically oxidized with dioxygen (eq 3).⁶ The stoichiometry of reaction 3 was established by manometric

$$\text{III} + \text{O}_2 \rightarrow (\text{DENC})_3\text{Cu}_3\text{CoX}_4\text{O}_2 + \text{N}_2\text{S}_2 \quad (3)$$

dioxygen uptake measurements,^{6,8} and the kinetics with excess III were measured by conventional spectrophotometry.⁶ The products IV and N_2S_2 were separated by gel-permeation chromatography (methylene chloride eluant).^{3,6} Product IV was isolated by vacuum solvent evaporation from the first brown eluted band. The product of oxidation of coordinated NS^- , N_2S_2 , was identified by thin-layer chromatography of the solids isolated from subsequent fractions, as described previously.⁶

The spectrum of the black filtrate from reaction 2 was not affected by exposure to dioxygen. The first two products were easily separated by gel-permeation chromatography (methylene chloride eluant).³ The dimeric product, VI, eluted first as a bright blue band, was obtained by vacuum solvent evaporation. Species V, a homologue of III (Scheme I), is proposed as an intermediate in the formation of VI (Results and Discussion).

Synthesis of Heterometallic Complexes. Dimers. The dimers $(\text{DENC})_4\text{CoMX}_4 \cdot 2\text{H}_2\text{O}$ (VIII) (Scheme I) were obtained by treatment of the product mixture from reaction 1 with 1 equiv of $\text{M}(\text{NS})_2$ under dinitrogen (eq 4). The reactions were all complete within 6 h at room

$$\text{III} + \text{M}(\text{NS})_2 \rightarrow (\text{DENC})_4\text{CoMX}_4 + \text{Cu}(\text{NS})_2 + 2\text{Cu}(\text{NS})(\text{s}) \quad (4)$$

temperature in methylene chloride (see below). Stoichiometries of eq 4 were established by weighing the precipitated $\text{Cu}(\text{NS})(\text{s})$. The first two products in eq 4 were easily separated by gel-permeation chromatography (methylene chloride eluant)³ and products VIII were isolated by vacuum solvent evaporation from the first eluted band in each system.

Trimers. Trimeric transmetalation products IX were obtained by treating the product mixture from reaction 1 with 2 equiv of $\text{M}(\text{NS})_2$ under dinitrogen (eq 5). The precipitated $\text{Cu}(\text{NS})_2$ was filtered

$$(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4 + 2\text{M}(\text{NS})_2 \rightarrow (\text{DENC})_3\text{Co}(\text{NS})_2\text{M}_2\text{X}_4 + \text{Cu}(\text{NS})_2 + 2\text{Cu}(\text{NS})(\text{s}) \quad (5)$$

(Schlenk) and determined gravimetrically.⁶ The filtrate was then either added to excess anhydrous hexane under dinitrogen (to precipitate the trimer) or treated with excess dioxygen (eq 6).



The stoichiometries of reactions 6 were established by manometric dioxygen uptake measurements. Products X were isolated by gel-permeation chromatography and characterized as described previously.⁶

Trimeric products XI and X were also obtained by treatment of IV, (eq 3) with 1 or 2 equiv of $\text{M}(\text{NS})_2$ in methylene chloride at room temperature (eq 7 and 8, respectively). Products X and XI were isolated

$$\text{IV} + \text{M}(\text{NS})_2 \rightarrow (\text{DENC})_3\text{CoCuMX}_4\text{O} + \text{Cu}(\text{NS})_2 + (\text{DENC})\text{CuO} \quad (7)$$

$$\text{IV} + 2\text{M}(\text{NS})_2 \rightarrow (\text{DENC})_3\text{CoM}_2\text{X}_4\text{O} + 2\text{Cu}(\text{NS})_2 + (\text{DENC})\text{CuO} \quad (8)$$

by vacuum evaporation from the first eluted bands from gel-permeation chromatography of product solutions.

Analytical and spectral data for transmetalation products are collected in Tables I and II, respectively.

