phenylantimony difluoride and dibromide is then almost surely similar to that of $(C_6H_5)_3SbCl_2$. The apparent lack of a large value for η in the benzyl compounds places a restriction on the arrangement which the R groups can assume. The threefold X–M–X axis cannot be appreciably disturbed.

Two crystallographically different sites for bismuth in $(C_6H_5)_3BiCl_2$ are evident from the nqr data. In agreement with this, Hawley and Ferguson[14] found that there are two molecular groups in the asymmetric unit of the crystallographic cell. Our nqr data indicate that $(C_6H_5)_3BiBr_2$ is probably isostructural with $(C_6H_5)_3BiCl_2$. Three bromine sites apparently exist in $(C_6H_5)_3BiBr_2$ giving the resonance frequency intensity ratios of 2:1:1. The Bi–Cl bond lengths in one molecule of $(C_6H_5)_3BiCl_2$ were found[14] to be 2.615 and 2.530 Å while in the other molecule they were much less different, 2.579 and 2.560 Å. A similar situation might exist in the bromine compound. The chlorine resonances in $(C_6H_5)_3BiCl_2$ were too weak to be observed.

Acknowledgment.—We wish to thank Dr. M. H. O'Brien for his work on the synthesis of many of the compounds used in this study.

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Isolation of Pure Mixed μ_4-Oxo-hexa-μ-carboxylato-tetraberyllium Compounds of the General Formula $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{6-x}$[1]

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The mixed μ_4-oxo-μ-hexacarboxylato-tetraberyllium derivatives $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$, $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$, and $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$ have been prepared by fractional crystallization from equilibrated chloroform solutions of $Be_4O(CH_3CO_2)_6$ and $Be_4O(CCl_3CO_2)_6$. The mass and proton nuclear magnetic resonance spectra were important in providing evidence for the existence of pure compounds. A study of the proton nmr spectrum *vs.* time on solutions of the mixed carboxylates indicated carboxylate scrambling occurred with increasing rate in the order $Be_4O(CH_3CO_2)_5(CCl_3CO_2) < Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3 < Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. It is postulated that carboxylate scrambling occurs *via* the ionic dissociative process $Be_4O(RCO_2)_x(R'CO_2)_{6-x} \rightarrow Be_4O(RCO_2)_x(R'CO_2)_{5-x}^+ + R'CO_2^-$.

A number of investigators have claimed the preparation of mixed μ_4-oxo-hexa-μ-carboxylato-tetraberyllium species.[2] However Marvel[3a] and Hardt[3b] have demonstrated that the "compounds" were actually mixtures of mixed carboxylates of the general formula $Be_4O(RCO_2)_x(R'CO_2)_{6-x}$, where $0 < x < 6$.

Isolation of pure mixed carboxylates seemed desirable for several reasons. We were interested in determining qualitatively the rate of carboxylate scrambling in a mixed species. The mechanism of the exchange process as well as the relative donor abilities of differing carboxylate ligands was also of interest. We sought to isolate a mixed compound in which the carboxylate groups would differ appreciably in base strength and molecular weight and found the trichloroacetate–acetate system fit these requirements. We have communicated the findings of our initial study,[4] the complete results of which are reported below.

Experimental Section

The usual precautions for working with beryllium compounds were observed.[5] Generally, operations were carried out in nitrogen-filled polyethylene bags regardless of whether the material being worked with was hygroscopic. This approach helped limit beryllium contamination in the laboratory. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU-6E mass spectrometer. Proton nmr spectra were obtained by means of a Varian HA 100 nuclear magnetic resonance spectrometer. Chemical shifts are reported *vs.* internal tetramethylsilane reference.

μ_4-Oxo-hexa-μ-acetato-tetraberyllium was prepared by refluxing beryllium oxide in a twofold excess of acetic acid and purified as previously reported.[6]

Beryllium Trichloroacetate Dihydrate.—The preparation of this compound was similar to the method of Parsons and Sargent,[7] although we used $Be(OH)_2$ in place of $BeCO_3$. *Anal.* Calcd for $C_4H_4BeCl_6O_6$: C, 12.99; H, 1.09; Cl, 57.52. Found: C, 12.98; H, 1.38; Cl, 56.47.

