constants of phosphorus and fluorine atoms, which is due to the presence of low-lying excited states in the metal–phosphorus bond, is increased on complexation. This contribution is larger in the case of molybdenum complexes than in nickel complexes.

(2) The data may best be interpreted as providing evidence in support of the view that there is an appreciable amount of d_π–d_π bonding between the phosphorus atom and the metal atom. The extent of d_π–d_π bonding appears to be larger in the case of the nickel complexes than in molybdenum complexes.

(3) The hybridization and bond angles of the ligand change (phosphorus orbitals possess less s character) on complexation. These changes are presumably more pronounced for chlorophosphine ligands than for the corresponding fluorophosphine ligands.

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Notes

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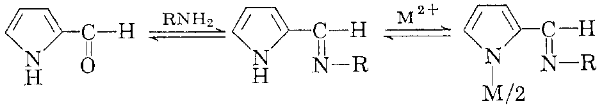
Synthesis and Properties of Some Metal Chelates of 2-Pyrrolealdimines[1]

By Kwan-nan Yeh and Robert H. Barker

Received October 8, 1966

Because of their high degree of stability and their prominence in areas of biological interest, the metal chelate complexes of condensed pyrrole ring systems have been quite thoroughly studied and characterized.[2] Metal derivatives of the dipyrromethenes, the phthalocyanines, and the complex porphyrins have been known for almost 50 years. It is thus somewhat surprising that only a few complexes have been reported in which the ligand contains a single pyrrole ring. The use of pyridylpyrrole as a ligand for nickel(II), aluminum(III), and cadmium(II) was reported by Emmert in 1929.[3] Pyrrole-2-carboxaldehyde (I) and its methylimine (IIb) were also used. Organopalladous compounds of pyrrole and indole have been claimed as products from the interaction of the heterocycle with palladium(II) chloride in aqueous solution, but this has been questioned recently.[4] The X-ray structure of bis(2-pyrrolealdmethylimino)copper(II) (IIIb, M = Cu) has been determined and the compound was found to be bimolecular, *trans*, and probably planar.[5]

The previously described procedures for the synthesis of the complexes of both the aldehyde and its methylimine with copper(II) involved heating the ligand together with the metal oxide at reflux in a high-boiling solvent such as xylene or anisole.[3] Since the methylimine was known to be quite unstable toward heat, light, and moisture and since there was no reason to expect the higher homologous imines to be any more stable, such high-temperature methods did not seem to offer the best routes to the desired chelates. The work described herein provides more widely applicable synthetic routes to the pyrrolealdimines and their copper(II), mercury(II), and palladium(II) complexes.



I

IIa, R = H
b, R = CH_3
c, R = CH_2CH_3
d, R = $CH(CH_3)_2$
e, R = $C(CH_3)_3$
f, R = C_6H_5

IIIa, R = H
b, R = CH_3
c, R = CH_2CH_3
d, R = $CH(CH_3)_2$
e, R = $C(CH_3)_3$
f, R = C_6H_5

The free methyl-, ethyl-, and phenylpyrrolealdimines were prepared by a modification of the procedure used by Emmert and co-workers for the methyl compound.[3] The instability of these materials precluded the usual characterization by elemental analysis but their infrared and nuclear magnetic resonance spectra were in complete agreement with the proposed structures. This instability is apparently greater for those imines having larger N-alkyl groups and all attempts to isolate the analogous N-isopropyl- and N-*t*-butylimines, IId and IIe, were unsuccessful. That this was due to unfavorable equilibria in the additions and not failure of the amines to add to the pyrrolealdehyde was shown by the fact that treatment of the crude amine–aldehyde reaction mixture with copper(II) produced the corresponding pyrrolealdimine chelates. Similar procedures were used for the synthesis of the mercury(II) and palladium(II) complexes of the isopropyl and *t*-butyl imine ligands. The N-methyl and N-ethyl complexes of mercury(II) and palladium(II) were best prepared from the purified ligands. The much more stable N-phenyl ligand, IIf, was also isolated and purified before complexation. The resulting chelates were characterized by elemental analysis, melting point, infrared spectra, and, when possible, nuclear magnetic resonance spectra.

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(1) Taken from a thesis submitted by Kwan-nan Yeh to the Graduate School of Tulane University in partial fulfillment of the requirements for the M.S. degree.

