C′, D′ and F′ were recrystallized twice. The rotations of the fractions are given in Table II.

TABLE II

ROTATIONAL DATA OF FINAL FRACTIONS

Fraction	Wt. of sample, mg.	Obsd. rotation	$[\alpha]_D$, deg.
A″	10	−0.068°	−68
C″	10	+ .072	+72
D″	10	− .060	−60
F″	10	+ .061	+61

The specific rotations of succeeding fractions were diverging and this is further evidence of the presence of four fractions.

Thirty-milligram samples of fractions A″, C″, D″ and F″ were dissolved in water and 30 mg. of 48% hydrobromic acid (10% excess) was added to each solution. The solutions were filtered and evaporated to small volume at room temperature, and acetone was added to precipitate the complex bromide, $[\text{Coen}_2\text{dabp}]\text{Br}_3$. This was washed with acetone and dried.

The rotatory dispersion curves for the four isomers of the bromide are plotted in Figs. 2 and 3.

It can be seen from the rotatory dispersion curves that the samples are not completely pure since the rotations do not pair up exactly.

The complex bromide is reasonably stable to racemization. Solutions of isomers A″ and C″ were made up in approximately equal concentrations—0.05 and 0.045%—and the rate of loss of optical activity was determined. There is very little difference in the rate of change in the two isomers (Table III).

TABLE III

RACEMIZATION DATA

	A″		C″	
Time, hr.	Obsd. rotation, deg.	Specific rotation, deg.	Obsd. rotation, deg.	Specific rotation, deg.
0	−0.040	−77	+0.030	+67
5	− .040	−77		
24	− .031	−60	+ .030	+67
48	− .025	−48	+ .020	+44
70			+ .010	+22
96			+ .005	+11
121			+ .001	∼ 0

The authors wish to express their thanks to the Socony-Vacuum Laboratories, whose financial support made this work possible.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XX. The Tetradentate and Bidentate Complexes of Ethylenediaminetetraacetic Acid

BY DARYLE H. BUSCH AND JOHN C. BAILAR, JR.

RECEIVED AUGUST 4, 1955

Two types of ethylenediaminetetraacetic acid complexes may be prepared with platinum(II) and palladium(II). In one, the ligand acts as a bidentate group and in the other, as a tetradentate group. The complex compounds have been characterized on the basis of analysis, equivalent weight, pK_{av} of the free acids, infrared spectra and isomer studies. These compounds provide proof that the hexafunctional ethylenediaminetetraacetic acid may use only a few of its donor atoms in the formation of certain complexes.

Introduction

In an earlier paper,[1] the authors confirmed the ability of ethylenediaminetetraacetic acid (EDTA) to act as a hexadentate and as a pentadentate donor molecule when combined with cobalt(III). It is commonly assumed that this ligand acts as a tetradentate donor in combination with metal ions having a coördination number of four. This has not been proven, however, and it was the purpose of this investigation to determine whether or not EDTA utilizes four or fewer groups in the formation of coördinate bonds in such cases. The dipositive ions of platinum and palladium were chosen for these studies since an invariable coördination number of four is best established for them. In the event that EDTA acts as a tetradentate chelate, in combination with platinum(II) or palladium(II), it is to be expected that the two nitrogen atoms and two of the carboxyl groups will be involved in the bonding. Since these metal ions normally form square planar complexes, the two carboxyl groups involved in bond formation must be parts of acetate groups attached to the two different nitrogen atoms. The resulting complex might be expected to exist in racemic and *meso* forms as a result of the asymmetry of the two nitrogen atoms. Study of the Fisher–Hirschfelder–Taylor models shows that the *meso* isomer is strained. It would be expected that the *meso* form would find its greatest stability in the acid form since a slight attraction might be gained through hydrogen bonding of the two carboxyl groups, while the two charges of the dinegative anion would cause the carboxyl groups to be strongly repelled from each other. The acids derived from the two geometrical isomers should differ greatly in their pK_1 and pK_2 values since they are comparable to the *cis* and *trans* forms of an unsaturated dicarboxylic acid.[2]

Palladium(II) and platinum(II) complexes of EDTA have not previously been prepared, and only recently has it been realized that complexes are formed in solutions of these substances.[3] In the present study, it has been found that EDTA reacts in a stepwise manner with platinum(II) chloride, palladium(II) chloride, tetrachloroplatinate(II) ion or tetrachloropalladate(II) ion, first replacing two chlorides with the two nitrogen atoms and then replacing the remaining two chlorides with two carboxyl oxygen atoms. Free acids of both

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(1) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953).

