

Metal Ion Scrambling in Hexanuclear $M_6(\text{Et}_2\text{NCO}_2)_{12}$ Complexes ($M = \text{Co}, \text{Mg}$). Synthesis, Solid State Structure, and Solution Dynamics of Heteronuclear $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ Complexes

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Heteronuclear diethylcarbamato complexes of the form $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ were prepared from the isostructural homonuclear precursors $\text{Mg}_6(\text{Et}_2\text{NCO}_2)_{12}$, **1**, and $\text{Co}_6(\text{Et}_2\text{NCO}_2)_{12}$, **2**, via a solvothermal methodology. Two materials were selected for single-crystal X-ray diffraction analysis: $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$. Both compounds crystallize in the orthorhombic space group *Ccca*, as do **1** and **2**. The molecular structure is best described as two trinuclear M_3 units cross-linked by diethylcarbamate ligands and twisted about one another, so that the complex has overall D_2 symmetry and is chiral. Each trinuclear unit consists of two terminal pentacoordinate metal ions and one central hexacoordinate metal ion. The X-ray diffraction data were unambiguous that the Co^{2+} ions migrate exclusively to the pentacoordinate sites in the heteronuclear complexes, thus demonstrating that metal ion scrambling at the molecular level must occur. The composition of individual crystals can be continuously varied for Co^{2+} mole fractions $\chi_{\text{Co}} < 0.5$, and the *a* and *c* unit cell distances are linearly related to χ_{Co} . This indicates that the compounds behave as solid solutions. There appears to be either a chemical or crystallographic phenomenon inherent in the synthetic methodology that prevents isolation of heteronuclear materials having $\chi_{\text{Co}} > 0.5$. Solution electronic spectroscopy and molecular weight measurements show that **2** can dissociate in chloroform and cyclohexane solution to give a dimeric complex **2'**. This behavior contrasts with the stability of **1** in solution, as shown by NMR. The kinetic rate profile for formation of $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ reveals saturation kinetics and is consistent with direct attack by **2'** on **1** to give the heteronuclear complex via a higher nuclearity intermediate. This study illustrates a general method for the preparation of solids based on heteronuclear Werner-type complexes of the $M_6(\text{Et}_2\text{NCO}_2)_{12}$ structure type, and the mechanism by which such compounds can be formed from isostructural homonuclear precursors.

There is a large body of literature on heteronuclear metal clusters supported by metal–metal bonds¹ which have found application in materials and catalysis, and which have provided fundamental information about the formation of such complex species. However, the design and preparation of complex heteronuclear Werner-type cages and frameworks is not as advanced. There has been recent success in the preparation of heterometallic coordination solids in which the metal ion composition can be varied in a rational manner^{2,3} by variation of the bulk metal ion ratio. This strategy is seen as a potential means for affecting the electrical, magnetic, and optical properties of the solids.

There has been less success in controlling the metal ion composition of discrete polynuclear coordination complexes containing more than one type of metal ion.^{4,5} This results from a propensity to form mixtures of homonuclear complexes and the difficulty in controlling the metal ion composition at the molecular level. The complicated and dynamic interactions leading to formation of such species

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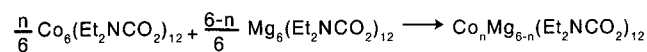
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Scheme 1



are also poorly understood. A general strategy that does sometimes result in formation of heteronuclear complexes is to utilize multinuclear complexes with symmetry-inequivalent sites. If the two types of sites have affinities for different metal ions, heteronuclear complexes may be prepared by exploiting the site preference.⁶

The crystal and solution structure of the hexanuclear magnesium carbamate complex $\text{Mg}_6(\text{Et}_2\text{NCO}_2)_{12}$,^{7,8} **1**, was recently reported. This complex is a diamagnetic analogue of the isostructural hexanuclear transition metal series $\text{M}_6(\text{Et}_2\text{NCO}_2)_{12}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) prepared by Calderazzo et al.^{9,10} The ability to measure high-resolution carbon and proton NMR spectra for **1** permitted us to conclusively demonstrate that the hexanuclear structure observed in the solid state is maintained in nonaqueous solution.⁷ This extended as far as to show that the helical symmetry of the discrete molecular units observed in the crystal structure must also be maintained in solution. At the molecular level, **1** is topologically identical to the Co^{2+} derivative $\text{Co}_6(\text{Et}_2\text{NCO}_2)_{12}$, **2**.¹⁰ One predicted consequence is that Co^{2+} should be able to replace one or more of the Mg^{2+} ions in **1** without a change in the molecular topology, thus permitting preparation of heteronuclear complexes as shown in Scheme 1. In other words, metal ion scrambling should occur between multinuclear complexes, thereby permitting isolation of heteronuclear complexes from mixtures of structurally identical homonuclear precursors. In this context, it may be important that **1** has two different metal sites with different coordination geometry, which may facilitate a degree of control over formation of heteronuclear complexes.

In this paper we report on the synthesis and characterization of molecular solids consisting of discrete $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ complexes in which the parameter n can be controlled by varying the bulk metal ion composition. We demonstrate that scrambling occurs at the molecular level and not simply at the crystallographic level, and that metal

ion site preferences play a role in the composition of the products. We present data showing that the heteronuclear complexes exhibit behavior in the solid state that is reminiscent of inorganic solid solutions. Solid solutions consisting of mixtures of mononuclear metal complexes are well-known,¹¹ but those consisting of discrete multinuclear Werner-type molecules appear to be rare. With the $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ complexes, we have the opportunity to understand a novel solid-solution-like system in some detail.

