

The Bis[di(2-aminoethyl)sulfide]rhodium(III) Ion. Preparation of the *u-fac* Isomer, its Resolution, and the Determination of the Absolute Configuration of the (+)_D-Enantiomer

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Bis[di(2-aminoethyl)sulfide]rhodium(III) chloride has been prepared and characterized as the *unsymmetrical facial* geometric isomer. Resolution into the catoptric forms has been accomplished by the use of arsenyl (+)_D-tartrate. The absolute configuration of the (+)_D-isomer of the complex ion has been determined to be Δ by a new modification of the method of active racemates. The circular dichroism of this isomer is very similar to that of the corresponding Δ -(-)_D-cobalt(III) complex.

Recently, a study of several synthetic pathways leading to bis[di(2-diaminoethyl)sulfide]cobalt(III), [Co(daes)₂]³⁺, was published.¹ It was shown that one geometrical isomer is formed exclusively and the latter was assigned the *u-fac* geometry on the basis of the circular dichroism of the resolved complex. This assignment has been verified by determination of the crystal structure of Δ -(-)_D-[Co(daes)₂]Cl₃·2H₂O.² At present it is not known why only the *u-fac* and not the *s-fac* and *mer* geometrical isomers are formed. The stability of [Co(daes)₂]³⁺ is much lower than that of [Co(dien)₂]³⁺ (dien = diethylenetriamine),³ all three possible geometrical isomers of the latter being formed in approximately equal amounts when a preparative route involving equilibration is employed.⁴

There is a general tendency for the metals of the second transition series to exhibit a greater affinity towards sulfur than do the elements in the first transition series. Therefore, it seems possible that both *facial* isomers of [Rh(daes)₂]³⁺ could be prepared. However, in the work described here only the *u-fac* isomer was found and characterized.

EXPERIMENTAL

Instrumentation. Absorption spectra were recorded on a Cary 118 spectrophotometer, and circular dichroism spectra on a Roussel Jouan Dichrographe III. Optical rotations were measured at 25 °C on a Perkin-Elmer 141 polarimeter. X-Ray powder diffraction photographs were obtained with a Hägg-Guinier focusing camera XDC 700 using CuK α radiation (quartz monochromator).

Preparations

[Rh(daes)₂]Cl₃·2H₂O. To doubly distilled di(2-aminoethyl)sulfide (6.60 g, 55.0 mmol) in 35 ml of water was added a solution of RhCl₃·3H₂O (6.57 g, 25 mmol; Johnson Matthey Chemicals Ltd.) in 30 ml of water over a period of 6 h. The reaction mixture was kept at 55–60 °C and vigorously stirred during the addition and for 1 h after it was completed. Carbon dioxide was excluded by the attachment of an absorption tube containing CaO. After dilution with 50 ml of water a yellowish solid byproduct was removed by filtration and the orange filtrate was evaporated to dryness on a rotary vacuum evaporator. The residue was subsequently heated at 130 °C for 20 min. The resulting sticky product was dissolved in 10 ml of boiling water and to this solution was added 10 ml of ethanol. Crystallization was initiated by stirring and scraping and aided by slow addition of a further 10 ml of ethanol and subsequent cooling to 0 °C. The creamcoloured crystalline product was filtered off, washed twice with a mixture of 1.5 ml of water and 8 ml of ethanol and then twice with ethanol. Yield 6.0 g. Prolonged standing of the mother liquor resulted in the formation of a second crop of 1.5 g. Total yield 7.5 g (62 %). Anal. C₈H₂₆Cl₃N₄O₂S₂Rh: C, H, N.

Resolution of $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. Sodium arsenyl (+)_D-tartrate⁵ (1.96 g, 7.5 mmol) was dissolved in a hot solution of $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (2.43 g, 5.0 mmol) in 15 ml of water. A slight amount of precipitate was removed by filtration while hot. Slow cooling of the solution to 0 °C resulted in the formation of a crystalline precipitate. The latter was filtered off, washed with 8 ml of ice-cold water, 8 ml of 50 % ethanol and 8 ml of absolute ethanol. Yield 1.6 g (60 %) of (+)_D- $[\text{Rh}(\text{daes})_2][\text{AsO}(+)\text{D-tart}]_3 \cdot \text{H}_2\text{O}$ having $[\alpha]_{578} = 40.7$, $[\alpha]_{546} = 46.3$, and $[\alpha]_{436} = 71.5$. The product was recrystallized from boiling water until the specific rotations remained unchanged (4 times) giving the values (0.6 % solution, 1 dm cell length) $[\alpha]_{578} = 58.5$, $[\alpha]_{546} = 66.2$, and $[\alpha]_{436} = 103$. Anal. $\text{C}_{20}\text{H}_{38}\text{N}_4\text{O}_{22}\text{S}_2\text{As}_3\text{Rh}$: C, H, N, S.

The diastereoisomer was converted into the chloride salt by cation exchange on Bio-Rex 70. 0.54 g (0.5 mmol) of (+)_D- $[\text{Rh}(\text{daes})_2][\text{AsO}(+)\text{D-tart}]_3 \cdot \text{H}_2\text{O}$ was dissolved in 75 ml of 0.03 M LiOH and the cation was adsorbed on a column (1.5 cm long, 1.2 cm diameter) of the ion exchanger in the Li-form. After careful washing of the resin the complex was eluted with 10 ml of 1 M HCl. The last 8 ml of the eluate was collected and evaporated to dryness, and the residue was recrystallized from 2 ml of water by addition of 8 ml of ethanol and cooling in ice. The precipitate was removed by filtration and washed with 85 % and 96 % ethanol. Yield 0.17 g of (+)_D- $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. Specific rotations at 25 °C: $[\alpha]_{589} = 101$, $[\alpha]_{578} = 107$, $[\alpha]_{546} = 120$, $[\alpha]_{436} = 190$, and $[\alpha]_{364} = -187$.

