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A Study of Heterotetranuclear Transmetalation Products by Fast Atom Bombardment Mass Spectrometry

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Transmetalation is the stoichiometric replacement of the metals in a polymetallic target with other metals from reagents called transmetalators. The family of heteropolymetallic complexes $(\mu_4\text{-O})L_4Cu_{4-x}M_xCl_6$ (M = Ni and x = 0–4 in **I–V**, respectively) was obtained by transmetalating the parent (x = 0) with x mol of $Ni(NS)_2$, where L is *N,N*-diethylnicotinamide and NS is *S*-methyl isopropylidenehydrazinecarbodithioate. These and other neutral polymetallic complexes **VI–XI** containing different combinations of Co, Ni, Cu, and Zn were evaluated by fast atom bombardment mass spectrometry (FAB/MS). Ionization of **I–XI** by FAB/MS produced no molecular ions under the analysis conditions employed, but the production of characteristic fragments as well as the formation of several metal–ligand complexes was observed. No heteropolymetallic fragments were observed in this study. The spectral patterns of the mixed metal complexes **II–IV** and **VI–X** indicate that metal exchange occurs in the matrix as a result of exposure to the FAB beam. $(\mu_4\text{-O})L_4CuNi_3Cl_6$ produces a fragmentation pattern indistinguishable from that of $(\mu_4\text{-O})L_4Cu_4Cl_6$ in the mass range from m/z 650 and above, yet produces ions at m/z 419 and 449 (CuL_2^+ and $[NiCl]L_2^+$, respectively) in ratios expected from the stoichiometric metal content of the original complex. It appears that the m/z 419 and 449 peaks do not result from an ionically induced fragmentation of the parent complex but rather from decomposition of the complex and recombination of neutral ligand and metal species in the nitrobenzyl alcohol matrix. Isotopic abundance calculations were used to determine fragmentation pathways and fragment compositions. A mixture of $(\mu_4\text{-O})L_4Cu_4Cl_6$ (**I**) and $(\mu_4\text{-O})L_4Ni_4Cl_6$ (**V**) in 3-nitrobenzyl alcohol produced a spectrum whose major fragments were remarkably different from those of the heteropolymetallic copper/nickel complexes (**II–IV**).

Introduction

There is great current interest in the synthesis, characterization, and properties of heteropolymetallic complexes.[1,2] Such species are made by a variety of methods, but the complex of interest often has to be extracted from a complicated product mixture because metal replacement in many targets is rarely rapid, stoichiometric, or specific under mild conditions.[1,2] Recently, it has been found that large, homologous families of heteropolymetallic complexes containing simple ligands may easily be obtained by transmetalation, which is defined as the stoichiometric replacement of the metals in a polymetallic target with other metals from reagents called transmetalators.[3]

Reaction 1 is an example of a useful system of transmetalation reactions. Here, L is *N,N*-diethylnicotinamide, X is Cl or Br, x is 1–4, M is Co, Ni, or Zn, and NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate in transmetalators $M(NS)_2$.[3-6] The molecular structures of A[4] and transmetalator B[5] (M = Ni) are shown in Figure 1.

$$\underset{\text{A}}{(\mu_4\text{-O})L_4Cu_4X_6} + \underset{\text{B}}{xM(NS)_2} \rightarrow \underset{\text{C}}{(\mu_4\text{-O})L_4Cu_{4-x}M_xX_6} + \underset{\text{D}}{xCu(NS)_2} \qquad (1)$$

Reaction 1 proceeds in rapid,[6] stoichiometric[7,8] steps at room temperature in aprotic solvents. The stepwise character means that transmetalation can be used, for example, to generate the molecule $(\mu_4\text{-O})L_4CuNi_3X_6$ by fixing x at 3 with M = Ni[7] and that molecules $(\mu_4\text{-O})L_4(Co,Ni,Cu,Zn)_4X_6$ containing up to four different metals can be obtained by use of different metal transmetalators.[8]

The heteropolymetallic products of reaction 1 are readily separated from coproduct $Cu(NS)_2$ by gel permeation chromatography.[4,6-9] Heteropolymetallic complexes should exist in equilibrium with more stable homopolymetallic forms because the coordination requirements of each element are different. Thus a molecule that has been modified by metal substitution may not be at equilibrium. Whether it equilibrates or not depends on the lability of its metal centers, which ultimately depends on the relative strength of its metal–ligand bonds.

There are several indications that such factors are important in determining the temporal existence of the heteropolymetallic products of transmetalation reactions; first, attempts to assemble them from discrete Cu and M complexes have been unsuccessful.[3]

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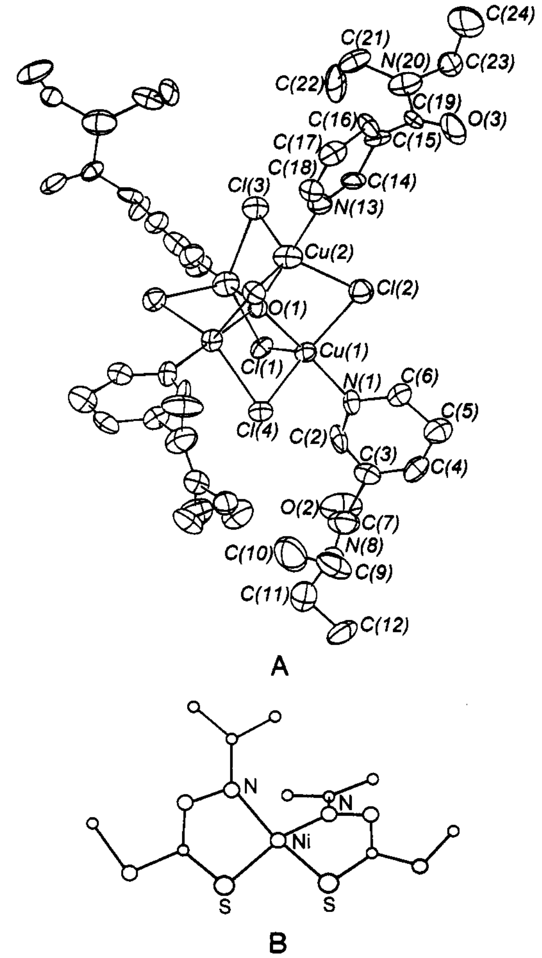

