Inorg. Chem. **2008**, *47*, 6393−6403

Inorganic Chemistry
Article

Mechanism of Single Metal Exchange in the Reactions of $[M_4(SPh)_{10}]^{2-}$ (M = Zn or Fe) with CoX_2 (X = Cl or NO_3) or $FeCl_2$

Valerie Autissier and Richard A. Henderson*

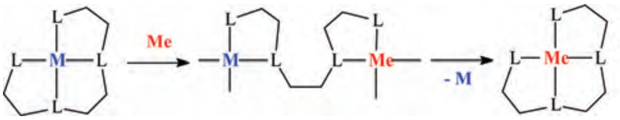
Chemistry, School of Natural Sciences, Newcastle University Newcastle upon Tyne,
NE1 7RU, U.K.

Received March 18, 2008

The kinetics of the reactions between $[Zn_4(SPh)_{10}]^{2-}$ and an excess of MX_2 (M = Co, X = NO_3 or Cl; M = Fe, X = Cl), in which a Zn^{II} is replaced by M^{II}, have been studied in MeCN at 25.0 °C. ^1H NMR spectroscopy shows that the ultimate product of the reactions is an equilibrium mixture of clusters of composition $[Zn_nM_{4-n}(SPh)_{10}]^{2-}$, and this is reflected in the multiphasic absorbance-time curves observed over protracted times (several minutes) using stopped-flow spectrophotometry to study the reactions. The kinetics of only the first phase have been determined, corresponding to the equilibrium formation of $[Zn_3M(SPh)_{10}]^{2-}$. The effects of varying the concentrations of cluster, MX_2, and $ZnCl_2$ on the kinetics have been investigated. The rate law is consistent with the equilibrium nature of the metal exchange process and indicates a mechanism for the formation of $[Zn_3M(SPh)_{10}]^{2-}$ involving two coupled equilibria. In the initial step binding of MX_2 to a bridging thiolate in $[Zn_4(SPh)_{10}]^{2-}$ results in breaking of a Zn-bridging thiolate bond. In the second step replacement of the cluster Zn involves transfer of the bridging thiolates from the Zn to M, with breaking of a Zn-bridged thiolate bond being rate-limiting. The kinetics for the reaction of $ZnCl_2$ with $[Zn_3M(SPh)_{10}]^{2-}$ (M = Fe or Co)} depends on the identity of M. This behavior indicates attack of $ZnCl_2$ at a M-μ-SPh-Zn bridged thiolate. Similar studies on the analogous reactions between $[Fe_4(SPh)_{10}]^{2-}$ and an excess of CoX_2 (X = NO_3 or Cl) in MeCN exhibit simpler kinetics but these are also consistent with the same mechanism.

Introduction

Metal exchange (transmetalation) reactions have been studied for many years but predominantly at mononuclear complexes containing multidentate ligands.[1] In such systems, the result of transferring a ligand from one metal to another is effectively metal exchange (eq 1), but, from a mechanistic viewpoint, is more usually viewed as a transfer of ligand.



(1)

However, in metal clusters, where the structural integrity of the cluster (including the ligands) can be maintained by the bulk of the cluster framework, metal exchange can occur while the ligands remain in place. Understanding how free metal ions exchange with the metal sites in polynuclear clusters is important not only for the fundamental mechanistic challenge but also in the rational synthesis of clusters containing more than one type of metal, and in understanding how metal aggregates (nanoparticles) and biological clusters (e.g., metallothioneins[2]) behave. Despite this, metal exchange reactions in clusters have been little studied.

In many clusters the metals are tightly held and metal exchange is not possible without severe disruption of the cluster, and consequently does not occur on any practical time scale. However, in the few studies of metal exchange in clusters that have been reported[3,4] the predominant mechanism involves loss of a metal from the cluster then incorporation of the new metal. These reactions are often slow since they require prior dissociation of ligands. Drawing

---

* To whom correspondence should be addressed. E-mail: r.a.henderson@ncl.ac.uk.

[1] (a) Tobe, M. L.; Burgess, J. B. *Inorganic Reaction Mechanisms*; Longman: Harlow, U.K., 1999; p 323 and refs therein. (b) Kolopajlo, L. *J. Coord. Chem.* **2006**, *59*, 891; and refs therein.

[2] Kägi, J. H. R.; Schäffer, A. *Biochemistry* **1988**, *27*, 8509; and refs therein.

[3] (a) Vahrenkamp, H. *Comments Inorg. Chem.* **1985**, *4*, 253. (b) Dunn, J. A.; Britten, J. F.; Durran, J.-C.; McGlinchey, M. J. *Organometallics* **2001**, *20*, 4690.

10.1021/ic800485t CCC: $40.75

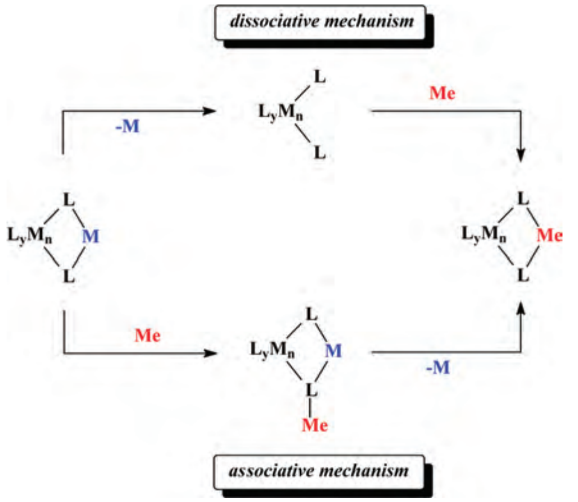


Figure 1. Schematic representation of the dissociative and associative mechanisms for metal exchange reactions of clusters.

a mechanistic comparison with the ligand substitution processes of mononuclear complexes[5] such metal exchange pathways could be described as a dissociative mechanism (Figure 1). In contrast, an associative metal exchange mechanism would involve initial binding of a free metal ion to the cluster prior to loss of a metal from the cluster.

Earlier investigations[6] have shown that mixtures of the "adamantane-shaped" clusters, $[M_4(SPh)_{10}]^{2-}$ and $[M'_4(SPh)_{10}]^{2-}$ (M = Fe, M′ = Co, Zn or Cd; M = Co, M′ = Zn or Cd) undergo rapid metal exchange to produce equilibrium mixtures of $[M_{4-n}M'_n(SPh)_{10}]^{2-}$. While these observations demonstrate that metal exchange occurs at $[M_4(SPh)_{10}]^{2-}$ with retention of the core topology, we considered these systems too complicated to be studied mechanistically. A stoichiometrically simpler system was sought to determine the kinetics of metal exchange. We found that the reactions of: (i) $[Zn_4(SPh)_{10}]^{2-}$ with $CoCl_2$, $Co(NO_3)_2$ or $FeCl_2$ in MeCN and (ii) $[Fe_4(SPh)_{10}]^{2-}$ with $CoCl_2$ (in MeCN as solvent) result in metal exchange. It is to be noted that the counteranion is included with these simple metal salts when discussing the reactions in MeCN (e.g., we write $CoCl_2$ rather than Co^{2+}). This is because, as we will show later in the Results section, our kinetic studies indicate that the counter-anions are strongly associated with the metal ion in MeCN. Consequently, the reactivity of a particular metal salt depends on the nature of the counteranion.

It is the kinetics and mechanisms of the first act of metal exchange in $[M_4(SPh)_{10}]^{2-}$ (M = Zn or Fe) which we report herein, and show that the exchange of the first metal (as described by eq 2) is an associative mechanism (Figure 1). To the best of our knowledge this is the first *kinetic study* of metal exchange in clusters.

$$[M_4(SPh)_{10}]^{2-} + M'X_2 \rightleftharpoons [M_3M'(SPh)_{10}]^{2-} + MX_2 \quad (2)$$

Clusters of the type $[M_4(SPh)_{10}]^{2-}$ have been prepared and structurally characterized for M = Zn,[7] Cd,[6] Co,[8] and Fe.[9] In all these clusters, each metal is divalent, tetrahedral, and coordinated to three bridged thiolates and a single terminal thiolate to produce a cluster with an overall "adamantane-shaped" structure. Because only the "adamantane-shaped" clusters with M = Zn, Cd, Co, and Fe have been structurally characterized, we have limited our choice of metal salts in the kinetic studies to the metal ions M'^{2+} = Co, Fe or Zn.

Experimental Section

All manipulations in both the synthesis of the compounds and the kinetic studies were performed under an atmosphere of dinitrogen using Schlenk or syringe techniques as appropriate. All solvents were freshly distilled from the appropriate drying agent immediately prior to use: MeCN (CaH_2); thf (Na-benzophenone) and diethyl ether (Na).

