Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Davies, Geoffrey , El-sayed, Mohamed A. and El-toukhy, Ahmed(1989) 'Transmetalation: A New Route to Heteropolymetallic Molecules and Materials', Comments on Inorganic Chemistry, 8: 5, 203 — 220
To link to this Article: DOI: 10.1080/02603598908035795
URL: http://dx.doi.org/10.1080/02603598908035795

Transmetalation: A New Route to Heteropolymetallic Molecules and Materials

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The newly discovered transmetalation of polymetallic molecules by mononuclear transmetalators is an excellent source of a wide variety of related heteropolyatomic molecules and materials that cannot be obtained by other means. The systems discussed involve easily obtained reactants, stoichiometric reactions and easily separated products. Among the factors that affect specific transmetalation patterns are target structure, transmetalator identity and relative stability, redox phenomena, intramolecular ligand transfer and specific types of primary product fragmentation. A feature of reported transmetalation systems that make them excellent candidates for the production of new materials is that they are stoichiometric and flexible. Prospects for extending known systems to new targets and elements are discussed.

Key Words: *cobalt, electron transfer, fragmentation, heteropolymetallic molecules, intramolecular ligand transfer, nickel, oxocopper(II), S-methyl hydrazinecarbodithioate Schiff base, supported catalysts, trans-effect, transmetalation, transmetalation limits, zinc*

Comments Inorg. Chem.
1989, Vol. 8, No. 5, pp. 203–220
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The availability of bimetallic and related heteropolymetallic systems is essential to a deeper understanding of the effect of one metal on reactions at another.[1-4] For example, there are obvious benefits from an ability to generate families of discrete entities $M_vM'_xM''_yM'''_z$, where the sum of integers $v \ldots z$ is fixed and M . . . M''' represent different elements. We need simple, reproducible means of varying $v \ldots z$ and M . . . M''' in atomic clusters on surfaces or in polyatomic molecules.

Bearing in mind that metal complexes are potential precursors of supported metal clusters,[5,6] we are interested in efficient methods of generating large numbers of heteropolymetallic molecules having different fixed core structures. For example, there are 20 possible entities of stoichiometry $(M,M',M'',M''')_3$, where M . . . M''' represent four different elements in a fixed geometry like trigonal CuRuZn. What are the chances that all such metallic clusters can be obtained on a support either by reduction of different sources of each element[5,6] or by conventional demetalation/remetalation procedures on particular molecular precursors?[7] We would be fortunate indeed to obtain just a few examples from the list by these methods. A more fruitful approach would be to directly substitute one metal, M, in a polymetallic complex with another, M', as in Eq. (1).

$$A \equiv M + M'B \rightarrow A \equiv M' + MB \qquad (1)$$

These are the thoughts of some coordination chemists who came upon the direct, stoichiometric replacement of metals M in polymetallic complexes with different metals M' under very mild conditions. The discovery was accidental,[8] in that we were expecting adduct formation, Eq.(2),

$$(\mu\text{-}O)_2N_4Cu_4X_4 + [Zn(N_2S_2)]_2 \rightarrow \mathbf{I} \cdot (Zn(N_2S_2))_2 \qquad (2)$$

between the basic sites of polynuclear dioxocopper(II) complexes **I** (N is a monodentate pyridine, X = Cl or Br; Fig. 1) and the molecule $[Zn(N_2S_2)]_2$ **A** (Fig. 2), whose dimeric structure is broken by Lewis bases such as pyridines, Eq. (3).[9]