Decomposition of $Be(CCl_3CO_2)_2 \cdot 2H_2O$ in a sealed capillary began at 100° with further observations being dependent on the rate of heating. If the sample was heated slowly (2°/min), quiet evolution of vapor was observed up to the melting point (270°) where vigorous bubbling occurred. The liquid appeared stable to 300°. When the sample was cooled and reheated some of the sample melted at 210°. However, if the sample temperature was initially raised rapidly (50°/min) melting and bubbling took place at 160–175° followed by solidification. After this, observations at higher temperatures were identical with the

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[1] Paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] (a) S. M. Tanator and E. K. Kurovski, *Zh. Fiz. Khim.*, **39**, 936 (1907); *Chem. Abstr.*, **2**, 1128 (1908); (b) W. Bragg and G. T. Morgan, *Proc. Roy. Soc., Ser. A*, **104**, 437 (1923).

[3] (a) C. S. Marvel and M. M. Martin, *J. Amer. Chem. Soc.*, **80**, 619 (1958); (b) H. Hardt, *Z. Anorg. Allg. Chem.*, **314**, 210 (1962).

[4] K. J. Wynne and W. Bauder, *J. Amer. Chem. Soc.*, **91**, 5920 (1969).

[5] D. A. Everest, "The Chemistry of Beryllium," Elsevier Publishing Co., New York, N. Y., 1964.

[6] T. Moeller, A. J. Cohen, and E. Marvell, *Inorg. Syn.*, **3**, 9 (1950).

[7] C. L. Parsons and G. J. Sargent, *J. Amer. Chem. Soc.*, **31**, 1202 (1909).

sample heated slowly. Rapid heating of $Be(CCl_3CO_2)_2 \cdot 2H_2O$ probably gave rise to a nonequilibrium situation whereby the compound was brought to its melting point where rapid evolution of H_2O produced anhydrous $Be(CCl_3CO_2)_2(s)$. In contrast, slow heating would cause gradual H_2O loss so that the melting point of the dihydrate would not be observed.

μ_4-Oxo-hexa-μ-trichloroacetato-tetraberyllium.—In a vacuum sublimator (0.1 mm) beryllium trichloroacetate dihydrate (47 g, 0.1 mol) was gradually heated to 200° over a 2-hr period. The temperature was maintained at 200–250° overnight while volatiles were collected in a −196° trap. Trichloroacetic acid and impure product collected on the cold finger. A considerable amount of decomposition of starting material took place resulting in a beryllium oxide residue. The product was purified by repeated sublimation (usually three times) until no residue remained; yield, 7.7 g (30%); mp 210–211°. Molecular weight (cryoscopic). Calcd, 1026; found, 1000 (benzene), 1040 (nitrobenzene). *Anal.* Calcd for $C_{12}Be_4Cl_{18}O_{13}$: Cl, 62.18. Found: Cl, 62.45. We were unsuccessful in preparing this compound by refluxing either BeO or $Be(OH)_2$ with trichloroacetic acid in benzene.

μ_4-Oxo-penta-μ-acetato-μ-trichloroacetato-tetraberyllium.—Pure $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ was prepared in two ways. Amounts of materials involved in a typical run are given in parentheses. A 9:1 mole ratio of $Be_4O(CH_3CO_2)_6$ (6.57 g, 16.1 mmol) to $Be_4O(CCl_3CO_2)_6$ (1.85 g, 1.8 mmol) was allowed to equilibrate for 6 days in chloroform (50 ml). When no further change was observed in the proton nmr spectrum of the solution, petroleum ether (bp 60–110°) was added until a quantity of precipitate (*ca.* 0.9 g) appeared. This material was filtered, dissolved in chloroform, and reprecipitated with petroleum ether two times (final yield 0.4 g). No change in the nmr spectrum, melting point (217–218.5°), or ir spectrum was observed in going from the second to the third precipitation. $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ can also be prepared by refluxing $Be_4O(CH_3CO_2)_6$, (30.0 g, 0.074 mol) with trichloroacetyl chloride (81.5 g, 0.449 mol) in benzene for 48 hr presumably according to the reaction

$$Be_4O(CH_3CO_2)_6 + CCl_3COCl \longrightarrow Be_4O(CH_3CO_2)_5(CCl_3CO_2) + CH_3COCl$$

