

Tin and Lead Complexes With 1,10-Phenanthroline¹

WARREN W. BRANDT and E. ELAINE ZIMMERMAN, Purdue University

A search of the literature revealed that although very little work has been done on polyamine complexes of tin and lead, a few such compounds and complexes have been prepared. 1,10-Phenanthroline is known to form complexes with many metal ions. Since the order of stability of phenanthroline complexes differs from many other systems, it would be of interest to determine the position of the tin and lead complexes in this series. The complexes of Sn(II), Sn(IV) and Pb(II) with phenanthroline were therefore investigated.

Experimental

Qualitative evidence for complex formation was obtained in two ways. Both were indirect methods since the ions in question do not form colored complexes or insoluble precipitates with the phenanthroline. The first method which gave evidence for complex formation consisted in studying the behavior of the metallic ions with and without the reagent present. Their reactions with various anions were compared. Of 16 anions used, two (IO_4^- and I^-) gave different reactions with Sn(II) when phenanthroline was present than they did when it was absent. $\text{S}_2\text{O}_3^{2-}$ gave a difference with Sn(IV). $\text{S}_2\text{O}_3^{2-}$, $\text{Fe}(\text{CN})_6^{4-}$ and SCN^- gave differences with Pb(II). These differences can be attributed to some type of interaction, presumably complexing, which had occurred between the metallic ion and the phenanthroline.

The second evidence that Sn(II), Sn(IV) and Pb(II) form complexes with phenanthroline was obtained from the fact that their presence caused a decrease in the intensity of the color of the ferroin complex in solution. The ferroin complex, the tris-1,10-phenanthroline iron(II) ion, has a reddish orange color with maximum absorbance at $510\text{m}\mu$. Part of the ferroin complex originally present was destroyed by the addition of stannous, stannic or plumbous ions. Apparently the interfering ions reacted with the trace of free phenanthroline which was in equilibrium with the ferroin complex. This caused more and more of the ferroin to dissociate until a new equilibrium was established which involved the tin- or lead-phenanthroline complex.

By letting ferrous and plumbous or stannic ions compete for a limited amount of phenanthroline in solution it was possible to calculate equilibrium constants and thus get some idea of the formulas of the tin- and lead-phenanthroline complexes. By comparison with ferroin it was also possible to calculate the dissociation constants of the complexes. Calculations were based upon absorbance values measured at $510\text{m}\mu$ with a Beckman spectrophotometer-model B using 1 cm. cells.

The pH was a very important factor which had to be carefully controlled in order to get consistent results. In the range pH 4.5-8.0 the

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ferroin was satisfactorily stable. To eliminate the possibility that variations in absorbance could be due to variations in pH, the pH of each series of test solutions was adjusted to within ± 0.1 pH unit. The pH was measured with a Beckman pH meter Model H-2. The pH of the Sn(IV)-phenanthroline solutions was adjusted by using ammonium hydroxide and hydrochloric acid. No satisfactory means of adjusting the pH of the Sn(II)-phenanthroline solutions to the desired value was found. The Sn(II) precipitated from solution almost quantitatively even at pH 3. Ammonium hydroxide and acetic acid were used to adjust the Pb(II)-phenanthroline solutions to the desired pH.

It was necessary to remove dissolved oxygen from the solutions by bubbling nitrogen through them. When the oxygen was removed a stable equilibrium was obtained. When oxygen was not removed there was a gradual decrease in the intensity of the color of the solutions on standing due to oxidation of the ferrous ions.

Calculations

The absorbance at $510m\mu$ gave a measure of the amount of ferroin in the test solutions. Correction was made for the amount of the 1:1 ferrous-phenanthroline complex by using the formula derived by Kolthoff, et al. (2). The concentration of the 1:2 ferrous-phenanthroline complex was neglected because this complex is not stable in aqueous solutions. For the very dilute solutions used, approximately 10^{-4} molar, the activity coefficients were assumed to be the same for the complexed forms as for the uncomplexed forms. The phenanthroline not complexed with iron was assumed to be completely complexed with lead or tin. The values of the equilibrium constants were determined for the equilibria of the general type: Ferroin + stannic or plumbous ions \rightleftharpoons stannic or plumbous-phenanthroline complex + ferrous ions. The equilibrium constants were calculated assuming a 1:1, a 1:2 and a 1:3 ratio for the tin- and lead-phenanthroline complexes.

Assuming that only one of the three possible tin-phenanthroline complexes was formed in each case, the equilibrium constants for the reactions involving the 1:3, the 1:2, and the 1:1 complexes varied by factors of 35, 500 and 80 respectively. This seems to indicate that while the 1:3 complex was perhaps the major stannic-phenanthroline complex present, at least one or perhaps both of the other were also present. By assuming that both the 1:3 and the 1:1 complexes were present and using successive approximations, it was possible to obtain somewhat better constants. The equilibrium constants obtained by successive approximations agreed fairly well with those obtained assuming that the 1:1 complex was the major one in the solutions in which the tin to ferroin ratio was 15:1 and the 1:3 complex was the major one in the solutions in which the tin to ferroin ratio was 1:1 or 2:1.

By assuming that only one of the three possible plumbous phenanthroline complexes was formed in each case, the equilibrium constants obtained for the reactions involving the 1:3, the 1:2 and the 1:1 complexes varied by factors of 7, 20 and 2.8 respectively. The average value for the equilibrium constant for the reaction involving the 1:1 complex obtained from

solutions in which the lead to ferroin ratio was 150:1 or higher and the average value for the equilibrium constant for the reaction involving the 1:3 complex obtained from solutions in which the lead to ferroin ratio was 10:1 or 20:1 were in fair agreement with the equilibrium constants obtained by assuming that both complexes were present and using the more laborious method of successive approximations.

The dissociation constant of ferroin has been reported by Cook and Long as 7×10^{-22} (1) and by Lee et al. as 5×10^{-22} (3). Knowing this and the equilibrium constants calculated above, the dissociation constants of the two tin-phenanthroline and the two lead-phenanthroline complexes can be calculated. The following dissociation constants were calculated: for the 1:3 stannic-phenanthroline complex, 5×10^{-20} ; for the 1:1 stannic-phenanthroline complex, 8×10^{-7} ; for the 1:3 plumbous-phenanthroline complex, 3×10^{-18} ; for the 1:1 plumbous-phenanthroline complex, 2×10^{-5} . These values give an indication of the strength of the complexes, but they should be considered as only rather rough approximations of the true values. The 1:2 plumbous and stannic-phenanthroline complexes which may also be present in the solutions were disregarded in the calculations as were also any complexes between the metal ions and acetate, chloride and ammonia, which were added in adjusting the pH.

Conclusion

Since the tin- and lead-phenanthroline complexes are colorless as well as soluble in water, they do not afford a convenient method for the determination of tin or lead in solution. Both interfere in the colorimetric determination of ferrous iron using phenanthroline. Tin interferes seriously in the +4 oxidation state. Iron solutions to be determined by the phenanthroline method should, therefore, not be reduced using stannous chloride as the reducing agent.

Summary

Evidence was obtained for the formation of stannous- stannic- and plumbous-phenanthroline complexes. Approximate values of the dissociation constants of the 1:1 and 1:3 complexes of Sn(IV) and Pb(II) were calculated. The stannic-phenanthroline 1:3 complex is slightly weaker and the 1:1 complex is slightly stronger than the corresponding ferrous-phenanthroline complexes. The plumbous-phenanthroline complexes are weaker than either the stannic- or ferrous-phenanthroline complexes.

Literature Cited

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