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Selective Transmetalation and Demetalation of Heteropolynuclear Metal Complexes[1]

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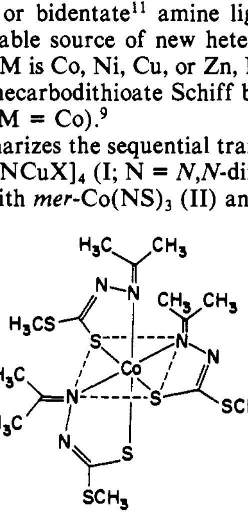
It is shown that tetranuclear complexes $[NCuX]_4$ (I: N = *N,N*-diethylnicotinamide; X = Cl or Br) can be sequentially or simultaneously transmetalated with *mer*-$Co(NS)_3$ (II) and different $M(NS)_2$ reagents (M = Co, Ni, Cu, Zn; NS = *S*-methyl isopropylidenehydrazinecarbodithioate) in stoichiometric reactions to give dimeric products $N_4M_2X_4$ (VIII) that are predictable (a) from II as the fastest transmetalator for I and $N_3Cu_3Co(NS)_2X_4$ (III) and (b) from the stability decrease for $M(NS)_2$ complexes in the order M = Cu > Ni > Co > Zn. Oxidation of III with dioxygen gives $N_3Cu_3CoX_4O_2$, which is simultaneously transmetalated by II and $M(NS)_2$ reagents to give trimers $N_3M_3X_4O$ (X) containing a variety of different metal centers. The spectra of X are discussed, and it is shown that complexes VIII and X, including those that contain no copper, can be transmetalated completely and predictably on the basis of the complete stability order $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$. These differences in stability allow the selective demetalation of complexes VIII and X with HNS. Syntheses of polynuclear complexes containing a variety of different metals can be designed from knowledge of established transmetalation patterns and relative transmetalation reagent stabilities.

Introduction

Transmetalation of polynuclear halocopper complexes containing mono-[3-10] or bidentate[11] amine ligands with $M(NS)_n$ reagents is a valuable source of new heteropolynuclear metal complexes. Here, M is Co, Ni, Cu, or Zn, NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base ligand, and *n* is 2[3-8,10,11] or 3 (for M = Co).[9]

Scheme I summarizes the sequential transmetalation of copper(I) complexes $[NCuX]_4$ (I; N = *N,N*-dimethylnicotinamide; X = Cl or Br)[12] with *mer*-$Co(NS)_3$ (II) and $M(NS)_2$ reagents,



II

where NS is *S*-methyl isopropylidenehydrazinecarbodithioate.[9] Electron transfer from I to II precedes transmetalation of copper(I), and all the products contain cobalt(II).[9] The coproduct Cu(NS)(s) is virtually insoluble in methylene chloride and nitrobenzene and can be separated and weighed to establish transmetalation stoichiometries.[6,9] Coproducts $Cu(NS)_2$ and N_2S_2 (the latter from oxidation of coordinated NS)[6,9] are easily separated from desired polynuclear products by gel permeation chromatography or selective precipitation.

There are competing processes in Scheme I. For example, reaction of $N_3Cu_3Co(NS)_2X_4$ (III) with 1 mol of $M(NS)_2$ under dinitrogen gives heterometallic dimers VIII. Coproduct $Cu(NS)_2$ arises from NS ligand transfer in proposed intermediate VII, which is prevented by faster transmetalation of copper(II) in VII by 1 additional mol of $M(NS)_2$ to give IX. Products IX are aprotically oxidized by dioxygen to trimers X with the same CoM_2 constitutions. Products VI and VIII–X are easily distinguishable by specific metal analysis and other techniques.[9]

Product IV is obtained by aprotic oxidation of III with dioxygen via rate-determining insertion of O_2 into its M_4X_4 molecular core. Product IV characteristically loses a CuO unit on transmetalation with $M(NS)_2$ reagents: reaction of IV with 2 mol of $M(NS)_2$ gives trimeric complexes X.[9]

The following questions are addressed in this paper.

1. The reactions of I with II and $M(NS)_2$ were carried out sequentially; that is, III was allowed to form completely before $M(NS)_2$ was added.[9] Are the same products obtained by simultaneous transmetalation of I?
2. Do simultaneous reactions of III with 1 equiv each of $M(NS)_2$ and $M'(NS)_2$, where M and M′ are different metals, give IX (containing three different metals) or VIII (containing M or M′)?
3. Do the corresponding reactions of IV give X (containing three different metals)?
4. Can polynuclear complexes containing no copper by transmetalated with $M(NS)_n$ reagents?
5. Are heteropolymetallic complexes demetalated[3,11] selectively by HNS, the ligand from which $M(NS)_n$ reagents are made?[3]

Experimental Section

Materials. The syntheses of I, II, and $M(NS)_2$ (NS = *S*-methyl isopropylidenehydrazinecarbodithioate) followed literature methods.[9] Transmetalation reactions were run sequentially[9] or simultaneously in methylene chloride or nitrobenzene at room temperature. Twelve hours was sufficient to ensure completion of each process described in this paper. The products were separated and isolated as solids as described previously.[3-11]

Analytical Methods. Metal contents of isolated solid products were determined with a Leeman Laboratories inductively coupled plasma spectrometer after standard sample preparation.[3] The analytical wavelengths (nm) and detection limits (ng/mL) were as follows: Co (228.62, 8), Ni (231.60, 20), Cu(324.75, 3) and Zn (213.86, 7). Halogens were determined by titration with $Hg(NO_3)_2$ (diphenylcarbazone indicator) after decomposition with KOH/H_2O_2 in dioxygen.[13] Carbon, hydrogen, and nitrogen analyses were performed by MicroChem Laboratories, Lowell, MA. Analytical data are given in Tables I and II.

