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Progressive Transmetalation of Tetranuclear Dioxocopper(II) Complexes with Cobalt Reagents

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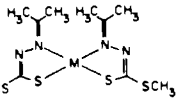
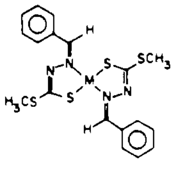
Aprotic oxidation of tetranuclear copper(I) complexes $N_4Cu_4X_4$ (I) (N is monodentate *N*,*N*-diethylnicotinamide; X is Cl or Br) with dioxygen gives tetranuclear dioxocopper(II) complexes $(\mu\text{-O})_2N_4Cu_4X_4$ (II). These targets are transmetalated by excess transmetalators bis(*S*-methyl isopropylidenehydrazinecarbodithioato)nickel(II) (A) and bis(*S*-methyl benzylidenehydrazinecarbodithioato)nickel(II) (B) to give isomers of $(\mu\text{-O})_2[NCuNi(H_2O)X_2]_2$, Te_1 and Te_2, respectively. However, if complexes I are first monotransmetalated by A (the metal is Co, Ni, Cu, or Zn) or tris(*S*-methyl isopropylidenehydrazinecarbodithioato)cobalt(III) (C) and then oxidized, the products are tetramers $(\mu_4\text{-O},\mu\text{-O})N_3Cu_3M(H_2O)X_4$ (IV). Complexes IV react with excess A (M = Ni) or C to give trimers $(\mu_3\text{-O})N_3M_3X_4$ (Tr_1) or, when M in IV is Cu (specified as III), with excess A to give the six-member family $(\mu_4\text{-O},\mu\text{-O})N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ (Te_3). It is shown that II (X = Cl) reacts with 1–4 mol of C to give the tetranuclear family $(\mu\text{-O})_2N_4Cu_{4-x}Co_xCl_4$ (x = 0–4), which includes the analogue of isomer Te_2. Transmetalation of $(\mu_3\text{-O})N_3Cu_3Cl_4$ (XIV) with 1–3 mol of C gives the family of Tr_1 trimers $(\mu_3\text{-O})N_3Cu_{3-x}Co_xCl_4$ (x = 1–3). Structurally different trimers $(\mu\text{-O})N_3(Co,Cu)_3Cl_4$ (Tr_2) are obtained by two methods: (1) transmetalation of III with 1–3 mol of C; (2) the four-step sequence (a) transmetalation of I with C and 2 mol of A (M = Cu), (b) oxidation of the product with dioxygen, and (c) transmetalation with 1 or 2 mol of C. These two methods give five of the six expected members of the Tr_2 family that are distinguishable from Tr_1 and from each other by ESR and electronic spectral measurements and by magnetic moment determinations. A trans effect with Co > Cu across μ-oxo bridges influences the course of progressive transmetalations of II and $(\mu\text{-O})N_3(Co,Cu)_3Cl_4$ isomers by C.

Introduction

Transmetalation is the stoichiometric replacement of metals in a polymetallic complex target with other metals from reagents called transmetalators.[1] The products are families of closely related, heteropolymetallic molecules that cannot be obtained by other means. We are systematically studying the patterns of transmetalation of specific polymetallic copper targets with different transmetalators.[1-4] Scheme I summarizes the results of our work on the oxidation and transmetalation[1-7] of tetranuclear copper(I) complexes $N_4Cu_4X_4$ (I), where N is *N*,*N*-diethylnicotinamide, X is Cl or Br, A–C are neutral bis- and tris(*S*-methyl hydrazinecarbodithioato)metal transmetalators, and the oxidant is dioxygen.[8]


A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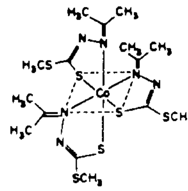
C

Our previous work demonstrates that tetranuclear dioxometal complexes with core structures III[9] and IV are obtained instead of II if I is transmetalated with A or C before it is oxidized.[2-4] We shall refer to this as a T/O sequence. The alternative core structures II–IV arise from fundamental differences in the steps involved in 4-electron dioxygen reduction by copper(I) and coordinated NS ligands.[2,3] Also evident is that structures II[10,11] and III[1] give tetramers Te_1–Te_3 of different metal stoichiometries and structures on transmetalation with excess A (M = Ni), while structures IV give trimers Tr_1 with characteristic loss of 1 mol of CuO.[2-4] This is one of several means of distinction of structures II–IV, which cannot be distinguished directly because of disproportionation on attempted crystallization.[1,6,7,10,11]

The conversion of IV to Tr_1 structures by transmetalation with A (M = Co, Ni, Zn) and C has been investigated thoroughly,[2-4] as has the conversion of structures II to isomeric tetramers Te_1 and Te_2 by A and B (M = Ni), respectively.[10,11] Evidence for trans effects across μ-oxo bridges in determining the steric course of stoichiometric transmetalation of $(\mu\text{-O})_2L_4Cu_4$ complexes (L = 6-methyl-2-hydroxypyridinate)[12] led us to investigate the transmetalation of II (X = Cl) by A (M = Co) and by C; the results reported in the first part of this paper indicate that isomer Te_2 (Scheme I: X = Cl; NCo replaces $(H_2O)Ni$) is one member of the complete tetranuclear family $(\mu\text{-O})_2N_4Cu_{4-x}Co_xCl_4$ (x = 0–4).

Scheme I also indicates that III (X = Cl) reacts stoichiometrically with excess A (M = Ni) to give tetranuclear Te_3, which is the last of the six-member[13] family $(\mu_4\text{-O},\mu\text{-O})N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ (x = 0–4).[1] The second part of this paper reports that III (X = Cl) reacts stoichiometrically with C to give a family of μ-oxo trimers Tr_2 instead of tetramers Te_3. Isomeric Tr_2 products also are obtained from the sequence (1) transmetalation of $N_3Cu_3Co(NS)_2Cl_4$ with 2 mol of A (M = Cu), (2) oxidation with dioxygen, and (3) transmetalation with C, while trans-

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(1) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 4479.

(2) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Gilbert, T. R.; Nabih, K. *Inorg. Chem.* **1986**, *25*, 1929.

(3) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Gilbert, T. R. *Inorg. Chem.* **1986**, *25*, 2373.

(4) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Kasem, T. S.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 3904.

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

(6) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, *22*, 1257.

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

(8) Abbreviations: A are bis(*S*-methyl isopropylidenehydrazinecarbodithioate)metal(II) complexes; B are bis(*S*-methyl benzylidenehydrazinecarbodithioate)metal(II) complexes; C is *mer*-tris(*S*-methyl isopropylidenehydrazinecarbodithioate)cobalt(III). See: Onan, K. D.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chim. Acta* **1986**, *119*, 121. Reagent C also is an oxidant: its transmetalation of I is preceded by electron transfer from copper(I) to cobalt(III) and its coordinated NS is oxidized to the disulfide N_2S_2 in eq 5.[3,4]

(9) Reference 1 singled out III as a special case of IV, Scheme I. The present work shows that III and IV react with C to give trimers of core structure Tr_2 and Tr_1, respectively (see text).

(10) El-Toukhy, A.; Cai, G.-Z.; Davies, G.; Gilbert, T. R.; Onan, K. D.; Veidis, M. *J. Am. Chem. Soc.* **1984**, *106*, 4596.

(11) Cai, G.-Z.; Davies, G.; El-Toukhy, A.; Gilbert, T. R.; Henary, M. *Inorg. Chem.* **1985**, *24*, 1701.

(12) Cai, G.-Z.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Onan, K. D. *Inorg. Chem.* **1986**, *25*, 1935.

