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Note

A paper electrophoretic study of ion-pair formation

XII. Interaction between Co(III) complexes and solutions of orthophosphate, pyrophosphate and metaphosphate

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We have been conducting a survey of ion-pair formation between anions and Co(III) complexes, the results of which obtained so far have been published in a series of papers¹⁻³.

On examining chromate and bichromate, we noted a remarkable inversion

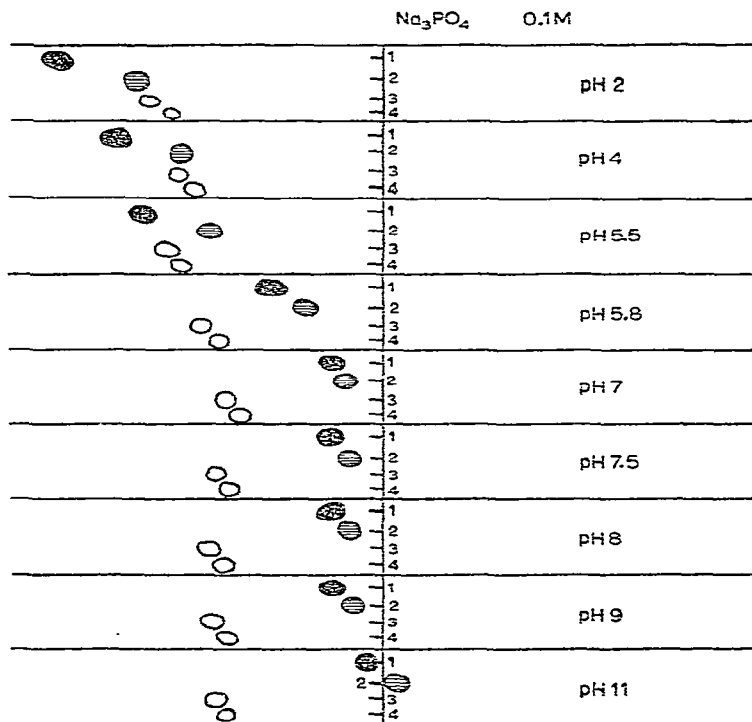


Fig. 1. Electrophoretic movement of (1) $\text{Co}(\text{NH}_3)_6^{3+}$, (2) $\text{Co}(\text{en})_3^{3+}$, (3) $\text{Co}(\text{dip})_2^{5+}$ and (4) $\text{Co}(\text{o-phen})_3^{3+}$ in 0.1 M sodium orthophosphate at the pH values indicated on the right. Conditions: Whatman No. 1 paper, 1500 V for 30 min at 6°.

