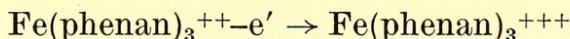


THE RESOLUTION OF THE TRIS o,PHENANTHROLINE FERROUS ION AND THE OXIDATION OF THE ENANTIOMORPHOUS FORMS.

By F. P. DWYER, D.Sc.
and (Miss) E. C. GYARFAS, M.Sc.

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When o,phenanthroline is added to ferrous salt solutions, red compounds result which have been shown to have the constitution $\text{Fe(phenan)}_3\text{X}_2\cdot n\text{H}_2\text{O}$ (Blau, 1898). The tris o,phenanthroline ferrous ion is reversibly oxidisable to the blue tris o,phenanthroline ferric ion the redox potential for the reaction



being 1.12 volts (Smith and Richter, 1944; Dwyer and McKenzie, 1947). In this paper the resolution of the ferrous complex and the oxidation of the enantiomorphous forms is described.

The resolution was carried out through the antimonyl tartrates, and it was found that on adding potassium antimonyl tartrate to a racemic solution of Fe(phenan)_3^{++} in water the l-complex d-antimonyl tartrate separated as a highly insoluble precipitate, whilst the d-complex remained in solution and could be precipitated from the mother liquid as the sparingly soluble perchlorate. The perchlorate of the laevo form was obtained by dissolving the antimonyl tartrate precipitate in caustic soda solution (thus destroying the antimonyl tartrate radicle) and adding sodium perchlorate. The active perchlorates were more soluble in water than the racemate.

The resolution of the analogous tris o,phenanthroline ruthenium II and nickel II complexes and recently that of the osmium II complex has been carried out in a similar way (Dwyer and Gyarfás, 1949*a, b, c*). In all of these complexes the d-Me(phenan)₃ d-antimonyl tartrate (Me = Ru II, Ni II, Os II), formed the highly insoluble compound. It is reasonable to suppose, therefore, that the form of the ferrous complex precipitated as the d-antimonyl tartrate has the same configuration as the dextrorotatory Ru II, Ni II and Os II complexes. The sign of the rotation is of no significance since all these ions possess a strongly abnormal rotatory dispersion, the investigation of which is now being carried out, and will be published in a subsequent communication.

The optical forms were more stable than the active forms of the tris 2:2' dipyridyl ferrous ion resolved by Werner (1912*a*). Thus whilst the rotations of solutions of this substance dropped to half of its original value in half an hour the phenanthroline complexes in solution have a half life of approximately one hour, and the solids possess some rotation even after a period of six months. The same relation was found between the stabilities of the corresponding Ni(dipy)₃⁺⁺ and Ni(phenan)₃⁺⁺ complexes (Morgan and Burstall, 1931; Dwyer and Gyarfás, 1949*b*). On standing from a racemic solution of the ferrous complex containing excess antimonyl tartrate, the whole of the complex precipitated slowly as the l-complex d-antimonyl tartrate, leaving a colourless solution behind. This is due to the racemisation of the solution. The equilibrium between the d and l complex ions is being shifted towards the latter, which is continuously eliminated from the solution as the insoluble antimonyl

tartrate, and finally none of the d-complex remains. A similar reaction was, observed on the resolution of the trioxalato chromiates with strychnine (Werner 1912*b*).

In a previous paper (Dwyer and Gyarfás, 1949*a*), the oxidation of the enantiomorphous forms of the tris o,phenanthroline ruthenium II complex was described. It was found that on oxidation of the active solutions of this complex the solutions of the blue ruthenium III complex were still optically active, although the magnitude of rotation was different, and that on reduction the ruthenium II complex was obtained with its rotation unchanged. If the same experiment is carried out on the active tris o,phenanthroline ferrous ion at room temperature, as stated by the authors in a note in *Nature* (Dwyer and Gyarfás, 1949), the rotation is lost on oxidation due to the rapid racemisation of the ferric complex. However, at 6° C. the rate of racemisation being reduced, active solutions of the ferric complex could be obtained. The rate of racemisation even at 6° C. was too rapid to permit measurement of the specific rotation with any degree of accuracy, but it is approximately 60% of that of the ferrous complex in the NaD line.

EXPERIMENTAL.

Owing to the racemisation of the active substances standard solutions could not be made up for measurements of rotations. The determinations of specific rotations was done by shaking the active substance in ice-cold water for a few seconds, filtering off the undissolved material on the filter pump, and measuring the angle of rotation immediately. The concentration of the solution was determined subsequently by comparing it with a standard solution in a photo-electric colorimeter.

A 2 dm. tube was used in all experiments.

l-Tris o,Phenanthroline Iron II d-Antimonyl Tartrate Tetrahydrate.

d,l Tris o,phenanthroline ferrous sulphate was prepared by the addition of finely divided o,phenanthroline monohydrate (2.2 g.) to a solution of ferrous sulphate heptahydrate (1.2 g.) in water (100 ml.). The mixture was stirred until the phenanthroline had dissolved completely. To the deep red solution of tris o,phenanthroline ferrous sulphate a solution of potassium d-antimonyl tartrate (2.5 g.) in water (20 ml.) was added slowly. On scratching the sides of the vessel a dark red crystalline substance was obtained. The reaction mixture was cooled rapidly in ice and the precipitate filtered off immediately. The crystalline substance was found to be pure l-tris o,phenanthroline ferrous d-antimonyl tartrate. It was practically insoluble in water but could be recrystallised by solution in 0.1 N caustic soda (50 ml.) and reprecipitation with the addition of acetic acid and a little potassium antimonyl tartrate. The substance crystallised in dark red needles.

A 0.0100% solution in water gave $\alpha_D = -0.19^\circ$, whence $[\alpha]_D^{25} = -950^\circ$.

Found: Fe = 4.37%; Sb = 19.54%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{SbO}_2\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$: Fe = 4.50%; Sb = 19.63%.

l-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The l-tris o,phenanthroline ferrous d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 ml.) by shaking at about 5° C., and the solution filtered. Sodium perchlorate solution was then added slowly and on scratching the sides of the vessel a red crystalline precipitate was obtained. This, after immediate filtration, washing with ice water and drying, gave the pure l-perchlorate in microprismatic needles. The substance was appreciably soluble in water, very soluble in acetone and sparingly soluble in alcohol.

A 0.0144% solution in water gave $\alpha_D = -0.41^\circ$, and a 0.0126% solution in water gave $\alpha_D = -0.355^\circ$, whence $[\alpha]_D^{25} = -1416^\circ$.

Found: Fe = 6.53%; N = 10.04%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$: Fe = 6.58%; N = 9.90%.

d-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The mother liquid of the original precipitate with potassium antimonyl tartrate was strongly dextrorotatory. The cold solution (5° C.) was treated immediately with sodium perchlorate solution. (Avoiding an excess to prevent the precipitation of potassium perchlorate.) The resulting red crystalline precipitate was the pure perchlorate of the dextro complex forming microprisms and needles.

A 0.0111% solution in water gave $\alpha_D = +0.32^\circ$ and a 0.0123% solution in water gave $\alpha_D = +0.35^\circ$, whence $[\alpha]_D^{25} = +1432^\circ$.

Found: Fe = 6.53%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$: Fe = 6.58%.

SUMMARY.

Tris o,phenanthroline iron II perchlorate has been resolved through the d-antimonyl tartrate. The optical forms were stable in the solid state for some months, but racemised rapidly in solution. After oxidation of the enantiomorphous forms with ceric sulphate at 6° C., the resulting blue iron III complex was found to possess a fleeting activity.

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Department of Chemistry,
University of Sydney.



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