THE THERMAL DECOMPOSITION OF METAL ETHYLENEDIAMINE OXALATE COMPLEXES

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Bis- and tris(ethylenediamine) metal complexes, such as $[Cu(en)_2][CdI_4]$[1], $[Cr(en)_3]SbS_4$[2], $[Cu(en)_2][HgI_4]$[3], $[Co(en)_2(SCN)_2][Ag(SCN)_2]$[4], and others, have long been used in gravimetric analysis. Of great importance in these determinations are the drying and/or ignition temperatures of the precipitated complexes. DUVAL[5] has studied the thermal stability of a large number of compounds of the above formulas as well as others. WENDLANDT and his coworkers have also studied the thermal dissociation of a large number of ethylenediamine complexes; among them are: $[Cr(en)_3]X_3$[6], $[Cr(en)_2(H_2O)_4]X_3$[7], $[Ni(en)_3]X_2$[8,9], platinum ethylenediamine complexes[10], cobalt ethylenediamine complexes[11], and copper ethylenediamine complexes[12]. In continuing with this work, the thermal decomposition of a series of metal ethylenediamine oxalates was studied by thermogravimetry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and high temperature reflectance spectroscopy.

EXPERIMENTAL

Thermobalance

The automatic recording thermobalance was previously described[11]. Sample sizes ranged in weight from 50 to 70 mg and were pyrolyzed in a static air atmosphere at a heating rate of 5°/min.

DTA apparatus

The DTA apparatus was previously described[13]. Sample sizes ranged in weight from 60 to 70 mg and were pyrolyzed in a dynamic helium atmosphere at a furnace heating rate of 10°/min.

DSC apparatus

A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was employed. Sample sizes ranged in weight from 2 to 5 mg and were pyrolyzed in a static air atmosphere at a heating rate of 5°/min.

Reflectance studies

The reflectance spectra of the samples at ambient and elevated temperatures

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were measured with a Beckman Model DK-2A spectroreflectometer equipped with a heated sample holder[14,15]. Measurements were made at fixed elevated temperatures in the 350–750 mμ wavelength range.

Preparation of complexes

Although a number of nickel, zinc, copper, and cadmium ethylenediamine complexes were prepared by WERNER[16], the oxalate compounds were not synthesized. However, in connection with the purification of ethylenediamine, BAILAR[17] described the preparation of $Zn(en)C_2O_4$. The methods described here were developed for the synthesis of the ethylenediamine metal oxalates.

The metal oxalates of Zn, Cd, Co, Ni, and Cu were prepared by the addition of an equivalent amount of a sodium oxalate solution to solutions containing the above metal ions. The precipitated compounds were all air-dried for 24 h at room temperature before use in the synthesis of the ethylenediamine complexes.

All of the tris(ethylenediamine) metal oxalates were prepared in the same general manner, such as is illustrated here by $[Zn(en)_3]C_2O_4$. A two-fold excess of ethylenediamine was added to 2 g of zinc oxalate. The latter was covered completely with the amine, triturated, and allowed to stand for 1 h. The resulting white precipitate was filtered off and dissolved in a minimum amount of hot water. Acetone was then added to the solution to effect crystallization of $[Zn(en)_3]C_2O_4$. The crystals were filtered off, washed with acetone, and dried in a vacuum desiccator. The yield was approximately quantitative. The cobalt and cadmium complexes were not redissolved in hot water but were washed with 100% ethanol and then acetone. The $[Cd(en)_3]C_2O_4$ required storage at 0° to prevent decomposition.

TABLE I

ANALYTICAL RESULTS FOR METAL COMPLEXES

Compound	*% Metal*		*% N*		*% C_2O_4*	
	Theoretical	*Found*	*Theoretical*	*Found*	*Theoretical*	*Found*
$[Zn(en)_3]C_2O_4$	19.59	20.2	25.19	23.4	26.38	26.8
$[Cd(en)_3]C_2O_4$	29.52	29.6	—	—	23.12	22.7
$[Cu(en)_2(H_2O)_2]C_2O_4$	20.64	20.4	18.20	18.8	28.60	27.6
$[Cu(en)_3]C_2O_4$	19.15	19.6	25.32	25.0	26.52	25.8
$[Ni(en)_3]C_2O_4 \cdot 2H_2O$	16.17	15.2	23.15	24.6	24.24	24.8
$[Co(en)_3]C_2O_4$	18.01	18.8	25.68	24.5	—	—