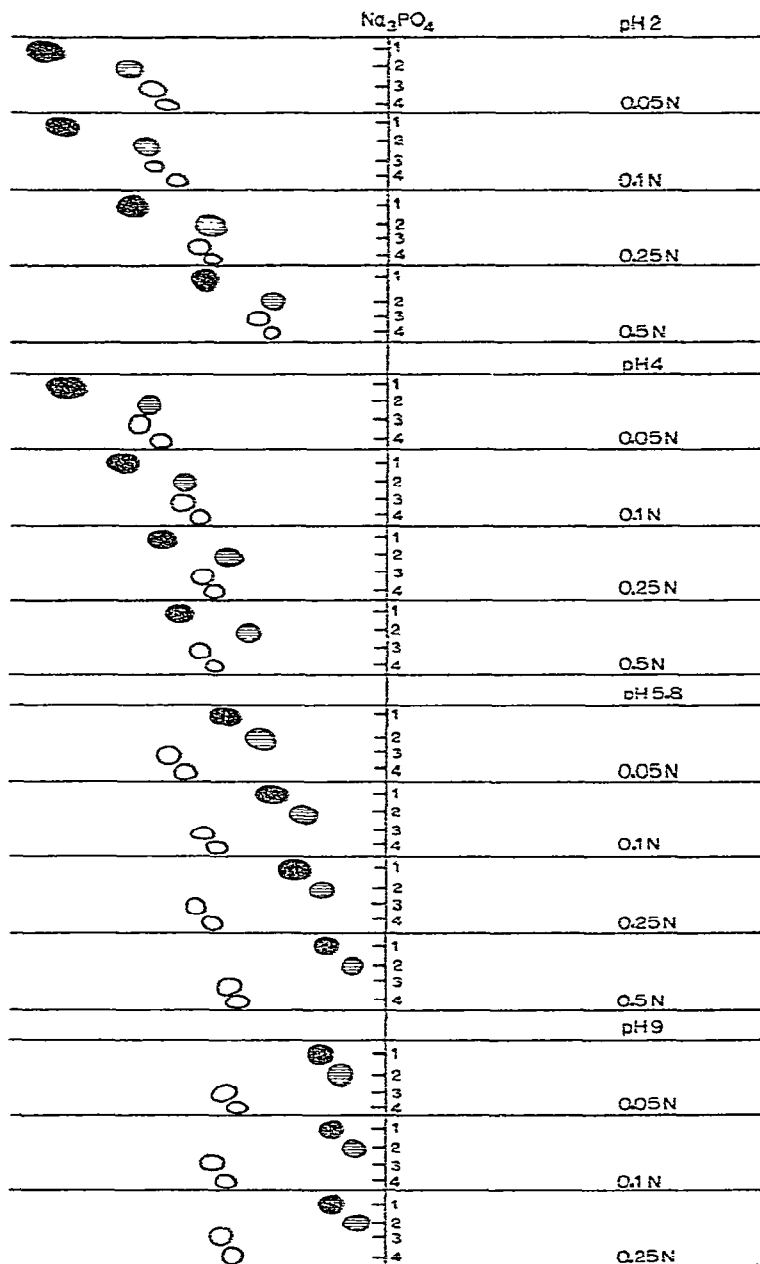


Fig. 2. Electrophoretic movement of the complexes as in Fig. 1 in various concentrations of sodium orthophosphate. The concentrations and pH values are shown on the right. Conditions as in Fig. 1.

effect: while in chromate the greatest affinity towards the anion was given by $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ * and little effect was noted with $\text{Co}(\text{dip})_3^{3+}$ and

* The following abbreviations are used: en = ethylenediamine; dip = dipyriddy; *o*-phen = *ortho*-phenanthroline.