The compounds $Co(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2 \cdot 6H_2O$, and $FeCl_2$ were purchased from Aldrich and used as received. $[NEt_4]Cl$ was also purchased from Aldrich and dried at 80 °C in vacuo for 10 h, then stored under a dry dinitrogen atmosphere prior to use. $[NEt_4]SPh$ was prepared by the literature method.[10]

The clusters $[NEt_4]_2[M_4(SPh)_{10}]$ (M = Zn, Co or Fe) and $[NBu^n_4]_2[Fe_4(SPh)_{10}]$ were prepared by the literature methods.[6–9] The compounds were characterized by comparison of the ^{1}H NMR spectra with those reported in the literature {For $[Zn_4(SPh)_{10}]^{2-}$: δ 7.5 (multiplet, *o*-H_b); 7.2 (multiplet, *o*-H_t); 7.0 (multiplet, *p*-H); 6.9 (multiplet, *m*-H_b, *m*-H_t, *p*-H). For $[Fe_4(SPh)_{10}]^{2-}$: δ 16.0 (*m*-H_b and *m*-H_t); −3.3 (*o*-H_t); −9.2 (*o*-H_b); −9.4 (*p*-H_t); −12.7 (*p*-H_b). For $[Co_4(SPh)_{10}]^{2-}$: δ 13.0 (*m*-H_t); 11.5 (*m*-H_b); −12.0 (*p*-H_t); −14.9 (*p*-H_b), −16.5 (*o*-H_t), −24.0 (*o*-H_b)}. All the clusters were dioxygen sensitive. Furthermore, the dioxygen sensitivity appears to depend on the countercation. In particular, $[NEt_4]_2[Fe_4(SPh)_{10}]$ was too air sensitive to be handled at the low concentrations employed for the stopped-flow studies reported herein, but $[NBu^n_4]_2[Fe_4(SPh)_{10}]$ was slightly less air sensitive and so the kinetic studies were performed on this salt.

Systems Studied. In this paper we describe the kinetics of the first metal exchange reactions of $[Zn_4(SPh)_{10}]^{2-}$ with CoX_2 (X = Cl or NO_3) or $FeCl_2$, and $[Fe_4(SPh)_{10}]^{2-}$ with CoX_2. We were unsuccessful in our attempts to study the analogous reactions of $[Co_4(SPh)_{10}]^{2-}$ with $FeCl_2$. The specific problem with this cluster is that the products of the reaction contained an insoluble material which deposited on the cell windows of the stopped-flow apparatus. Consequently, between each experiment the light intensity observed by the photomultiplier got progressively less. Furthermore, the deposit could not be removed easily by treatment with acid or alkaline solutions and needed overnight soaking in 2 M HCl to be

---

(4) (a) Song, L.-C.; Yu, G.-H.; Liu, Y.; Zhang, X.-G.; Hu, Q.-M. *Organometallics* **2007**, *26*, 1966. (b) Usher, A. J.; Lucas, N. T.; Dalton, G. T.; Randles, M. D.; Vian, L.; Humphrey, M. G.; Petrie, S.; Stranger, R.; Willis, A. C.; Rae, A. D. *Inorg. Chem.* **2006**, *45*, 10859. (c) Zhang, J.; Zhang, Y.-H.; Chen, X.-N.; Ding, E.-R.; Yin, Y.-Q. *Organometallics* **2000**, *19*, 5032. (d) Song, L.-C.; Guo, D.-S.; Hu, Q.-M.; Huang, X.-Y. *Organometallics* **2000**, *19*, 960.

(5) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; Benjamin: New York, 1965.

(6) Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3928.

(7) Hucher, J. L.; Khan, M.; Said, F. F.; Tuck, D. G. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 287.

(8) (a) Dance, I. G.; Calabrese, J. C. *J. Chem. Soc., Chem. Comm.* **1975**, 762. (b) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264.

(9) (a) Hagen, K. S.; Berg, J. M.; Holm, R. H. *Inorg. Chim. Acta* **1980**, *45*, L17. (b) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.

(10) Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173.

(11) Cui, Z.; Henderson, R. A. *Inorg. Chem.* **2002**, *41*, 4158.

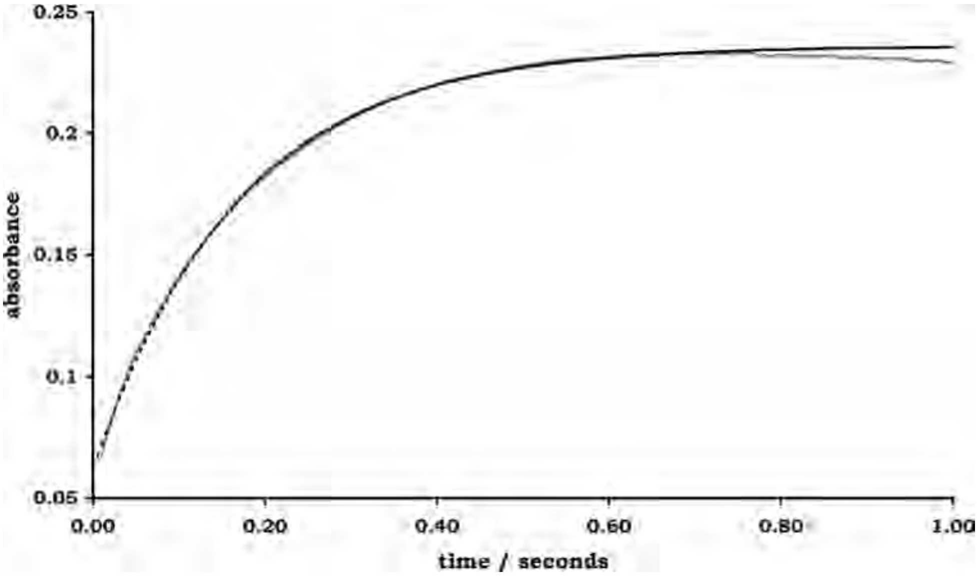


Figure 2. Typical stopped-flow absorbance-time trace (black curve) for the reaction of $[Zn_4(SPh)_{10}]^{2-}$ (0.1 mmol dm^{-3}) with $FeCl_2$ (1.25 mmol dm^{-3}) in MeCN at 25.0 °C, measured at $\lambda = 450$ nm. The exponential curve fit (gray curve) is defined by the equation $A_t = 0.236 - 0.174e^{-6.0t}$.

removed. Although some data was collected on the reaction between $[Co_4(SPh)_{10}]^{2-}$ and $FeCl_2$ (which seemed to show similar kinetics to that reported herein for the other clusters) we had concerns about the possible long-term effect the deposited precipitate might have on the kinetics, and the integrity of the stopped-flow apparatus, so have not pursued this system. The insoluble material which was deposited in the reaction between $[Co_4(SPh)_{10}]^{2-}$ and $FeCl_2$ has not been identified.

Product Analysis. ^1H NMR spectroscopy shows that upon mixing $[Zn_4(SPh)_{10}]^{2-}$ and MX_2 a complex spectrum is obtained, apparently containing an equilibrium mixture of $[Zn_{4-n}M_n(SPh)_{10}]^{2-}$ (an example is presented in Supporting Information, Figure S1). Similar complex spectra have been reported[6] for the mixtures of two different adamantane-shaped clusters.

Kinetic Studies. All kinetic studies were performed in CH_3CN. ^1H NMR spectroscopic studies show that, in the time required to record the spectra (at least 10 min), solutions of $[Zn_4(SPh)_{10}]^{2-}$ and CoX_2 or $FeCl_2$ produce a mixture of clusters where multiple metal exchange has occurred to form all $[Zn_{4-n}Co_n(SPh)_{10}]^{2-}$. When the reactions of: (i) $[Zn_4(SPh)_{10}]^{2-}$ with $CoCl_2$, $Co(NO_3)_2$ or $FeCl_2$, or (ii) $[Fe_4(SPh)_{10}]^{2-}$ with $CoCl_2$ were studied by stopped-flow spectrophotometry, at least three phases could be identified over the time scale 2 ms to 100 s. In this paper we focus on the initial phase which logically and most reasonably corresponds to the exchange of the first metal. This proposal is substantiated by the kinetic studies reported herein. In particular, analysis of the kinetics of the first phase (vide infra) of the reactions between $[M_4(SPh)_{10}]^{2-}$ and M'^{2+} shows that, in all systems studied, this phase corresponds to the binding of one M'^{2+}; and the replacement of one M in the parent cluster ($[M_4(SPh)_{10}]^{2-}$). Notably, the kinetics exhibit a dependence on the concentration of M^{2+} which is consistent with an equilibrium reaction, as described by eq 2. In addition to the first act of metal exchange being the conceptually simplest to interpret, we found that the first phase could always be analyzed. Complications associated with the rapidity of the reaction, sensitivity to traces of dioxygen over protracted periods for the slowest phases, and the intense color of the solutions when using relatively high concentrations of cluster and metal salts prohibited an analysis of the complete reaction.

All kinetic studies were performed using an Applied Photophysics SX.18 MV stopped-flow spectrophotometer, modified to handle air-sensitive solutions, connected to a RISC pc. The temperature was maintained at 25.0 ± 0.1 °C using a Grant LTD 6G thermostat tank with combined recirculating pump. The solutions of cluster and reactants were prepared under an atmosphere of dinitrogen and transferred to the spectrophotometer using gas-tight, all-glass syringes. The solutions of all reagents were prepared by dilution from freshly made stock solutions and used within 1 h. Most of the kinetics were performed under pseudo first order conditions with all reactants in a large excess over the concentration of the cluster. The absorbance-time traces were fitted to exponential curves using the Applied Photophysics software to obtain the observed rate constants (k_{obs}). A typical stopped-flow absorbance-time trace, together with corresponding exponential curve fit is shown in Figure 2. This figure also shows the goodness of the fit of the experimental data to a single exponential curve. A small deviation from the exponential fit can be observed after about 0.8 s, because of interference by the slower second phase. However, the exponential fit is good for at least 6 half-lives (ca. 98% reaction). In cases where the kinetics were not studied under strict pseudo first order conditions ($[M'X_2] \sim 5[M_4(SPh)_{10}{}^{2-}]$) the observed rate constant was determined from the *initial slope* of the plot of $\log_e \{[M_4(SPh)_{10}{}^{2-}]_t - [M_4(SPh)_{10}{}^{2-}]_\infty\}$ versus time. The observed rate constants obtained in this way were in good agreement with those obtained from exponential curve fits to the *initial* part of the corresponding stopped-flow absorbance-time traces. Furthermore, the values of the observed rate constants determined by the intial slope method fitted the pattern defined by analysis of other data collected under pseudo first order conditions.