(13) The six members of the family $(\mu_4\text{-O},\mu\text{-O})N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ (x = 0–4) from transmetalation of III with xA (M = Ni) include two isomeric pairs.[1]

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Scheme I

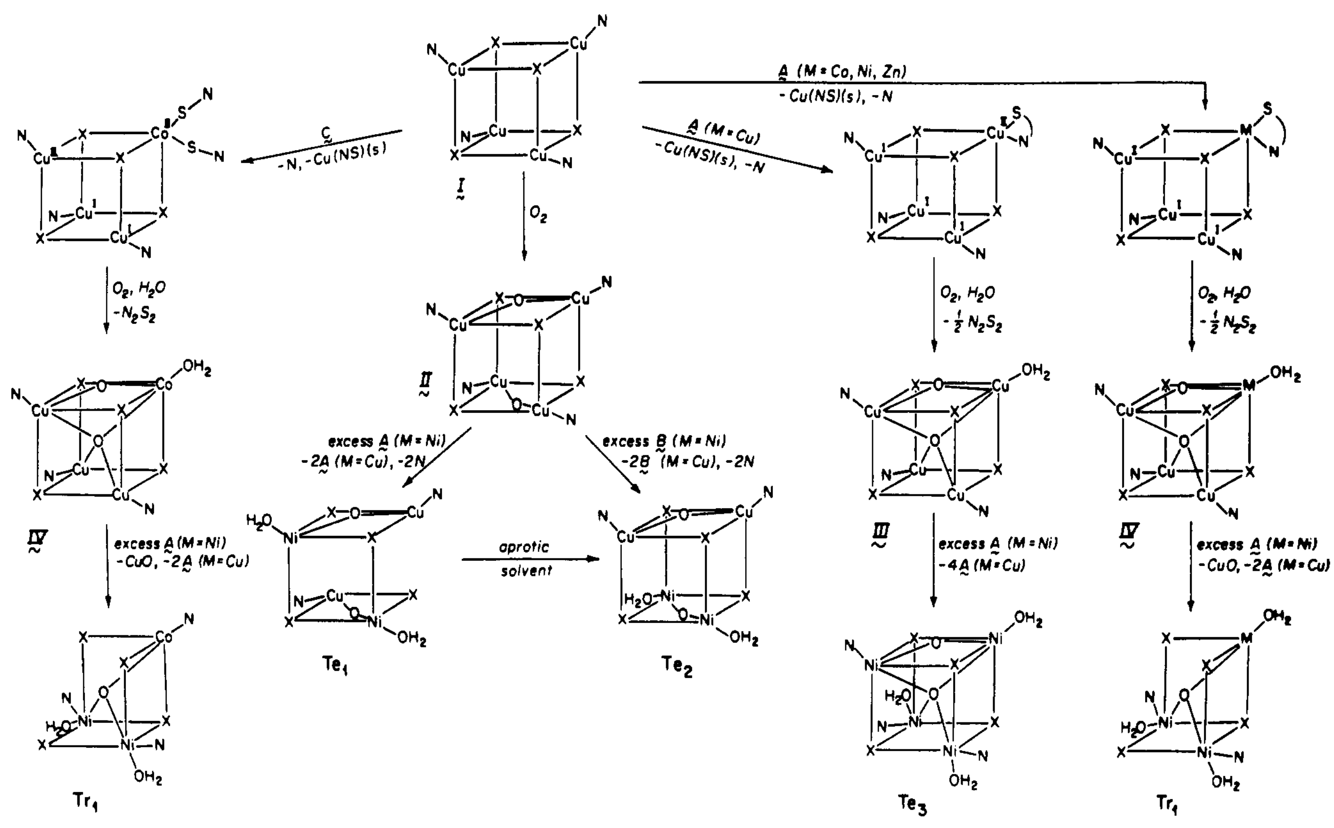

Table I. Analytical and Electronic Spectral Data for Products of Transmetalation of $(\mu\text{-O})_2N_4Cu_4Cl_4$ (II) with $Co(NS)_3$ Reagent C

symbol[a]	complex	% anal.[b] C	H	N	Cl	Cu	Co	M_r[b,c]	λ_{max},[d] nm (ϵ_λ, M^{-1} cm^{-1})
II	$(\mu\text{-O})_2N_4Cu_4Cl_4$	41.5 (42.1)	5.1 (4.9)	9.8 (9.8)	12.9 (12.4)	22.1 (22.3)		1140 ± 20 (1141)	850 (740) 775 (680)
V	$(\mu\text{-O})_2N_4Cu_3CoCl_4$	42.0 (42.2)	4.5 (4.9)	9.7 (9.9)	13.2 (12.5)	16.3 (16.8)	5.1 (5.2)	1130 ± 20 (1137)	850 (625) 775 (600) 610 (220)
VI	$(\mu\text{-O})_2N_4Cu_2Co_2Cl_4$	42.5 (42.4)	4.4 (4.9)	9.5 (9.9)	12.2 (12.5)	10.7 (11.2)	9.8 (10.4)	1160 ± 20 (1132)	850 (560) 775 (540) 610 (290)
VII	$(\mu\text{-O})_2N_4CuCo_3Cl_4$	42.1 (42.6)	4.7 (5.0)	9.4 (9.9)	11.9 (12.6)	4.9 (5.6)	15.2 (15.7)	1120 ± 20 (1128)	830 (365) 775 (350) 630 (280) 600 (340) 575 (285)
VIII	$(\mu\text{-O})_2N_4Co_4Cl_4$	41.8 (42.7)	4.2 (5.0)	9.4 (10.0)	12.1 (12.6)		20.7 (21.0)	1130 ± 20 (1123)	675 (700) 630 (860) 600 (1170) 575 (1010)
IX	$(\mu\text{-O})_2N_3Cu_2CoNiCl_4\cdot H_2O$[e]	36.7 (37.0)	4.2 (4.6)	8.4 (8.6)	14.2 (14.6)	12.8 (13.1)	5.4 (6.1)	940 ± 20 (972)	850 (419) 775 (391)

[a] Symbols as used in Scheme II; data for II were taken from ref 1. [b] Calculated values in parentheses. [c] Measured cryoscopically in nitrobenzene in the range (3–5) × 10^{-2} *m*. [d] In methylene chloride. [e] Anal. for nickel: 5.8 (6.1). The water molecule indicated is very probably bonded to the nickel center in IX.[1,10,11,23]

metalation of $(\mu_3\text{-O})Cu_3Cl_4$ (XIV) gives Tr_1 complexes containing cobalt and copper. ESR and electronic spectral measurements together with magnetic moment determinations enabled the assignment of different core structures to Tr_1 and Tr_2 transmetalation products.

Experimental Section

Materials and Procedures. Copper(I) chloride, prepared by the literature method,[14] was used throughout this work. The syntheses of $N_4Cu_4Cl_4$ (I) and its oxidized product $(\mu\text{-O})_2N_4Cu_4Cl_4$ (II) have been described.[1,5,6] Complexes III and IV were obtained from the T/O sequences of Scheme I.[1,2–4] Experimental procedures for transmetalation of II[10,11] and III[1] were as described previously.

The complex $(\mu_3\text{-O})N_3Cu_3Cl_4$ (XIV) was obtained from the reaction of $(\mu_4\text{-O})N_4Cu_4Cl_6$[10] with 1 mol of $Hg(NS)_2$ and isolated by gel permeation chromatography (methylene chloride eluant).[15] The complex $N_3CoCu_2Cl_4O$ (XVIII) was obtained by reaction of $N_3Cu_3Co(NS)_2Cl_4$ with 2 mol of A (M = Cu) in methylene chloride, followed by in situ oxidation of the product with dioxygen.[3] Stepwise transmetalations of XIV and XVIII with reagent C were conducted as previously described.[2–4]

Product isolation techniques, analytical methods, and most of the physical measurement techniques employed are detailed in our earlier papers.[1–7,10–12] ESR spectra of 1.0 mM solutions of Tr_1 and Tr_2 products

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(14) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(15) Abu-Raqabah, A.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M., to be submitted for publication. All the properties of XIV are consistent with its formulation as $(\mu_3\text{-O})N_3Cu_3Cl_4$.