Figure 1. Structure A: Core molecular structure of the target (μ_4-O)$L_4Cu_4Cl_6$.[4] Structure B: Molecular structure of transmetalator $M(NS)_2$, M = Ni.[5]

Second, although the products of reaction 1 can be isolated as stable solids, attempted single-crystal growth invariably leads to disproportionation to homometallic products.[3,4,7-9] Third, there are limits to the replacement of copper with particular metals. For example, attempted replacement of three copper(II) centers in (μ_4-O)$L_4Cu_4Cl_6$ with Zn from $Zn(NS)_2$[5] is accompanied by disproportionation of the desired product (μ_4-O)$L_4CuZn_3Cl_6$.[8] Fourth, thermal treatment of (μ_4-O)$L_4Cu_{4-x}Ni_xX_6$ products in an inert atmosphere at 350 °C directly leads to copper–nickel alloy formation.[10] It would thus appear that transmetalation products (μ_4-O)$L_4Cu_{4-x}M_xX_6$ are trapped in relatively high-energy potential wells that are separated from more stable states by kinetic barriers to disproportionation.

This is the first reported study of the fast atom bombardment mass spectrometry of the transmetalation product family (μ_4-O)L_4(Co,Ni,Cu,Zn)$_4X_6$.[11] We find that the fragmentation patterns strongly depend on the metal constitution of these molecules in a manner that indicates significant differences in metal–ligand bond strengths. The data indicate that (μ_4-O)$L_4Cu_{4-x}M_xX_6$ molecules do indeed exist in kinetically-controlled equilibria with more thermodynamically stable forms. Fast atom bombardment mass spectrometry was utilized to conduct the analysis because, as a less energetic ionization process, it was considered a suitable technique for the analysis and characterization of these labile materials.

Table 1. Molecular Weight Data and Figure Citations for Complexes I–XII

complex	formula	molecular weight (amu)[a]	Figure no.
I	(μ_4-O)$L_4Cu_4Cl_6$	1194.0	2a
II	(μ_4-O)$L_4Cu_3NiCl_6$	1189.0	2b
III	(μ_4-O)$L_4Cu_2Ni_2Cl_6$	1184.0	2c
IV	(μ_4-O)$L_4CuNi_3Cl_6$	1179.0	2d
V	(μ_4-O)$L_4Ni_4Cl_6$	1176.0	2e
VI	(μ_4-O)$L_4Cu_3CoCl_6$	1190.0	7a
VII	(μ_4-O)$L_4Cu_2NiZnCl_6$	1192.0	7b
VIII	(μ_4-O)$L_4Cu_3ZnCl_6$	1197.0	7c
IX	(μ_4-O)$L_4CuCoNiZnCl_6$	1186.0	7d
X	(μ_4-O)$L_4CoNi_3Cl_6$	1175.0	not shown
XI	(μ_4-O)$L_4Co_4Cl_6$	1176.0	not shown
I and V	mixture of complexes I and V	1194.0, 1176.0	6

[a] The molecular mass computed on the basis of the most intense peak within the mass envelope (see text).

Experimental Section

Materials. The target A[4] and transmetalators B[5] were synthesized and crystallized in accordance with literature procedures. Transmetalation reactions 1 were conducted in methylene chloride at room temperature, and the heteropolymetallic products C were isolated by gel permeation chromatography on Biobeads SX-12 resin with methylene chloride as the eluent, as described previously.[3-6] Molecular weight data for polymetallic complexes of this study are given in Table 1.

Solvents evaluated as potential matrices for this FAB-MS study of heteropolymetallic transmetalation products were tetramethylene sulfone, 3-nitrobenzyl alcohol, dichloromethane, and glycerol (Aldrich), which were used as received. The analyte concentration was 100 μg/L throughout.

Apparatus and Procedures. All FAB-MS analyses were conducted on a VG70-250SE mass spectrometer equipped with a direct insertion FAB probe. Xenon (Matheson, research grade) was used as the FAB gas. The ion accelerating voltage was 8 kV. The FAB gun was operated at 8 kV and a current of 1 mA. The probe and ion source were operated at 25 °C throughout the analyses. The MS system was tuned and calibrated with cesium iodide. The static probe was cleaned and prepared prior to each analysis.[12]

The analytical mass range was generally from m/z 400 to 1300 with a scan time of 10 s/scan. The mass spectrometer data acquisition system was allowed to complete one scan prior to the activation of the xenon beam. Spectra were normally summed from the fifth to fifteenth scans and averaged. No significant variations in spectral patterns were observed with time except with the mixture of complexes I and V as described in the text.

