

# OPTICAL ACTIVITY OF COMPOUNDS FORMED BY AMMINO COMPLEXES OF COBALT(III) AND CARBOHYDRATES—II. D-ARABINOSE COMPLEXES

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**Abstract**—Two sugar-containing chiral complexes are formed by the reaction of *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> and D-arabinose at pH 6. Complex I is a mixed valence cobalt(II)/cobalt(III) paramagnetic species, whereas complex II is a mononuclear cobalt(III) complex. Their syntheses and characterization are described. Visible absorption spectra and IR spectra were recorded. Optical activity was measured via circular dichroism spectra and optical rotatory dispersion. Complex I undergoes anomerization in aqueous solution, the rate of this process being pH and chiral complex dependent. Complex II does not retain its optical activity in aqueous solution as a result of decomposition. Spectral data support the coordination scheme proposed for each complex.

In previous work we reported the preparation and optical activity of amino complexes of cobalt(III) containing D-ribose, L-sorbose and D-glucosamine as the second ligand.<sup>1</sup> We also reported the optical rotatory dispersion (ORD) curves of amino complexes of cobalt(III) and L- or D-arabinose in aqueous solutions.

This work was initially aimed at isolating D-arabinose complexes which we assumed would have a composition similar to that of the complexes previously mentioned. However, two kinds of chiral compounds containing the sugar were obtained in the same reaction: one of them unexpectedly turned out to be the salt of a mixed valence binuclear cobalt(II)/cobalt(III) complex, I; whereas the other was a mononuclear complex salt, II.

This paper reports the optical, spectral, magnetic and chemical characteristics of these complexes and we relate these properties to structural models.

## EXPERIMENTAL

### Materials

Most of the carbohydrates were from Merck. All were used without further purification.

### Methods

Visible absorption spectra were measured on a Zeiss PMQ-2 spectrophotometer in 10<sup>-2</sup>–10<sup>-3</sup> M aqueous solutions. Optical rotatory dispersion measurements were run on a Perkin-Elmer 141 polarimeter modified with a Bausch & Lomb monochromator, with 10<sup>-2</sup> M aqueous solutions, using a 2 cm pathlength cell, connected to a thermostated bath.

The circular dichroism spectra were recorded on a Cary 60 spectropolarimeter using 10<sup>-2</sup> M aqueous solutions in 1 cm pathlength cells. IR spectra of complexes were recorded on a DIGILAB FTIR with a spectral resolution of 2 cm<sup>-1</sup> and KBr pellets, and also on a Leitz Wetzlar III G IR spectrometer. The chloride forms of complexes I and II were employed to avoid the strong sulphate bands.

Carbon, hydrogen and nitrogen were analysed with a Perkin-Elmer 240-C analyser. The Co content was determined by atomic absorption spectroscopy with a Perkin-Elmer 305 spectrometer. The sulphate content was determined by conductimetric titration with a standard BaCl<sub>2</sub> solution<sup>2</sup> in a YSI model 32 conductivity meter.

Magnetic susceptibility measurements at 298 K were carried out by the Gouy method. The susceptibility was also determined in the 2.5–300 K

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range with an SHE magnetometer connected to an SQUID sensor.

### Kinetic measurements

The anomerization process developed by the binuclear complex was studied at 15°C in buffered (acetic acid (1M)/sodium acetate) solutions. Optical activity changes were followed on  $8.5 \times 10^{-3}$  M solutions at 550 nm, using 2 cm pathlength thermostated cells and a modified Perkin-Elmer 141 polarimeter, until constant rotations were achieved.

### Preparation of the binuclear compound, complex I

*Cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>)<sub>3</sub> · 3H<sub>2</sub>O (1.685 g, 2.5 mmol) and D-arabinose (3.750 g, 25 mmol) were dissolved in 50 cm<sup>3</sup> of water, and the pH was adjusted to 6 with ammonia. The mixture was maintained at 25°C and the reaction was complete after 3 h. The products were then isolated. Methanol (60 cm<sup>3</sup>) was added dropwise to the solution with constant stirring and a well-known tetranuclear amino complex, [Co{(OH)<sub>2</sub>Co(NH<sub>3</sub>)<sub>4</sub>}(SO<sub>4</sub>)<sub>3</sub> · *n*H<sub>2</sub>O, (*n* = 2–9),<sup>3</sup> was first precipitated, which was separated by filtration. Methanol (100 cm<sup>3</sup>) was then added to the stirred solution and a red microcrystalline solid precipitated on the walls of the beaker. This product was collected by vacuum filtration, washed with methanol and ethanol, and dried in a vacuum desiccator. The yield was approximately 300 mg. The residual solution was a deep pink colour and was optically active.

