

CHROM. 15,265

## RATE AND EQUILIBRIUM STUDIES OF THE REACTION BETWEEN BERYLLIUM OXYACETATE AND BERYLLIUM OXYPROPIONATE BY GAS CHROMATOGRAPHY

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(Received August 6th, 1982)

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### SUMMARY

Gas chromatography has proved to be suitable for monitoring the rate of the reaction between two beryllium oxycarboxylates. The rate curves have been described qualitatively by consideration of the ligand exchange processes occurring in the system. Equilibrium data indicate that the beryllium oxyacetate-oxypropionate system shows excellent agreement with the theoretical predictions for a completely random distribution.

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### INTRODUCTION

The gas-liquid chromatography (GLC) of volatile neutral metal chelates is now well established as a technique for trace metal analysis<sup>1-4</sup>. In contrast, only a few reports have been made on the use of GC in the study of redistribution reactions of mixed-ligand metal chelate systems. Moshier and Sievers<sup>4</sup> claimed that preliminary GC studies indicated the presence of seven compounds in the reaction of trifluoroacetylacetone and hexafluoroacetylacetone with chromium(III), but detailed results were not presented. More recently, Uden *et al.*<sup>5</sup> reinvestigated the same redistribution reaction using a porous-layer open tubular (PLOT) column (Dexsil 300GC) and observed five clearly separated components with Cr(hfa)<sub>3</sub> unresolved from the solvent. Linck and Sievers<sup>6</sup> briefly described the formation and separation of mixed-ligand complexes in mixtures of aluminium acetylacetonate and aluminium hexafluoroacetylacetonate.

We have recently reported that GC can be used to monitor ligand exchange (carboxylate scrambling) reactions in mixtures of beryllium oxyacetate and beryllium oxypropionate<sup>7</sup>. Wynne and Bauder<sup>8</sup> used nuclear magnetic resonance (NMR) spectroscopy to investigate carboxylate scrambling of several mixed-ligand species of the beryllium oxyacetate-oxytrichloroacetate system. Other inorganic systems also exhibit this type of reorganisation or scrambling and their reaction kinetics and equilibria have been studied quantitatively or semi-quantitatively by NMR or GC. Systems studied include the condensed phosphates<sup>9</sup>, phosphoryl and thiophosphoryl halides<sup>10</sup>, tetramethyltin with tetrachlorotin, germanium or silicon<sup>11</sup>, various tetra-substituted germanium compounds<sup>12</sup> and dimethylsilicon and methylphosphorus moieties<sup>13</sup>. Several of the above systems are quite complex involving up to ten mixed-ligand

species but they have been analysed using the random reorganisation theory of Parks and Van Wazer<sup>9</sup>.

In this paper, the carboxylate scrambling reactions in the beryllium oxyacetate–oxypropionate system are examined in greater detail in order to generate rate and equilibrium data.

## EXPERIMENTAL

Beryllium oxyacetate and oxypropionate were prepared by the method of Moeller<sup>14</sup>, recrystallised twice from dry chloroform and sublimed under vacuum.

Chromatographic conditions were identical to those described previously<sup>7</sup>. Pyrex glass columns (1 m × 0.4 mm I.D.) were packed with 5% Apiezon L on exhaustively silanized (DMCS) Universal B (60–80 mesh) and the column temperature was maintained at 140°C, injector and detector at 200°C and nitrogen flow-rate at 60 cm<sup>3</sup> min<sup>-1</sup>.

Ligand exchange reactions of beryllium oxyacetate and oxypropionate were carried out by mixing appropriate volumes of acetone solutions (0.01 M) of each complex. Rate data were generated by following the decrease in reactants and the increase in products at 43.5 and 57°C for initial mole ratios of reactants of 2:1, 1:1 and 1:2. The reaction flask, fitted with a water-cooled condenser, was submerged in a constant-temperature oil bath; the higher temperature (57°C) corresponds to a refluxing acetone solution (oil bath maintained at 90°C). The reaction mixtures were sampled (1–2 μl) every 30 min, analysed immediately by GC, and the amount of each species in the reaction mixture was computed from the chromatographic peak area and the response factor (mole cm<sup>-2</sup>) for each component. As it was not possible to isolate pure samples of each mixed-ligand complex, the responses for the latter were assumed to be identical to that for the two initial reactants, determined to be  $(0.42 \pm 0.2) \cdot 10^{-8}$  mole cm<sup>-2</sup> from their linear calibration plots of peak area (cm<sup>2</sup>) vs. amount of metal complex injected (moles).

