243. The Identity of the gamma Modification of Basic Lead Azide Type I

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Summary. Published information on the basic lead azide series is discussed with particular reference to the gamma modification of basic lead azide I. A sample of this product has been prepared and the absence of significant impurity confirmed by *X*-ray diffraction analysis. Infrared absorption analysis has indicated the presence of Pb–O bonding and the absence of H–O bonding. The product is therefore an oxyazide containing neither hydroxide nor water of crystallisation. Chemical analysis confirms that the $Pb(N_3)_2$:PbO ratio is less than one.

Feitknecht & Sahli [1] [2] have carried out a survey of the various basic lead azides prepared by the following four methods: (a) reaction of water with a suspension of lead azide; (b) reaction of aqueous sodium hydroxide with a suspension of lead azide; (c) reaction between aqueous suspensions of 'lead hydroxide' [3] and lead azide; (d) reaction between aqueous lead nitrate and an aqueous mixture of sodium azide and sodium hydroxide.

Products were analysed by *X*-ray diffraction, and in particular fifteen preparations believed to be fairly pure were analysed chemically for lead and azide nitrogen. Results are shown plotted in Figure 1.

From the grouping of these results, five basic lead azide types were postulated and assigned values for x and y in a general formulation $x\,Pb\,(N_3)_2 \cdot yPbO \cdot z\,H_2O$. The five types with their suggested digital values of x and y are shown in the Table.

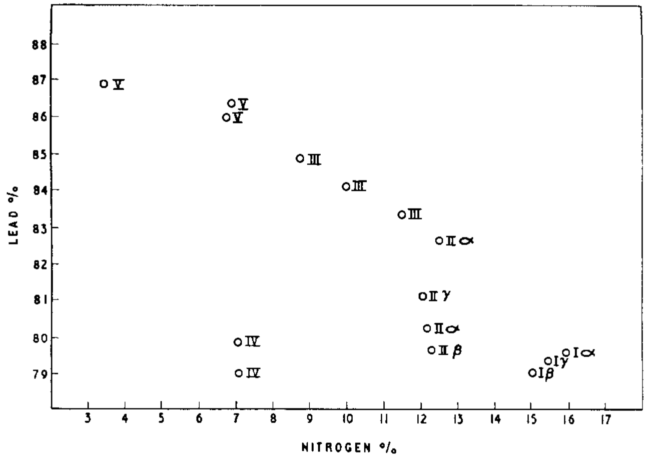

Fig. 1. *Analytical figures for the suggested basic lead azide types*

The values for z were obtained by difference; their uncertainty results from a combination of analytical error, impurity content, and water content where the

Basic lead azides, $xPb(N_3)_2 \cdot yPbO \cdot zH_2O$

Type	I	II	III	IV	V
x	1	3	1	2	1
y	1	5	2–3	7	4–9
z	0.4–0.8	1.2–5.0	0.3–0.8	3.6–4.5	1.0–5.0

water could exist as water of crystallisation or combined with oxygen as hydroxyl ions.

X-ray diffraction analysis showed that types I and II each existed as three crystalline modifications (α, β and γ) whereas III, IV, and V existed as one modification only. A superficial examination of the published diffraction patterns [1] suggests that those of Iβ, Iγ, IIα, and IIβ are similar in major detail.

In the course of a study of the thermal decomposition of the alpha modification of normal lead azide in air *Todd* [4] noted that the initial decomposition product gave diffraction data similar to those of types Iβ/Iγ/IIα/IIβ. In view of the elevated temperature of decomposition (250 °C) an oxyazide was suggested. More recent work on the hydrolysis of α-lead azide by moist air at 60 °C [5] has again indicated formation of this crystal modification, and since this product is almost certainly the same as the hydrolysis product previously obtained by *Feitknecht* & *Sahli* [2] it is proposed to call this important recurring modification Iγ in deference to the earlier nomenclature.