The solvent was evaporated and the resulting solid dissolved in chloroform (50 ml). Petroleum ether was added and the solution was evaporated to one-third its volume with dry nitrogen yielding 9.8 g (0.0192 mol, 26%) of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$. Addition of more petroleum ether gave a mixture of the monotrichloroacetate and higher melting material which was discarded. We were surprised at the result as it had been our original intent to prepare $Be_4O(CCl_3CO_2)_6$ *via* this route. Evidently the above replacement reaction is sufficiently slow to allow isolation of the monotrichloroacetate derivative even after 2 days refluxing in benzene. *Anal.* Calcd for $Be_4O_{13}C_{12}H_{15}Cl_3$: C, 28.28; H, 2.96; Cl, 20.87. Found: C, 28.77; H, 3.15; Cl, 20.38, 20.84. Molecular weight: calcd, 509.7; found, 494 (cryoscopic, benzene).

μ_4-Oxo-tri-μ-acetato-tri-μ-trichloroacetato-tetraberyllium.—$Be_4O(CH_3CO_2)_6$ (7.8 g, 0.019 mol) and $Be_4O(CCl_3CO_2)_6$ (19.7 g, 0.019 mol) were dissolved in 125 ml of benzene and 15 ml of $CHCl_3$. After equilibration for 3 days the volume of the solution was reduced to 40 ml and cooled (+8°) overnight. Filtration yielded 5 g of material with a wide melting point range, 110–120°. The product was redissolved in 3 ml of $CHCl_3$ and petroleum ether was added until precipitation began. The solution was cooled rapidly to −20° for 1 hr. Filtration yielded 2 g of material, mp 146–148°. The product was dissolved in 1 ml of $CHCl_3$ and 5 ml of petroleum ether. Evaporation of solvent to one-third its original volume with dry nitrogen yielded 0.7 g of $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$, mp 146–148°. *Anal.* Calcd for $C_{12}H_{19}Be_4Cl_9O_{13}$: C, 20.12; H, 1.27; Cl, 44.54. Found: C, 20.92; H, 1.45; C, 43.40.

μ_4-Oxo-μ-acetato-penta-μ-trichloroacetato-tetraberyllium.—$Be_4O(CH_3CO_2)_6$ (1.6 g, 3.94 mmol) and $Be_4O(CCl_3CO_2)_6$ (28.3 g, 27.6 mmol) were dissolved in 50 ml of $CHCl_3$ and the solution was allowed to equilibrate for 4 days. The solution was evaporated to 15 ml and a small quantity of petroleum ether was added until precipitation began. Further evaporation of the solution to one-third original volume followed by filtration gave 5 g of product, mp 110–150° (mostly 145–150°). Reprecipitation from $CHCl_3$-petroleum ether gave 1 g of $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$, mp 150–152°. A second reprecipitation gave 0.2 g of material, mp 154–155°. *Anal.* Calcd for $C_{12}H_3Be_4Cl_5O_{13}$: C, 15.62; H, 0.32; Cl, 57.62. Found: C, 16.03; H, 1.67; Cl, 56.14.

Attempted Preparations of Other Mixed Carboxylates.—$Be_4O(CH_3CO_2)_2(CCl_3CO_2)_4$ and $Be_4O(CH_3CO_2)_4(CCl_3CO_2)_2$ should exhibit *cis–trans* isomerism (Table III) and should have proton chemical shifts in between mono- and trichloroacetate and tri- and pentaacetate, respectively. We made numerous attempts to isolate these compounds without success. Through fractional precipitation from suitable $Be_4O(CH_3CO_2)_6$–$Be_4O(CCl_3CO_2)_6$ solutions we did obtain solids whose nmr spectra suggested enrichment in the desired compounds. However, solubility differences between the desired compounds and other mixed carboxylates were small enough to make isolation of pure compounds impossible.

