

Limits of Direct Transmetalation of Polynuclear Copper(II) Complexes with $M(NS)_n$ Reagents. Scissor Transmetalators. Synthesis and Properties of the Trimers $(\mu_3-O)(N,py)_3Cu_3X_4$ ($N = N,N$ -Diethylnicotinamide; $py =$ Pyridine, $X = Cl, Br$)

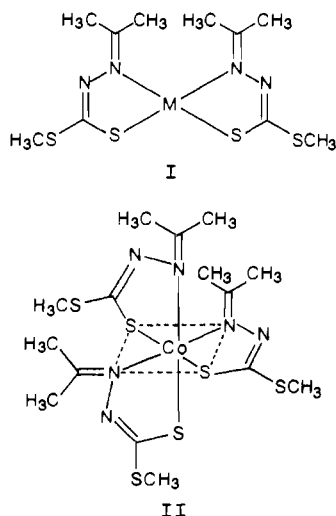
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The practical limit of direct, stoichiometric transmetalation of the tetranuclear copper(II) complexes $(\mu_4-O)(N,py)_4Cu_4Cl_6$ (IIIa,c) with $M(NS)_2$ and $Co(NS)_3$ reagents to give the heterotetranuclear products $(\mu_4-O)(N,py)_4(Co,Ni,Cu,Zn)_4Cl_6$ (IV) is reagent-dependent. Here, N is monodentate *N,N*-diethylnicotinamide (DENC), py is pyridine, M is Co, Ni, Zn, Cd, Hg, or Sn, and NS is *S*-methyl isopropylidenehydrazinecarbodithioate. Products IV prepared with $Co(NS)_2$ and $Zn(NS)_2$ are unstable if they contain more than two cobalt(II) or zinc centers, and even monotransmetalated tetramers containing Cd, Hg, and Sn are unstable. In contrast, the complete tetranuclear families $(N,py)_4Cu_{4-x}M_xCl_6$ ($x = 0-4$; $M = Co^{II}, Ni$) are obtained from stoichiometric reactions of IIIa and IIIc with 0-4 mol of the reagents $Co(NS)_3$ and $Ni(NS)_2$, respectively. All 19 reported complexes $(N,py)_4(Co,Ni,Cu,Zn)_4X_6O$ appear to have a (μ_4-oxo) metal core structure. Five-coordinate cobalt(II) and copper(II) centers are assigned to the majority from spectral measurements; six-coordinate cobalt(II) is assigned for monocobalt species. Reactions of IIIa, IIIc, and $(\mu_4-O)N_4Cu_4Br_6$ (IIIb) with equimolar amounts of $Cd(NS)_2$, $Hg(NS)_2$, and $Sn(NS)_2$ proceed stoichiometrically as follows to give the new oxotrimers V: $III + (Cd,Hg,Sn)(NS)_2 \rightarrow (\mu_3-O)(N,py)_3Cu_3X_4$ (V) + $N(Cd,Hg,Sn)X_2Cu(NS)_2$. These $M(NS)_2$ reagents are called scissor transmetalators. The kinetics of the reaction of excess IIIa with $Hg(NS)_2$ are consistent with rate-determining monotransmetalation of copper(II) by mercury. The instability of monotransmetalated products $(\mu_4-O)(N,py)_4Cu_3MX_6$ ($M = Cd, Hg, Sn$) is attributed to the disparately large size of M. Spectral and other properties of tetranuclear III and trimeric V are compared. The spectra of V, 12 of their transmetalated derivatives $(N,py)_3(Co,Ni,Cu,Zn)_3Cl_6O$ (VII), and oxometal trimers from other transmetalation systems indicate a common (μ_3-oxo) metal core structure. Products VII containing one Cd, Hg, or Sn or three Zn atoms are unstable, which also indicates closely similar core structures for III and V. ESR measurements show that the copper(II) centers of $(\mu_3-O)Cu_{3-x}M_xCl_4$ complexes ($x = 0-2$; $M = Co, Zn$) are sensitive to the identity of M.

Introduction

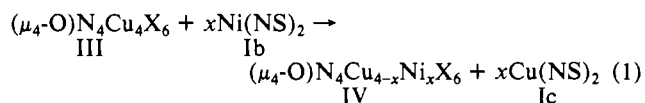
Transmetalation of neutral polynuclear copper(I) and copper(II) complexes with $M(NS)_n$ reagents is an excellent, quantitative source of many new polymetallic molecules, including examples containing two oxidation states of copper¹⁻³ and up to four different metals.⁴ Here, NS has most often been the monoanionic Schiff base ligand *S*-methyl isopropylidenehydrazinecarbodithioate, with $M = Co, Ni, Cu, Zn$ in $M(NS)_2$ complexes Ia-d or in $Co(NS)_3$ (II).^{2,3,6} Specific heteropolymetallic products result



from reactant-dependent transmetalation patterns;¹⁻¹² reactions with transmetalators containing different metals often can be conducted simultaneously to give predictable mixed-metal products,³ and the transmetalation phenomenon is not restricted to polynuclear copper targets.³ Transmetalation systems are im-

pressive in the number and variety of specific new molecules that they are easily capable of generating.¹⁻¹²

Equation 1 summarizes a series of quantitative transmetalation reactions. Here, N is monodentate *N,N*-diethylnicotinamide



(DENC), X is Cl or Br, and x is 1, 2, 3, or 4.^{5,7-10} Each replacement of copper(II) in III is quantitative because of the high stability of the coproduct $Cu(NS)_2$ (Ic)⁷ and is *direct* because all

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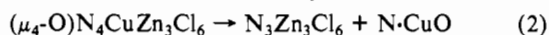
Table I. Analytical, Cryoscopic, and Electronic Spectral Data for Transmetalation Reactants

symbol	complex	anal., ^a %						M_r^b	λ_{max}, nm^c ($\epsilon_\lambda, M^{-1}\cdot cm^{-1}$)
		C	H	N	X or S	Cu	M		
Ie	Cd(NS) ₂	27.1 (27.6)	3.8 (4.1)	13.3 (12.9)	29.1 (29.4)		25.2 (25.8)	400 ± 20 (434)	d
If	Hg(NS) ₂	24.2 (24.5)	3.1 (3.4)	11.0 (10.7)	24.2 (24.5)		38.1 (38.4)	495 ± 20 (522)	d
Ig	Sn(NS) ₂	27.5 (27.2)	3.7 (4.1)	12.2 (12.7)	28.2 (29.0)		26.2 (27.0)	e	d
IIIa	(μ_4 -O)N ₄ Cu ₄ Cl ₆	29.9 (40.1)	4.5 (4.7)	9.2 (9.4)	17.7 (17.8)	20.9 (21.3)		1180 ± 20 (1196)	850 (1630), 775 (1400)
IIIb	(μ_4 -O)N ₄ Cu ₄ Br ₆	32.7 (32.8)	3.7 (3.9)	7.5 (7.7)	32.7 (32.8)	17.6 (17.5)		1420 ± 50 (1462)	850 (2200), 775 (1930)
IIIc	(μ_4 -O)(py) ₄ Cu ₄ Cl ₆	30.6 (30.0)	2.3 (2.5)	7.5 (7.0)	25.8 (26.5)	31.5 (31.8)		820 ± 20 (799)	850 (1400), 775 (1260)

^aCalculated values in parentheses. ^bIn nitrobenzene at the (3–5) × 10⁻² m level. ^cIn methylene chloride. ^dNo absorbance in the visible region. ^eNot sufficiently soluble in nitrobenzene for accurate measurements.

eight members of the product family IV are tetranuclear and stable.¹⁰

Direct transmetalation of a fixed polynuclear target with reagents containing different metals is a powerful means of generating large numbers of related new molecules. For example, 35 different tetranuclear molecules can, in principle, be obtained by sequential or simultaneous direct transmetalation of III (N, X fixed) and its (μ_4 -O)N₄(Cu,Co,Ni,Zn)₄X₆ homologues with reagents Ia,b,d and II in eq 1.¹⁴ Twelve such molecules are described in this paper. The practical number is reduced if any molecules disproportionate, for example via eq 2, before they can be isolated or further transmetalated by I or II.^{13,15}

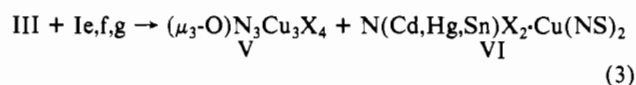


Disproportionation via intramolecular NS ligand transfer is commonly observed on progressive transmetalation of tetranuclear copper(I) complexes with M(NS)_n reagents.^{1–4,12a} In contrast, many total transmetalations of tetranuclear copper(II) complexes by excess nickel reagent Ib are direct. Examples are eq 1^{7,8,10} and the total transmetalations of (μ -O)₂L₄Cu₄ (L = 6-methyl-2-hydroxypyridinate)^{4,12a} and (μ_4 -O, μ -O)N₃Cu₃Cu(H₂O)Cl₄.¹¹ Others are direct but stop at a particular point, as in the transmetalations of (μ -O)₂N₄Cu₄X₄ complexes to give Cu₂Ni₂-containing products.^{7,8} Others are not direct, as in transmetalations of (μ_4 -O, μ -O)N₃Cu₃M(H₂O)X₄ targets (M = Co, Ni, Zn), which extrude CuO at the first step.^{1–3,6,16} Transmetalation patterns are thus target specific. Transmetalator specificity is the focus of this paper.

Reagents III (eq 1) are particularly appropriate targets for studies of transmetalator specificity. Their structures are known to contain equivalent copper sites,^{5,7,9,10,17} which eliminates the complication of site-selective transmetalation.^{4,6–8,11} The appearance of III as crystalline disproportionation products of the attempted crystallization of many different heteropolynuclear dioxo molecules containing copper^{1–3,5–12} suggests inherent stability that should favor direct transmetalation of III.

We report here that transmetalation of (μ_4 -O)N₄Cu₄Cl₆ (IIIa) by reagents Ia and Id is direct only for x ≤ 2 in eq 1, whereas every step of transmetalation of IIIa and (μ_4 -O)(py)₄Cu₄Cl₆ (IIIc) by II is direct. The electronic spectra of the tetranuclear products IV containing cobalt, nickel, copper, and zinc suggest a common core structure. We also report for the first time that the size of M in the monotransmetalated products (μ_4 -O)(N,py)₄Cu₃MX₆ is important in determining their stability. Thus, eq 3 is a

quantitative source of the new trimers V. The properties of III and V are compared, and the characteristics of the transmetalation of V with reagents I and II are discussed.