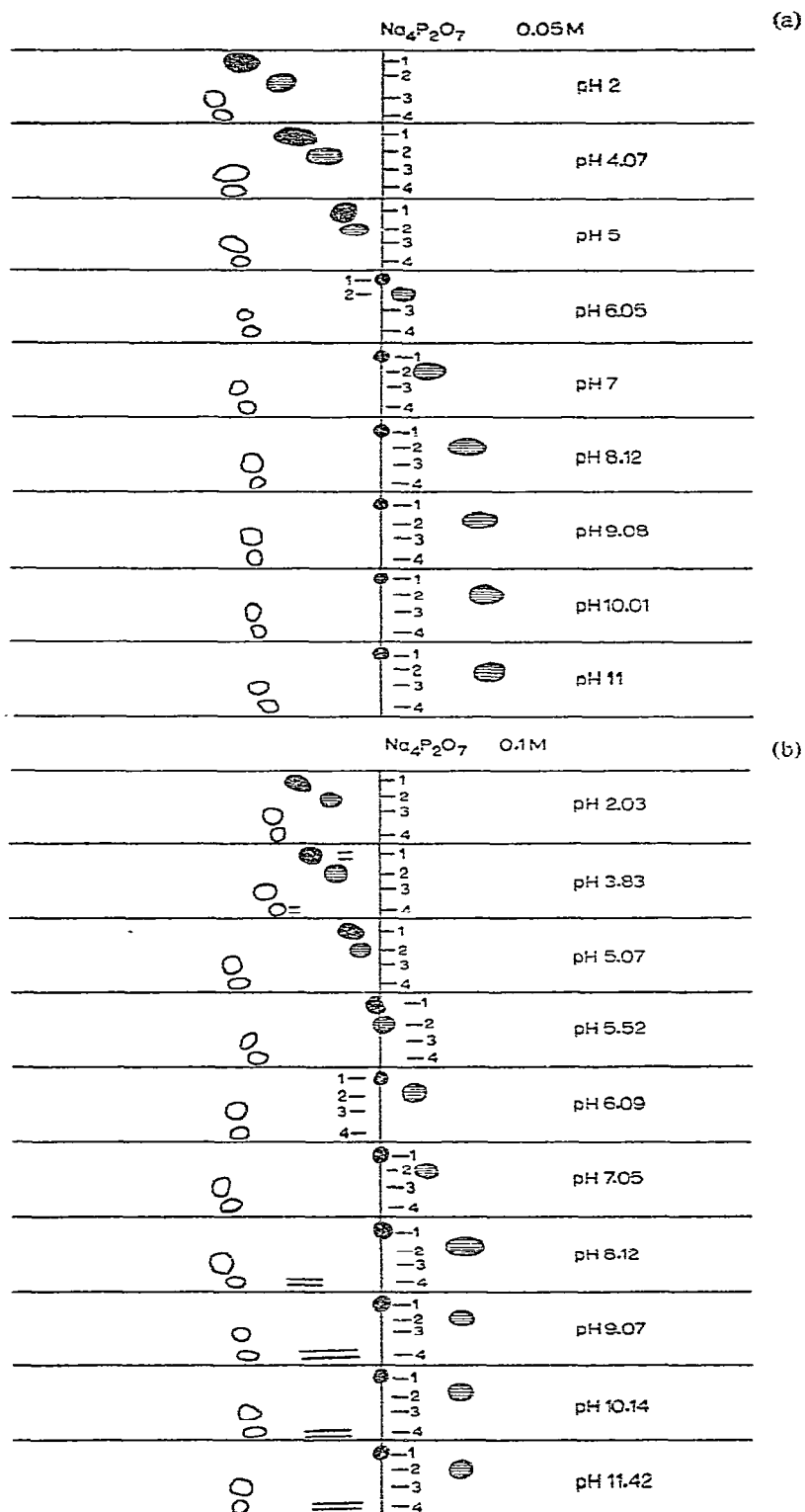


Fig. 3.

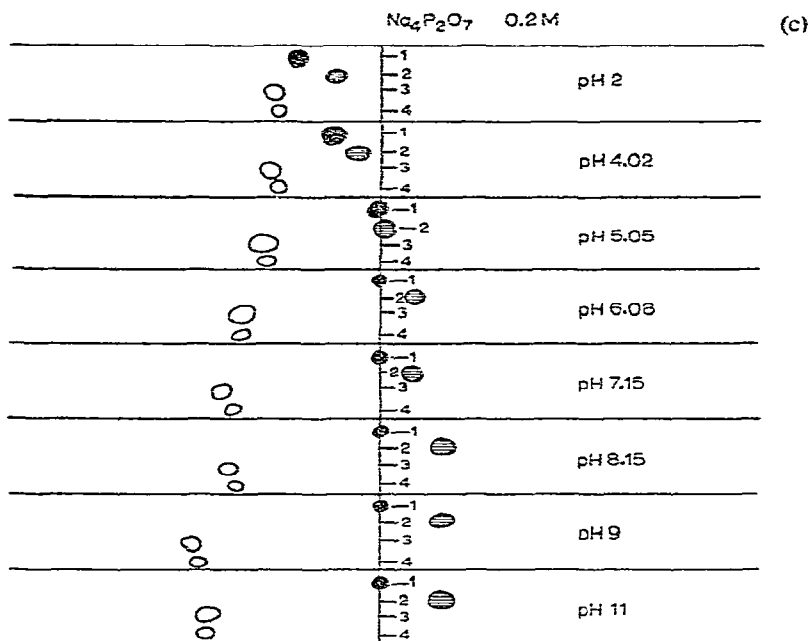


Fig. 3. Electrophoretic movement of the complexes as in Fig. 1 in sodium pyrophosphate, (a) 0.05 *M*, (b) 0.1 *M* and (c) 0.2 *M*, at the pH values indicated on the right. Conditions as in Fig. 1.

$\text{Co}(o\text{-phen})_3^{3+}$, the opposite occurred in dichromate. This effect led us to conclude that two entirely different ion-pair mechanisms operate in chromate and dichromate and we have discussed the types of interactions that are possible in another paper⁴.

An obvious extension of these unexpected results was to continue the survey of the ion-pairing properties of condensed anions, and in this paper we report on the results obtained with various phosphates. Our interest in phosphates stems from the facts firstly that condensed phosphates have important industrial and biological functions and secondly that pyrophosphate is much more stable than dichromate, thus permitting the pH to be varied without interfering with the degree of polymerization of the anion.

