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## A FEW REMARKS ON THE IDENTIFICATION OF INORGANIC COMPOUNDS

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In inorganic chemistry we have two distinct identification problems, *viz.* (a) the indication of an element in a sample, and (b) the identification of an inorganic compound by chromatography.

## IDENTIFICATION OF AN ELEMENT

The identification of an element in a sample, *i.e.* to tell whether there is copper or bismuth in a sample, has been dealt with repeatedly and can be approached in numerous ways. I do not intend to discuss it here because methods better than chromatography are usually available; the only exception is perhaps the identification of carrier-free radioactive isotopes. Chromatography is only preferred in certain types of qualitative analysis, such as geochemical prospecting, where it is simpler than many instrumental methods.

## IDENTIFICATION OF AN INORGANIC COMPOUND

Here we have a homologous series such as the polyphosphates, polyarsenates and polythionates to discuss as well as the stable coordination complexes, such as the cobalt(III)ammine series or the platinum(II)ammine series, the many stable halo-aquocomplexes of most of the platinum metals and many others. I propose to discuss here only a few of the pitfalls in the apparently simple techniques now used and shall do this by selecting a few examples in which we were interested.

*Example I*

When  $\text{SnCl}_2$  is added to a solution of  $\text{Rh(III)Cl}_6^{3-}$  in dilute 2*N* hydrochloric acid, an intensely red coloration is produced. Similar intense colorations are given by Pt, Pd and Ir. The first explanation of this coloration was that colloidal solutions of the metal were produced<sup>1</sup>. AYRES<sup>2</sup> and MEYER AND AYRES<sup>3</sup> poured the solution of the platinum complex over a sulphonic resin and found it to be adsorbed strongly, and thus, after analysis, they formulated the cation  $[\text{PtSn}_4\text{Cl}_4]^{4+}$ . SHUKLA<sup>4</sup> examined the Rh, Pt and Pd compounds by paper electrophoresis with  $\text{SnCl}_2\text{-HCl}$  as electrolyte and observed anionic movement for all three complexes. This induced later workers to precipitate the anion with quaternary ammonium cations and thus isolate a crystalline compound.

Which of these results is correct? Actually none of them are. AYRES should have examined the behaviour of his solution not only on a cationic resin. He would have found still stronger adsorption on an anionic resin. But even this stronger adsorption would not have excluded the possibility of a neutral species being present, which

adsorbs strongly on all non-polar surfaces. It would only have avoided the conclusion that the species is cationic.

SHUKLA indeed had an anion but more recent work with a wide range of metal salts as electrolytes<sup>5</sup> has shown that ion pairing could have associated a cationic rhodium complex with  $\text{SnCl}_4^{2-}$  and produced anionic movement. A spectacular example of this kind of phenomenon is the cationic movement of  $\text{Fe}(\text{CN})_6^{3-}$  in acidified zirconium(IV) chloride as electrolyte.

The formation of a precipitate with a heavy cation is better evidence than either cation-exchange chromatography or paper electrophoresis, but even this classical method is inadequate with the complexes under study because the precipitate obtained with Rh is not red but yellow. The same yellow species can be obtained by electrophoresis of a red solution in dilute HCl (in the absence of  $\text{SnCl}_2$ ), and it can be shown that Sn(II) moves away from it. By allowing the yellow band to migrate through a band of Sn(II) in its path, it will regain the red colour and lose it when it has moved out of the Sn(II). This process may be repeated several times. We believe that this indicates that there is a reversible reaction with at least one Sn(II) and that the precipitates obtained are not likely to correspond to the species in solution. In summation, so far no suitable method for the study of the red Rh(III)- $\text{SnCl}_2$  complex(es) has been found. While cation exchange yielded erroneous results, paper electrophoresis gave the correct result, more by good luck than by good management, however.