Experimental Section

Materials. Purification procedures for methylene chloride and nitrobenzene have been described.⁷ The tetranuclear oxocopper(II) reactants (μ_4 -O)N₄Cu₄X₆ (N = DENC, X = Cl (IIIa), Br (IIIb)) and (μ_4 -O)(py)₄Cu₄Cl₆ (py = pyridine; IIIc) were prepared and purified by the literature method.¹⁸ Transmetalators I were obtained by reacting S-methyl isopropylidenehydrazinecarbodi-thioate (HNS; 50 mmol) with the respective metal acetate (25 mmol) in ethanol. The reactions with M = Cd, Hg¹⁹ proceed rapidly at room temperature, whereas those with M = Co, Ni, Cu, Zn,²⁰ Sn require heating at reflux for 30 min. The reaction with M = Co must be conducted under dinitrogen because the microcrystalline product Co(NS)₂ (Ia) is air-sensitive.^{1–3} The transmetalator mer-Co(NS)₃ (II) was prepared by reacting cobalt(II) acetate with a 3-fold molar excess of HNS in dioxygen-saturated, refluxing ethanol.²¹ The crude M(NS)_n products were washed with ethanol and recrystallized from chloroform–light petroleum ether. Analytical data for products Ie–g are given in Table I. N,N,N',N'-Tetraethylethylenediamine (TEED, Alfa) was vacuum distilled immediately before use in spectrophotometric titrations employing standard techniques.^{7,11}

Transmetalation Procedures. General Observations. Most of our previous transmetalation work has been conducted in anhydrous methylene chloride under dinitrogen. Neutral reactants of the type being considered here are very soluble in this solvent, and the transmetalation reactions are rapid:^{5,9} gel permeation chromatography (BioBeads SX-12 resin, methylene chloride eluant, positive dinitrogen pressure)⁷ separates the desired polynuclear transmetalation products from monomeric coproducts M(NS)₂; the degree of separation is an excellent early indicator of product molecularity. The solvent is easily removed by vacuum evaporation of the respective bands. Water is often coordinated by the new metal centers during this total isolation procedure.^{7,9} Another approach in cases where the transmetalated products are unstable to chromatographic separation is to complete the transmetalation reaction in anhydrous nitrobenzene under dinitrogen, pour the product mixture into a 3-fold volumetric excess of anhydrous hexane, and stir the resulting mixture at room temperature overnight under dinitrogen. We have found that this latter procedure gives 65–95% yields of solid, polynuclear transmetalation products that are not contaminated with coproducts such as Cu(NS)₂ (Ic). We verified that the nitrobenzene–hexane procedure gives exactly the same products as chromatographic separation where the latter does not result in product decomposition. Inherently unstable

(14) Because of stability differences, Ic > Ib > Ia > II > Id³, a given molecule can be obtained from different targets. The theoretical total includes the two enantiomers of (μ_4 -O)N₄CuCoNiZnX₆. See Appendix for complete list.

(15) The reactant of eq 2 is not a stable, tetranuclear species (see text).

(16) Extrusion of CuO also is observed in reactions of (μ_4 -O, μ -O)N₃Cu₃M(H₂O)X₄ complexes with excess Ia, Ic, and II.^{1–3,6}

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tetranuclear products could be isolated by neither procedure.

Transmetalation of Tetranuclear Copper(II) Complexes III with M(NS)_n Reagents (Eq 1 and 3). Reactions 1 with M(NS)_n reagents Ia, d-g and II replacing Ni(NS)₂ (Ib) at x = 1-4 were conducted in methylene chloride or nitrobenzene at room temperature under dinitrogen. Analytical data for the stable, isolated tetranuclear products IV (eq 1) and trinuclear products V (eq 3) are given in Table II.

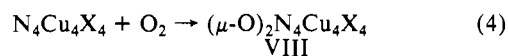
Transmetalation of Trinuclear Copper(II) Complexes V with M(NS)_n Reagents. The title reactions were conducted with x molar equiv of the respective M(NS)_n reagents, and the desired trinuclear transmetalation products VII were isolated as described above. Analytical data for stable examples of VII are given in Table II.

Analytical Methods. Metal analyses of all the reactants and products of this study were made with a computer-controlled Leeman Laboratories inductively coupled plasma spectrometer after standard sample preparation.^{7,11} Analytical wavelengths (nm) and detection limits (ng·mL⁻¹) for Cu, Co, Ni, and Zn have been given previously;³ the corresponding parameters for Cd, Hg, and Sn were 233.1 nm (6 ng·mL⁻¹), 244.4 (5), and 314.7 (8), respectively. Halides were determined by a literature procedure,²² and C, H, N, and S analyses were performed by Microchem Laboratories, Lowell, MA, or the Microanalysis Department, Cairo University, Cairo, Egypt. The molecular weights, M_r, of all neutral reactants and transmetalation products were determined by cryoscopy in nitrobenzene (mp 5.70 °C, K_f = 7.00 °C·m⁻¹).⁷ Cryoscopic data are included in Tables I and II.

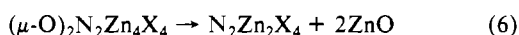
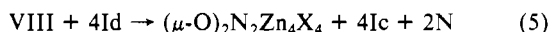
Physical Measurements. Instruments and procedures for obtaining electronic, ESR, and KBr-disk IR spectra have been described previously,¹⁻¹¹ as have procedures for spectrophotometric titrations with TEED and HNS.^{3,7,8} The kinetics of the reactions of IIIa with II in nitrobenzene were monitored in a computer-assisted stopped-flow apparatus.⁵ Monotransmetalation of IIIa was assured by maintaining at least a 10-fold excess of IIIa in all cases, as described previously.^{5,9}

Results and Discussion

The transmetalation phenomenon was discovered¹³ in attempts to use Zn(NS)₂ (Id) to measure the basicities of the μ-oxo groups of copper(II) products VIII (N = DENC, ethylnicotinate) from eq 4.²³ We instead found stoichiometric replacement of copper



by zinc. However, the presumed tetranuclear products of eq 5 are inherently unstable (eq 6).¹³ Later work showed that VIII

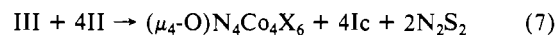


reacts with excess reagents Ib and II to give tetranuclear products of Cu₂Ni₂^{7,8,11} and Co^{II}₄⁶ metal stoichiometries, respectively, with retention of the core structure of VIII. All these *direct*^{7,11} transmetalations are driven by the high relative stability of the copper(II) coproduct Ic.^{3,7} However, complete transmetalations of VIII by excess Ia⁶ and Id (eq 5 and 6)¹³ are not direct and the question is "Why?". There are several reasons for using the μ₄-oxo complexes III instead of other transmetalation targets to seek an answer.

The complexes (μ₄-O)(py)_mCu₄X₄O (m = 3, 4)²³ and their transmetalated forms^{7,11} disproportionate on attempted isolation. Crystalline IIIc (Table I) is one of the disproportionation products. Complexes IIIa and IIIb often result from the attempted crystallization of VIII,²³ their dicarbonato derivatives²³ or transmetalated derivatives containing copper.^{7,8,11} This suggests that structures III have special stability, which should favor higher limits of direct transmetalation with a given reagent, as demonstrated by eq 1. Trans effects across μ-oxo bridges that affect the steric course of limited transmetalations of VIII and their carbonato derivatives⁶⁻⁸ and of complete transmetalations of (μ-O)₂L₄Cu₄ (L = 6-methyl-2-hydroxypyridinate)⁴ complicate establishment of the origins of limits to direct transmetalation. Such trans effects are irrelevant for III since all the transmetalation sites are equivalent.^{5,7-11,17,18}

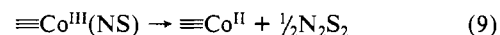
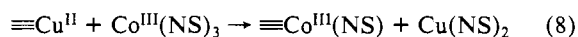
Direct Transmetalation of IIIa with Cobalt(II) Transmetalator Ia. We have already demonstrated direct monotransmetalations of IIIa and IIIb (Table I) with equimolar Ia.⁵ The product IVb (Table II) was easily isolated from the rapid reaction of IIIa with 2 mol of Ia in methylene chloride or nitrobenzene. Spectrophotometric titrations of IIIa with Ia at 600 nm²⁴ established the overall stoichiometry Δ(Ia)/Δ(IIIa) = 4.0 ± 0.1, but the reactions of IIIa with 3 and 4 mol of Ia were unexpectedly slow, and the isolated products were not tetranuclear.²⁵ It is evident that (μ₄-O)₄CuCo₃Cl₆ is formed and disproportionates to products of lower molecularity at comparable rates, as found for the transmetalation of VIII by Ia.⁶ The practical limit of direct transmetalation of IIIa by Ia is x = 2 in (μ₄-O)₄Cu_{4-x}Co_xCl₆; the products are IVa and IVb (Table II).

Direct Transmetalation of IIIa and IIIc with Cobalt(III) Transmetalator II. The stoichiometry Δ(II)/Δ(III) = 4.0 ± 0.1, corresponding to eq 7 (N = DENC, py) was established for the title reactions by spectrophotometric titration. The reactions of



IIIa and IIIc with 1, 2, 3, and 4 mol of II were all rapid and direct. Analytical data for the respective tetranuclear products IVa-d and IVm-p are given in Table II.

Transmetalations of VIII by II are also rapid, stoichiometric, and direct.⁶ We feel that tetranuclear products result in all cases because (a) II is less thermodynamically stable than Ia,³ leading to higher transmetalation rates with II, and (b) reaction 9 is the last step of transmetalation of copper(II) by II. Higher rates and the presence of ≡Co^{III}(NS) centers (rather than ≡Co^{II} from transmetalation by Ia) evidently prevent disproportionation of derivatives of III containing more than two cobalt centers.



Direct Transmetalation of III with Zinc Transmetalator Id. We have already demonstrated direct monotransmetalation of IIIa and IIIb by equimolar amounts of Id.⁵ The tetranuclear product IVj (Table II) was easily isolated from the reaction of IIIa with 2 mol of Id. Spectrophotometric titrations of IIIa with Id at 600 nm indicated the overall stoichiometry Δ(Id)/Δ(IIIa) = 4.0 ± 0.1, consistent with complete replacement of copper(II) in IIIa with zinc.¹³ An isosbestic point was observed at 744 nm. However, fast reactions of IIIa with 3 and 4 mol of Id did not give tetranuclear products,²⁵ as found for the cobalt(II) reactant Ia (see above). The practical limit of the title reactions is thus x ≤ 2 in the products (μ₄-O)₄Cu_{4-x}Zn_xCl₆.

We suggested above that one of the reasons that extensive direct transmetalations of III by Ia fail is comparable rates of transmetalation of (μ₄-O)₄Cu₂Co₂X₆ and disproportionation of the products. This cannot be the case for the zinc transmetalator Id, which reacts very rapidly⁵ and completely with IIIa, as expected from the stability order Ic > Ia > II > Id.³ The fact that no tetranuclear copper(II) complex has ever been completely transmetalated by zinc to give a stable tetranuclear product suggests that the d¹⁰ electron configuration of zinc is responsible: the transmetalated products simply are too electron rich,¹³ even when the core has a μ₄-oxo structure of special stability.

To test this hypothesis further, we reacted IIIa with 4 mol of II in methylene chloride and then treated the product (μ₄-O)₄Co₄Cl₆ (IVd) in situ with 3 mol of Id (eq 10-12) in an

(24) Coproduct Ic is the principal absorber at 600 nm in the product mixtures from such spectrophotometric titrations.⁷

(25) The ability of gel permeation chromatography to separate coproduct Ic from other transmetalation products decreases in the order tetramers > trimers > dimers.⁶ We have a great deal of experience in recognizing tetranuclear transmetalation products from their chromatographic behavior. We have made no attempt in the present work to determine the nature of disproportionation reactions that prevent direct transmetalation by particular reagents under typical conditions,¹⁻¹² and product analytical data are only presented to demonstrate the practical limits of direct transmetalation of III.