EXPERIMENTAL AND RESULTS

High-voltage electrophoresis was carried out in a Camag apparatus. All recorded electrophoretic movements were corrected for electroosmotic flow (using hydrogen peroxide and glycerine) and the spots of the Co(III) complexes were detected by spraying the paper sheets lightly with aqueous ammonium sulphide.

We limited the study to four Co(III) complexes, *viz.*, $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{dip})_3^{3+}$ and $\text{Co}(o\text{-phen})_3^{3+}$, which were allowed to migrate in solutions of phosphate (0.05–0.5 *M*) and pyrophosphate (0.05–0.2 *M*) at pH 2–11. Some work was also carried out with solutions of metaphosphate.

The results are best represented in the form of schematic graphs showing the actual electrophoretic movement of the various complexes. Fig. 1 shows the effect of

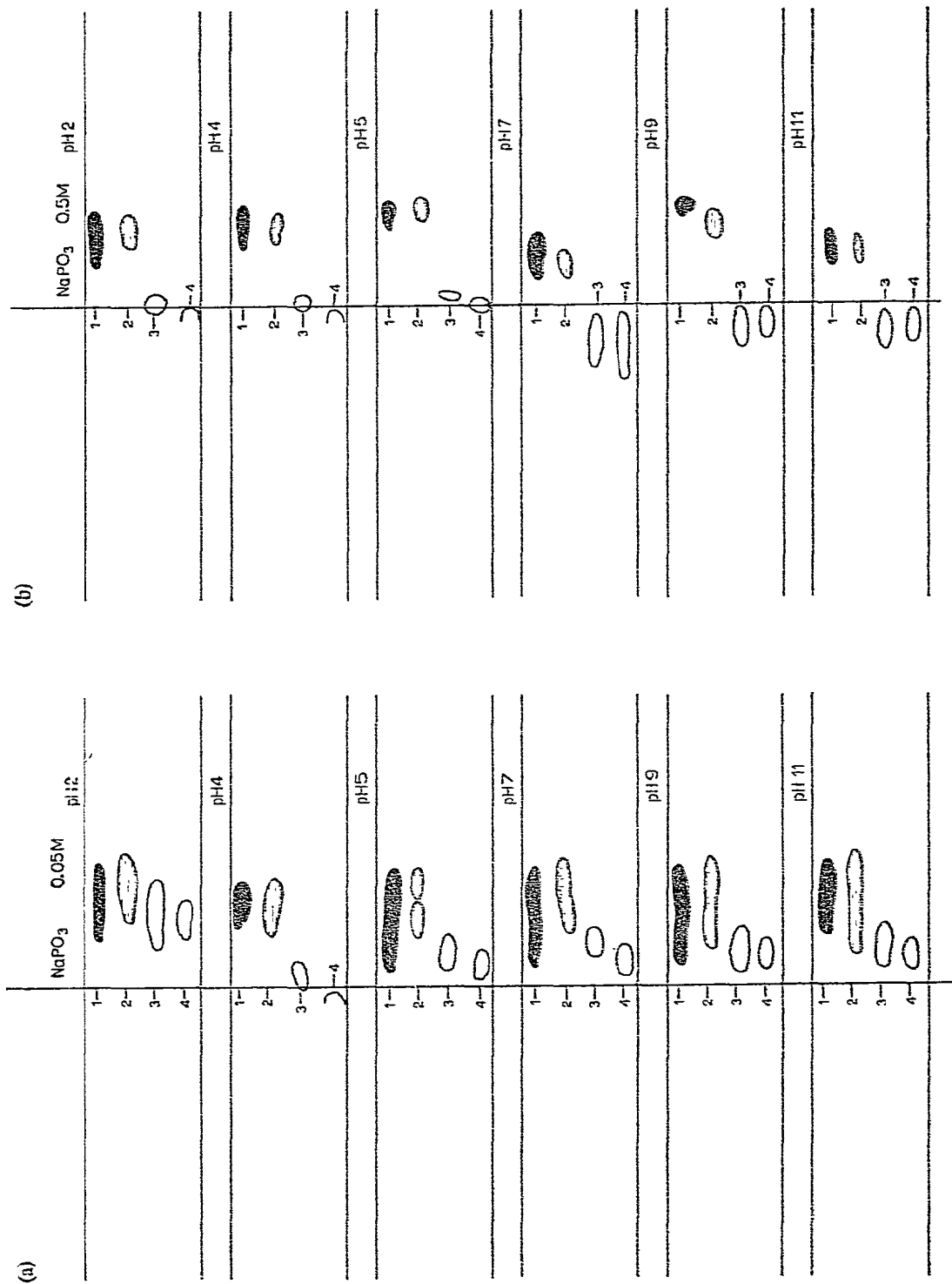


Fig. 4. Electrophoretic movement of the complexes as in Fig. 1 in "sodium metaphosphate" (actually a mixture of phosphate species), (a) 0.05 M and (b) 0.5 M, at the pH values indicated on the right. Conditions as in Fig. 1.

pH on the movement of the four complexes in 0.1 *M* orthophosphate. While Co(dip)_3^{3+} and $\text{Co}(o\text{-phen})_3^{3+}$ are relatively unaffected by changes in pH, *i.e.*, by the gradual change from H_2PO_4^- to HPO_4^{2-} and then to PO_4^{3-} , both $\text{Co}(\text{NH}_3)_6^{3+}$ and Co(en)_3^{3+} change their movement considerably to almost zero above pH 7. This change corresponds to the disappearance of H_2PO_4^- from solution and the gradual formation of more highly charged ions, principally HPO_4^{2-} .

Fig. 2 shows that the total concentration of phosphate used as electrolyte does not have a great influence within the range 0.05–0.5 *N* except that, of course, all ions move more slowly at higher electrolyte concentrations.

