

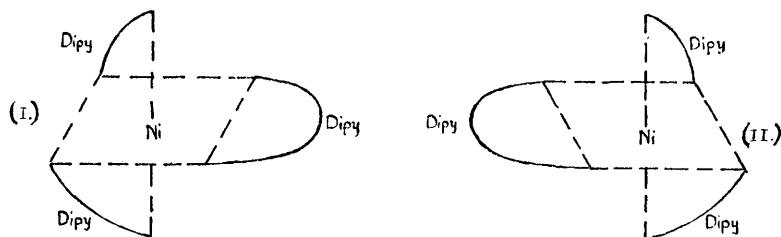
CCCII.—*Researches on Residual Affinity and Co-ordination. Part XXXIII. Optical Activity dependent on Co-ordinated Nickel.*

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WHEN treated with  $\alpha\alpha'$ -dipyridyl (dipy) in aqueous or alcoholic media, simple nickel salts furnish well-defined, stable, pink complex salts of general formula  $[\text{Ni } 3\text{dipy}]\text{X}_2 \cdot y\text{H}_2\text{O}$ , and the first member of this series, the bromide, was described as  $[\text{Ni } 3\text{dipy}]\text{Br}_2 \cdot 6\frac{1}{2}\text{H}_2\text{O}$  by Blau (*Monatsh.*, 1898, **19**, 647).

We have now prepared *tris- $\alpha\alpha'$ -dipyridylnickelous chloride, bromide, iodide, nitrate, carbonate, and tartrate*, all as hexahydrated salts, whereas *tris- $\alpha\alpha'$ -dipyridylnickelous thiocyanate* gives a trihydrate.

In stability and colour, these complex nickelous salts are comparable with the analogously constituted deep red co-ordination compounds obtained by Blau (*loc. cit.*) from ferrous salts and  $\alpha\alpha'$ -dipyridyl. Moreover, two of these ferrous compounds, namely, the tris- $\alpha\alpha'$ -dipyridylferrous bromide ( $6\text{H}_2\text{O}$ ) and iodide ( $5\text{H}_2\text{O}$ ), were resolved into optical forms by Werner (*Ber.*, 1912, **45**, 433), who thus demonstrated the octahedral distribution of  $\alpha\alpha'$ -dipyridyl chelate groups round the central ferrous atom. These facts encouraged the hope that similarly constituted complex nickel salts might prove to be resolvable into optically active enantiomorphous forms. We have now accomplished this resolution, and the following enantiomerides (I and II) of tris- $\alpha\alpha'$ -dipyridylnickelous chloride hexahydrate have been obtained in dextro- and lævo-rotatory forms, this optical activity being dependent on co-ordinated nickel.



When excess of ammonium *d*-tartrate was added to an aqueous solution of tris- $\alpha\alpha'$ -dipyridylnickelous chloride hexahydrate, *d*-tris- $\alpha\alpha'$ -dipyridylnickelous *d*-tartrate hexahydrate separated, having  $[\alpha]_{5461}^{18.5^\circ} + 590^\circ$  and  $[M] + 4621^\circ$ , and this salt when decomposed with ammonium chloride gave *d*-tris- $\alpha\alpha'$ -dipyridylnickelous chloride hexahydrate, with  $[\alpha]_{5461}^{17^\circ} + 529^\circ$  and  $[M] + 3735^\circ$ . Another specimen of this chloride, submitted for confirmation to Dr. Sugden, gave  $[\alpha]_{5791}^{20^\circ} + 550^\circ$  with  $[M] + 3883^\circ$ .

The corresponding *l*-tris- $\alpha\alpha'$ -dipyridylnickelous chloride hexahydrate was isolated by the use of ammonium *l*-tartrate and showed a rotation  $[\alpha]_{5461}^{15^\circ} - 501^\circ$  and  $[M] - 3536^\circ$ . These active salts racemise with great facility in aqueous solution at room temperature, so that after  $1\frac{1}{2}$  hours the *d*- and *l*-complex nickel chlorides become quite inactive. They are, however, more stable in the solid state, and may be kept for a few days without complete loss of activity.

Earlier attempts to isolate optically active co-ordinated nickel salts were made by Mann and Pope (*J.*, 1926, 486), who attempted unsuccessfully a resolution of the tris(aminotriethylamine)bis-nickelous complex, and by Bucknall and Wardlaw (*J.*, 1928, 2739), who failed to resolve trisethylenediaminonickelous chloride.

Meanwhile, Wahl had stated that he had obtained an active form

of bisaquobisethylenediamminonickel tartrate, but without mentioning the conversion of this tartrate into an optically active salt of any inactive acid [*Soc. Sci. Fennica Comm. Phys. Math.*, 1927, **4**, (14), 1]. The data on which this alleged resolution is based are very scanty.

