

# Chromatographic Separation and Optical Activity of Co(III) Complexes with Mixed Ethylenediamine—Trimethylenediamine Coordination Spheres

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A paper chromatographic method is developed for separation and purification of  $[\text{Co en}_3\text{tn}]^{3+}$  and  $[\text{Co en tn}_2]^{3+}$ . Both complexes are resolved in the form of their bromides by means of nitro-(+)<sub>D</sub>-camphor. The less soluble nitro-camphorates yield the (+)<sub>D</sub>-bromides.

Absorption, circular dichroism and rotatory dispersion spectra are presented, and dipole and rotatory strengths compared to those of  $[\text{Co en}_3]^{3+}$  and  $[\text{Co tn}_3]^{3+}$ .

It is concluded that the (+)<sub>D</sub> enantiomers of the mixed complexes have the same absolute configuration, *A*, as (+)<sub>D</sub>- $[\text{Co en}_3]^{3+}$  and (-)<sub>D</sub>- $[\text{Co tn}_3]^{3+}$ .

The "first absorption band" ( $450 < \lambda_{\text{max}} < 500$  nm) of tris(diamine) chelates of Co(III) and Cr(III), in which the central atom is a member of three identical five-membered rings exhibit rotatory strengths (in aqueous solution), which appear to be only slightly dependent upon the constitution of the diamine. The slight deviation from octahedral symmetry of a tris(diamine) Co(III) chromophore can be well approximated as  $D_3$ . Under this point group the  ${}^1T_{1g}$  state is split into  ${}^1E$  and  ${}^1A_2$  states. The rotatory strength of the  ${}^1A_1 \rightarrow {}^1E$  transition increases in the series 1,2-ethanediamine (en), 1,2-propanediamine (pn), 2,3-butanediamine (2,3-bn) and 2-methyl-1,2-propanediamine (i-bn).<sup>1,2</sup> The rotatory strength of the other component of the first band the  ${}^1A_1 \rightarrow {}^1A_2$  transition, increases on substitution by optically active pn and 2,3-bn, but decreases on substitution by *meso*-2,3-bn and i-bn. An increase in net rotatory strength ( $\sum R$ ) on substitution

by an optically inactive diamine is accompanied by an increase in molar extinction so that the dissymmetry factor  $g \equiv (\epsilon_l - \epsilon_d)/\epsilon^*$  remains almost unchanged. The average extinction coefficient  $\epsilon$  is defined as  $\epsilon^* = (\epsilon_l + \epsilon_d)/2$ . Note that a substance circularly dichroic at wavelength  $\lambda$  does not obey Lambert's (or Beer's) law for light of wavelength  $\lambda$  polarized otherwise than circularly,<sup>3</sup> and that it is therefore theoretically meaningless to speak of its "extinction coefficient,  $\epsilon$ , at  $\lambda$ ". In practice,  $\epsilon$  as measured without specification of the polarization state of the light is usually a satisfactory approximation<sup>3</sup> to  $\epsilon^*$ .

This suggests that changes in degree of "forbiddenness" of the electronic transitions rather than changes in the relative steric disposition of their electric and magnetic dipole moments are responsible for the changes in rotatory strengths.

An effect of a different nature could be expected when the diamines of the type mentioned above were replaced by a diamine, the chelation of which results in the formation of a six-membered ring, and this expectation caused us to undertake a study of tris(diamine) chelates involving 1,3-propanediamine ("trimethylenediamine", tn). The most conspicuous effect, a drastic reduction of the rotatory strengths occurring with a coordination sphere consisting of three trimethylenediamine molecules, has been reported earlier by one of us.<sup>4</sup> The present paper deals with our subsequent investigations of the tris(trimethylenediamine)

and the mixed en-tn Co(III) complexes. Among the results are the preparation and resolution of  $[\text{Co en tn}_2]^{3+}$  and the resolution of  $[\text{Co en}_2\text{tn}]^{3+}$ , which are here reported for the first time. Part of our results were presented in a preliminary communication.<sup>5</sup>

After the completion of this work, the methods developed here were used in a study of the analogous Cr(III) complexes.<sup>6</sup>

## EXPERIMENTAL

"Pure complexes".  $(+)\text{-D-}[\text{Co en}_3]^{3+}$  and  $(-)\text{-D-}[\text{Co tn}_3]^{3+}$  were obtained by standard methods, using *d*-tartaric acid and nitro- $(+)\text{-D-}$  camphor as resolving agents.