Table II. Analytical and Electronic Spectra Data for Products of Transmetalation of $N_3Cu_3Cu(H_2O)Cl_4O_2$ (III) with $Co(NS)_3$ Reagent C

		% anal.[b]							
symbol[a]	complex	C	H	N	Cl	Cu	Co	M_r[b,c]	λ_{max},[d] nm (ϵ_λ, M^{-1} cm^{-1})
III	$N_3Cu_4Cl_4O_2 \cdot H_2O$	35.8 (36.7)	4.1 (4.5)	8.6 (8.6)	14.2 (14.5)	25.3 (25.9)		950 ± 20 (981)	850 (770) 775 (750)
X	(μ-O)$N_3Cu_2CoCl_4$	39.9 (40.9)	4.7 (4.8)	9.2 (9.6)	15.3 (16.1)	13.8 (14.4)	6.3 (6.7)	840 ± 20 (879)	850 (620) 775 (600) 610 (260)
XI	(μ-O)$N_3CuCo_2Cl_4$	40.5 (41.2)	4.6 (4.9)	9.3 (9.6)	15.8 (16.2)	6.8 (7.3)	12.8 (13.5)	860 ± 20 (874)	850 (380) 750 (360) 630 (390) 610 (495) 575 (380)
XII	(μ-O)$N_3Co_3Cl_4$	40.9 (41.4)	5.0 (4.9)	9.7 (9.6)	16.3 (16.3)		19.9 (20.4)	920 ± 20 (869)	650 (770) 630 (980) 610 (1300) 575 (1100)

[a] Symbols as used in Schemes I and IV. [b] Calculated values in parentheses. [c] Measured cryoscopically in nitrobenzene in the range (3–5) × 10^{-2} *m*. [d] In methylene chloride.

Table III. Analytical and Electronic Spectral Data for Products of Transmetalation of (μ_3-O)$N_3Cu_3Cl_4$ (XIV) with $Co(NS)_3$ Reagent C

		% anal.[a]							
symbol	complex	C	H	N	Cl	Cu	Co	M_r[a,b]	λ_{max},[c] nm (ϵ_λ, M^{-1} cm^{-1})
XIV	(μ_3-O)$N_3Cu_3Cl_4$	40.4 (40.7)	4.8 (4.8)	9.4 (9.5)	16.5 (16.1)	21.2 (21.6)		900 ± 20 (883)	850 (1000) 775 (880)
XV	(μ_3-O)$N_3Cu_2CoCl_4$	40.6 (41.0)	4.7 (4.8)	9.3 (9.6)	16.2 (16.0)	13.7 (14.4)	12.8 (13.4)	900 ± 20 (873)	850 (690) 775 (640) 630 (365) 600 (410) 575 (360)
XVI	(μ_3-O)$N_3CuCo_2Cl_4$	39.1 (41.1)	4.9 (4.8)	9.1 (9.6)	16.7 (16.2)	6.7 (7.3)	12.8 (13.4)	890 ± 20 (875)	850 (215) 630 (690) 610 (780) 580 (680)
XVII	(μ_3-O)$N_3Co_3Cl_4$	39.4 (41.4)	5.4 (4.8)	9.4 (9.7)	15.0 (16.3)		19.9 (20.3)	890 ± 20 (869)	630 (850) 610 (990) 580 (800)

[a] Calculated values in parentheses. [b] Measured cryoscopically in nitrobenzene in the range (3–5) × 10^{-2} *m*. [c] In methylene chloride.

Table IV. Analytical and Electronic Spectral Data for Products of Transmetalation of (μ-O)$N_3Cu_2CoCl_4$ (XVIII) with $Co(NS)_3$ Reagent C

		% anal.[b]							
symbol[a]	complex	C	H	N	Cl	Cu	Co	M_r[b,c]	λ_{max},[d] nm (ϵ_λ, M^{-1} cm^{-1})
XVIII	(μ-O)$N_3Cu_2CoCl_4$	40.3 (40.9)	4.8 (4.8)	9.4 (9.6)	15.8 (16.1)	13.3 (13.6)	7.1 (6.7)	850 ± 20 (873)	850 (260) 630 (710) 610 (840) 580 (680)
XIX	(μ-O)$N_3CuCo_2Cl_4$	43.9 (41.2)	4.9 (5.1)	9.3 (9.6)		7.1 (7.0)	12.8 (13.0)	860 ± 20 (875)	850 (190) 630 (890) 610 (1020) 575 (880)
XX	(μ-O)$N_3Co_3Cl_4$	41.4 (41.4)	4.5 (4.9)	9.6 (9.6)	16.2 (16.3)		20.1 (20.4)	850 ± 20 (869)	650 (770) 630 (980) 610 (1300) 575 (1100)

[a] Symbols as used in Scheme V. [b] Calculated values in parentheses. [c] Measured cryoscopically in nitrobenzene in the range (3–5) × 10^{-2} *m*. [d] In methylene chloride.

in methylene chloride were obtained with a Bruker ESR-300 instrument. Magnetic moments were determined at the 6 mg/mL level in 30% v/v DMSO-d_6/D_2O by the Evans method[16] (Me_4NCl standard) with a Varian spectrometer. All physical measurements were made at 25 °C. Analytical, cryoscopic, and spectral data for all polynuclear reactants and products are given in Tables I–IV.

Results and Discussion

Cobalt Transmetalators. Like other $M(NS)_2$ complexes, cobalt(II) complex A (M = Co) directly transmetalates copper(I) centers via eq 1 and copper(II) centers via eq 2.[2-4] The corresponding reactions of cobalt(III) complex C are summarized in eq 3 and 4, respectively.[3,4] Gravimetric determination of the

$$\equiv Cu^{I} + Co(NS)_2 \rightarrow \equiv Co^{II}(NS) + Cu(NS)(s) \qquad (1)$$

$$\equiv Cu^{II} + Co^{II}(NS)_2 \rightarrow \equiv Co^{II} + Cu(NS)_2 \qquad (2)$$

$$\equiv Cu^{I} + Co^{III}(NS)_3 \rightarrow \equiv Co^{II}(NS)_2 + Cu(NS)(s) \qquad (3)$$

$$\equiv Cu^{II} + Co^{III}(NS)_3 \rightarrow \equiv Co^{III}(NS) + Cu(NS)_2 \qquad (4)$$

insoluble coproduct Cu(NS)(s) confirms the stoichiometries of eq 1 and 3.[2-4] Analytical data and spectral measurements indicate the presence of cobalt(II) in all of the polynuclear products of copper(I) and copper(II) transmetalation by A (M = Co) and C.[2-4] Equation 5 is responsible for cobalt(II) formation in copper(II)/C systems.[3,4]

$$\equiv Co^{III}(NS) \rightarrow \equiv Co^{II} + {}^{1}/_{2}N_2S_2 \qquad (5)$$

There are several reasons why the transmetalations of copper(I) and copper(II) complexes with A (M = Co) and C are fast and

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[16] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

selective, including their relatively low thermodynamic stability in the order $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$.[4,17] Another advantage of their use as transmetalators is that cobalt(II) centers in the transmetalated products often exhibit a strong, structured absorption centered at ca. 600 nm ($\epsilon \gtrsim 300$ L (mol of Co)$^{-1}$ cm^{-1}).[2-4] When observed, this absorption is taken to indicate the presence of five-coordinate cobalt(II) in species $N_3Cu_3Co(NS)X_4$ (see Figure 1 of ref 2) and $N_3Cu_3Co(NS)_2X_4$ (see Figure 1 of ref 3), leading to the proposed respective structures in Scheme I. The formulation of $N_3Cu^I_2Cu^{II}Co^{II}(NS)_2X_4$ as mixed-valence species arises from structured absorption at 600 nm together with significant absorption at 700–900 nm due to copper(II).[3,4] Lack of significant structured absorption at 600 nm (with $\epsilon \lesssim 100$ L (mol of Co)$^{-1}$ cm^{-1}) indicates six-coordinate cobalt(II) in products IV, Scheme I.[3,4] We can thus spectrally assign five- or six-coordinate cobalt(II) and copper(II) in a given molecule. In the following sections we propose the use of absorptions at 600 and 700–900 nm and other techniques to delineate transmetalation patterns and assign product core structures for isomeric polynuclear copper–cobalt molecules.