The $[Cu(en)_2(H_2O)_2]C_2O_4$ was prepared by the addition of an excess of ethylenediamine to solid copper oxalate hemihydrate followed by enough water to effect solution. The dark purple colored solution was filtered, and acetone was added to the filtrate to cause crystallization of $[Cu(en)_2(H_2O)_2]C_2O_4$. After filtration, the crystals were washed with acetone and dried in a vacuum desiccator. Yield was approximately quantitative.

The compounds were analyzed for nitrogen content by use of a Coleman Nitrogen Analyzer; for oxalate content by titration with standard potassium permanganate; and for metal ion content by ignition of the compounds to the metal oxide. The results of the analyses are given in Table I.

RESULTS AND DISCUSSION

Weight-loss studies

The weight-loss curves of the ethylenediamine metal complexes are given in Figs. 1 and 2.

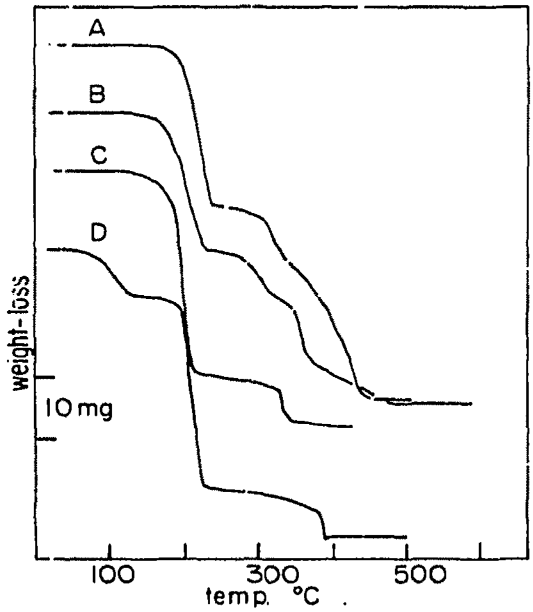


Fig. 1. Weight-loss curves of metal complexes. (A) $[Zn(en)_3]C_2O_4$; (B) $[Cd(en)_3]C_2O_4$; (C) $[Cu(en)_3]C_2O_4$; (D) $[Cu(en)_2(H_2O)_2]C_2O_4$.

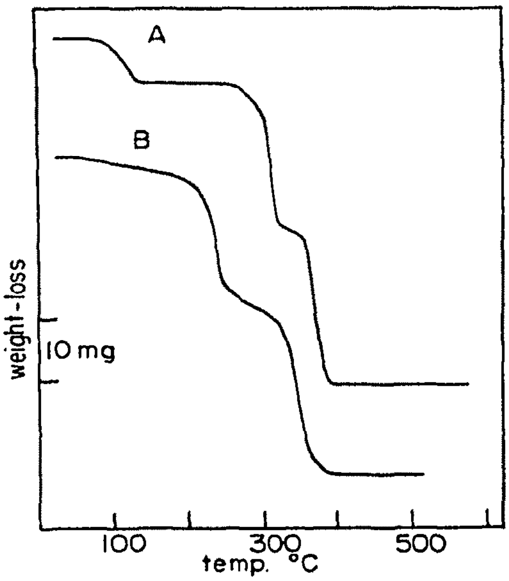


Fig. 2. Weight-loss curves of metal complexes. (A) $[Ni(en)_3]C_2O_4 \cdot 2H_2O$; (B) $[Co(en)_3]C_2O_4$.

In general, the tris(ethylenediamine) complexes evolved 2 moles of amine per mole of complex, to form the mono(ethylenediamine) complex. Well-defined curve plateaus were observed, indicating that the monoamine compounds were quite stable. The remainder of the ethylenediamine was evolved at still higher temperatures but no curve plateaus were observed for the anhydrous metal oxalate. Instead, the oxalate ion began to dissociate before all of the amine was evolved, resulting in only a curve inflection point rather than a plateau.