## RESULTS AND DISCUSSION

Typical chromatograms for the sampling of the reaction in refluxing acetone (57°C) have been presented previously<sup>7</sup>. As expected for ligand exchange in the reaction of beryllium oxyacetate and beryllium oxypropionate, seven peaks were observed corresponding to the species Be<sub>4</sub>OAc<sub>n</sub>Pr<sub>6-n</sub>, where 0 ≤ n ≤ 6, Ac = acetate and Pr = propionate. The order of elution was Be<sub>4</sub>OAc<sub>6</sub> (4.2) < Be<sub>4</sub>OAc<sub>5</sub>Pr (5.8) < Be<sub>4</sub>OAc<sub>4</sub>Pr<sub>2</sub> (7.8) < Be<sub>4</sub>OAc<sub>3</sub>Pr<sub>3</sub> (10.2) < Be<sub>4</sub>OAc<sub>2</sub>Pr<sub>4</sub> (13.7) < Be<sub>4</sub>OAcPr<sub>5</sub> (18.2) < Be<sub>4</sub>OPr<sub>6</sub> (24.2), with the respective retention times (min) given in parenthesis. Identification of eluted samples was performed by mass spectrometry<sup>7</sup>.

### Rate measurements

Rate curves for the disappearance of the reactants and the production of the five mixed-ligand species for equimolar concentrations (initially 10<sup>-5</sup> mole of each complex) of reagents at 57°C are shown in Fig. 1. Qualitative understanding of the curves can be obtained by considering the ligand exchange processes which are likely to occur. In order to simplify such a highly complex system, it is assumed that (i) only

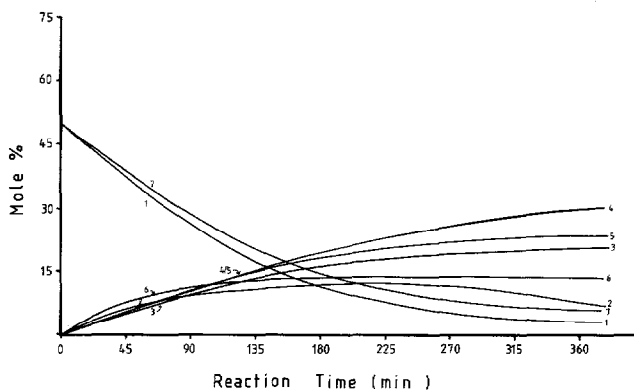
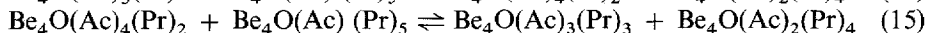
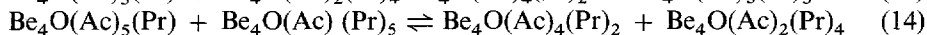
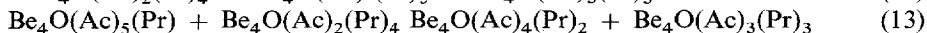
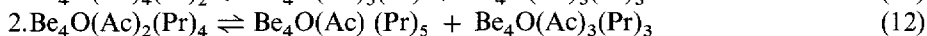
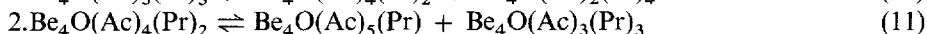
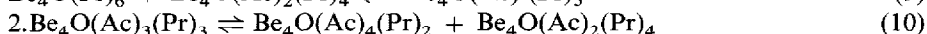
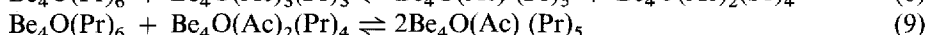
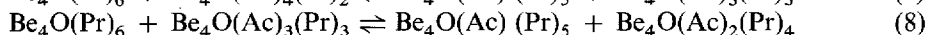
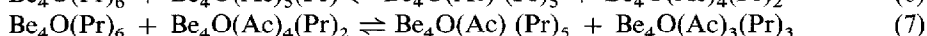
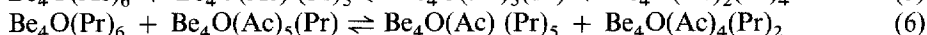
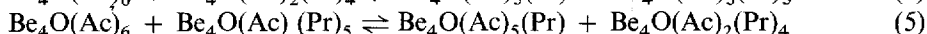
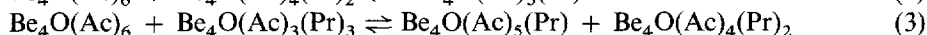
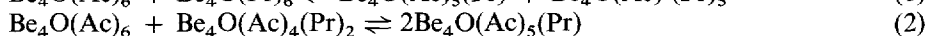
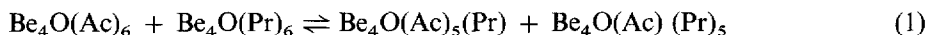


