

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF SYDNEY]

The Preparation of the Optical Forms of Tris-2,2'-Dipyridyl Iron(III) and Tris-1,10-phenanthroline Osmium(III) Perchlorates

BY F. P. DWYER AND E. C. GYARFAS

RECEIVED MARCH 4, 1952

Dextro and levo tris-2,2'-dipyridyl-iron(II) perchlorates were oxidized by ceric ammonium nitrate in 0.1 *N* nitric acid, and the resulting solution precipitated with sodium perchlorate the active blue crystalline perchlorates $\text{Fe}(\text{dipy})_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ for which $[\alpha]_{5461}^{16} \pm 260^\circ$. This is the first iron(III) cationic complex to be obtained in enantiomorphic forms. Tris-1,10-phenanthroline osmium(II) salts were oxidized by chlorine to the corresponding red osmium(III) compounds. In this way *d*- and *l*-tris-1,10-phenanthroline osmium(III) perchlorates were obtained for which $[\alpha]_{5461}^{20} \pm 400^\circ$.

The well known red tris-2,2'-dipyridyl iron(II) salts are reversibly oxidized to the blue iron(III) salts—the potential of the reaction being approximately 1 volt.^{1,2} The chloroplatinate³ and perchlorate² of the iron(III) complex have been obtained in crystalline form. Werner⁴ isolated *l*-tris-2,2'-dipyridyl iron(II) bromide and iodide hexahydrates through the *d*-tartrate for which $[\alpha]_{20D}^{20}$ was -520 and -440° , respectively. Recently⁵ both antipodal forms of the perchlorate dihydrate were prepared through the iodide antimony tartrate, $[\text{Fe}(\text{dipy})_3]_3 \cdot \text{I}_2 \cdot (\text{SbOTart.})_4 \cdot 18\text{H}_2\text{O}$ with the very much higher rotations of $+4800$ and -4100° . When the active perchlorates were suspended in ice-water and treated with chlorine or ceric ammonium nitrate and nitric acid they dissolved giving blue solutions from which the active perchlorates were precipitated with sodium perchlorate. Since the half-life of the active iron(III) complex ion in solution is only a few minutes the various operations must be conducted very quickly. Although oxidation with chlorine is preferable, since the subsequent purification of the precipitated perchlorate is easier, the rate of oxidation was found to be surprisingly slow, and even though it was increased by the addition of the finely powdered substance to chlorine-saturated ice-water containing an electrolyte such as sodium nitrate, appreciable racemization was found to occur. The method ultimately used was the addition of ice-cold 0.5 *N* nitric acid to a finely powdered mixture of ceric ammonium nitrate and the active ferrous perchlorate. The solid iron(III) complex became grayish and finally purplish after a week in a desiccator over phosphorus pentoxide but still possessed some activity. In solution no rotation was evident after five minutes at 15° . Like the *dl*-perchlorate and chloroplatinate, the blue color was stable in slightly acid solution, but rapidly changed to purplish and then red in neutral solution, and instantly, to red in alkaline solution. This reaction was observed by Blau,³ and also occurred with the phenanthroline iron(III) complex and the complexes of both chelate groups with ruthenium(III) and osmium(III). An odor of ozone is associated with the reduction, and after a short time hydrogen peroxide can also be detected by

the perchromic acid test if amyl acetate is substituted for ether as the extractant. If the alkaline solution is immediately acidified the complex is re-oxidized—but not on standing. Since neither ozone nor hydrogen peroxide oxidizes the bivalent complex ion at room temperature an unstable intermediate oxidation product of hydroxyl ion must be formed, which decomposes irreversibly to yield ozone or hydrogen peroxide. This intermediate is probably the O_2^- ion.

As noted previously,⁶ *d*- and *l*-tris-1,10-phenanthroline iron(II) salts could be oxidized to the active ferric compounds in solution. The activity, however, was so fleeting that the rotation could not be measured even at 6° .

Tris-1,10-phenanthroline osmium(II) salts were recently prepared and resolved.⁷ The intensely dark greenish-brown ion $\text{Os}(\text{phenan})_3^{++}$ was found to be reversibly oxidized to the red $\text{Os}(\text{phenan})_3^{+++}$ ($E = 0.859$ in 0.1 *N* HCl).⁸

The *dl*-perchlorate and chloride and the active perchlorates have now been prepared by oxidation with chlorine at $0-4^\circ$ and isolated in crystalline form. The solid substances varied in color from red to blue-gray depending on the particle size. The solutions were dichroic being blue in dilute solution and red in more concentrated solution. The active perchlorates were optically stable in solution at room temperature and had $[\alpha]_{5461}^{20} +380^\circ$ and -360° —but no rotation was observed in the NaD line.