(2) See, for example, A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(3) B. Emmert, K. Diehl, and F. Gollwitzer, *Ber.*, **62**, 1733 (1929).

(4) F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955).

(5) M. V. Stackelberg, *Z. Anorg. Chem.*, **253**, 136 (1947).

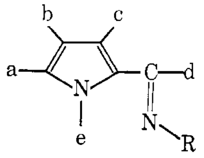
Attempts to isolate either the free imine IIa or its copper chelate were unsuccessful. Treatment of a cupric acetate solution with pyrrolealdehyde and ammonia did produce a dark crystalline copper complex similar to the other pyrrolealdimine chelates IIIb, c, d, e, and f, but this was apparently a complex of some polymerized form of IIa. Imines of this type are known to polymerize and that this was the case here was indicated by the lack of any band attributable to an N–H moiety in the infrared spectrum of the complex and the low H content found on elemental analysis. Also, it was noted that this material decomposed rather than melting and was quite insoluble in common solvents.

Although the structures of the complexes were not rigorously established, it seemed most likely that the copper(II) compounds in which the N-alkyl group was methyl, ethyl, or isopropyl were all in a simple *trans*, square-planar configuration. However, this was not necessarily the case when the N-alkyl group was *t*-butyl. Examination of the melting points of the N-alkyl chelates showed a progressive decrease in melting point as the bulk of the alkyl group increased. The *t*-butyl compound was anomalous in that its melting point was more than 30° higher than that of the isopropyl analog which could be indicative of a configuration less symmetrical than *trans* square-planar. The same general trends were noted in the decomposition temperatures in the palladium(II) series. The *t*-butyl compound in this series was quite unstable and could not be isolated in a form sufficiently pure for characterization.

The infrared and nmr spectra of those complexes which were sufficiently soluble in appropriate solvents showed nothing incompatible with the structures postulated. The chemical shift values are tabulated in Tables I and II. Since the solubilities of all four of the N-alkyl chelates in the mercury(II) series were high enough to permit measurement of their spectra, these data are of particular interest. All of the protons are shifted to lower field relative to those in the free ligands and the magnitudes of the shifts for the different protons are surprisingly similar. One might expect that the complexed ligands would be more anionic in character than in the free state. However, this would increase the electron density of the ring and thus should cause an increase rather than a decrease in shielding. Alternatively, increased anionic character could increase the magnitude of the ring current in the pyrrole nucleus thus deshielding the ring hydrogens by the increased anisotropy. However, on this basis, it would be difficult to explain the large effect on H_d. It would seem more plausible to invoke an explanation based on a continuous π system about the entire periphery of the ligand and perhaps even involving two electrons from one of the metal d orbitals. This would produce a closed π cycle containing ten electrons and thus impart some extra aromatic character to the compound.

TABLE I

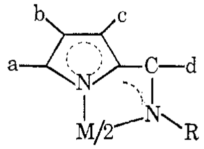
NMR CHEMICAL SHIFTS OF THE IMINES (τ)



						R	
Compd	a	b	c	d	e	CH_3	CH_2
R = CH_3	3.54	3.80	3.17	2.00	−1.20	6.59	
	3.56	3.85				6.61	
	3.60	3.86					
	3.63	3.91					
R = CH_2CH_3	3.45	3.72	3.16	1.91	−1.19	8.67	6.24
	3.48	3.77				8.80	6.37
	3.52	3.82				8.92	6.48
	3.54						6.59

TABLE II

NMR CHEMICAL SHIFTS OF THE CHELATES (τ)



						R	
Compd	a	b	c	d	CH_3	CH_2	CH
		M = Hg					
R = CH_3	3.23	3.48	3.07	1.73	6.68		
	3.29	3.54			6.70		
R = CH_2CH_3	3.20	3.46	3.00	1.67	8.79	6.24	
	3.23	3.50			8.92	6.37	
					9.04	6.49	
						6.62	
R = $CH(CH_3)_2$	3.18	3.45	3.00	1.68	8.92		6.18
					9.03		6.28
							6.38
R = $C(CH_3)_3$	3.15	3.45	3.00	1.62	8.89		
	3.24	3.49					
		M = Pd					
R = $CH(CH_3)_2$	3.20	3.70	2.94	2.43	8.50		5.66
	3.27	3.74			8.62		5.78
	3.77						5.90
	3.80						
R = $C(CH_3)_3$	3.61	4.01	3.06	2.43	8.56		
	3.63	4.03	3.08		8.66		
	3.68	4.08	3.10		8.76		
	3.70	4.10	3.12		8.86		
	3.73	4.16					
	3.77						
	3.80						