Fig. 1. Concentration-time profiles for the reaction between beryllium oxyacetate and beryllium oxypropionate in acetone at 57°C using an initial mole ratio of 1:1. The numbers on the curves correspond to the complexes according to (1)  $\text{Be}_4\text{OAc}_6$ , (2)  $\text{Be}_4\text{OAc}_5\text{Pr}$ , (3)  $\text{Be}_4\text{OAc}_4\text{Pr}_2$ , (4)  $\text{Be}_4\text{OAc}_3\text{Pr}_3$ , (5)  $\text{Be}_4\text{OAc}_2\text{Pr}_4$ , (6)  $\text{Be}_4\text{OAcPr}_5$  and (7)  $\text{Be}_4\text{OPr}_6$ .

two species react with each other at any one time, (ii) processes where a single species exchanges two carboxylate ligands, *e.g.*



are not permissible, and (iii) geometrical isomers are not formed by those species likely to exhibit isomerism<sup>8</sup>. Therefore, interactions corresponding to the equilibrium eqns. 1–15 represent the total number of chemically nontrivial exchange processes that can occur.



The predominant reaction for the equimolar mixture at 57°C in the initial stage of the ligand exchange process is eqn. 1, consistent with the immediate increase in the concentration of species  $\text{Be}_4\text{OAc}_5\text{Pr}$  and  $\text{Be}_4\text{OAcPr}_5$  and the similarity between initial rates of disappearance of  $\text{Be}_4\text{OAc}_6$  and  $\text{Be}_4\text{OPr}_6$  and rates of formation of

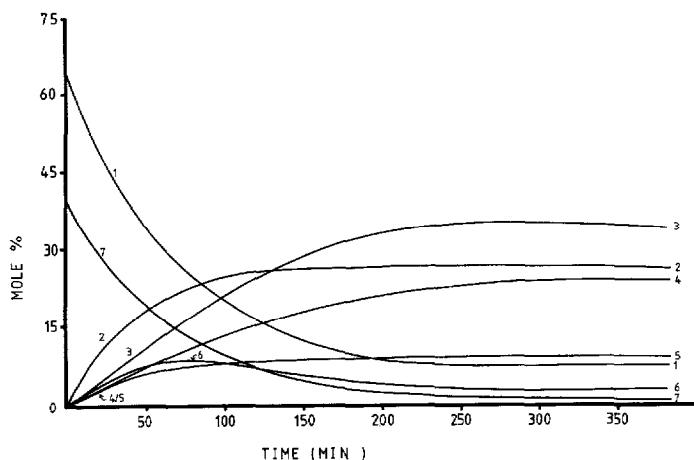


Fig. 2. Concentration-time profiles for the reaction between beryllium oxyacetate and beryllium oxypionate in acetone at 57°C for an initial mole ratio of 2:1. Numbers on curves as in Fig. 1.