Results and Discussion

Our basis for discussion of the transmetalation and oxidation chemistry of I and their transmetalated derivatives is a cubane structure for I consisting of a tetrahedron of halogen atoms with a $(\text{DENC})\text{Cu}$ center in each tetrahedral hole.⁸

The following evidence indicates that electron transfer from I to III (eq 9) precedes transmetalation.¹¹ First, all the products



contain cobalt(II), and not cobalt(III), as indicated by characteristic blue colors and electronic spectral features.^{6,7} Second, formation of blue colors in reactions 1 and 2 occurs very soon after the reactants are mixed and is much faster than the formation of pale yellow $\text{Cu}(\text{NS})(\text{s})$ and black $\text{Cu}(\text{NS})_2$. Third, we have observed that transmetalations of copper(II) complexes with II, in which electron transfer is not expected, are slower than the corresponding transmetalations with $\text{M}(\text{NS})_2$ reagents. Indeed, reactions 1 and 2 proceed at rates similar to those of the $[(\text{DENC})\text{CuX}]_4/\text{M}(\text{NS})_2$ reactions reported earlier.⁶ Thus, the effective transmetalating agent in these systems is cobalt(II), tentatively formulated as $\text{Co}(\text{NS})_3^-$ in eq 9.¹¹

Reaction 1. The stoichiometry of eq 1 was confirmed by gravimetric determination of the precipitated $\text{Cu}(\text{NS})(\text{s})$.⁶ Tetranuclear products III were precipitated from the product filtrates by addition to excess hexane under dinitrogen. Cryoscopic

(11) Although eq 9 is written as an outer-sphere redox reaction it seems likely that an inner-sphere mechanism obtains, perhaps within the Cu-X-M-S rings that are believed to be necessary in copper(II)/ $\text{M}(\text{NS})_2$ systems.⁵ We are currently exploring this possibility.

