

## Short Communications

## Correction to "Studies on Polynuclear Complexes. II"

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In a recent paper by us<sup>1</sup> the slow formation of an orange-red compound in solutions of aquahydroxo-(tren)cobalt(III) perchlorate {tren = tris(2-aminoethyl)amine} was discussed at length. This compound, which was assumed to be a polynuclear complex, has now been identified as the carbonato-(tren)cobalt(III) cation. In Fig. 1 (lower figure) the spectrum of this compound is compared with that of the orange-red compound (isolated from the aged solutions on Sephadex columns). The similarity of the two spectra is convincing, the extinction coefficients and wavelengths for the two maxima (at 500 and 353 nm) being nearly identical; also all the other properties found for the orange-red compound agree well with those of the carbonato-(tren) complex.

Dasgupta and Harris<sup>2</sup> have recently reported a study of carbon dioxide uptake and intramolecular carbonato ligand chelation in solutions of the aquahydroxo(tren)cobalt(III) perchlorate. According to these authors even rather acid buffers of the diaqua(tren)cobalt(III) system show a high affinity for carbon dioxide. We attribute the partial formation of the carbonato-complex in the dilute (~0.01 M) tren-cobalt(III) buffers employed by us to the fact that the solutions were allowed to stand in sintered glass-stoppered bottles at room temperature for periods of weeks or of months.

When carbon dioxide replaces two water molecules in the diaqua(tren) complex, two hydrogen ions are released. It is this reaction and not the formation of a polynuclear tren complex which is the reason for the observed fall in pH in the aged solutions. When release of somewhat less than two hydrogen ions per diaqua ion was found, it is due to the fact that some decomposition reactions of the tren complex take place in the more basic

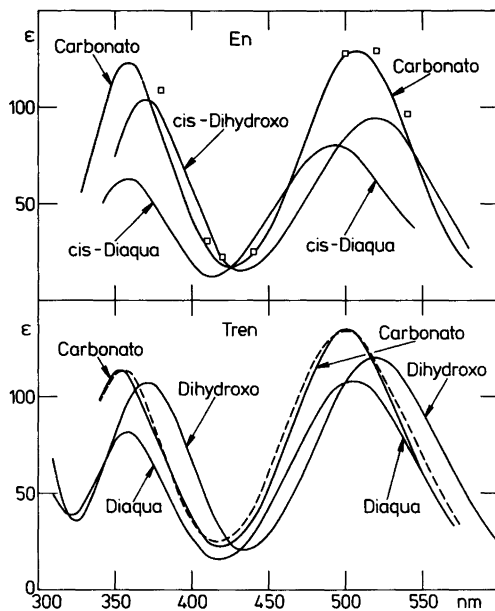


Fig. 1. In the lower part of the figure our spectrum of the orange-red compound (----) is compared with that of an analyzed preparation of carbonato-(tren)cobalt(III) perchlorate in 1 M NaClO<sub>4</sub>. Our spectra of diaqua- and dihydroxo(tren)cobalt(III) in the same medium are shown for comparison.

In the upper part of the figure the calculated points (□) for the hypothetical compound formed in aged bis(ethylenediamine)cobalt(III) solutions are compared with that of an analyzed preparation of carbonatobis(ethylenediamine)cobalt(III) chloride. The spectra of *cis*-diaqua- and *cis*-dihydroxobis(ethylenediamine)cobalt(III) are also shown.

solutions with the formation of polynuclear complexes with less than 4 nitrogen per cobalt atom.

In Fig. 1 (upper part) the spectrum of carbonatobis(ethylenediamine)cobalt(III) chloride (maxima at 508 and 359 nm) is compared with some values for the extinction coefficients of the hypothetical compound formed in aged solutions of aquahydroxobis(ethylenediamine)cobalt(III) nitrate.

These values were calculated on the basis of data given by Rasmussen and Bjerrum<sup>3</sup> and it can be seen that they agree also reasonably well with the assumption that it is the carbonato complex which is formed during the long period of ageing.

Addition of large amounts of iodide to solutions of the carbonato(tren) complex results in formation of a precipitate of aquahydroxo(tren)cobalt-(III) iodide after some hours. The same was found to be the case for the orange-red compound and this was one of the observations which led us to false conclusions.

What must be learned from our experience is that the utmost care with regard to protection against carbon dioxide is necessary in prolonged experiments of the kind employed in this work.

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2. Dasgupta, T. P. and Harris, G. M. *J. Am. Chem. Soc.* 97 (1975) 1733.
3. Rasmussen, S. E. and Bjerrum, J. *Acta Chem. Scand.* 9 (1955) 735.

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