In view of the relative ease with which the copper(II), mercury(II), and palladium(II) complexes formed with these aldimines, it was somewhat surprising to find that the analogous platinum(II) chelates did not form under similar conditions. Instead, when treated with the previously purified ligands, platinum(II) seemed to have very little affinity for chelate formation and reacted preferentially with the small amount of free amine present in equilibrium with the imine. The elemental analyses of the four complexes obtained from attempts to prepare the platinum(II) chelates indicated in each case an empirical formula of $[(RNH_2)_2PtCl_2]_n$. In the N-methyl and N-ethyl series, identical products were obtained from treatment of the potassium tetrachloroplatinite with either the aldimines or the free amines in the absence of any pyrrolealdehyde. The solubilities and colors of these products were very similar to those reported by Yamada and Tsuchida[6] for the Magnus green salt complexes $[(RNH_2)_4Pt][PtCl_4]$ known to be produced by the interaction of alkyl amines and potassium tetrachloroplatinite. It is not clear why this type of complex formation should be preferred over chelate formation.

Experimental Section[7]

Pyrrolealdmethylimine (IIb).—The crude product was prepared and precipitated according to the procedure of Emmert, *et al.*[3] The precipitate and mother liquor were then extracted with two 25-ml portions of chloroform and the separated organic layer was dried over calcium chloride. Heptane (20 ml) was added to the chloroform solution and the resulting solution was concentrated under vacuum at room temperature to a volume of *ca.* 15 ml. Storage in a refrigerator overnight yielded 0.43 g (44%) of the pure methylimine as long white needles, mp 56–58° (lit.[3] 57°). The infrared spectrum (KBr disk) showed methyl stretching frequencies at 2890 and 2879 cm^{-1} and N–H stretching at 3460 cm^{-1}. The N–H frequency of the parent 2-pyrrolealdehyde is reported at 3458 cm^{-1}.[8] The instability of this imine precluded satisfactory elemental analysis.

Pyrrolealdethylimine (IIc).—The procedure was the same as for IIb except that 70% aqueous ethylamine was used as the amine source. This produced 0.44 g (40%) of the ethylimine as pale yellow needles, mp 46°. The infrared spectrum showed C–H frequencies at 2940, 2895, and 2860 cm^{-1} attributable to the ethyl group and an N–H mode at 3460 cm^{-1}. The compound was too unstable for satisfactory elemental analysis.

Pyrrolealdphenylimine (IIf).—A 0.50-g sample (5 mmoles) of the 2-pyrrolealdehyde and 0.5 ml (*ca.* 5 mmoles) of aniline were dissolved in 5 ml of benzene and the resulting solution was stored in an open flask at room temperature until the benzene had evaporated. After recrystallization from heptane, 0.81 g (95%) of the phenylimine was obtained as white needles, mp 92°. The infrared spectrum showed strong aromatic absorption at 693 cm^{-1} and N–H stretching at 3460 cm^{-1}. The instability of the product precluded satisfactory elemental analysis.

Bis(pyrrolealdimino)copper(II) (IIIa, M = Cu).—To 25 ml of concentrated aqueous ammonia was added 0.95 (10 mmoles) of 2-pyrrolealdehyde, and the solution was stirred at 45–50° until a yellow color appeared. A solution containing 1.45 g (8 mmoles) of cupric acetate in 50 ml of ethanol was then added and stirring was continued for 2 hr. The precipitate which formed was washed with 20 ml of 95% ethanol and dried under vacuum to yield 0.28 g (23%) of fine black crystals, dec pt 140°.

Bis(pyrrolealdmethylimino)copper(II) (IIIb, M = Cu).—The procedure was the same as for IIIa except that 40% aqueous methylimine was used in place of the concentrated ammonia. Recrystallization from heptane produced 0.84 g (60% yield) of black cubic crystals, mp 162–164° (lit.[3] 163°).

Bis(pyrrolealdethylimino)copper(II) (IIIc, M = Cu).—The procedure was the same as for IIIa and IIIb except for the use of 70% aqueous ethylamine. After recrystallization, 0.94 g (62%) of fine black crystals was obtained, mp 127°.