Results and Discussion

General Observations. It may be shown theoretically that 36 different molecules (μ_4-O)L_4(Co,Ni,Cu,Zn)$_4Cl_6$ can be obtained from reaction 1 by employing target A and transmetalators $Co(NS)_2$, $Ni(NS)_2$, and $Zn(NS)_2$.[8] One example is (μ_4-O)$L_4Co_2NiCuCl_6$, which contains three different metals. The solid polymetallic products are identified after isolation by analytical, cryoscopic, and spectral measurements. Linear variations of the molar absorptivities of these tetranuclear products as a function of copper(II) and cobalt(II) content indicates a common molecular core structure.[8] This core structure presumably[13] consists of a central μ_4-oxo group surrounded by a tetrahedron of metal ions, as in the structure of target A.[4] Each pair of metal centers is bridged by chlorides. The stability of any particular tetranuclear molecule (μ_4-O)L_4(Co,Ni,Cu,Zn)$_4Cl_6$ depends on the ability of the oxo and chloro ligands to retain each metal in the molecule.

It has been found in practice that the number and identity of the metals are very important in determining the stability of

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products $(\mu_4\text{-O})L_4(Co,Ni,Cu,Zn)_4Cl_6$. For example, the complete families $(\mu_4\text{-O})L_4Cu_{4-x}Ni_xCl_6$ and $(\mu_4\text{-O})L_4Cu_{4-x}Co_xCl_6$ with L = *N,N*-diethylnicotinamide or pyridine and X = Cl or Br have been obtained by reaction of *x* mol of $Ni(NS)_2$ or $Co(NS)_3$[13] with 1 mol of the respective copper(II) targets.[7,8] Although products $(\mu_4\text{-O})L_4Cu_{4-x}M_xX_6$ with M = Zn and *x* = 1 or 2 may be isolated, those with higher *x* values disproportionate.[8] The occurrence of reactions 2 with M = Cd, Hg, or Sn indicates that the size of the substituted metal M is important in determining the stability of products $(\mu_4\text{-O})L_4Cu_{4-x}M_xX_6$.[8]

$$(\mu_4\text{-O})L_4Cu_4Cl_6 + M(NS)_2 \rightarrow (\mu_3\text{-O})L_3Cu_3Cl_4 + L + Cu(NS)_2 + MCl_2 \quad (2)$$

Mass Spectra of Copper–Nickel Complexes (I–V). Five heteropolynuclear complexes containing nickel and copper were prepared and analyzed by FAB-MS in 3-nitrobenzyl alcohol. The spectra of complexes $(\mu_4\text{-O})L_4Cu_{4-x}Ni_xCl_6$, where *x* = 0–4, are shown in Figure 2a–e, respectively. As expected, the combination of the transition metals Co, Ni, Cu, and Zn with chloride ions produces an envelope of ion masses based upon the naturally occurring isotopic abundances of the elements present. For any given ion fragment, the masses cited in this paper refer to the most abundant mass observed within the mass envelope. An example of this is shown in Figure 3, where a comparison of observed and theoretical isotopic abundances is provided for the *m/z* 981 fragment in complex **I**.

Complex $(\mu_4\text{-O})L_4Cu_4Cl_6$ (**I**) contains four coppers (*x* = 0) and has a molecular weight of 1195.8 amu. Figure 2a is the mass spectrum of this compound. No molecular ion (M^+) peak is observed under the conditions of this analysis. The isotopic pattern of $[M - Cl]^+$ (*m/z* 1159) corresponds to that expected theoretically from five chloride and four copper ions. This unique spectral pattern allows the isotopic content of the fragments to be readily recognized. The fragment at *m/z* 981 results from the additional loss of a neutral *N,N*-diethylnicotinamide ligand, which has a mass of 178 amu. The molecular structure of the complex (Figure 1) would suggest that the primary fragmentation pathway involves the repeated loss of this neutral ligand from the complex.[14,15] However, the most abundant fragment at *m/z* 419 results from decomposition of the original complex and recombination of metal ions and neutral *N,N*-diethylnicotinamide ligands in solution to form a stable copper(I) complex CuL_2^+.

The fragments appearing in the mass spectrum of Figure 2a result from three different fragmentation pathways. Repetitive losses of metal ions and ligands are observed in both pathways a and b. In pathway a, copper remains in the +2 oxidation state while in pathway b copper is rapidly reduced to copper(I). The third pathway c is a decomposition sequence in which the complex breaks apart and several stable metal–ligand complexes form from the fragments. This fragmentation sequence is shown in Figure 4.

The fragmentation pathway proposed in Figure 4 is supported by both linked scans (B^2/E and B/E) and by comparison of theoretical isotopic abundances to those observed in the mass spectrum.

Additional solvents and matrices were evaluated in an attempt to generate conditions for detection of the molecular ion at *m/z* 1194. However, neither glycerol nor tetramethylene sulfone in combination with dichloromethane was capable of producing a detectable molecular ion M^+ or other molecular adduct ion peak.

The spectrum of $(\mu_4\text{-O})L_4Cu_3NiCl_6$ (**II**) (Figure 2b) was subsequently examined under the same conditions as the all-copper complex (**I**). Surprisingly, the spectral details of complex **II** demonstrate a fragmentation pattern remarkably similar to that of the all-copper complex (**I**). The isotopic calculations as well as the linked scans confirm that, above *m/z* 650, the mass spectra of complexes **I** and **II** are similar in all respects. However, close examination of the spectral patterns show significant differences in the mass range below *m/z* 650. For instance, the appearance of *m/z* 449 in the spectrum of complex **II** indicates the formation of $[NiCl]L_2^+$ which results from decomposition products of the parent complex.