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Table II. Analytical, Cryoscopic, and Electronic Spectral Data for Products of the Transmetalation of III and V with I and II

symbol	complex ^{b,c}	anal., ^a %								M_r^d	λ_{max} , nm (ϵ_λ , M ⁻¹ ·cm ⁻¹)
		C	H	N	Cl	Cu	Co	Ni	Zn		
IVa ^e	N ₄ Cu ₃ CoCl ₆ O·H ₂ O	39.2 (39.7)	4.3 (4.8)	9.1 (9.3)	16.8 (17.6)	14.9 (15.8)	4.3 (4.9)			1190 ± 20 (1209)	850 (1300), 775 (1200)
IVb ^e	N ₄ Cu ₂ Co ₂ Cl ₆ O	39.4 (40.5)	4.4 (4.7)	9.0 (9.4)	16.7 (17.8)	9.5 (10.7)	9.3 (9.9)			1180 ± 20 (1186)	850 (600), 775 (630), 650 (775), 630 (800), 600 (990), 575 (995)
IVc	N ₄ CuCo ₃ Cl ₆ O	38.2 (40.6)	4.2 (4.7)	8.9 (9.5)	16.1 (17.9)	4.8 (5.3)	12.9 (14.9)			1180 ± 20 (1181)	875 (450), 675 (1000), 650 (1200), 600 (1390), 575 (1380)
IVd	N ₄ Co ₄ Cl ₆ O	39.9 (40.8)	4.3 (4.8)	8.9 (9.5)	16.4 (18.0)		19.5 (20.1)			1140 ± 20 (1176)	650 (1100), 630 (1380), 600 (1750), 575 (1380)
IVe ^f	N ₄ Cu ₃ NiCl ₆ O·H ₂ O	40.0 (39.7)	4.9 (4.8)	8.9 (9.3)		16.3 (15.8)		4.6 (5.0)		1240 ± 20 (1208)	850 (1160), 775 (1030)
IVf ^f	N ₄ Cu ₂ Ni ₂ Cl ₆ O·2H ₂ O	36.6 (39.4)	4.6 (4.9)	8.7 (9.2)		11.0 (10.4)		10.2 (9.6)		1250 ± 20 (1223)	850 (840), 775 (740)
IVg ^f	N ₄ CuNi ₃ Cl ₆ O·3H ₂ O	36.5 (38.9)	4.7 (5.1)	8.7 (9.1)		5.5 (5.1)		15.1 (14.3)		1260 ± 20 (1236)	840 (360), 770 (340)
IVh ^f	N ₄ Ni ₄ Cl ₆ O·4H ₂ O	37.8 (38.5)	5.1 (5.2)	8.7 (9.0)				18.5 (18.8)		1270 ± 20 (1249)	g
IVi	N ₄ Cu ₃ ZnCl ₆ O·H ₂ O	38.9 (39.6)	4.4 (4.7)	9.2 (9.2)		16.2 (15.7)			4.1 (5.4)	1240 ± 20 (1215)	850 (1130), 775 (1020)
IVj	N ₄ Cu ₂ Zn ₂ Cl ₆ O·2H ₂ O	38.1 (38.9)	4.2 (4.7)	9.7 (9.1)	18.0 (17.2)	11.2 (10.3)			11.5 (10.5)	1200 ± 20 (1235)	850 (560), 775 (525)
IVk	N ₄ Co ₂ Ni ₂ Cl ₆ O·2H ₂ O				18.2 (17.5)		9.4 (9.8)	9.1 (9.6)		1194 ± 20 (1210)	650 (590), 630 (665), 610 (831), 575 (600)
IVl	N ₄ CuCoNiZnCl ₆ O· 2H ₂ O	38.7 (39.1)	4.4 (5.1)	8.8 (9.1)	16.1 (17.1)	4.3 (5.1)	4.3 (4.7)	3.7 (4.7)	5.0 (5.2)	1210 ± 20 (1227)	860 (390), 775 (345), 630 (360), 610 (420), 575 (395)
IVm	(py) ₄ Cu ₃ CoCl ₆ O·H ₂ O	29.1 (29.5)	2.3 (2.7)	7.4 (6.9)	26.9 (26.1)	24.0 (23.4)	6.9 (7.3)			820 ± 20 (799)	850 (980), 775 (890)
IVn	(py) ₄ Cu ₂ Co ₂ Cl ₆ O	29.2 (29.7)	2.2 (2.7)	7.6 (6.9)	25.6 (26.2)	15.1 (15.7)	15.2 (14.6)			835 ± 20 (809)	850 (600), 775 (550), 630 (780), 610 (800), 575 (740)
IVo	(py) ₄ CuCo ₃ Cl ₆ O	30.3 (29.8)	2.3 (2.7)	7.7 (7.0)	27.0 (26.4)	7.1 (7.9)	21.5 (22.0)			830 ± 20 (805)	850 (240), 775 (250), 630 (1140), 610 (1100), 575 (980)
IVp	(py) ₄ Co ₄ Cl ₆ O	30.5 (29.9)	3.0 (2.7)	7.4 (7.0)	26.0 (26.5)		30.1 (29.5)			830 ± 20 (801)	630 (1620), 610 (1640), 575 (1340)
Va	N ₃ Cu ₃ Cl ₄ O	40.4 (40.7)	4.7 (4.8)	9.4 (9.7)	16.5 (16.1)	21.2 (21.6)				900 ± 20 (883)	850 (990), 775 (880)
Vb	N ₃ Cu ₃ Br ₄ O	34.2 (33.9)	4.4 (4.0)	8.4 (7.9)	31.1 (30.2)	18.8 (18.0)				1040 ± 20 (1061)	850 (1460), 775 (1260)
Vc	(py) ₃ Cu ₃ Cl ₄ O	29.8 (30.7)	2.7 (2.6)	6.9 (6.2)	23.7 (24.3)	31.8 (32.5)				610 ± 20 (586)	850 (870), 775 (790)
VIIa	N ₃ Cu ₂ CoCl ₄ O	39.6 (40.0)	4.7 (4.8)	9.3 (9.6)	16.2 (16.0)	13.7 (14.4)	6.2 (6.7)			900 ± 20 (878)	850 (690), 775 (640), 630 (365), 610 (410), 575 (360)
VIIb	N ₃ CuCo ₂ Cl ₄ O	39.1 (41.1)	4.9 (4.8)	9.1 (9.6)	16.7 (16.2)	6.7 (7.3)	12.8 (13.4)			900 ± 20 (874)	850 (260), 775 (220), 630 (700), 610 (780), 575 (680)
VIIc	N ₃ Co ₃ Cl ₄ O	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), 575 (800)
VIIId	N ₃ Cu ₂ NiCl ₄ O·H ₂ O	40.3 (40.1)	4.7 (4.9)	9.1 (9.4)	15.2 (15.8)	14.9 (14.2)		7.1 (6.6)		880 ± 20 (896)	850 (670), 775 (620)
VIIe	N ₃ CuNi ₂ Cl ₄ O·2H ₂ O	39.2 (39.6)	4.8 (5.1)	9.0 (9.2)	16.0 (15.6)	6.1 (6.9)		13.4 (12.9)		950 ± 20 (910)	850 (230), 775 (230)
VIIIf	N ₃ Ni ₃ Cl ₄ O·3H ₂ O	39.3 (39.0)	5.4 (5.2)	9.3 (9.1)	15.9 (15.4)			18.7 (19.1)		h (923)	g
VIIg	N ₃ Cu ₂ ZnCl ₄ O·H ₂ O	39.1 (39.9)	4.4 (4.9)	8.9 (9.3)	16.2 (15.7)	13.4 (14.1)			6.2 (7.2)	890 ± 20 (923)	850 (620), 775 (580)
VIIh	N ₃ CuZn ₂ Cl ₄ O·2H ₂ O	38.4 (39.0)	4.6 (5.0)	8.8 (9.1)	15.9 (15.4)	6.3 (6.9)			12.8 (14.1)	h (923)	850 (170), 775 (175)
VIIi	N ₃ CoNiZnCl ₄ O· 2H ₂ O	38.9 (38.0)	5.6 (4.9)	7.8 (8.9)	16.3 (15.0)		7.1 (6.2)	5.4 (6.1)	6.0 (6.9)	h (947)	630 (290), 610 (330), 575 (285)
VIIj	(py) ₃ Cu ₂ CoCl ₄ O	29.5 (31.0)	2.9 (2.5)	6.6 (7.2)	24.9 (24.4)	21.0 (21.9)	9.3 (10.1)			610 ± 20 (581)	850 (590), 775 (480), 630 (260), 610 (320), 575 (220)
VIIk	(py) ₃ CuCo ₂ Cl ₄ O	31.8 (31.3)	2.8 (2.6)	6.9 (7.3)	23.9 (24.6)	10.0 (11.0)	19.0 (20.0)			540 ± 20 (576)	850 (230), 775 (220), 630 (640), 610 (700), 575 (570)
VIII	(py) ₃ Co ₃ Cl ₄ O	30.8 (31.5)	2.2 (2.6)	7.0 (7.3)	25.3 (24.9)		29.2 (30.9)			690 ± 20 (571)	630 (680), 610 (900), 575 (770)

^a Calculated values in parentheses. ^b N = DENC; py = pyridine. ^c See text for discussion of coordination of aquo ligands. ^d In nitrobenzene at (3–5) × 10⁻² m. ^e Obtained from reaction of IIIa with 2 mol of Ia or II (see text). ^f Data from ref 10. ^g Insoluble; see ref 10. ^h Solubility too low in nitrobenzene for accurate measurements.

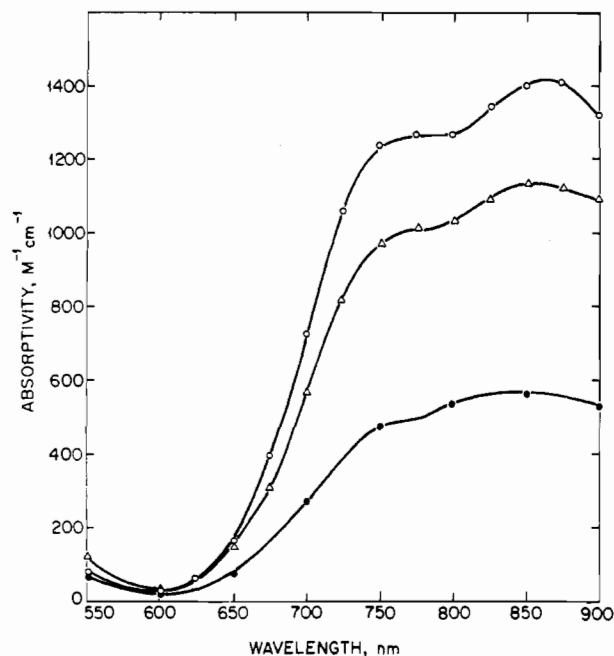
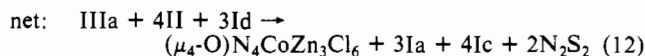
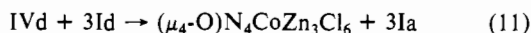
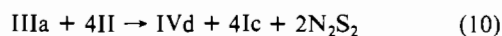


Figure 1. Electronic spectra of IIIa (O), IVi (Δ), and IVj (●) in methylene chloride at 25 °C. See Tables I and II for identification.

attempt to isolate $(\mu_4\text{-O})\text{N}_4\text{CoZn}_3\text{Cl}_6$. Equation 11 is driven by the stability order $\text{Ia} > \text{Id}$.³



Gel permeation chromatography (methylene chloride eluant) of the final product solution resulted in a single band, which was black because it contains $\text{Cu}(\text{NS})_2$ (Ic) from eq 10. This result indicates that the anticipated tetranuclear first product of eq 12 is unstable.²⁵ No better result was obtained by running reaction 12 in nitrobenzene and attempting to precipitate a tetranuclear product selectively with hexane. It thus appears that all μ_4 -oxo molecules containing more than two zinc centers are inherently unstable; as indicated in the Appendix, this reduces the number of possible μ_4 -oxo molecules $(\mu_4\text{-O})\text{N}_4(\text{Co}, \text{Cu}, \text{Ni}, \text{Zn})_4\text{Cl}_6$ from 36 to 32.