Analysis of the dependence of k_{obs} on the concentrations of the various reactants was accomplished by graphical methods as detailed in the Results and Discussion sections. The values of k_{obs} presented in the figures in the Results and Discussion sections are the average of at least three experiments, with the agreement between the repeat experiments being within 5%. The error bars shown in the plots in Figures 4, 5, 6, 7, 8, and 9 represent this 5% uncertainty.

Results

The only previous kinetic studies on the reactions of $[M_4(SPh)_{10}]^{2-}$ involved the irreversible cluster disruption

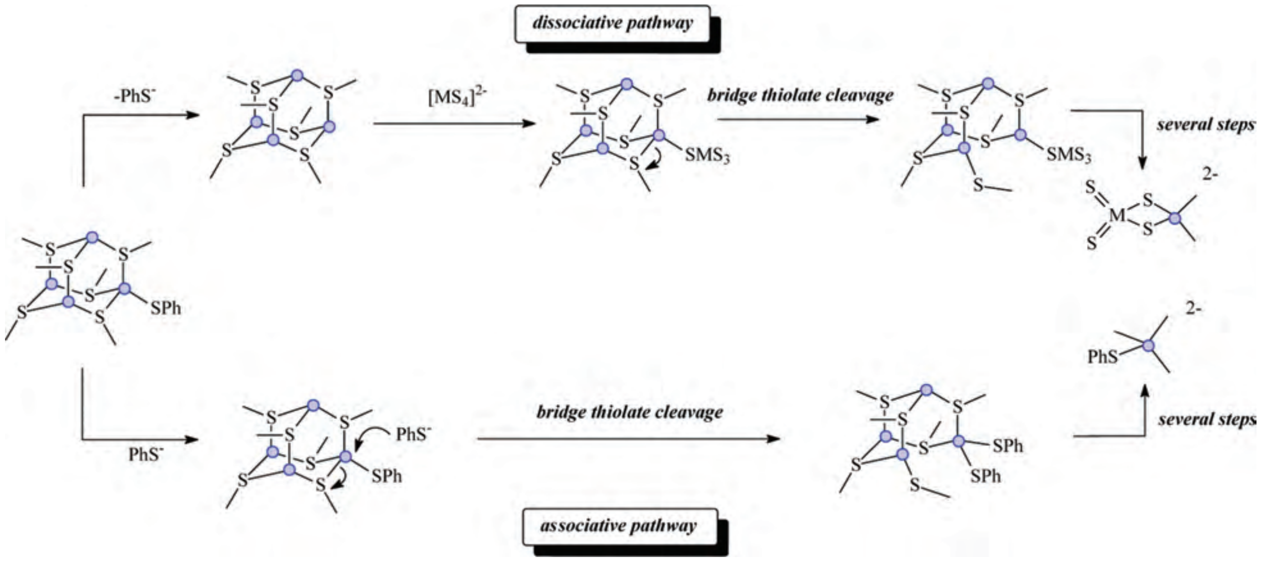


Figure 3. Summary of the initial (substitution) steps in the cluster disruption reactions of $[M_4(SPh)_{10}]^{2-}$ (M = Fe or Co) with the nucleophiles PhS^- or $[MS_4]^{n-}$ in MeCN. The full details of these pathways are in reference 11.

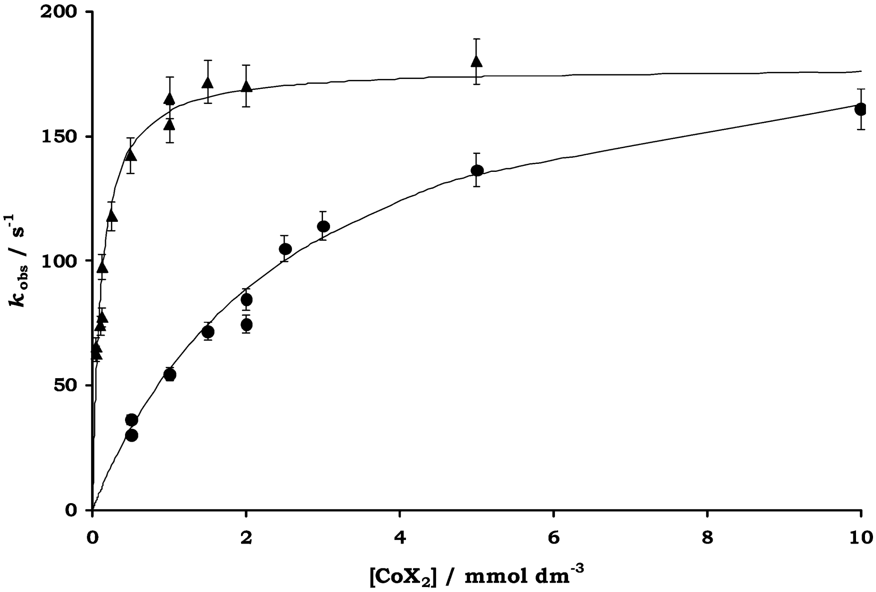


Figure 4. Kinetics of the reactions between $[Zn_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) and CoX_2 {X = NO_3 (▲); Cl (●)} in MeCN at 25.0 °C. Curves drawn are those defined by eq 3 and the parameters presented in the text. The duplicate points shown at some concentrations are presented to indicate the reproducibility of the experiments.

reactions of the M = Fe or Co derivatives with the nucleophiles PhS^- (to produce $[M(SPh)_4]^{2-}$) and with $[M'S_4]^{n-}$ to produce $[S_2M'S_2Fe(SPh)_2]^{2-}$ (M′ = Mo or W, $n = 2$) or $[(PhS)_2FeS_2VS_2\text{-}Fe(SPh)_2]^{3-}$ (M′ = V, $n = 3$)[11], as outlined in Figure 3. These reactions involve attack by nucleophiles which initiate disruption of the clusters and highlight the lability of both terminal and bridged thiolates in $[M_4(SPh)_{10}]^{2-}$. This lability is a key feature of the facile transmetalation reactions of $[M_4(SPh)_{10}]^{2-}$ presented in this paper.

In the presentation below the kinetics of the metal exchange reactions with $[Zn_4(SPh)_{10}]^{2-}$ will be described first since, with this cluster, the kinetics are the more complicated and give the most insight into the mechanism. Subsequently, the kinetics for the analogous metal exchange reactions of $[Fe_4(SPh)_{10}]^{2-}$ will be presented. The kinetics of both systems are consistent with the same mechanism.

Nature of Metal Salts in MeCN. Before describing the kinetics of the reactions of $[M_4(SPh)_{10}]^{2-}$ with various metal salts it is essential to briefly address the nature of the metal salts in MeCN since this is crucial in the interpretation of the kinetics. Upon dissolution of the salt MX_2 in MeCN, what species are present in solution? Clearly, the principal candidates are M^{2+}, MX^+ or MX_2 (in the last two cases the association of the anion and cation could represent coordination or tight ion-pair association). Although there is limited information in the literature about the solution nature of metal salts in acetonitrile, some general features are evident.

It would be anticipated that ion-pairs or even coordination between metal cations and anions would be prevalent in the dipolar, aprotic solvent MeCN ($\varepsilon = 36.0$)[12] which can only poorly solvate anions. A significant amount of quantitative information is available about the reactions of Ni^{II} com-

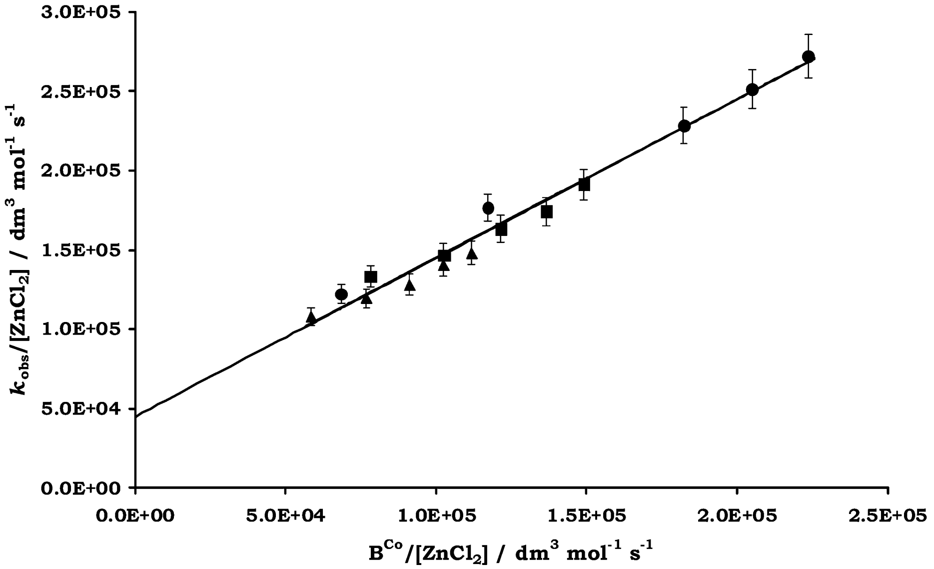


Figure 5. Kinetic data for the reaction of $[Zn_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) with $CoCl_2$ in MeCN at 25.0 °C. Plot shows dependence of $k_{obs}/[ZnCl_2]$ on $B^{Co}/[ZnCl_2]$ (where $B^{Co} = 7.8 \times 10^4[CoCl_2]/(1 + 380[CoCl_2])$, see text). Data points correspond to studies where $[CoCl_2] = 0.5 - 3.0$ mmol dm^{-3} and $[ZnCl_2] = 1.0$ mmol dm^{-3} (▲); $[ZnCl_2] = 0.5$ mmol dm^{-3} (●); $[ZnCl_2] = 0.75$ mmol dm^{-3} (■). Line drawn is that defined by eq 4 and the parameters presented in the text.