"Mixed complexes". According to Bailar and Work<sup>7</sup>  $[\text{Co en}_2\text{tn}]\text{Cl}_3$  may be prepared by the reaction of  $[\text{Co en}_2\text{Cl}_2]^+$  with tn. As we have shown by the chromatographic procedure described below, the products thus prepared are generally contaminated by  $[\text{Co en}_3]^{3+}$  and/or  $[\text{Co en tn}_2]^{3+}$ , and the mere analytical result corresponding stoichiometrically to the formula  $[\text{Co en}_2\text{tn}]^{3+}$  is therefore no indication of purity. Salts of  $[\text{Co en tn}_2]^{3+}$  are not easily obtained by an analogous procedure, and we have been able to obtain only rather impure preparations<sup>8</sup> by, e.g., reacting  $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$  or  $[\text{Co tn}_2\text{CO}_3]^+$  with en at various acidities in water or dimethylsulfoxide as solvents. Again the impurities in the salts isolated are the different tris(diamine)chelates. In view of the kinetic inertness characteristic of all of these chelates once they are formed this tendency to "randomisation of the sphere of coordination" is a somewhat unexpected feature of the reactions described.

*Chromatographic separation.* Being unable, e.g. by repeated recrystallization and by fractional precipitation, to isolate pure preparations of either of the mixed complexes directly from the mixtures resulting from the above-mentioned substitution reactions, we resorted to develop a preparative chromatographic method capable of separating all of the four possible tris(diamine) complex ions. For the purpose of preparing  $[\text{Co en tn}_2]^{3+}$  we have chosen to apply this method to the mixtures obtained from the oxidation of solutions of cobalt(II) chloride containing ethylenediamine and trimethylenediamine in amounts sufficient for the complete conversion of the cobalt to tris(diamine)complexes and in a ratio promoting the formation of the desired complex. Such reaction mixtures invariably contain all of the four possible tris(diamine)complexes (in ratios partly depending upon the initial concentration ratio of en and tn), and when the oxidation is carried out in the presence of activated charcoal these account for almost all of the cobalt present. (In the

absence of charcoal varying amounts of unidentified, probably polynuclear species are formed.)

Numerous publications deal with the separation of transition metal complexes by chromatographic methods. Suffice it to mention Jensen *et al.*,<sup>9</sup> Dwyer *et al.*<sup>10</sup> and Druding and Hagel,<sup>11</sup> who describe separation of luteo complexes, among others, by column, paper and thin-layer chromatography. A paper chromatographic technique was chosen for the present work.

All experiments were carried out using 1 mm thick Whatman 3MM paper. Three techniques were employed: ascending chromatography on  $10 \times 140 \text{ mm}^2$  strips, and descending on  $155 \times 190 \text{ mm}^2$  and on  $460 \times 570 \text{ mm}^2$  sheets. The first-mentioned was used for the initial screening of eluent formulations, the second for further development of the more promising ones, and the third for chromatography on a preparative scale.

After a long series of experiments, the following eluent formation was found satisfactory: 1-butanol-acetone-"liquid phenol" (90% phenol, 10% water)-pyridine-benzene-water-80% acetic acid (14:14:30:14:14:4:7 by volume).

$[\text{Co en}_2\text{tn}]^{3+}$  was conveniently obtained as a by-product from the preparation of  $[\text{Co en tn}_2]^{3+}$ . However, for the purpose of isolating solely  $[\text{Co en}_2\text{tn}]^{3+}$  we recommend the application of the chromatographic separation to the mixture obtained by the preparation of  $[\text{Co en}_2\text{tn}]\text{Cl}_3$  according to Bailar and Work,<sup>7</sup> which contains  $[\text{Co en}_2\text{tn}]^{3+}$  in a higher proportion (>ca. 60% of the Co) than any of the mixtures obtainable directly from the oxidation.