The decomposition temperatures for the tris- to mono(ethylenediamine) transition were as follows: $[Zn(en)_3]C_2O_4$, 150–240°; $[Cd(en)_3]C_2O_4$, 140–230°; $[Ni(en)_3]C_2O_4$, 250–325°; and $[Co(en)_3]C_2O_4$, ambient–*ca.* 300°. The curve for $[Cu(en)_3]C_2O_4$ did not show a weight-change which corresponded to the above transition but instead, evolved all 3 amines in one step, from 140–220°.

Water of hydration of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ was evolved in the temperature range 70°–130°, resulting in the formation of anhydrous $[Ni(en)_3]C_2O_4$. The coordinated water in $[Cu(en)_2(H_2O)_2]C_2O_4$ was evolved over a similar temperature range, 60°–130°, resulting in the formation of $Cu(en)_2C_2O_4$. The two ethylenediamines were then evolved from 170°–230°.

In all cases, the residue of the thermal decomposition reaction was the metal oxide.

DTA studies

The DTA curves of the complexes are given in Figs. 3 and 4.

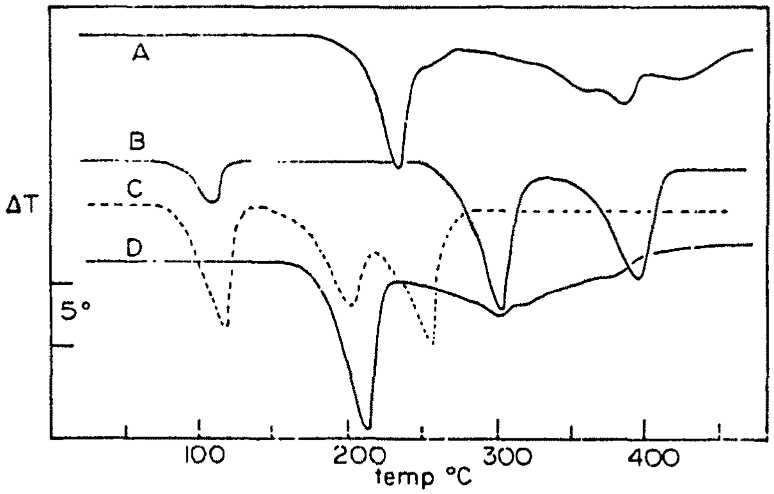


Fig. 3. DTA curves of metal complexes. (A) $[Co(en)_3]C_2O_4$; (B) $[Ni(en)_3]C_2O_4 \cdot 2H_2O$; (C) $[Cu(en)_2(H_2O)_2]C_2O_4$; (D) $[Zn(en)_3]C_2O_4$.

The curves all contained endothermic peaks which were due to dehydration, deamination, and decomposition reactions. The transitions involved were the same as previously discussed in the weight-loss studies. The curve for $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ contained 3 endothermic peaks. The first peak, with a T_{max} of 110° was due to the dehydration reaction; the second at 300°, due to the loss of 2 moles of ethylenediamine; and the third, at 400°, to the loss of the remaining ethylenediamine and the decomposition of the oxalate ion. A similar interpretation can be made for $[Cu(en)_2(H_2O)_2]C_2O_4$. The first peak, at 115°, to the dehydration reaction; the other peaks, at 200° and 255°, to the deamination and decomposition reactions.

The DTA curves of $[Zn(en)_3]C_2O_4$, $[Co(en)_3]C_2O_4$, and $[Cd(en)_3]C_2O_4$ were all similar to each other. The first endothermic peak was due to the tris → mono amine transition, while the other smaller peaks were due to the deamination and decomposition reactions of the mono(ethylenediamine) complex.

Gas evolution (GE) curves were obtained simultaneously with the DTA curves, but only the GE curve for $[Cu(en)_3]C_2O_4$ is shown. The GE curves for the other compounds indicated that all of the DTA curve peaks involved gaseous products, as was expected. The GE curve for $[Cu(en)_3]C_2O_4$ indicated that each DTA peak was due to a reaction which evolved a gaseous product. However, an exact interpretation of the peaks was not possible because from the weight-loss curve, no stable amine intermediates were observed.