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Table I. Analytical and Cryoscopic Data for Products of Reaction of $N_3Cu_3Co(NS)_2Cl_4$ (III) and $N_3Cu_3CoCl_4O_2\cdot H_2O$ (IV) with Equimolar II, $M(NS)_2$, and $M'(NS)_2$ Reagents[a]

reaction	M, M′[c]	product, M[d]	C	H	N	X	Co	Ni	Cu	Zn	M_r[e]
					(i) Reactions of III[b]						
8, 9	Co, Ni	VIII, Co	46.0	6.1	10.8	13.5	11.5				1030 ± 20
	Co, Cu		(46.51)	(5.99)	(11.11)	(14.06)	(11.69)				(1009)
8, 9	Co, Zn	VIII, Zn	47.0	6.0	11.0	14.5	5.3			7.2	980 ± 20
	Ni, Zn		(47.29)	(5.96)	(11.03)	(13.97)	(5.81)			(6.45)	(1015)
	Cu, Zn										
8, 9	Ni, Cu	VIII, Ni	46.2	5.9	10.0	13.8	5.5	6.7			890 ± 20
			(46.51)	(5.99)	(11.11)	(14.06)	(5.9)	(5.9)			(1009)
8, 9	Co, Zn[f]	VIII, Zn	40.1	4.9	9.3	26.3	5.4			6.2	1160 ± 20
			(40.23)	(5.07)	(9.4)	(26.79)	(4.95)			(5.42)	(1193)
7	Co, Co[g]	IX, Co	40.8	5.0	11.8	11.6	15.0				1220 ± 30
			(40.83)	(5.15)	(11.90)	(12.07)	(15.06)				(1175)
7	Ni, Ni[g]	IX, Ni	40.6	5.7	10.7	12.6	5.5	9.3			1140 ± 30
			(40.83)	(5.15)	(11.90)	(12.07)	(5.02)	(10.03)			(1175)
7	Zn, Zn[g]	IX, Zn	40.2	4.9	11.6	12.4	4.2			9.93	1130 ± 30
			(40.43)	(5.05)	(11.79)	(11.95)	(4.97)			(10.95)	(1187)
13 + 14	II, Zn	X, Co, Zn	42.0	5.7	10.2	15.9	10.7			7.0	890 ± 20
			(41.18)	(5.26)	(9.61)	(15.55)	(11.6)			(6.4)	(912)
13 + 14	II, Co	X, Co	41.4	4.5	9.6	14.9	20.1				950 ± 20
			(41.43)	(4.87)	(9.67)	(15.66)	(19.55)				(906)
15, 5	II, Ni	VI	46.0	5.5	11.0	13.7	10.6				1000 ± 20
			(46.51)	(5.99)	(11.11)	(14.06)	(11.69)				(1009)
7	Cu, Cu[g]	X, Cu[h]	40.3	4.8	9.4	15.3	7.1		13.3		850 ± 20
			(40.96)	(4.82)	(9.56)	(15.2)	(6.23)		(13.6)		(933)
					(ii) Reactions of IV						
18	Ni, Ni[g]	X, Ni	39.8	5.3	9.0	15.4	6.2	11.4			930 ± 20
			(39.74)	(5.12)	(9.27)	(15.65)	(5.8)	(12.26)			(906)
18	Co, Co[g]	X, Co	41.4	4.7	9.6	15.6	19.2				830 ± 20
			(41.43)	(4.87)	(9.67)	(15.66)	(19.55)				(906)
18	Zn, Zn[g]	X, Zn	39.0	5.0	9.2	14.6	5.7			13.5	940 ± 20
			(39.22)	(5.05)	(9.15)	(14.86)	(6.18)			(13.62)	(954)
19	Ni, Zn	X, Ni, Zn	42.9	5.7	10.3	14.3	5.87	4.3		6.0	900 ± 20
			(41.18)	(5.26)	(9.61)	(14.06)	(4.99)	(4.99)		(5.55)	(912)
22b	II	XI, Co, Cu	43.9	5.7	10.4	15.4	11.7		2.3		830 ± 20
			(41.18)	(5.26)	(9.61)	(15.58)	(12.96)		(6.4)		(910)
23b	II, II	X, Co	41.1	4.9	9.6	15.9	20.2				875 ± 20
			(41.43)	(4.87)	(9.67)	(15.66)	(19.55)				(905)
24	II, Ni	VIII, Co	46.0	6.2	10.8	14.6	11.90				980 ± 20
			(46.51)	(5.99)	(11.11)	(14.06)	(11.69)				(1009)

[a] Analytical data are given for desired polynuclear products separated by gel permeation chromatography from each system. $M(NS)_2$ coproducts were identified from their distinctive spectra.[17] Product N_2S_2, where formed, was isolated and identified as described previously.[6] Calculated values are in parentheses. X = Cl except where noted. [b] Simultaneous reactions of I with II and the species in column 2 give the same respective products in each system (see text). [c] equimolar $M(NS)_2$ and $M'(NS)_2$ are given in the order of their appearance in the equations of column 1. [d] Symbols in Scheme I. [e] Measured cryoscopically in nitrobenzene at (3–5) × 10^{-2} molal. [f] X = Br. [g] Data from ref 9. [h] Obtained after aprotic oxidation of IX (M = Cu from eq 7; see text) with O_2.