$$\mathbf{A} + 2py \rightarrow 2Zn(N_2S_2) \cdot py \qquad (3)$$

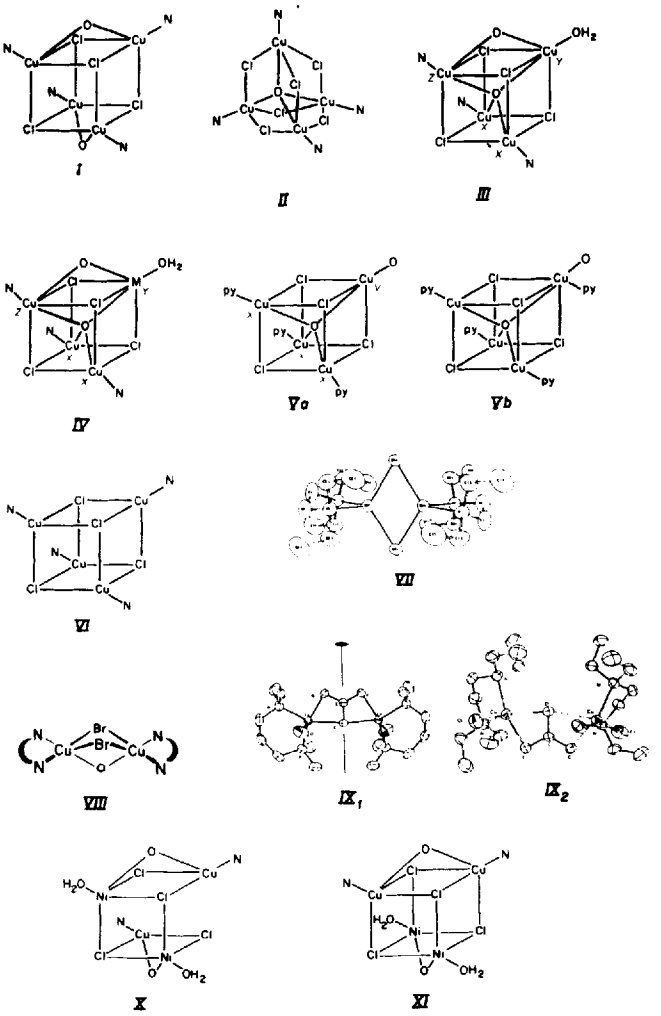

FIGURE 1 Some easily obtained, neutral copper transmetalation targets. Complexes **I** and **V** are obtained by aprotic oxidation of **VI** (N = monodentate N,N-diethylnicotinamide, py = pyridine) with dioxygen (Ref. 31 and citations). Attempted crystallization of **I** and **V** usually gives core structure **II** (Refs. 12 and 14). Complexes **III** and **IV** are obtained by transmetalation of **VI** with **B**, **C**, or **E** followed by oxidation with dioxygen (Refs. 15, 20, 21). Oxidation of complexes of type **VII** with dioxygen gives postulated structures **VIII** (Ref. 26 and citations). In the presence of CO_2 the products are represented by carbonates **IX** (Ref. 26 and citations). Isomers **X** and **XI** result from the transmetalation of **I** with excess **C** and **D**, respectively (Refs. 14, 18).

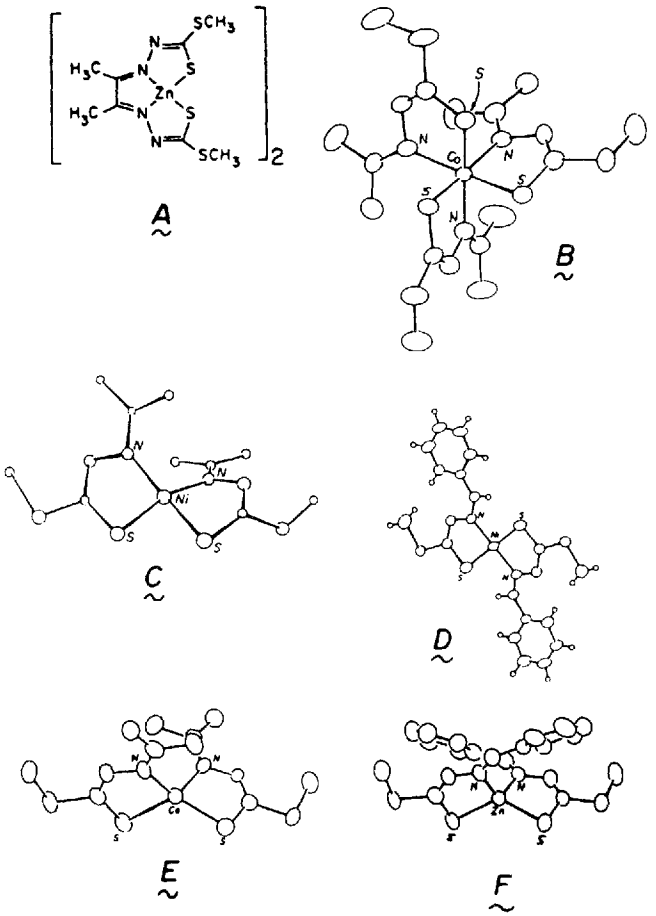

FIGURE 2 Some neutral hydrazinecarbodithioate transmetalators (Ref. 10).