Transmetalation of II with A (M = Co) and C. Aprotic oxidation of $N_4Cu_4X_4$ with dioxygen obeys the stoichiometry of eq 6 (Scheme I).[1,5-7] Transmetalation of II with excess A and B (M

$$I + O_2 \rightarrow II \qquad (6)$$

= Ni) gives respective isomers Te_1 and Te_2;[10,11] although the corresponding reactions with M = Zn result in complete replacement of copper(II) with Zn, the primary tetranuclear products are unstable.[18] We investigated the title reactions to see if the products are tetranuclear and stable.

Spectrophotometric titrations of II (X = Cl) with A (M = Co) and C in methylene chloride at 600 nm[19] showed that both reactions have the stoichiometry $\Delta(A \text{ or } C)/\Delta(II) = 4.0 \pm 0.1$. This corresponds to complete transmetalation of II by cobalt.[18] Coproduct $Cu(NS)_2$ from eq 2 and 4 was identified in the second of two colored bands eluted on gel permeation chromatography (methylene chloride eluant) of the products of reactions of II with 1–4 mol of A (M = Co) or C.

Transmetalation of II with Equimolar A (M = Co) and C. Analytical and cryoscopic data (Table I) show that the transmetalated polynuclear product isolated from the title reactions is tetranuclear $(\mu\text{-}O)_2N_4Cu_3CoCl_4$ (V). The reaction of II with C was especially rapid and gave coproduct N_2S_2 (eq 5). The core structure of V was confirmed through reaction 7,[20] which is specific

$$V + 2CO_2 \rightarrow (\mu\text{-}CO_3)_2N_4Cu_3CoX_4 \qquad (7)$$

to II and their transmetalated derivatives Te_1 and Te_2 (Scheme I),[10,11] and by lack of ability to initiate the oxidative coupling of 2,6-dimethylphenol by dioxygen.[1,5-7] The data in Table I show that V contains four ligands N, which are all monodentate (sharp, single IR band at 1635 cm^{-1}).[10] Product V is clearly different from IV (M = Co) (Scheme I), which contains three N ligands and an aquo ligand incorporated during product isolation.[2,3]

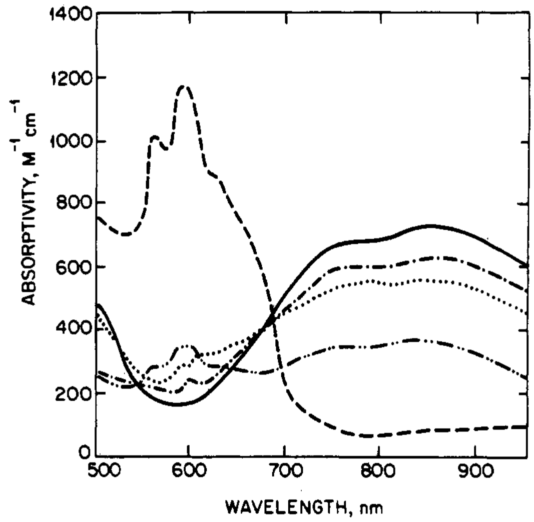

Figure 1. Electronic spectra of II (—), V (- -), VI (···), VII (-··-), and VIII (-·-) in methylene chloride at 25 °C. See Table I, Scheme II, and text.

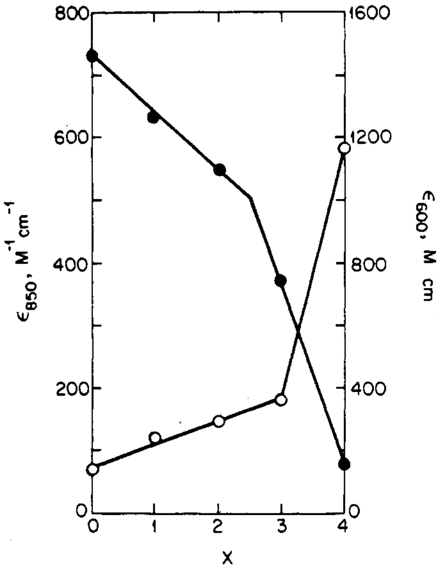

Figure 2. Plots of ϵ_{850} (left ordinate, ●) and ϵ_{600} (right ordinate, ○) vs x from the data in Figure 1. See text for definitions.

Attempted Progressive Transmetalation of II with A (M = Co). Gel permeation chromatography (methylene chloride eluant) of the products of reaction of II with 2–4 mol of A (M = Co) in methylene chloride resulted in poor separation of a blue band, analyzed as $N_4Co_2Cl_4{\cdot}2H_2O$[22] from a mixture of $Cu(NS)_2$ and unidentified coproducts. This result is similar to those obtained with A and B (M = Zn)[18] and indicates that the anticipated transmetalated products VI–VIII (next section) are unstable if prepared by this route. We recommend the use of C for extensive, direct transmetalation of II with cobalt (see below).

Progressive Direct Transmetalation of II with C. We are pleased to report that the transmetalation of II (X = Cl) with 2, 3, and 4 mol of C gives tetranuclear molecules VI–VIII, respectively, each of which contains four ligands N (Table I). Products VI–VIII were easily separated from coproducts $Cu(NS)_2$ and N_2S_2 by gel permeation chromatography (methylene chloride eluant). The IR spectra of isolated solids VI–VIII exhibit a sharp, single band at 1635 cm^{-1}, indicating monodentate N.[10] Products VI–VIII all react with CO_2 (eq 7) to give solids containing carbonate,[20] indicating that they retain the μ-oxo groups of II.

We feel that the direct transmetalation of II by C to give a family of stable, tetranuclear products VI–VIII is due to reaction 5 as the last stage of each transmetalation step. This corresponds to replacement of copper(II) by *cobalt(III)*, which prevents the

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(17) Reasons for different rates and rate laws of transmetalation of copper(II) by A and B have been proposed: Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 1925, 3899.

(18) Davies, G.; El-Toukhy, A.; Veidis, M.; Onan, K. D. *Inorg. Chim. Acta* **1984**, *84*, 41.

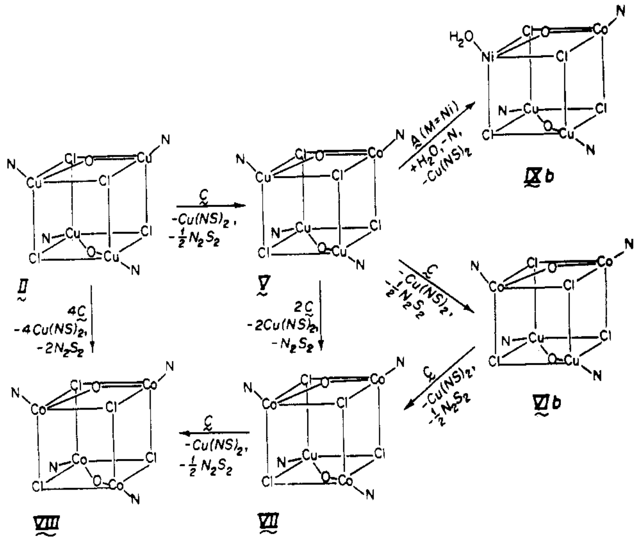
(19) A (M = Cu) is the principal absorber at 600 nm in the product mixtures from such spectrophotometric titrations.[10]

(20) Replacement of copper(II) with cobalt(II) generally gives water-sensitive products;[12,21] although freshly prepared μ-oxo products containing cobalt, nickel and zinc react with CO_2 to give products that contain carbonate, these products are much less stable[21] than those that contain only copper.[1,5-7,10,11] For example, for the monocarbonato derivative of XI the analysis is as follows. Anal. Calcd for $N_3CuCo_2Cl_4CO_3$: CO_3, 6.54. Found: CO_3, 4.1.