Table II. Products of Transmetalation of Polynuclear Complexes Containing No Copper[a]

reaction	products, M	C	H	N	Cl	Co	Ni	Cu	Zn	M_r[c]
31, 32	X, Co[b]	41.0	4.5	9.3	15.4	20.1				920 ± 20
		(41.43)	(4.87)	(9.67)	(15.66)	(19.55)				(905)
33	VIII, Zn[b]	47.0	6.2	11.3	13.5	6.5			5.7	960 ± 20
		(47.29)	(5.96)	(11.06)	(13.97)	(5.8)			(6.4)	(1015)
34, 36, 39	VI[b]	45.9	6.2	10.8	14.3	12.0				960 ± 20
		(46.51)	(5.94)	(11.11)	(14.06)	(11.69)				(1009)
35	X, Zn[b]	39.0	5.0	9.3	15.0	6.3			13.0	1000 ± 30
		(39.22)	(5.05)	(9.15)	(14.86)	(6.18)			(13.68)	(954)
40	$N_4Zn_2Cl_4\cdot 2H_2O$	46.8	5.8	14.0	13.8				12.8	920 ± 20
		(47.56)	(6.15)	(14.22)	(14.41)				(13.21)	(984)
41	$N_3Co_2Cl_4\cdot 3H_2O$	45.45	5.5	10.6	17.1	14.2				730 ± 20
		(45.34)	(5.59)	(10.58)	(17.85)	(14.86)				(794)

[a] Analytical data are given for desired polynuclear products separated by gel permeation chromatography for each system. $M(NS)_2$ coproducts were identified from their distinctive spectra.[17] Product N_2S_2, where formed, was isolated and identified as described previously.[6] Calculated values are in parentheses. [b] Symbols in Scheme I. [c] Measured cryoscopically in nitrobenzene at (3–5) × 10^{-2} molal.

The molecular weights, M_r, of transmetalation products were established by cryoscopy at the (3–5) × 10^{-2} molal level in nitrobenzene.[3,12] Standard techniques were followed in spectrophotometric titrations of products IV, VI, VIII, and X with *S*-methyl isopropylidenehydrazinecarbodithioate, HNS,[3] in methylene chloride at room temperature to determine reactant ratios for selective, stoichiometric demetalation.

Relative $M(NS)_2$ Reagent Stabilities. The spectra of solutions obtained by reacting equimolar amounts of anhydrous $M(NS)_2$ and $M'Cl_2$ in ethanol[14] at room temperature overnight (eq 1) were measured with a Beckman DK-1A spectrophotometer with matched quartz cells. The

$$M(NS)_2 + M'Cl_2 \rightarrow MCl_2 + M'(NS)_2 \qquad (1)$$

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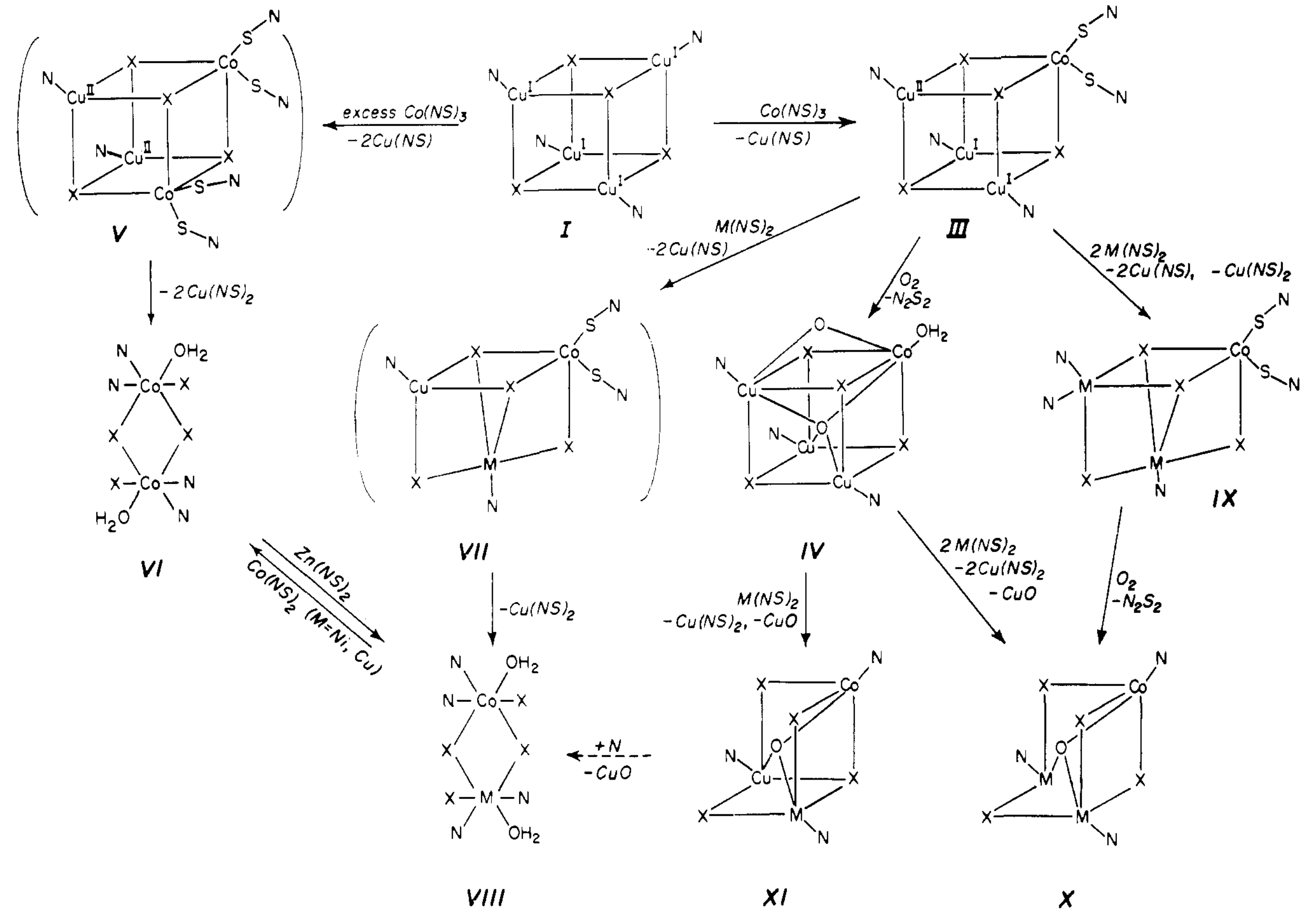
(14) The metal chlorides are insoluble in methylene chloride and nitrobenzene, which necessitated the use of ethanol as the solvent in eq 1.