Bis(pyrrolealdisopropylimino)copper(II) (IIId, M = Cu).—To 10 ml of neat isopropylamine was added 0.48 g (5 mmoles) of 2-pyrrolealdehyde and the resulting solution was warmed at 50° with constant stirring until the yellow color appeared. A solution containing 0.75 g (4 mmoles) of cupric acetate in 50 ml of ethanol was then added and heating and stirring were continued for 1 hr. Crystallization was completed by storage in a refrigerator overnight. After washing with ethanol and recrystallization from heptane, 0.45 g (55%) of fine black crystals was obtained, mp 118–119°.

TABLE III

ANALYTICAL DATA FOR PYRROLEALDIMINE CHELATES

Compd	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N	Mp, °C
IIIa, M = Cu	48.08	4.47	22.21	48.16	4.01	22.24	140 dec
IIIb, M = Cu	51.89	5.04	20.18	51.82	4.96	20.38	163–164
IIIc, M = Cu	54.99	5.89	18.33	54.78	6.00	18.26	127
IIId, M = Cu	57.57	6.59	16.79	57.54	6.80	16.94	118–119
IIIe, M = Cu	59.75	7.19	15.49	59.81	7.11	15.58	153
IIIf, M = Cu	65.74	4.48	13.92	65.90	4.62	13.87	181
IIIb, M = Hg	34.73	3.37	13.50	34.83	3.47	13.39	152–154
IIIc, M = Hg	37.96	4.07	12.65	37.97	4.25	12.60	135–136
IIId, M = Hg	40.79	4.67	11.89	40.95	4.99	11.85	133
IIIe, M = Hg	43.22	5.21	11.23	43.11	5.03	11.13	147–148
IIIf, M = Hg	49.00	3.34	10.39	48.87	3.51	10.24	182
IIIb, M = Pd	45.00	4.38	17.50	44.94	4.49	17.61	260 dec
IIIc, M = Pd	48.26	5.17	16.10	48.36	5.16	16.20	241 dec
IIId, M = Pd	51.07	5.85	14.90	50.86	5.68	14.88	215 dec
IIIf, M = Pd	59.50	4.06	12.61	58.17	4.06	12.77	280 dec

Bis(pyrroleald-*t*-butylimino)copper(II) (IIIe, M = Cu).—The procedure was the same as that for IIId above except for the use of *t*-butylamine as the solvent. The product was isolated in 33% yield as black crystals, mp 153°.

Bis(pyrrolealdphenylimino)copper(II) (IIIf, M = Cu).—A 1.70-g (10-mmole) sample of the pyrrolealdphenylimine was dissolved in 95% ethanol and 20 ml of an aqueous solution containing 1.20 g (7 mmoles) of cupric acetate was added dropwise with stirring. After stirring 1 hr at room temperature, the black precipitate was collected, washed with ethanol, dried *in vacuo*, and recrystallized from heptane to yield 1.60 g (80%) of fine black crystals, mp 181°.

Bis(pyrrolealdmethylimino)mercury(II) (IIIb, M = Hg).—A solution containing 0.98 g (10 mmoles) of the pyrrolealdmethylimine in 100 ml of benzene was mixed with a large excess of mercury(II) oxide and stirred for 1 hr at 50°. Filtration to remove the excess oxide gave a brown filtrate which yielded light yellow crystals upon slow evaporation under vacuum. Recrystallization from heptane produced 1.51 g (73%) of white needles, mp 152–154°.

Bis(pyrrolealdethylimino)mercury(II) (IIIc, M = Hg).—The procedure was the same as that for IIIb except that pyrrolealdethylimine was used. An 80% yield of white needles was obtained, mp 135–136°.

Bis(pyrrolealdisopropylimino)mercury(II) (IIId, M = Hg).—The parent 2-pyrrolealdehyde (0.95 g, 10 mmoles) was dissolved in 15 ml of isopropylamine and the solution stirred at 50° for 30 min. The reaction mixture was diluted with 100 ml of benzene, and a large excess of mercury(II) oxide was added. After stirring for 1 hr, the solution was filtered, dried over calcium chloride, and evaporated slowly under vacuum to produce dark brown crystals. Recrystallization from heptane produced 1.45 g (50%) of brown crystals, mp 133°.