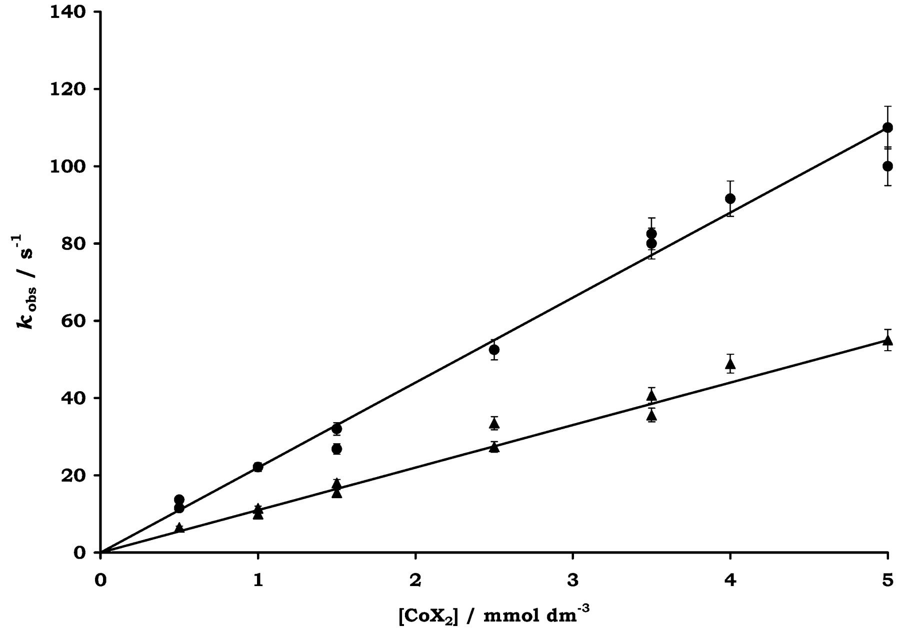


Figure 6. Kinetic data for the reactions of $[Fe_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) with CoX_2 {X = Cl (●); NO_3 (▲)} in MeCN at 25.0 °C. Lines drawn are those defined by eq 6 and the parameters presented in the text. The duplicate points shown at some concentrations are presented to indicate the reproducibility of the experiments.

plexes.[13] Thus, enhanced outer-sphere stabilization has been observed in the chemistry of Ni^{II} in MeCN and even outer-sphere complexes of Ni^{II} with neutral pyridine-based ligands possess stabilities greater than those predicted by the Eigen−Fuoss equation.[14] Measurements of the equilibrium constants for formation of Ni^{II} complexes (K_f) with a variety of ligands shows that K_f is appreciably higher in MeCN than in water. For example, in the binding of NCS^- to Ni^{II}, log $K_f = 1.8$ in water and log $K_f = 5.5$ in MeCN at 20 °C.[15]

All the kinetic analyses presented in this paper, indicate that upon dissolution of salts of MX_2 in MeCN at millimolar concentrations, $[MX_2(NCMe)_n]$ ($n = 2$ or 4, presumably) is the predominant solution species, and there is no appreciable amount of free X^-. This conclusion is consistent with earlier conductivity measurements on salts in acetonitrile.[12,13] For brevity and convenience we will refer to these solution species as MX_2. Specifically, the strong association of

---

[12] Burgess, J. *Metal Ions in Solution*; Ellis Horwood Ltd.: Chichester, U.K., 1978; p 30

[13] (a) Coetzee, J. F. *Solute-Solvent Interactions* Coetzee, J. F., Ritchie, C. D., Eds.; Marcel-Dekker: New York, 1976; Vol. *2*, Chapter 14, and refs therein. (b) Caldin, E. F. *Pure Appl. Chem.* **1979**, *51*, 2067. (c) Coetzee, J. F. *Pure Appl. Chem.* **1977**, *49*, 27. (d) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. (e) Grzyblowski, W. *J. Chem. Soc., Dalton Trans.* **1987**, 2863.

[14] (a) Chattopadhyay, P. K.; Coetzee, J. F. *Inorg. Chem.* **1976**, *15*, 400. (b) Coetzee, J. F.; Gilles, D. M. *Inorg. Chem.* **1976**, *15*, 405.

[15] Chattopadhyay, P. K.; Coetzee, J. F. *Anal. Chem.* **1974**, *46*, 2014.

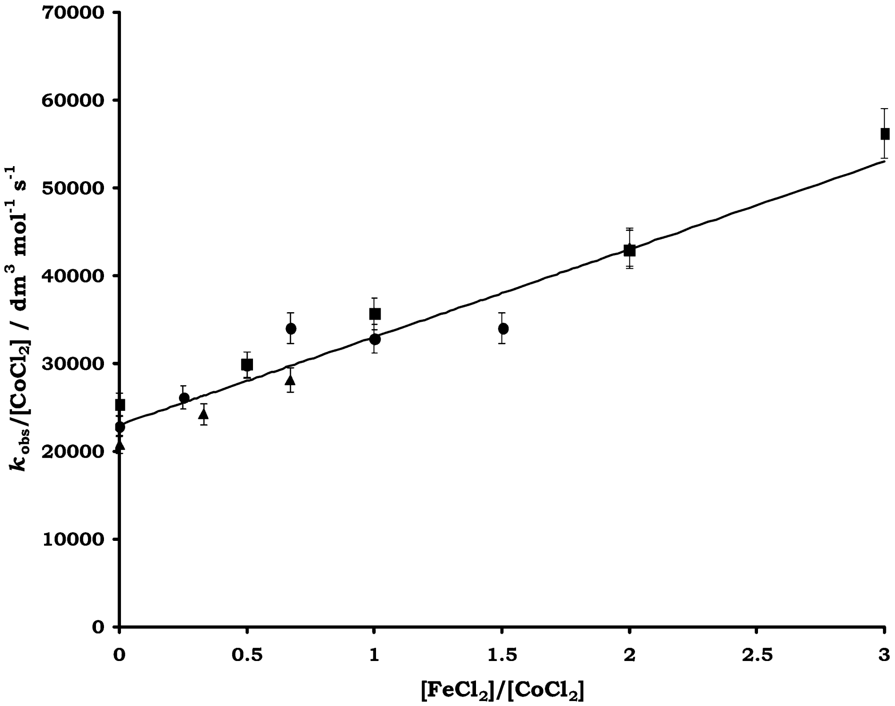


Figure 7. Kinetic data for the reaction of $[Fe_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) with $CoCl_2$ in the presence of $FeCl_2$. Plot shows the dependence of k_{obs}/[$CoCl_2$] on [$FeCl_2$]/[$CoCl_2$]. Data points correspond to [$FeCl_2$] = 0.5−3.0 mmol dm^{-3} and [$CoCl_2$] = 1.0 mmol dm^{-3} (■); [$CoCl_2$] = 2.0 mmol dm^{-3} (●); [$CoCl_2$] = 1.5 mmol dm^{-3} (▲). Line drawn is that defined by eq 7 and the parameters presented in the text.

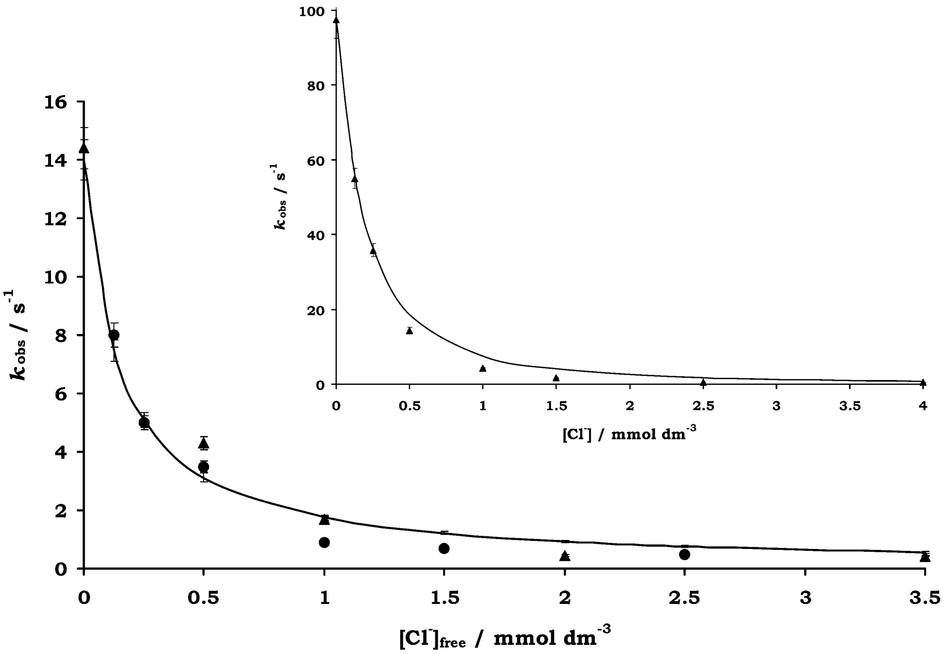


Figure 8. Main plot showing the effect of Cl$^-$ on the rate of the reaction between $[Zn_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) and $CoCl_2$ (0.25 mmol dm^{-3}), (▲), and comparison with the effect that Cl$^-$ has on the rate of the reaction between $[Zn_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) and $Co(NO_3)_2$ (0.25 mmol dm^{-3}) in the presence of $[Cl^-]_{free}$ (●), where $[Cl^-]_{free} = [Cl^-]_{total} - 0.5 \times 10^{-3}$ mol dm^{-3} (see text). Temperature = 25.0 °C. The curve is that defined by eq 8. Inset plot showing the effect of Cl$^-$ on the rate of the reaction between $[Zn_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) and $Co(NO_3)_2$ (0.25 mmol dm^{-3}) over the entire range of Cl$^-$ concentration.

chloride to the metal ion results in the following two important features of the kinetics: (i) the rates of the reactions of $Co(NO_3)_2$ and $CoCl_2$ with $[M_4(SPh)_{10}]^{2-}$ depends on the Co^{II} salt and (ii) in solutions made from dissolution of $CoCl_2$, $FeCl_2$ or $ZnCl_2$ no free chloride is present. These studies will be described in detail in a later section.