Scheme I



reactions involving M or M′ = Co were conducted under dinitrogen because Co(NS)$_2$ is air-sensitive.[6]

NS Ligand Removal from II by N$_4$M$_2$Cl$_4$ Complexes. The products of reactions of Co(NS)$_3$ (II) with 0.5 mol of dimers N$_4$M$_2$Cl$_4$ (M = Ni, Co, Cu, Zn)[6,9] in methylene chloride under dinitrogen at room temperature were separated by gel permeation chromatography and identified from their spectra.[6,9]

Results and Discussion

Sequential or Simultaneous Transmetalation. Our previous work on the transmetalation of I by M(NS)$_2$[6] and Co(NS)$_3$[9] reagents in aprotic solvents is summarized in eq 2–5 and Scheme I.

$$\mathrm{I + M(NS)_2 \rightarrow N_3Cu_3M(NS)X_4 + N + Cu(NS)(s)} \quad (2)$$

$$\mathrm{I + 2M(NS)_2 \rightarrow N_4M_2X_4 + 4Cu(NS)(s)} \quad (3)$$

$$\mathrm{I + II \rightarrow III + N + Cu(NS)(s)} \quad (4)$$

$$\mathrm{I + 2II \rightarrow VI + 2Cu(NS)_2 + 2Cu(NS)(s)} \quad (5)$$

Reactions 3 and 5 give dimeric products even in the presence of excesses of the respective transmetalating agents.[6,9] We have found in subsequent work that reactions 3 and 5 can be conducted in steps via reactions 2 and 4, respectively, and that there is no effect of removing the precipitated Cu(NS)(s) if these routes to homodimeric products N$_4$M$_2$X$_4$ are followed.

Scheme I illustrates the products obtained by sequential transmetalation of I with II (to give III) and then M(NS)$_2$ reagents.[9] In subsequent work we have found that reactions 6 and 7 can both be run in one step, without the need to preform

$$\mathrm{I + II + M(NS)_2 \rightarrow VIII + Cu(NS)_2 + 3Cu(NS)(s)} \quad (6)$$

$$\mathrm{I + II + 2M(NS)_2 \rightarrow IX + Cu(NS)_2 + 3Cu(NS)(s) + N} \quad (7)$$

III. Incorporation of cobalt in products IX indicates that II transmetalates I faster than any of the M(NS)$_2$ complexes (M = Co, Ni, Cu, or Zn) at comparable concentrations. There is evidence that electron transfer from I to II precedes transmetalation (Scheme I),[9] which may be the origin of the highest relative reactivity of II as a transmetalating agent for I.[15]

Curious Behavior of Cu(NS)$_2$ in Eq 7. Reaction of III with 1 mol of M(NS)$_2$ gives intermediate VII, which contains one copper(II) center and collapses by intramolecular NS ligand transfer to give VIII.[9] We have concluded that a second 1 mol of M(NS)$_2$ (M = Co, Ni, or Zn) transmetalates the copper(II) of VII to give IX. This should not be the case with M = Cu since Cu(NS)$_2$ should not transmetalate VII. Nevertheless, reaction 7 proceeds to give IX (M = Cu) and not VIII (M = Cu). We conclude that excess Cu(NS)$_2$ inhibits NS ligand transfer from cobalt(II) to copper(II) in VII.

Simultaneous Transmetalation of I with II, M(NS)$_2$, and M′(NS)$_2$ Reagents, Where M and M′ Are Different Metals. We found that reactions 8 take place when I is simultaneously reacted with 1 mol each of II, M(NS)$_2$, and M′(NS)$_2$, where M and M′ are different metals (cf. eq 7). The same respective products VIII

$$\mathrm{I + II + M(NS)_2 + M'(NS)_2 \rightarrow VIII + M'(NS)_2 + Cu(NS)_2 + 3Cu(NS)(s)} \quad (8)$$

(Table I) were obtained by treating III (preformed in eq 4) simultaneously with 1 mol each of M(NS)$_2$ and M′(NS)$_2$ (eq 9).

$$\mathrm{III + M(NS)_2 + M'(NS)_2 \xrightarrow{N} VIII + M'(NS)_2 + Cu(NS)_2 + 2Cu(NS)(s)} \quad (9)$$

In each case we found that M′ in isolated products VIII was below its limit of detection, indicating that the reactions follow eq 6 as if no M′(NS)$_2$ were present. The exclusion of M′ arises, at least in part, from differences in stability of M(NS)$_2$ complexes, as described in the next section.

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[15] There is a good possibility that inner-sphere electron transfer takes place in $\overline{\mathrm{Cu^{I}{-}X{-}Co^{III}{-}S}}$ rings like those felt to be necessary for transmetalation of copper(II) by M(NS)$_2$.[5,10]

Table III. Products of Reaction of $M(NS)_2$ with Equimolar $M'Cl_2$ in Ethanol at 25 °C (Equation 1)

	M'			
M	Cu	Ni	Co[b]	Zn
Cu	*a*	*a*	*a*	*a*
Ni	$Cu(NS)_2$, $NiCl_2$	*a*	*a*	*a*
Co[b]	$Cu(NS)_2$, $CoCl_2$	$Ni(NS)_2$, $CoCl_2$	*a*	*a*
Zn	$Cu(NS)_2$, $ZnCl_2$	$Ni(NS)_2$, $ZnCl_2$	$Co(NS)_2$, $ZnCl_2$	*a*

[a] No reaction observed. [b] Conducted under N_2 (see text).