### Purification of the binuclear complex

Freshly-prepared binuclear complex was dissolved in 10 cm<sup>3</sup> of water and was poured dropwise into 80 cm<sup>3</sup> of methanol containing 100 mg NaClO<sub>4</sub>, which prevented formation of a colloidal suspension. Constant stirring was maintained during this process and a pink solid precipitated, which was isolated by vacuum filtration, washed with methanol and ethanol, and dried in a vacuum desiccator. This procedure was repeated until the amplitude of the Cotton-effect, centred at 545 and 475 nm, levelled off. The yield of pure binuclear complex was *ca* 150 mg.

The product is very soluble in water, but insoluble in most organic solvents. It is stable as a solid and retains its optical activity when stored in a dry atmosphere. The compound is also paramagnetic. Optical activity of the aqueous solution of this compound drops slowly until the sign of the Cotton-effect, centred at 500 nm, reverses (see Fig. 1), while the absorption spectrum suffers no variation.

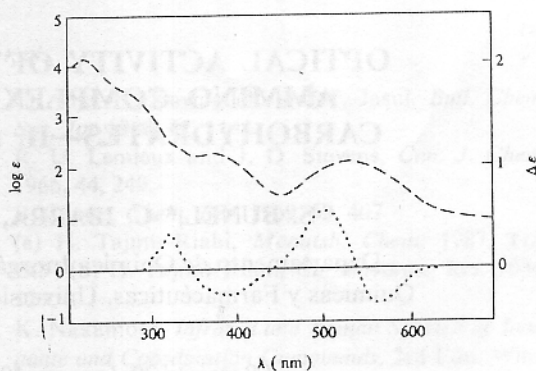


Fig. 1. Visible absorption spectrum (---) and circular dichroism (.....) of aqueous solutions of Complex I.

Analysis for [Co<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> D-arabinose]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 4H<sub>2</sub>O: Found: Co, 20.5; SO<sub>4</sub>, 24.8; C, 10.4; H, 4.8; N, 9.5. Calc: Co, 20.8; SO<sub>4</sub>, 25.3, C, 10.6; H, 5.3; N, 9.9%.

### Preparation of the mononuclear compound, complex II

400 cm<sup>3</sup> of the methanolic residual solution from the previous preparation were concentrated to 120 cm<sup>3</sup> on a 2 dm<sup>3</sup> evaporating dish under a cool air stream. The aqueous solution obtained was precipitated by dropwise addition of 200 cm<sup>3</sup> of absolute ethanol, under vigorous stirring for 30 min. Once pink crystals appeared, the resulting solution was kept at 4°C in the dark for a further 1/2 h before the next stage.

Precipitation was continued by adding another 500 cm<sup>3</sup> of absolute ethanol dropwise to the cold solution. A hygroscopic purple solid appeared, which covered the walls of the beaker. The resulting pink supernatant was discarded and the purple solid was redissolved in 5 cm<sup>3</sup> of distilled water. This concentrated solution was added dropwise to 120 cm<sup>3</sup> of a cold methanol–propanone (1 : 2) mixture, with vigorous stirring. The purple solid quickly covered the bottom of the beaker and a pink suspension developed. Once again the pink supernatant was discarded and the purple solid was easily washed off using 80 cm<sup>3</sup> of cold propanone with vigorous magnetic stirring. The purple solid obtained was quickly transferred to a dark container and dried *in vacuo* overnight. The yield of the purple solid was 230 mg.

Elemental analysis for [Co(NH<sub>3</sub>)<sub>4</sub> D-arabinose](NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub> · 3H<sub>2</sub>O: Found: Co, 10.6; SO<sub>4</sub>, 35.5; C, 11.8; H, 5.9; N, 12.5. Calc: Co, 10.9; SO<sub>4</sub>, 35.5; C, 11.1; H, 5.2; N, 12.9%.

The resulting mononuclear compound is heat- and light-sensitive, so it was kept in the refrigerator

in a dry container. Under these conditions the compound lasted for at least 3 months without loss of optical activity. Optical activity of the aqueous solutions of this complex decreases very slowly at room temperature in the dark. However, this process speeds up in dim light or acidic media. Cobalt(II) was identified as one of the decomposition products.

The chloride form of complexes **I** and **II** were obtained either by anion exchange on Dowex 1X8 or by precipitation with  $\text{BaCl}_2$  solution. Aqueous solutions so obtained were evaporated and dried in a desiccator.