(2) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 396.

(3) W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **26**, 1768 (1954).

types of complex have been isolated and identified by total analysis, equivalent weight, pK_a, thermal dehydration and infrared spectra. In the case of the tetradentate complex, a search for the predicted isomers has been made.

Experimental

Complexes of Bidentate EDTA.—Disodium dihydrogen ethylenediaminetetraacetate reacted with $PtCl_2$, $PdCl_2$, K_2PtCl_4 or K_2PdCl_4 to form a bidentate complex of EDTA which crystallized from concentrated hydrochloric acid as bright crystals of the composition $H_4M^{II}YCl_2 \cdot 5H_2O$. (Here the symbol "Y" indicates the tetranegative anion of EDTA.) With either metal ion, the complex tetrachloro anion provided the smoother reaction; however, in the case of palladium, the difference was slight. The same procedure is applicable in both cases; however, the platinum(II) reacts more slowly and its complex is more soluble so that under identical treatment, higher yields of the palladium(II) complex are obtained. The procedure is given for the palladium compound.

Preparation of Dichloro-(tetrahydrogen-ethylenediaminetetraacetate)-palladium(II) 5-Hydrate.—To a solution of 8.2 g. of ethylenediaminetetraacetic acid (0.028 mole) in 130 ml. of 0.45 *N* potassium hydroxide (0.058 mole) was added 5.0 g. of palladium(II) chloride (or 9.2 g. of K_2PdCl_4) (0.028 mole) and the mixture was heated and stirred for 30 minutes. During this time, the palladium(II) chloride dissolved. The solution was cooled and 10 ml. of concentrated hydrochloric acid was added, whereupon crystallization occurred.[4] The product was filtered, washed with a few milliliters of water and dried over calcium chloride. It crystallized in the form of bright, golden-brown octahedra. *Anal.* Calcd. for $[Pd(C_{10}H_{16}N_2O_8)Cl_2] \cdot 5H_2O$: C, 21.40; H, 4.64; N, 5.00; Cl, 12.68; Pd, 19.1. Found: C, 20.95; H, 4.64; N, 4.88; Cl, 12.67; Pd, 19.5. The corresponding platinum compound was isolated as a canary yellow microcrystalline solid. *Anal.* Calcd. for $[Pt(C_{10}H_{16}N_2O_8)Cl_2] \cdot 5H_2O$: C, 18.50; H, 4.02; N, 4.33; Cl, 10.95; Pt, 30.10. Found: C, 18.38; H, 4.21; N, 4.06; Cl, 11.00; Pt, 30.44.

The equivalent weight of the palladium compound was found to be 141.9 by *p*H titration; the theoretical value is 140. pK_{av} for four equivalents of strong acid, on the basis of the equivalent weight, is 2.40. The weight loss *in vacuo* at 44° corresponded closely to the five molecules of water reported in the analysis. Calcd. % wt. loss, 16.07; found 15.73. In view of the possibility that the chloride might be present as molecular hydrogen chloride of crystallization, chloride analysis was run on a sample after treatment *in vacuo*.

Anal. Calcd. for $[Pd(C_{10}H_{16}N_2O_8)Cl_2]$: Cl, 15.10. Found: Cl, 14.97. The equivalent weight was also estimated after dehydration. Calcd.: 117.5. Found: 121.3. Further attempts to remove the HCl *in vacuo* by raising the temperature resulted in no weight change until the complex decomposed at 125°.

Infrared Spectra of Complexes of Bidentate EDTA.—The infrared spectra of these complexes (Fig. 1) are consistent with the supposition that the four carboxyl groups are uncomplexed and that the EDTA is bound to the metal through the two nitrogens. Very strong split carbonyl bands are observed at 1707 and 1730 cm.$^{-1}$ for palladium and at 1715 and 1730 cm.$^{-1}$ for platinum. Other possible assignments are: resonance C=O stretching, 1420 cm.$^{-1}$ (Pd) and 1425 cm.$^{-1}$ (Pt); C–O stretching 1230 cm.$^{-1}$ (Pd) and 1230 cm.$^{-1}$ (Pt); O–H stretching (acid), 2540 cm.$^{-1}$ (Pd) and 2500 to 2700 cm.$^{-1}$ (Pt); O–H stretching (hydrate), 3450 cm.$^{-1}$ (Pd) and 3460 cm.$^{-1}$ (Pt).