Experimental

All rotations were measured in a 1-dm. tube using a mercury vapor lamp with filter as the source of the 5461 Å. line.

***d*-Tris-2,2'-dipyridyl Iron(III) Perchlorate Trihydrate.**—*d*-Tris-2,2'-dipyridyl iron(II) perchlorate dihydrate (0.5 g.) and dry ceric ammonium nitrate (0.4 g.) were placed in a mortar, cooled on ice and finely ground. Ice-cold 0.5 *N* nitric acid (12 ml.) was added immediately and the mixture stirred for 10–15 seconds before filtering through a cold sintered glass filter. The bright blue filtrate was treated at once with cold 20% sodium perchlorate solution (2 ml.), crystallization was induced both by scratching the sides of the vessel and by vigorous shaking. The blue microcrystalline precipitate was filtered rapidly. The above operations were carried out approximately in one minute. The precipitate was washed successively with a 5% sodium perchlorate (2 ml.) containing a little chlorine, absolute alcohol (5 ml.) and finally pure ether. It was then placed in a desiccator containing phosphorus pentoxide and chlorine, and allowed to dry for 15 minutes at a pressure of 0.5 atmos-

(1) G. H. Walden, L. P. Hammett and R. P. Chapman, *THIS JOURNAL*, **53**, 3909 (1931).

(2) F. P. Dwyer and H. A. McKenzie, *J. Proc. Roy. Soc. N.S.W.*, **81**, 97 (1947).

(3) F. Blau, *Monatsh.*, **10**, 647 (1898).

(4) A. Werner, *Ber.*, **46**, 433 (1912).

(5) F. P. Dwyer and E. C. Gyarfás, *J. Proc. Roy. Soc. N.S.W.*, **85**, 126 (1951).

(6) F. P. Dwyer and E. C. Gyarfás, *ibid.*, **83**, 263 (1949).

(7) F. P. Dwyer, E. C. Gyarfás and N. A. Gibson, *ibid.*, **84**, 68 (1950).

(8) F. P. Dwyer, E. C. Gyarfás and N. A. Gibson, *ibid.*, **84**, 80 (1950).

phere before its rotation was determined. A 0.05% solution in 0.01 *N* HNO₃ containing a trace of ceric ammonium nitrate gave $\alpha_{5461} + 0.13^\circ$, whence $[\alpha]^{15}_{5461} + 260^\circ$ and $[M]^{15}_{5461} + 2400^\circ$. The rotation in the NaD line was slightly dextro. The degree of hydration of the substance was variable owing to the use of a strong desiccant.

Anal. Calcd. for Fe(C₁₀H₈N₂)₃(ClO₄)₃·3H₂O: Fe, 6.37; N, 9.59. Found: Fe, 6.28; N, 9.50.

1-Tris-2,2'-dipyridyl Iron(III) Perchlorate Trihydrate.—This was obtained in the same manner as the dextro compound, using instead *l*-tris-2,2'-dipyridyl ferrous perchlorate as a microcrystalline powder. A 0.05% solution in the same medium as above gave $\alpha_{5461} - 0.13^\circ$, whence $[\alpha]^{15}_{5461} - 260^\circ$.

Anal. Calcd. for Fe(C₁₀H₈N₂)₃(ClO₄)₃·3H₂O: Fe, 6.37; N, 9.59. Found: Fe, 6.40; N, 9.63.

***dl*-Tris-1,10-phenanthroline Osmium(III) Chloride Monohydrate.**—*dl*-Tris-1,10-phenanthroline osmium(II) chloride octahydrate (0.2 g.) in methanol (10 ml.) at 0°, was treated with chlorine gas until the dark brown solution became bluish-red. The osmic complex was immediately precipitated with ether, and the precipitate washed first with 50% methanol ether and then ether.

The dark red micro needles were very soluble in water giving a brilliant bluish-red solution which rapidly turned brown due to reduction. The substance was more stable in the solid state.

Anal. Calcd. for Os(C₁₂H₈N₂)₃·Cl·H₂O: Os, 22.24; N, 9.83. Found: Os, 22.1; N, 9.9.

***dl*-Tris-1,10-phenanthroline Osmium(III) Perchlorate Monohydrate.**—*dl*-Tris-1,10-phenanthroline osmium(II) perchlorate dihydrate (0.5 g.) was suspended in 20 ml. of water, cooled to 0° and treated with chlorine until the substance went

into solution. The deep reddish-blue solution was warmed to 20°, 10% sodium perchlorate was added until the solution became cloudy and then precipitation was brought about by cooling the mixture on ice and by scratching the sides of the vessel. The precipitate was filtered through a sintered glass filter, washed quickly first with cold absolute alcohol, then with ether and dried in warm air.