Relative $M(NS)_2$ Stabilities. Table III summarizes the results of metal-exchange reactions 1[14] and indicates that the stabilities of $M(NS)_2$ complexes decrease in the order M = Cu > Ni > Co > Zn, as expected from data for many other ligands.[16] The $M(NS)_2$ complexes cited have very different electronic spectra and are easily distnguishable in mixtures.[17] Product spectra indicated that, when observed, reactions 1 are quantitative; for example, $Ni(NS)_2$ formation was at least 98% complete with M = Co and M' = Ni in eq 1. Thus, the stabilities of $M(NS)_2$ reagents are substantially different.

Interpretation of Reactions 8. The results in Table I indicate that the metal incorporated in product VIII of eq 8 and 9 is that which forms the weaker $M(NS)_2$ complex (Table III).

We interpret reactions 8 as follows.

1. Intermediate VII forms in reaction 10 because (a) II transmetalates I faster than do equimolar $M(NS)_2$ and $M'(NS)_2$, the product being III (eq 3), (b) $M(NS)_2$ transmetalates III faster than does $M'(NS)_2$, and (c) copper(I) in III is transmetalated in preference to copper(II) by $M(NS)_2$ because Cu(NS)(s) is more stable than dissolved $Cu(NS)_2$.[9]

$$\mathrm{I + II + M(NS)_2 \rightarrow VII + 3Cu(NS)(s)} \qquad (10)$$

2. NS ligand transfer from cobalt(II) to copper(II) in VII (eq 11) is faster than transmetalation of this copper(II) by $M'(NS)_2$ (eq 12).

$$\mathrm{VII \xrightarrow{N} VIII + Cu(NS)_2} \qquad (11)$$

$$\mathrm{VII + M'(NS)_2 \xrightarrow{N} IX + Cu(NS)_2} \qquad (12)$$

3. When M = M' (eq 7), the three copper centers of III are transmetalated at similar rates so that VII does not accumulate. This eliminates the possibility of NS ligand transfer from cobalt to copper to give VIII.

4. The rates of transmetalation of copper(I) and copper(II) centers in III by $M(NS)_2$ reagents decrease in the order M = Zn > Co > Ni > Cu, which is the reverse of stabilities of the respective $M(NS)_2$ complexes.

We conclude that reactions 8 and 9 with any combination of different M and M' = Co, Ni, Cu, or Zn are not a source of trimers IX and X containing three different metals, where one is cobalt, because of particular relationships between the rates of competing reactions in Scheme I.

Relative Reactivities of II and $M(NS)_2$ as Transmetalating Agents for III. Reactions 7 and 8 indicate that II transmetalates I more rapidly than $M(NS)_2$ to give III as an intermediate product. The relative reactivities of II and $M(NS)_2$ as transmetalators for III are indicated by simultaneous reactions 13 and 15. We interpret these reactions as follows.

$$\mathrm{III + II + M(NS)_2\ (M = Zn, Co) \rightarrow N_3CoMCo(NS)_2X_4 + 2Cu(NS)_2 + Cu(NS)(s)} \qquad (13)$$

$$\mathrm{N_3CoMCo(NS)_2X_4 + {}^1/_2O_2 \rightarrow N_3Co_2MX_4O + N_2S_2} \qquad (14)$$

$$\mathrm{III + II + Ni(NS)_2 \xrightarrow{N} VI + Ni(NS)_2 + 2Cu(NS)_2 + Cu(NS)(s)} \qquad (15)$$

1. The production of 1 mol of Cu(NS)(s), established gravimetrically, indicates that III, like I, is most rapidly transmetalated by II to give V[15] (Scheme I): if $M(NS)_2$ were the primary transmetalator, we would have observed 2 mol of Cu(NS)(s) (eq 16; cf. eq 9).[6]

$$\mathrm{III + II + M(NS)_2 \rightarrow VII + II + 2Cu(NS)(s)} \qquad (16)$$

2. One of the two copper(II) centers in V is transmetalated by $M(NS)_2$ (M = Co or Zn) at significantly higher rates than NS ligand transfer from cobalt(II) to copper(II) to give VI. This is not the case with M = Ni, and reaction 17 proceeds as if $Ni(NS)_2$ were absent.

$$\begin{tikzcd} \mathrm{III + II} \arrow[r] & \mathrm{V + Cu(NS)(s)} \arrow[d, "\mathrm{N}"'] & \\ & \mathrm{VI + 2Cu(NS)_2} & (17) \end{tikzcd}$$

Transmetalation of IV by Equimolar $M(NS)_2$ and $M'(NS)_2$. Aprotic oxidation of III with dioxygen removes its NS ligands (as the disulfude N_2S_2) and gives IV.[9] Reactions 18 are a source

$$\mathrm{IV + 2M(NS)_2 \rightarrow X + 2Cu(NS)_2 + CuO} \qquad (18)$$

of trimers X (Scheme I) and are characteristic of structure IV.[6,9] We found that reaction 19 gives a trimeric product containing three different metals (Table I) irrespective of the great difference of transmetalating agent stabilities (Table III). From the previous results we anticipate that IV is first transmetalated by $Zn(NS)_2$. The result of reaction 19 indicates that reaction 20, like eq 18, prevents reaction 21, which slowly gives VIII.[9]

$$\mathrm{IV + Zn(NS)_2 + Ni(NS)_2 \rightarrow N_3CoNiZnCl_4O + 2Cu(NS)_2 + CuO} \qquad (19)$$

$$\mathrm{XI\ (M = Zn) + Ni(NS)_2 \rightarrow N_3CoNiZnCl_4O + Cu(NS)_2} \qquad (20)$$

$$\mathrm{XI\ (M = Zn) \xrightarrow{N} VIII + CuO} \qquad (21)$$

Transmetalation of IV by II. Reactions 22c and 23b occurred on treatment of dioxo complex IV with 1 and 2 mol of II, respectively.