(21) (a) Davies, G.; El-Kady, N.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chim. Acta* **1985**, *104*, 131. (b) Davies, G.; El-Kady, N.; El-Sayed, M. A.; El-Toukhy, A.; Onan, K. D.; Shomaly, W., submitted for publication in *Inorg. Chim. Acta*.

(22) Anal. Calcd for $N_4Co_2Cl_4{\cdot}2H_2O$: Co, 11.5; Cl, 14.1. Found: Co, 10.64; Cl, 14.7. Dimers are much more difficult to separate from $Cu(NS)_2$ by gel permeation chromatography (methylene chloride eluant)[21a] than are trimers and tetramers.[1,2-4,10-12,15,21]

Scheme II



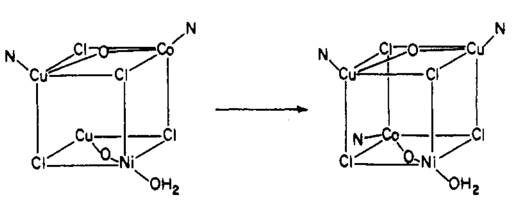
primary tetranuclear products from disproportionating before reduction of cobalt(III) to cobalt(II) by coordinated NS (eq 5).

Electronic Spectra of V–VIII. The electronic spectra of II and V–VIII are compared in Figure 1. Substitution of cobalt(II) for copper(II) in II results in a progressive decrease in molar absorptivities ϵ at 700 nm and longer wavelengths and the gradual appearance of spectral evidence for five-coordinate cobalt(II) near 600 nm. Plots of ϵ_{600} and ϵ_{850} vs x, where x is the number of cobalt atoms in a particular molecule, are linear to $x = 3$ and $x = 2$, respectively (Figure 2). Linear behavior of ϵ_{850} vs x in the family $(\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ has been shown from ESR measurements to correspond to the same local geometry of copper(II) throughout.[23] Figures 1 and 2 strongly suggest that the molecular geometries of V, VI, and possibly VII[24] (from ϵ_{600} linearity to $x = 3$, Figure 2) are largely dictated by the requirements of their copper(II) centers.

The electronic spectra of isomers Te_1 and Te_2 (Scheme I) are very different:[10,11] Te_2 is identified by its spectral similarity with II but with half the maximum molar absorptivity, while Te_1 has a single absorption maximum at 700 nm and no features at longer wavelengths. These differences are accounted for by the coordination of less than three chlorides per copper(II) center in Te_1.[1,10,11] Distinction of Te_1 and Te_2 is possible because nickel is essentially transparent in these ligand systems.[1,10,11]

The similarity of the 700–900-nm spectra of II and V–VII (Figure 1) and the linearity of ϵ_{850} vs x (Figure 2) suggest $NCuCl_3$ chromophores in II and V–VI (i.e. that VI is the analogue of Te_2); however, the absorptivity of VI ($\epsilon_{850} = 550 \pm 20$ M^{-1} cm^{-1}) is 75%, not 50%, of that of II, indicating that the absorptivity of $NCuCl_3$ chromophores is increased by cobalt(II). This confounds the assignment of the isomeric structure of VI from its electronic spectrum, although the evidence leans toward VI being the analogue of Te_2 (NCo replaces $(H_2O)Ni$ in Scheme I) for the following reasons.

We simultaneously transmetalated II with equimolar A (M = Ni) and C and isolated the tetranuclear product $(\mu\text{-O})_2N_3Cu_2CoNi(H_2O)Cl_4$ (IX) (Table I). If this product had isomeric structure IXa, we would expect it to isomerize spontaneously to IXb (eq 8) because (a) it has a $(H_2O)Ni\text{–O–}CuN$ unit in its bottom face and (b) IXb has an additional $NCuCl_3$ center.[1] However, product IX has a spectrum similar to that of II (with $\epsilon_{850,II} \approx 2\epsilon_{850,IX}$, Table I), and the spectra of IX and VI were invariant over long periods of time in methylene chloride, indicating no isomerization.[1] We thus conclude that progressive transmetalation of II by C gives the products in Scheme II, which is consistent with the data in Figures 1 and 2. Preferential formation of isomers Te_1 (Scheme I) and VIb and IXb (Scheme II) evidently is due to the trans-directing influence cobalt > Cu^{II} > Ni^{II} across μ-oxo groups, as found for transmetalation of $(\mu\text{-O})_2L_4Cu_4$ (L = 6-methyl-2-hydroxypyridinate) with $M(NS)_2$ reagents.[12]



IXa IXb (8)

The above transmetalation of II with A (M = Ni) and C was repeated in sequence as follows. First, II was treated with 1 mol of C, and reaction 9 was allowed to go to completion. The product

$$\text{II} + \text{C} \rightarrow \text{V} + Cu(NS)_2 + {}^1/_2N_2S_2 \quad (9)$$

solution was treated with 1 mol of A (M = Ni), and product IXb was isolated. Formation of product IXb from simultaneous or sequential transmetalation of II with equimolar C and A (M = Ni) indicates that II is first transmetalated by C and not by A (M = Ni): the tetranuclear product of eq 10 would react with

$$\text{II} + \text{A (M = Ni)} \rightarrow (\mu\text{-O})_2N_4Cu_3NiCl_4 + Cu(NS)_2 \quad (10)$$

C to give isomer IXa because of the trans-directing Cu > Ni.[10,11] If the simultaneous transmetalation of II with C and A (M = Ni) actually proceeds via eq 11–13, then the trans-directing order is

$$\text{II} + \text{C} \rightarrow (\mu\text{-O})_2N_3Cu_3Co^{III}(NS)Cl_4 + Cu(NS)_2 + N \quad (11)$$

$$(\mu\text{-O})_2N_3Cu_3Co^{III}(NS)Cl_4 + \text{A (M = Ni)} \rightarrow (\mu\text{-O})_2N_3Cu_2Co^{III}(NS)NiCl_4 + Cu(NS)_2 \quad (12)$$

$$(\mu\text{-O})_2N_3Cu_2Co^{III}(NS)NiCl_4 \rightarrow \text{IXb} + {}^1/_2N_2S_2 \quad (13)$$

(Co^{III}(NS), Co^{II}) > Cu > Ni in II. However, if the time course of eq 12 and 13 is reversed, eq 14 and 15, then we can only specify Co^{II} > Cu^{II} > Ni as the trans-effect order.

$$(\mu\text{-O})_2N_3Cu_3Co^{III}(NS)Cl_4 \xrightarrow{N} \text{V} + {}^1/_2N_2S_2 \quad (14)$$

$$\text{V} + \text{A (M = Ni)} \rightarrow \text{IXb} + Cu(NS)_2 + N \quad (15)$$

Transmetalation of III with A (M = Co). Transmetalation of III with A (M = Ni) is site selective and gives a family of six tetranuclear products $(\mu_4\text{-O},\mu\text{-O})N_mCu_{4-x}(Ni(H_2O))_xCl_4$[13] whose core structures can be distinguished because of the very low absorptivity of nickel and the negligible influence of nickel on the absorptivities of copper(II).[1] We had hoped to replicate the previous work[1] with A (M = Co) because absorption of cobalt(II) in the products might supplement spectral information on site-selective transmetalation of III from copper(II) absorption.[1] However, the reactions of III with 1–4 mol of A (M = Co) were unexpectedly slow, as indicated by spectrophotometric monitoring of coproduct $Cu(NS)_2$ formation. Gel permeation chromatography of final product solutions gave poor separation from $Cu(NS)_2$, suggesting that the transmetalated products are not stable tetranuclear species.[21a] Because of this poor separation, analytical data for cobalt-containing fractions were irreproducible, and transmetalation of III with A (M = Co) was therefore abandoned.