The monoclinic prisms were dark red with a grayish-blue reflex. The aqueous solutions rapidly underwent self reduction except in the presence of chlorine or acid.

Anal. Calcd. for Os(C₁₂H₈N₂)₃(ClO₄)₃·H₂O: Os, 18.17; N, 8.03. Found: Os, 18.3; N, 8.1.

***d*-Tris-1,10-Phenanthroline Osmium(III) Perchlorate Monohydrate.**—*d*-Tris-1,10-phenanthroline osmium(II) perchlorate was treated as the *dl*-perchlorate above. The bluish-red prisms of the active perchlorate were more soluble than the racemate. A 0.01% solution in water containing a trace of chlorine gave $\alpha = +0.04^\circ$, whence $[\alpha]^{20}_{5461} + 400^\circ$, and $[M]^{20}_{5461} + 4200^\circ$. No rotation was observed in the NaD line.

Anal. Calcd. for Os(C₁₂H₈N₂)₃(ClO₄)₃·H₂O: Os, 18.17; N, 8.03. Found: Os, 18.3; N, 8.10.

***l*-Tris-1,10-Phenanthroline Osmium(III) Perchlorate Monohydrate.**—The bluish-red prisms of this substance were prepared from *l*-tris-1,10-phenanthroline osmium perchlorate in the same manner as the *dl*-compound. A 0.01% solution in water containing chlorine gave $\alpha - 0.04^\circ$, whence $[\alpha]^{20}_{5461} - 400^\circ$.

Anal. Calcd. for Os(C₁₂H₈N₂)₃(ClO₄)₃·H₂O: Os, 18.17; N, 8.03. Found: Os, 18.1; N, 8.0.

SYDNEY, AUSTRALIA

NOTES

Preparation of Alkyl Isocyanates Using Alkyl Phosphates

BY THEODORE I. BIBBER¹

RECEIVED APRIL 10, 1952

Isocyanic esters are generally prepared by the phosgenation of primary amines or by the Curtius rearrangement of acyl azides, but the alkylation of an inorganic cyanate constitutes a convenient method in some cases. Ethyl isocyanate may thus be prepared by the reaction of potassium cyanate with potassium ethyl sulfate,² ethyl sulfate³ or ethyl *p*-toluenesulfonate.³ A satisfactory yield is obtainable only with ethyl sulfate as the ethylating agent. However, the resulting ethyl isocyanate has been observed by us to polymerize very readily, even after several redistillations. It appears likely that this polymerization is catalyzed by sulfur dioxide, a known decomposition product of ethyl sulfate at the alkylation temperature used, and that distillation does not achieve the complete separation of this gas from the low-boiling ethyl isocyanate.

We have found that triethyl phosphate, a readily

available substance, is capable of ethylating potassium cyanate at about 200°, affording ethyl isocyanate in good yield. The product so obtained does not polymerize on standing. It should be pointed out that triethyl phosphate is stable at its boiling point (216°), whereas ethyl sulfate boils with considerable decomposition (208°). The reaction of ethyl sulfate with potassium cyanate is rather violent and requires a moderator, like sodium carbonate³; the analogous reaction of triethyl phosphate, however, is smooth and unlikely to get out of control. The fact that triethyl phosphate, in contrast to ethyl sulfate, has no corroding action and is safe to handle, also deserves mention.

The ratio of phosphoric ester to potassium cyanate employed in this reaction is considerably greater than one (on a molar basis), so that the principal reaction leading to ethyl isocyanate must be

$$(C_2H_5O)_3PO + KNCO \longrightarrow (C_2H_5O)_2PO_2K + C_2H_5NCO$$

only one ethyl group of triethyl phosphate being utilized. The use of triethyl phosphate in limited amount gives unsatisfactory results.

Butyl isocyanate was similarly prepared, but in smaller yield, by the reaction of potassium cyanate with tributyl phosphate. Butyl isocyanate has previously been obtained by the Curtius rearrangement of valeryl azide but was not separated from

(1) Address correspondence concerning this paper to the author at 80-40 Lefferts Blvd., Kew Gardens 15, N. Y.

(2) A. Wurtz, *Compt. rend.*, **27**, 241 (1848); *Ann. chim.*, [3] **42**, 43 (1854).

(3) K. H. Slotta and L. Lorenz, *Ber.*, **58**, 1320 (1925).