Table I. Analytical Data for Transmetalation Products^a

symbol ^b	complex	anal., %										M _r ^c
		C	H	N	X	Cu	Co	Ni	Zn			
IIIa	N ₃ Cu ₃ Co(NS) ₂ Cl ₄	38.3 (38.46)	4.8 (4.81)	11.1 (11.22)	12.4 (11.36)	15.9 (15.30)	4.95 (4.73)					1200 ± 20 (1248)
IIIb	N ₃ Cu ₃ Co(NS) ₂ Br ₄	33.4 (33.66)	4.0 (4.24)	9.8 (9.82)	21.59 (22.4)	12.6 (13.38)	3.9 (4.14)					1460 ± 20 (1426)
IVa	N ₃ Cu ₂ Co(H ₂ O)Cl ₄ O ₂	37.2 (36.90)	4.6 (4.54)	8.6 (8.61)	14.3 (14.52)	18.9 (19.51)	5.8 (6.04)					980 ± 20 (976)
IVb	N ₃ Cu ₃ Co(H ₂ O)Br ₄ O ₂	31.7 (31.69)	3.8 (3.90)	7.3 (7.39)	27.8 (28.13)	16.1 (16.76)	6.0 (5.19)					1100 ± 20 (1136)
Vla	N ₄ Co ₂ Cl ₄ ·2H ₂ O	46.0 (46.51)	6.1 (5.99)	10.8 (11.11)	14.6 (14.06)	11.9 (11.69)	11.9 (11.69)					990 ± 20 (1009)
Vlb	N ₄ Co ₂ Br ₄ ·2H ₂ O	40.5 (40.44)	5.0 (5.09)	9.2 (9.44)	26.0 (26.92)	9.3 (9.94)	9.3 (9.94)					1150 ± 20 (1187)
VIIIa	N ₄ CoNiCl ₄ ·2H ₂ O	46.2 (46.51)	5.9 (5.99)	11.0 (11.11)	13.8 (14.06)	5.9 (5.85)	5.9 (5.85)					1140 ± 20 (1009)
VIIIb	N ₄ CoNiBr ₄ ·2H ₂ O	40.3 (40.44)	5.0 (5.09)	9.3 (9.44)	26.1 (26.92)	4.2 (4.97)	4.2 (4.97)					1150 ± 20 (1187)
VIIIc	N ₄ CoZnCl ₄ ·2H ₂ O	47.0 (47.29)	6.0 (5.96)	11.0 (11.03)	13.1 (13.97)	5.4 (5.81)	5.4 (5.81)					990 ± 20 (1015)
VIIIId	N ₄ CoCuCl ₄ ·2H ₂ O	47.4 (47.38)	5.9 (5.97)	11.0 (11.06)	14.8 (13.99)	5.8 (6.27)	6.6 (5.82)					1050 ± 20 (1013)
IXa	N ₃ Ni ₂ Co(NS) ₂ Cl ₄	40.8 (40.83)	5.7 (5.15)	10.7 (11.90)	12.6 (12.07)	5.5 (5.02)	5.5 (5.02)					1140 ± 20 (1175)
IXb	N ₃ Co ₃ (NS) ₂ Cl ₄	40.8 (40.83)	5.0 (5.15)	11.8 (11.90)	11.6 (12.07)	15.0 (15.06)	15.0 (15.06)					1220 ± 20 (1175)
IXc	N ₃ Zn ₂ Co(NS) ₂ Cl ₄	40.2 (40.43)	4.9 (5.05)	11.6 (11.79)	12.4 (11.95)	4.2 (4.97)	4.2 (4.97)					1130 ± 20 (1187)
Xa	N ₃ CoNi ₂ Cl ₄ O·2H ₂ O	39.8 (39.74)	5.3 (5.12)	9.0 (9.27)	15.0 (15.65)	5.8 (6.50)	5.8 (6.50)					880 ± 20 (906)
Xb	N ₃ CoCu ₂ Cl ₄ O·2H ₂ O	40.3 (40.96)	4.7 (4.82)	9.4 (9.56)	15.3 (15.2)	7.1 (6.33)	7.1 (6.33)					850 ± 20 (933)
Xc	N ₃ CoZn ₂ Cl ₄ O·2H ₂ O	39.0 (39.22)	5.0 (5.05)	9.2 (9.15)	14.6 (14.86)	5.7 (6.18)	5.7 (6.18)					940 ± 20 (954)
Xd	N ₃ Co ₂ Cl ₄ O·2H ₂ O	41.4 (41.43)	4.7 (4.87)	9.6 (9.67)	15.6 (15.66)	19.2 (19.55)	19.2 (19.55)					830 ± 20 (905)
Xe	N ₃ CoNi ₂ Br ₄ O·2H ₂ O	33.0 (33.21)	4.2 (4.28)	8.0 (7.75)	30.2 (29.50)	4.8 (5.44)	4.8 (5.44)					1120 ± 20 (1084)
XIa ^d	N ₃ CoNiCuCl ₄ O·2H ₂ O	44.2 (41.18)	5.7 (5.26)	10.6 (9.61)	15.5 (15.58)	3.45 (6.97)	7.1 (6.40)					815 ± 20 (910)
XIb ^e	N ₃ Co ₂ CuCl ₄ O·2H ₂ O	43.9 (41.18)	5.7 (5.26)	10.3 (9.61)	15.6 (15.58)	1.8 (6.97)	11.8 (12.97)					860 ± 20 (910)

^aCalculated values in parentheses. ^bSee Scheme I; N = DENC. ^cMeasured cryoscopically in nitrobenzene at (3–5) × 10⁻² m. ^dPoor analytical data fit indicates loss of CuO to give product VIIIa (see text). ^ePoor analytical data fit indicates loss of CuO to give product VIa (see text).

Table II. Spectral Data

complex ^a	λ _{max} , ^b nm (ε, M ⁻¹ cm ⁻¹)	ν _{M-O} , ^c cm ⁻¹
IIIa	575 (715), 610 (890), 675 (720), 825 (600) ^d	
IIIb	575 (1370), 625 (1680), 675 (1160), 825 (880)	
IVa	775 (790), 875 (870)	535
IVb	775 (1410), 875 (1500)	525
VIa	575 (1020), 610 (1300), 630 (1030)	500
VIb	575 (1300), 610 (1380), 630 (1350)	435
VIIIa	575 (440), 610 (610), 630 (530)	475
VIIIb	575 (730), 610 (945), 630 (815)	410
VIIIc	575 (340), 610 (500), 630 (445)	420
VIIIId	575 (570), 610 (790), 630 (615), 850 (200)	545
IXa	575 (400), 610 (520), 630 (430) ^d	
IXb	575 (720), 610 (940), 630 (785) ^d	
IXc	575 (150), 610 (230), 630 (169) ^d	
Xa	575 (310), 610 (330), 630 (302)	500
Xb	575 (650), 610 (830), 635 (660), 850 (290)	550
Xc	575 (139), 610 (189), 630 (142)	430
Xd	575 (780), 610 (998), 630 (820)	495
Xe	575 (890), 625 (1295), 630 (985)	515

^aSee Table I; no data given for products XIa,b because of poor analytical data (see text). ^bIn methylene chloride. ^cKBr disk. ^dIn nitrobenzene.

