Ultraviolet Absorption Spectra of Lead Aldose-cysteinate[*]

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When the present authors studied metal complexes of HGC[**], lead glucose-cysteinates in solution were found to form a gel like agar-agar and to have an ultraviolet absorption maximum at 270 mμ[1]. The other HSCs[**] with lead acetate in solution also show the same absorption spectra as HGC. These absorption spectra have not been known thus far. Moreover, no absorption spectrum of lead cysteinate has been reported.

In the study of the mechanism of gelation, one of the most important projects is to clarify the structure of lead aldose-cysteinate in solution.

In this paper, the results of spectrophotometric study related to the structure of lead aldose-cysteinates are described.

Experimental

HSCs were prepared in the same manner as was described in the previous paper[1]. Cysteine was prepared by the addition of pyridine to cysteine hydrochloride (monohydrate) in hot ethanol, filtration, and washing with ethanol until the pyridine odor had vanished; d. p., 218°C. The cysteine methyl ester was prepared by the electrolytic reduction of the cystine dimethyl ester which had been obtained by the usual method. Thiazolidine carboxylic acid-4 was prepared by the treatment of cysteine hydrochloride in an aqueous solution with formalin.

The spectrophotometric measurements were carried out in an aqueous solution with a Hitachi spectrophotometer, model EPU-2.

The pH value of the solution was adjusted by the addition of an appropriate amount of nitric acid or sodium hydroxide.

Results and Discussion

The absorption spectra in the solution containing different HSCs and lead acetate, and HGC and different metal salts are shown in Figs. 1 and 2 respectively. Only the lead complex of HSC in solution shows an absorption maximum at 270 mμ. Neither HSCs nor metal salts in solution show an absorption in the range between 250 and 600 mμ.

The lead complexes of different amino acids, except cysteine, show no absorption in the range between 250 and 300 mμ (Fig. 3). On the other hand, the lead complexes of various thiol-containing compounds have an absorption maximum at about 270 mμ (Fig. 4). From

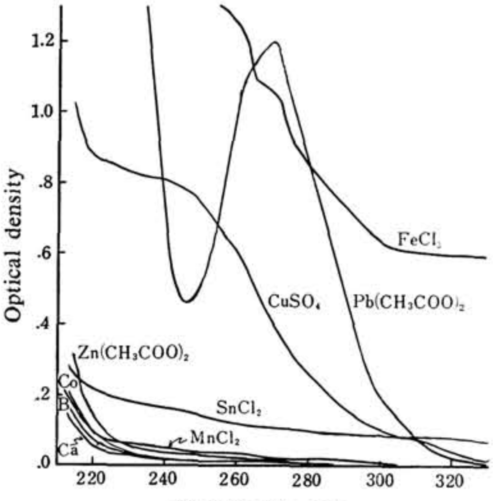

Fig. 1. HGC-various metal salts
0.5 mM HGC, 0.5 mM metal salt.
B: Only HGC (metal free)
Co: $CoCl_2$+HGC
Ca: $CaCl_2$+HGC

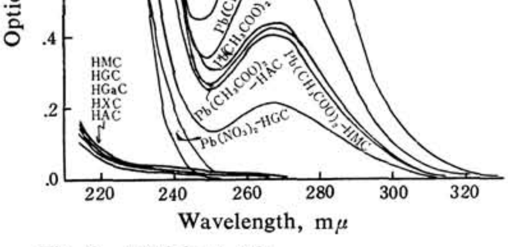

Fig. 2. HSC-lead salt.
0.5 mM HSC, 0.5 mM $Pb(CH_3COO)_2$ or $Pb(NO_3)_2$

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[*] Gelation of Lead Aldose-cysteinate Part II.

[**] See this Bulletin 35, 1819 (1962).

1) F. Takahashi and J. Mizuguchi, This Bulletin 35, 1818 (1962).