The heteropolymetallic complexes **III** and **IV** were also examined by FAB/MS. Their mass spectra are shown in Figure 2c,d, respectively. As with complex **II**, the nickel in complexes **III** and **IV** is replaced by copper to form the all-copper complex **I** with a resultant peak at *m/z* 1159 ($(\mu_4\text{-O})L_4Cu_4Cl_5^+$).

The final complex **V** evaluated in this family of copper–nickel complexes contained only nickel (*x* = 4). Its spectrum is shown in Figure 2e. Present in the nickel mass spectrum are ions with *m/z* 414 (NiL_2^+), *m/z* 449 ($[NiCl]L_2^+$), and *m/z* 1046 ($M - NiCl_2^{+\bullet}$). Complex **V** has a fragmentation pathway (Figure 5) that demonstrates similarities to the fragmentation pattern of the all-copper complex (**I**). Significantly, in the complexes containing copper (**I–IV**), the highest observed mass was at *m/z* 1159 corresponding to $[M - Cl]^+$. For the all-nickel complex (**V**), the highest mass observed was *m/z* 1046 corresponding to $[M - NiCl_2]^{+\bullet}$. Complexes **I–IV** all exhibit the same spectral pattern above *m/z* 650, while the all-nickel complex (Figure 2e) exhibits no similarities to complexes **I–IV** in this region of the spectrum. The most abundant ion observed in the spectrum of complex **I** (containing only copper) is at *m/z* 419, corresponding to CuL_2^+. On the other hand, the most intense peak in the spectrum of the complex containing only nickel (**V**) is at *m/z* 449, corresponding to $[NiCl]L_2^+$.

The molecular stoichiometry in terms of the copper and nickel content was reflected in the ratio of the signals at *m/z* 419 (CuL_2^+) and *m/z* 449 $[NiCl]L_2^+$). The relative abundance of the 419 peak in Figure 2d is lower than the anticipated abundance because three copper ions are required for the replacement of three nickel ions in the molecular structure. This creates a deficit of available copper ions necessary to form significant quantities of the CuL_2^+ complex. It was also observed that no fragment in the complexes in Figure 2b–d exhibits any evidence for the simultaneous presence of copper with nickel; all fragments contained either nickel or copper, but not both. This information was confirmed by both linked scans and examination of the isotopic patterns.

A comparison of the relative abundance of *m/z* 419 (CuL_2^+) and *m/z* 449 ($[NiCl]L_2^+$) demonstrates the dependence of fragment production on the stoichiometry of parent complexes **I–V**. The data are shown in Table 2 and are also illustrated in the insets shown in Figure 2a–e. In an attempt to assess whether this apparent metal exchange occurs in the vapor phase or in the NBA matrix, a further experiment was conducted using a FAB probe tip with a 200-μm split in the center. Half of the probe tip was coated with copper(II) chloride, while the other was coated with $(\mu_4\text{-O})L_4Ni_4Cl_6$. The FAB beam was directed equally across the 200-μm gap separating the two compounds. No metal exchange product was observed under these conditions. This suggests that the metal exchange occurs in the matrix solution.

A 2:1 mixture of the all-nickel complex and the all-copper complex was prepared and allowed to stand for 12 h in the 3-nitrobenzyl alcohol matrix. It was expected that if metal exchange occurred in solution at room temperature, the all-nickel complex would have disappeared prior to the FAB analysis. The mass spectrum in Figure 6 shows the result of this experiment. The spectrum shows the presence of high mass fragments (e.g., *m/z* 1159 and *m/z* 1046) attributable to both the all-copper (**I**) and all-nickel (**V**) complexes. This confirms that complexes **I–V** are all unique compounds with the correct stoichiometric amounts