#### EXPERIMENTAL.

*Tris- $\alpha\alpha'$ -dipyridylnickelous Chloride Hexahydrate.*—When  $\alpha\alpha'$ -dipyridyl (23.4 g.) was added to nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 11.8 g.), dissolved in water, the crystals of the base acquired a pink tint, and on warming dissolved with formation of a deep red solution. The pink complex salt separated on cooling. This salt and the following halides were crystallised from warm water and dried over concentrated sulphuric acid (Found: Ni, 8.02, 8.27; Cl, 10.06, 9.92; N, 11.50.  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$  requires Ni, 8.31; Cl, 10.04; N, 11.91%). This stable complex salt was easily soluble in water, and on slow crystallisation of its aqueous solution gave large, deep red prisms. The chloride and the two succeeding halides also dissolved readily in alcohol, but were insoluble in other organic solvents. The complex nickel salt was precipitated unchanged from its aqueous solution by addition of an excess of a soluble chloride, but was decomposed into its generators on heating with dilute hydrochloric acid. Furthermore, tris- $\alpha\alpha'$ -dipyridylnickelous chloride was not affected by dilute aqueous alkalis, although cold 50% caustic potash gave a pink microcrystalline precipitate of the free complex base, which, however, decomposed on warming or keeping into hydrated nickel oxide and  $\alpha\alpha'$ -dipyridyl. The water of crystallisation in the hexahydrated complex chloride was firmly held, but on heating at  $110^\circ$  half was eliminated (Found:  $\text{H}_2\text{O}$ , 7.25.  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$  requires  $3\text{H}_2\text{O}$ , 7.64%). This tris- $\alpha\alpha'$ -dipyridylnickel chloride was produced even on using excess of nickel chloride.

*Tris- $\alpha\alpha'$ -dipyridylnickelous Bromide Hexahydrate.*—An excess of aqueous sodium bromide was added to a warm solution of the foregoing chloride, whereupon the complex bromide separated as a pink crystalline precipitate, which was recrystallised from boiling water (Found: Ni, 7.19; Br, 20.18; N, 10.71.  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Br}_2\text{Ni} \cdot 6\text{H}_2\text{O}$  requires Ni, 7.38; Br, 20.11; N, 10.58%).

*Tris- $\alpha\alpha'$ -dipyridylnickelous iodide hexahydrate* was deposited as a sparingly soluble precipitate from solutions of the corresponding chloride by addition of aqueous sodium iodide; it separated from a large volume of hot water in very pale pink plates (Found: Ni, 6.46; I, 28.46; N, 9.56.  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{I}_2\text{Ni} \cdot 6\text{H}_2\text{O}$  requires Ni, 6.60; I, 28.49; N, 9.46%). The crystals of this complex iodide acquired a brown tint on keeping, but their composition was not materially affected.

*Tris- $\alpha\alpha'$ -dipyridylnickelous nitrate hexahydrate* was formed when

concentrated ammonium nitrate was added to a solution of the corresponding chloride, or when nickel nitrate and  $\alpha\alpha'$ -dipyridyl were heated in aqueous solution; it crystallised from a small quantity of warm water and was air-dried (Found: Ni, 7.62; N, 15.05.  $C_{30}H_{24}O_6N_8Ni \cdot 6H_2O$  requires Ni, 7.83; N, 14.96%). This complex nickel nitrate lost five of its six molecules of water of crystallisation over concentrated sulphuric acid or when heated at  $100^\circ$  (Found: loss, 11.80.  $C_{30}H_{24}O_6N_8Ni \cdot 6H_2O$  requires  $5H_2O$ , 12.03%).

*Tris- $\alpha\alpha'$ -dipyridylnickelous thiocyanate trihydrate* separated when aqueous solutions of the analogous chloride and concentrated potassium thiocyanate were mixed. The pink leaflets were crystallised from warm water. This salt and the two succeeding preparations were dried over concentrated sulphuric acid (Found: Ni, 8.31; N, 16.10, 15.80.  $C_{32}H_{24}N_8S_2Ni \cdot 3H_2O$  requires Ni, 8.42; N, 16.08%). The complex thiocyanate resembled the bromide in its solubility.

*Tris- $\alpha\alpha'$ -dipyridylnickelous tartrate hexahydrate* was produced by adding the equivalent quantity of tartaric acid to a solution of tris- $\alpha\alpha'$ -dipyridylnickelous hydroxide (see below), and isolated by evaporating the solution to small volume or by precipitation with acetone; it crystallised in small salmon-pink needles, very soluble in water and alcohol (Found: C, 51.90; H, 5.30; Ni, 7.41.  $C_{34}H_{28}O_6N_6Ni \cdot 6H_2O$  requires C, 52.11; H, 5.15; Ni, 7.49%).