$$\begin{tikzcd} \mathrm{IV + II} \arrow[r] & \mathrm{XI\ (M = Co^{III}(NS)) + Cu(NS)_2 + CuO} \arrow[d] & (22a) \\ & \mathrm{XI\ (M = Co^{II}) + NS\cdot} \arrow[d, "\mathrm{N}"'] & (22b) \\ & \mathrm{VIII\ (M = Co^{II}) + CuO} & (22c) \\ \mathrm{IV + 2II} \arrow[r] & \mathrm{X\ (M = Co^{III}(NS)) + 2Cu(NS)_2 + CuO} \arrow[d] & (23a) \\ & \mathrm{X\ (M = Co^{II}) + N_2S_2} & (23b) \end{tikzcd}$$

Overall reaction 22c is analogous to transmetalation of IV with 1 mol of $Co(NS)_2$ (Scheme I[9]), and the product also contains cobalt(II) (Table I). We invoke eq 22b to explain cobalt(II) formation (see next section). In both cases the copper content of the product is low because XI from (22b) slowly loses CuO to give VIII (eq 22c).[9] This process is prevented in reaction 23, which is the analogue of reactions 18. Reaction 23 was run in the absence of dioxygen, but the product contained cobalt(II). The two $Co^{III}(NS)$ units of X evidently are unstable (eq 23b), as expected for cobalt(III) centers containing a preponderance of O and/or X donor atoms[18] and demonstrated in the next section.

We also examined competitive transmetalation of IV by II and $Ni(NS)_2$ (eq 24). The analytical data for the isolated product

$$\mathrm{IV + II + Ni(NS)_2 \xrightarrow{N} VIII\ (M = Co) + Cu(NS)_2 + Ni(NS)_2 + 2CuO + NS\cdot} \qquad (24)$$

(Table I) indicate negligible copper, very low nickel, and a cobalt content approaching that of dimer VIII (M = Co). This is consistent with most rapid transmetalation of IV by II followed by unusually rapid loss of 1 mol of CuO from XI (M = Co(NS))

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(17) (a) El-Sayed, L.; El-Toukhy, A.; Iskander, M. F. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1739. (b) El-Sayed, L.; El-Toukhy, A.; Iskander, M. F. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 300. (c) Iskander, M. F.; Mishrikey, M. M.; El-Sayed, L.; El-Toukhy, A. *J. Inorg. Nucl. Chem.* **1979**, *41*, 815. (d) Iskander, M. F.; El-Sayed, L.; El-Toukhy, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1145.

(18) Bodek, I.; Davies, G. *Inorg. Chem.* **1976**, *15*, 922 and references therein.

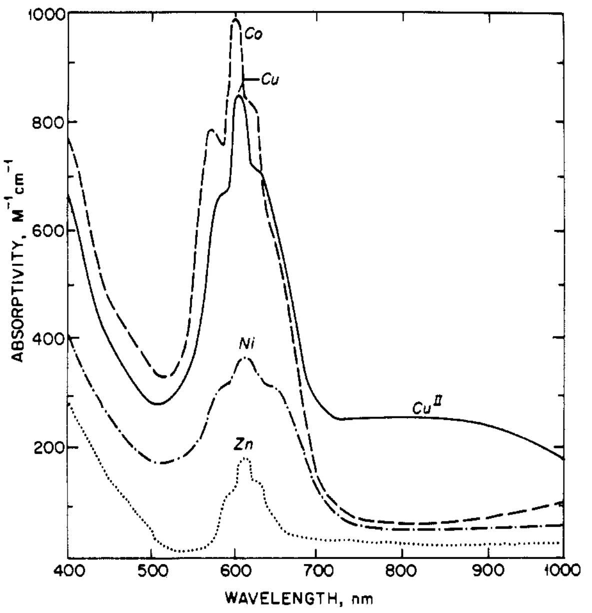

Figure 1. Electronic spectra of $N_3CoM_2(H_2O)_3Cl_4O$ complexes in methylene chloride at 25 °C.

to give VIII (M = Co) and NS·. The latter dimerizes to the disulfide in eq 25.[9]

$$2NS\cdot \rightarrow N_2S_2 \qquad (25)$$

High Reactivity of II for the Transmetalation of IV. All the reactions of the previous section involve transmetalation of copper(II) in IV by cobalt(III) in II. The quantitative production of $Cu(NS)_2$ indicates that $Cu(NS)_2$, the most stable of the $M(NS)_2$ complexes (Table III), is more stable than II. We observed reaction 28 at room temperature in methylene chloride. The products were separated by gel permeation chromatography and identified from their spectra.[9,17] We propose that reaction 28 proceeds via reactions 26[19] and 27. Reaction 26 removes two

$$II + N_2CuCl_2 \rightarrow Co^{III}(NS) + Cu(NS)_2 \qquad (26)$$

$$Co^{III}(NS) \rightarrow N_2Co^{II}Cl_2 + NS\cdot \qquad (27)$$

$$\text{net:}\quad II + N_2CuCl_2 \rightarrow N_2Co^{II}Cl_2 + Cu(NS)_2 + NS\cdot \qquad (28)$$

NS ligands from II; the product $Co^{III}(NS)$ (other ligands omitted) decomposes by electron transfer from NS to cobalt(III) to give cobalt(II) and NS·. The disulfide N_2S_2 is then formed in eq 25.