Results

Infrared data on the mixed carboxylates prepared in this study are listed in Table I while mass spectroscopic data are presented in Table II. Only the principal peaks above approximately 200 mass units are listed. The two main chlorine isotopes caused numerous peaks for a given trichloroacetate-containing species. Close agreement was obtained between observed and cal-

TABLE I
INFRARED SPECTRA OF $Be_4O(CCl_3CO_2)_6$ AND MIXED CARBOXYLATES[a,b]

Band, cm⁻¹ (±10)	A[c]	B[c]	C[c]	D[c]
670	m	m	m	m
710	m	m	m	m
750		ms	ms	m
780	s		m	ms
790	s	ms		
810		ms	m	m
820		ms		m
830		m	m	m
865	m	m	m	m
930			wm	
970		wm	wm	
980	m	m		
1000			m	m
1030	wm	wm	wm	
1055	wm	wm	wm	
1150	w	wm	w	w
1165		wm	w	w
1200		wm	w	w
1310		w	wm	wm
1350	w	wm	wm	wm
1480	s	ms	m	
1490	s	ms		
1560	wm		w	
1580	m	m	wm	
1590	m	m		
1620			wm	w
1630	ms	m	wm	
1660		m	m	
1690	m	ms	m	m

[a] Nujol mulls. [b] Intensity key: s, strong; m, medium; w, weak. [c] A, $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$; B, $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$; C, $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$; D, $Be_4O(CCl_3CO_2)_6$.

TABLE II

MASS SPECTRA OF $Be_4O(CCl_3CO_2)_6$ AND MIXED CARBOXYLATES

m/e[b]	Rel intens[c]	Ion
	$Be_4O(Ac)_5(TCA)$[a]	
551–557	1[d]	$Be_4O(Ac)_3(TCA)_2^+$
449–457	100	$Be_4O(Ac)_4(TCA)^+$
414–457	30	$Be_4O(Av)_4(CCl_2CO_2)^+$
347–349	52	$Be_4O(Ac)_5^+$
346	1	$Be_4O(Ac)_4(CH_2CO_2)^+$
322–327	5	$Be_3O(Ac)_2(TCA)^+$
287–291	1	$Be_4O(Ac)_4^+$
245–247	5	$Be_4O(Ac)_3O^+$
219–223	30	$Be_3O(Ac)_3^+$
202–206	5	$Be_4O(Ac)_2OH^+$
	$Be_4O(Ac)_3(TCA)_3$	
755–771	1[e]	$Be_4O(Ac)(TCA)_4^+$
653–665	20	$Be_4O(Ac)_2(TCA)_3^+$
617–627	1	$Be_4O(Ac)_2(TCA)_2(CCl_2CO_2)^+$
596–603	1	$Be_4O(Ac)(TCA)_3^+$
583–591	1	$Be_4O(Ac)_2(TCA)(CCl_2CO_2)_2^+$
551–565	100	$Be_4O(Ac)_3(TCA)_2^+$
524–535	10	$Be_2O(TVA)_3^+$
514–523	10	$Be_3O(Ac)_3(TCA)(CCl_2CO_2)^+$
489–496	10	$Be_4O(Ac)_2(TCA)_2^+$
480–486	5	$Be_3O(Ac)_2(TCA)_2^+$
445–451	5	$Be_4O(Ac)_3(TCA)Cl^+$
420–430	10	$Be_4O(Ac)(TCA)_2^+$
382–390	10	$Be_3O(Ac)_3(TCA)^+$
315–323	20	$Be_3O(Ac)_2(TCA)^+$
281–286	20	$Be_3O(Ac)(TCA)O^+$
212–218	5	$Be_3O(Ac)_3^+$
193–198	5	$Be_3O(TCA)^+$
	$Be_4O(AcO)(TCA)_5$	
857–877	9	$Be_4O(TCA)_5^+$
755–771	100	$Be_4O(AC)(TCA)_4^+$
695–705	1	$Be_3O(TCA)_4^+$
653–665	7[f]	$Be_4O(Ac)_2(TCA)_3^+$
628–642	30	$Be_4O(TCA)_2(CCl_2CO_2)_2^+$
590–605	5	$Be_4O(Ac)(TCA)_3^+$
526–536	5	$Be_2O(TCA)_3^+$
503–513	5	$Be_4O(TCA)_2(CCl_2CO_2)^+$
490–502	1	$Be_3O(TCA)_2(CCl_2CO_2)^+$
424–433	10	$Be_3O(Ac)(TCA)_2^+$
390–400	10	$Be_3O(Ac)(TCA)(CCl_2CO_2)^+$