We instead observed the complete replacement of copper by zinc, Eq. (4).

$$\mathbf{I} + 2\mathbf{A} \rightarrow (\mu\text{-O})_2N_2Zn_4X_4 + 2[Cu(N_2S_2)]_2 + 2N \qquad (4)$$

whose stoichiometry was easily established by spectrophotometric measurements of coproduct $[Cu(N_2S_2)]_2$. We called this phenom-

enon *transmetalation*.[8] However, the other transmetalation product, $(\mu\text{-O})_2N_2Zn_4Cl_4$, was found to be inherently unstable, Eq. (5),

$$(\mu\text{-O})_2N_2Zn_4X_4 \rightarrow N_2Zn_2X_4 + 2ZnO(s) \quad (5)$$

and so we had not succeeded in preserving the core structure of the target molecule, **I**.[8] Such *direct* transmetalation was subsequently achieved by substituting other metals like Ni for Zn in Eq. (4) and employing mononuclear transmetalators like **B-F**[10] that substitute single metal sites rather than pairs.

The key to this discovery was the very special properties of S-methyl hydrazinecarbodithioate Schiff base ligands, which can easily be varied.[9b,11] The results are exciting because there are no other general methods of obtaining the simple heteropolymetallic molecules to be described.

TRANSMETALATION REQUIREMENTS

With many desirable attributes of easily obtained, related heteropolymetallic molecules in mind, we present a "wish-list" of requirements for useful transmetalation systems through an example.

Equation (6) summarizes a series of transmetalation reactions.

$$(\mu_4\text{-O})N_4Cu_4X_6 + xM(NS)_2 \rightarrow (\mu_4\text{-O})N_4Cu_{4-x}M_xX_6 + xCu(NS)_2 \quad (6)$$

Here, N is a monodentate amine, X is Cl or Br, x is 0-4 and NS is the monoanionic Schiff base ligand S-methyl isopropopylidenehydrazinecarbodithioate in **B**, **C** and **E**. The very useful attributes of this series of reactions are as follows.

1. *Easy Reactant Synthesis from Readily Available Materials.* Reactants **II**, Fig. 1, are obtained in high yield by treating equimolar amounts of CuX_2 and N with NaOMe in methanol, or by substitution of amines for acetone in $(\mu_4\text{-O})\text{-(acetone)}_4Cu_4X_6$.[12] Transmetalator **C** is obtained in high yield by reacting nickel acetate with two equivalents of HNS, which comes from a straightforward

three-step synthesis. In this case the third step condenses acetone with S-methyl hydrazinecarbodithioate.[13]

2. *High Reactant Solubility in Easily Purified and Recovered, Non-Coordinating Aprotic Solvents.* The reactants of Eq. (6) are neutral and highly soluble as unassociated molecules in easily recoverable, aprotic solvents like methylene chloride.[14] As a result, the transmetalation products are independent of reactant concentration at fixed molar reactant ratio, and large scale syntheses are thus possible at minimal cost. Acid–base interactions with the solvent or any reactant molecularity changes would have given rise to different products under different experimental conditions.

3. *Stoichiometric Reactions.* Each of the four steps of Eq. (6) is stoichiometric because (a) coproduct $Cu(NS)_2$ is much more stable than **C**[15] and (b) transmetalation of $(\mu_4\text{-O})N_4Cu_3NiX_6$ is slower than that of $(\mu_4\text{-O})N_4Cu_4X_6$ and so on.[16] Attribute (a) ensures that each reaction step goes to completion. Attribute (b) leads to pure products like $(\mu_4\text{-O})N_4Cu_3NiX_6$ rather than, say, mixtures of fully transmetalated $(\mu_4\text{-O})N_4Ni_4X_6$ and unreacted $(\mu_4\text{-O})N_4Cu_4X_6$ at $x = 1$.[17]

4. *Rapid Reactions under Mild Conditions.* Reactions (6) are rapid at 25°C in methylene chloride or nitrobenzene.[22,26] More severe conditions could easily have resulted in changes in target molecularity or caused reactant decomposition, leading to mixtures of products that are difficult to separate.

5. *Easy Product Separation.* Because of their very different molar volumes, the products of Eq. (6) are easily separated at room temperature by gel permeation chromatography on inert cross-linked styrene–divinylbenzene resin supports with the reaction solvent as eluant.[14] Methylene chloride works well for this separation despite minimal support swelling and is easily evaporated from eluant fractions. The separated products are uncontaminated with mobile phase additives because none are needed.