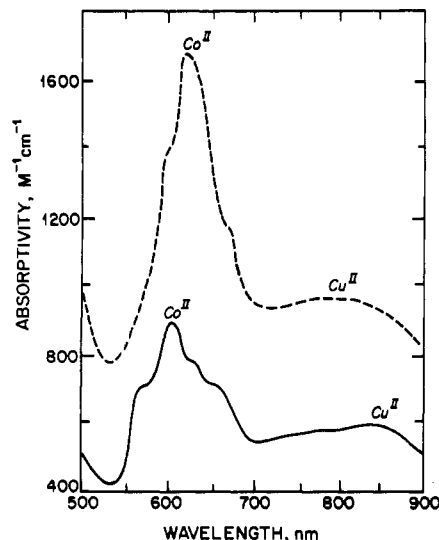


Figure 1. Electronic spectra of IIIa (full line) and IIIb (dotted line) in nitrobenzene at 25 °C.

measurements on the product filtrates ((3–5) × 10⁻² m) in nitrobenzene under dinitrogen indicated the presence of equimolar amounts of tetranuclear IIIa,b and DENC (e.g., M_r found for IIIa solutions 690 ± 20; calcd 713). The molar ratio (DENC):Cu = 1 in isolated solid products III (Table I) indicates that DENC is almost certainly coordinated to copper and not to cobalt.^{6,8} The KBr disk IR spectrum of these solids contain bands at 1635 cm⁻¹ (monodentate DENC)^{3,6,12} and 1000 cm⁻¹ (coordinated NS⁻).^{6,9} Products III are formal analogues of (DENC)₃Cu₃M(NS)₄, obtained in reaction 10,⁶ but III contain copper(II), as indicated

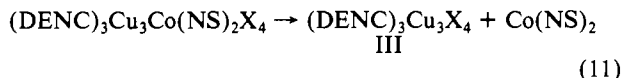
$$I + M(NS)_2 \rightarrow (DENC)_3Cu_3M(NS)_4 + Cu(NS)(s) \quad (10)$$

by electronic spectra under dinitrogen in methylene chloride (Figure 1), which contain bands characteristic of 4- or 5-coordinate cobalt(II) (575, 610 nm)^{6,13} and copper(II) (850 nm).^{5,8} Negligible

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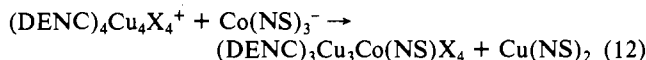
absorption by copper(I) is expected in this region.^{6,8}

Complexes III are discrete tetranuclear species (Table I). Their proposed core structure (Scheme I) retains most of the features of the structures of I.⁸ The apparent presence of 4- or 5-coordinate cobalt(II) can be reconciled in two ways. The cobalt(II) center could consist of bidentate NS ligands with long bonds to bridging X. This would tend to destabilize the tetranuclear structure (eq 11), which is contrary to cryoscopic evidence. We prefer alter-



native structure III in Scheme I, since there is evidence for opening of $\text{M}(\text{NS})_n$ chelate rings on coordination of additional ligands.¹⁵

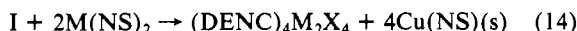
Whatever their detailed structures, products III are formed by transmetalation of copper(I) (eq 1) and not copper(II) (eq 12)



after electron transfer (eq 9). This is consistent with reaction 13 $\text{I} + \text{Cu}(\text{NS})_2 \rightarrow (\text{DENC})_3\text{Cu}_3\text{Cu}(\text{NS})\text{X}_4 + \text{Cu}(\text{NS})(\text{s})$ (13)

observed previously.⁶ Reactions 1, 2 and 13 occur because $\text{Cu}(\text{NS})(\text{s})$ is more thermodynamically stable than dissolved $\text{Cu}(\text{NS})_2$.