Regarding the synthesis of the chiral complexes, it must be remembered that the reacting complex  $\text{cis}[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$  in aqueous solution at pH 6 and  $25^\circ\text{C}$ , spontaneously forms the tetranuclear ammino complex of cobalt(III) previously mentioned. The formation of this product is enhanced as the pH and temperature increase. The same chiral products containing arabinose were even obtained from a reaction with a 1:1 mole ratio of the reagents, although poorer yields were achieved. The large excess of carbohydrate employed in the present synthesis shifts the course of the reaction with formation of the sugar-containing chiral complexes.

## RESULTS AND DISCUSSION

Magnetic susceptibility measurements of the binuclear complex at 298 K and 1 kG gave a magnetic moment,  $\mu = 4.49$  BM. The data were corrected to compensate for the diamagnetism of the constituent atoms (Pascal constants). Susceptibilities measured over the range 2–300 K showed a linear dependence of the reciprocal susceptibility on temperature, confirming the presence of one cobalt(II) in the complex. The calculated value of the magnetic moment is higher than the spin only moment for three unpaired electrons (3.89 BM). This is the normal situation for high-spin octahedral cobalt(II) complexes, since they have a very high orbital contribution.<sup>4</sup>

Conductimetric titrations of the binuclear complex with hydrochloric acid showed two inflections due to non-bridged OH groups.<sup>5</sup> This agrees with the Co- $\text{SO}_4$  molar ratio, thus indicating the coordination of two OH ligands.

Table 1 shows that the visible absorption spectrum of the binuclear complex consists of two bands: the first one has  $\lambda_{\text{max}} = 527$  nm, ( $\epsilon = 109$ ), whereas the second one is a shoulder at 370 nm, which corresponds to a  $d-d$  absorption overlapped by a charge-transfer absorption, Fig. 1. This spectrum is similar to that found for ammino complexes

Table 1. Visible absorption and circular dichroism data

	Absorption		CD	
	$\lambda$ (nm)	$\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ )	$\lambda$ (nm)	$\Delta\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ )
Complex <b>I</b>	527	109	562	-0.568
			497	0.994
	370(s)	129	380	-0.419
		318	0.426	
Complex <b>II</b>	530	46.38	560	0.38
			495	-0.65
	373	80	375	0.31
			310	-0.567

of cobalt(III) containing ribose, sorbose and glucosamine,<sup>1</sup> where cobalt(III) is surrounded by four nitrogen and two oxygen atoms.

Two circular dichroism signals of opposite sign appear under the first absorption band, detected at 562 and 497 nm. Of the two CD signals, the one with the lower energy corresponds to the  ${}^1A_2$  state, and the other to the  ${}^1E$  state, both of them derived from the first  ${}^1T_{1g}$  excited state of cobalt(III) in octahedral symmetry, see Fig. 2. These CD signals exhibit the same signs sequence as that of the chiral compounds formed by an ammino complex of cobalt(III) with D-glucosamine, L-sorbose and D-ribose.

The CD spectrum of the binuclear complex also has two signals at 380 and 318 nm, corresponding to the low wavelength visible absorption spectrum. The lower energy signal should correspond to an  ${}^1E$  state derived from the magnetically forbidden  ${}^1T_{2g}$  state of cobalt(III).<sup>6</sup> The higher energy signal could correspond to a ligand-to-metal charge-transfer state (see Table 1).

The visible spectra of the mononuclear and binuclear complexes are similar, Table 1. In the mononuclear complex, the first band appears at

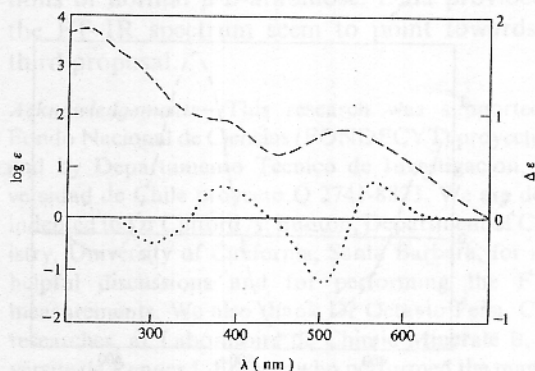


Fig. 2. Visible absorption spectrum (---) and circular dichroism (.....) of aqueous solutions of Complex II.



530 nm ( $\epsilon = 46$ ) and there is a shoulder at 373 nm ( $\epsilon = 180$ ), which is better resolved than that of the binuclear species. There are two circular dichroism signals under the first visible absorption band, Fig. 2. Their signs are opposite to those of the corresponding band of the binuclear complex: one is at 565 nm and the other one at 505 nm.