Fig. 3 shows the electrophoretic movement of the four complexes in pyrophosphate solutions. There are several interesting features: firstly, there is no inversion of the general effect as was observed with chromate–dichromate; secondly, the ion-pairing effect on $\text{Co}(\text{NH}_3)_6^{3+}$ and Co(en)_3^{3+} is more pronounced even at low pH values; and finally, while $\text{Co}(\text{NH}_3)_6^{3+}$ precipitates above pH 6, Co(en)_3^{3+} becomes negatively charged, suggesting an interaction principally of one tri-charged Co(III) cation with one tetra-charged pyrophosphate anion.

Metaphosphates gave rather disappointing results, some of which are shown in Fig. 4. Only elongated trails are formed, the most interesting feature of which is the anionic movement of virtually all complexes. At higher concentrations of sodium metaphosphate (0.5 *M*), there is a pronounced difference between the complexes $\text{Co}(\text{NH}_3)_6^{3+}$ and Co(en)_3^{3+} on the one hand and the complexes Co(dip)_3^{3+} and $\text{Co}(o\text{-phen})_3^{3+}$ on the other.

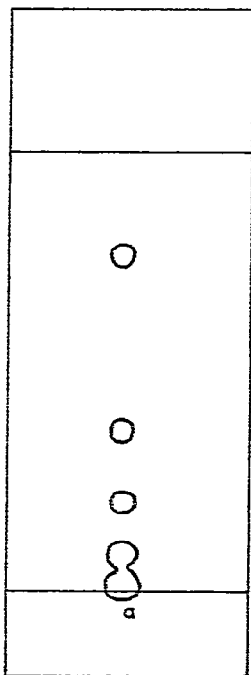


Fig. 5. Chromatogram of sample of "sodium metaphosphate". Solvent: isopropanol–water–trichloroacetic acid–ammonia (75:25:5:0.3). Ascending development on Whatman No. 1 paper; a = point of application.

We had also planned to examine the electrophoretic movement of complexes in tripolyphosphate, but none of the preparative methods available yielded a product of sufficient purity. The same applied to the solution of metaphosphate, and therefore, when considering the results shown in Fig. 4, it should be borne in mind that the solution contained different phosphates; a typical paper chromatogram of our "metaphosphate" is shown in Fig. 5.

In conclusion, there is no fundamental difference between the types of outer-sphere complexing (or ion pairing) encountered with orthophosphate and with pyrophosphate, both giving the type of interaction already observed with other polyvalent anions such as sulphate, chromate and thiosulphate. Owing to the high charge on the anion, the complexes are often found to migrate anionically, which is not so typical with divalent anions such as sulphate.

ACKNOWLEDGEMENTS

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