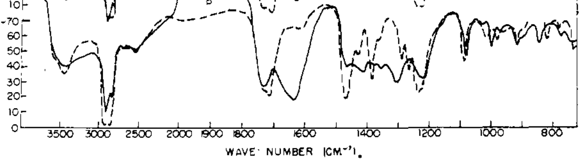

Fig. 1.—(A) $[Pd(C_{10}H_{14}N_2O_8)] \cdot 3H_2O$, —; $[Pd(C_{10}H_{16}N_2O_8)Cl_2] \cdot 5H_2O$, - - -; (B) $[Pt(C_{10}H_{14}N_2O_8)] \cdot 3H_2O$, —; $[Pt(C_{10}H_{16}N_2O_8)Cl_2] \cdot 5H_2O$, - - -.

Discussion

On the basis of these data, the structure shown in Fig. 2 is assigned to these compounds.

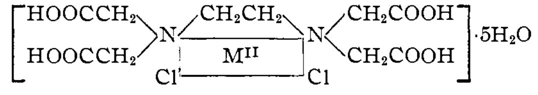

Fig. 2.

The ease with which the water of hydration is lost and the fact that dehydration does not disrupt the crystal structure of the complex indicates that the chloride, and not the water, is attached to the metal. The equivalent weight and pK_{av} indicate that there are four acidic groups of similar strength, leading to the conclusion that the protons are all associated with the carboxyl groups, and, consequently, that coördination of the metal is through the nitrogen atoms only. The fact that disodium dihydrogen ethylenediaminetetraacetate reacts with tetrachloroplatinate(II) or tetrachloropalladate(II) to form a tetradentate species is explained on the basis that the nitrogen atoms easily displace chloride from the coördination spheres of these metal ions but that carboxyl oxygen will displace chloride only with the aid of some additional driving force. This interpretation is consistent with the structure assigned to these compounds and with the actual conditions necessary for the preparation of complexes of these metal ions which contain tetradentate EDTA.

Experimental

Complexes of Tetradentate EDTA.—The platinum(II) and palladium(II) complexes of tetradentate EDTA (Fig. 3) are most conveniently prepared from the bidentate complexes. The reaction is carried out by neutralization of two of the carboxyl groups of the complexed EDTA and simultaneous removal of the chloride groups with silver ion. The products were isolated as the free acids and in the form of salts with optically active cations. The salts were fractionated in an attempt to obtain evidence for the presence of the predicted isomers. Fractionation of the free acid of the platinum(II) complex was also carried out in an attempt to isolate the two predicted geometrical isomers.

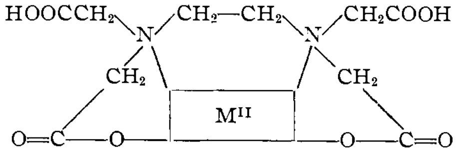

Fig. 3.

Preparation and Fractionation of Dihydrogen-ethylenediaminetetraacetatoplatinum(II) 3-Hydrate.—The complex was prepared in solution by homogeneous reactions yielding quantitatively insoluble by-products. The final product was isolated in a series of fractions. Twenty grams of $H_4M^{II}YCl_2 \cdot 5H_2O$ (0.0309 mole) was dissolved in 350 ml. of water heated just to the boiling point and mixed with a solution of 9.65 g. of silver sulfate (0.0309 mole) in 750 ml. of boiling water. When the silver chloride had coagulated, the solution was filtered and the precipitate was washed with several portions of water. Calcd. wt., of AgCl, 8.5 g.; found 8.5

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[4] In order to obtain an appreciable yield of the platinum complex it is necessary to concentrate the solution with an air stream. By such a process a yield of approximately 70% is realized.