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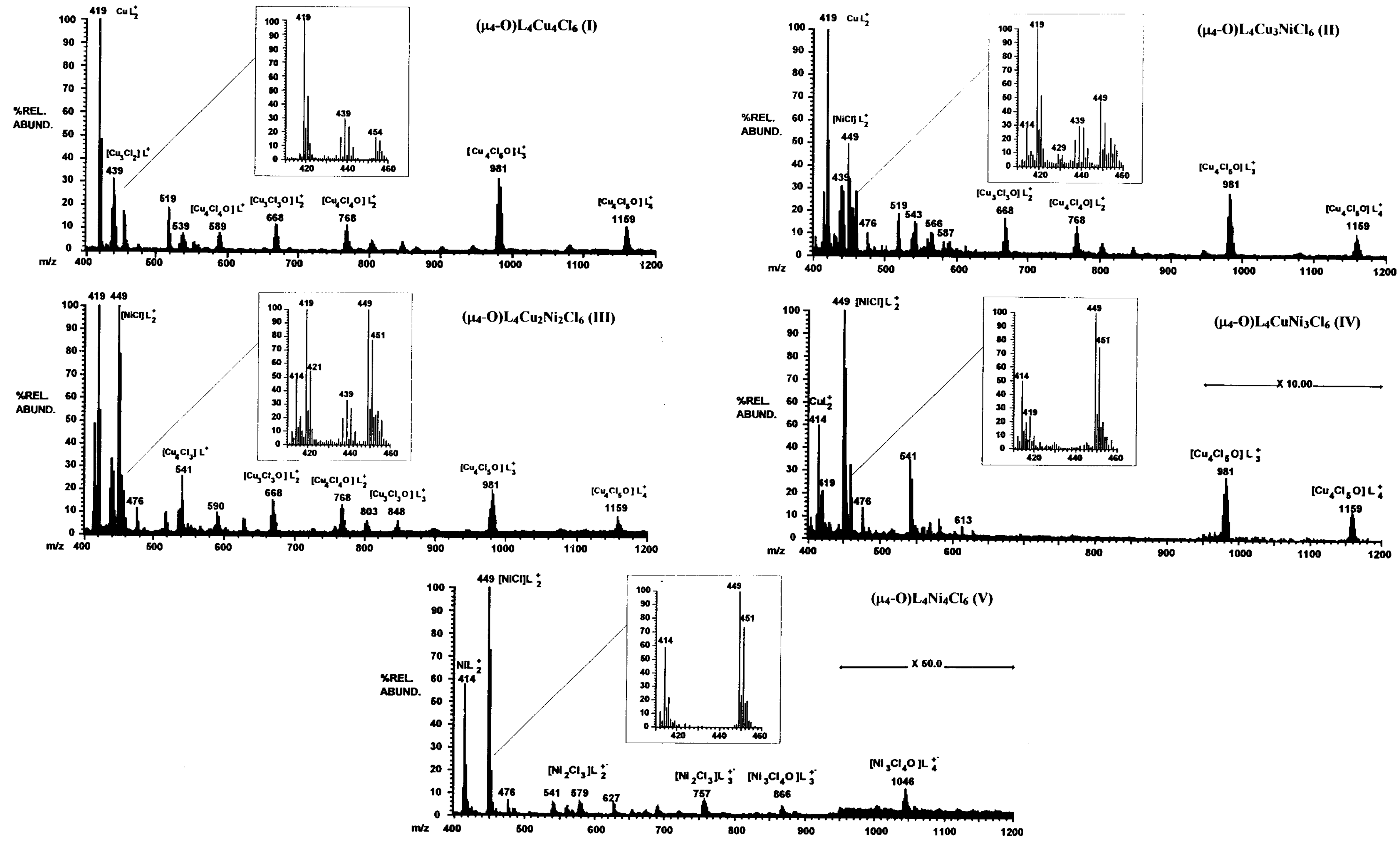


Figure 2. FAB mass spectra of complexes I-V, (μ_4-O)$L_4Cu_{4-x}Ni_xCl_6$, where $x = 0$–4 in (a)–(e), respectively. No molecular ion is observed for any of these polymetallic complexes, and no heteropolymetallic ions were observed. The highest mass observed for (μ_4-O)$L_4Cu_4Cl_6$ (a) is at m/z 1159 ((μ_4-O)$L_4Cu_4Cl_5^+$) and represents $M-Cl^+$. The most abundant signal observed is at m/z 419 and represents the formation of CuL_2^+. A fragment at m/z 1159 is also observed for (μ_4-O)$L_4Cu_3NiCl_6$ (b), indicating that a metal exchange to give complex I (a) has occurred. The appearance of a metal–ligand complex at m/z 449 ($[NiCl]L_2^+$) indicates the presence of nickel. The ratio of the m/z 419 for copper and m/z 449 for nickel reflects the stoichiometry of the parent complex (insets of (a)–(e)). The presence of the m/z 1159 fragment in the remaining two complexes $x = 2$ and $x = 3$ (c, d) also indicates that metal exchange has occurred to form complex I (a). The homometallic complex (μ_4-O)$L_4Ni_4Cl_6$ (e) has none of the spectral features observed in complexes I–IV above m/z 650.

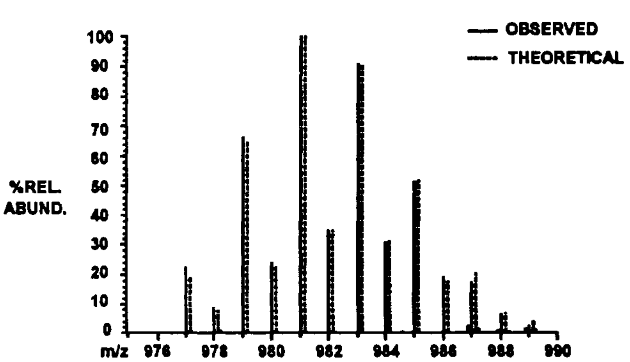


Figure 3. Mass envelope for the fragment $(\mu_4\text{-O})L_3Cu_4Cl_5^+$. Only the most abundant mass (*m*/*z* 981) within the mass envelope is cited in this paper. The observed and theoretical isotopic abundances are shown for this fragment.

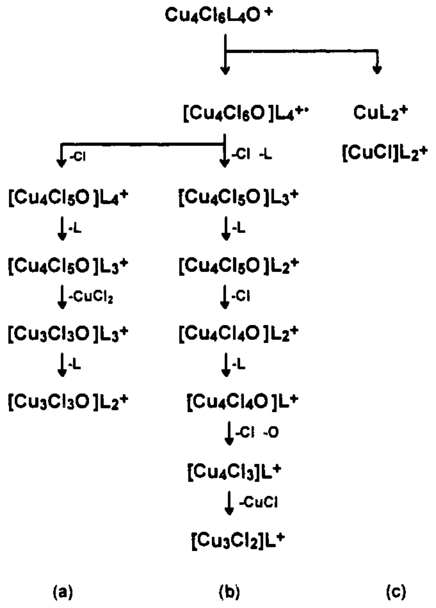


Figure 4. Fragmentation pathways for $(\mu_4\text{-O})L_4Cu_4Cl_6$ (**I**) in NBA. The loss of neutral ligand L occurs in both pathways a and b. The copper remains primarily as copper(II) in pathway a. The copper in pathway b is rapidly reduced to copper(I). Decomposition results in the formation of stable metal–ligand complexes CuL_2^+ and $[CuCl]L_2^+$ in solution (pathway c).