Circular dichroism signals under the second visible absorption band of cobalt(III) are detected at 385 and 310 nm. The lower energy signal has *d-d* character, corresponding to a transition derived from the  ${}^1T_{2g}$  state. The positive circular dichroism signal at 218 nm in the binuclear complex and the negative one at 310 nm in the mononuclear complex have similar  $\Delta\epsilon$  values. Considering their energies we think that both signals correspond to a ligand-to-metal charge-transfer transition.<sup>7</sup>

The different rotation signs for the same kind of transition in the mono- and the binuclear complexes might originate from an opposite helical distribution of the chelate ring around the cobalt(III) ion in each species.

Solutions of the binuclear complex suffer an inversion of the Cotton-effect signs in the visible spectral region (Fig. 3). This process follows first-order kinetics with complex concentration. It is also first order regarding proton concentration. The specific rate constant at 15°C (288 K), measured under pseudo-first-order conditions at pH 5.4 (buffered solution) is  $1.5 \times 10^{-3} \text{ min}^{-1}$ . We ascribe this behaviour to anomerization. It is slower than that of D-arabinose solutions at the same pH and temperature, ( $k = 1.99 \times 10^{-2} \text{ min}^{-1}$ ).

D-Arabinose is known to exist in the alternative form, with an anomeric composition, 68%  $\alpha$ - and 34%  $\beta$ -anomers.<sup>8,9</sup> The cobalt(III) ion can coordinate to this carbohydrate forming five-membered chelate rings through the O(1)H—O(2)H, or O(2)H—O(3)H or O(3)H—O(4)H positions.

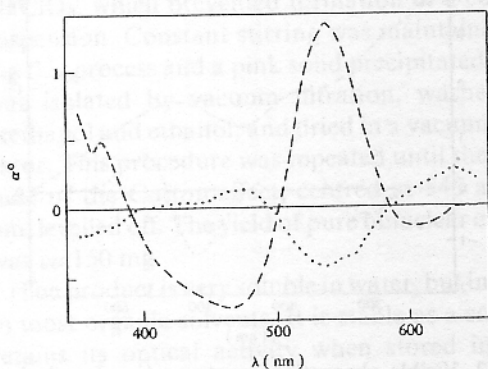


Fig. 3. Optical rotatory dispersion change of a 0.0055 M solution of Complex I, pH 5.4, 15°C, 1 cm pathlength cell. Starting solution (---); same solution after 100 min. (.....).

Chirality is the same,  $\lambda$ , for each one of these in the case of the  $\beta$ -anomer [Fig. 4(a)]. In the case of the  $\alpha$ -anomer, chirality originating by bonding through the O(1)H—O(2)H positions is opposite,  $\delta$ , to that resulting from bonding through the two other coordination positions [Fig. 4(b)].

The Cotton-effect signs under the first visible absorption band and the phenomenon of complex anomerization led us to think that the cobalt(III) ion bonds to the O(1)H group of the  $\beta$ -D-arabinose, in which case the other site of coordination would be O(2)H. Bonding to the ring oxygen atom O(5) is sterically hindered for the alternative conformation of D-arabinose.

Coordination of D-arabinose to the cobalt(II) ion in the binuclear complex has not been discussed yet. Scale models show that simultaneous bonding of O(3)H and O(4)H, or O(4)H and ring oxygen O(5) atoms of the sugar to the metal are feasible.

The FTIR spectrum of the chloride form of complex I is not as well-resolved as that of complex II in the 3500–3200  $\text{cm}^{-1}$  range. However, a clear shift of the CO group ring vibrations of the carbohydrate to lower frequencies can be observed. In this way, the bands in the neighbourhood of 1136, 1093, 1052, 1000 and 943  $\text{cm}^{-1}$ , assigned as  $\nu(\text{CO})+$

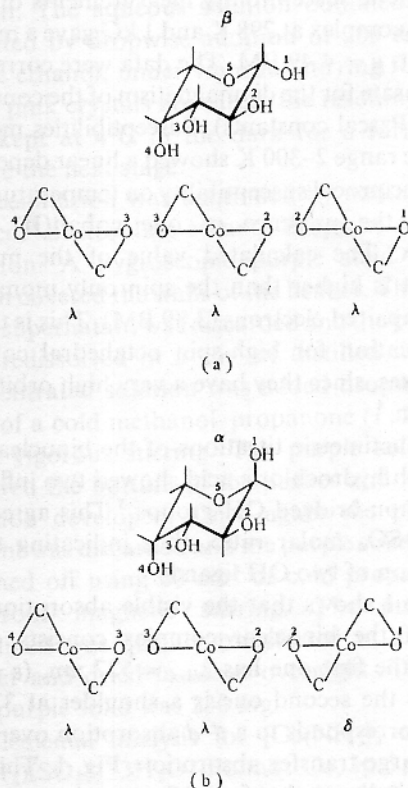


Fig. 4. (a)  $\beta$ -D-Arabinose; (b)  $\alpha$ -D-arabinose, alternative form, and their corresponding five-membered ring conformations around cobalt(III).