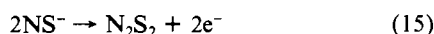
Reaction 2. Reaction 2 is the analogue of reaction 14 observed previously.⁶ However, because of prior electron transfer, only 2 mols of $\text{Cu}(\text{NS})(\text{s})$ are precipitated in eq 2. The likely respective



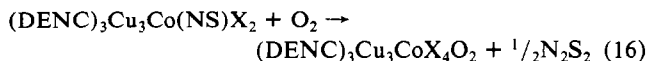
intermediates $(\text{DENC})_2\text{Cu}_2(\text{Co}(\text{NS})_2)_2\text{X}_4$ (V) and $(\text{DENC})_2\text{Cu}_2(\text{M}(\text{NS})_2)_2\text{X}_4$ ⁶ are not stable tetranuclear species. They lose 2 mol of $\text{Cu}(\text{NS})_2$ and 2 mol of $\text{Cu}(\text{NS})(\text{s})$, respectively, presumably because of major core structural changes on transmetalation of more than one copper(I) center. These decompositions must be faster than transmetalation because $\text{V} \rightarrow \text{VI}$ is not intercepted by excess $\text{Co}(\text{NS})_3$ and reaction 14 proceeds even in the presence of excess $\text{M}(\text{NS})_2$.⁶

Analytical (Table I) and spectral data (Table II) for product VI ($\text{X} = \text{Cl}$) from reactions 2 and 14 ($\text{M} = \text{Co}$)⁶ are identical, indicating formation of the same dimeric product.

Reaction 3. Stoichiometry and Products. Manometric dioxygen uptake measurements confirmed the stoichiometry of eq 3. The chromatographically isolated product IV is tetranuclear (Table I). Its IR spectrum contains bands at 1635 cm^{-1} (monodentate DENC)^{3,6,8,12} and no absorption at 1000 cm^{-1} (no coordinated NS^-).⁹ Reaction 3 is thus analogous to the corresponding aprotic reactions of I⁸ and $(\text{DENC})_3\text{Cu}_3\text{M}(\text{NS})\text{X}_4$ ⁶ with dioxygen, in which a total of 4 electrons are transferred to dioxygen to give *oxo*-metal(II) products. These four electrons are donated by the two copper(I) centers and the two coordinated NS^- ligands of III (eq 15).



Product IV has previously been obtained through reaction 16.⁶ Evidence has been presented for its proposed core structure (Scheme I).⁶ One of the curious features of its electronic spectrum



(Table II) is that it contains little or no absorption from the cobalt(II) center.

Kinetics and Mechanism of Reaction 3. Reactions of excess III with dioxygen in methylene chloride and nitrobenzene were easily monitored by conventional spectrophotometry in the wavelength range 700–900 nm. The concentrations of III were always sufficient to ensure pseudo-first-order conditions. Plots of $\ln(A_\infty - A_t)$ vs. A_t , where A_t is the absorbance at time t under fixed experimental conditions, were linear to at least 4 half-lives

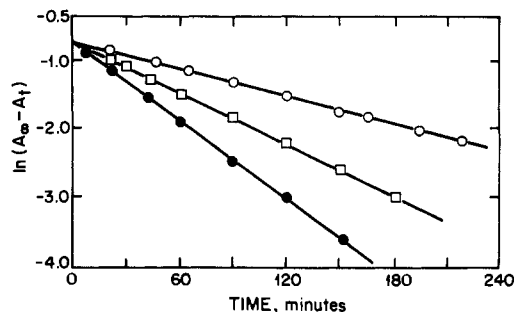


Figure 2. First-order kinetic plots for reaction of excess IIIa with dioxygen ($1 \times 10^{-4} \text{ M}$) at 32°C and monitoring wavelength 900 nm. $10^2[\text{III}]_0 = 0.66$ (O), 1.66 (□), 2.00 (●).