#### *Example II*

In studies on the equilibrium between metal ions and organic solvent-HCl mixtures, KORKISCH AND TERA<sup>6</sup> noted that Th(IV) was strongly retained on Dowex-I and proposed that an anionic thorium chloride complex was formed in organic solvents. The existence of the anionic complex was disproved by a rather simple experiment. Th(IV) was developed with some of the solvent mixtures of KORKISCH AND TERA both on ordinary cellulose paper and on SB-2 anion-exchange paper (45% resin). On both papers Th had the same  $R_F$  value<sup>7</sup>.

Evidently a ternary system consisting of a mixture of organic solvent, HCl and water in equilibrium with the resin produces a water-rich HCl phase on the resin surface (which is very polar due to the many ionised ammonium groups) and a more solvent-rich phase as the mobile solvent. In such a partition system Th(IV) remains in the aqueous phase.

#### *Example III*

KRISTJANSON AND LEDERER<sup>8</sup> studied the rhodium chloride species present in concentrated HCl solutions by column chromatography on Dowex-2 anionic resin.  $\text{RhCl}_6^{3-}$  is known to hydrolyse very readily, and they used 6 N and more concentrated HCl as eluent throughout the work. On heating  $\text{Rh}(\text{OH})_3$  in 6 N HCl they obtained several solutions at various time intervals and these separated into variously coloured bands on the column. The slowest and most intensely coloured red band was tacitly assumed to be  $\text{RhCl}_6^{3-}$ . Later work<sup>9</sup> with anion-exchange resin papers showed this to be wrong:  $\text{RhCl}_6^{3-}$ ,  $\text{Rh}(\text{H}_2\text{O})\text{Cl}_5^{2-}$  and  $\text{Rh}(\text{H}_2\text{O})_2\text{Cl}_4^-$  do not separate in 6 N HCl but only in 2 N or less concentrated HCl.

When electrophorising rhodium(III) aquo-chloro complexes in dilute HCl,

several anionic bands were obtained<sup>10</sup>, and the fastest was assumed to be  $\text{RhCl}_6^{3-}$ , the slower  $\text{Rh}(\text{H}_2\text{O})\text{Cl}_5^{2-}$  and the slowest  $\text{Rh}(\text{H}_2\text{O})_2\text{Cl}_4^-$ . Later work by BLASIUS AND PREETZ<sup>11</sup> proved this to be correct but it was another case of good luck because we now realise that polyvalent acids often move more slowly than monovalent ones due to a greater tendency to form ion pairs. It is not justified to assume a higher charge on a faster ion unless the electrolyte is very dilute and does not contain cations with a tendency to form ion pairs.

## REFERENCES

- 1 F. FEIGL, *Spot Tests, Vol I, Inorganic Applications*, 4th Ed., Elsevier, Amsterdam, 1954, p. 129.
- 2 G. H. AYRES, *Anal. Chem.*, 25 (1953) 1622.
- 3 A. S. MEYER AND G. H. AYRES, *J. Am. Chem. Soc.*, 77 (1955) 2671.
- 4 S. K. SHUKLA, *Thèse de doctorat*, Paris, 1962.
- 5 M. LEDERER AND M. MAZZEI, *J. Chromatog.*, 35 (1968) 201.
- 6 J. KORKISCH AND F. TERA, *J. Inorg. Nucl. Chem.*, 15 (1960) 177.
- 7 M. LEDERER AND F. RALLO, *J. Chromatog.*, 7 (1962) 552.
- 8 A. M. KRISTJANSON AND M. LEDERER, *J. Less Common Metals*, 1 (1959) 245.
- 9 G. BAGLIANO AND L. OSSICINI, *J. Chromatog.*, 19 (1965) 412.
- 10 M. LEDERER, *Zh. Neorgan. Khim.*, 3 (1958) 1799.
- 11 E. BLASIUS AND W. PREETZ, in M. LEDERER (Editor), *Chromatographic Reviews*, Vol. 6, Elsevier, Amsterdam, 1964, p. 191.

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