6. *Easy Extension to Other Targets.* Most of the above desirable attributes apply to transmetalation of the polynuclear molecules

in Fig. 1, which includes copper(I) and copper(II) targets carrying neutral monodentate[8,14,17–22] and bidentate[23–26] amine ligands and even a monoanionic bridging ligand.[27]

We have found that progressive transmetalation is more likely to be direct for copper(II) centers than for copper(I)[15,20,21,24] (see below). An important attribute of the copper(I) transmetalation systems is the very high stability of coproduct (S-methyl isopropylidehydrazinecarbodithioato)copper(I), Cu(NS), which make reactions (7) irreversible.

$$N_4Cu_4X_4 + xM(NS)_2 \begin{cases} \xrightarrow[x=1]{} N_3Cu_3M(NS)X_4 + N + Cu(NS)(s) & (7a) \\ \xrightarrow[x=2]{} N_4M_2X_4 + 4Cu(NS)(s) & (7b) \end{cases}$$

$$N_4Cu_4X_4 + Cu(NS)_2 \rightarrow N_3Cu_3Cu(NS)X_4 + N + Cu(NS)(s) \quad (7c)$$

In addition, its very low solubility in methylene chloride and nitrobenzene makes product isolation easy and is a useful means of establishing reaction stoichiometries.[20,21,24]

Depite its high stability, Cu(NS)(s) precipitates quite slowly in Eqs. (7), presumably because it forms adducts with the other transmetalation products (molecular Cu(NS) would be two-coordinate).[24] By contrast, $Cu(NS)_2$ is rapidly formed on transmetalation of copper(II) targets because this coproduct is coordinatively saturated.[19,22,26]

Another very important attribute of transmetalation with $M(NS)_n$ is that it is not restricted to copper targets.[15] Reactions like (8) and (9)

$$N_4CoNiX_4 + Co(NS)_2 \rightarrow N_4Co_2X_4 + Ni(NS)_2 \quad (8)$$

$$N_4Co_2X_4 + Zn(NS)_2 \rightarrow N_4CoZnX_4 + Co(NS)_2 \quad (9)$$

are quantitative because of large differences of stability in the order $Cu(NS)(s) > Cu(NS)_2 > Ni(NS)_2 > Co(NS)_2 > Co(NS)_3 >$

$Zn(NS)_2$.[15] This means that there are several potential routes to the same heteropolynuclear product and that a rational synthesis can be mapped out once target- and transmetalator-specific transmetalation patterns are delineated.

LIMITS OF DIRECT TRANSMETALATION

Equation (6) can be extended to give products containing up to four different metals. Table I shows that there are 36 possible molecules $(\mu_4\text{-O})N_4(M_1,M_2,M_3,M_4)_4X_6$ with N and X fixed.[28] In principle, all of these products can be obtained by simultaneous reaction of $(\mu_4\text{-O})N_4Cu_4X_6$ with the appropriate number of equivalents of each transmetalator. In this case, the order of transmetalation of the target by different $M(NS)_2$ is irrelevant because all the sites are equivalent and the relative stability of $M(NS)_2$ is the

TABLE I

Thirty-six possible tetranuclear metal (II) complexes $(\mu_4\text{-O})N_4(Cu,Co,Ni,Zn)_4Cl_6$[a]

Cu	Co	Ni	Zn	Cu	Co	Ni	Zn
4	0	0	0	0	0	2	2
0	4	0	0	2	0	0	2
0	0	4	0	2	0	2	0
(0	0	0	4)	0	2	0	2
3	1	0	0	1	2	1	0
0	3	1	0	0	1	2	1
0	0	3	1	1	0	1	2
(1	0	0	3)	2	1	0	1
3	0	1	0	1	0	2	1
(0	3	0	1)	1	1	0	2
1	0	3	0	2	1	1	0
0	1	0	3	0	2	1	1
3	0	0	1	1	2	0	1
1	3	0	0	1	1	2	0
0	1	3	0	0	1	1	2
0	0	1	3	2	0	1	1
2	2	0	0	1	1	1	1[b]
0	2	2	0	1	1	1	1[b]

[a]Products known to be unstable in parentheses (see Ref. 28).
[b]Enantiomeric forms of $(\mu_4\text{-O})N_4CuCoNiZnCl_6$.

determining factor. For example, $Ni(NS)_2$ is excluded in Eq. (10) because of the stability order **C** >> **F**, **B**.[15]

$$\mathbf{II} + 3\mathbf{C} + \mathbf{B} + \mathbf{F} \rightarrow (\mu_4\text{-O})N_4CoNi_2ZnX_6 + \mathbf{C} + 1/2\,N_2S_2 \quad (10)$$

An idea of the potential scope of transmetalation can be obtained by recalling that Dieck reported 42 examples of $(\mu_4\text{-O})N_4Cu_4X_6$, where N are different amines.[12]