of copper and nickel and not physical mixtures of the all-copper complex (**I**) and the all-nickel (**V**) complex. However, the higher mass fragments from the all-nickel portion of the mixture began to disappear rapidly after about a 1-min exposure of the mixture to the FAB beam indicating that metal exchange to form the all-copper complex (**I**) was occurring. This also indicates that the metal exchange observed with complexes **II–IV** occurs as a result of exposure of the matrix to the FAB beam.

In order to determine the fragmentation pathway responsible for producing the *m*/*z* 419 and 449 fragments, linked scans (B^2/E and B/E) were conducted. No ionic precursors of the *m*/*z* 419 or 449 ions could be found, which lends further credence to the hypothesis that the source of these lower mass complexes is likely to be the recombination of decomposition products in the matrix and that they are not fragments of the original complex.

Mass Spectra of Complexes VI–XI. The observation that copper exchanges with nickel in the spectra of **II–IV** prompted further study of potential interactions between other heteropolymetallic complexes. Mixed complexes of copper–cobalt (**VI**) and nickel–cobalt (**X**) were also evaluated. In addition, one complex in which the four metal sites were occupied by four different metals $(\mu_4\text{-O})L_4CuNiCoZnCl_6$ (**IX**) was also examined.

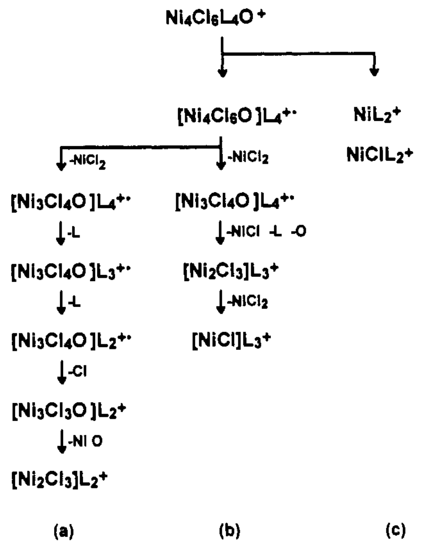


Figure 5. Fragmentation pathways for complex V, $(\mu_4\text{-O})L_4Ni_4Cl_6$, the all-nickel complex. As with copper, nickel remains primarily nickel(II) in pathway a; some nickel reduction is observed in pathway b. The decomposition products form charged metal–ligand complexes observed at *m*/*z* 449 and *m*/*z* 414 (pathway c).

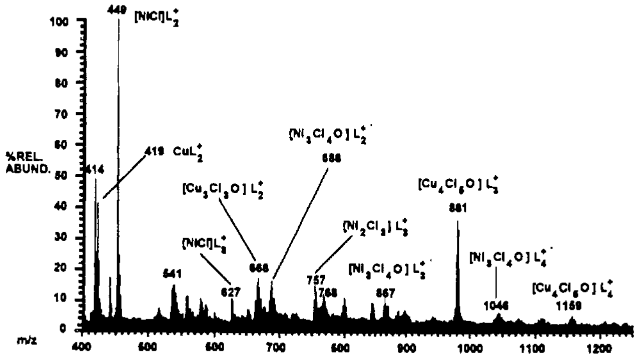


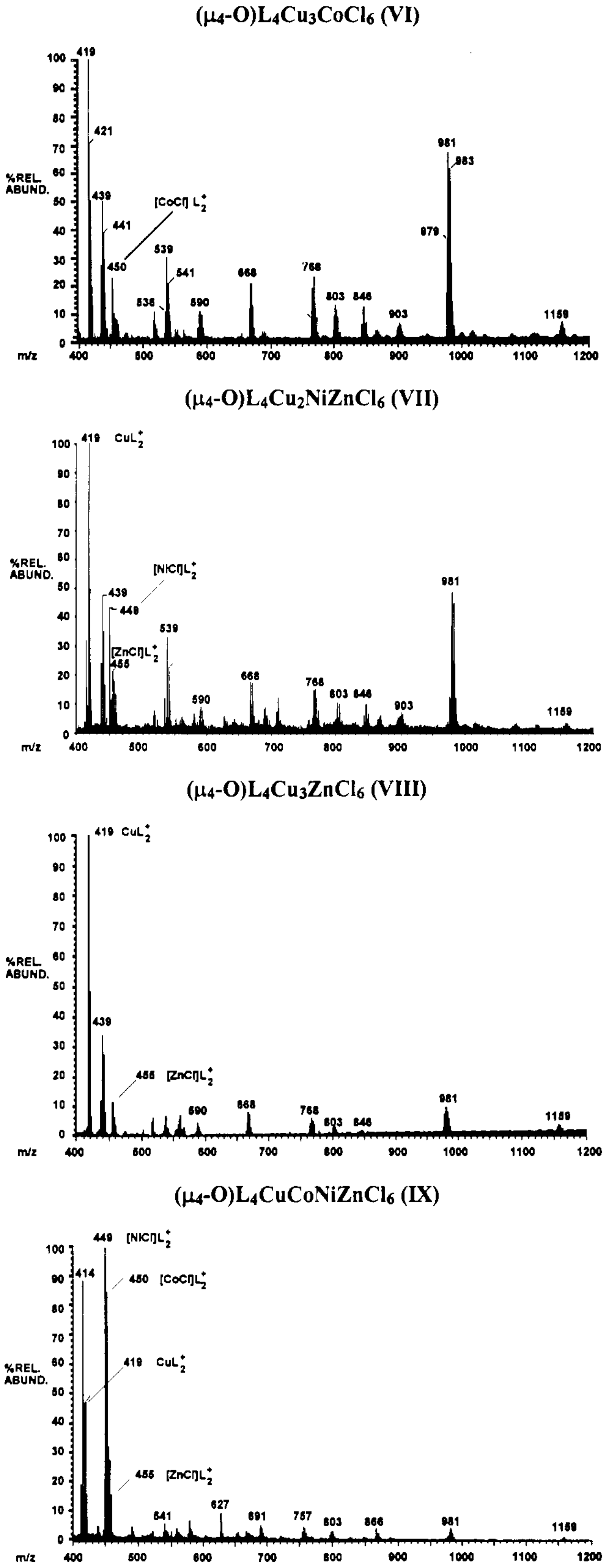
Figure 6. Physical mixture of complex **I** ($(\mu_4\text{-O})L_4Cu_4Cl_6$) and complex **V** ($(\mu_4\text{-O})L_4Ni_4Cl_6$) producing a mass spectrum with features common to both parts a and e of Figure 2, confirming that complexes **II–IV** are unique compounds and not stoichiometric mixtures of complexes **I** and **V**.