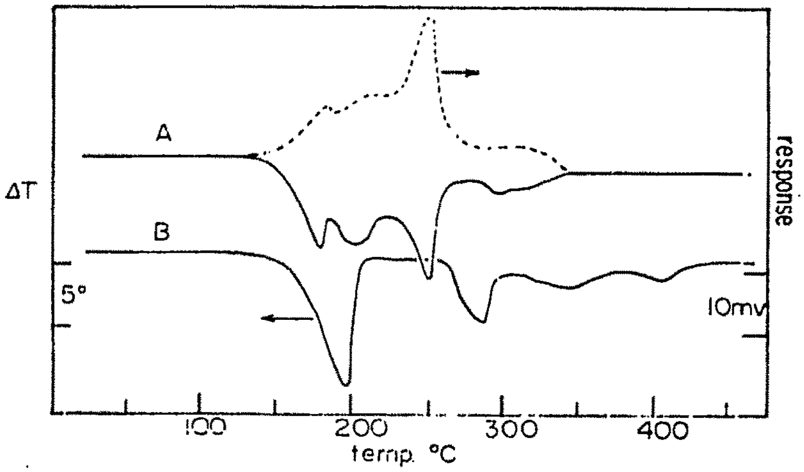


Fig. 4. DTA and GE curves of metal complexes. (A) $[Cu(en)_3]C_2O_4$; (B) $[Cd(en)_3]C_2O_4$.

DSC studies

It was possible to study only some of the dehydration and deamination reactions calorimetrically. Difficulty was encountered due to the overlapping of curve peaks. Results that were obtained, however, are shown in Table II. The heat of dissociation of the coordinated water, such as in $[Cu(en)_2(H_2O)_2]C_2O_4$, was greater than for the hydrate-bound water in $[Ni(en)_3]C_2O_4 \cdot 2H_2O$. In fact, on the basis of kcal per mole of water, the values are 13.1 and 7.2, respectively. Practically identical ΔH values were obtained for the deamination of the cadmium and zinc complexes; both values were higher than those obtained for the dehydration reactions.

TABLE II

HEATS OF DISSOCIATION OF THE METAL COMPLEXES

Reaction	ΔH *(kcal/mole)*	*Temperature (°K)*
$[Ni(en)_3]C_2O_4 \cdot 2H_2O(s) \rightarrow [Ni(en)_3]C_2O_4(s) + 2H_2O(v)$	14.2 14.7	350– 405
$[Cu(en)_2(H_2O)_2]C_2O_4(s) \rightarrow [Cu(en)_2C_2O_4](s) + 2H_2O(v)$	26.2 26.3	335– 385
$[Zn(en)_3]C_2O_4(s) \rightarrow [Zn(en)C_2O_4](s) + 2en(v)$	36.7 35.7	
$[Cd(en)_3]C_2O_4(s) \rightarrow [Cd(en)C_2O_4](s) + 2en(v)$	35.8 35.9	

Reflectance studies

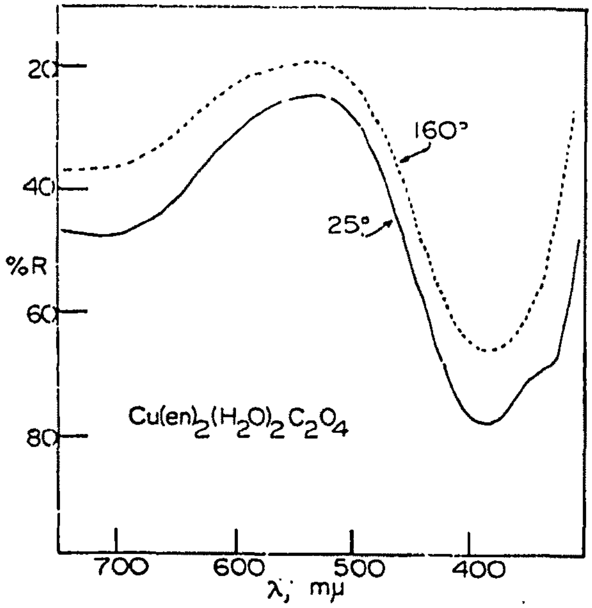
The total diffuse reflectance curves of $[Cu(en)_2(H_2O)_2]C_2O_4$ and $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ are shown in Figs. 5 and 6. The reflectance curve of $[Cu(en)_2(H_2O)_2]C_2O_4$ contained a single absorption peak (reflectance minimum) at 535 mμ. On heating the compound to 160°, the peak intensity changed but did not shift to a different wavelength. Thus, the anhydrous complex, $[Cu(en)_2C_2O_4]$, was of a lighter blue color than the initial compound. This behavior was similar to that observed for the dehydration of $[Cu(en)(H_2O)_2]SO_4$[12].