Other Products of Transmetalation. The product $(\mu_4\text{-O})\text{N}_4\text{Co}_2\text{Ni}_2\text{Cl}_6$ (IVk), obtained by transmetalating IVb (Table II) with 2 mol of the nickel reagent Ib, was easily separated by gel permeation chromatography (methylene chloride eluant). Analytical data are given in Table II. The product $(\mu_4\text{-O})\text{N}_4\text{Co}_3\text{ZnCl}_6$ from transmetalation of IVc (Table II) with 1 mol of Id was unstable.²⁵ The placement of Co_2Zn in one face of IIIa is evidently fatal to its stability.

Synthesis of a Molecule Containing Four Different Metals. In previous papers^{4,12a} we reported the synthesis of the products $\text{L}_4\text{CoNiCuZnY}_2$ from the sequential transmetalation of $\text{L}_4\text{Cu}_4\text{Y}_2$ (L = 6-methyl-2-oxopyridinate; Y = O, CO_3) with equimolar amounts of Id, Ib, and Ia followed by chromatographic product separation. At that time we did not appreciate that such reactions can, in principle, be conducted simultaneously, partly because of the decreasing reagent stability $\text{Ib} > \text{Ia} > \text{Id}$.^{3,5} We are pleased to report that $(\mu_4\text{-O})\text{N}_4\text{CoNiCuZnCl}_6 \cdot 2\text{H}_2\text{O}$ (IVl, Table II) is quantitatively obtained by gel permeation chromatographic separation of the products of simultaneous or sequential transmetalation of IIIa with equimolar amounts of Ia, Ib, and Id. We presume that III is transmetalated by $\text{M}(\text{NS})_2$ in the order Id, Ia, Ib, which is the reverse of their respective stabilities.³ No attempt was made to separate the enantiomers of IVl (see Appendix).

Spectra of Products IV. The IR spectra of the products IVa–l all exhibit sharp, single bands at 1635 cm^{-1} , indicating mono-

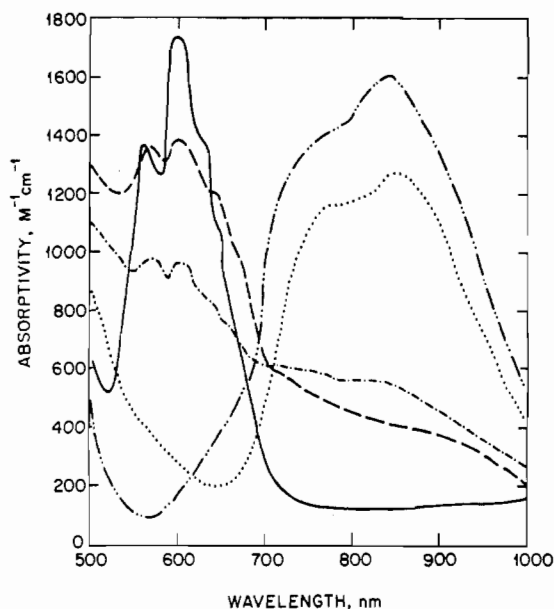


Figure 2. Electronic spectra of IIIa (---), IVa (---), IVb (---), IVc (---), and IVd (—) in methylene chloride at 25 °C. See Tables I and II for identification.

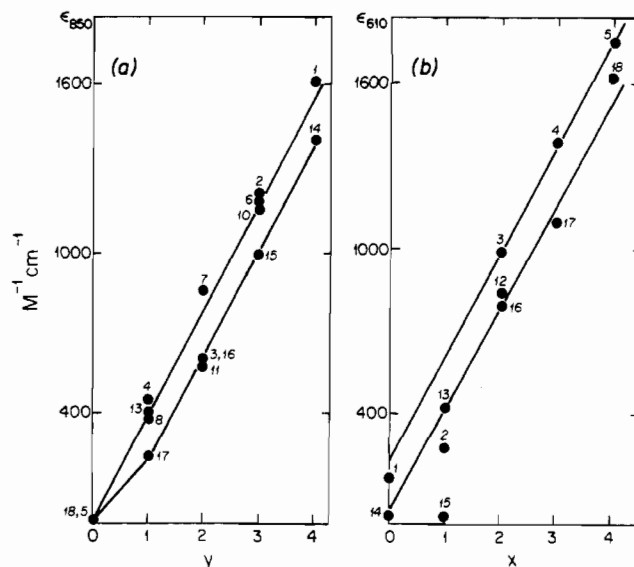


Figure 3. Plots of (a) ϵ_{850} vs y and (b) ϵ_{610} vs x for the following complexes in methylene chloride at 25 °C: (1) IIIa; (2) IVa; (3) IVb; (4) IVc; (5) IVd; (6) IVe; (7) IVf; (8) IVg; (9) IVh; (10) IVi; (11) IVj; (12) IVk; (13) IVl; (14) IVm; (15) IVn; (16) IVo; (17) IVp. See text for definitions and Tables I and II for identification.

dentate N.¹⁰ Representative electronic spectra are shown in Figures 1 and 2.

Figure 1 illustrates the progressive decrease of characteristic^{10,11} absorption due to copper(II) in IIIa on progressive replacement with zinc. Progressive replacement of copper(II) in IIIa with cobalt(II) (Figure 2) causes absorption decreases in the same wavelength region that are accompanied by structured increases centered at 610 nm. The latter are characteristic of five-coordinate cobalt(II).¹⁻³

In Figure 3 we examine the molar absorptivities ϵ_{610} and ϵ_{850} as a function of x and y in the general formula $(\mu_4\text{-O})\text{N}_4(\text{Co}_x\text{Cu}_y\text{M}_z)\text{Cl}_6$ ($\text{M} = \text{Ni}, \text{Zn}; x + y + z = 4$). Each complex considered is labeled in the legend of Figure 3.

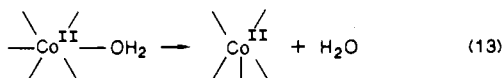
A linear relation, within experimental error, of points 1, 2, 4–8, 10, and 13 (for DENC ligands) and points 14–17 (for py ligands) in Figure 3a strongly suggests an invariant copper(II) geometry and μ_4 -oxo molecular core structure for the cited complexes. This opinion is supported by ESR and IR evidence for points 6–8.¹⁰ The deviation of points 3 and 11 from the upper line refers to

$(\mu_4\text{-O})\text{N}_4\text{Cu}_2\text{M}_2\text{Cl}_6$ complexes IVb and IVj (Table II). The ϵ_{850} values for these complexes are ca. 75% of the expected value. The origin of the deviation could not be determined since all IV species containing copper disproportionate on attempted crystallization.²⁶

A linear relation, within experimental error, of points 1 and 3–5 (for DENC ligands) and of points 14 and 16–18 (for py ligands) in Figure 3b strongly suggests an invariant cobalt(II) geometry and μ_4 -oxo molecular core structure for the cited complexes. We ascribe the deviation of point 12 (for $\mu_4\text{-O})\text{N}_4\text{Co}_2\text{Ni}_2\text{Cl}_6$, IVk) from the upper line to no effect of nickel on the atomic absorptivity of cobalt(II): higher values for points 3–5 are due to enhancement of ϵ_{610} specifically by copper(II) (see below).

Since points 2, 13, and 15 all refer to copper(II)-containing molecules, the deviation of these points from their respective lines must have a different origin. Inspection of the electronic spectra of IVa (Figure 2), IVl, and IVm indicates little evidence for five-coordinate cobalt(II) from structured features near 600 nm: ϵ_{610} values for IIIc and IVm are essentially the same.

Complexes IVa, IVl, and IVm are the only tetranuclear copper-cobalt complexes of this study that show IR evidence for coordinated water (broad absorption centered at 3400 cm^{-1}). It appears that the single cobalt(II) center of these particular molecules coordinates a water molecule, resulting in six-coordinate cobalt(II). In support of this explanation, we found that ϵ_{610} values for IVa, IVl, and IVm increase with decreasing concentration of the respective complexes in methylene chloride, suggesting shifts to the right in equilibrium 13, with five-coordinate cobalt(II) having a far greater ϵ_{610} value than the six-coordinate aquated center.



In summary, spectral data at 850 and 610 nm favor the assignment of invariant copper(II) and cobalt(II) geometries, respectively, in 13 of the 18 molecules examined. Three of the five "deviant" molecules are proposed to contain six-coordinate cobalt(II), and the other two evidently contain geometrically different copper(II) atoms.²⁶

New Trimers from Reactions of III with Equimolar Amounts of Ie–g. The metal centers of reagents Ie–g all contain 10 d electrons, as in the zinc reagent Id. Our objective was to demonstrate direct transmetalation of copper(II) with the three new elements Cd, Hg, and Sn and to compare the spectra and other properties of the family $(\mu_4\text{-O})(\text{N},\text{py})_4(\text{Cu},\text{Zn},\text{Cd},\text{Hg},\text{Sn})_4\text{Cl}_6$. We instead found a very convenient route to the new μ_3 -oxo trimers V (Table II) from eq 3.