Transmetalation of III with C. In sharp contrast with the results of the previous section, we found that III is rapidly transmetalated by C in ambient methylene chloride and nitrobenzene and that the products X–XII (Table II) are easily separated from coproducts $Cu(NS)_2$ and N_2S_2 (eq 4 and 5) by gel permeation chromatography. The analytical and cryoscopic data for products X–XII in Table II indicate that they are trimers $N_3Cu_{3-x}Co_xCl_4O$ (x = 0–3) and not analogues of the tetranuclear family $N_3Cu_{4-x}(Ni(H_2O))_xCl_4O_2$ obtained from stepwise transmetalation of III with A (M = Ni).[1]

Spectral Properties of Trimers X–XII. The IR spectra of isolated solid trimers X–XII all exhibit sharp, single bands at 1635

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[23] Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 2269.

[24] Competitive domination of the structure of product VII by the local geometrical requirements of copper(II) and cobalt(II) is suggested by the nonisosbestic behavior of V–VII in Figure 1.

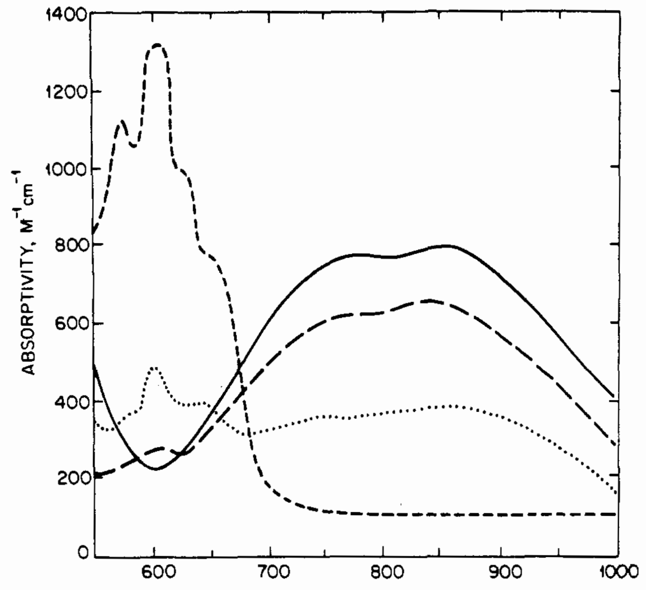
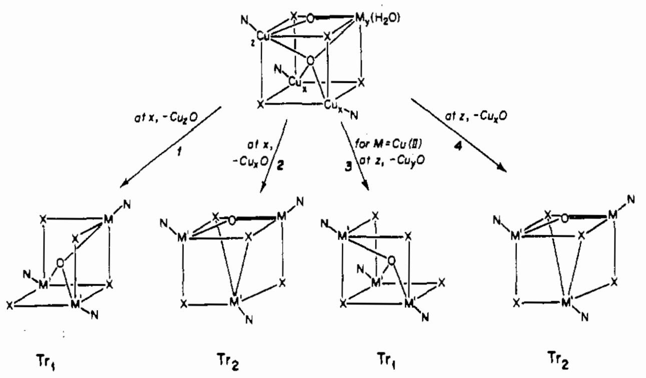


Figure 3. Electronic spectra of III (—), X (– –), XI (···), and XII (- -) in methylene chloride at 25 °C. See Table II, Scheme IV, and text.

Scheme III



cm^{-1}, indicating monodentate N.[23] The electronic spectra of III and X–XII in methylene chloride (Figure 3) exhibit (a) increasing absorptivity near 600 nm and (b) decreasing absorptivity at 700 nm and longer wavelengths on progressive replacement of copper(II) with cobalt(II).

The production of trimers with loss of a CuO unit in the reactions of III with C and in the transmetalations of IV (M = Co, Ni) with excess A (M = Co, Ni, Zn; Scheme I) or C[2-4] indicates that III is only a special case of IV with respect to its reaction with A (M = Ni), where no CuO loss occurs and the products are μ_4-, μ-oxo tetramers Te$_3$.[1] The reactions of III with A (M = Ni) are site selective, commencing at site Z of Scheme III and ending with the transmetalation of site Y by A (M = Ni).[1] Alternative site-selective transmetalations of structures IV with excess M'(NS)$_2$ that result in the loss of Cu$_x$O, Cu$_y$O, or Cu$_z$O are considered in Scheme III: for example, "at X, –Cu$_z$O" denotes (a) selective monotransmetalation at an X site of IV with concomitant loss of Cu$_z$O, followed by (b) transmetalation of the second X site by M'(NS)$_2$ to give a μ_3-oxo trimer Tr$_1$ (sequence 1). The retention of M of IV in the trimeric products N$_3$MM'$_2$X$_4$O[2-4] indicates that sequence 3 is only possible with M = Cu in Scheme III.

The conclusion of Scheme III is that μ_3-oxo trimers Tr$_1$ (from sequences 1 and 3) and μ-oxo trimers Tr$_2$ (from distinguishable sequences 2 and 4) are possible products of transmetalations of IV that result in CuO loss. Before turning to distinction of Tr$_1$ from Tr$_2$, we will describe two other methods of obtaining trimeric products N$_3$M$_3$X$_4$O from transmetalation reactions.

Trimers from Transmetalation of (μ_3-O)N$_3$Cu$_3$Cl$_4$ (XIV). We have recently discovered that transmetalation of (μ_4-O)N$_4$Cu$_4$Cl$_6$ (XIII)[10] with 1 mol of A (M = Hg) proceeds in aprotic solvents via eq 16.[15] Analytical and cryoscopic data for product XIV and

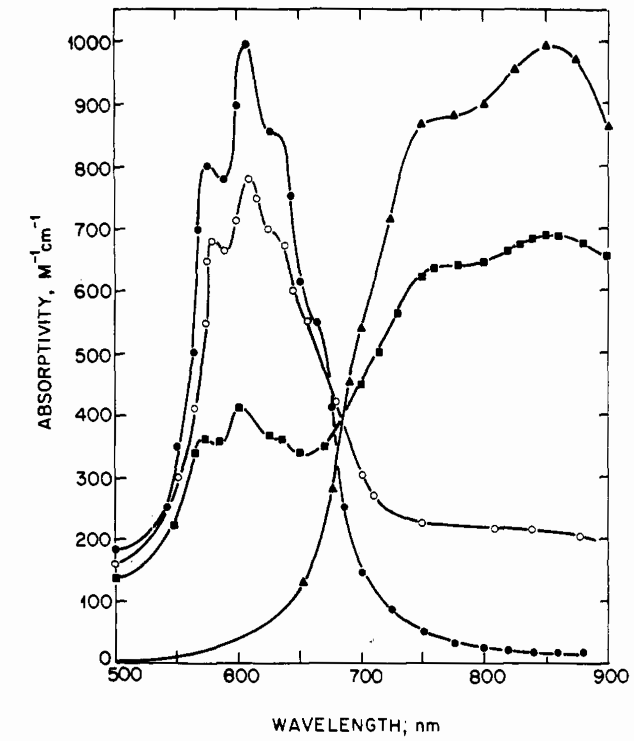


Figure 4. Electronic spectra of XIV (▲), XV (■), XVI (○), and XVII (●) in methylene chloride at 25 °C. See Table III for identification.

$$\underset{\text{XIII}}{\text{XIII}} + \text{A (M = Hg)} \rightarrow \underset{\text{XIV}}{(\mu_3\text{-O})N_3Cu_3Cl_4} + Cu(NS)_2{\cdot}HgCl_2 \qquad (16)$$

for the trimeric products XIV–XVII of its transmetalation by 1, 2, and 3 mol of C, respectively, are given in Table III. The electronic spectra of XIV–XVII, Figure 4, show the effects of progressive replacement of copper(II) in XIV with cobalt(II). The growth of cobalt(II) absorption at 600 nm on progressive transmetalation is very different in Figures 3 and 4, indicating different product core structures (see below).