Solution spectroscopy and kinetic measurements on the formation of heteronuclear complexes suggest that metal ion scrambling is controlled by the dissociation of **2** into an intermediate of lower nuclearity, which then directly attacks **1** via an intermediate of higher nuclearity. Evidence is presented to show that unimolecular dissociation of **1** cannot be a viable kinetic step in the metal ion scrambling reaction. This metal ion scrambling reaction is of chemical interest on several levels. First, the dynamics of complex multinuclear Werner-type complexes is not as well understood as dynamics on mononuclear complexes. Metal ion scrambling reactions such as Scheme 1 provide an opportunity to monitor and study molecular dynamics in a multinuclear metal assembly. Second, Scheme 1 may emerge as the most convenient pathway for synthesis of a series of heteronuclear complexes whose chemical and/or physical properties might be tuned by varying the metal ion ratio, and so we are interested in the chemical details of how such compounds form.

Experimental Section

Materials. Diethylamine was distilled from potassium hydroxide and stored over 4 Å molecular sieves. Anhydrous MgBr_2 and CoCl_2 were obtained from Aldrich and stored under nitrogen. Toluene, chloroform, *n*-hexane, and *n*-heptane were distilled by standard procedures. Chloroform-*d* was obtained from Cambridge Isotope Laboratories and distilled from calcium hydride prior to use. All preparative and analytical manipulations were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques.

Infrared spectra were measured using a Nicolet Avatar 360 FTIR instrument. UV–visible spectra were measured on a Hewlett-Packard 8453 diode array instrument. Carbon NMR spectra were measured using a Varian Unity-500 instrument.

$\text{Mg}_6(\text{Et}_2\text{NCO}_2)_{12}$, **1.** The preparation of **1** has been reported previously.⁷ Briefly, 1.5 g of MgBr_2 (8.15 mmol) and 3.4 mL of diethylamine (32.6 mmol) were combined in 50 mL of *n*-hexane under N_2 . The reaction flask was evacuated and charged with approximately 1 atm of CO_2 , and the solution was stirred overnight. This gave a colorless precipitate identified as diethylammonium bromide, which was removed by filtration. Evaporation of the hexane solvent gave 1.48 g (71%) of **1** as a colorless microcrystalline powder. This material was recrystallized once from warm *n*-heptane. The ^1H and ^{13}C NMR spectra and IR spectra were

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Table 1. Analytical Data for Isolated $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ Complexes

bulk soln		crystals		fw ^a	n	C, H, N		X-ray
$\chi(\text{Co})$	$\chi(\text{Mg})$	$\chi(\text{Co})$	$\chi(\text{Mg})$			exptl	theor	
0	1	0	1	256	0	<i>b</i>	<i>b</i>	full ^b
0.16	0.84	0.15	0.85	261	0.9	45.4, 7.8, 10.7	45.9, 7.6, 10.7	unit cell
0.25	0.75	0.28 (0.27 ^c)	0.72 (0.73 ^c)	266	1.7	43.9, 7.7, 10.4	45.1, 7.5, 10.5	full
0.32	0.67	0.30	0.70	266	1.8	43.7, 7.6, 10.5	45.1, 7.5, 10.5	none
0.49	0.51	0.52	0.48	274	3.1	43.1, 7.5, 10.6	43.7, 7.4, 10.2	none
0.66	0.34	0.39 (0.44 ^c)	0.60 (0.56 ^c)	271	3.1			full
1	0	1	0	291	6	<i>d</i>	<i>d</i>	full ^d

^a Formula weight per metal ion ^b Full refinement at 173 K from ref 7. Unit cell was measured again at 298 K for this work. ^c Determined from crystallographic refinement. ^d Previous full crystallographic refinement from ref 9. Unit cell was measured again at 298 K for this work.

identical to previously prepared material.⁷ Unit cell (298 K): orthorhombic *Ccca*, $a = 20.893 \text{ \AA}$, $b = 25.105 \text{ \AA}$, $c = 16.362 \text{ \AA}$, $V = 8582 \text{ \AA}^3$.

$\text{Co}_6(\text{Et}_2\text{NCO}_2)_{12}$, 2. Complex **2** was prepared by a modification of the literature preparation.¹⁰ Briefly, 1.70 g (13 mmol) of anhydrous CoCl_2 and 5.4 mL of (52 mmol) diethylamine were combined in 100 mL of *n*-hexane under N_2 . The reaction flask was evacuated and charged with approximately 1 atm of CO_2 , and the mixture was stirred overnight. This gave a white precipitate, identified as diethylammonium chloride, and a blue solution. Careful evaporation of the hexane solvent gave a blue/violet crystalline solid. This solid was stirred with anhydrous acetonitrile for 15 min to remove a blue cobalt-containing impurity,¹² leaving 0.75 g (20%) of violet crystalline **2**. Anal. Found (calcd): C, 40.8 (41.2); H, 6.9 (6.9); N, 9.3(9.6). IR (cm^{-1} , KBr): 1597 (asymm $-\text{CO}_2$), 1484 (symm $-\text{CO}_2$), 799 ($-\text{CO}_2$ bend). Unit cell (298 K): orthorhombic *Ccca*, $a = 20.712 \text{ \AA}$, $b = 25.040 \text{ \AA}$, $c = 16.498 \text{ \AA}$, $V = 8557 \text{ \AA}^3$.

$\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$. The heteronuclear Co/Mg complexes were prepared by the reaction of **1** with **2** in *n*-heptane, followed by crystallization of the material. In a typical preparation, 0.108 g (0.062 mmol) of **2** and 0.299 g (0.19 mmol) of **1** were combined in 10 mL of *n*-heptane in a sealed heavy-walled glass pressure flask. The flask was heated to 120 °C for 24 h, during which time all of the solid material dissolved to give a violet solution. The flask was then cooled back to room temperature over the course of 2 days, giving large violet single crystals suitable for X-ray diffraction study. Analytical data show these crystals to have a composition consistent with $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$. Crystalline solids of different metal ion compositions were made by the same procedure, but using different bulk ratios of **1** and **2**. Preparative and analytical data for all of the complexes isolated is provided in Table 1. All of the complexes have an IR spectrum qualitatively identical to the spectra of **1** and **2**.