Reaction of $[Zn_4(SPh)_{10}]^{2-}$ with Co^{II} or Fe^{II} Salts. The kinetics of the reaction between $[Zn_4(SPh)_{10}]^{2-}$ (0.1 mmol dm^{-3}) and an excess of CoX_2 (X = NO_3 or Cl) in MeCN exhibits a first order dependence on the concentration of cluster as demonstrated by the fit of the absorbance-time traces to exponential curves (see example in Figure 2). Furthermore, in experiments where [$CoCl_2$] = 2.5 mmol dm^{-3}, but the concentration of $[Zn_4(SPh)_{10}]^{2-}$ is varied over the range [$Zn_4(SPh)_{10}{}^{2-}$] = 0.05 − 0.5 mmol dm^{-3}, k_{obs} is constant (k_{obs} = 100 ± 8 s^{-1}). The dependence of the rate

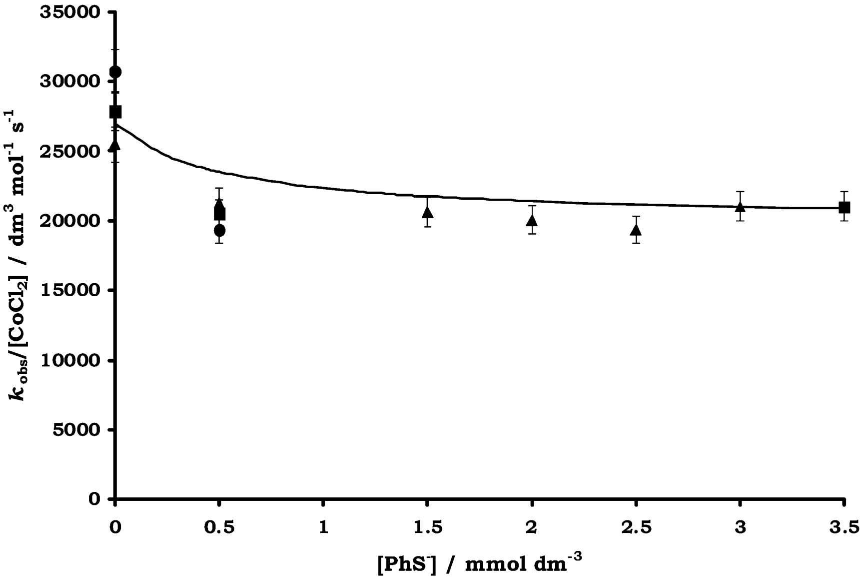


Figure 9. Effect of PhS^- on the rate of the reaction between $[Fe_4(SPh)_{10}]^{2-}$ and $CoCl_2$ in MeCN at 25.0 °C. Data points correspond to $[CoCl_2] = 0.5$ mmol dm^{-3} (●); $[CoCl_2] = 1.0$ mmol dm^{-3} (■); $[CoCl_2] = 2.0$ mmol dm^{-3} (▲).

on the concentration of CoX_2 is complicated and exhibits a nonlinear dependence as shown in Figure 4. Thus, at low concentrations of CoX_2 the rate of the reaction exhibits a first order dependence on the concentration of CoX_2, but at high concentrations of CoX_2 the rate is independent of the concentration of CoX_2.

Analysis of these data by the usual graphs of $1/k_{obs}$ versus $1/[CoX_2]$ gave straight line plots[16] from which the rate law shown in eq 3 can be determined. For X = NO_3: $a = 1.6 \pm 0.2 \times 10^6$ dm^3 mol^{-1} s^{-1}, $b = 9.0 \pm 0.2 \times 10^3$ dm^3 mol^{-1}; for X = Cl: $a = 7.8 \pm 0.2 \times 10^4$ dm^3 mol^{-1} s^{-1}, $b = 3.8 \pm 0.2 \times 10^2$ dm^3 mol^{-1} s^{-1}.

$$\frac{-d[Zn_4(SPh)_{10}{}^{2-}]}{dt} = \frac{a[CoX_2][Zn_4(SPh)_{10}{}^{2-}]}{1 + b[CoX_2]} \qquad (3)$$

^{1}H NMR spectroscopy indicates that the reactions between $[Zn_4(SPh)_{10}]^{2-}$ and CoX_2 produce an equilibrium mixture (Supporting Information). The stopped-flow absorbance-time curves also indicate equilibrium reactions. For example, in the reactions of $[Zn_4(SPh)_{10}]^{2-}$ (0.1 mmol dm^{-3}) with $CoCl_2$, the initial absorbance is about 0.31; however, when $[CoCl_2] = 0.5$ mmol dm^{-3} the absorbance change (ΔA) is about 0.063 but when $[CoCl_2] = 5.0$ mmol dm^{-3}, ΔA is about 0.205. In principle, we can use these spectrophotometric changes to calculate the equilibrium constant for the reaction. However, the multiphasic nature of these reactions precludes sufficiently accurate measurement of the absorbance changes for a full quantitative analysis.

Because the spectroscopic changes for the reaction between $[Zn_4(SPh)_{10}]^{2-}$ and CoX_2 are consistent with an equilibrium reaction, we have investigated the effect of $ZnCl_2$ on the rate of the reaction. When the kinetics of the reactions between $[Zn_4(SPh)_{10}]^{2-}$ and CoX_2 (X = NO_3 or Cl) are measured in the presence of $ZnCl_2$, at constant concentration of CoX_2, the rate increases with increasing concentration of $ZnCl_2$ as shown, for the reaction with $CoCl_2$, in Figure 5. In analyzing the data from a series of such experiments it is necessary to allow for the nonlinear dependence of the rate on the concentration of $CoCl_2$ described by eq 3. Figure 5 shows the plot of $k_{obs}/[ZnCl_2]$ versus $B^{Co}/[ZnCl_2]$ {where $B^{Co} = 7.8 \times 10^4[CoCl_2]/(1 + 380[CoCl_2])$}. From the resulting straight line the rate law shown in eq 4 was determined.

$$\frac{-d[Zn_4(SPh)_{10}{}^{2-}]}{dt} = \left\{\frac{a[CoX_2]}{1 + b[CoX_2]} + (4.5 \pm 0.2) \times 10^4[ZnCl_2]\right\}[Zn_4(SPh)_{10}{}^{2-}] \qquad (4)$$

Similar studies have been performed for the reaction between $[Zn_4(SPh)_{10}]^{2-}$ and $FeCl_2$ in the presence of $ZnCl_2$, and analogous kinetic behavior was observed (kinetic data presented in Supporting Information, Supplementary Tables). Analysis of the kinetic data, by the graphical methods described above, gives the rate law for the reaction of $[Zn_4(SPh)_{10}]^{2-}$ with $FeCl_2$ in the presence of $ZnCl_2$ shown in eq 5.

$$\frac{-d[Zn_4SPh_{10}{}^{2-}]}{dt} = \left\{\frac{(7.8 \pm 0.5) \times 10^3[FeCl_2]}{1 + (4.8 \pm 0.2) \times 10^2[FeCl_2]} + (1.8 \pm 0.2) \times 10^3[ZnCl_2]\right\}[Zn_4SPh_{10}{}^{2-}] \qquad (5)$$

Reaction of $[Fe_4(SPh)_{10}]^{2-}$ with Co^{II} Salts. The kinetics of the reaction between $[Fe_4(SPh)_{10}]^{2-}$ (0.05 mmol dm^{-3}) and an excess of CoX_2 (X = NO_3 or Cl) exhibit a first order dependence on the concentration of cluster as demonstrated by the fit of the absorbance-time curves to exponential curves. In addition, in experiments where $[CoCl_2] = 2.5$ mmol dm^{-3} but the concentration of $[Fe_4(SPh)_{10}]^{2-}$ was varied over the range $[Fe_4(SPh)_{10}{}^{2-}] = 0.05 - 0.5$ mmol dm^{-3}, k_{obs} was constant ($k_{obs} = 52 \pm 3$ s^{-1}). The rate of the reaction exhibits a first order dependence on the concentration

---

(16) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991; p 3.