Equations like (6) are the most useful types of transmetalation systems because they are direct and thus generate large families of molecules with the same total metal stoichiometry. The equivalent sites of $(\mu_4\text{-O})N_4Cu_4X_6$ and their high stability relative to other oxocopper(II) targets[14,18] make them excellent candidates for studies of the limits of direct transmetalation. We have found that $(\mu_4\text{-O})N_4Cu_{4-x}Zn_xCl_6$ molecules with $x > 2$ are unstable to disproportionation, most obviously because they contain too many electrons.[8,28] Even molecules $(\mu_4\text{-O})N_4Cu_3MX_6$, M = Cd, Hg, Sn (all d^{10}), are unstable: they spontaneously lose MX_2 to give new trimers $(\mu_3\text{-O})N_3Cu_3X_4$, Eq. (11).[28]

$$\mathbf{II} + M(NS)_2\ (M = Cd, Hg, Sn) \rightarrow (\mu_3\text{-O})N_3Cu_3X_4 + NMX_2 \cdot Cu(NS)_2 \quad (11)$$

The most obvious reasons for this are the disparately large size of M and relatively strong MX_2 bonds.[28]

Another indication of transmetalator specificity is that $(\mu_4\text{-O})N_4Cu_{4-x}Co_xCl_6$ is unstable to disproportionation with $x > 2$ if the transmetalator is $Co(NS)_2$. This occurs because $(\mu_4\text{-O})N_4Cu_2Co_2Cl_6$ disproportionates faster than it can be transmetalated by $Co(NS)_2$. By contrast, $(\mu_4\text{-O})N_4Co_4Cl_6$ can be easily obtained with transmetalator $Co(NS)_3$, evidently because (a) $Co(NS)_3$ (Eq. 12) is a faster transmetalator than $Co(NS)_2$[15] and (b) Eq. (13) is the last step of each substitution.

$$\mathbf{II} + 4\mathbf{B} \rightarrow (\mu_4\text{-O})N_4(Co^{III}(NS))_4X_6 + 4Cu(NS)_2 \quad (12)$$

This brings up another factor requiring attention in other trans-

metalation systems. We observe that Fe(NS) centers created by transmetalation of copper(II) with $Fe(NS)_3$ are, unlike Eq. (13), oxidatively stable, Eq. (14).

$$(\mu_4\text{-O})N_4(Co^{III}(NS))_4X_6 \rightarrow (\mu_4\text{-O})N_4Co_4X_6 + 2N_2S_2 \quad (13)$$

$$\mathbf{II} + Fe(NS)_3 \rightarrow (\mu_4\text{-O})N_4Cu_3Fe(NS)X_6 + Cu(NS)_2 \quad (14)$$

We do not yet know the reason for this difference, but it considerably broadens the scope of transmetalation: we can simultaneously introduce new metals and new ligands into a polymetallic molecule![29]

TARGET SPECIFICITY

Other reported direct tetranuclear transmetalation systems mostly involve transmetalation of copper(II) centers (Fig. 1) with **B** or **C**. Changing the target to a tetranuclear dioxocopper(II) complex sometimes results in CuO fragmentation and a trinuclear heterometallic product, Table II.[15,20,21]

Intramolecular NS Ligand Transfer

Only the first step of transmetalation of tetranuclear copper(I) targets is direct. The products in Table III include five very interesting mixed-valence molecules $N_mCu_3M(NS)_nX_4$. Further transmetalation of these molecules with $M(NS)_n$ results in intramolecular NS ligand transfer from $M(NS)_n$ to copper and dimeric products, Table IV. This process will be prevented by discovery of new transmetalating agents M(NS), Eqs. (15).

$$N_4Cu_4X_4 + xM(NS) \rightarrow N_4Cu_{4-x}M_xX_4 + xCu(NS) \quad (15)$$

If M is redox-inactive this creates the possibility of having a family of 4-, 3-, 2- and 1-electron reducing agents, a very valuable resource in studies of reactions with multi-electron oxidants like dioxygen.

TABLE II

Trinuclear products resulting from CuO and MX_2 fragmentation on transmetalation of tetranuclear oxocopper(II) targets with $M(NS)_n$ transmetalators B, C and E