Crystallography. Crystallographic studies were performed using a Bruker SMART APEX system. Crystals of $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ were coated in mineral oil and mounted on a glass fiber inside a sealed capillary tube. Data were collected at room temperature and SHELXS-97 and SHELXL-97 used for structure solution and least-squares refinement. The metal ion occupancy of the two symmetry-inequivalent coordination sites was permitted to float independently, giving a crystallographically determined Co:Mg ratio and relative metal ion occupancies of the two sites. See Table 1 and the Supporting Information for details on the crystallographic data collection and refinement. For unit cell measurements where full refinement was not performed, the space group was confirmed by systematic absences and lattice constants were determined by refinement of 192 reflections.

Kinetics. Kinetic measurements were made by the stopped-flow method using a home-built rapid mixing device with a Starna UV-vis flow cell, and using an HP 8453 diode array spectrometer for detection. Time-dependent spectra were measured between 400 and 800 nm. Observed rate constants were determined from first-order exponential fits to absorbance decay curves taken at three well-separated wavelengths.

Results and Discussion

Isolation and Structural Characterization of Heteronuclear Complexes. When **1** was reacted with **2** in organic solvent, we were able to isolate single crystals whose optical density was visibly less than that of **2**. Inspection under magnification revealed these crystals to be of the same morphology as the starting products **1** and **2**. However, it was apparent from compositional analysis that individual crystals contained both magnesium and cobalt. As can be seen from Table 1, the mole fraction of Co^{2+} and Mg^{2+} in the isolated crystals was essentially identical to the bulk mole fraction when $\chi_{\text{Co}} < 0.5$. This provided us with a simple means to prepare a series of heteronuclear materials in which the composition of Co^{2+} and Mg^{2+} can be rationally controlled.

The molecular structure of the heteronuclear complexes is represented by the single-crystal diffraction data on two complexes, $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$, whose basic crystallographic data are provided in Table 2. Both materials contain the same molecular unit, which is shown in ORTEP view in Figure 1a. This structure is topologically identical to that previously determined for the homonuclear magnesium complex **1**⁷ and cobalt complex **2**.¹⁰ The most pertinent structural feature is the presence of two equivalent hexacoordinate sites (green) and four equivalent pentacoordinate sites (violet) in the molecular unit. The central six-coordinate metal ions have distorted octahedral ligand geometry. The four terminal five-coordinate metal ions are best described as a distorted square pyramid as judged by the τ parameter,¹³ which is 0.40 for both complexes. The bond metrical parameters for $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$ are qualitatively similar to those observed in **1** and **2**. A list of selected bond distances and angles for the core of the two complexes is provided as Table S1.¹⁴

(12) This impurity was identified as $\text{Co}_4\text{O}(\text{Et}_2\text{NCO}_2)_6$ by compositional analysis, IR, visible spectroscopy, and X-ray diffraction. It arises from partial hydrolysis of **2** during preparation.

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(14) Deposited in Supporting Information.

Table 2. Single-Crystal Diffraction Data for $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_6$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_6$ Complexes

	$\text{Co}_{1.6}\text{Mg}_{4.4}$	$\text{Co}_{2.7}\text{Mg}_{3.3}$
formula	$\text{C}_{60}\text{H}_{120}\text{Co}_{1.6}\text{Mg}_{4.4}\text{N}_{12}\text{O}_{24}$	$\text{C}_{60}\text{H}_{120}\text{Co}_{2.68}\text{Mg}_{3.32}\text{N}_{12}\text{O}_{24}$
fw	1593.89	1632.49
cryst size (mm)	$0.22 \times 0.17 \times 0.12$	$0.4 \times 0.3 \times 0.2$
cryst syst	orthorhombic	orthorhombic
space group	<i>Ccca</i>	<i>Ccca</i>
color	violet	violet
<i>a</i> (Å)	20.8064(10)	20.7534(8)
<i>b</i> (Å)	25.1198(12)	25.1200(10)
<i>c</i> (Å)	16.4196(8)	16.4750(7)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
<i>V</i> (Å ³)	8581.7(7)	8588.8(6)
<i>Z</i>	4	4
temp (K)	298(2)	298(2)
λ (Å)	0.71073	0.71073
measd rflns	41109	40811
indep rflns	4931	4935
obsd rflns	1549	2110
R_{all}^a	0.1555	0.1033
R_{obs}^a	0.0447	0.0424
$R_{\text{w}}(\text{all})^a$	0.1092	0.1122
$R_{\text{w}}(\text{obs})^a$	0.0896	0.0968
GOF	0.689	0.783

^a Refined on F_o^2 .

When inspected from the point of view of the metal ion coordination polyhedra, the complex consists of two trinuclear M_3 units cross-linked by diethylcarbamate ligands, which is best viewed in Figure 1b. Each trinuclear unit consists of a central six-coordinate ion (green) and two terminal five-coordinate ions (violet). Two trinuclear M_3 units are twisted about each other forming a short double helix. This is consistent with the D_2 symmetry of the molecular unit, which lacks any improper axis of rotation and is therefore chiral with a right-handed (Δ) or left-handed (Λ) stereoisomerism. Compounds **1** and **2** and all of the heteronuclear complexes $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ crystallize from aliphatic hydrocarbons in the same centrosymmetric space group, *Ccca*, with four molecular units per unit cell, two of Δ and Λ two of configuration. Isomers of opposing stereochemistry are symmetry related by the crystallographic inversion center.