Table 1. Summary of the Elementary Rate and Equilibrium Constants for the Reactions of $[Zn_4(SPh)_{10}]^{2-}$ with CoX_2 ($X = NO_3$, Cl or SPh) or $FeCl_2$, and $[Fe_4(SPh)_{10}]^{2-}$ with CoX_2 in MeCN at 25.0 °C

cluster $[M_4(SPh)_{10}]^{2-}$	metal salt MX_2	K_1^M/dm^3 mol^{-1}	k_2^M/s^{-1}	$K_1^M k_2^M$/dm^3 mol^{-1} s^{-1}	k_{-2}^M/dm^3 mol^{-1} s^{-1}	$K_1^M K_2^M$
$[Zn_4(SPh)_{10}]^{2-}$	$Co(NO_3)_2$	$9.0 \pm 0.2 \times 10^3$	$1.8 \pm 0.2 \times 10^2$	$1.6 \pm 0.2 \times 10^6$	$4.2 \pm 0.2 \times 10^4$	38.6 ± 0.3
	$CoCl_2$	$3.8 \pm 0.2 \times 10^2$	$2.1 \pm 0.2 \times 10^2$	$7.8 \pm 0.2 \times 10^4$	$4.5 \pm 0.2 \times 10^4$	1.7 ± 0.2
	$FeCl_2$	$4.8 \pm 0.2 \times 10^2$	16.3 ± 1	$7.8 \pm 0.2 \times 10^3$	$1.8 \pm 0.2 \times 10^3$	4.3 ± 0.3
$[Fe_4(SPh)_{10}]^{2-}$	$Co(NO_3)_2$	≤ 20[a]	$\geq 5.5 \times 10^2$	$1.1 \pm 0.2 \times 10^2$	$1.0 \pm 0.2 \times 10^4$	1.1 ± 0.2
	$CoCl_2$	≤ 20[a]	$\geq 1.2 \times 10^3$	$2.3 \pm 0.2 \times 10^4$	$1.2 \pm 0.2 \times 10^4$	1.9 ± 0.2

[a] Limits for K_1M and k_2^M established assuming the full rate law for the reactions with $[Fe_4(SPh)_{10}]^{2-}$ is the same as that with $[Zn_4(SPh)_{10}]^{2-}$. Because, at the highest concentration of $[CoX_2]_{max}$, there is no evidence of departure from a first order dependence on the concentration of $[CoX_2]$ and hence $K_1^{Co}[CoX_2]_{max} \leq 0.1$.

of CoX_2 over the concentration range of CoX_2 amenable to study ($[CoX_2] = 0 - 5.0$ mmol dm^{-3}), as shown in Figure 6. The rate law derived from these kinetics is shown in eq 6, for $X = NO_3$: $c = (1.1 \pm 0.2) \times 10^4$ dm^3 mol^{-1} s^{-1}; $X = Cl$: $c = (2.3 \pm 0.2) \times 10^4$ dm^3 mol^{-1} s^{-1}. As with the studies on $[Zn_4(SPh)_{10}]^{2-}$, the spectroscopic changes for the reaction between $[Fe_4(SPh)_{10}]^{2-}$ and CoX_2 are consistent with an equilibrium reaction, so we have investigated the effect of $FeCl_2$ on the rate of the reaction. The addition of $FeCl_2$ to the reaction between $[Fe_4(SPh)_{10}]^{2-}$ and CoX_2 leads to an increase in the rate of the reaction as shown (for the reaction with $CoCl_2$) in Figure 7. Analysis of the data gives the rate law shown in eq 7. The plot in Figure 7 differs from that shown in Figure 5 (for the reaction of $[Zn_4(SPh)_{10}]^{2-}$), in that the abscissa corresponds to $[FeCl_2]/[CoCl_2]$ because the reaction of $[Fe_4(SPh)_{10}]^{2-}$ with CoX_2 exhibits a simple first order dependence on the concentration of $[CoX_2]$.

$$\frac{-d[Fe_4(SPh)_{10}{}^{2-}]}{dt} = c[CoX_2][Fe_4(SPh)_{10}{}^{2-}] \qquad (6)$$

$$\frac{-d[Fe_4(SPh)_{10}{}^{2-}]}{dt} = \{c[CoX_2] + (1.0 \pm 0.2) \times 10^4[FeCl_2]\}[Fe_4(SPh)_{10}{}^{2-}] \qquad (7)$$

Effect of Cl^- on the Rate of Metal Exchange in $[M_4(SPh)_{10}]^{2-}$. Earlier in this paper the problem of what solution species are present upon dissolution of CoX_2 or $FeCl_2$ in MeCN was outlined. Our studies on the reactions of $[M_4(SPh)_{10}]^{2-}$ with MX_2 salts reinforce the proposal that the anions are strongly associated with the metal cation. In particular, we have investigated the nature of $CoCl_2$ in MeCN, and those studies are described in this section.

It is evident from Figures 4 and 6 that, at low concentrations of CoX_2, the rate of the first metal exchange in $[M_4(SPh)_{10}]^{2-}$ depends on the *nature* of the metal salt. For example, the reaction of $[Zn_4(SPh)_{10}]^{2-}$ with $Co(NO_3)_2$ is faster than that with $CoCl_2$ at the same concentration of metal salt. For the reaction between $[Zn_4(SPh)_{10}]^{2-}$ and $Co(NO_3)_2$ (0.25 mmol dm^{-3}), addition of chloride (added as $[NEt_4]Cl$) leads to a decrease in the rate, as shown in Figure 8 (inset). The decrease in k_{obs} is quantitatively consistent with the formation of $CoCl_2$. For example, when $[Cl^-] = 0.5$ mmol dm^{-3} and $[Co(NO_3)_2] = 0.25$ mmol dm^{-3}, $k_{obs} = 14.4$ s^{-1}. This value is in good agreement with the kinetics for the reaction between $[Zn_4(SPh)_{10}]^{2-}$ and $CoCl_2$ ($[CoCl_2] = 0.25$ mmol dm^{-3}), calculated using eq 3 which gives $k_{obs} = 17.8$ s^{-1}. This result is consistent with association of two chloride ions with Co^{2+}. However, it is also evident from Figure 8 that further increase in the concentration of chloride (when $[Cl^-] > 2[Co]$), results in a further decrease in the rate. In separate experiments the addition of chloride was shown to lead to a decrease in the rate of the reaction between $CoCl_2$ (0.25 mmol dm^{-3}) and $[Zn_4(SPh)_{10}]^{2-}$, as shown in Figure 8 (inset).

The following analysis shows that the effect that chloride has on the rates of the reactions of $[Zn_4(SPh)_{10}]^{2-}$ with $Co(NO_3)_2$ and $CoCl_2$ is the same, giving a consistent picture of the solution species of these two Co^{II} salts in MeCN. In the experiments with $Co(NO_3)_2$ (0.25 mmol dm^{-3}), if we assume that at $[Cl^-] = 0.5$ mmol dm^{-3} stoichiometric amounts of $CoCl_2$ have been formed, then the plot shown in Figure 8 (main) can be produced, where $[Cl^-]_{free} = [Cl^-]_{total} - 0.5 \times 10^{-3}$ mol dm^{-3}. In the same plot is shown the data {replicated from Figure 8 (inset)} showing the effect that chloride has on the rate of the reaction between $CoCl_2$ (0.25 mmol dm^{-3}) and $[Zn_4(SPh)_{10}]^{2-}$. It is evident that the data corresponding to the effect that chloride has on the rate of the reaction between $Co(NO_3)_2$ and $[Zn_4(SPh)_{10}]^{2-}$ and the data corresponding to the effect that chloride has on the rate of the reaction between $CoCl_2$ and $[Zn_4(SPh)_{10}]^{2-}$ follow the same curve, defined by eq 8. It is important to stress that we have included this curve, drawn through the data in Figure 8 (main), principally to guide the eye. The quality of the data is not sufficiently good to be sure that the region $[Cl^-] = 0 - 0.5$ mmol dm^{-3} exhibits a linear dependence, corresponding to the stoichiometric addition of chloride to the metal salt.

$$k_{obs} = \frac{B^{Co}}{1 + 7000[Cl^-]_{free}} \qquad (8)$$

In summary, the data presented in Figure 8 indicates the following. (i) In solutions of $CoCl_2$ both chlorides strongly associate with the Co^{2+} and no appreciable amounts of free chloride is present. It seems likely that the solutions of $CoCl_2$ principally contain $[CoCl_2(NCMe)_n]$, where $n = 2$ or 4. The conclusion that in solutions of $CoCl_2$ there is effectively no free Cl^- is consistent with other kinetic studies reported herein. Thus, in the studies involving $ZnCl_2$ and $FeCl_2$, analysis of the data shows no evident dependence on the concentration of chloride. (ii) In solutions containing $CoCl_2$ in the presence of an excess of chloride, the inhibition is due to further association (or binding) of chloride to form

