

CHROM. 9694

Note

Formation of polymeric species by reaction of cobalt(III) complexes with ammonium sulphide

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(Received October 4th, 1976)

This investigation was based on an observation made during the thin-layer and paper chromatography of cobalt(III) complexes. When the chromatograms are sprayed with ammonium sulphide, cobalt in the form of cobalt(II) yields intense black spots while cobalt(III) complexes such as $\text{Co(en)}_3\text{Cl}_3$, $\text{Co(pn)}_3\text{Cl}_3$ and $\text{Co(dip)}_3\text{Cl}_3$ yield brown spots, and moreover each complex gives a different hue of brown. These colours are reproducible from one chromatogram to another and from one day to another.

We therefore wondered whether a different kind of compound is formed. Reflectance spectra of the spots gave little information as they have a continuous form (see, for example, Fig. 1) and show no definite peaks, nor do they differ very much from one complex to another.

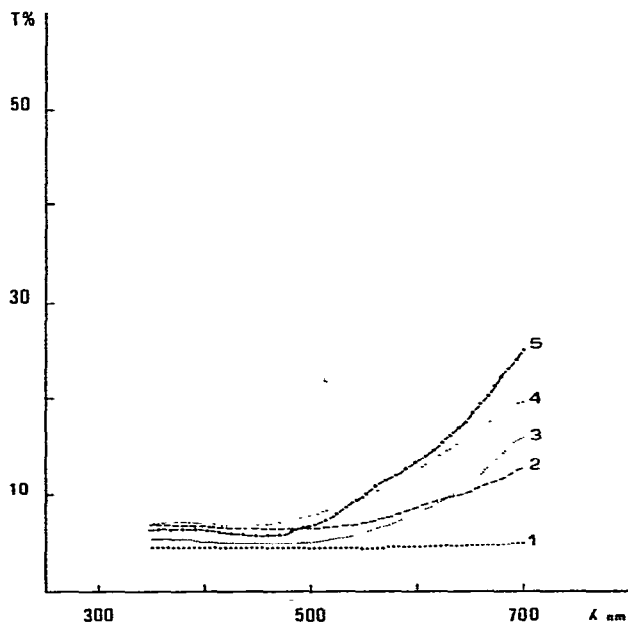


Fig. 1. Reflectance spectra obtained for 5 mg/ml aqueous solutions of Co(III) complexes adsorbed on cellulose thin layers and sprayed with ammonium sulphide solution: 1 = $\text{Co}(\text{NH}_3)_6\text{Cl}_3$; 2 = $\text{Co}(\text{tn})_3\text{Cl}_3$; 3 = $\text{Co}(\text{pn})_3\text{Cl}_3$; 4 = $\text{Co}(\text{en})_3\text{Cl}_3$; 5 = $\text{Co}(\text{dip})_3\text{Cl}_3$.

When one adds ammonium sulphide solution to solutions of various cobalt(III) complexes, an intense black precipitate is formed immediately, which presumably is the well known cobalt(II) sulphide. It was possible, however, to reproduce the reactions that occur on chromatograms by adding small amounts of ammonium sulphide carefully to solutions of cobalt(III) complexes. This was first achieved by spraying a solution of the complex in a measuring cylinder with ammonium sulphide with a sprayer as used for chromatograms, but later it was found more convenient to expose the solutions to an ammonium sulphide-saturated atmosphere in a desiccator for 45 min. The solutions so obtained are dark brown and, depending on the complex, form a black precipitate more or less slowly, usually overnight.

When these solutions are chromatographed on Sephadex gels, it can be shown that they contain a dark excluded band, *i.e.*, a polymer. We can suggest only one explanation for this polymer, namely that it is a sulphur analogue of the well known hydroxy- or oxy-polymers. In other words, intermediates are formed in which $-S-$ links (probably) with a number of cobalt(III) moieties that still have the remainder of their coordination groups attached to the central metal atom.

To our knowledge, this type of polymer has not been observed before. It could also occur with other types of trivalent metal complexes and may belong to one of the mechanisms of ore formation from sulphurous springs.