$\text{Be}_4\text{OAc}_5\text{Pr}$  and  $\text{Be}_4\text{OAcPr}_5$ . The dominance of this reaction is short-lived as the product species now react with the starting ingredients according to eqns. 5 and 6 to produce  $\text{Be}_4\text{OAc}_4\text{Pr}_2$  and  $\text{Be}_4\text{OAc}_2\text{Pr}_4$ , which in turn can react according to eqns. 4 and 7 to produce eventually the dominant mixed-ligand complex,  $\text{Be}_4\text{OAc}_3\text{Pr}_3$ . As soon as significant concentrations of all mixed-ligand species are attained, reactions in eqns. 10–15 increasingly become important until equilibrium is achieved in about 360 min. The dominant species at equilibrium is  $\text{Be}_4\text{OAc}_3\text{Pr}_3$  (28.5 mole %), followed by  $\text{Be}_4\text{OAc}_4\text{Pr}_2$  (22.5 mole %),  $\text{Be}_4\text{OAc}_2\text{Pr}_4$  (20.1 mole %),  $\text{Be}_4\text{OAcPr}_5$  (11.5 mole %),  $\text{Be}_4\text{OAc}_5\text{Pr}$  (7.6 mole %),  $\text{Be}_4\text{OPr}_6$  (5.8 mole %) and  $\text{Be}_4\text{OAc}_6$  (2.5 mole %). As expected for a reaction which is statistically controlled (see below), the observed rate curves for the pairs of species  $\text{Be}_4\text{O}(\text{Ac})_n(\text{Pr})_{6-n}$  and  $\text{Be}_4\text{O}(\text{Ac})_{6-n}(\text{Pr})_n$  (where  $n = 0, 1$  or  $2$ ) are similar. The general form of the concentration-time curves is rather similar to that observed in the scrambling reaction between  $\text{CH}_3\text{PSCl}_2$  and  $(\text{CH}_3)_2\text{SiBr}_2$  (ref. 13). On the other hand, there is no evidence for the induction period observed in the reaction between  $(\text{CH}_3)_4\text{Sn}$  and  $\text{SnCl}_4$  (ref. 11).

Concentration-time profiles at 57°C were also obtained for the reaction between  $\text{Be}_4\text{OAc}_6$  and  $\text{Be}_4\text{OPr}_6$  at an initial mole ratio of 2:1 (see Fig. 2). Equilibrium is established in a similar time period to the equimolar reaction above. Concentrations of species at equilibrium were  $\text{Be}_4\text{OAc}_4\text{Pr}_2$  (31.2 mole %),  $\text{Be}_4\text{OAc}_5\text{Pr}$  (23.5 mole %),  $\text{Be}_4\text{OAc}_3\text{Pr}_3$  (20.3 mole %),  $\text{Be}_4\text{OAc}_6$  (11.0 mole %),  $\text{Be}_4\text{OAc}_2\text{Pr}_4$  (8.5 mole %),  $\text{Be}_4\text{OAcPr}_5$  (3.0 mole %) and  $\text{Be}_4\text{OPr}_6$  (1.0 mole %). As expected, the distribution has shifted towards species with a higher Ac/Pr ratio. The initial process is that described by eqn. 1 but the rate profiles for formation of  $\text{Be}_4\text{OAc}_5\text{Pr}$  and  $\text{Be}_4\text{OAcPr}_5$  are distinctly different, the concentration of the latter passing through a maximum at about 70 min. This is presumably a consequence of the continuous removal of  $\text{Be}_4\text{OAcPr}_5$  by reaction with excess  $\text{Be}_4\text{OAc}_6$  according to eqn. 5.

Analogous results were also obtained at 57°C for an initial mole ratio of  $\text{Be}_4\text{OAc}_6$  to  $\text{Be}_4\text{OPr}_6$  of 1:2. At equilibrium the distribution shifts towards species of