The treatment of the brown complexes III with an equimolar amount of Ie, If, or Ig at ambient temperature in methylene chloride or nitrobenzene under dinitrogen results in a very rapid color change to dark black, characteristic of $\text{Cu}(\text{NS})_2$ (Ic).⁷ The product solutions were easily separated by gel permeation chromatography (methylene chloride eluant) or by addition to a 3-fold volumetric excess of anhydrous hexane under dinitrogen. Gel permeation chromatography cleanly separated brown V from a diffuse, black band, which was shown by analysis to contain Cl, Cu, and NS and Cd, Hg, or Sn.²⁷ Chromatography gave higher

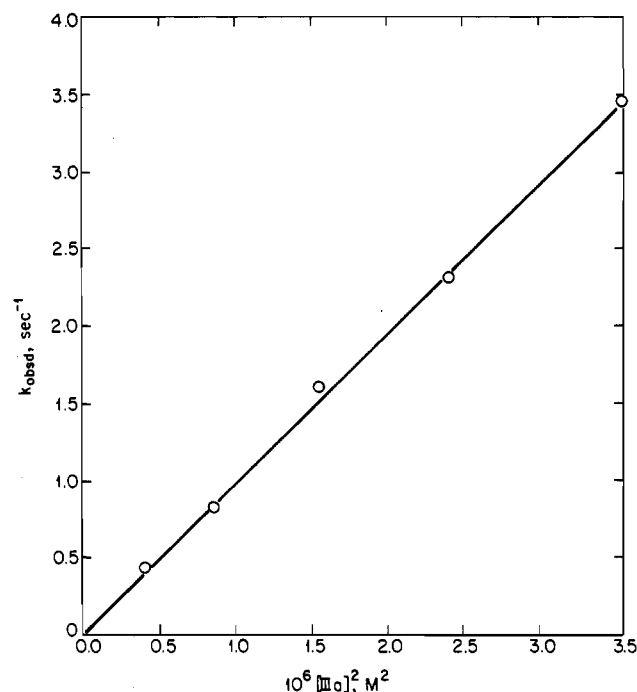


Figure 4. Plot of k_{obsd} (s^{-1}) vs $[\text{IIIa}]^2$ for the reaction of excess IIIa with mercury complex If in nitrobenzene at 25 °C.

Table III. Kinetic Data for Monotransmetalation of Excess IIIa by $\text{M}(\text{NS})_2$ Reagents I in Aprotic Solvents

reactant	solvent ^a	temp ^b	$10^{-5}k^c$	ΔH^{*d}	ΔS^{*e}	
If	N	17.1	9.1	12.2 ± 0.3	11 ± 3	
		21.0	9.8			
		26.2	10.2			
		30.1	22.9			
		35.3	31.6			
40.0	42.7					
Ia ^f	N	21.0	8.6	20.0 ± 0.4	36 ± 3	
		M	21.0	3.4	19.5 ± 0.4	33 ± 3
Ib ^f	N ^g	21.0	0.162	20.0 ± 0.4	29 ± 3	
		21.0	2.5×10^{-3}	24.0 ± 0.4	35 ± 3	
		N ^h	21.0	0.189	20.4 ± 0.4	30 ± 3
		M	21.0	0.97	16.5 ± 0.4	20 ± 3
Id ^f	N	21.0	1.64	20.0 ± 0.3	33 ± 3	
		M	21.0	4.75	14.0 ± 0.4	15 ± 3

^aN = nitrobenzene; M = methylene chloride. ^bGiven in °C. ^cUnits are $\text{M}^{-2}\text{s}^{-1}$ in rate law 14. ^dUnits are $\text{kcal}\cdot\text{mol}^{-1}$. ^eUnits are $\text{cal}\cdot\text{deg}\cdot\text{mol}^{-1}$ at 25 °C. ^fData from Table IIIa of ref 5. ^gCopper reactant is $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{Br}_6$ (IIIb). ^hLigand is py; all others have DENC as ligand.

yields of V than addition of product solutions to excess hexane (yields from the latter were 50–70% of the pure complexes V).

Kinetics of the Reaction of Excess IIIa with $\text{Hg}(\text{NS})_2$ (If). Equation 3 results in the net transfer of two NS ligands from Ie,f to copper(II) and the loss of MX_2 from the presumed product of monotransmetalation of III, $(\mu_4\text{-O})\text{N}_4\text{Cu}_3\text{MX}_6$ ($\text{M} = \text{Cd}, \text{Hg}, \text{Sn}$). The kinetics of the reaction of IIIa (6.25–19.0 mM) with If (0.05 mM) were investigated at 575 nm over the temperature range 17.1–40.0 °C in nitrobenzene. The objective was to see if more than one process could be observed. At least a 10-fold excess of IIIa was maintained in all cases to ensure that only one copper(II) center of IIIa is replaced.^{5,9}

Plots of $\ln(A_\infty - A_t)$ vs t , where A_t is the absorbance at time t , were linear to at least 4 half-lives, indicating that only one process, first-order in [If], is observed. Plots of the pseudo-first-order rate constant at fixed temperature, k_{obsd} , were a linear function of $[\text{IIIa}]^2$ (Figure 4), indicating third-order rate law 14.

$$-\text{d}[\text{IIIa}]/\text{d}t = k[\text{If}][\text{IIIa}]^2 \quad (14)$$

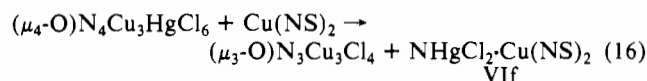
Values for the third-order rate constant k and its activation pa-

(26) The fact that ϵ_{610} for IVb (point 3) conforms to data points 1, 4, and 5 of Figure 3b strongly suggests that the low ϵ_{850} value (point 3 of Figure 3a) is due to a local geometrical change for copper(II) in this complex and for $(\mu_4\text{-O})\text{N}_4\text{Cu}_2\text{Zn}_2\text{Cl}_4$ (IVj, point 11). This distortion could be movement along $(\mu_4\text{-O})\text{-Cu}$ axes caused by the presence of cobalt(II) and zinc(II). Distortion at copper(II) evidently does not greatly affect the local geometry of cobalt(II) in IVb (point 3 of Figure 3b).

(27) Under identical experimental conditions, the diffuseness of the second, black chromatographic band increased with $\text{M} = \text{Hg} < \text{Cd} < \text{Sn}$. Fractionation of this band with $\text{M} = \text{Hg}$ gave fractions with molar ratios N:Cu:Hg:Cl close to 1:1:1:2 and solids with IR spectra very similar to that of N and $\text{Cu}(\text{NS})_2$ (Ic); however, attempted crystallization gave only crystalline $\text{Cu}(\text{NS})_2$ (Ic). The molar ratios Cu:M:Cl of chromatographic fractions were much more variable with $\text{M} = \text{Cd}, \text{Sn}$, suggesting that the stability of coproducts VI (eq 3) decreases in the order $\text{M} = \text{Hg} > \text{Cd}, \text{Sn}$.

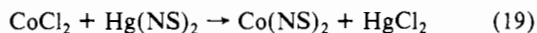
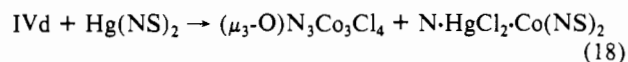
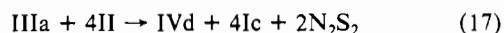
rameters are collected with third-order data for other monometalations of IIIa^{5,9} in Table III.

The observations of (i) rate law 14^{5,9} and (ii) A_{∞} readings for the one observable process that are stable for many half-lives indicate that the reaction of IIIa with the mercury reagent proceeds via the rate-determining monometalation of copper(II) (eq 15) followed by rapid fragmentation of the primary



product.²⁸ Another indication of rate-determining monometalation is that a linear plot of ΔH^\ddagger vs ΔS^\ddagger accommodates all the data in Table III.²⁹

Trimers V. Although oxometal trimers result from transmetalation of a variety of tetranuclear dioxocopper targets,^{1-3,6} eq 3 is the only known method of obtaining oxometal trimers containing just copper by transmetalation. The kinetic evidence (previous section) strongly suggests that reaction 3 of III with Ia-g gives the monometalated species $(\mu_4\text{-O})\text{N}_4\text{Cu}_3\text{MX}_6$. Such species are stable with M = Co, Ni, Cu, Zn (Table II) but not with Hg, Cd, or Sn, evidently because the latter metals are too large to conform to a core structure dominated by the requirements of (a) the central μ_4 -oxo group and (b) the preferred local geometry of copper(II). To test requirement b, we reacted IIIa with 4 mol of II and then treated the product IVd in situ with equimolar Hg(NS)₂ (If; eq 17 and 18). The isolated product



was the trimer $(\mu_3\text{-O})\text{N}_3\text{Co}_3\text{Cl}_4$ (VIIc), which can be obtained directly from Va (see below). This result is important for three reasons.

First, it demonstrates the stability order $\text{Co}(\text{NS})_2 > \text{Hg}(\text{NS})_2$, which was independently verified through reaction 19 in ethanol.³ Second, it again emphasizes that the transmetalation phenomenon is by no means restricted to polynuclear copper targets³ and that a knowledge of relative transmetalator stabilities is the guide to obtaining a desired product from particular targets.³⁰ Third, it indicates that the requirements of the central μ_4 -oxo group dominate the geometries of $(\mu_4\text{-oxo})$ metal complexes and that the tetrahedral sites can only accommodate metals that are smaller than ca. 1.0 Å.³¹

We have delineated the different patterns of extrusion of CuO from $(\mu_4\text{-O}, \mu\text{-O})\text{N}_3\text{Cu}_3\text{M}(\text{H}_2\text{O})\text{Cl}_4$ complexes (M = Co, Ni, Cu, Zn) on transmetalation with excess $\text{M}(\text{NS})_n$ reagents; the alternative trimeric products $(\mu\text{-O})\text{N}_3(\text{Cu}, \text{Co})_3\text{Cl}_4$ and $(\mu_3\text{-O})\text{N}_3(\text{Cu}, \text{M})_3\text{Cl}_4$ have been identified.^{1-3,6} The great interest of reaction 3 is that it results in the loss of MX_2 , not CuO, from $(\mu_4\text{-O})\text{N}_3\text{Cu}_3\text{MX}_6$. This indicates a greater strength of the Cu-O

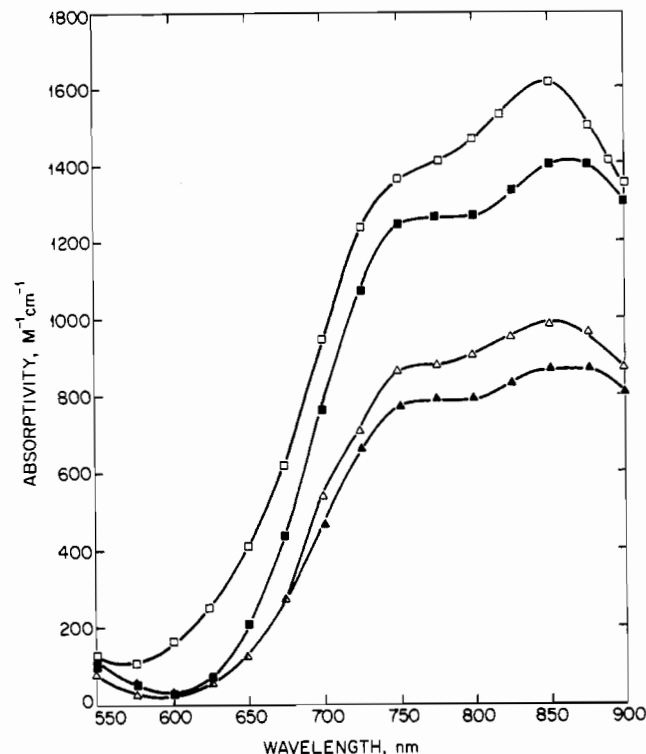


Figure 5. Electronic spectra of IIIa (□), Va (Δ), IIIc (■), and Vc (▲) in methylene chloride at 25 °C. See Tables I and II for identification.