[a] Ac = acetate; TCA = trichloroacetate. [b] *m/e* values give the range of peaks observed for each ion. [c] Relative intensity is the total relative intensity of peaks arising from a particular ion. [d] From $Be_4O(Ac)_4(TCA)_2$. [e] From $Be_4O(Ac)_2(TCA)_4$. [f] From $Be_4O(Ac)_2(TCA)_4$.

culated peak intensities for a given ion. Nmr spectra *vs.* time for the mixed carboxylates, except for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$,[4] are shown in Figures 1 and 2. Figures 3 and 4 show nmr spectra *vs.* time for solutions of $Be_4O(CH_3CO_2)_6$ and $Be_4O(CCl_3CO_2)_6$ in 8.8:1 and 1:7.5 mole ratios, respectively.

Discussion

In a $Be_4O(RCO_2)_6$ molecule the carboxylate groups roughly form an octahedral arrangement about the Be_4O core. Close correlation is therefore found with regard to isomeric possibilities between $Be_4OX_nY_{6-n}$ mixed carboxylate and octahedral Ma_nb_{6-n} systems. Structural representations of compounds in the series $Be_4OX_nY_{6-n}$ (n = 0–6) are shown in Table III. A difference in isomeric possibilities between this series and the octahedral case arises for $Be_4OX_3Y_3$ where two *cis* isomers are possible. We were interested in whether specific mixed carboxylates in a favorable system could be isolated.

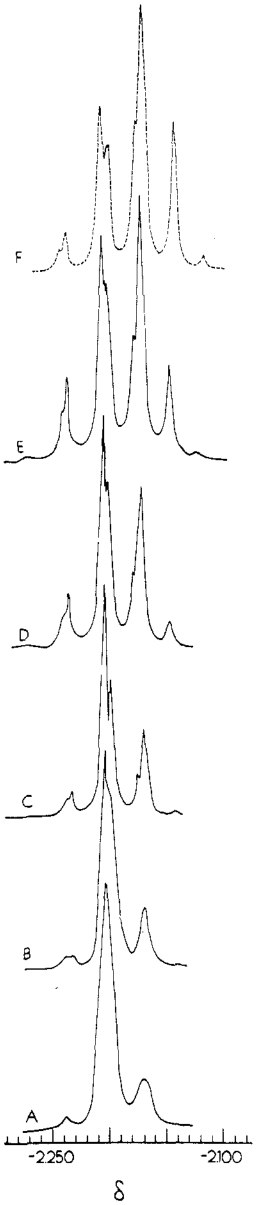

Figure 1.—Proton nmr spectrum of $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$. Time in hours: A, 17; B, 2.14; C, 8.39; D, 13.44; E, 112; F, an equimolar $Be_4O(CH_3CO_2)_6$–$Be_4O(CCl_3CO_2)_6$ solution after 100 hr.

Preliminary experiments showed that mixed carboxylates in the acetate–*p*-nitrobenzoate system could be obtained but that acetate proton chemical shifts in the various mixed carboxylates were nearly the same making identification of a particular isomer by this technique impossible. With the idea of preparing mixed trifluoroacetate–acetate compounds we next made an unsuccessful attempt to prepare $Be_4O(CF_3CO_2)_6$ by the thermal decomposition of beryllium trifluoroacetate. We were successful, however, in preparing $Be_4O(CCl_3CO_2)_6$, a colorless, crystalline moisture-sensitive compound, from the thermal decomposition of $Be(CCl_3CO_2)_2 \cdot 2H_2O$ presumably *via* the reaction

$$4Be(CCl_3CO_2)\cdot 2H_2O \longrightarrow Be_4O(CCl_3CO_2)_6 + (CCl_3CO_2)_2O + 8H_2O$$

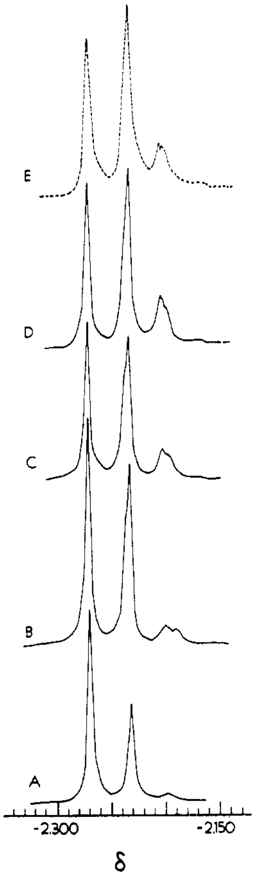

Figure 2.—Proton nmr spectrum of $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. Time in hours: A, 0.20; B, 0.57; C, 5.0; D, 71; E, a solution of $Be_4O(CH_3CO_2)_6$ and $Be_4O(CCl_3CO_2)_6$ in a 1.00:4.93 mole ratio after 23 hr.