A heteronuclear crystal consisting of $\text{M}_6(\text{Et}_2\text{NCO}_2)_{12}$ molecular units can result in one of two ways, as shown in Figure 2. Case a represents a crystal in which **1** and **2** cocrystallize, but no metal ion scrambling has occurred at the molecular level. Case b represents crystallization of heteronuclear complexes in which metal ion scrambling has occurred between molecular units. In the absence of any metal ion site preference at the molecular level, the two cases will be crystallographically indistinguishable since the Co/Mg occupancy in each molecular site would reflect the bulk metal ion composition in either case. It is therefore important that the molecular unit contains two different types of metal coordination sites, which have different relative affinities for Co^{2+} and Mg^{2+} . Since cobalt and magnesium have very different X-ray scattering factors, they can be differentiated by X-ray crystallography. In refining the X-ray data, we permitted the relative Co/Mg occupancies of the pentaco-

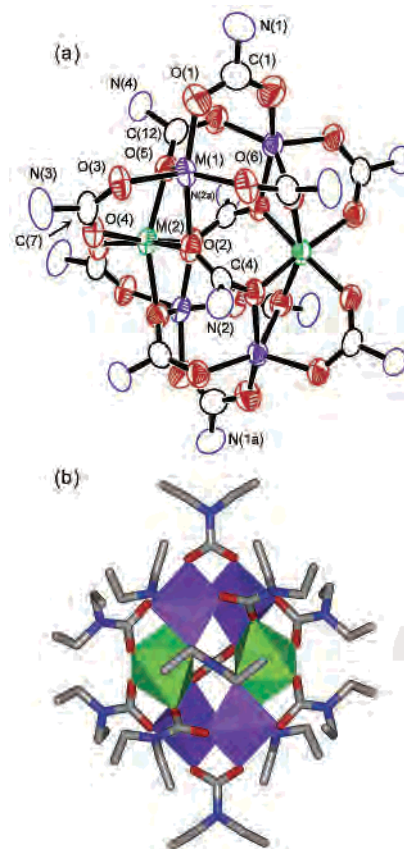


Figure 1. (a) ORTEP diagram (50% ellipsoids) of $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ showing the core structure and metal site occupancies. $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$ has the same molecular structure. Blue = N, red = O, white = C, green = Mg. The violet ellipsoids represent the pentacoordinate sites partially occupied by both Mg and Co. The ethyl groups on the ligands have been removed from this view for clarity. (b) View of the structure of the hexanuclear complexes showing the metal ions as coordination polyhedra, and the complete diethylcarbamate ligands.

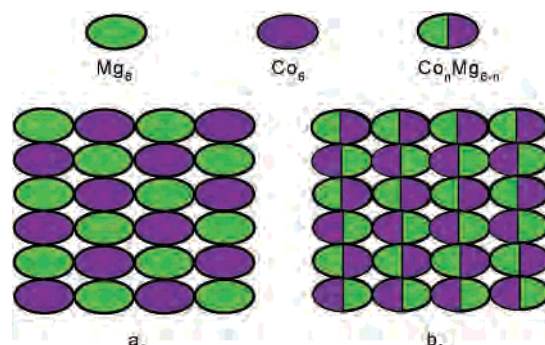


Figure 2. Schematic representation of metal ion mixing at the crystallographic level (a) vs the molecular level (b).

ordinate and hexacoordinate sites to float independently. This final result showed conclusively that, for both $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$, the hexacoordinate site was occupied exclusively by magnesium. The pentacoordinate site had a Co/Mg ratio of 0.39/0.61 for the former complex and 0.67/0.33 for the latter. This inhomogeneous distribution of Co^{2+} within the molecular unit rules out case a, in which the hexacoordinate and pentacoordinate sites must have equivalent occupancy. We therefore conclude that metal ion scrambling has occurred between individual molecular units, as implied by case b.

Table 3. Unit Cell Parameters for $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ as a Function of Cobalt Mole Fraction

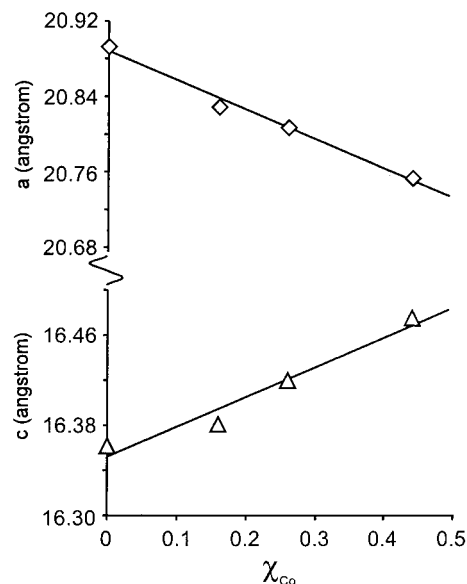
n	χ_{Co}^a	a (Å)	b (Å)	c (Å)	V (Å ³)
0 ^b	0	21.548(2)	25.094(2)	15.4485(11)	8353.5(1)
0 ^c	0	20.893(4)	25.105(4)	16.362(3)	8582(3)
0.9 ^c	0.16	20.829(3)	25.134(5)	16.381(3)	8576(3)
1.6 ^d	0.26	20.806(1)	25.120(1)	16.4196(8)	8581.7(7)
2.7 ^d	0.44	20.7534(8)	25.120(1)	16.4750(7)	8588.8(6)
6 ^e	1	20.712(6)	25.040(4)	16.498(3)	8557(3)

^a Cobalt as a fraction of total metal ion content. ^b $T = 173$ K, refinement of full data set, from ref 7. ^c $T = 298$ K, unit cell only. ^d $T = 298$ K, refinement of full data set. ^e The original report on the structure of **2** gave the monoclinic space group $C2/c$ with $\beta = 95.9^\circ$, ref 10. Our determination of the unit cell at 298 K gave the orthorhombic space group $Ccca$. It seems unlikely that the space group in the original report was mistakenly assigned, and we expect that different crystallization conditions resulted in a slightly different crystal morphology.