*Preparation of  $[\text{Co en tn}_2]\text{Cl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  and  $[\text{Co en}_2\text{tn}]\text{Cl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ .* To a solution of 8.0 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (34 mmol) in 35 ml 1 M HCl was added 6.0 ml (anhydrous) trimethylenediamine (70 mmol), 2.8 ml ethylenediamine monohydrate (34 mmol) and 1.0 g of activated charcoal (in that order). After oxidation for 17 h by a stream of air sufficiently vigorous to keep the charcoal suspended, the charcoal was removed by filtration and the filtrate condensed to 30 ml by evaporation in a stream of air at room temperature. The precipitate formed by the addition of 150 ml abs. ethanol was recovered by filtration and washed with ethanol. Yield after drying in the air 11.3 g (~80%) based upon the reaction scheme  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{enH}_2\text{O} + 2 \text{tn} + \text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow [\text{Co en tn}_2] \cdot 3\frac{1}{2}\text{H}_2\text{O} + 4\text{H}_2\text{O}$ . The mixture of tris(diamine) complex salts thus obtained was separated by descending paper chromatography as follows. The salt mixture was applied to sheets ( $460 \times 570 \text{ mm}^2$ ) in straight lines along the shorter edge (2.5 g of salt to 16 sheets, or approximately 1 mmol per meter).

The chromatograms were developed in glass tanks (Shandon Pangloss Chromatank 2192 Model 500-20 in., four sheets to a tank)

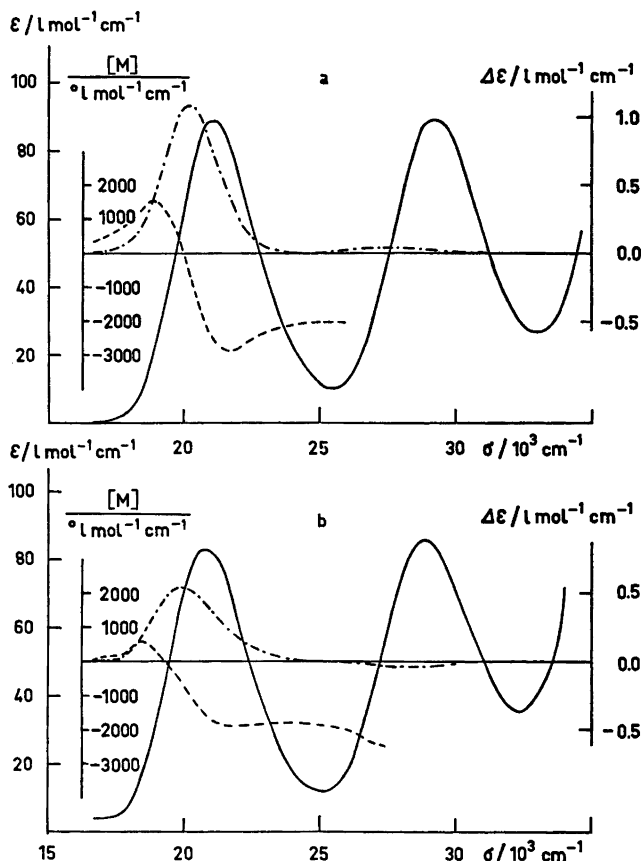


Fig. 1. Absorption (—), rotatory dispersion (---) and circular dichroism (— · —) spectra of (a) (+)<sub>D</sub>-[Co en<sub>2</sub>tn]<sup>3+</sup> and (b) (+)<sub>D</sub>-[Co en tn<sub>2</sub>]<sup>3+</sup>.

at 25 °C for ca. 150 h using the final eluent described above in a quantity of ca. 0.5 liter per sheet.

The chromatogram consisted of four well separated zones representing from top to bottom the ions [Co en<sub>3</sub>]<sup>3+</sup>, [Co en<sub>2</sub>tn]<sup>3+</sup>, [Co en tn<sub>2</sub>]<sup>3+</sup>, and [Co tn<sub>3</sub>]<sup>3+</sup>. The (16 times) two zones containing the desired complexes were cut out (cutting along the front of the [Co en tn<sub>2</sub>]<sup>3+</sup> and [Co en<sub>2</sub>tn]<sup>3+</sup> zones and the tail of the [Co en<sub>2</sub>tn]<sup>3+</sup> zone, this zone being separated from the following zone of [Co en<sub>3</sub>]<sup>3+</sup> by ca. 5 cm of white paper) and extracted each by four successive 200 ml portions of water. The four extracts of each complex were combined, evaporated to dryness in a stream of air at room temperature and the residue dissolved in the smallest possible volume of water (1–2 ml). 130 ml of ethanol: ether (75:25) were added and the chlorides precipitated by subsequent addition of 2.5 ml 4 M HCl. The precipitates were filtered off, rinsed with 96 % ethanol and dried in the air at room

temperature. Yields and analyses: [Co en<sub>2</sub>tn]Cl<sub>3</sub>·3½H<sub>2</sub>O 2.42 g (17 %): found C 19.85; H 6.63; N 19.97; Cl 25.38; Co 12.56; calc. C 19.89; H 6.20; N 19.89; Cl 25.16; Co 13.94. [Co en tn<sub>2</sub>]Cl<sub>3</sub>·3½H<sub>2</sub>O 3.68 g (25 %): found C 21.56; H 7.04; N 19.42; Cl 24.22; Co 12.08; calc. C 22.00; H 6.47; N 19.24; Cl 24.36; Co 13.49.