*Tris- $\alpha\alpha'$ -dipyridylnickelous carbonate hexahydrate*, formed when carbon dioxide was passed through a solution of tris- $\alpha\alpha'$ -dipyridylnickelous hydroxide (see below), crystallised from a small quantity of water (Found: C, 53.27; H, 5.50; N, 11.77; Ni, 8.21.  $C_{31}H_{24}O_3N_6Ni \cdot 6H_2O$  requires C, 53.51; H, 5.22; N, 12.10; Ni, 8.44%). This salt, which was readily soluble in water or alcohol, crystallised from these solvents in small pink needles.

*Tris- $\alpha\alpha'$ -dipyridylnickelous Hydroxide*.—A solution of this base was formed when one of the corresponding halides was treated with freshly prepared silver oxide. It could not, however, be isolated, since evaporation led to considerable decomposition with deposition of hydrous nickel oxide.

#### *Optical Resolutions of Complex Nickel Salts.*

*d-Tris- $\alpha\alpha'$ -dipyridylnickelous d-Tartrate*.—Tris- $\alpha\alpha'$ -dipyridylnickelous chloride hexahydrate (2.5 g.) was dissolved in cold distilled water (110 c.c.), and neutral ammonium *d*-tartrate (60 g.) was added all at once to the mechanically stirred solution. Small pink needles of the *d*-tris- $\alpha\alpha'$ -dipyridylnickelous *d*-tartrate hexahydrate soon appeared, and when the mixture had been stirred for 45 minutes,

the solution was decanted from any undissolved ammonium *d*-tartrate, cooled to 0°, left in the melting ice with occasional shaking for 45 minutes, and then drained from the precipitated complex nickel salt. A portion of this tartrate was well pressed on a porous plate and dried over sulphuric acid for an hour. A 0.5% solution in a 2-dm. tube gave  $\alpha = +5.90^\circ$ ,  $[\alpha]_{5461}^{18.5^\circ} = +590^\circ$ ,  $[M] + 4621^\circ$ . This rotation fell to a constant value of  $+0.14^\circ$  after one hour.

*d*-Tris- $\alpha'$ -dipyridylnickelous Chloride Hexahydrate.—The foregoing freshly prepared and undried tartrate was dissolved in 40–50 c.c. of cold water, and excess of 2*N*-ammonium chloride was added; the *d*-tris- $\alpha'$ -dipyridylnickelous chloride then separated in small, very pale pink plates, which were at once collected and washed with cold ammonium chloride solution until free from tartrate. The active chloride was then pressed on porous porcelain and dried over sulphuric acid for an hour. A 0.5% solution in a 2-dm. tube gave  $\alpha = +5.29^\circ$ ;  $[\alpha]_{5461}^{17^\circ} + 529^\circ$ ,  $[M] + 3735^\circ$ . Another specimen examined by Dr. Sugden gave  $\alpha = +5.50^\circ$ ,  $[\alpha]_{5791}^{20^\circ} = +550^\circ$ ,  $[M] + 3883^\circ$ .

The following table gives the racemisation of the active chloride in aqueous solution;  $k$  was calculated according to the equation  $k = 1/t \cdot \log_{10} \theta_0/\theta_t$ .

1st Series (at 17°).			2nd Series (at 20°) (Dr. Sugden).		
<i>t</i> (mins.).	$\alpha$ .	<i>k</i> .	<i>t</i> (mins.).	$\alpha$ .	<i>k</i> .
—	5.29°	—	—	5.50°	—
5	4.35	0.017	3	4.14	0.041
10	3.51	0.018	5	3.68	0.035
15	2.54	0.021	7	3.23	0.033
20	2.05	0.020	10	2.35	0.037
30	1.35	0.019	15	1.70	0.034
42	0.82	0.019	30	0.64	0.031
48	0.52	0.023	45	0.18	0.033
60	0.29	0.021	60	0.08	—
83	0.13	0.019			
115	0.01	—			

Although the active chloride racemised rapidly in aqueous solution, the dried chloride could be kept for some time in a cool dry place without undue loss of activity. For instance, after 5 days the activity of the substance had only dropped to about half its original value,  $\alpha = +2.87^\circ$ ,  $[\alpha]_{5461}^{19^\circ} + 287^\circ$  ( $c = 0.5$ ,  $l = 2$ ).

*l*-Tris- $\alpha'$ -dipyridylnickelous Chloride Hexahydrate.—This active chloride was prepared in exactly the same manner as the foregoing dextrorotatory complex chloride, ammonium *l*-tartrate being substituted for ammonium *d*-tartrate, but only half the actual quantities of material being employed. A 0.5% solution at 18° in a 2-dm. tube gave  $\alpha = -5.01^\circ$ ,  $[\alpha]_{5461}^{18^\circ} - 501^\circ$ ,  $[M] - 3536^\circ$ .

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