The reflectance curve of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$ at 25° contained 2 absorption peak maxima, at 525 mμ and 335 mμ, respectively. On heating the compound to 130°, the 525 mμ peak shifted slightly to 535 mμ and also increased in intensity. The 335 mμ peak shifted to 325 mμ but underwent a pronounced intensity change. Thus, the visual change in color was from a dark pink to a lighter pink. Apparently, no structural change in the coordination of ligands to the nickel or copper ions was involved in either dehydration reaction.

Kinetics studies

BORCHARDT AND DANIELS[18] have derived general expressions for calculating kinetic data from enthalpy measurements. If it is assumed that the heat evolved (or absorbed) is proportional to the number of moles reacted, then

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{n_0}{A}\frac{\mathrm{d}H}{\mathrm{d}t}$$



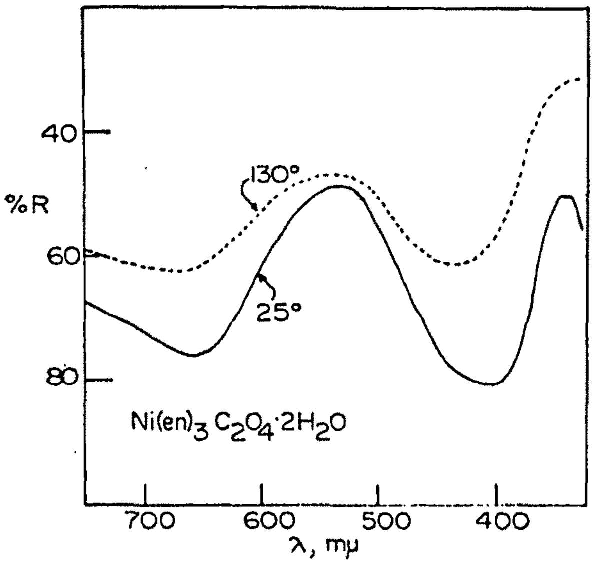


Fig. 5. Reflectance curves of $[Cu(en)_2(H_2O)_2]C_2O_4$.

Fig. 6. Reflectance curves of $[Ni(en)_3]C_2O_4 \cdot 2H_2O$.

where n_0 is the initial number of moles of reactant, and $A = A\ H$, the relationship between total peak area to heat transferred. The amount of reactant present at any instant is given by

$$n = n_0 - \frac{n_0 a}{A}$$

where a is the peak area up to a certain time or temperature. The rate constant, k, is given by

$$k = \frac{\left(\dfrac{AV}{n_0}\right)^{x-1} \dfrac{\mathrm{d}H}{\mathrm{d}t}}{(A - a)^x}$$

where V/n_0 is the reciprocal of the initial concentration of reactants. Then, assuming a first order reaction, the previous equation becomes

$$k = \frac{\mathrm{d}H/\mathrm{d}t}{(A - a)}$$

The assumptions under which the above equations apply have previously been discussed[18] in detail.

Typical kinetics plots for the deamination of $[\mathrm{Cd(en)_3}]\mathrm{C_2O_4}$ and $[\mathrm{Zn(en)_3}]\mathrm{C_2O_4}$ are given in Fig. 7. Activation energies, E_a, for these 2 complexes were both 51 kcal/mole. Kinetics data were also obtained for the dehydration of $[\mathrm{Cu(en)_2(H_2O)_2}]\mathrm{C_2O_4}$, $E_a = 38$ kcal/mole, and $[\mathrm{Ni(en)_3}]\mathrm{C_2O_4} \cdot 2\mathrm{H_2O}$, $E_a = 27$ kcal/mole. The value for the