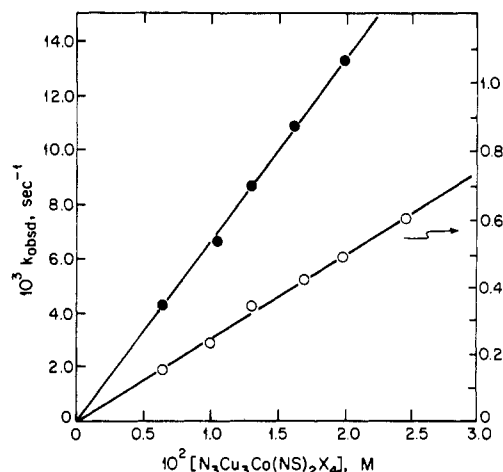


Figure 3. Plots of k_{obsd} vs. $[\text{III}]_0$ in reaction 3 for $\text{X} = \text{Cl}$ at 32.0°C (●) and $\text{X} = \text{Br}$ at 25°C (O) in nitrobenzene.

Table III. Kinetic Parameters for Oxidation of $\text{N}_4\text{Cu}_4\text{X}_4$, $\text{N}_3\text{Cu}_3\text{Co}(\text{NS})\text{X}_4$, and $\text{N}_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ Complexes ($\text{N} = \text{DENC}$; $\text{X} = \text{Cl}, \text{Br}$) by Dioxygen in Aprotic Solvents

reactant	k_T^a , $\text{M}^{-1} \text{s}^{-1}$	ΔH_T^* , kcal mol^{-1}	ΔS_T^* , $\text{cal deg}^{-1} \text{mol}^{-1}$
$\text{N}_4\text{Cu}_4\text{Cl}_4^{b,c}$	5.4	2.1 ± 0.3	-48 ± 3
$\text{N}_4\text{Cu}_4\text{Cl}_4^{b,d}$	16.2	3.9 ± 0.3	-40 ± 3
$\text{N}_4\text{Cu}_4\text{Br}_4^{b,d}$	0.66	5.9 ± 0.6	-40 ± 3
$\text{N}_3\text{Cu}_3\text{Co}(\text{NS})\text{Cl}_4^{d,e}$	5.4	4.3 ± 0.3	-41 ± 3
$\text{N}_3\text{Cu}_3\text{Co}(\text{NS})_2\text{Cl}_4$ (IIIa) ^d	0.53	3.1 ± 0.3	-49 ± 3
$\text{N}_3\text{Cu}_3\text{Co}(\text{NS})_2\text{Br}_4$ (IIIb) ^d	0.026	5.2 ± 0.3	-48 ± 3

^a Given at 25°C . ^b Data from ref 8. ^c In methylene chloride. ^d In nitrobenzene. ^e Data from ref 6.

(Figure 2) with no spectrophotometric evidence for precursors or intermediates, indicating that the rate-determining step in reaction 3 is first order in $[\text{O}_2]$. The pseudo-first-order rate constants, k_{obsd} , were accurately proportional to $[\text{III}]$ (Figure 3), indicating that reaction 3 has the second-order rate law 17. Rate constants k_T

$$d[\text{IV}]/dt = k_T[\text{III}][\text{O}_2] \quad (17)$$

and their respective activation parameters are compared with those for aprotic oxidation of $[(\text{DENC})\text{CuX}]_4$ ⁸ and $(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})\text{X}_4$ ⁶ complexes in Table III.

Interpretation of the Kinetic Data. It has previously been concluded that the rate-determining step in the aprotic oxidation of $\text{N}_4\text{Cu}_4\text{X}_4$ complexes ($\text{X} = \text{Cl}$ or Br) by dioxygen is insertion of O_2 into the halo core of the copper(I) reactant.⁸ 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.⁸

These features are observed in the corresponding oxidations of $(\text{DENC})_3\text{Cu}_3\text{M}(\text{NS})\text{X}_4$ ⁶ and $(\text{DENC})_3\text{Cu}_3\text{Co}(\text{NS})_2\text{X}_4$ (III) (Table III). The data for III fit the $\Delta H_T^*/\Delta S_T^*$ correlation noted previously,⁶ indicating that insertion of O_2 into the cores of all