TABLE I

Fraction	Weight, g.	Strychnine salt *α*	Strychnine salt $[\alpha]_D$	Sodium salt *α*	Sodium salt $[\alpha]_D$
1	1.05	−0.009 ± 0.003°	.....	0.000 ± 0.002°	.....
2	0.326	− .030 ± .002°	− 4.64°	+ .020 ± .001°	+ 7.90°
3	.112	− .011 ± .003°	− 5.14°	+ .018 ± .002°	+20.4°
4	.470	− .058 ± .003°	−12.4°	+ .019 ± .002°	+10.8°
5	.167	− .019 ± .003°	− 5.69°	.000 ± .003°	.....

g. A solution of 9.75 g. of barium hydroxide 8-hydrate (0.0309 mole) in 60 ml. of hot water was added to the filtrate. The mixture was allowed to stand for 3 hours before the precipitate was filtered and washed. Calcd. wt. of $BaSO_4$, 6.9 g.; found 6.8 g. Concentrating the filtrate in an air stream to 400 ml. produced a precipitate which contained small amounts of barium sulfate and silver chloride as well as a portion of the major reaction product. This portion of the product was obtained in two fractions by extraction with five 75-ml. portions of acetone and two 75-ml. portions of ethanol (fraction 1) and then by heating the remaining solid with 150 ml. of water. The respective solutions were then evaporated to obtain the pure complex. The original mother liquor was evaporated slowly by pulling a stream of filtered air over its surface. Fractions 3 through 5 were isolated at intervals of from 2 to 10 hours. When fraction 5 was isolated, approximately 50 ml. of solution remained. Further evaporation to 25 ml. failed to yield an additional fraction; however, upon the addition of 70 ml. of acetone, fraction 6 separated. The remaining solid was isolated by evaporation of the solvent. Attempts to dry this residue *in vacuo* resulted in decomposition as evidenced by a strong odor of formic acid over the solid. The total recovery was 15.9 g. of a theoretical 16.6 g. *Anal.* of fraction 4. Calcd. for $[Pt(C_{10}H_{14}N_2O_8)]\cdot 3H_2O$: C, 22.25; H, 3.71; N, 5.19; Pt, 36.17. Found: C, 22.14; H, 3.67; N, 4.98; Pt, 35.46. Most of the fractions were titrated potentiometrically with a Beckman line-operated *p*H meter using glass electrodes, to determine the equivalent weights. The values found varied between 269 and 276; the calculated value is 269.5. Approximate values for pK_{av} were determined from the titration curves, all of which give single breaks, at the half-equivalence points. The values found were 3.69, 3.64, 3.95, 3.62 and 3.63.

The general agreement, both of the equivalent weight and pK_{av} values, is interpreted as meaning that all of the samples contain two equivalents of acid per platinum atom and that the fractions probably all contain the same geometrical isomer of the complex acid. The pK_{av} value given for the third fraction is probably in error since it alone deviates from the pattern Its infrared spectrum is virtually identical with that o other fractions, lending support to this hypothesis.

Preparation of Dihydrogen-ethylenediaminetetraacetatopalladium(II).—Approximately 0.5 g. of freshly precipitated silver oxide was added to a solution of 1.0 g. of $H_4PdYCl_2\cdot 5H_2O$ in 100 ml. of water and the mixture was stirred for 3 hours at room temperature. After removal of the excess silver oxide and precipitated silver chloride, the product was obtained by evaporation of the solution. *Anal.* Calcd. for $[Pd(C_{10}H_{14}N_2O_8)]\cdot H_2O$: N, 6.75. Found: N, 6.85.

Preparation of the Strychnine Salt of the Palladium Complex.—Two and one-tenth grams of freshly precipitated silver oxide (0.009 mole) was ground with 5 g. of $H_4PdYCl_2\cdot 5H_2O$ (0.009 mole) until the dark mixture turned light yellow. A few milliliters of water were added and the mixture was triturated for 15 minutes. The silver chloride was removed by filtration and the filtrate was added to 3 g. of strychnine (0.009 mole) dissolved in 350 ml. of ethanol. The strychnine salt was obtained by evaporation of this solution.