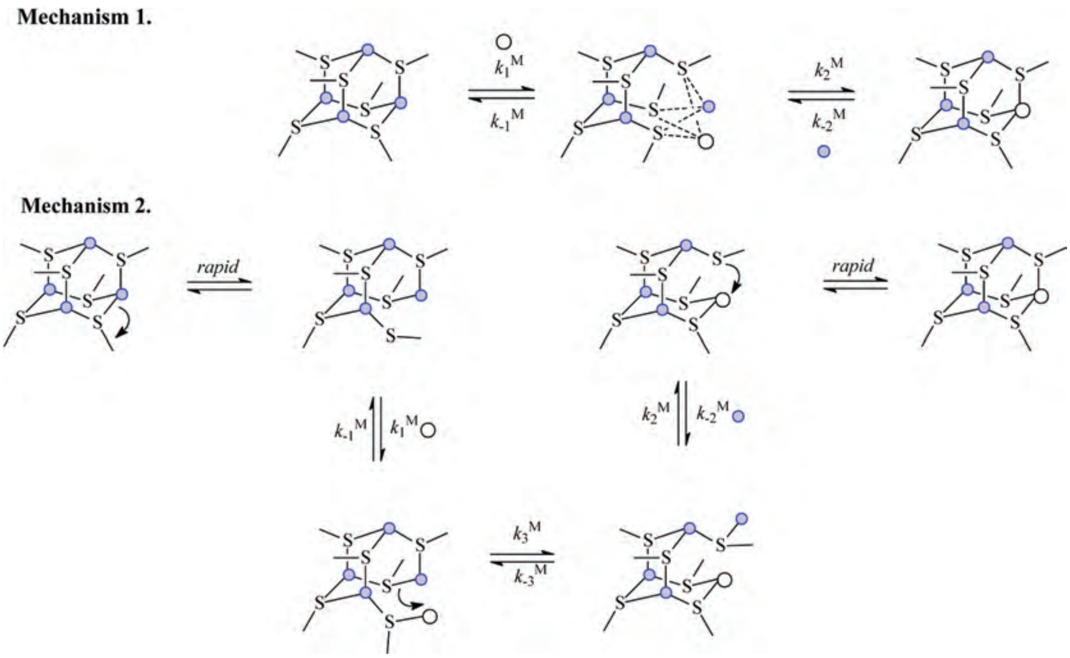


Figure 10. Two possible mechanisms for the metal exchange reactions of $[M_4(SPh)_{10}]^{2-}$ (M = Zn or Fe) with $M'X_2$ (M′ = Co, X = NO_3 or Cl; M′ = Fe, X = Cl) in MeCN. Top: Mechanism 1, involving attack of $M'X_2$ at bridging thiolate of cluster. Bottom: Mechanism 2, involving initial bridged thiolate cleavage prior to attack of $M'X_2$ at pendant thiolate. For simplicity, in neither mechanism are the terminal thiolate ligands shown.

$CoCl_3^-$, or that the equilibrium involving $CoCl^+$ and $CoCl_2$ is disturbed to favor $CoCl_2$. Irrespective of the explanation, it is clear that the $CoCl_2$ and $CoCl_3^-$ species are less reactive in the transmetalation reactions than Co^{2+} or $CoCl^+$.

Effect of PhS^- on the Rate of Metal Exchange. Studies on the reaction between $CoCl_2$ and $[Fe_4(SPh)_{10}]^{2-}$ in the presence of PhS^- ($[PhS^-] \leq 3.5$ mmol dm^{-3}) show that PhS^- has no appreciable effect on the rate of metal exchange (Figure 9). We have chosen to study the reactions with $[Fe_4(SPh)_{10}]^{2-}$ so that the complicating side-reaction involving direct reaction of the cluster with PhS^- can be avoided.

Previous studies showed that PhS^- reacts with $[Fe_4(SPh)_{10}]^{2-}$ to form $[Fe(SPh)_4]^{2-}$ (eq 9). The kinetics of this $[Fe(SPh)_4]^{2-}$ forming reaction exhibits simple first order dependences on the concentrations of both cluster and PhS^- ($k = 2.5 \times 10^2$ dm^3 mol^{-1} s^{-1}).[11] Thus, under the conditions used in the metal exchange studies (when $[PhS^-] \leq 3.5$ mmol dm^{-3}), the formation of $[Fe(SPh)_4]^{2-}$ is associated with $k_{obs} \leq 0.88$ s^{-1}. In the data presented in Figure 9, for the reaction between $CoCl_2$ and $[Fe_4(SPh)_{10}]^{2-}$ in the presence of PhS^-, the smallest measured value of $k_{obs} = 3.5$ s^{-1}. Consequently, the reaction forming $[Fe(SPh)_4]^{2-}$ makes no significant contribution.

$$[M_4(SPh)_{10}]^{2-} + 6PhS^- \rightarrow 4[M(SPh)_4]^{2-} \qquad (9)$$

It is evident from Figure 9 that PhS^- has a negligible effect on the rate of the reaction between $[Fe_4(SPh)_{10}]^{2-}$ and $CoCl_2$. We suggest that the small decrease in k_{obs} evident at low concentrations of PhS^- is due to the formation of $Co(SPh)_2$ or $Co(SPh)^+$ which react slower with $[Fe_4(SPh)_{10}]^{2-}$ than $CoCl_2$. Thus, there is no evidence for binding of PhS^- to $[Fe_4(SPh)_{10}]^{2-}$ to form $[Fe_4(SPh)_{11}]^{3-}$ which undergoes slower metal exchange than the parent cluster. However, since binding of the thiolate to $[Fe_4(SPh)_{10}]^{2-}$ would (most reasonably) only significantly affect the rate of metal exchange of one Fe site, leaving the other three Fe sites in the cluster little perturbed, we cannot rule out this possibility altogether.

Discussion

Mechanism of Metal Exchange in $[M_4(SPh)_{10}]^{2-}$. The rate laws for the reactions of $[Zn_4(SPh)_{10}]^{2-}$ with $CoCl_2$ (eq 4) or $FeCl_2$ (eq 5) in the presence of $ZnCl_2$ are both consistent with a mechanism comprising coupled equilibria.[17] Two possible mechanisms are shown in Figure 10. On the basis of the rate law these two mechanisms are indistinguishable. The two mechanisms are similar, and only differ in the timing of the elementary steps: notably, the degree of bond-making of the thiolates to the incoming metal and bond-breaking of the same thiolates from the parent metal in the cluster. Mechanism 1 represents a concerted process while Mechanism 2 shows the stepwise mechanism. The absence of a dependence on the concentration of PhS^- in the rate of metal exchange means that dissociation of a (presumably terminal) thiolate ligand prior to a metal exchange process is not involved in the mechanism, at least up to the rate-limiting step.

In both mechanisms, the equilibrium nature of the metal exchange is reflected in the symmetrical nature of the proposed mechanisms, which is dictated by the reversibility of the transmetalation. In Mechanism 1, shown at the top of Figure 10, the initial step is the attack of $M'X_2$ at a sulfur of a bridged thiolate in $[M_4(SPh)_{10}]^{2-}$. Subsequently, there is progressive transfer of the three (labile) bridging thiolates from the parent metal (M) to the incoming metal (M′), with an intermediate in which all these thiolates are bound symmetrically to both parent and incoming metal. In Mechanism 2, initial cleavage of a bridged thiolate precedes attack of MX_2. The bridged thiolate does not dissociate from the cluster completely, but becomes a terminal thiolate. Subsequently the thiolates of the cluster transfer by dissociation from the parent metal (M) then attachment to the new metal (M′).

The rate constants for the reaction of $ZnCl_2$ with $[Zn_3M(SPh)_{10}]^{2-}$ (k_{-2}^M) shows a marked dependence on the nature of M (Table 1), and this reveals further details about the mechanisms. For Mechanism 1, this observation indicates that the interaction of $ZnCl_2$ with the cluster occurs close to the M site. Specifically, the observation indicates that the reverse pathway involves attack of $ZnCl_2$ at a bridged thiolate still bound to the M site and hence would exhibit a rate dependent on the nature of M. For Mechanism 2, the dependence of k_{-2}^M on the nature of M would necessitate that initial dissociation of a M-μ-SPh bond in $[Zn_3M(SPh)_{10}]^{2-}$ occurs before or during the rate-limiting step. It would be anticipated that the rate constant for attack of $ZnCl_2$ at a pendant thiolate which has dissociated (and hence remote) from M would be essentially independent of the nature of M. Parenthetically, it is worth stressing that a full description of the metal exchange processes occurring on $[Zn_3M(SPh)_{10}]^{2-}$ in both mechanisms would also include pathways in which $ZnCl_2$ attacks a bridged thiolate which is not attached to M. Such a pathway would be nonproductive, merely exchanging one zinc atom for another.

The rate law associated with Mechanism 1 is shown in eq 10[17,18] and the associated elementary rate constants for the studies on $[Zn_4(SPh)_{10}]^{2-}$ and $[Fe_4(SPh)_{10}]^{2-}$ are summarized in Table 1.

$$\frac{\mathrm{d}[MM'_3(SPh)_{10}{}^{2-}]}{\mathrm{d}t} = \left\{\frac{K_1{}^M k_2{}^M[MX_2]}{1+K_1{}^M[MX_2]} + k_{-2}[MCl_2]\right\}[M'_4(SPh)_{10}{}^{2-}] \quad (10)$$

The rate law shown in eq 10 is observed in the reactions of all MX_2 with $[Zn_4(SPh)_{10}]^{2-}$. However, in the studies on the reactions of CoX_2 with $[Fe_4(SPh)_{10}]^{2-}$ a simpler rate law is observed (eq 7). This simpler rate law is a limiting form of eq 10, when $K_1^M[MX_2] \ll 1$, resulting in eq 11.

$$\frac{\mathrm{d}[MM'_3(SPh)_{10}{}^{2-}]}{\mathrm{d}t} = \{K_1{}^M k_2{}^M[MX_2] + k_{-2}{}^M[MCl_2]\}[M'_4(SPh)_{10}{}^{2-}] \quad (11)$$