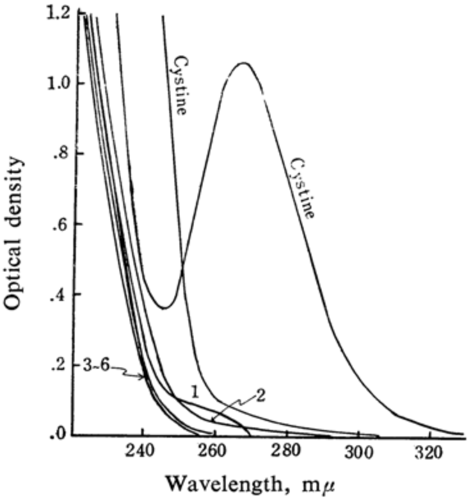

Fig. 3. Various amino acids-Pb(CH_3COO)$_2$.
0.5 mM amino acid, 0.5 mM Pb(CH_3COO)$_2$.

1 Phenylalanine
2 Thiazolidine carboxylic acid-4
3 Glycine
4 Glutamic acid
5 Serine
6 Lysine-HCl

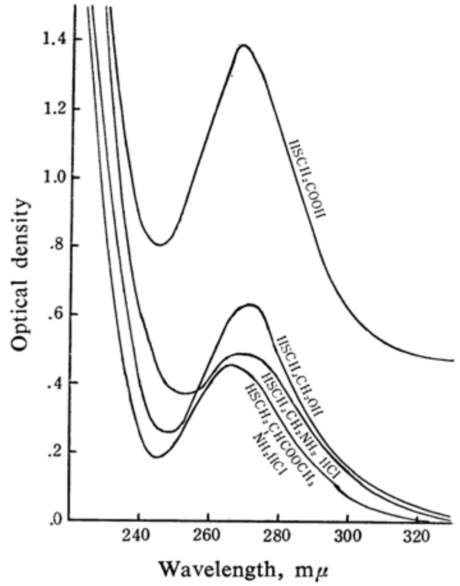

Fig. 4. Pb(CH_3COO)$_2$-thiol containing compounds.
0.5 mM Pb(CH_3COO)$_2$, 0.5 mM thiol-containing compounds

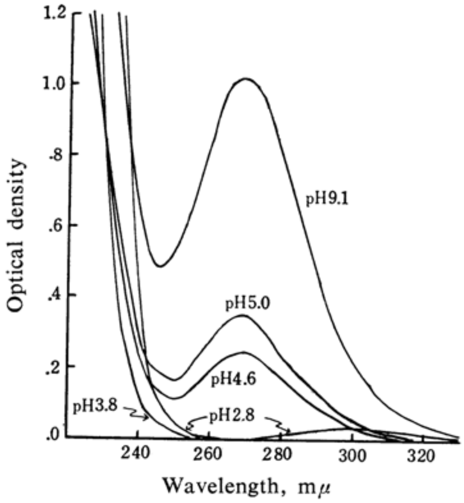

Fig. 5. HGC-lead salt in various pH.
0.25 mM HGC, 0.25 mM lead salt.

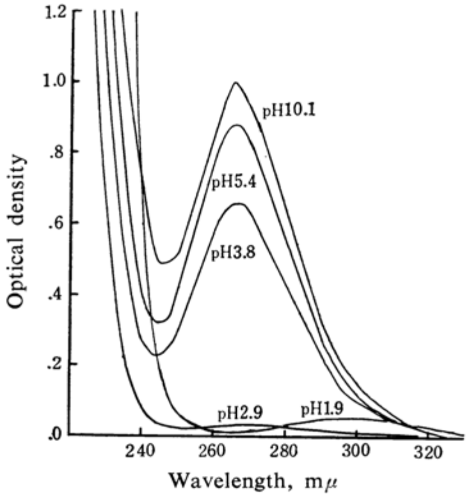

Fig. 6. Cysteine-lead salt in various pH.
0.5 mM cysteine, 0.25 mM lead salt

these results, it can be concluded that lead is coordinated through the sulfur atom of thiol-containing compounds.