Results of Fractionation of the Strychnine Salt.—Three and one-half grams of the strychnine salt was stirred with 200 ml. of water at room temperature for 8 hours, during which time a considerable amount of the salt dissolved. Long stirring with an additional 150 ml. of water resulted in no apparent change in the amount of remaining solid. The solid was removed and was dried over calcium chloride. The weight of fraction 1 was 1.05 g. Ignition of a weighed sample revealed that the substance was probably a distrychnine salt. *Anal.* Calcd. for $(C_{21}H_{22}N_2O_2)_2\cdot H_2[Pd(C_{10}H_{12}N_2O_8)]\cdot 4H_2O$: Pd, 9.41. Found: Pd, 9.38. The mother liquor was concentrated to 35 ml. without the appearance of a second fraction. However, the addition of 150 ml. of absolute ethanol to the concentrated solution yielded 0.326 g. of a solid (fraction 2). Fraction 3 (0.112 g.) was obtained by the further dilution with 100 ml. of absolute ethanol. Addition of 600 ml. of acetone was followed by the separation of fraction 4 (0.470 g.). Fraction 5 was then obtained by concentration to 20 ml. and standing *in vacuo* (0.167 g.). Attempts to isolate additional fractions were curtailed by the decomposition of the complex accompanied by deposition of metallic palladium. Fractions 2, 3, 4 and 5 were each dissolved in 50 ml. of water and their optical rotations were measured at the D-line of sodium. The strychnine was then removed by treatment with a 10% excess of 0.1 *N* sodium hydroxide and extraction with 30 ml. of chloroform. The extractions of all fractions and of the similar platinum complex were performed by shaking vigorously, allowing approximately 30 minutes for the separation of the layers, and then drawing off the heavier chloroform solution. The aqueous solution was poured through a fine sintered glass crucible before the rotations were measured to remove any tiny emulsified globules of chloroform. Because of its very slight solubility in water, fraction 1 was dissolved in the calculated amount of base and, after the determination of the rotation of its solution, it was treated in the same manner as the other fractions. The polarimetric data are summarized in Table I. Fractions 1 and 5 provide a control indicating the effectiveness of the method employed in the removal of the alkaloid.

Attempted resolution of the platinum(II) complex of tetradentate EDTA with strychnine, quinine and with *d*-tris-(ethylenediamine)-cobalt(III) ion gave only negative and ambiguous results and further studies will be carried out.

Infrared Spectra of the EDTA Complexes of Platinum(II) and Palladium(II).—Two strong carbonyl bands are observed in the spectrum (Fig. 1) of dihydrogen-ethylenediaminetetraacetatoplatinum(II) at 1730 and 1635 cm.$^{-1}$. The 1730 cm.$^{-1}$ band is attributed to the presence of carboxylic acid groups, while the band at 1635 cm.$^{-1}$ is associated with the complexed carboxyl groups. The similarity in the intensities of the bands is in agreement with the supposition that the two types of carboxyl group are present in equal numbers (two coördinated and two in the acidic form). These two bands are both manifestations of the C=O stretching vibration. Other possible assignments are: O–H stretching (carboxylic acid), 2600 cm.$^{-1}$; resonance C=O stretching (carboxylate), 1425 cm.$^{-1}$; resonance C=O stretching (carboxylic acid), 1408 cm.$^{-1}$; C–O stretching, 1220 cm.$^{-1}$; O–H bonding, 914 cm.$^{-1}$; O–H stretching (hydrate), 3460 cm.$^{-1}$. The spectrum of the palladium(II) compound (Fig. 1) is quite similar, and its interpretation is the same as that given for the platinum(II) compound. Assignments: complexed carboxylate, 1625 cm.$^{-1}$; carboxylic acid carbonyl stretching, 1740 cm.$^{-1}$.

Discussion

The failure of two geometrical forms to appear either in the resolution of the palladium complex or during the fractionation of the free acid $[Pt(H_2Y)]$ indicates that the *meso* form does not exist. It was suggested above that the *meso* form might be less stable than the racemate for steric reasons. It should also be pointed out that up to the present time, no evidence has appeared for the existence of *meso* complexes, whose structures depend on the configurations of donor atoms, in spite of determined efforts to isolate them. Bennett, Mosses and

Statham[5] investigated complexes of the types shown in Fig. 4.

They were unable to secure any evidence for the two predicted geometrical isomers. On the other hand, racemates containing coördinated sulfur[6] and coördinated nitrogen[7] as the centers of asymmetry have been proven to exist.