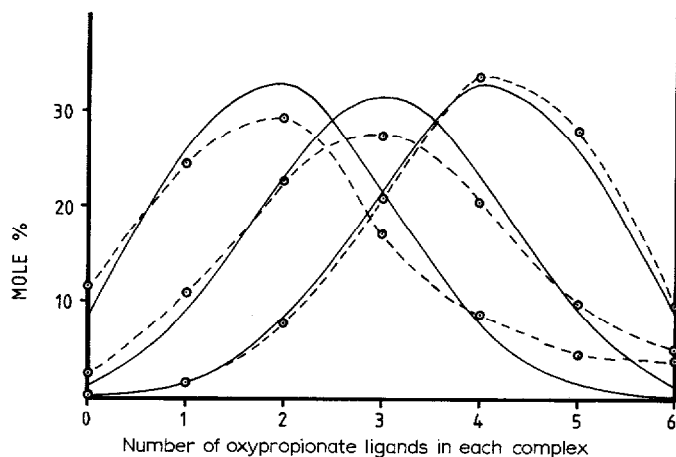


Fig. 3. Theoretical (solid lines) and experimental (dashed lines) equilibrium distribution of reactants and products in the reaction between beryllium oxyacetate and beryllium oxypropionate at 43.5°C.

higher propionate content so that  $\text{Be}_4\text{OAc}_2\text{Pr}_4$  (30.6 mole %) and  $\text{Be}_4\text{OAcPr}_5$  (27.2 mole %) predominate.

Rate curves for 1:1, 2:1 and 1:2 mole ratios were also obtained at 43.5°C. The concentration-time profiles are rather similar to those obtained at 57°C but the reactions are much slower, equilibration requiring about 30 h.

#### *Equilibration measurements*

The experimentally determined distributions of beryllium oxycarboxylates at equilibrium for initial mole ratios of 1:2, 1:1 and 2:1 are presented in Figs. 3 and 4 (dashed lines) at 43.5 and 57°C, respectively.

These results are compared with completely random distributions of reactants

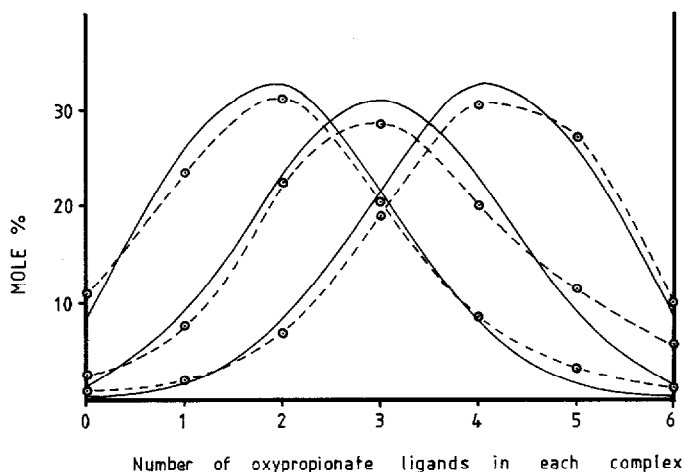


Fig. 4. As in Fig. 3 for the reaction at 57°C.

TABLE I

EQUILIBRIUM CONSTANTS FOR CARBOXYLATE SCRAMBLING BETWEEN BERYLLIUM OXYACETATE AND BERYLLIUM OXYPROPIONATE AT 57°C

$$K_n = [\text{Be}_4\text{OAc}_{n+1}\text{Pr}_{5-n}] [\text{Be}_4\text{OAc}_{n-1}\text{Pr}_{7-n}] / [\text{Be}_4\text{OAc}_n\text{Pr}_{6-n}]^2$$

$K_n$	Mole ratio			Ideal randomness
	1:1	2:1	1:2	
$K_1$	$0.97 \pm 0.14$	$0.62 \pm 0.03$	$1.08 \pm 0.40$	0.417
$K_3$	$0.43 \pm 0.02$	$0.49 \pm 0.02$	$0.81 \pm 0.16$	0.533
$K_3$	$0.56 \pm 0.02$	$0.64 \pm 0.03$	$0.59 \pm 0.03$	0.5625
$K_4$	$0.81 \pm 0.04$	$0.84 \pm 0.11$	$0.55 \pm 0.02$	0.533
$K_5$	$0.88 \pm 0.07$	$0.94 \pm 0.35$	$0.41 \pm 0.02$	0.417

and products in the carboxylate scrambling of  $\text{Be}_4\text{OAc}_6$  and  $\text{Be}_4\text{OPr}_6$ , where it is assumed that Ac and Pr are monofunctional, *i.e.* each carboxylate ion occupies one site although it is, strictly speaking, a bidentate ligand. If the Ac/Pr ratio is  $a/p$  (with  $a + p = 1$ ), then the probability of having a  $\text{Be}_4\text{O}$  moiety with  $n$  acetates and  $6 - n$  propionates in the six available sites is given by

$$P(n, 6 - n) = \frac{6!}{n! (6 - n)!} \cdot a^n \cdot p^{6-n}$$

for  $0 \leq n \leq 6$  (ref. 10). The experimental initial mole ratio was used to calculate the probability for each species in each reaction mixture and the distributions on a purely random basis are represented by the solid lines in Figs. 3 and 4.