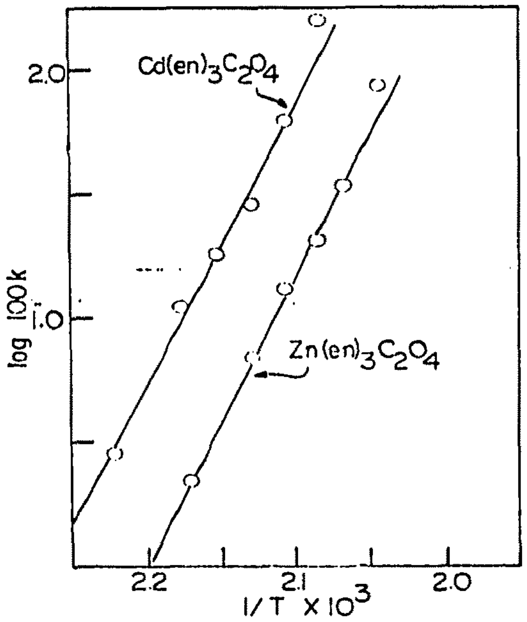


Fig. 7. Kinetics plots.

copper complex was somewhat larger than the $E_a = 29$ kcal/mole, previously calculated for $[Cu(en)(H_2O)_2]SO_4$ using a DTA method[12].

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SUMMARY

The thermal dehydration and deamination of some ethylenediamine complexes of Zn, Cd, Cu, Ni and Co oxalate were studied by TGA, DTA, DSC, reflectance spectroscopy, and by GE. The tris(amine) complexes deaminated to mono(amine) compounds which then decomposed directly to the metal oxide. The kinetics and heats of dehydration and deamination of several of the complexes were determined.

RÉSUMÉ

Les auteurs ont examiné la décomposition thermique de complexes oxalates métalliques (Zn, Cd, Cu, Ni, Co)-éthylènediamine, par analyse thermogravimétrique, analyse thermique différentielle, calorimétrie différentielle, spectroscopie et par dégagement gazeux. Les complexes étudiés donnent d'abord des composés monoaminés; ils se décomposent ensuite directement en oxyde métallique.

ZUSAMMENFASSUNG

Die thermische Zersetzung einiger Äthylendiaminkomplexe der Oxalate des Zn, Cd, Cu, Ni und Co wurden mit verschiedenen Methoden wie z.B. der TGA, DTA u.a. untersucht. Die Trisaminkomplexe zersetzen sich zu Monoaminverbindungen und weiter direkt zum Metalloxyd.

REFERENCES

1 G. Spacu and G. Suciu, *Z. Anal. Chem.*, 77 (1929) 340.
2 G. Spacu and A. Pop, *Z. Anal. Chem.*, 111 (1937–38) 254.
3 G. Spacu and G. Suciu, *Z. Anal. Chem.*, 78 (1929) 329.
4 G. Spacu, *Bull. Soc. Stiinte Cluj*, 7 (1934) 568.
5 C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd Ed., Elsevier, Amsterdam, 1963.
6 W. W. Wendlandt and J. L. Bear, *J. Inorg. & Nucl. Chem.*, 17 (1961) 286.
7 W. W. Wendlandt and W. R. Robinson, *J. Inorg. & Nucl. Chem.*, 26 (1964) 531.
8 T. D. George and W. W. Wendlandt, *J. Inorg. & Nucl. Chem.*, 25 (1963) 395.
9 T. D. George and W. W. Wendlandt, *Texas J. Sci.*, 14 (1962) 47.
10 W. W. Wendlandt, *Texas J. Sci.*, 14 (1962) 264.
11 W. W. Wendlandt, T. D. George and K. V. Krishnamurty, *J. Inorg. & Nucl. Chem.*, 21 (1961) 69.
12 W. W. Wendlandt, *J. Inorg. & Nucl. Chem.*, 25 (1963) 833.
13 W. W. Wendlandt, *Anal. Chim. Acta*, 27 (1962) 309.
14 W. W. Wendlandt, P. H. Franke and J. P. Smith, *Anal. Chem.*, 35 (1963) 105.
15 W. W. Wendlandt and T. D. George, *Chemist-Analyst*, 53 (1964)100.
16 A. Werner, *Z. Anorg. Allgem. Chem.*, 21 (1899) 201.
17 J. C. Bailar, *J. Am. Chem. Soc.*, 56 (1934) 955.
18 H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.