The mass spectra of a number of $Be_4O(RCO_2)_6$ compounds have revealed very weak or nonexistent parent ion peaks. Instead the ion of highest mass (and also of high intensity) is $Be_4O(RCO_2)_5^+$.[8] Consistent with these observations the mass spectrum of $Be_4O(CCl_3CO_2)_6$ showed $Be_4O(CCl_3CO_2)_5^+$ to be the ion of highest mass.

$Be_4O(CH_3CO_2)_5(CCl_3CO_2)$, $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$, and $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$ were prepared by fractional crystallization from equilibrated chloroform solutions of $Be_4O(CCl_3CO_2)_6$ and $Be_4O(CH_3CO_2)_6$ in suitable mole ratios. Quite surprisingly, an alternate route to $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ was found by refluxing $Be_4O(CH_3CO_2)_6$ with trichloroacetyl chloride for 48 hr. Relatively large amounts of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ may be prepared in this way. The three mixed carboxylates gave satisfactory molecular weight and analytical data. In addition the presence of both bridging acetate and trichloroacetate groups was ascertained from infrared spectra (Table I). Asymmetric CO_2 stretching frequencies[9] were found at 1630 and 1690 cm^{-1} for acetate and trichloroacetate groups, respectively. These data do not provide definitive evidence for pure compounds. It could be argued that we have isolated mixtures which fortuitously gave the above results. Compelling evidence for the purity of the three compounds came from nmr and mass spectroscopic data. The mass spectroscopic data were especially important in establishing the purity of these compounds because sampling is direct from the solid state where carboxyl exchange does not occur. All the mixed carboxylates are stable in the solid state for at least 2 months as evidenced by the constancy of the mass spectrum.

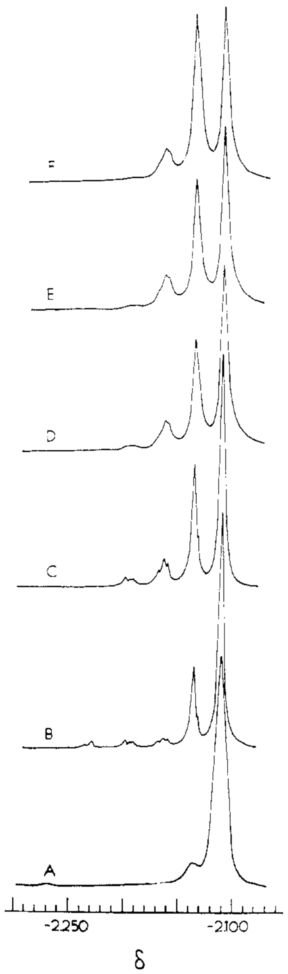

Figure 3.—The nmr spectrum of a $Be_4O(CH_3CO_2)_6$–$Be_4O(CCl_3CO_2)_6$ solution ($CHCl_3$) in 8.8:1 mole ratio. Time in hours: A, 0.12; B, 1.08; C, 2.47; D, 3.59; E, 6.83; F, 100.

Mass spectroscopic and nmr data for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ have been discussed in adequate detail previously.[4] We have, however, listed the peaks observed in the mass spectrum of this compound in Table II.

The mass spectrum of $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$ (Table II) was of special aid in providing evidence for the existence of this compound as a pure mixed carboxylate. The possibility of significant amounts of $Be_4O(CH_3CO_2)_4(CCl_3CO_2)_2$ or $Be_4O(CH_3CO_2)_2(CCl_3CO_2)_4$ was ruled out due to the absence of peaks corresponding to $Be_4O(CH_3CO_2)_4(CCl_3CO_2)^+$ and the presence of $Be_4O(CH_3CO_2)(CCl_3CO_2)_4^+$ peaks in only 1% relative intensity.

The nmr spectrum of $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$

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[8] J. G. Vogel and B. G. Hobrock, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967, No. L103.