Reaction 28 was also observed for Ni and Co, but not Zn, replacing copper(II). Thus, the complete stability order of the transmetalating agents is $Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 > Zn(NS)_2$. We can now predict that $Zn(NS)_2$ and II will transmetalate cobalt(II),[20] nickel(II), and copper(II) centers, as demonstrated after discussion of trimers X.

Trimers X. Trinuclear complexes X (Scheme I) are members of a new class of oxometal complexes obtained by transmetalation of IV with $M(NS)_n$ reagents (eq 18, 19, or 23) or by oxidation of IX with dioxygen (Scheme I). Other examples can be obtained by oxidizing $N_3Cu_3M(NS)X_4$ complexes from eq 2 (M = Ni, Co, or Zn) with dioxygen (eq 29) and then transmetalating the products IV[6] with $M(NS)_n$ reagents as in eq 18, 19, or 23.

$$N_3Cu_3M(NS)X_4 + O_2 \rightarrow \underset{IV}{N_3Cu_3MX_4O_2} + {}^1/_2N_2S_2 \qquad (29)$$

Figure 1 shows electronic spectra for complexes $N_3Co(M(H_2O))_2Cl_4O$ obtained from reactions 18 with M = Co, Ni, Cu, or Zn. All the complexes contain 4- or 5-coordinate cobalt(II), as indicated by intense maxima at 610 nm and shoulders at 575 and 630 nm.[9]

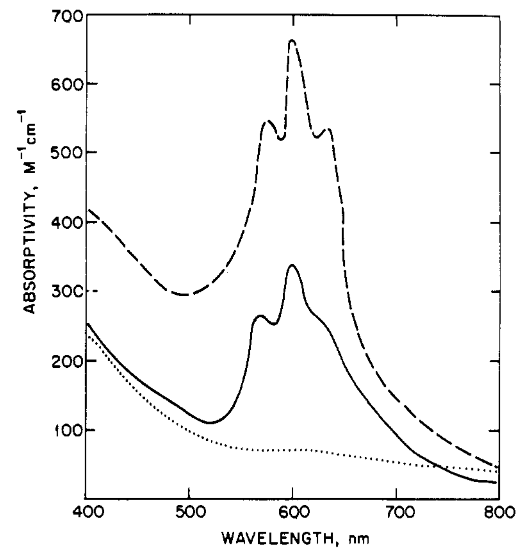

Figure 2. Electronic spectra of $N_3Co_2Zn(H_2O)_3Cl_4O$ (---), $N_3CoNiZn(H_2O)_3Cl_4O$ (—), and $N_3Ni_3(H_2O)_3Cl_4O$ (···) complexes in methylene chloride at 25 °C.

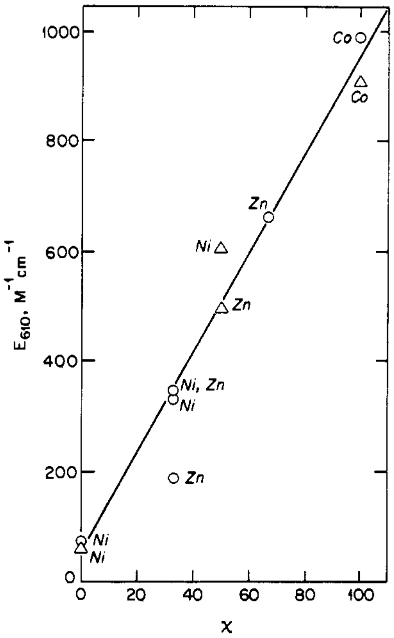

Figure 3. Plot of E_{610} vs. x (see text for definitions) for dimers VIII (M = Co, Ni, Zn) (△) and trimers X (○) in methylene chloride at 25 °C. The metal M present in each product is indicated for each point.

Figure 2 shows the electronic spectrum of $N_3(Ni(H_2O))_3Cl_4O$, obtained from reactions 29 (M = Ni, X = Cl)[6] and 30.[21] Its

$$N_3Cu_3NiX_4O_2 + 2Ni(NS)_2 \rightarrow N_3(Ni(H_2O))_3X_4O + 2Cu(NS)_2 + CuO \qquad (30)$$

features at 410 nm (ϵ 230 M^{-1} cm^{-1}), 610 nm (70), and 750 nm (45) are similar to those in $N_4(Ni(H_2O))_2Cl_4$ from eq 3 after chromatographic separation.[6] Also shown in Figure 2 are the electronic spectra of $N_3Co_2Zn(H_2O)_3Cl_4O$ (from eq 13; M = Zn, X = Cl) and $N_3CoNiZn(H_2O)_3Cl_4O$ (from eq 19). Absorption due to cobalt(II)[9] dominates these spectra, as found for the $N_3CoM_2(H_2O)_3Cl_4O$ complexes (Figure 1).

In Figure 3 we show E_{610} vs. x for complexes VIII (M = Ni or Zn) and X (containing Co, Ni, or Zn). Here, E_{610} is the molar

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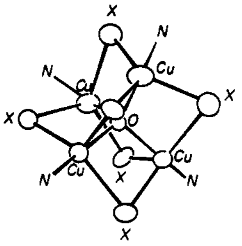
(19) Dimers $N_4M_2Cl_4$ are represented as monomers N_2MCl_2 in eq 26 and 28 to simplify description of the stoichiometry.

(20) No new metal centers are introduced by transmetalation of cobalt(II) with II, although N_2S_2 is obtained because of electron transfer from NS to cobalt(III) (see text).