Table IV. Comparative Properties of IIIa and Va

property	IIIa	Va
IR, cm ⁻¹	$\nu_{\text{Cu-O}}$ 510	$\nu_{\text{Cu-O}}$ 540
spectrum, ^a nm ^b	850 (1630),	850 (990),
(M ⁻¹ ·cm ⁻¹) ^c	775 (1400)	775 (880)
tit. ^d Ib	1:4 ^f	1:3 ^e
tit. If	1:4 ^f	1:3
tit. HNS	1:8 ^f	1:6
tit. TEED	1:4	1:2
ESR ^g	inactive	active (g) = 2.13

^a Electronic spectrum in methylene chloride at 25 °C. ^b Wavelength. ^c Absorbivity. ^d Spectrophotometric titration with reagents shown. ^e Example: reaction stoichiometry $\Delta(\text{Ib})/\Delta(\text{Va}) = 3$. ^f Data from ref 7. ^g At room temperature in methylene chloride (see Figure 9b).

bonds in III than in tetranuclear dioxocopper(II) complexes and explains the frequent appearance of crystalline III on the attempted crystallization of all manner of tetranuclear dioxometal complexes containing copper.

Although pairs such as IIIa and Va have very similar electronic spectral features (Figure 5) and elemental analyses (Tables I and II), they can be distinguished by cryoscopic molecular weight measurements in nitrobenzene. However, because the attempted crystallization of Va-c gave products that are isomorphous with their parents IIIa-c, respectively, more means of distinction were mandatory.

The results in Table IV indicate that IIIa and Va are distinguishable by a number of means, including spectrophotometric titrations with HNS, Ib, If, and TEED and ESR measurements. The titration results indicate that compounds V are easily and totally transmetalated with $\text{M}(\text{NS})_n$ reagents (see below). We have no ready explanation for the stoichiometry $\Delta(\text{TEED})/\Delta(\text{Va}) = 2$, but this is clearly different from the result of the reaction with IIIa.³²

Our opinion that V compounds are μ_3 -oxo species is supported by (a) their inability to form carbonato derivatives, a characteristic property of μ -oxo complexes,^{6-8,23} (b) their inability to initiate the

(28) We do not know if coproduct $\text{Cu}(\text{NS})_2$ from eq 15 is a reactant in eq 16. However, this same coproduct does not demetallate $(\mu_4\text{-O})\text{N}_4\text{Cu}_3\text{MX}_6$ complexes (M = Co, Ni, Zn),^{5,9} which strongly suggests that the analogues with M = Cd, Hg, Sn are inherently unstable to disproportionation of MX_2 (see text).

(29) We generally take a common rate law with correlated ΔH^\ddagger and ΔS^\ddagger to indicate the same rate-determining step for related reactions.¹ The ΔS^\ddagger data for reactions of Ia with IIIa and for Id with IIIa in nitrobenzene are 5-8 cal-deg-mol⁻¹ larger than expected from the other data at $\Delta H^\ddagger = 20$ kcal-mol⁻¹.

(30) The point here is that a product such as $(\mu_3\text{-O})\text{N}_3\text{Co}_3\text{X}_4$ can be obtained from transmetalations $(\mu_3\text{-O})\text{N}_3\text{Ni}_3\text{X}_4/3$ Ia, V/3 Ia, etc.

(31) The effective ionic radii of five-coordinate Zn, Cd, and Hg²⁺ are 0.82, 1.01, and ~1.12 Å, respectively: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. Space-filling models based on the known⁷ dimensions of IIIa suggest loose binding of Cd, Hg, and Sn in tetrahedral holes. This mismatch of sizes and strong M-X bonds evidently is responsible for specific MX_2 loss.

(32) One possible explanation is that reaction of III with 1 mol of TEED results in $(\mu\text{-O})\text{N}_3\text{Cu}_2\text{Cu}(\text{TEED})\text{X}_4$; such μ -oxo molecules would only be expected to react with an additional 1 mol of TEED.⁷

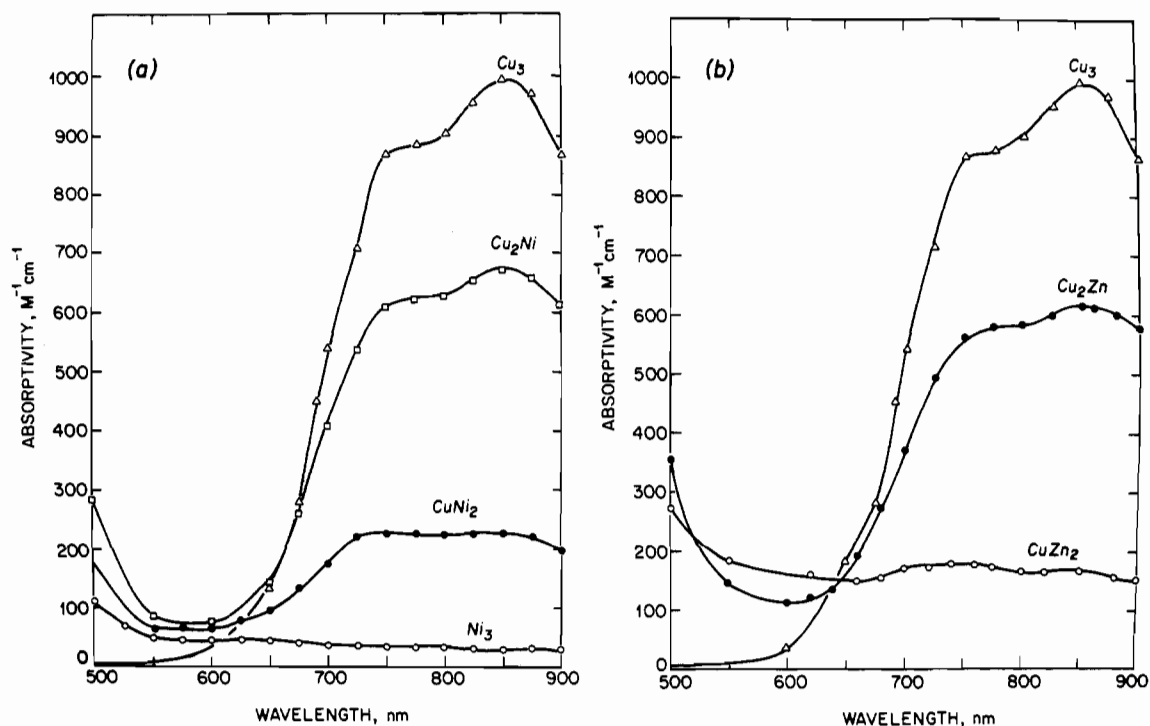
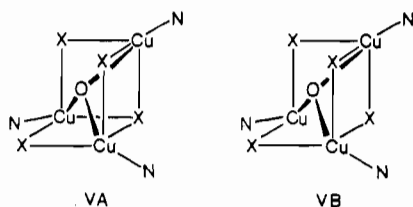


Figure 6. Electronic spectra of the following complexes in methylene chloride at 25 °C: (a) Va (Δ), δ IIId (\square), VIIe (\bullet), VIIf (\circ); (b) Va (Δ), VIIg (\bullet), VIIh (\circ). See Table II for identification.

oxidative coupling of phenols by dioxygen, which is characteristic of terminal oxo groups,^{3,23} and (c) the insensitivity of the electronic spectrum to large excesses of pyridine ligands, which also is characteristic of the μ_4 -oxo complexes III.³³

Core Structures of V. Alternative core structures for V differ only in the presence of three-coordinate halide in the symmetrical alternative VA, which contains equivalent copper(II) sites around a C_3 axis. Structure VB contains one four-coordinate copper(II)



site. The fact that the molar absorptivities of V are close to 75% of those of their respective μ_4 -oxo parents strongly suggests that all the copper(II) sites in III and V are $NCuX_3$ chromophores,¹⁰ which favors structure VA. Mild support for the presence of three-coordinate halide in V is the fact that compounds V do not react with equimolar amounts of CuX_2 in methylene chloride to give III in the presence or absence of equimolar amounts of pyridine ligands (eq 20).³⁴

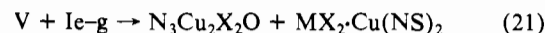


Transmetalation of Copper(II) Trimers V with Reagents I and II. General Observations. Spectrophotometric titration in methylene chloride showed that all transmetalations of V with reagents I and II obey the stoichiometry $\Delta(I \text{ or } II)/\Delta(V) = 3.0 \pm 0.1$ (Table IV). Gel permeation chromatography of the products of the reactions of Va and Vc with 3 mol of each reagent resulted in clean separation of trimeric products from the coproduct Ic only with reagents Ib and II. The anticipated trimeric products $N_3Co_3Cl_4O$, $N_3Zn_3Cl_4O$, $N_3Cd_3Cl_4O$, $N_3Hg_3Cl_4O$, and $N_3Sn_3Cl_4O$ could not be isolated intact from the reactions of IIIa with

3 mol of Ia,d-g, respectively, by chromatography or by addition of transmetalation product mixtures in nitrobenzene or methylene chloride to excess hexane. These methods work well for the isolation of many other heteropolynuclear metal complexes,¹⁻¹⁰ and so we can be sure that the cited complexes are inherently unstable if prepared from the reactions of IIIa with Ia,d-g.

The successful isolation of $N_3Co_3Cl_4O$ (VIIc) and $(py)_3Co_3Cl_4O$ (VIIi) from the reactions of Va and Vc with 3 mol of II, respectively, emphasizes the advantages of II over Ia as a direct transmetalator of copper(II) through eq 7-9.

From earlier observations (eq 3) we might have expected reaction 21 with equimolar amounts of reagents Ie-g, where M is Cd, Hg, or Sn. However, only one black band was observed on



gel permeation chromatography of product solutions from eq 21, indicating that the anticipated first products do not associate to form tetranuclear VIII (eq 22) or its tetranuclear dioxocopper(II) isomers, which would be easily separated by chromatography.¹⁻¹⁰



The instability of $N_3Zn_3Cl_4O$ and $(py)_3Zn_3Cl_4O$ suggests the analogy of V with one of the four equivalent faces of the parents III.^{7,10,17} This instability and the limit of direct transmetalation of III by Id to $CuZn_2$ stoichiometries (see above) indicate that such faces cannot accommodate more than two zinc centers; this also is good support for closely similar metal-metal distances and geometries in III and V.

Direct Transmetalation of V with Reagents Ib, Id, and II. There are 23 possible complexes $N_3(Co,Ni,Cu,Zn)_3Cl_4O$ (VII) if (a) no product can contain more than two zinc centers and (b) there is a fixed core structure. This total includes four enantiomeric pairs of molecules containing any three different metals (Appendix). Table II gives analytical and cryoscopic data for Va and nine of its transmetalated derivatives. Data for Vc and molecules Vj-l obtained from their reactions with 1, 2, and 3 mol of II, respectively, also are included.

Spectra of V and VII. Sharp bands at 1635 cm^{-1} in the IR spectra of all DENC-containing molecules Va,b and VIIa-i indicate monodentate N.^{10,23} Representative electronic spectra (Figures 6 and 7) show the effects of progressive replacement of copper(II) in V with other metals: we observe decreasing ab-

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

(34) Five-coordinate copper(II) is often observed in neutral halooxocopper(II) complexes.^{1-3,6-8} Addition of MX_2 is more likely for VB, which contains a four-coordinate copper(II) if all halo ligands are two-coordinate.