The strong preference of Co^{2+} for the pentacoordinate site is perhaps surprising given the similar pentacoordinate and hexacoordinate ionic radii of Mg^{2+} (80, 86 pm) and Co^{2+} (81, 88 pm).¹⁵ However, if the pentacoordinate site is modeled as a distorted square pyramid, then the site preference is consistent with the more favorable ligand field stabilization energy for Co^{2+} in an idealized C_{4v} environment ($-9.14 D_q$) versus an idealized O_h environment ($-8.00 D_q$). Therefore, the driving force for the formation of heteronuclear crystals of this type arises in part from the favorable enthalpy to shift Co^{2+} from the hexacoordinate to pentacoordinate sites, and also from the favorable entropy of mixing that results when Co^{2+} and Mg^{2+} are permitted to randomize throughout the available pentacoordinate sites.

For any individual heteronuclear complex $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$, n must be an integer quantity. The nonstoichiometric composition of the crystalline preparations therefore results from a mixture of stoichiometric molecular units. What is observed crystallographically is then an average of several different stoichiometric molecular units distributed throughout the crystal. This system therefore exhibits a number of properties often associated with solid solutions.¹⁶ For example, n can be varied nonstoichiometrically between 0 and 3, and so the mole fraction of cobalt, χ_{Co} , varies continuously over a range between 0 and 0.5. Within the framework provided by the pentacoordinate sites in the array of molecular units, we can say that Co^{2+} and Mg^{2+} are miscible for $0 < \chi_{\text{Co}} < 0.5$. The unit cell lengths vary continuously as a function of the composition of the crystal over this range of compositions, as shown in Table 3. Although the variation in the a and c unit cell distances is small, they are linearly correlated with χ_{Co} , Figure 3. The b parameter is essentially invariant over the same range of χ_{Co} . The decrease in a as χ_{Co} increases is compensated by an increase in c , and so cell volume changes little as a function of χ_{Co} .

We have been unable to isolate heteronuclear materials having $\chi_{\text{Co}} > 0.5$, and all attempts to do so have resulted in isolation of heteronuclear complexes with $\chi_{\text{Co}} < 0.5$ plus unreacted **2** ($\chi_{\text{Co}} = 1$). This arises partly from the fact that

**Figure 3.** Dependence of the a (\diamond) and c (\triangle) unit cell parameters on χ_{Co} in crystals of $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ complexes. See Table 3 for unit cell data.

Co^{2+} is excluded from the hexacoordinate sites in the molecular unit, but if this were the only factor, we should observe a maximum fraction of Co^{2+} to be 0.67 in the heteronuclear compounds. We find no evidence from solution titration data for special stability associated with the $\text{Co}_3\text{-Mg}_3(\text{Et}_2\text{NCO}_2)_{12}$ complex (vide infra), and so there would appear to be no obvious molecular mechanism that precludes the formation of $\text{Co}_4\text{Mg}_2(\text{Et}_2\text{NCO}_2)_{12}$ in vitro. This leaves a precipitation mechanism that thermodynamically disfavors crystallization of heteronuclear materials with $0.5 < \chi_{\text{Co}} < 1$, and instead favors disproportionation into two crystals, one containing $\chi_{\text{Co}} < 0.5$ and the other containing $\chi_{\text{Co}} = 1$. In the language of solid solutions, this would correspond to a region of immiscibility where two phases richer in Mg^{2+} and Co^{2+} are favored over phases having χ_{Co} in the range between 0.5 and 1. In such a case, we might form complexes such as $\text{Co}_4\text{Mg}_2(\text{Et}_2\text{NCO}_2)_{12}$ in solution, but crystallization of materials containing a 2:1 ratio of $\text{Co}^{2+}:\text{Mg}^{2+}$ would not occur.

It is worthwhile examining the unit cell parameters in Table 3 in light of this latter hypothesis. The lengths of a and c in **2** are nearly identical to those predicted for crystalline $\text{Co}_3\text{Mg}_3(\text{Et}_2\text{NCO}_2)_{12}$ by using the linear correlations in Figure 3 ($a_{\text{theor}} = 20.732$, $c_{\text{theor}} = 16.485$). On the other hand there is a substantial difference in b between $\chi_{\text{Co}} \approx 0.5$ and $\chi_{\text{Co}} = 1$ and an associated decrease in cell volume that would indicate more efficient packing. At the point where favorable packing of **2** balances the unfavorable entropy for crystallization of **2**, we would expect the system to disproportionate into one set of crystals containing **2** and another set consisting of a magnesium-enriched composition. This might in turn explain why crystals or “phases” having $0.5 < \chi_{\text{Co}} < 1$ are not accessible.

Mechanism for Metal Ion Scrambling. When dissolved in organic solution, the cobalt complex **2** has been shown to exhibit a series of overlapping visible electronic transitions

(15) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

(16) West, A. R. *Solid-state chemistry and its applications*; John-Wiley & Sons: New York, 1989.

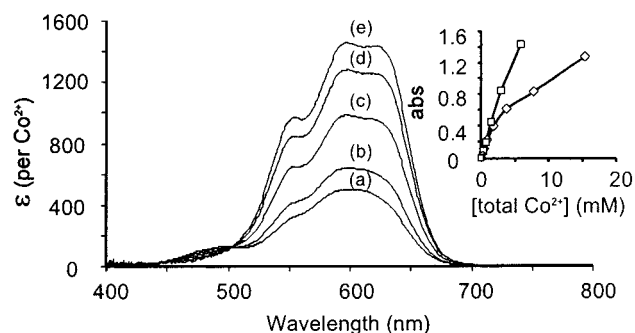


Figure 4. Concentration-normalized absorbance spectra of **2** in toluene as a function of concentration. Spectra were measured at total Co^{2+} concentrations of (a) 15.4, (b) 7.9, (c) 3.8, (d) 1.9, and (e) 0.95 mM. Inset: Absorbance (596 nm) of **2** in toluene (\diamond) and chloroform (\square) as a function of total Co^{2+} concentration. Solid lines are for viewing convenience and do not represent a theoretical fit to the data.