**Resolution.** *Isolation of (+)<sub>D</sub>-[Co en<sub>2</sub>tn]Br<sub>3</sub> and (+)<sub>D</sub>-[Co en tn<sub>2</sub>]Br<sub>3</sub>·1½H<sub>2</sub>O.* 2.00 g of the complex chloride to be resolved (ca. 4.6 mmol) and 1.50 g sodium nitro-(+)<sub>D</sub>-camphor (6.8 mmol) were dissolved in the smallest sufficient amounts of water at room temperature, and the solutions were mixed. When necessary, a little more water was added in order to obtain a clear solution. The solution was evaporated at room temperature under stirring. A stream of air was applied until the first crystals appeared. The crystallisation was fractionated so that the first fraction of the nitrocamphorate amounted to 1.00–1.20 g (ca. 1.3 mmol) after filtration and rinsing with chilled water. (Caution: The nitrocamphorate of [Co en tn<sub>2</sub>]<sup>3+</sup>

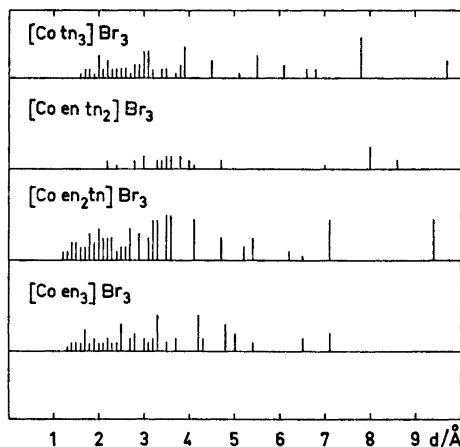


Fig. 2. X-Ray powder diagrams of the bromides. Heights indicate relative intensities.

is considerably more soluble in water than that of  $[\text{Co en}_2\text{tn}]^{3+}$ . Further fractions may be obtained by the addition of 0.5 g sodium nitrocamphor so that the (+)<sub>D</sub>-enantiomer may in both cases be almost quantitatively isolated.

The first fractions of the nitrocamphorates were converted to bromides. 1.15 g of the  $[\text{Co en}_2\text{tn}]^{3+}$  salt was agitated with 1.5 ml 48 % HBr and 30 ml ethanol for 4 h, filtered, washed with ethanol and air-dried; yield 0.59 g (82 %). 1.00 g of the  $[\text{Co en tn}_2]^{3+}$  salt was dissolved in 1.5 ml 48 % HBr, precipitated with 250 ml ethanol, centrifuged, washed with ethanol and air-dried; yield 0.53 g (84 %). Analyses: (+)<sub>D</sub>- $[\text{Co en}_2\text{tn}]\text{Br}_3$ ; found C 17.13; H 5.37; N 17.00; Br 48.82; calc. C 17.06; H 5.32; N 17.05; Br 48.63. (+)<sub>D</sub>- $[\text{Co en tn}_2]\text{Br}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ; found C 17.74; H 5.39; N 15.62; Br 44.85; calc. C 17.99; H 5.57, N 15.74; Br 44.90.

Microanalyses for C, H, N and halogens were made by Mr. Preben Hansen, Chemistry Department II, The H. C. Ørsted Institute, University of Copenhagen. Microanalyses for Co were carried out by atomic absorption.<sup>13</sup> Since the completion of our work, similar compounds have been resolved successfully on sephadex resins.<sup>1,2</sup>

## Measurements

*Absorption spectra* were recorded at 25 °C by means of a Cary 14 spectrophotometer. The concentration of the solutions measured was  $10^{-2}$  mol l<sup>-1</sup> with respect to the complex bromides.

*Circular dichroism* was recorded at 25 °C by means of a Roussel-Jouan Dichrographe at concentrations of  $10^{-2}$  mol l<sup>-1</sup>.