Table 2. Stoichiometry of Metal Content in Complexes I–V Compared to the Signal Intensity of the *m*/*z* 419 $(CuL_2)^+$ and *m*/*z* 449 ($[NiCl][L_2^+]$) Complexes

complex	metal content	relative abundance ratios *m*/*z* 419 $(CuL_2)^+$	 *m*/*z* 449 ($[NiCl]L_2^+$)
I	Cu_4	100	
II	Cu_3Ni	100	50
III	Cu_2Ni_2	100	100
IV	$CuNi_3$	25	100
V	Ni_4		100

Complex **VI** contains copper and cobalt in a 3:1 molar ratio. Its FAB/MS spectrum (Figure 7a) suggests that metal exchange leading to the all-copper complex (**I**) has again occurred. The CuL_2^+ ion is observed at *m*/*z* 419, and a fragment corresponding to the complex $[CoCl]L_2^+$ appears at *m*/*z* 450. Cobalt is monoisotopic, and therefore, the isotopic pattern of a single chloride at *m*/*z* 450 is readily recognized. The presence of *m*/*z* 419 and *m*/*z* 450 confirms that both cobalt and copper are present in the complex $(\mu_4\text{-O})L_4Cu_3CoCl_6$ (**VI**). It may be further concluded that metal exchange leading to the all-copper complex (**I**) occurs irrespective of the actual stoichiometry of the initial complex. This suggests that the all-copper complex (**I**) is more stable than an all-cobalt complex. In this case, as with the copper–nickel complexes **II–IV**, no fragment that contained both copper and cobalt was observed.

Three additional copper containing heteropolymetallic complexes were evaluated, and all three underwent similar metal


$(\mu_4\text{-O})L_4Cu_3CoCl_6$ (VI)

$(\mu_4\text{-O})L_4Cu_2NiZnCl_6$ (VII)

$(\mu_4\text{-O})L_4Cu_3ZnCl_6$ (VIII)

$(\mu_4\text{-O})L_4CuCoNiZnCl_6$ (IX)

Figure 7. FAB mass spectra of heteropolymetallic complexes **VI–IX**. These copper-containing complexes demonstrate similarities to the all-copper homometallic complex (**I**) shown in Figure 2a at mass 650 and greater. Below *m/z* 650, the ions observed result primarily from a recombination of metal and ligands in the NBA matrix. The presence of copper in complexes **VI–IX** is confirmed by the appearance of *m/z* 419 (a–d), the presence of nickel in complexes **VII** and **IX** (b, d) by the appearance of *m/z* 449 ($[NiCl]L_2^+$), the presence of cobalt in complexes **VI** and **IX** (a, d) at *m/z* 450 ($[CoCl]L_2^+$), and the presence of zinc in complexes **VII–IX** (b–d) at *m/z* 455, $[ZnCl]L_2^+$. The relative intensities of the metal–ligand complexes are consistent with the stoichiometry of the parent molecule.

exchange to form the copper complex. Complexes containing three or more zinc cations readily undergo decomposition during preparation.[8] However, several stable complexes of zinc have been prepared. The first of these complexes that was examined by FAB/MS was $(\mu_4\text{-O})L_4Cu_2NiZnCl_6$ (**VII**).

The most abundant fragment in the mass spectrum of $(\mu_4\text{-O})L_4Cu_2NiZnCl_6$, Figure 7b, is at *m/z* 419 and results from the formation of CuL_2^+. Other significant ions observed include $[Cu_3Cl_2]^+$ (*m/z* 439), $[NiCl]L_2^+$ (*m/z* 449), $[ZnCl]L_2^+$ (*m/z* 455), $[Cu_4Cl_3]L^+$ (*m/z* 539), and $(\mu_4\text{-O})L_3Cu_4Cl_5^+$ at *m/z* 981. The fragment at *m/z* 981 indicates that an intact core molecular structure exists with four coppers present and that metal exchange must have occurred in order for this to happen.