Target[a]	Transmetalator	R[b]	Product	Ref.
	a. μ_3-*oxo Complex Products from CuO Fragmentation*			
$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3Ni(H_2O)Cl_4$	C	2	$[NNi(H_2O)]_3Cl_4O$	20
$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3Co(H_2O)Cl_4$	C	2	$N_3CoNi_2Cl_4O{\cdot}2H_2O$	21
	E[c]	2	$N_3CoZn_2Cl_4O{\cdot}2H_2O$	21
	E	2	$N_3Co_3Cl_4O{\cdot}2H_2O$	21
	C,E	1,1	$N_3Co_2NiCl_4O{\cdot}2H_2O$	21
	E,E[c]	1,1	$N_3Co_2ZnCl_4O{\cdot}2H_2O$	15
	C,E[c]	1,1	$N_3CoNiZnCl_4O{\cdot}H_2O$	15
	C	1	$N_3CoNiCuCl_4O$[d]	21
$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3Co(H_2O)Br_4$	C	2	$N_3CoNi_2Br_4O{\cdot}2H_2O$	21
	b. μ-*Oxo Complex Products*[e] *from CuO Fragmentation*			
$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3Cu(H_2O)Cl_4$	B	1	$N_3Cu_2CoCl_4O$	31
	B	2	$N_3CuCo_2Cl_4O$	31
	B	3	$N_3Co_3Cl_4O$	31
	c. μ-*Oxo Complex Products*[e] *from* MX_2 *Fragmentation*			
$(\mu_4\text{-O})N_4Cu_4Cl_6$	E[f]	1	$N_3Cu_3Br_4O$	28
$(\mu_4\text{-O})N_4Cu_4Br_6$	E[f]	1	$N_3Cu_3Br_4O$	28
$(\mu_4\text{-O})py_3Cu_4Cl_6$	E[f]	1	$py_3Cu_3Cl_4O$	28

[a]N = N, N-diethylnicotinamide, py = pyridine.

[b]*R* = molar reactant ratio [transmetalator]/[target]. Examples: R = [C]/[target] = 2 (data set 1); R_1 = [C]/[target] = 1, R_2 = [E]/[target] = 1 (data set 5).

[c]Zn substituted for Co in E (Fig. 2: see Ref. 10).

[d]Product is impure because of further CuO loss to give $N_3CoNiCl_4{\cdot}2H_2O$ (see ref. 21).

[e]Spectral distinction of isomers is discussed in Ref. 30.

[f]M = Cd, Hg, Sn substituted for Co in E (Fig. 2: Ref. 28).

TABLE III

Mixed-valence transmetalation products

Reactants	Product	Ref.
$N_4Cu_4Cl_4$, $Co(NS)_3$	$N_3Cu_2^{I}Cu^{II}Co^{II}(NS)_2Cl_4$	15,21
$N_4Cu_4Br_4$, $Co(NS)_3$	$N_3Cu_2^{I}Cu^{II}Co^{II}(NS)_2Br_4$	15,21
$N_4Cu_4Cl_4$, $Fe(NS)_3$	$N_4Cu_2^{I}Cu^{II}Fe^{II}(NS)_2Cl_4$	29
$N_4Cu_4Br_4$, $Fe(NS)_3$	$N_4Cu_2^{I}Cu^{II}Fe^{II}(NS)_2Br_4$	29
$N_4Cu_4Cl_4$, $Cu(NS)_2$	$N_3Cu_2^{I}Cu^{II}(NS)Cl_4$	20

EXTENSION TO OTHER ELEMENTS

Our transmetalators contain the elements Co, Ni, Cu, Zn, Cd, Hg and Sn. None of these substituted elements are air-sensitive or catalytic. If they were we could probably link polynuclear molecules through oxo bridges by reacting them with dioxygen, Eq. (16).

$$4 \equiv M^{II} + O_2 \rightarrow 2[\equiv M^{III}\text{-}O\text{-}M^{III} \equiv] \qquad (16)$$

We are busy trying to make $Fe(NS)_2$, $V(NS)_2$ and other transmetalators that would provide air-sensitive sites in heteropolynuclear molecules. We also wish to make heteropolymetallic molecules containing catalytic metals like Ru, Os and Rh. Imagine the satisfaction of understanding the catalytic properties of a family like $(\mu_4\text{-}O)N_4Cu_{4-x}Ru_xX_6$, x = 0-4! And we should be able to

TABLE IV

Products resulting from intramolecular NS ligand transfer processes

Reactants	Product	Ref.
$N_4Cu_4Cl_4$, $2Cu(NS)_2$	$N_4Cu_2Cl_4$	20
$N_4Cu_4Br_4$, $2Cu(NS)_2$	$N_4Cu_2Br_2$	20
$N_4Cu_4Cl_4$, $2Ni(NS)_2$	$N_4Ni_2Cl_4(H_2O)_2$	20
$N_4Cu_4Cl_4$, $2Co(NS)_2$ or $2Co(NS)_3$	$N_4Co_2Cl_4$	15,20
$N_4Cu_4Br_4$, $2Co(NS)_2$	$N_4Co_2Br_4(H_2O)_2$	20
$N_4Cu_4Cl_4$, $2Zn(NS)_2$	$N_4Zn_2Cl_4$	20
$N_4Cu_4Cl_4$, $Co(NS)_3$, $Ni(NS)_2$	$N_4CoNiCl_4(H_2O)_2$	21
$N_4Cu_4Br_4$, $Co(NS)_3$, $Ni(NS)_2$	$N_4CoNiBr_4(H_2O)_2$	21
$N_4Cu_4Cl_4$, $Co(NS)_3$, $Zn(NS)_2$	$N_4CoZnCl_4$	21
$N_4Cu_4Cl_4$, $Co(NS)_3$, $Cu(NS)_2$	$N_4CoCuCl_4$	21

reduce such molecules to $Cu_{4-x}Ru_x$ alloys either as bulk materials or as supported catalysts of well-defined and variable metal stoichiometry.[6] This will require the development of labile precious metal targets or transmetalators, a subject that we are vigorously pursuing.