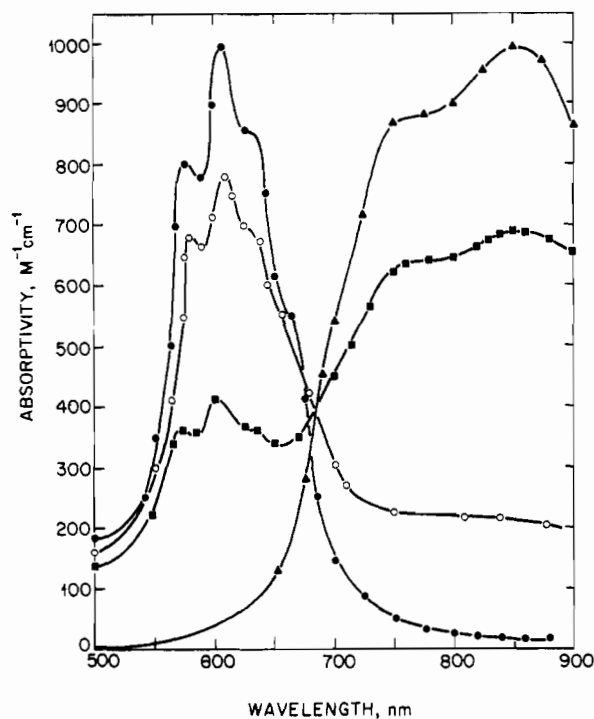


Figure 7. Electronic spectra of Va (▲), VIIa (■), VIIb (○), and VIIc (●) in methylene chloride at 25 °C. See Table II for identification.

sorbance at wavelengths greater than 700 nm and the gradual appearance of a structured absorbance centered at 610 nm due to five-coordinate cobalt(II) (Figure 7).

In Figure 8 we have plotted ϵ_{610} vs x and ϵ_{850} vs y in the general formula $N_3(Co_xCu_yM_z)Cl_4O$, where $x + y + z = 3$. Each complex considered is specifically labeled in the legend of Figure 9. Closed circles refer to pyridine complexes.

A central line drawn through points 1, 4, 10, and 15–17 in Figure 8a relates the trimer Va, the product VIIc of its total

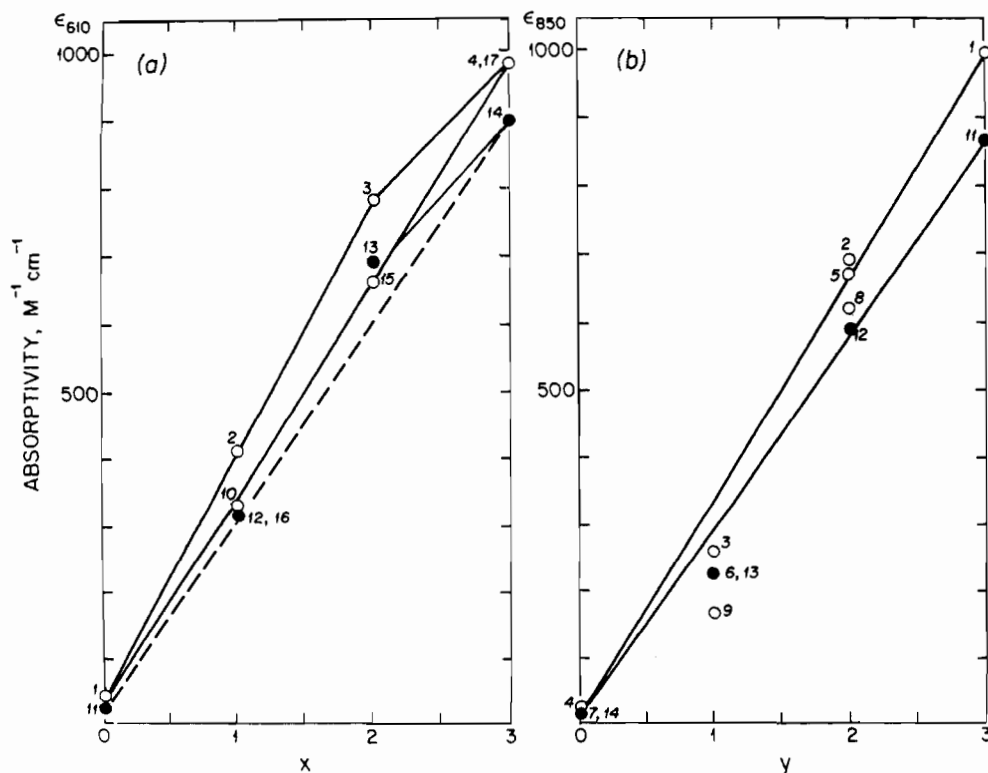


Figure 8. Plots of (a) ϵ_{610} vs x and (b) ϵ_{850} vs y for the following complexes in methylene chloride at 25 °C: (1) Va; (2) VIIa; (3) VIIb; (4) VIIc; (5) VIId; (6) VIIe; (7) VIIf; (8) VIIg; (9) VIIh; (10) VIIi; (11) Vc; (12) VIIj; (13) VIIk; (14) VIII; (15) $(\mu_3-O)(DENC)_3Co_2ZnCl_6$; (16) $(\mu_3-O)(DENC)_3CoNi_2Cl_6$; (17) $(\mu_3-O)(DENC)_3Co_3Cl_4$ from reaction of $(\mu_4-O,\mu-O)(DENC)_3Cu_3Co(H_2O)Cl_4$ with excess II.⁷ See Tables I and II for identification.

Table V. Twenty-Four Possible Trimeric Metal(II) Complexes for $(\mu_3-O)N_3(Cu,Co,Ni,Zn)Cl_6$ ^a

example ^b	Cu	Co	Ni	Zn	example ^b	Cu	Co	Ni	Zn
Va,c	3	0	0	0	VIIg	2	0	0	1
VIIc,l	0	3	0	0 ^{c,d}	VIIb,k	1	2	0	0 ^e
VIIIf	0	0	3	0		0	1	2	0 ^{c,d}
	(0)	(0)	(0)	(3)		0	0	1	2 ^f
VIIa,j	2	1	0	0 ^c		1	1	1	0
	0	2	1	0		1	1	1	0
	0	0	2	1 ^g	VIIi	0	1	1	1
VIIh	1	0	0	2		0	1	1	1
VIIId	2	0	1	0		1	0	1	1
	0	2	0	1 ^d		1	0	1	1
VIIe	1	0	2	0		1	1	0	1
	0	1	0	2 ^{c,d}		1	1	0	1

^a Products known to be unstable in parentheses. ^b See Table II for identification. ^c See ref 2. ^d See ref 3. ^e Attempted syntheses in other systems give unstable products.² ^f Enantiomeric pairs. ^g No 500–900-nm spectral features anticipated. ^h Example: this complex could be obtained by transmetalation of Va with equimolar amounts of Ia and Id.

transmetalation by 3 mol of II, the product VIIi, and three products of reaction 23, respectively, where M and M' are Co, Ni, or Zn.³ All the complexes contain three DENC ligands, and $(\mu_4-O,\mu-O)(DENC)_3Cu_3Co(H_2O)Cl_4 + M(NS)_2 + M'(NS)_2 \rightarrow (\mu_3-O)(DENC)_3(Co,Ni,Zn)_3Cl_4 + CuO + 2Cu(NS)_2$ (23)

only Va contains copper(II). The relationship of these points and, in particular, the coincidence of points 4 and 17 for the common product Vc from the total transmetalation of Va with II or from eq 23 ($M = M' = Co$) indicate a common μ_3 -oxo core structure.

Points 1–3 form a separate line in Figure 8a. Copper(II) evidently increases the atomic absorptivity of cobalt(II) in the same μ_3 -oxo core structure. The same trends for points 1–4 (DENC ligand) and 11–14 (py ligand) indicate a μ_3 -oxo core structure for Vc and VIIj–l. We anticipate that ϵ_{610} data for $(\mu_3-O)(py)_3(Co,Ni,Zn)_3Cl_4$ complexes would fit the dashed line of Figure

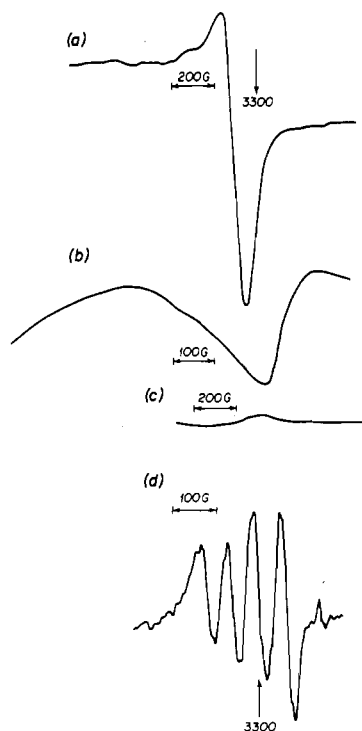


Figure 9. ESR spectra in methylene chloride for (a) Va at 10 K (instrument gain 1.6×10^3), (b) Va at room temperature (gain 1.0×10^3), (c) VIIg at room temperature (gain 3.2×10^3), and (d) VIIa at room temperature (gain 1.0×10^3). All concentrations are 1.00 mM. The cobalt(II) complex VIIa has a room-temperature spectrum similar to (d); see text.

8a because of the negligible effects of Ni and Zn on cobalt(II) absorptivity.

We now turn to Figure 8b. We are confident that complexes Va (point 1) and Vc (point 11) are (μ_3 -oxo)copper complexes. We therefore take the linear relationship of points 1, 2, 4, 5, and 7 and of points 11, 12, and 14 to indicate common μ_3 -oxo core structures for the respective complexes. The slight deviation of ϵ_{850} for $N_3Cu_2ZnCl_4O$ (VIIg, point 8) from the upper line suggests a small local copper(II) geometry change in this particular case.³⁵

Of particular importance is the fact that ϵ_{850} values are lower than expected for the following molecules containing one copper(II) center: $N_3CuCo_2Cl_4O$ (point 3), $N_3CuNi_2Cl_4O$ (point 6), $N_3CuZn_2Cl_4O$ (point 9), and $(py)_3CuCo_2Cl_4O$ (point 13). The fact that two Co, Ni, or Zn centers are present in these "deviant" molecules and that points 1, 2, and 3 of Figure 8a are linearly related suggests that the local copper(II) geometry in (μ_3 -O)-(N,py)₃CuM₂Cl₄ has to conform to those of the M centers.³⁶ Similar deviations noted for the μ_4 -oxo complexes $N_4Cu_2Co_2Cl_6O$ and $N_4Cu_2Zn_2Cl_6O$ in Figure 3b were earlier ascribed to copper(II) center distortions.²⁶ The "deviant" trimers approximate one of the four faces of the "deviant" tetramers. Copper(II) centers in such faces and trimer molecules evidently are subject to induction of the same kinds of distortions by M = Co, Zn. We thus feel that closely similar core structures are responsible for the analogous spectral behavior in III and V and their transmetalated derivatives. We will continue with attempts to crystallize these interesting molecules intact, but experience suggests that this is difficult, if not impossible, to achieve with transmetalated derivatives of III and molecules with core structures V, all of which

(35) Transmetalation of core structure VB could take place at alternative four- or five-coordinate copper(II) sites. We are currently investigating product spectra, rates, and rate laws for monotransmetalation of copper(II) sites of known, different geometries and coordination numbers.
 (36) There is no analytical or IR evidence for coordinated water in products VIIc and VIII (Table II). It is possible that complexes (μ_3 -O)-(N,py)₃CuM₂Cl₄ adopt core structure VB, with the remaining four-coordinate copper(II) center having a lower ϵ_{850} value than the equivalent sites in VA.