*Rotatory dispersion* was measured with a Perkin-Elmer polarimeter model 141 and was also recorded by means of a Cary 11 spectrophotometer with ORD attachment<sup>10</sup>. All measurements were carried out at a concentration of  $10^{-2}$  mol l<sup>-1</sup> and at 25 °C.

*Optical spectra* of (+)<sub>D</sub>- $[\text{Co en}_2\text{tn}]^{3+}$  and (+)<sub>D</sub>- $[\text{Co en tn}_2]^{3+}$  are shown in Fig. 1. The data for the maxima of the first band are, with  $(\sigma, \epsilon)$  and  $(\sigma, \Delta\epsilon)$  in (10<sup>3</sup>cm<sup>-1</sup>, l mol<sup>-1</sup>cm<sup>-1</sup>): (+)<sub>D</sub>- $[\text{Co en}_2\text{tn}]^{3+}$  ABS (21.10, 89), CD (20.20, 1.09); (+)<sub>D</sub>- $[\text{Co en tn}_2]^{3+}$  ABS (20.79, 83), CD (19.92, 0.54).

<sup>1</sup>H NMR spectra were recorded at 25 °C by means of a Varian A 60 spectrometer. Deuteration of the amino groups was accomplished by triple recrystallisation from D<sub>2</sub>O (99.8 %). The solutions measured contained (20 ± 1) % of the complex chlorides in D<sub>2</sub>O.

The spectra of the four possible tris(diamine)-chelates are individually characteristic so that the spectra of the mixed chelates cannot be reproduced by linear combinations of the pure en and tn complexes. In each of the three spectra of the mixed en-tn and the pure tn complexes the methylene protons give rise to two band systems, one attributable to protons at carbon atoms bonded to one nitrogen (low field), and one attributable to protons at C<sub>2</sub> in tn (high field). The ratios of the areas of these two band systems in each case correspond to the theoretical ratios (12:2, 12:4, and 12:6, respectively).

*X-Ray powder photographs* were taken using CoK $\alpha$  radiation and are shown in Fig. 2. Crystals of the racemic bromides were prepared by evaporation of a saturated solution at room temperature. The comminuted crystals were washed with ethanol and dried in air. Attempts at preparing large crystals of the active (+)<sub>D</sub>- $[\text{Co en tn}_2]$ -salt have not been successful. The powder diagrams confirm that the prepared compounds are pure, mixed complexes rather than mixtures of pure complexes.

*Infrared and far infrared spectra* have been reported elsewhere.<sup>15</sup> They also confirm the individuality of the compounds.

## DISCUSSION

The absolute configurations of (+)<sub>D</sub>- $[\text{Co en}_2]^{3+}$  and (-)<sub>D</sub>- $[\text{Co tn}_2]^{3+}$  are known from X-ray work<sup>16,17</sup> to be identical and of the type designated *A*. The gradual change in CD observed in the sequence of complexes shown in the figure strongly suggests that (+)<sub>D</sub>- $[\text{Co en}_2\text{tn}]^{3+}$  and (+)<sub>D</sub>- $[\text{Co en tn}_2]^{3+}$  both possess same absolute configuration (*A*). This is in accordance with the "solubility criterion" when applied to the nitro-(+)<sub>D</sub>-camphorates. After this work was carried out, (+)<sub>D</sub>- $[\text{Co en}_2\text{tn}]^{3+}$

Table 1. Rotatory and dipole strengths of the first absorption band.

	$S \times 10^{38}$ esu	$S_{act} \times 10^{38}$ esu	$\sum R_{obs}$ Biot	$\chi \times 10^{21}$ esu <sup>†</sup>		$\sum R_{calc}$ Biot		
				II	III	I	II	III
(+) <sub>D</sub> -[Co en <sub>3</sub> ] <sup>3+</sup> A-configuration	13.75	4.00	4.68	1.36	0.73			
(+) <sub>D</sub> -[Co en <sub>2</sub> tn] <sup>3+</sup>	14.30	4.55	3.17			3.02	3.11	3.07
(+) <sub>D</sub> -[Co en tn <sub>2</sub> ] <sup>3+</sup>	13.49	3.74	1.87			1.46	1.08	1.36
(-) <sub>D</sub> -[Co tn <sub>3</sub> ] <sup>3+</sup> A-configuration	10.58	0.83	-0.31	-0.20	-0.05			

was found<sup>18</sup> to have the A configuration.