(21) Anal. Calcd for $N_3(Ni(H_2O))_3Cl_4O$: Ni, 19.6; M_r = 906. Found: Ni, 20.4; M_r = 1020 ± 30.

absorptivity at 610 nm and x is the atomic percentage of metal as cobalt in a given complex (50% for N_4CoMCl_4 cores VIII, and so on). We observe that E_{610} increases linearly with x: eight of ten cobalt(II) centers in dimers VIII and trimers X containing different combinations of cobalt, nickel, and zinc are spectrally indistinguishable.[22]

Many attempts to crystallize a variety of complexes IV and X have resulted in disproportionation[6,9] or crystals of insufficient quality for X-ray structural characterization. However, we have presented evidence for proposed structure IV[9] and now wish to consider structures for X.



XII

The structure of $N_4Cu_4Cl_6O$ (XII) consists of a central μ_4-oxo group and 2-coordinate halide on each tetrahedral edge.[3] This last structural feature is also present in VIII.[6,9] Structures VIII, X, and XII all contain monodentate N (single IR band at 1630–1635 cm^{-1}).[3] They all can be completely transmetalated with appropriate $M(NS)_n$ reagents with no change in their nuclearity: further examples for X are given in eq 31 and 32. We

$$N_3(Ni(H_2O))_3Cl_4O + 3Co(NS)_2 \rightarrow N_3(Co(H_2O))_3Cl_4O + 3Ni(NS)_2 \quad (31)$$

$$N_3(Ni(H_2O))_3Cl_4O + 3II \rightarrow N_3(Co(H_2O))_3Cl_4O + 3Ni(NS)_2 + {}^3/_2N_2S_2 \quad (32)$$

also find that progressive replacement of copper(II) with nickel(II) in XII[3,10] and cobalt(II) with nickel or zinc in structures VIII or X (Figure 3) results in linear changes in their respective dominant spectral features. The representative structure X in Scheme I reflects our tentative opinion that the cores of VIII, X, and XII all contain 2-coordinate halo bridges, which would be consistent with their distinctive spectral and transmetalation properties. The μ_3-oxo group in proposed X is retained solely because it is also believed to be present in IV.[6,9] Similar spectral behavior on transmetalation of VIII, X, and XII indicates that no specific or limiting function can be ascribed to bridging oxo groups in structures X and XII. In sharp contrast, the μ-oxo groups in $(\mu\text{-oxo})_2N_4Cu_4X_4$ complexes (N = *N,N*-diethylnicotinamide[3] or ethyl nicotinate[4]) definitely limit the extent of their transmetalation by $Ni(NS)_2$ reagents[3,4] and their substitution by *N,N,N′,N′*-tetraethylethylenediamine.[3]

Transmetalation of Centers Other Than Copper. Reactions 31–36 demonstrate that products VI, VIII, and X containing no copper can indeed be transmetalated with $M(NS)_n$ reagents of low relative stability. The indicated $M(NS)_2$ products were

$$VI + Zn(NS)_2 \rightarrow VIII\ (M = Zn) + Co(NS)_2 \quad (33)$$

$$VIII\ (M = Ni) + Co(NS)_2 \rightarrow VI + Ni(NS)_2 \quad (34)$$

$$X\ (M = Ni) + 2Zn(NS)_2 \rightarrow X\ (M = Zn) + 2Ni(NS)_2 \quad (35)$$

$$N_4Ni_2Cl_4 + 2II \rightarrow VI + 2Ni(NS)_2 + N_2S_2 \quad (36)$$

identified as the second of two well-separated colored bands eluted by gel permeation chromatography (methylene chloride eluant) of product mixtures. All the reactions were quantitative.

Selective Demetalation of Heteropolynuclear Metal Complexes by HNS. The high stabilities of Cu(NS)(s) and $Cu(NS)_2$ lead to complete, stoichiometric demetalation of copper(I) and copper(II) complexes by HNS (eq 37 and 38, respectively).[3,11]

$$I + 4HNS \rightarrow 4Cu(NS)(s) + 4N + 4HX \quad (37)$$

$$N_4Cu_4X_4O_2 + 8HNS \rightarrow 4Cu(NS)_2 + 4N + 4HX + 2H_2O \quad (38)$$

We found that products VI, VIII, and X can also be stoichiometrically demetalated with HNS and that demetalation is selective and predictable from our study of $M(NS)_n$ stabilities. For example, reactions 39–41 in methylene chloride were demonstrated by separation of the products by gel permeation chromatography.

$$VIII\ (M = Ni) + 2HNS \rightarrow {}^1/_2N_4Co_2X_4 + Ni(NS)_2 + 2HX \quad (39)$$

$$VIII\ (M = Zn) + 2HNS \rightarrow {}^1/_2N_4Zn_2X_4 + Co(NS)_2 + 2HX \quad (40)$$

$$X\ (M = Ni) + 4HNS \rightarrow {}^1/_2N_3Co_2X_4 + 2Ni(NS)_2 + H_2O + 2HX \quad (41)$$

In each case the second of two colored bands was identified from its spectrum[17] as a solution of the indicated $M(NS)_2$ complex.

Conclusions. $M(NS)_n$ complexes are excellent, quantitative transmetalating agents for polynuclear metal complexes containing mono- or bidentate amine ligands. Transmetalation proceeds at convenient rates at room temperature, and the products are easily separated. Syntheses can be designed to give products that are predictable on the basis of established transmetalation patterns and the relative stabilities of $M(NS)_n$. These stabilities are sufficiently different for sequential transmetalation to be unnecessary. Polynuclear complexes can be selectively demetalated by HNS. The products are predictable from the relative $M(NS)_n$ stability order.

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[22] The large deviation for $N_3CoZn_2(H_2O)_3Cl_4O$ (X, Scheme I, M = Zn: E_{610}(calcd) = 340; E_{610}(found) = 190) in Figure 3 suggests a substantially different cobalt(II) environment in this particular complex.