PHENOMENA AND FUTURE WORK IN TRANSMETALATION SYSTEMS

1. *Limits of Practicability.* Practical transmetalation reactions are rapid and irreversible under mild conditions. This requires labile targets and transmetalators, strong driving forces and conformity to basic structural requirements in reaction precursors.[19,22,24,26] It appears that copper(II) systems carrying tridentate ligands do not react at practical rates with $M(NS)_n$ transmetalators and that $Pd(NS)_2$ is too inert to substitute copper that is easily replaced with nickel. If a labile form of any metallic element is available, or can be made so by accepting an electron from copper(I), we have the chance to make many heteropolymetallic derivatives. Even in inert systems there is considerable scope for chemical or photochemical catalysis of transmetalation leading to catalytic heteropolymetallic products.

2. *Mixed Ligand Systems.* We regard the halide ligands of polynuclear halocopper complexes as the *core.* For example, in $N_4Cu_4X_4$ complexes the copper occupies the tetrahedral holes of an X_4 tetrahedron.[30] We could, in principle, construct molecules like $N_4Cu_4ClBrI_2$, with four questions in mind. First, given that $N_4Cu_4I_4$ is air-stable, are all the copper(I) centers in $N_4Cu_4ClBrI_2$ oxidized by dioxygen? Second, what is the order of transmetalation of the different copper(I) sites in $N_4Cu_4ClBrI_2$, bearing in mind that $N_4Cu_4I_4$ is not transmetalated? Third, what is the order of transmetalation of the different copper sites in oxidized $N_4Cu_4ClBrI_2$? Fourth, how does coordination of newly introduced M to different halides affect its affinity for different exogenous ligands?

3. *Different Transmetalators.* We already know that the choice of NS transmetalator ligand affects the rates and rate laws of copper transmetalation.[19,22,25,26] It also has important practical conse-

quences. For example, Cu(NS)(s) (NS = S-methyl isopropylidenehydrazinecarbodithioate) insolubility simplifies copper(I) transmetalation[15,20,21,24] and $Cu(NS)_2$ (NS = S-methyl benzylidenehydrazinecarbodithioate) insolubility eases the pain of $L_2Ni_2X_2CO_3$ isolations.[23]

There are three other phenomena related to the choice of transmetalator ligand.

(a) *Intramolecular NS Ligand Transfer.* Transmetalation of the second copper(I) site in $N_3Cu_3M(NS)X_4$ with $M(NS)_2$ leads to intramolecular NS ligand transfer from M to copper(I),[15,20,21] Eq. (7b). Although this leads to new products, it is undesirable because it reduces the target molecularity. Prevention of NS ligand transfer would result in direct total transmetalation of copper(I) by M. The alternative approaches to this goal are (a) to increase the NS ligand transfer distance[24]; (b) choose a non-transferring ligand; or (c) transmetalate with M(NS) reagents, Eq. (15).

(b) *Electron Transfer.* Equations (17) and (18)

$$N_4Cu_4X_4 + \mathbf{B} \rightarrow N_3Cu_3Co(NS)_2X_4 + Cu(NS)(s) + N \quad (17)$$

$$N_4Cu_4X_4 + Fe(NS)_3 \rightarrow N_4Cu_3Fe(NS)_2X_4 + Cu(NS)(s) \quad (18)$$

proceed by electron transfer to give very interesting mixed-valence copper complexes (Table III). Unfortunately, NS ligand transfer occurs after electron transfer in the second step and leads to dimeric products, Eq. (19).

$$N_3Cu_3Co(NS)_2X_4 + \mathbf{B} \xrightarrow{N} N_4Co_2X_4 + Cu(NS)(s) + 2Cu(NS)_2 \quad (19)$$

The situation would be very different if either electron transfer, NS ligand transfer or both phenomena could be eliminated by choice of the transmetalator metal and ligand.