between 450 and 650 nm,¹⁰ a range characteristic of Co^{2+} in weak ligand fields. The concentration-normalized absorption spectrum of **2** in toluene is strongly dependent on the concentration, Figure 4. The extinction coefficient at λ_{max} (596 nm) is $250 \text{ M}^{-1} \text{ cm}^{-1}$ per Co^{2+} at low concentration, which is considerably higher than would normally be expected for Co^{2+} in an octahedral ligand field.¹⁷ At higher concentrations, the extinction coefficient per Co^{2+} decreases considerably and suggests a shift to a distorted octahedral ligand field. A weak band also appears in the near-infrared at higher concentrations, and this band is typically associated with the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ transition in octahedral Co^{2+} complexes. The normalized spectra exhibit an isosbestic point at 505 nm, which shows that only two different Co^{2+} complexes give rise to this series of spectra. We interpret these observations in terms of equilibrium dissociation of **2** into a single Co^{2+} -containing species of lower nuclearity. The dissociation equilibrium is markedly solvent dependent, as shown by comparing absorbance measurements in toluene and chloroform, Figure 4 (inset). At low concentrations, the spectra in chloroform and toluene are nearly identical. However, at concentrations greater than 2.5 mM total Co^{2+} , the data in chloroform and toluene diverge, with the absorbance spectrum being considerably more intense in chloroform. The Beer's law plot is only slightly curved in chloroform, and the positions and intensities of absorbance bands more closely resemble the low-concentration spectra in toluene. These data taken together indicate that the complex exists largely in the dissociated form in chloroform over the entire concentration range studied. Below a total Co^{2+} concentration of 3.5 mM in cyclohexane, visible spectra show that **2** exists almost exclusively in its dissociated form. Cryoscopic molecular weight determination under these conditions gave a molecular mass of 624 amu, and conductance measurements show that **2** is a nonelectrolyte. These solution data when combined with the visible spectroscopy are consistent with formulation of the dissociated complex as the dimer $\text{Co}_2(\text{Et}_2\text{NCO}_2)_4$ (fw = 582 amu). This is consistent with the structure of cobalt benzoate complexes,¹⁸ which can adopt a copper acetate like dinuclear structure.

(17) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.

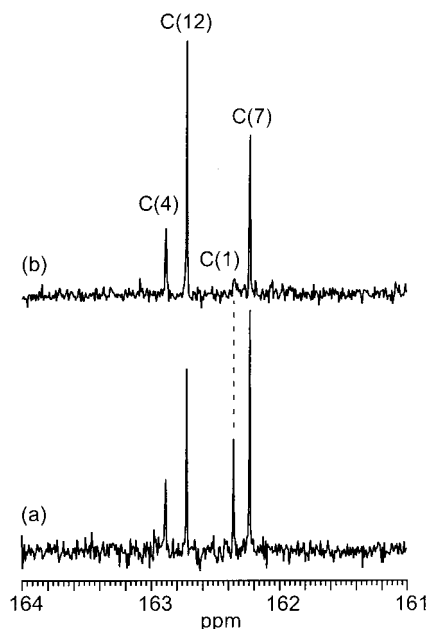
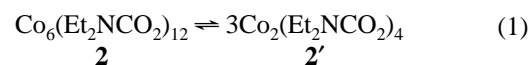


Figure 5. ${}^{13}\text{C}$ NMR spectra of **1** in CDCl_3 . (a) Complex **1** containing natural abundance ${}^{13}\text{C}$. (b) Complex **1** selectively enriched by exposure to ${}^{13}\text{CO}_2$ and aged for 24 h.

The instability of $\text{Co}_6(\text{Et}_2\text{NCO}_2)_{12}$ is consistent with qualitative observations made previously on this complex.¹⁰ The most chemically appealing interpretation for the solution characterization data is that **2** dissociates into a dimeric complex according to eq 1. This solution behavior contrasts



with that of the magnesium analogue **1**. The hexameric $\text{Mg}_6(\text{Et}_2\text{NCO}_2)_{12}$ complex has a characteristic NMR spectrum that is unchanged over a range of concentrations.⁷ However, the most dramatic evidence for the solution stability of **1** comes from examination of the carbon NMR spectrum of the complex selectively enriched in ${}^{13}\text{C}$ at the carboxyl sites. Exposure of **1** to ${}^{13}\text{CO}_2$ results in ${}^{13}\text{C}$ incorporation into C(4), C(7), and C(12), but not into C(1), Figure 5.¹⁹ Even after 24 h, there was no observable enrichment in the C(1) site. This result precludes dissociation of **1** into dimers or trimers on this time scale, since such dissociation would scramble the carbamate ligands in the complex and result in eventual ${}^{13}\text{C}$ enrichment in all of the carboxyl carbon atoms in the complex. Since metal ion scrambling occurs on the second time scale in chloroform and on the hour time scale in toluene, the ${}^{13}\text{C}$ NMR spectra also preclude any scrambling mechanism dependent on unimolecular dissociation of **1** to give lower nuclearity intermediates.

The interaction between **1** and **2** in solution is readily monitored by the change in the visible absorption spectrum, which we interpret to arise from the change in the coordination environment of the Co^{2+} as it is incorporated into the

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(19) The mechanism for selective ${}^{13}\text{C}$ enrichment in **1** is presently under investigation.