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

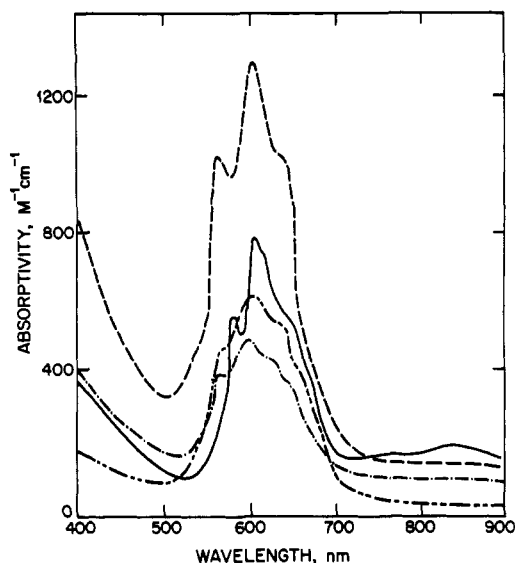


Figure 4. Electronic spectra for VI (---), VIIIa (---), VIIIc (---), and VIIIId (—) in methylene chloride at 25 °C.

of these complexes is rate-determining. Relatively low k_T values for oxidation of III in Table III are ascribed (a) to insertion obstructed by the two NS ligands on cobalt(II) and (b) to the presence of one formal copper(II) center in III that "stiffens" the core relative to those in $N_4Cu_4X_4$ ⁸ and $(DENC)_3Cu_3M(NS)X_4$ ⁶ which contain no copper(II).

Because insertion is rate-determining we have no information on the rates of electron transfer from copper(I) and NS^- to dioxygen. However, if dioxygen is preferentially inserted through a face of III that is unobstructed by NS, then rapid transfer of 2 electrons from the two formal copper(I) centers in III would give O_2^{2-} in the intermediate that is capable of aprotic, intramolecular oxidation of coordinated NS^- (eq 15). The resulting disulfide is easily lost,⁶ particularly if NS^- is monodentate in III, as proposed in Scheme I.

Reactions 4. Reactions 4 are stoichiometric transmetalation reactions that provide a valuable route to heterobimetallic complexes VIII. The proposed intermediate VII presumably decomposes because of marked instability of a species with M on a C_2 axis of the tetrahalo core, which may facilitate NS^- ligand transfer to copper(II)—product III, which also contains one copper(II) and two NS^- ligands, is much more stable.

The IR spectra of isolated dimers VIII contain bands for coordinated water (3400 cm^{-1})¹⁴ monodentate DENC (1635 cm^{-1})^{6,8,12} and no bands for coordinated NS^- at 1000 cm^{-1} .⁹

Comparison of the electronic spectra of VI and VIII (Figure 4) allows an assessment of the effects of replacement of one of the cobalt(II) centers of VI with M in what are almost certainly common μ, μ -dihalo-bridged structures.¹² The bands at 570–630 nm are due to 4- or 5-coordinate cobalt(II).^{6,13} The molar absorptivity per cobalt(II) center decreases progressively with M = Cu, Co (in VI), Ni, and Zn in VIII (Table II).

Reactions 5. Trimeric products IX are obtained by treatment of III with 2 equiv of $M(NS)_2$ in methylene chloride under dinitrogen. Stabilization of intermediate VII occurs through transmetalation of its copper(II) center by M, which is evidently faster than NS^- ligand transfer VII \rightarrow VIII.

Analytical data (Table I) and the presence of an IR band at 1000 cm^{-1} confirm that IX are trimeric species with coordinated NS^- ligands.^{6,9} Their IR spectra also indicate the presence of monodentate DENC ligands and coordinated water molecules (see above).

The molar absorptivities per cobalt(II) of $(DENC)_3Co(NS)_2M_2X_4$ complexes IX in the 570–630 nm region decrease as M is varied from Cu to Zn, as found for dimers VIII (see above).