The spectrum of a complex containing copper and zinc, $(\mu_4\text{-O})L_4Cu_3ZnCl_6$ (**VIII**), was evaluated next, and the results are shown in Figure 7c. As in the case of $(\mu_4\text{-O})L_4Cu_2NiZnCl_6$ (**VII**), the most abundant ion observed results from the decomposition of the complex and the formation of CuL_2^+ (*m/z* 419) from the individual fragments. The appearance of *m/z* 981 suggests that metal exchange occurred to form an all-copper complex during the bombardment process. The fragment at *m/z* 455 confirms the presence of $[ZnCl]L_2^+$, and the fragment at *m/z* 439 represents $[Cu_3Cl_2]L^+$.

The final copper-containing complex examined was $(\mu_4\text{-O})L_4CoCuNiZnCl_6$ (**IX**), which contains a total of four different metals. Its FAB/MS spectrum is shown in Figure 7d. Again, the most abundant ions observed resulted from small stable complexes that form from decomposition products of the original complex. The most abundant fragment at *m/z* 449 is $[NiCl]L_2^+$, with a slightly lower abundance of NiL_2^+ observed at *m/z* 414. Lower abundances of CuL_2^+ (*m/z* 419) than expected result from the transmetalation of the original complex to the all-copper analog $(\mu_4\text{-O})L_4Cu_4Cl_5^+$ (*m/z* 1159) and other fragments consistent with the ionization of the all-copper complex creating a net deficiency of available copper ions. The formation of $[ZnCl]L_2^+$ is also observed in this spectrum but is partially obscured by the intensity of the $[NiCl]L_2^+$ (*m/z* 449) signal.

Since any complex containing copper produces highly ordered fragments consistent with those found in Figure 2, it is suggested that cobalt-, nickel-, and zinc-containing heteropolymetallic complexes undergo metal exchange to form $(\mu_4\text{-O})L_4Cu_4Cl_6$ when exposed to the FAB beam.

Finally, the spectrum of the complex $(\mu_4\text{-O})L_4CoNi_3Cl_6$ (**X**) was evaluated in order to ascertain whether products consisting of either nickel or cobalt predominated. However, this spectrum provided few spectral details in the mass region above *m/z* 650 and was therefore not included.

Thus, the metal exchange characteristics of complex **X** could not be determined despite attempts to modify the matrix and pre-analysis conditions. The lower end of the spectrum <650 Da exhibits signals at *m/z* 414 (NiL_2^+) and *m/z* 449 ($[NiCl]L_2^+$) as well as *m/z* 450 ($[CoCl]L_2^+$) with signal intensities that were in general agreement with the metal stoichiometry of the complex.

The energy required to ionize complex **X** is likely to be greater than the energy required to break the bonds of this complex.[3,4,7–9] Therefore, insufficient concentrations of intact complex **X** remain in the NBA matrix to undergo metal exchange, ionization, and detection.

The all-cobalt complex $(\mu_4\text{-O})L_4Co_4Cl_6$ (**IX**) did not produce structurally informative fragments in the spectral region >650 Da. A signal observed at *m/z* 450 is that of $[CoCl]L_2^+$. It would appear that cobalt within the molecular structure fails to provide sufficient stability for ionization and detection of high molecular weight fragments.

Other complexes with different combinations of metals were evaluated but failed to generate sufficient significant mass spectral information unless copper was present.

Conclusions

1. Competing decomposition, metal exchange, ionization, and fragmentation reactions during FAB/MS limit the amount of structural information that can be obtained for the heteropolymetallic transmetalation products of reaction 1 in a range of commonly used matrices.

2. It appears that for the complexes $(\mu_4\text{-O})L_4M_4Cl_6$ (where M_4 may be any combination of Cu, Ni, Co, and Zn) a metal exchange reaction occurs to form homopolymetallic complexes during ionization. Complexes containing copper and any other combination of metal ions undergo metal exchange to form the copper complex $(\mu_4\text{-O})L_4Cu_4Cl_6$. No fragments or ions were observed that contained two different transition metals together.

3. The primary species observed by FAB/MS are metal–ligand complexes formed by decomposition of the original complex when exposed to the FAB beam. Metal–ligand complexes formed from decomposition products contain two neutral *N,N*-diethylnicotinamide ligands. The most intense signal generally occurs in the presence of chloride ion ($[MCl]L_2^+$) because the metal is in a +2 oxidation state. The exception is copper, where ML_2^+ predominates because the copper ion is reduced to copper (I). Spectral information suggests that the original heteropolymetallic complex will convert to the most thermodynamically stable complex during exposure of the matrix to the FAB xenon beam.

4. A mixture of $(\mu_4\text{-O})L_4Cu_4Cl_6$ and $(\mu_4\text{-O})L_4Ni_4Cl_6$ produces a spectrum (Figure 6) that differs significantly from that of $(\mu_4\text{-O})L_4Cu_3NiCl_6$ (Figure 2b), $(\mu_4\text{-O})L_4Cu_2Ni_2Cl_6$ (Figure 2c), or $(\mu_4\text{-O})L_4CuNi_3Cl_6$ (Figure 2d). This indicates that complexes **II**–**IV** are uniquely different complexes and not physical mixtures of complexes **I** and **V**. The mixture of complexes **I** and **V** are relatively stable together in 3-nitrobenzyl alcohol and do not undergo metal exchange until they are exposed to the FAB beam.

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