The lead complexes of HSCs, which have a thiazolidine ring and no thiol group, show the same absorption spectra as that of thiol-containing compounds. In the beginning of this work, it was thought that the material which shows an absorption maximum was not the lead complexes of HSC but lead cysteinate, because HSC can be hydrolized to form cysteine in an aqueous solution. However, from the results of iodide-iodate determination[2], it was found to show no cysteine in the solution prepared for the determination of absorption spectra. Therefore, it is suggested that lead is doubtless coordinated through the sulfur atom of HSC and that the absorption maximum appears by means of this Pb–S bond.

Lead aldose-cysteinate, which has hydroxyl groups, shows the absorption maximum, but thiazolidine carboxylic acid, which has no

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[2] M. Sato, T. Hirano and T. Kan, *J. Agr. Chem. Soc.* (*Japan*), 15, 783 (1938).

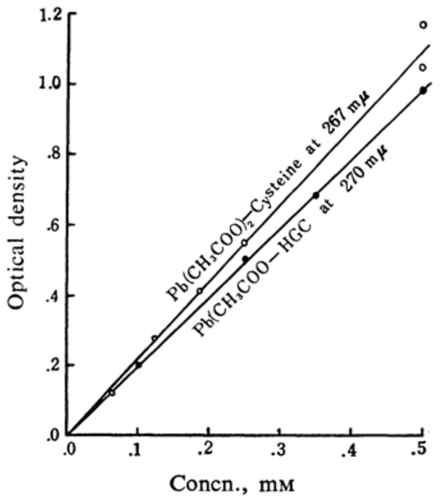

Fig. 7. $Pb(CH_3COO)_2$-HGC or cysteine in various concentration. (Molar ratio 1 : 1)

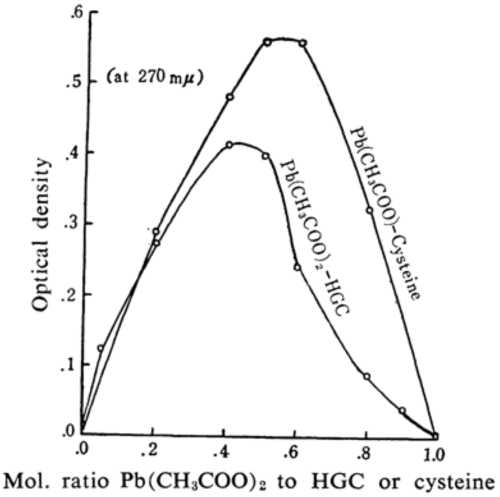

Fig. 8. Graphical determination of the composition of lead glucose-cysteinate or cysteinate. Total concn. 0.5 mM

hydroxyl group, does not show it, as is shown in Fig. 3. It is suggested that an absorption maximum appears when lead is coordinated through not only the sulfur atom but also hydroxyl groups of HSC.

It seems that these coordinations exist in the pH range between 3 and 10. In this pH range, the curves exhibit the same general contour and the same peak, as is shown in Fig. 5. The characteristic absorption spectra could not be observed in the pH range of 6 to 8 because the solution became turbid. In the lower pH range below 3, an absorption maximum was found to shift from 270 to 300 mμ. This fact presumably means that the complex is transformed.

Lead cysteinate was found to show the same absorption spectra as lead glucose-cysteinate (Fig. 6).

The absorption spectra of lead glucose-cysteinate was found to obey Beer's law in the range of 250 to 300 mμ (Fig. 7). When the absorption spectra were measured according to Job's method(3), the optical density at 270 mμ was found to be at a maximum at the molar ratio of about 1 : 1 (Fig. 8). It can be concluded that the highest order lead aldose-cysteinates and lead cysteinate are 1 : 1. These results can be supported by the suggestion obtained from the potentiometric study of Li and Manning(4).

Summary

Lead Aldose-cysteinates in solution were found to show an ultraviolet absorption maximum at 270 mμ. Moreover, lead complexes of various thiol-containing compounds were found to show the same absorption spectra as aldose-cysteine. From these results, it has been suggested that the absorption maximum appears when lead is coordinated through the sulfur atom.

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3) P. Job, *Ann. chim.*, **9**, 113 (1928).
4) N. C. Li and R. A. Manning, *J. Am. Chem. Soc.*, **77**, 5225 (1955).