Transmetalation of N$_3$Cu$_3$Co(NS)$_2$Cl$_4$ with 2 mol of A (M = Cu) Followed by in Situ Reaction with Dioxygen. We have previously reported that the title sequence gives 2 mol of Cu(NS)(s), 1 mol of N$_2$S$_2$, and the trimeric product N$_3$CoCu$_2$Cl$_4$O (XVIII).[4] We transmetalated product XVIII with 1 and 2 mol of C to give trimers N$_3$Co$_2$CuCl$_4$O (XIX) and N$_3$Co$_3$Cl$_4$O (XX), respectively. Analytical, cryoscopic, and spectral data for XVIII–XX are collected in Table IV, and their electronic spectra are shown in Figure 5.

Electronic Spectral Distinction of Trimeric Products. Trimeric products of transmetalation that contain cobalt(II) exhibit structured spectra centered near 600 nm (Figures 3–5). In Figure 6 we have plotted ϵ_{600} vs x, where x is the number of cobalt atoms in the general formula N$_3$Co$_x$(M,M')$_{3-x}$Cl$_4$O and M and M' are Co, Ni, Cu, or Zn. Each point is identified with a specific complex in the legend of Figure 6.

We have previously concluded that linear variations of ϵ_{600} vs x in the spectra of families N$_3$Co$_x$(M,M')$_{3-x}$Cl$_4$O, (M, M' = Co, Ni, Zn) are diagnostic of the same local geometry for cobalt(II) throughout.[25] The linear relationship of points 1–5 in Figure 6 strongly suggests that the complexes exhibiting the respective molar absorptivities have a common core structure that results in the same local geometry for cobalt(II). Since point 1 refers to (μ_3-O)N$_3$Cu$_3$Cl$_4$ (XVI) from eq 16,[15] we conclude that trimers responsible for data points 2–5 have a common core μ_3-oxo structure Tr$_1$ (Scheme III).

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(25) See Figure 3 of reference 4.

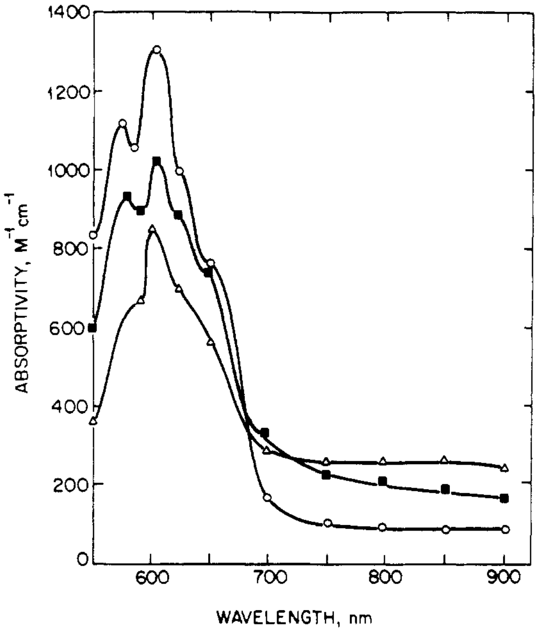


Figure 5. Electronic spectra of XVIII (△), XIX (■), and XX (○) in methylene chloride at 25 °C. See Table IV for identification.

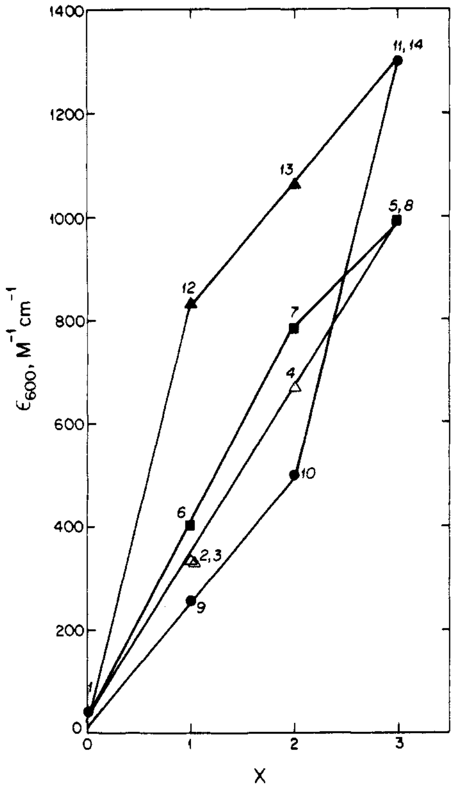
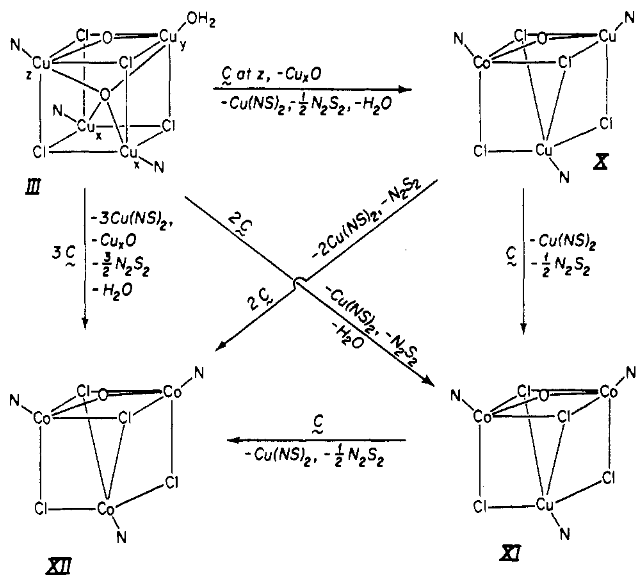


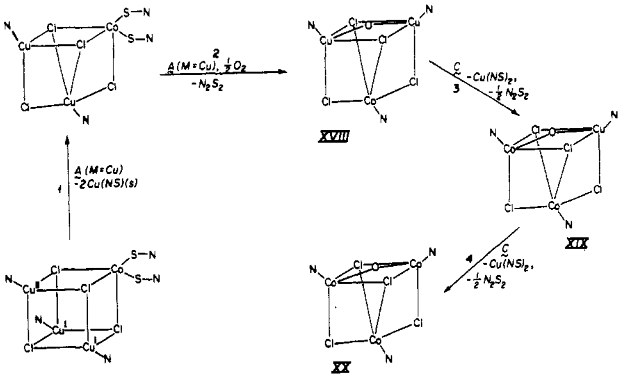
Figure 6. Plots of ϵ_{600} vs x in methylene chloride for the following complexes: 1, XIV; 2, $N_3CoNi_2Cl_4O$;[3] 3, $N_3CoNiZnCl_4O$;[4] 4, $N_3Co_2ZnCl_4O$;[4] 5, $N_3Co_3Cl_4O$;[2-4] 6, XV; 7, XVI; 8, XVII; 9, X; 10, XI; 11, XII; 12, XVIII; 13, XIX; 14, XX. See text for definitions.

Points 6–8 are ϵ_{600} for products XV–XVII of transmetalation of the (μ_3-oxo)copper(II) trimer XIV, eq 16, with 1, 2, and 3 mol of C.[15] The coincidence of points 5 and 8 and the linear relationship of points 1, 6, and 7 indicate that products XV–XVII also have core structure Tr_1. Points 1–8 are not colinear because M = copper(II) enhances the atomic absorptivity of cobalt(II) in (μ_3-O)$N_3CoM_2Cl_4$ (point 6) and (μ_3-O)$N_3Co_2MCl_4$ (point 7), while M = Ni and Zn (points 2–4) do not.