[9] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," Wiley, New York, N. Y., 1963.

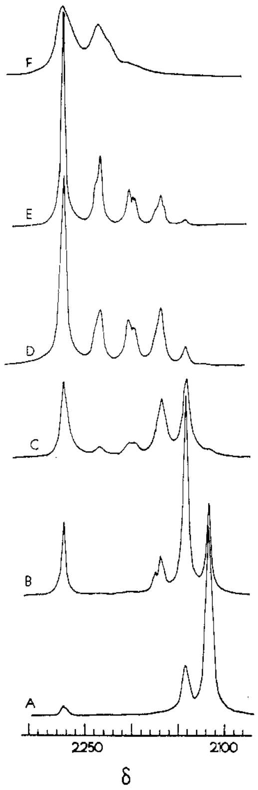

Figure 4.—The nmr spectrum of a $Be_4O(CH_3CO_2)_6$–$Be_4O(CCl_3CO_2)_6$ solution ($CHCl_3$) in a 1:7.5 mole ratio. Time in hours: A, 0.17; B, 2.52; C, 6.85; D, 14.1; E, 17.7; F, 100.

(Figure 1) shows two main peaks in a 3:1 ratio shifted to low field from $Be_4O(CH_3CO_2)_6$ (δ 2.116). The chemical shift may be simply understood in terms of the poor donor properties of the trichloroacetate ligand leaving beryllium(II) ions to which it is coordinated electron deficient. This in turn causes relatively more electron density to be shifted from acetates to beryllium. We suggest that the observation of two peaks may be rationalized in terms of the *trans* isomer schematically shown in Table III. Two peaks would be expected for this isomer in a 2:1 ratio and the peak of highest intensity would be expected furthest downfield as observed. Carboxylate scrambling (*vida infra*) could account for the disagreement between expected and calculated peak height ratios.

If we assume that none of the three $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$ isomers is energetically more stable than the others we may calculate which is statistically favored. It is interesting that *trans*-$Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$ is favored 3:1 over the other two isomers. Barring any drastic solubility differences, it is reasonable that the species in greatest abundance should be the one isolated by fractional precipitation.

Our arguments concerning the purity of $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$ are also strongly based on mass spectroscopic data. Again the principal ion observed in the mass spectrum was due to loss of a single carboxylate group (Table II). Approximately 4% contamination with $Be_4O(CH_3CO_2)_2(CCl_3CO_2)_4$ was suggested by the presence of the $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3{}^+$ ion. The nmr spectrum (Figure 2) agrees with the mass spectroscopic data in showing $Be_4O(CH_3CO_2)_2(CCl_3CO_2)_4$ impurity (δ 2.231). One must halve the peak intensity for $Be_4O(CH_3CO_2)_2(CCl_3CO_2)_4$ to obtain a true estimate of its concentration relative to $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. As expected the furthest downfield ^1H chemical shift was observed for $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. Unfortunately neither nmr nor mass spectroscopic data could help us estimate $Be_4O(CCl_3CO_2)_6$ impurity. However, the combination of mass spectroscopic and analytical data together with the observation that the hexatrichloroacetate is extremely soluble in chloroform suggests the level of impurity from this source is low.

TABLE III

REPRESENTATIONS OF SPECIES IN A $Be_4OX_nY_{6-n}$ SYSTEM[a]

n	Isomer	Structure[b]
0	. . .	
1	. . .	
2	*cis*	
2	*trans*	
3	*α-cis*	
3	*β-cis*	
3	*trans*	
4	*trans*	
4	*cis*	
5	. . .	
6	. . .	

[a] X and Y are differing carboxylate groups. [b] A beryllium atom is at each vertex of the tetrahedron; an oxygen atom is at the center of the tetrahedron; – – – – and ——— represent X and Y groups, respectively, which bridge two beryllium atoms.