There are several points about the values of the rate and equilibrium constants presented in Table 1 which warrant discussion since they give further insight into the intimate mechanism of the metal exchange reactions of $[M_4(SPh)_{10}]^{2-}$. (i) For the reactions between $[Zn_4(SPh)_{10}]^{2-}$ and CoX_2, the values of K_1^{Co} depend on the nature of X ($K_1^{CoNO3} > K_1^{CoCl}$). This is consistent with the conclusion, presented earlier, that in MeCN the metal salt (MX_2) in solution has the anion strongly associated (or coordinated) to the metal. (ii) The value of K_1^M depends on the nature of the cluster. Thus, for $[Zn_4(SPh)_{10}]^{2-}$, $K_1^{CoNO3} = 8.8 \times 10^3$ dm^3 mol^{-1} and $K_1^{CoCl} = 3.8 \times 10^2$ dm^3 mol^{-1}; while for $[Fe_4(SPh)_{10}]^{2-}$ it can be estimated that both K_1^{CoNO3} and $K_1^{CoCl} < 20$ dm^3 mol^{-1} since $K_1^M[CoX_2] < 0.1$, even at the highest concentration of CoX_2 used. This difference in the binding affinities of the different cobalt salts toward $[Zn_4(SPh)_{10}]^{2-}$ and $[Fe_4(SPh)_{10}]^{2-}$ is presumably attributable to the effect that the metals in the cluster have on the Lewis basicity of the bridging thiolate ligands. It appears that the bridging thiolate ligands in $[Zn_4(SPh)_{10}]^{2-}$ are more Lewis basic than those in $[Fe_4(SPh)_{10}]^{2-}$. (iii) The values of k_2^M for the reactions of $CoCl_2$ or $FeCl_2$ with $[Zn_4(SPh)_{10}]^{2-}$ correspond to the transfer of thiolate ligands from Zn to M′ (M′ = Co or Fe), and depend, as might be expected, on the nature of M′ ($k_2^{Co} = 2.1 \times 10^2$ s^{-1}; $k_2^{Fe} = 16.3$ s^{-1}). This indicates that in the transfer of these ligands bond-making to M′ as well as bond-breaking from Zn is important. (iv) The values of k_2^{CoX} for the reactions of CoX_2 with $[Zn_4(SPh)_{10}]^{2-}$ are essentially insensitive to the nature of X ($k_2^{CoNO3} = 1.8 \times 10^2$ s^{-1}; $k_2^{CoCl} = 2.1 \times 10^2$ s^{-1}). Bearing in mind our conclusion from point (iii), where the reactants were MCl_2, it seems likely that the sensitivity of k_2^M is principally to the metal (M′) and not the ligands on M′. (v) Finally, we have already pointed out that the values of k_{-2}^M for the reaction of $ZnCl_2$ with $[Zn_3M(SPh)_{10}]^{2-}$ are dependent on the nature of M. However, studies on the reactions between $CoCl_2$ or $Co(NO_3)_2$ with $[Zn_4(SPh)_{10}]^{2-}$ give the same value of k_{-2}^{Co}. This observation is consistent with the product of the forward reaction being $[Zn_3Co(SPh)_{10}]^{2-}$, and the anion X is no longer associated with the Co.

The work by others has shown that metal exchange occurs between clusters.[6] A feature of the kinetics of the reactions between $[M_4(SPh)_{10}]^{2-}$ and $M'X_2$ is the strict first order dependence on the concentration of the cluster (up to about 98% completion). If metal exchange between clusters was occurring we would expect to see a contribution from a second order dependence on the concentration of $[M_4(SPh)_{10}]^{2-}$. The absence of such behavior indicates that metal exchange between clusters is slower than metal exchange between clusters and $M'X_2$. While others have monitored the exchange between $[M_4(SPh)_{10}]^{2-}$ and $[M'_4(SPh)_{10}]^{2-}$ using ^{1}H NMR spectroscopy,[6] a mechanism was not proposed. On the basis of our conclusions about the mechanism of metal exchange between cluster and $M'X_2$, we can suggest how metal exchange occurs between clusters. Our suggested mechanism is shown in Figure 11. The key features of this mechanism are analogous to those described for the reactions of $[M_4(SPh)_{10}]^{2-}$ with $M'X_2$. Initial attack of the metal from one cluster on the thiolate bridge of another produces an intermediate with both clusters joined through this thiolate. Subsequent transfer of the bridging thiolates from one metal to another results in transfer of the two metals coupling the two cluster fragments.

Metal Exchange Mechanisms of Other Clusters. While metal exchange in clusters has been known for some time,

---

[17] Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991; p 4.

[18] The rate law derived from Mechanism 2 is of the same form as that shown in Equation (10) and is as follows, where $K_C{}^M = K_1{}^M/(1 + K_3{}^M)$, $\mathrm{d}[MM'_3(SPh)_{10}{}^{2-}]/\mathrm{d}t = \{K_C{}^M k_2{}^M[MX_2]/(1 + K_C{}^M[MX_2]) + k_{-2}{}^M[MCl_2]\}[M'_4(SPh)_{10}{}^{2-}]$.

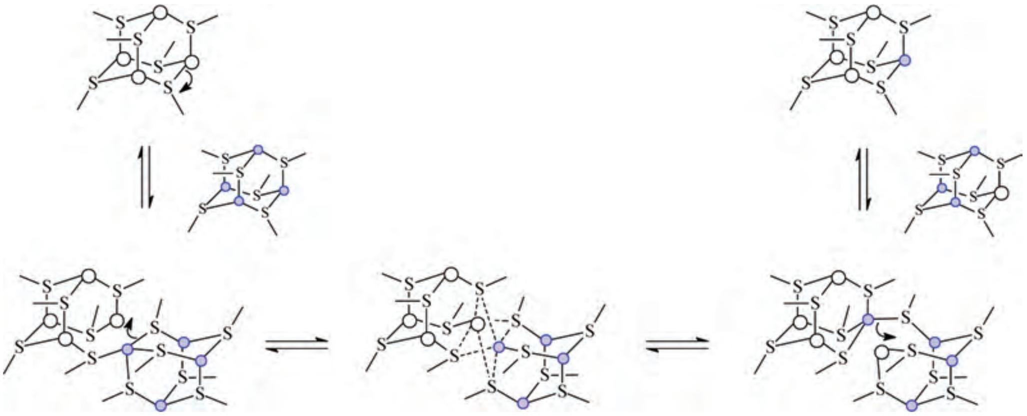


Figure 11. Suggested mechanism for the metal exchange between $[M_4(SPh)_{10}]^{2-}$ and $[M'_4(SPh)_{10}]^{2-}$

there have been few studies to elucidate the mechanisms of such reactions. The mechanisms for transmetalation in clusters containing 4, 5, or 6 metals involve replacement by isolobal units and can occur by the following mechanisms: (i) fragmentation−reconstruction; (ii) elimination−addition (equivalent to the dissociative pathway shown in Figure 1) or (iii) addition−elimination (equivalent to the associative pathway shown in Figure 1).[3a] The use of isolobal relationships does not really define a mechanism in the sense of timing of bond-making and bond-breaking processes. Rather, it just describes what fragment might replace another and as such is a more helpful guide to synthesis than mechanism. The three types of mechanisms outlined above can be augmented in clusters where ligands contain potential sites of metal coordination, in which cases the attacking metal can attach to such binding sites and subsequent rearrangements and dissociation of another metal ultimately results in metal exchange.

There are few kinetic studies on metal exchange reactions involving metal clusters or aggregates. The possible relevance of the synthetic clusters $[M_4(SR)_{10}]^{2-}$ to metallothioneins has been discussed by other authors,[6,19] but principally from a structural point of view. Metallothioneins are a class of small proteins characterized by a high metal and sulfur (cysteine) content.[2,19] These proteins are found in many organisms from fungi to mammals and although their role has not been established unambiguosly, it is believed that metallothioneins are involved in the metabolism and detoxification of both essential and nonessential trace metals.

There have been several kinetic studies of metal ions binding to apo-metallothioneins,[20] and others involving one metal ion replacing another already bound to the protein.[21] In general, these are complicated, multiphasic reactions which involve inter- and intraprotein metal exchange. It is not clear yet whether the results from our studies on metal exchange in $[M_4(SPh)_{10}]^{2-}$ operate by similar mechanisms to these natural metal ion aggregates. We have limited our studies so far to systems where the metal exchange involves replacement of one divalent metal ion for another, with no gross change in topology of the cluster. Future studies will explore the mechanisms for metal exchange where changes in the topology of the cluster occur as a consequence of replacing a cluster metal for another metal ion with different charge and coordination requirements.

Acknowledgment. We thank EPSRC for supporting this research through a postdoctoral fellowship (to V.A.).

Supporting Information Available: ^{1}H NMR spectrum of the reaction products of the reaction between $[Zn_4(SPh)_{10}]^{2-}$ and $CoCl_2$ and listings of tables containing the observed rate constants for all the reactions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC800485T

---

(19) Chan, J.; Huang, Z.; Merrifield, M. E.; Salgado, M. T.; Stillman, M. J. *Coord. Chem. Rev.* **2002**, *233*, 319.

(20) (a) Ejrik, J.; Robinson, J.; Zhu, J.; Fösterling, H.; Frank Shaw III, C.; Petering, D. H. *J. Inorg. Biochem.* **2002**, 144. (b) Roschitzki, B.; Vašák, M. *Biochemistry* **2003**, *42*, 9822. (c) Ngu, T. T.; Stillman, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 12473.

(21) (a) Li, H.; Otvos, J. D. *Biochemistry* **1996**, *35*, 13929. (b) Li, H.; Otvos, J. D. *Biochemistry* **1996**, *35*, 13937. (c) Zelazowski, A. J.; Stillman, M. J. *Inorg. Chem.* **1992**, *31*, 3363. (d) Frank Shaw III, C.; Laib, J. E.; Saras, M. M.; Petering, D. H. *Inorg. Chem.* **1990**, *29*, 403. (e) Johnson, B. A.; Armitage, I. M. *Inorg. Chem.* **1987**, *26*, 3139.