Bis(pyrroleald-*t*-butylimino)mercury(II) (IIIe, M = Hg).—The procedure was the same as that used for IIId above except that *t*-butylamine was used as solvent. A 58% yield of pale pink crystals was obtained, mp 147–148°.

Bis(pyrrolealdphenylimino)mercury(II) (IIIf, M = Hg).—The procedure was the same as that used for the methyl compound IIIb, M = Hg above. A yield of 55% was obtained, mp 182°.

Bis(pyrrolealdmethylimino)palladium(II) (IIIb, M = Pd).—To a solution of 1.12 g (10 mmoles) of pyrrolealdmethylimine in 30 ml of ethanol was added 150 ml of an aqueous solution containing 0.90 g (5 mmoles) of palladium(II) chloride. After stirring for 4 hr at room temperature, the yellow-green precipitate was collected, washed with water and ethanol, dried at 80°, and recrystallized from chloroform. This produced 0.46 g (28%) of fine yellow crystals, dec pt 260°.

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[6] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 813 (1958).

[7] All melting points are uncorrected and were measured on a Thomas-Hoover melting point apparatus. Nmr spectra were obtained on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were obtained on a Beckman Model IR-8 spectrophotometer. Analytical data are presented in Table III.

[8] P. Mirone, A. M. Drusiani, and V. Lorenzelli, *Ann. Chim.* (Rome), **51**, 7149 (1957).

Bis(pyrrolealdethylimino)palladium(II) (IIIc, M = Pd).—The procedure was the same as that used for the methyl compound above except that pyrrolelaldethylimine was used. Recrystallization from chloroform gave 0.40 g (46%) of yellow needles, dec pt 241°.

Bis(pyrrolealdisopropylimino)palladium(II) (IIId, M = Pd).—The pyrrolealdehyde (0.49 g, 5 mmoles) was dissolved in 10 ml of neat isopropylamine with stirring until a clear yellow solution was obtained. A solution of 0.45 g (2.5 mmoles) of palladium(II) chloride in 80 ml of water was added and stirring was continued for an additional 6 hr. After collection of the yellow-green precipitate, drying at 80°, and recrystallization from chloroform, 0.80 g (82% yield) of yellow needles was obtained, dec pt 215°.

Bis(pyrroleald-*t*-butylimino)palladium(II) (IIIe, M = Pd).—The same procedure was used as for the isopropyl compound above except that the isopropylamine was replaced by *t*-butylamine. The resulting fine yellow crystals were obtained in 65% yield, mp 170°. Unlike the other palladium(II) complexes in this series, this product was highly soluble in chloroform and could never be obtained in a state of purity sufficient for satisfactory elemental analysis. Its nmr spectrum showed two different kinds of methyl groups present.

Bis(pyrrolealdphenylimino)palladium(II) (IIIf, M = Pd).—The procedure was the same as used for the methyl and ethyl compounds in this series. The product exhibited very limited solubility in common organic solvents and was recrystallized from hot chloroform only with great difficulty to yield 0.20 g (20%) of yellow-green needles, dec pt 280°.

Interaction of Platinum(II) with Pyrrolealdimines.—A 0.24-g (2.4-mmole) portion of pyrrolealdmethylimine was dissolved in 20 ml of *n*-propyl alcohol and 15 ml of a solution containing 0.50 g (1.2 mmoles) of K_2PtCl_4 (prepared according to the method of Keller[9]) added dropwise with stirring. After 3 hr of stirring at room temperature, the light blue crystals were collected, washed with water and ethanol, dried at 80°, and washed again with boiling chloroform. This produced 0.27 g of solid which was insoluble in common organic solvents but very slightly soluble in hot water, dec pt 205°.

Anal. Calcd for $C_6H_{14}N_4Pt$: C, 35.20; H, 3.44; N, 13.70. Calcd for $C_4H_{20}N_4Cl_4Pt_2$: C, 7.00; H, 2.90; N, 7.80. Found: C, 7.29; H, 3.03; N, 8.53. With pyrrolealdethylimine 0.28 g of light pink crystals was obtained, dec pt 190°.

Anal. Calcd for $C_{14}H_{18}N_4Pt$: C, 38.04; H, 4.14; N, 12.81. Calcd for $C_8H_{28}N_4ClPt_2$: C, 13.58; H, 3.92; N, 7.82. Found: C, 13.48; H, 3.93; N, 7.87.