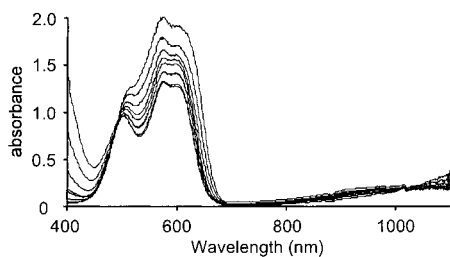


Figure 6. Spectrum of **2** in chloroform in the presence of increasing concentrations of **1**. $[\mathbf{2}] = 1.6 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, $[\mathbf{1}] = 0\text{--}134 \text{ mM}$.

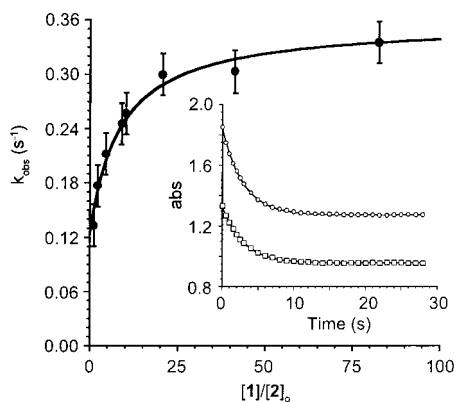
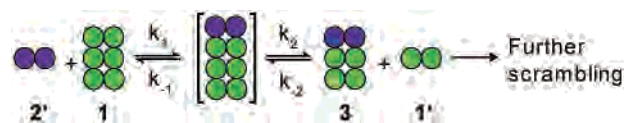


Figure 7. First-order rate constant, k_{obs} , for metal ion scrambling as a function of $[\mathbf{1}]/[\mathbf{2}]_0$ in chloroform at $25 \text{ }^\circ\text{C}$. The solid line is a best fit of eq 3 to the data. Inset: Electronic absorbance decay profiles for metal ion scrambling at (O) 596 nm and (\square) 498 nm. The solid lines are a least-squares fit of $A - A_\infty = (A_0 - A_\infty)e^{-k_{\text{obs}}t}$ to the data, from which values for k_{obs} were obtained.

heteronuclear $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ product. Titration of **2** with **1** in chloroform results in a substantial decrease in molar extinction coefficient per cobalt, Figure 6. It is initially about $250 \text{ M}^{-1} \text{ cm}^{-1}/\text{Co}^{2+}$, a value that reflects the molar absorbance of the dissociated intermediate **2'**. It decreases to $130 \text{ M}^{-1} \text{ cm}^{-1}/\text{Co}^{2+}$ when **1** is in large excess, a value more representative of Co^{2+} in the intact hexanuclear complex. The change in the absorption spectrum therefore provides us with a spectroscopic observable that can be used to measure the rate for incorporation of Co^{2+} into the heteronuclear complexes. Rapidly mixing **2** with an excess of **1** in chloroform and monitoring the absorbance decay at 596 nm shows that the reaction is complete within about 30–60 s, Figure 7(inset). The absorbance decay profile at multiple wavelengths is fit very well to a first-order decay with pseudo-first-order rate constant k_{obs} . When k_{obs} is determined as a function of $[\mathbf{1}]$, we see that the reaction exhibits saturation kinetics, Figure 7, a rate profile indicative of two consecutive kinetic processes.

It was qualitatively observed that metal ion scrambling was considerably more rapid in chloroform than in toluene. Since **2** is also more dissociated in chloroform than in toluene, this suggested the hypothesis that metal ion scrambling in this system is driven in part by the dissociation of **2** to give **2'**. The chemical mechanism must also account for the kinetic stability of **1** on the time scale of the experiment, which precludes any mechanism dependent on unimolecular dissociation of **1**, and must give a rate law consistent with a saturation kinetic profile. We are led to reject pathways involving mononuclear intermediates since

Scheme 2



it seems chemically unlikely for **1** or **2** to form complexes CoL_2 or MgL_2 ($L = \text{diethylcarbamate}$) in noncoordinating solvents. We also reject pathways having ionic intermediates, since this should be disfavored in nonpolar solvents such as chloroform, toluene, and aliphatic hydrocarbons where we still observe metal ion exchange. Finally, we must take account of the general topological properties of the system, in which Co^{2+} ions migrate exclusively to the terminal pentacoordinate sites.

The simple mechanism presented in Scheme 2 satisfies all of these requirements. The green and violet circles represent Mg^{2+} and Co^{2+} ions, respectively. The metal ions are arranged schematically as they would be in the hexanuclear complex, with the four terminal ions being pentacoordinate and the two internal ions being hexacoordinate. The first step is the formation of **2'** by dissociation of **2**, but since the dissociation appears to be essentially complete in chloroform, we can assume that $[\mathbf{2}']_0 = 3[\mathbf{2}]_0$. The first kinetic step involves fusion of **2'** and **1** to give an expanded octanuclear complex. This obviates the need to dissociate **1** into complexes of lower nuclearity, which is not kinetically competitive with metal ion scrambling. This intermediate can dissociate back to a hexanuclear complex in two ways. Loss of $\text{Co}_2(\text{Et}_2\text{NCO}_2)_4$ regenerates the reactants. However, loss of $\text{Mg}_2(\text{Et}_2\text{NCO}_2)_4$ leads to formation of a heteronuclear complex $\text{Co}_2\text{Mg}_4(\text{Et}_2\text{NCO}_2)_{12}$, **3**. The dimagnesium complex is unstable to complex reassociation, and will be quickly reincorporated into a hexanuclear complex in a rapid postkinetic step. By assuming that the octanuclear intermediate exists in a steady state condition, we can derive the rate law for Scheme 2, which is

$$\frac{d[\mathbf{3}]}{dt} = \frac{3k_2[\mathbf{2}]_0 - k_2(3+x)[\mathbf{3}]}{(3+x) + (k_{-1} + k_2)/k_1[\mathbf{2}]_0} \quad (2)$$

where $x = [\mathbf{1}]/[\mathbf{2}]_0$. This in turn gives the analytical expression for k_{obs} .

$$k_{\text{obs}} = \frac{k_2(3+x)}{(3+x) + (k_{-1} + k_2)/k_1[\mathbf{2}]_0} \quad (3)$$

The solid line in Figure 7 is the best fit of eq 3 to the rate profile, and gives values for $k_2 = 0.35(1) \text{ s}^{-1}$ and $(k_{-1} + k_2)/k_1[\mathbf{2}]_0 = 5.6(6)$.