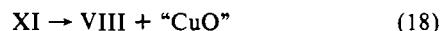
Reactions 6. Stoichiometry and Products. The stoichiometry of reactions 6 was established by manometric dioxygen uptake

measurements in nitrobenzene, and the trimeric oxidation products $(DENC)_3CoM_2X_4O$ (X) were easily separated by gel-permeation chromatography (methylene chloride eluent).³

The trimeric products X (Table I) have IR spectra indicating the presence of coordinated water and monodentate DENC and the absence of coordinated NS^- . Their electronic spectra (Table II) are dominated by bands due to 4- or 5-coordinate cobalt(II). Once again, the molar absorptivities per cobalt in X decrease in the order M = Cu > Co > Ni > Zn. Products X probably do not contain terminal oxo groups because they are not initiators for the oxidative coupling of phenols by dioxygen.⁸ We suggest a μ_3 -oxo core structure because complexes containing μ_4 -oxo groups (as in IV) can be completely transmetalated,^{1,3,6} but in this case the (μ -oxo)copper unit is lost to give X before this occurs. We have been unable to monitor the kinetics of reactions 6 by spectrophotometry because of negligible differences in the electronic spectra of reactants IX and products X. However, these reactions are not slow on a synthetic scale: coordinated NS^- oxidation by O_2 could be catalyzed by transient cobalt(III) formation in IX.

Reactions 7 and 8. Our study of reactions 7 and 8 is an extension of previous work⁶ in which we transmetalated the nickel(II) analogue of IV, $(DENC)_3Cu_3NiCl_4O_2$, with 2 or 3 equiv of bis(*S*-methyl isopropylidenehydrazinecarbodithioato)nickel(II) ($Ni(NS)_2$) and obtained X (Co = M = Ni). Satisfactory analytical data were also obtained with M = Co and Zn in X (Table I). Loss of a formal CuO unit¹⁶ on transmetalation of IV with 2 or more equiv of an $M(NS)_2$ reagent thus appears to be characteristic of core structure IV and distinguishes it from the alternative bis(μ -oxo) structure.^{3,6}

We have investigated reaction 7 with M = Co, Ni, and Zn. The analytical data (Table I) indicate that XI are not particularly stable species. Lower than expected copper contents indicate reaction 18 on the time scale of transmetalation. Products labeled



"XI" are thus best regarded as mixtures of IX and VIII that are difficult to separate by gel-permeation chromatography.

Species VII and XI are both trimers containing a single copper(II) center that disproportionate to give VIII. However, XI is definitely more stable than the intermediate VII, because CuO loss from XI can be prevented by faster transmetalation with $M(NS)_2$ (eq 8).

Proposed Core Structures. None of the transmetalated products of this study have been obtained as single crystals, but the core structures proposed in Scheme I are consistent with their spectral and other properties. When present, copper(II) has been assigned one terminal DENC ligand (except in dimer VIIIId) following our previous observations.^{1-8,12} In other cases we have arbitrarily allocated DENC ligands to give 5-coordinate metal centers throughout.

Relative Stabilities. Species III, V, and VII all contain copper(II) and coordinated NS^- but only III are stable to intramolecular NS^- ligand transfer to copper(II), which in the other cases results in the loss of $Cu(NS)_2$. Thus, although copper(I) is transmetalated in preference to copper(II), copper(I) in III retards intramolecular NS^- ligand transfer to copper.

On present evidence we suggest processes IV \rightarrow X and IV \rightarrow XI \rightarrow VIII as diagnostic of the proposed core structure IV.

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Registry No. Ia, 80105-82-4; Ib, 80105-83-5; II, 102282-27-9; IIIa, 102211-27-8; IIIb, 102211-28-9; IVa, 102109-36-4; IVb, 102109-40-0; VIa, 102211-29-0; VIb, 102233-41-0; VIIIa, 102211-30-3; VIIIb, 102211-31-4; VIIIc, 102211-32-5; VIIIId, 102211-33-6; IXa, 102211-34-7; IXb, 102211-35-8; IXc, 102211-36-9; Xa, 102211-37-0; Xb, 102211-38-1; Xc, 102211-39-2; Xd, 102211-40-5; Xe, 102211-41-6; XIa, 102211-42-7; XIb, 102211-43-8; $Cu(NS)_2$, 34156-34-8; $Cu(NS)_2$, 102211-44-9; $(DENC)CuO$, 102211-45-0; $Ni(NS)_2$, 34214-73-8; $Zn(NS)_2$, 72871-59-1.