A study of the proton nmr spectrum *vs.* time of solutions of the mixed carboxylates indicated carboxylate scrambling occurred (Figures 1 and 2). It is seen that the rate of carboxylate scrambling increases in the order $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ < $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$ < $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. This is also evident from Figures 3 and 4 which show the nmr spectra *vs.* time for solutions of $Be_4O(CH_3CO_2)_6$ and $Be_4O(CCl_3CO_2)_6$ in mole ratios of 1.0:7.5 and 8.8:1.0, respectively. The curves in Figure 4 show that species containing high ratios of acetate to trichloroacetate persist for some time in the initial stages of attaining equilibrium. In contrast Figure 3 shows that barely observable quantities of species containing high trichloroacetate to acetate ratios are built up at any stage in the attainment of equilibrium. This rapid scrambling seriously hampered our attempts to purify $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$.

That more rapid carboxylate scrambling occurs in mixed carboxylates with high trichloroacetate:acetate ratios (in spite of the bulk of the CCl_3 group) is consistent with the relatively weaker donor properties of the trichloroacetate group and suggests a dissociative mechanism for the exchange process

$$Be_4O(RCO_2)_x(R'CO_2)_{6-x} \rightleftharpoons Be_4O(RCO_2)_x(R'CO_2)_{5-x}{}^+ + R'CO_2{}^-$$

We note here that the mass spectra of the mixed carboxylates indicated that for the process involving loss of carboxylate from $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{6-x}$, loss of CCl_3CO_2 occurred consistently 2.4 (± 0.2) times the statistically calculated value. Thus for $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ one expects a 5:1 relative intensity ratio for $Be_4O(CH_3CO_2)_4(CCl_3CO_2)^+$:$Be_4O(CH_3CO_2)_5{}^+$ while a 1.9:1.0 ratio is observed. Once again these data are indicative of the relative ease of loss of trichloroacetate *vs.* acetate, although under quite different conditions with regard to nmr experiments.

In view of our observation of carboxylate scrambling the previous claim[10] for the preparation of pure acetate–monochloroacetate carboxylates simply by melting together appropriate amounts of starting materials appears untenable.

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Anion-Exchange Studies of Halo Complexes of Indium and Some Related Elements in Mixed Water–Alcohol Solutions

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The equilibrium distribution of anionic halo complexes of Au(III), In(III), and Ga(III) between solution and anion-exchange resin is profoundly affected by the addition of hydrophilic organic solvents. The solvents investigated were methanol, ethanol, 1-propanol, 1-butanol, and acetone. With Au(III) in aqueous HCl, the decrease in the distribution coefficient (K_d) is ascribed primarily to a change in the dielectric constant of the solution phase. For In(III), addition of the solvent affects the equilibria between the various species present in solution and K_d may increase, decrease, or go through a maximum depending on the halide present and on the solvent. With Ga(III), the results are similar to those for In(III). The results are in agreement with the previous solvent extraction studies of anionic In(III) complexes.

The use of anion exchange has provided much important information on the complexing behavior of positive ions in solution. For halide complexes, variations in the distribution coefficient (K_d) with hydrohalic acid concentration have been reported for a variety of elements in hydrofluoric,[1] hydrochloric,[2] and hydrobromic[3] acids. The values of K_d differ widely from element to element and often depend markedly on the acid concentration. The effect of adding electrolytes to the aqueous phase has been discussed by several authors, with special concern as to whether the observed changes in K_d arise from effects in the aqueous phase rather than in the resin.[4,5] There is much less information on anion exchange from nonaqueous solvents, or in mixed aqueous–nonaqueous systems; Korkisch and Janauer[6] have reviewed this field up to 1962, but with special reference to the behavior of uranium and thorium, and to the separation of these elements (see also ref 5).

The work described in this paper arose from a continuing interest in the nature of the indium(III) species present in aqueous solution. In particular, it is known that the extraction of anionic indium(III)–chloro complexes into basic oxygenated solvents is significantly less efficient than is the case for complexes of other tripositive elements. Results on the anion exchange of metal ions in aqueous hydrochloric acid solution[2] show a similar effect in that indium is removed from the solution phase less easily than other comparable elements. One possible explanation would be that indium(III) forms anionic complexes less strongly than the other elements in question. There are few reliable stability constant data[7] for the higher anionic complexes of elements such as indium, but in any case this explanation does not seem appealing when one compares (say) indium(III) and iron(III), since the available evidence shows that the complexing properties of these two elements are not very different quantitatively; in any case, the differences are not sufficient to explain fully the extraction and anion-exchange results.

An alternative explanation, advanced previously in connection with work on the extraction of indium by long-chain amines,[8] is that the predominant anionic

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