Todd & *Parry* [6] have reported upon the *X*-ray analysis of a number of attempted preparations of Iγ carried out by variants of method (d). Several of these preparations were found to be contaminated with α-lead azide, basic lead carbonate, and an unidentified compound but the product giving the simplest *X*-ray pattern was analysed chemically and found to contain 80.2% lead and 15.5% azide nitrogen. *X*-ray data for this product were quoted.

A second preparation of this type has now been carried out and chemically analysed as containing 80.3% lead and 15.6% azide nitrogen. This second preparation has further been subjected to infrared analysis and its absorption spectrum compared with those of 'lead hydroxide' and basic lead carbonate as shown in Fig. 2.

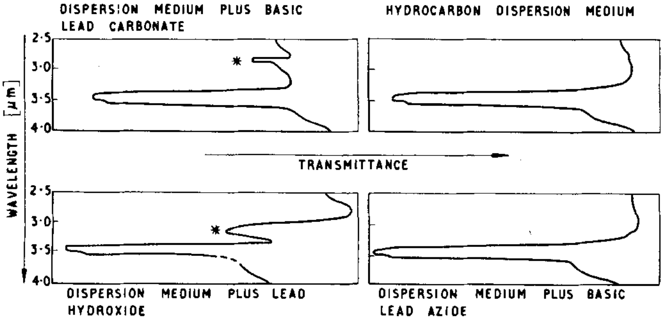

Fig. 2. *Infrared absorption spectra for γ-basic lead azide I, lead hydroxide, and basic lead carbonate*
Absorption due to hydroxyl is marked with an asterisk. The strong absorption common to all is due to the hydrocarbon dispersion medium.

It was noted that γ-basic lead azide I yielded absorption features for the azide grouping and for lead-oxygen bonding only. There was no evidence whatsoever for absorption due to the hydrogen-oxygen bond so that complete absence of hydroxyl ion and water of crystallisation must be concluded.

The results of this work indicate that γ-basic lead azide I is an oxyazide which does not conform to the formulation $Pb(N_3)_2 \cdot PbO$. Such a formula should yield analytical figures for lead and nitrogen of 80.6% and 16.3% and although the lower analytical figures for our two preparations could indicate an impure product, a complex of approximate formula $Pb(N_3)_{0.96}\,O_{0.66}$ is considered likely.

Results to date indicate that in any assessment of the purity of a γ-basic lead azide I sample by chemical methods, the lead and azide figures should be at least 80.3% and 15.6%, respectively. Frequent impurities are basic lead carbonate and normal lead azide. It is worth noting that the presence of basic carbonate will lower the azide figure without affecting the lead figure substantially whereas the presence of normal azide will lower the lead figure and raise the azide figure. The return of an acceptable azide figure but a low lead figure may indicate the presence of both basic lead carbonate and normal lead azide as impurity.

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244. Infrared Spectra of α-Thenoyl-trifluoroacetonates of Metal Ions of the First Transition Series

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Summary. The IR. spectra of α-thenoyl-trifluoroacetone (HTTA) and seventeen of its chelates with metal(II) and -(III) ions of the first transition series have been determined. Three series of complexes are represented: the anhydrous metal(II) species, $[M(TTA)_2]_n$ (M = Ca, Mn, Co, Ni, Cu, Zn); metal(II) dihydrates, $[M(TTA)_2(H_2O)_2]$ (M = Mn, Fe, Co, Ni, Zn); and the metal-(III) chelates, $[M(TTA)_3]$ (M = Sc, V, Cr, Mn, Fe, Ga). For each metal(II) complex, the spectra of the anhydrous and hydrated compounds are practically identical, suggesting that the anhydrous complexes have the polynuclear octahedral structure established for the corresponding acetylacetonates. Magnetic moment determinations reveal that complexes of the $3d^4$–$3d^7$ ions all have

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[1]) On leave during 1971 for study at the Laboratorium für anorganische Chemie, Eidg. Technische Hochschule Zürich.