Scheme IV



Scheme V



Points 9–11 for products X–XII of transmetalation of III with 1, 2, and 3 mols of C (Table II) are not colinear with points 2–5 or 6–8. Products X–XII cannot have the μ_3-oxo core structure Tr_1 in Scheme III because (a) the presence of copper(II) obviously *reduces* the atomic absorptivity of cobalt(II) in X and XI and the molar absorptivity of product XII is too large for it to be (μ_3-O)$N_3Co_3Cl_4$ (XVII). The unusually high absorptivity of product XII (point 11 of Figure 6) is strong evidence that XII contains a cobalt(II) center coordinated to four halogens, as in the well-known, strongly absorbing species CoX_4^{2-}.[26] The relation between points 9 and 10 suggests that all the products of transmetalation of III by C have μ-oxo core structures Tr_2 (Scheme IV). The first stage of transmetalation is step 2 or 4 of Scheme III. We are inclined to favor step 4, since (a) progressive transmetalation of III by A (M = Ni) commences at site Z and ends at site Y^1 and (b) placement of the first cobalt at site Z would favor attack of C at site Y because of a trans effect across the μ-oxo bridge (see above and ref 12): this effect would be enhanced if the Co–O–Cu angle increased on loss of the restraining central μ_4-oxo group of III as Cu_xO (Scheme IV).

Finally, we propose that product XVIII of transmetalation of $N_3Cu_3Co(NS)_2Cl_4$ (Scheme I) with 2 mol of A (M = Cu) followed by in situ oxidation with dioxygen has the core structure shown in Scheme V.[27] The very high absorptivity of XVIII (point 12 of Figure 6) is strong evidence for the presence of a cobalt(II) center with four coordinated halogens (see discussion of product

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[26] Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M. *J. Am. Chem. Soc.* **1961**, *83*, 4690. Angell, C. A.; Gruen, D. M. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2243.

[27] See earlier discussion of the "curious" behavior of $N_3Cu_3Co(NS)_2Cl_4$ (Scheme I and eq 7 of ref 4) in its specific reaction with 2 mol of A (M = Cu).[4] The effects of A (M = Cu) in restraining intramolecular NS ligand transfer[2-4] in the product of step 1 (Scheme V) and in causing the formation of XVIII rather than the μ_3-oxo product isomer in step 2 are not understood at this time.

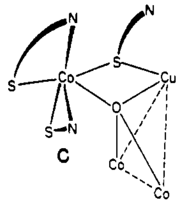
XII above and ref 26). The linear relationship of points 12, 13, and 14 in Figure 6 is consistent with the progressive transmetalation of equivalent copper(II) sites in XVIII by 1 and 2 mol of C. Parallelism of the lines for points 1, 9, and 10[28] and 12, 13, and 14 with points 11 and 14 coincident indicates that transmetalation of III by 1 mol of C (Scheme IV) and oxidation of the product of step 1 of Scheme V result in isomers, XIII and XVIII, respectively, of the same Tr_2 core structure. This is confirmed by the fact that products XII (Scheme IV) and XX (Scheme V) are identical.

Isomeric Trimers $N_3Cu_{3-x}Co_xCl_4O$. Complexes XIV–XVII are the four-membered Tr_1 family $(\mu_3\text{-O})N_3Cu_{3-x}Co_xCl_4$ (x = 0–3). Complexes X–XII and XVIII–XIX constitute five members of the Tr_2 family $(\mu\text{-O})N_3Cu_{3-x}Co_xCl_4$ (x = 0–3), which includes two isomeric pairs X, XVIII and XI, XIX. The missing member of the Tr_2 family is $(\mu\text{-O})N_3Cu_3Cl_4$, which we are currently attempting to synthesize.

We found that 1.0 mM solutions of the odd-electron trimers XI, XVI, and XIX (Tables II–IV) in methylene chloride at 25 °C have different ESR spectra. Trimer XI has an isotropic spectrum ($\langle g \rangle = 2.05$), while its μ_3-oxo isomer XVI is ESR-silent and its other isomer XIX exhibits a rhombic spectrum ($g_1 = 2.18$, $g_2 = 2.11$, $g_3 = 2.05$) under these conditions. The corresponding molecular magnetic moments measured by the Evans method[16] in 30% DMSO-d_6/D_2O are 4.51 ± 0.03, 5.12 ± 0.03, and 4.42 ± 0.04 μ_B, respectively, at 25 °C. Although the detailed origins of the different properties of Tr_1 and Tr_2 isomers are unknown, it is evident that room-temperature ESR and electronic spectra distinguish between them. We note that $(\mu_3\text{-O})N_3CuCo_2Cl_4$ (XVI) has a higher room-temperature magnetic moment than those of its Tr_2 isomers XI and XIX but that the latter are indistinguishable on this basis.

We found no spectral evidence for thermal interconversion of Tr_1 and Tr_2 complexes with x common or for isomerizations X $\rightleftarrows$ XVIII and XI $\rightleftarrows$ XIX. This indicates significant kinetic barriers for these respective processes and also supports spectral evidence for at least three halides per copper(II) center in all $N_3Cu_{3-x}Co_xCl_4O$ complexes[15] because formation of $NCuX_3$ units is the driving force for isomerizations in other systems.[1,10,11]

Also of great interest is the fact that Tr_1 and Tr_2 core structures do not interconvert when transmetalated by A or C. For example, reaction of $(\mu_3\text{-O})N_3Cu_2CoCl_4$ (XV) with 1 mol of C gives $(\mu_3\text{-O})N_3CuCo_2Cl_4$ (XVI) and not $(\mu\text{-O})N_3CuCo_2Cl_4$ (XI) or its isomer XIX. This suggests an associative, "S_N2" type of transmetalation mechanism in which the copper(II) being replaced and the cobalt(III) reactant are both bonded to an oxo group in the activated complex, perhaps as in the example shown here (ligands X in $(\mu_3\text{-O})CuM_2X_4$ have been omitted for clarity).



Opening one of the NS chelate rings to maintain six-coordination of cobalt(III) would promote NS transfer to copper(II) needed for coproduct $Cu(NS)_2$ formation. Preassociation of copper(II) with carbothioate S as illustrated above follows our earlier suggestions,[17] in particular that formation of the four-membered $\overline{\text{Co–S–Cu–O}}$ ring would facilitate transmetalation. We shall test this proposal in future kinetic work.

Acknowledgment. Support in the form of Grants RR07143 from the Department of Health and Human Services and INT-8512210 from the National Science Foundation is gratefully acknowledged. M.A.E.-S. and A.E.-T. are grateful to Alexandria University for study leave to collaborate on this project. We sincerely thank Dr. Arthur Heiss (Bruker Instruments, Inc.) and Adel Moussa for assistance with the ESR and magnetic moment measurements, respectively.

Registry No. II, 80105-85-7; III, 102109-38-6; V, 114058-49-0; VIb, 114058-50-3; VII, 114058-51-4; VIII, 114058-52-5; IXb, 114058-53-6; X, 114058-54-7; XI, 114058-55-8; XII, 114155-43-0; XIV, 114058-56-9; XV, 114130-27-7; XVI, 114130-26-6; XVII, 114058-57-0; XVIII, 114058-58-1; XIX, 114058-59-2; A (M = Cu), 34156-34-8; A (M = Co), 54166-06-2; C, 72043-56-2; $(\mu_4\text{-O})N_4Cu_4Cl_6$, 90741-95-0; $Hg(NS)_2$, 72871-79-5; $N_3Cu_3Co(NS)_2Cl_4$, 102211-27-8; $N_4Co_2Cl_4{\cdot}2H_2O$, 102211-29-0; CO_2, 124-38-9.

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(28) Points 1 and 9 and points 1 and 12 should not be joined in Figure 6 because point 1 refers to a Tr_1 core structure and points 9 and 12 refer to Tr_2 core structures, respectively. The data in Figure 6 serve to indicate that Tr_1 and Tr_2 core structures containing only copper(II) can not be distinguished by absorptivity measurements at 600 nm, where absorption minima are observed for copper(II).[1,5-7,10,11,23] However, Tr_1 and Tr_2 core structures are distinguishable on introduction of cobalt(II) (Figures 3–6).