Table VI. Thirty-Six Possible Tetranuclear Metal(II) Complexes for $(\mu_4-O)N_4(Cu,Co,Ni,Zn)_4Cl_6^a$

example ^b	Cu	Co	Ni	Zn	example ^b	Cu	Co	Ni	Zn
IIIa,c	4	0	0	0		0	0	2	2 ^c
IVd,p	0	4	0	0	IVj	2	0	0	2
IVh	0	0	4	0 ^c	IVf	2	0	2	0
	(0)	(0)	(0)	(4) ^c		0	2	0	2
IVb,m	3	1	0	0		1	2	1	0
	0	3	1	0		0	1	2	1
	0	0	3	1 ^c		1	0	1	2
	(1)	(0)	(0)	(3)		2	1	0	1
IVe	3	0	1	0		1	0	2	1
	(0)	(3)	(0)	(1)		1	1	0	2
IVg	1	0	3	0		2	1	1	0
	0	1	0	3		0	2	1	1 ^d
IVi	3	0	0	1		1	2	0	1
IVc,o	1	3	0	0		1	1	2	0
	0	1	3	0		0	1	1	2
	0	0	1	3 ^c		2	0	1	1
IVb,n	2	2	0	0	IVl	1	1	1	1 ^e
IVk	0	2	2	0	IVi	1	1	1	1 ^e

^a Products known to be unstable in parentheses (see text). ^b See Table II for identification. ^c No 500–900-nm spectral features anticipated. ^d Example: this complex could be obtained by transmetalation of IIIa with 2 mol of II, 1 mol of Ib, and 1 mol of Id. ^e Enantiomeric forms of $(\mu_4-O)N_4CuCoNiZnCl_6$ (IVl).

are neutral and subject to disproportionation.³⁷

ESR Spectra of Trimers Va and VII. The tetranuclear (μ_4 -oxo)copper(II) complexes IIIa and IIIb are ESR silent at room temperature.¹⁰ Figure 9b shows the isotropic ($g = 2.13$) ESR spectrum of the odd-electron molecule Va in methylene chloride at room temperature. Cooling to 10 K results in an axial spectrum ($g_{\parallel} = 2.26$; $A_{\parallel} = 180$ G; $g_{\perp} = 2.01$; Figure 9a). Replacement of one copper(II) with zinc to give the even-electron molecule VIIg results in a very broad, weak signal at room temperature (Figure 9c) that indicates that strong copper–copper coupling is allowed by zinc. In contrast, the odd-electron molecule (μ_3 -O)₃Cu₂CoCl₄ (VIIa) has a spectrum like that in Figure 9d at room temperature; this indicates that the two copper(II) centers of VIIa are decoupled by cobalt(II) and that the latter ($I = 7/2$) is ESR silent. Finally, the room-temperature ESR spectrum of the product (μ_3 -O)₃CuZn₂Cl₄ (VIIh; Figure 9d) is typical of that for an isolated copper(II) center.

These results (a) clearly distinguish V from III¹⁰ and (b) indicate that copper–copper coupling is either allowed (by M = Zn) or broken (by M = Co) in (μ_3 -O)₃Cu₂MCl₄ complexes.

Conclusions. We have found that the cobalt(III) reagent II transmetalates (μ_4 -oxo)copper(II) complexes in four direct steps, as found earlier with the nickel(II) reagent Ib.¹⁰ However, disproportionation is observed for products containing more than two zinc centers, which reduces the $(\mu_4-O)N_4(Co,Cu,Ni,Zn)_4Cl_6$ family to 32 members. The spectra of family members containing cobalt and copper indicate closely similar five-coordinate metal geometries.

tom Dieck¹⁷ reported 42 examples of $(\mu_4-O)N_4Cu_4X_6$ molecules prepared by reaction of the acetone complexes with a range of amines, N. Each is a potential source of many other heterotetranuclear molecules from direct transmetalation and of many heterotrimeric molecules by reaction with the scissor transmetalators Ie–g. It will be interesting to see if enantiomeric molecules containing four or three different metals (e.g., IVl and VIIi (Table II)) can be resolved.

Acknowledgment. Support from Grant RR07143 from the Department of Health and Human Services and Grants INT-8512210, CHE-8717556, and INT-8715384 from the National Science Foundation is gratefully acknowledged. We thank Neil Bastian and Professor William Orme-Johnson for help with ESR

(37) See ref 6 for further arguments in favor of μ_3 -oxo core structures for the complexes cited.

measurements and Mark Schure for valuable discussions. M. A.E.-S. and A.E.-T. thank Alexandria University for study leave.

Appendix

Consider a fixed molecular core geometry with m equivalent sites, each of which can be occupied by any one of n different metals. The number of possible metal stoichiometries is given

by eq A1. The total number of discrete molecules, N , depends

$$s = \frac{(n + m - 1)!}{m!(n - 1)!} \quad (\text{A1})$$

on the core geometry. Examples: (1) $N = 24$ when $n = 4$ for the trinuclear core structures VA and VB (Table V); (2) $N = 36$ when $n = 4$ for the tetrahedral core structure III (Table VI).

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Preparation and Characterization of a Binuclear Iron- μ -Dioxygen Complex: [(Ph₃PO)₄FeOFe(OPPh₃)₄·2H₂O](ClO₄)₄

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The combination of [Fe^{II}(OPPh₃)₄](ClO₄)₂ with HOOH, *m*-ClC₆H₄C(O)OOH, Me₃COOH, PhIO, PhI(OAc)₂, Bu₄N(IO₄), O₃, or NaOCl in anhydrous acetonitrile results in the formation of the binuclear complex [(Ph₃PO)₄FeOFe(OPPh₃)₄·2H₂O](ClO₄)₄ (1). The same material is produced from the addition of HOOH plus two ⁻OH ions to [Fe^{III}(Ph₃PO)₄](ClO₄)₃ in acetonitrile. The complex has been characterized by elemental analysis, electronic, vibrational, and ESR spectroscopy, solid- and solution-phase magnetic susceptibility measurements, and electrochemistry. Mechanistic pathways are proposed for the formation of 1 and for its reactivity with halide ions.

Hydrogen peroxide and related oxygen atom donors are activated by Fe^{II}(MeCN)₄²⁺ in anhydrous acetonitrile.^{1,2} The resulting systems mimic the substrate transformations by enzymes such as catalase,³ peroxidase,⁴ and cytochrome P-450⁵ and appear to involve a reactive iron(II)-oxene, [Fe^{II}(O)]²⁺.⁶ The present report describes the unique chemistry that results when triphenylphosphine (PPh₃) is the substrate for the [Fe^{II}(MeCN)₄]²⁺/H₂O₂/MeCN system.

The slow introduction of HOOH to an MeCN solution that contains Fe^{II}(MeCN)₄(ClO₄)₂ and PPh₃ causes the substrate to be converted to triphenylphosphine oxide (Ph₃PO), with the iron remaining as Fe(II) (consistent with the reactivity for other substrates).^{1,2} However, the rapid addition of HOOH to the same system results in the formation of a deep purple complex (1), which is identical with that formed by the addition of HOOH (or other oxygen atom donors such as PhIO, O₃, *m*-ClPhC(O)OOH, IO₄⁻, and ⁻OCl) to an MeCN solution that contains [Fe^{II}(OPPh₃)₄](ClO₄)₂. The same complex is formed by the addition of HOOH plus two ⁻OH to [Fe^{III}(OPPh₃)₄](ClO₄)₃. The purple product (1) has been isolated and characterized, and its reactivity investigated in relation to the activation of HOOH by [Fe^{II}(MeCN)₄]²⁺ in acetonitrile.

Experimental Section

Equipment. The resonance Raman spectra were recorded with the optics in a 90° scattering configuration on a computer-controlled Spex Industries Ramalog 6 spectrometer equipped with a thermoelectrically cooled Hamamatsu R955 photomultiplier tube and a photon-counting detection system. Excitation at 488 nm was provided by an argon ion laser (Coherent Innova 15). Resonance Raman spectra were collected at 2-cm⁻¹ intervals (0.5 s/point). The incident laser power was between 50 and 75 mW, and the spectral slit width was approximately 3 cm⁻¹. The spectra were recorded for solid samples prepared in KCl pellets (20 mg/200 mg of KCl) and MeCN solutions (20–40 mM) sealed in a glass capillary tube.

Diffuse-reflectance infrared (DRIFT) spectra were run on a Nicolet 60-SX FTIR spectrometer equipped with a Barnes diffuse-reflectance

attachment and a wide-range mercury-cadmium telluride detector. The spectra were collected at 4-cm⁻¹ resolution for 500 scans. Samples were run either in synthetic diamond (20 μm, Kay Industrial Diamond Corp.) or KCl. Conventional IR spectra were recorded of solid samples prepared in KCl pellets on a Perkin-Elmer Model 283B spectrometer (spectral resolution 2 cm⁻¹).

A Cary Model 219 spectrophotometer and a Hewlett-Packard Model 8451 diode-array spectrophotometer were used for the UV-visible spectrophotometric measurements.

The solution-phase magnetic susceptibility measurements were made with Varian EM-390 and XL-200 NMR spectrometers by the Evans method⁷ (as modified by Rettig⁸) and made use of the paramagnetic shift of the methyl protons of TMS (added as an internal standard). Solid-state magnetic susceptibility data were obtained with a variable-temperature superconducting susceptometer/magnetometer system (SQUID).⁹ Pascal constants were used for diamagnetic corrections.¹⁰

The ESR spectra were recorded with a Bruker Model 200 X-band spectrometer equipped with an Oxford Instruments liquid-helium cryostat and temperature controller for low-temperature measurements. Liquid-nitrogen ESR spectra (77 K) were obtained by immersing the sample tubes in a liquid-nitrogen finger Dewar that was placed within the ESR cavity.

A three-electrode potentiostat (Bioanalytical Systems Model CV-1 or CV-27) and a Houston Instruments Model 100 Omnigraphic X-Y recorder were used for the cyclic voltammetric experiments. Controlled-potential coulometric electrolysis was accomplished with either a Princeton Applied Research Model 173/179 potentiostat/digital coulometer or a Bioanalytical Systems Model CV-27 potentiostat.

A Bioanalytical Systems microcell assembly was adapted to use a glassy-carbon working electrode, a platinum-flag auxiliary electrode, and a Ag/AgCl reference electrode filled with aqueous tetraethylammonium chloride solution and adjusted to 0.000 V vs SCE.¹¹ The latter was contained in a Pyrex tube with a soft-glass cracked tip; this electrode was placed inside a luggin capillary that contained the MeCN electrolyte solution. The cell was closed with a Teflon cap that included holes for

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