Table 2. FT-IR transmittance bands ( $\text{cm}^{-1}$ ) with possible assignments

Arabinose	Assignments	Reference	[Co(NH <sub>3</sub> ) <sub>4</sub> D-arabinose]Cl <sub>3</sub>
3536 s	$\nu(\text{O}(4)\text{—H}\cdots\text{O}(2)\text{H})$	10(a)	3530 shoulder 3500 strong
3340 vs	$\nu(\text{O}(1)\text{—H}\cdots\text{O}(5))$		3370 sharp-medium 3330 sharp-weak
3321 sh	$\nu(\text{O}(3)\text{—H}\cdots\text{O}(2)\text{H})$	10(a)	3320 sharp-strong 3295 sharp-strong 3280 sharp-strong
3235 b	$\nu(\text{O}(2)\text{—H}\cdots\text{O}(3)\text{H})$		3239 shoulder 3195 sharp-strong 3175 sharp-strong 3159 sharp-strong
3000 w	$\nu(\text{C}(5)\text{—H})$	10(a)	3000 sharp-weak
2970 sh	$\nu(\text{C}(4)\text{—H})$	10(a)	— shoulder
2953 sh	$\nu(\text{C}(3)\text{—H})$	10(a)	— no band
2940 m	$\nu(\text{C}(2)\text{—H})$	10(a)	2945 medium
—	$\delta(\text{O—H}(2))$		1635 strong
—	$\delta(\text{N—H}(3))$	11	1595 strong
1402 vw	$\delta(\text{CH}(2)) + \delta(\text{COH})$	10(a)	1415 strong
—	$\delta(\text{N—H}(3))$	11	1308 medium
1134 vs	$\nu(\text{CO}) + \nu(\text{CC})$	10(a)	1145 sharp-weak 1115 sharp-weak
1002 s	$\nu(\text{CC}) + \nu(\text{CO})$	10(a)	1080 broad-medium 1045 sharp-weak
893 s	$\delta(\text{COH})\alpha$	10(b)	855 broad-weak

$\nu(\text{CC})$ ,  $\nu(\text{CO})$ ,  $\nu(\text{CO}) + \delta(\text{CCO})$  and  $\nu(\text{CO}) + \delta(\text{CCH})$ , respectively,<sup>10</sup> are broadened and shifted towards 1108, 1075, 1030 and 983  $\text{cm}^{-1}$ , thus suggesting that the CO group could be involved in bonding to the cobalt(II) ion.

In the mononuclear complex, under the same pH and temperature conditions, the optical activity drops to zero. At the same time, the intensity of the first visible absorption band decreases as a result of decomposition of the complex species.

The FT-IR spectra of complex II in the chloride form show three major frequency ranges (3500–3200, 1415 and 1145–1045  $\text{cm}^{-1}$ ), as shown in Table 2. From 3500 to 3200  $\text{cm}^{-1}$  the OH $\cdots$ O stretching bands are shifted towards lower frequencies compared with free sugar, thus showing shorter OH $\cdots$ O bridging between O(3)H and O(2)H. However, O(4)H and O(1)H were almost unperturbed compared to UO<sub>2</sub>-sugar complexes obtained by Tajmir-Riahi.<sup>10a</sup> In addition, no CH stretching bands were observed for C(4)H and C(3)H, but they were observed for C(1)H, C(2)H and C(5)H. COH and CCH deformation modes of sugar complexes appeared as a strong band at 1415  $\text{cm}^{-1}$ . This, together with a set of four unresolved bands ( $\nu(\text{CO}) + \nu(\text{CC})$  1145–1045  $\text{cm}^{-1}$ ), are indicative of metal-sugar coordination.<sup>10a</sup>

Complex II Cotton-effect signs under the first absorption band, which are opposite to those of I, might arise from coordination of cobalt(III) to O(1)H and O(2)H atoms of the  $\alpha$ -anomer of D-arabinose in its alternative form. This possibility looks more attractive to us, although it cannot be forgotten that the same sequence of Cotton-effect signs could arise from bonding of the metal ion to the O(1)H—O(2)H or O(3)H—O(4)H positions of normal  $\beta$ -D-arabinose. Data provided by the FT-IR spectrum seem to point towards the third proposal.

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