We believe that scrambling leads to eventual formation of complexes containing one, two, three, and possibly four Co^{2+} ions, but it should be recognized that the crystal data as well as the spectroscopic data are ambiguous on this point. Once Co^{2+} has been incorporated into the $\text{M}_6(\text{Et}_2\text{NCO}_2)_{12}$ complex, its visible spectrum (per Co^{2+}) does not depend on how many cobalt ions are present in the complex. Hence, the visible spectrum only monitors the initial incorporation of cobalt from **2'** into the hexanuclear complex. Subsequent

rearrangements will then be invisible insofar as electronic spectroscopy is concerned. Crystallography shows that all of the cobalt resides in pentacoordinate sites, but cannot distinguish between two adjacent Co^{2+} ions in the same molecule, two Co^{2+} ions in nonadjacent sites within the same molecule, or two Co^{2+} ions in different molecules. Hence a crystal consisting only of adjacent Co^{2+} ions (as would be expected if scrambling occurred exclusively via dimeric Co^{2+} complexes) is crystallographically indistinguishable from one in which Co^{2+} is randomly distributed throughout the pentacoordinate sites. Mass spectrometry could in principle resolve this problem, but we have thus far been unable to obtain MALDI or electrospray mass spectrometry data showing the intact $\text{M}_6(\text{Et}_2\text{NCO}_2)_{12}$ complexes.²⁰

We have collected solid state EPR data on heteronuclear manganese/magnesium complexes of this structure type, and these do show the presence of magnetically isolated manganese that indicates a scrambling pathway leading to random distribution of manganese(II).²¹ In the context of Scheme 2, randomization of the Co^{2+} could occur in one of two ways. If there is a secondary dissociation pathway that involves intermediates having an odd number of metal ions such as a trimer, then scrambling via a combination of dimeric and trimeric intermediates could result in metal ion randomization. On the other hand, an internal pseudorotation that shifted metal ions from hexacoordinate to pentacoordinate sites and vice versa, in parallel with Scheme 2, could also result in metal ion randomization. This latter hypothesis is supported by the work of Yang et al. in which a topologically different but compositionally related hexanuclear magnesium diphenylcarbamato complex, $\text{Mg}_6(\text{Ph}_2\text{NCO}_2)_{12}$, was prepared.⁸ This compound has an alternate hexanuclear structure type where all of the metal ions are in equivalent pentacoordinate sites. In principle, equilibration between the two structure types is possible without dissociation of the ligands. Hence the alternate structure could function as a fluxional intermediate for interconverting pentacoordinate and hexacoordinate sites in heteronuclear $\text{M}_6(\text{Et}_2\text{NCO}_2)_{12}$ complexes. The difference in energy between the two structure types must be small for the shift to be precipitated by a change

from diethylcarbamate to diphenylcarbamate ligands. This implies that it may be feasible for metal ions to be interconverted between five-coordinate and six-coordinate sites without dissociation of the complex, which would in turn provide the means for randomization of Co^{2+} .

Summary

In this paper, we demonstrated the facile metal ion scrambling that occurs in hexanuclear metal carbamate complexes by isolating heteronuclear complexes $\text{Co}_n\text{Mg}_{6-n}(\text{Et}_2\text{NCO}_2)_{12}$ with $n = 0-3$. We established the existence of a site preference within the heteronuclear complexes using single-crystal X-ray diffraction. We furthermore showed that the metal ion composition can be varied over a range of nonstoichiometric compositions with $0 < \chi_{\text{Co}} < 0.5$, and that the crystallographic unit cell parameters vary predictably with χ_{Co} . The crystalline compounds can therefore be treated as a novel example of a solid solution consisting of discrete multinuclear complexes. Equilibrium and kinetic spectroscopic experiments showed that the most probable mechanism for metal ion scrambling in this system involves unimolecular dissociation of the cobalt complex **2** to generate a dimeric species **2'**. This reactive dimer subsequently reacts with the intact magnesium hexamer **1** to generate the heteronuclear hexamers. The rate-limiting process would appear to be a transient core expansion in which the **2'** adds directly to **1**. This study provides the first example of a dynamic rearrangement in a multinuclear Werner-type complex whose structure, kinetics, and mechanism have been elucidated in detail. It therefore gives considerable insight into the formation of this unusual class of heteronuclear compounds.

Acknowledgment. The National Science Foundation is acknowledged for a summer fellowship to J.B.B. and C.K.M. (DBI 9988027), for support to M.T.C. (CHE 9985266), and for contribution toward the purchase of single-crystal instrumentation used in this study (CHE 9808440). We also acknowledge Professor Don Seo for useful discussion on this project.

Supporting Information Available: Table S1 containing selected bond lengths and angles for $\text{Co}_{1.6}\text{Mg}_{4.4}(\text{Et}_2\text{NCO}_2)_{12}$ and $\text{Co}_{2.7}\text{Mg}_{3.3}(\text{Et}_2\text{NCO}_2)_{12}$ and two crystallographic data files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) Mass spectrometry has recently been applied successfully to study metal substitution in different but related metal carbamates. See: Dell'Amico, D. B.; Bradicich, C.; Calderazzo, F.; Guarini, A.; Labella, L.; Marchetti, F.; Tomei, A. *Inorg. Chem.* **2002**, *41*, 2814–2816.

(21) Manuscript in preparation.