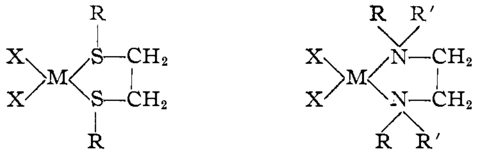

Fig. 4.—(M = Pt^{II} or Hg^{II}).

Certain conjectures about the relative coördinating power of tertiary nitrogen, chloride and carboxylate oxygen atoms toward palladium(II) and platinum(II) may be derived from the methods required for the preparation of the complexes of bidentate and tetradentate EDTA. The formation of two metal–nitrogen bonds in the initial reaction of EDTA with the anions $[MCl_4]^{=}$ implies that the strength of the metal–nitrogen bonds is comparable to that of the metal–chlorine bonds. The failure of the two free carboxylate groups to displace the remaining chloride groups, despite the increased stability expected from the formation of two additional chelate rings, is interpreted as meaning that chloride attaches itself more firmly to these metal ions than does oxygen. The introduction of an external driving force (removal of chloride with silver ion) allows the oxygen atoms to coördinate to the metal. This interpretation is in accord with the observations of others.[8]

Acknowledgment.—The authors wish to express their gratitude to the Bersworth Chemical Company whose financial support made this work possible.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE WATSON LABORATORY OF INTERNATIONAL BUSINESS MACHINES]

Preparation of Pure Potassium Metaniobate

BY ARNOLD REISMAN, FREDERIC HOLTZBERG, SOL TRIEBWASSER AND MELVIN BERKENBLIT

RECEIVED OCTOBER 7, 1955

Potassium metaniobate has been prepared in laboratory quantities by two procedures. The first method involves the fusion of potassium carbonate with niobium pentoxide and yields large polycrystalline aggregates exhibiting a slight degree of reduction. After leaching and grinding, a product of greater than 99.9% purity is obtained. Digesting the powder derived from the first process, in a flux of potassium carbonate, yields very finely crystallized, non-reduced, strain-free potassium metaniobate after water extraction. A rapid quantitative method for assaying the Nb_2O_5 content of potassium metaniobate has also been described

Introduction

Several compounds of the perovskite type are exceedingly interesting because of their ferroelectric properties. Potassium metaniobate was first characterized as a ferroelectric by Matthias, *et al.*,[1] who found a curie transition at 425° and a phase transformation at 215°. In order to complete a study of dielectric properties correlated with X-ray diffraction measurements it was felt desirable to obtain the pure material in a non-reduced strain-free state. Laboratory quantities of the *meta* salt were needed for crystal growing and the preparation of ceramics.

Starting with reagent grade Nb_2O_5 one would expect that the usual difficulties encountered in niobium analysis, could be circumvented, since one would not be faced with the problem of separating the compound from tantalum. It was expected, therefore, that a straightforward rapid analytical scheme could be devised to establish the purity of $KNbO_3$.

Joly[2] first reported the preparation of potassium metaniobate in 1877. The method was based on the fusion of stoichiometric quantities of K_2CO_3 and Nb_2O_5 with an unspecified amount of CaF_2 as a flux. All attempts to reproduce his experiments in this Laboratory have proved unsuccessful. More recently Matthias,[3] Vousden[4] and others[5,6] have prepared $KNbO_3$ by fusion of either KOH or K_2CO_3 with Nb_2O_5, in the absence of a flux. These procedures were successful in producing a few small crystals for X-ray studies and dielectric measurements, but were not readily adaptable to the preparation of laboratory quantities of the pure niobate, because the range of compositions and the methods of purification were not clearly defined.

A recent phase equilibrium study[7] of the system K_2CO_3–Nb_2O_5 indicates that $KNbO_3$ (I) can be contaminated by $2K_2O{\cdot}3Nb_2O_5$ (II) or $3K_2O{\cdot}Nb_2O_5$ (III), depending on the mole ratios of the original reactants. Separation of I from II could not be effected because of their similar solubilities. Fusion of stoichiometric quantities of K_2CO_3 with Nb_2O_5 often showed the presence of II in the reaction mixtures. It is evident from the phase diagram that any volatilization of K_2CO_3 or K_2O during the reaction would result in the appearance of II.

Uncertainty exists concerning the state in which

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