The lower symmetry of the mixed en-tn complexes as compared to the pure en and tn complexes is probably responsible for the fact that the mixed complexes exhibit relatively large dipole strengths within their "first" absorption band.

It has been suggested<sup>8</sup> that the rotatory strength of the "first" absorption band of a mixed tris(diamine) complex might be approximated by a sum of mutually independent contributions from the three chelate rings. Results of examining this hypothesis are presented in Table 1. The dipole and rotatory strengths  $S$  and  $\sum R_{obs}$  are obtained in the usual way from the absorption spectra and the dichrograms. The rotatory strengths of the mixed complexes are calculated under three schemes. In column I,  $\sum R_{calc}$  is obtained by simple linear interpolation between  $\sum R_{obs}$  of the pure complexes. In column II a scheme<sup>19</sup> is used in which the suggestion by Moffitt<sup>20</sup> that only a part,  $S_{act}$ , of the observed dipole strength contributes to the optical activity, is combined with an attempt at taking into consideration the nonlinear variation of the dipole strength caused by the stepwise contribution of en and tn. In this scheme

$$S_{act} = S - S_{[Co(NH_3)_6]^{3+}} = S - 9.75 \times 10^{-38} \text{esu}$$

$$\sum R_{calc} = [(3-x)\chi_{en} + x\chi_{tn}] \sqrt{S_{act}/3}$$

$$\chi = \sum R_{obs} / 3 \sqrt{S_{act}/3}$$

In column III, the same scheme is used, substituting  $S$  for  $S_{act}$ , i.e. disregarding the suggestion due to Moffitt.

In contrast to what is found for the analogous Cr(III) complexes,<sup>8</sup> the results of the three calculation schemes differ appreciably, par-

ticularly for [Co en tn<sub>2</sub>]<sup>3+</sup>. Under all three schemes it is implicitly assumed that the conformation of a five- and of a six-membered chelate ring either has no influence on the rotatory strength or is unchanged through the series. The disagreement suggests that such assumptions may be invalid.

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## REFERENCES

1. Kojima, M., Funaki, H., Yoshikawa, Y. and Yamasaki, K. *To be published.*
2. Kojima, M., Yoshikawa, Y. and Yamasaki, K. *Bull. Chem. Soc. Jap.* 46 (1973) 1687.
3. Woldbye, F. and Bagger, S. *Acta Chem. Scand.* 20 (1966) 1145.
4. Woldbye, F. *Proc. 7th ICCC*, Stockholm 1962, p. 41.
5. Bang, O., Engberg, A., Rasmussen, K. and Woldbye, F. *Proc. 3rd Symp. Coord. Chem. Vol. I*, Akadémiai Kiadó, Budapest 1970, p. 63.
6. Rancke-Madsen, M. and Woldbye, F. *Acta Chem. Scand.* 26 (1972) 3405.
7. Bailar, J. C., Jr. and Work, J. B. *J. Amer. Chem. Soc.* 68 (1946) 232.
8. Woldbye, F. In Snatzke, G., Ed., *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*, Heyden, London 1967, p. 101.
9. Jensen, A., Bjerrum, J. and Woldbye, F. *Acta Chem. Scand.* 12 (1958) 1202.
10. Dwyer, F. P., MacDermott, T. E. and Sargeson, A. M. *J. Amer. Chem. Soc.* 85 (1963) 2913.

11. Druding, L. F. and Hagel, R. B. *Anal. Chem.* **38** (1966) 478.
12. MacDermott, T. E. *Chem. Commun.* (1968) 223.
13. Engberg, A. *Anal. Chim. Acta* **50** (1970) 531.
14. Woldbye, F. *Acta Chem. Scand.* **13** (1959) 2137.
15. Rasmussen, K. *Spectrochim. Acta* **30** (1974) 1763.
16. Nakatsu, K., Shiro, M., Saito, Y. and Kuroya, H. *Bull. Chem. Soc. Jap.* **30** (1957) 158.
17. Nomura, T., Marumo, F. and Saito, Y. *Bull. Chem. Soc. Jap.* **42** (1969) 1016.
18. Schousboe-Jensen, H. V. F. *Acta Chem. Scand.* **26** (1972) 3413.
19. Woldbye, F. *Studier over Optisk Aktivitet*, Polyteknisk Forlag, Copenhagen 1969, p. 217 f.
20. Moffitt, W. J. *Chem. Phys.* **25** (1956) 1189.

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