(c) *M(NS) Stability.* $Co^{III}(NS)$ centers in halocopper(II) complexes are inherently unstable, Eq. (13),[15,21] while $Fe^{III}(NS)$ are not, Eq. (14).[29] On the other hand, the NS of $M(NS)_n$ centers are

oxidized to the disulfide N_2S_2 by dioxygen that has been partially reduced by copper(I) in the same molecule.[15,20,21,29]

Another decomposition route is via Eq. (20),

$$(NS)Cu(X,X)Cu(NS) \rightarrow 2Cu(NS)(s) + 2X\cdot \qquad (20)$$

which occurs with M = Cu but not Co or Ni.[24] These situations obviously could be changed by choice of different transmetalator ligands. The benefit would be families of molecules with fixed molecularities but different numbers of available electrons.

4. *Selectivity*. There are three kinds of selectivity in transmetalation systems.

(a) *Site Selectivity*. We have demonstrated marked selectivity in the transmetalation of structures **I** and **III** by $M(NS)_n$ reagents. For structure **I**,[14,18] the presence of μ-oxo or μ-carbonate groups leads to geometric isomers of $(\mu\text{-}O)_2N_4Cu_2M_2X_4$ and $(\mu\text{-}CO_3)_2N_4Cu_2M_2X_4$, respectively. The case with M = Ni is informative because transmetalation of **I** with excess **C** or **D** stops at the Cu_2Ni_2 stage and gives different isomers **X** and **XI**.[14,18] Actually, catalysis of isomerization of **X** to **XI** (M = Ni) by coproduct $Cu(NS)_2$ is responsible for this result.[18] By contrast, transmetalation of **I** by excess $Co(NS)_3$ proceeds to the Co_4 stage, apparently *via* isomeric structure **XI** (M = Co). This implies that the Co^{II} center in $(\mu\text{-}O)_2N_4Cu_3CoX_4$ directs transmetalation of the copper(II) which shares the same oxo bridge. However, the conclusion is invalid if isomerization of **X** (M = Co) is catalyzed or inherently fast. Fortunately, direct kinetic measurements indicate that this is not the case in halocopper–nickel systems or in a variety of heterometallic derivatives of L_4Cu_4 (L = 6-methyl-2-oxopyridinate).[27] Evidence for a *trans*-effect indicates that μ-oxo groups are an important means of communication between metals in heteropolymetallic molecules.[27,31]

The existence of a μ-oxo group in core structure **III** leads to distinct sites and selective transmetalation of copper(II) by nickel.[32] The Z,X,X,Y order of transmetalation of **III** (Fig. 1) is consistent with the preference of the Ni_z-O-Cu_y unit not to be transmetal-

ated when Cu_x sites are available. However, primary transmetalated forms of Cu_2Ni_2 and $CuNi_3$ isomerize because of a thermodynamic preference of copper for X sites. This is despite the fact that X sites are transmetalated more rapidly than Y sites.[32]

By contrast to the results with $Ni(NS)_2$, transmetalation of **III** with just 1 mol of $Co(NS)_3$ leads to CuO fragmentation,[31] an example of the second kind of transmetalation selectivity.

(b) *Fragmentation Selectivity.* Intramolecular NS ligand transfer and primary transmetalation product fragmentation both result in lowering of target molecularity. Fragmentation can be selective, as indicated by Eqs. (21).

$$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3MX_4 \xrightarrow{-MX_2} (\mu\text{-O},\mu_3\text{-O})N_3Cu_3X_2 \quad (21a)$$

$$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3MX_4 \xrightarrow{-CuO} (\mu_3\text{-O})N_3Cu_2MX_4 \quad (21b)$$

$$(\mu\text{-O},\mu_4\text{-O})N_3Cu_3MX_4 \xrightarrow{-CuO} (\mu\text{-O})N_3Cu_2MX_4 \quad (21c)$$

We have observed examples of Eqs. (21b) and (21c).[15,20,21,31] Fragmentation of MX_2 seems to be restricted to Eqs. (11) (M = Cd, Hg, Sn), which are a new source of a wide variety of μ_3-oxo trimers.[28]

(c) *Exogenous Ligand Selectivity.* The metals in a heteropolymetallic molecule have different affinities for a given ligand. Good examples are the very high relative affinity of copper for amine ligands in copper–nickel molecules: nickel very much prefers coordinated water.[14,18,23] This kind of ligand selectivity is well worth exploring, since catalytic properties of heterometallic clusters must, in some way, be related to the relative ligand affinities of their precursor heteropolymetallic molecules.

Transmetalation seems to be the best available means of exploring such relationships, providing, as it does, the opportunity to generate large numbers of different, but related, heteropolymetallic entities. There is still much good work to be done in developing this useful chemistry. We hope that the phenomenon will be applied to a wide variety of chemical and materials systems.

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