EXPERIMENTAL AND RESULTS

The complexes studied were $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{pn})_3^{3+}$, $\text{Co}(\text{tn})_3^{3+}$, $\text{Co}(\text{dip}_2\text{en})_3^{3+}$ and $\text{Co}(\text{dip}_2\text{oph})_3^{3+}$, where en = ethylenediamine, pn = 1,2-diaminopropane, tn = 1,3-diaminopropane, dip = dipyridyl and oph = *o*-phenanthroline. These complexes were prepared according to published methods: $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and $\text{Co}(\text{en})_3\text{Cl}_3$ according to Work¹, $\text{Co}(\text{dip}_2\text{en})\text{Cl}_3$ and $\text{Co}(\text{dip}_2\text{oph})\text{Cl}_3$ according to Proserpi *et al.*² and $\text{Co}(\text{pn})_3\text{Cl}_3$ and $\text{Co}(\text{tn})_3\text{Cl}_3$ by the method used for $\text{Co}(\text{en})_3\text{Cl}_3$.

Portions of 5 ml of solutions of the complexes (5 mg/ml) were placed in test-tubes in a desiccator in which was also placed a beaker containing 20 ml of 20% yellow ammonium sulphide solution (Carlo Erba, Milan, Italy). The solutions of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and $\text{Co}(\text{tn})_3\text{Cl}_3$ gave a black precipitate after a few minutes. The other complexes formed a dark brown zone on the surface and, on gently shaking the test-tube, a homogeneous transparent brown solution was obtained.

The brown solutions were chromatographed on columns (20 × 1 cm I.D.) of Sephadex LH-20 (Pharmacia, Uppsala, Sweden) using 0.01 *N* sodium nitrate solution as eluent. Two bands were always formed: a brown zone, which was completely excluded, and a slower orange band. The excluded band decomposed during development, leaving an orange-coloured trail and a dark precipitate along the column.

If very short columns (3 × 1 cm I.D.) were used, the brown band could be eluted from the column and its absorption spectrum measured (Fig. 2). However, the solutions so isolated decomposed, forming a precipitate within 30–50 min, depending on the complex.

$\text{Co}(\text{dip}_2\text{oph})\text{Cl}_3$ yielded a brown solution that was strongly adsorbed on Sephadex LH-20; however, if Dextran Blue was added to the column immediately after the sample, the brown band moved ahead of the blue band, apparently desorbed by the presence of the latter.

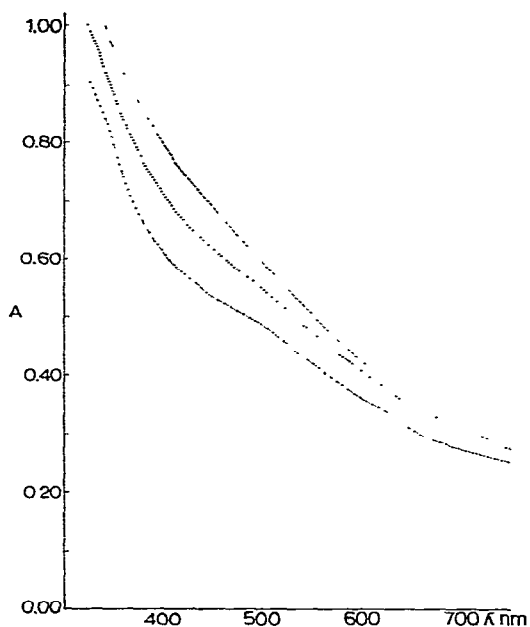


Fig. 2. Visible absorption spectra of the isolated first band when an aqueous concentrated solution of $\text{Co}(\text{pn})_3\text{Cl}_3$ exposed to ammonium sulphide vapour was eluted on a Sephadex column. Decomposition sequence: ----, just eluted; ·····, 30 min old; - · - ·, 50 min old.

These results give rise to two questions: what is the exact nature of the brown polymer and which other types of complexes form such polymers? We hope to be able to report on both questions in the future.

REFERENCES

- 1 J. B. Work, *Inorganic Syntheses*, Vol. II, McGraw-Hill, New York, 1946, pp. 217-221.
- 2 T. Prospero, M. Sinibaldi and M. Lederer, *Gazz. Chim. Ital.*, 103 (1973) 995.