The experimental data can also be presented in terms of equilibrium constants. The beryllium oxyacetate–oxypropionate system can be completely described by five equilibrium constants according to reorganisation theory<sup>9</sup> and these are listed in Tables I and II.

The equilibrium data above show that the behaviour of the beryllium oxyacetate–oxypropionate system approaches that calculated for a completely random reorganisation. In most of the reaction mixtures analysed, the concentrations of the initial reactants at equilibrium are slightly higher and the concentrations of the mixed-ligand species are lower than those based on random distributions. Therefore,

TABLE II

EQUILIBRIUM CONSTANTS FOR CARBOXYLATE SCRAMBLING AT 43.5°C

$K_n$	Mole ratio			Ideal randomness
	1:1	2:1	1:2	
$K_1$	$0.49 \pm 0.06$	$0.56 \pm 0.02$	$0.69 \pm 0.45$	0.417
$K_2$	$0.59 \pm 0.03$	$0.49 \pm 0.02$	$0.52 \pm 0.10$	0.533
$K_3$	$0.62 \pm 0.02$	$0.85 \pm 0.05$	$0.60 \pm 0.03$	0.5625
$K_4$	$0.64 \pm 0.03$	$1.02 \pm 0.10$	$0.52 \pm 0.02$	0.533
$K_5$	$1.09 \pm 0.10$	$1.54 \pm 0.28$	$0.41 \pm 0.02$	0.417

these results seem to indicate that the reaction mixtures may not have reached complete equilibrium; further reaction would tend to decrease the concentrations of the initial reactants and increase the concentrations of the mixed-ligand complexes. For one system, the reaction where the Ac/Pr ratio is 1:2 at 43.5°C, the experimental points closely match the theoretical distribution for a random process; this suggests that complete equilibrium may not have been achieved in the other reaction mixtures. Another equally plausible explanation for the slight differences between the experimental and theoretical results is the difficulty encountered in obtaining pure beryllium oxypropionate: GC consistently indicated that this starting material was contaminated with traces (1–2%) of mixed-ligand species, in particular  $\text{Be}_4\text{OAcPr}_5$ .

#### ACKNOWLEDGEMENT

We wish to thank Dr. M. W. Grant for constructive discussions on several aspects of this work.

#### REFERENCES

- 1 G. Guiochon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1973.
- 2 J. A. Rodriguez-Vasquez, *Anal. Chim. Acta*, 73 (1974) 1.
- 3 P. C. Uden and D. E. Henderson, *Analyst (London)*, 102 (1977) 1221.
- 4 R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
- 5 P. C. Uden, D. E. Henderson, F. P. DiSanzo, R. J. Lloyd and T. Tetu, *J. Chromatogr.*, 196 (1980) 403.
- 6 R. G. Linck and R. E. Sievers, presented at 148th Nat. Meet. Amer. Chem. Soc., Chicago, IL, Sept. 1964.
- 7 T. J. Cardwell and M. R. L. Carter, *J. Chromatogr.*, 140 (1977) 93.
- 8 K. J. Wynne and W. Bauder, *Inorg. Chem.*, 9 (1970) 1985.
- 9 J. R. Parks and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 79 (1957) 4890.
- 10 L. C. D. Groenweghe and J. H. Payne, *J. Amer. Chem. Soc.*, 81 (1959) 6357.
- 11 D. Grant and J. R. Van Wazer, *J. Organometal. Chem.*, 4 (1965) 229.
- 12 G. M. Burch and J. R. Van Wazer, *J. Chem. Soc. A*, (1966) 586.
- 13 K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 12 (1973) 2856.
- 14 T. Moeller, *Inorg. Syn.*, 3 (1950) 4.