Interaction of Platinum(II) with Amines in the Presence of Pyrrolealdehyde.—A 0.23-g (2.4-mmole) portion of pyrrolealdehyde was dissolved in 10 ml of isopropylamine and stirred constantly at 50° until the solution turned yellow. An aqueous solution containing 0.50 g (1.2 mmoles) of K_2PtCl_4 in 15 ml was added with stirring, and stirring was continued for 3 hr. After collection, washing with water and ethanol, drying at 80°, and washing again with boiling chloroform, 0.35 g of light gray crystals was obtained, dec pt 225°.

Anal. Calcd for $C_{16}H_{22}N_4Pt$: C, 41.27; H, 4.77; N, 12.04. Calcd for $C_{12}H_{36}N_4Pt_2Cl_4$: C, 19.14; H, 4.84; N, 7.28. Found: C, 18.75; H, 4.84; N, 7.28.

Use of *t*-butylamine produced 0.30 g of light green crystals, dec pt 260°.

Anal. Calcd for $C_{18}H_{26}N_4Pt$: C, 43.78; H, 5.32; N, 11.34. Calcd for $C_{16}H_{44}N_4Cl_4Pt_2$: C, 23.50; H, 5.39; N, 6.78. Found: C, 23.31; H, 5.32; N, 6.79.

Use of methylamine or ethylamine produced compounds which were identical in solubilities, decomposition points, and infrared spectra with those obtained previously from the pyrrolealdimines. The infrared spectra of all of the platinum(II) complexes exhibited one or more absorption bands in the 3100–3350-cm^{-1} region. All were insoluble in common organic solvents but slightly soluble in hot water.

Acknowledgment.—The authors are grateful to Mr. G. J. Boudreaux of the Southern Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, for the nmr spectra and to the American Cancer Society for partial support of this work.

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[9] R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

CONTRIBUTION FROM THE NUCLEAR TECHNOLOGY DEPARTMENT,
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Tentative Phase Diagram of Beryllia–Lithia System

BY P. P. TURNER AND S. F. BARTRAM

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In connection with some work done on materials for storing solar thermal energy, BeO was considered because it has the highest heat of fusion and thermal conductivity of the low-atomic-weight oxides. Other low-atomic-weight oxides of interest are Al_2O_3, CaO, Li_2O, and MgO. A search of the literature yielded information on the binary systems BeO–Al_2O_3, BeO–CaO, and BeO–MgO. Nothing was found on the BeO–Li_2O system nor on ternaries or quaternaries containing these two oxides; therefore, an examination of the high BeO side of the binary system was undertaken.

Melting point, total heat content, chemical analysis, and X-ray diffraction data were believed to be sufficient for an initial evaluation of this system. This note is, therefore, confined to these results and the tentative phase diagram derived from them.

Experimental Section

Specimen Preparation and Testing.—The raw materials used in this work were Brush Beryllium Co. UOX-grade BeO (800 to 1500 ppm total impurities) and analytical reagent grade Li_2CO_3 (Mallinckrodt Chemical Co.). Various proportions of these materials were mixed for 15 min in a Mix-R-Mill (Spex Industries) and then heated in argon in a tungsten resistance furnace in a platinum or rhenium crucible to the fusion point shown. A rhenium crucible was used for compositions fusing at temperatures above the melting point of platinum. All samples were furnace-cooled in approximately 2.5 hr. Melting temperatures were measured optically. Although the true heat of fusion was not measured, the amount of heat required to achieve complete melting from ambient was determined by the drop calorimeter technique.

Chemical Analysis.—Reaction products were leached in a hot 1:4 HNO_3 solution to dissolve any unreacted Li_2CO_3 and rhenium metal contamination resulting from reaction with the crucible. The compositions shown in Figure 1 were determined by wet chemical analysis of the leached residues. After dissolution in H_2SO_4–HNO_3, beryllium was precipitated with NH_4OH as Be(OH)$_2$. The hydroxide was filtered off and converted to BeO by ignition at 1000°. Lithium was recovered from the filtrate by addition of H_2SO_4 and evaporation to dryness. The Li_2O content was obtained by igniting the sulfate at about 500° and weighing as Li_2SO_4.

X-Ray Methods.—Powder diffraction photographs of the