"Active racemates". A: a solution of $\Delta(-)\text{D-}u\text{-fac}[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (22 mg, 0.05 mmol) and (+)_D- $u\text{-fac}[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (24 mg, 0.05 mmol) in 0.5 ml of water was allowed to evaporate slowly. Examination under a microscope showed that the resulting crystals were uniformly red coloured.

B: a solution of $\Delta(+)\text{D-}u\text{-fac}[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (22 mg) and (+)_D- $u\text{-fac}[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (24 mg) in 0.5 ml of water was similarly allowed to evaporate. Examination of the resulting crystals under a microscope revealed them to be a mixture of discrete white and red crystals.

RESULTS AND DISCUSSION

A compound having the correct analytical composition for bis[di(2-aminoethyl)sulfide]rhodium(III) has been prepared by a route similar to that used in the preparation of tris(diamine)rhodium(III)^{6,7} and has been resolved into enantiomers. The absorption and circular dichroism spectra of the (+)_D catoptric form are shown in Fig. 1 together with the spectra of the corresponding cobalt(III)

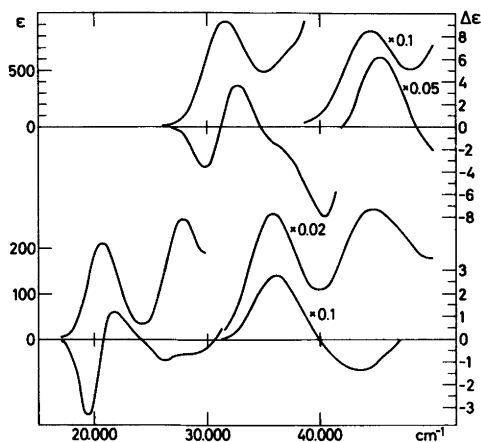


Fig. 1. The absorption and circular dichroism spectra of (+)_D- $[\text{Rh}(\text{daes})_2]^{3+}$ (top) and (-)_D- $[\text{Co}(\text{daes})_2]^{3+}$ (bottom).

complex which is known to be the Δ -*u-fac* isomer. A comparison of the two sets of spectra leaves little doubt that the (+)_D- $[\text{Rh}(\text{daes})_2]^{3+}$ ion also possesses the Δ -*u-fac* configuration. The racemic $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ and *u-fac*- $[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ give very similar X-ray powder diagrams (*vide infra*), thereby substantiating our conclusion that *u-fac*- $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ has indeed been isolated. The relatively low yield of this product (62 %), however, could indicate that a more soluble isomer has remained in solution. This possibility was examined by carrying out chromatography on Sephadex SP-C25, a procedure similar to that employed in previous work with the cobalt complex.¹ However, this procedure resulted in considerable reduction to rhodium metal and no absolutely conclusive results were obtained.

The absolute configuration of (+)_D- $[\text{Rh}(\text{daes})_2]^{3+}$ is predicted to be Δ on the basis of the similarity of the circular dichroism of this isomer to that of $\Delta(-)\text{D-}[\text{Co}(\text{daes})_2]^{3+}$ (see Fig. 1). Both cations are obtained as the less soluble diastereoisomeric arsenyl (+)_D-tartrates, information which provides further evidence for the assignment of the absolute configuration of the rhodium complex. However, in this particular case there is unequivocal proof of the Δ absolute configuration of (+)_D- $[\text{Rh}(\text{daes})_2]^{3+}$ since the absolute configuration of $\Delta(-)\text{D-}[\text{Co}(\text{daes})_2]^{3+}$ has been established³ by X-ray diffraction:

Table 1. Indexed Guinier X-ray powder diffraction lines for $\Delta(-)_D$ -*u-fac*-[Co(daes)₂]Cl₃·2H₂O, I; $\Delta(+)_D$ -*u-fac*-[Rh(daes)₂]Cl₃·2H₂O, II; and crystals containing a mixture of the two cations, III.

<i>hkl</i>	I			II			III		
	<i>I</i> _{obs}	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å	<i>I</i> _{obs}	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å	<i>I</i> _{obs}	<i>d</i> _{obs} Å	<i>d</i> _{calc} Å
0 2 0	mw	7.931	7.933	m	7.962	7.961	m	7.952	7.946
2 0 0	vs	7.338	7.339	s	7.434	7.437	vs	7.387	7.387
0 1 1	vs	7.156	7.146	vs	7.169	7.174	vs	7.155	7.156
1 2 0	vs	6.972	6.979	vs	7.011	7.019	vs	6.994	6.998
2 1 0							w	6.693	6.699
1 1 1	vs	6.430	6.425	vs	6.462	6.462	vs	6.435	6.440
0 2 1	mw	5.634	5.634	w	5.647	5.656	m	5.645	5.643
2 2 0	mw	5.393	5.387	mw	5.440	5.435	m	5.408	5.410
2 1 1	mw	5.119	5.120	m	5.166	5.163	m	5.142	5.140
2 2 1	m	4.467	4.469	m	4.503	4.502	ms	4.487	4.484
0 3 1	m	4.411	4.412	ms	4.429	4.429	ms	4.419	4.419
2 3 0	mw	4.291	4.291	mw	4.319	4.320	m	4.306	4.305
1 3 1				m	4.246	4.245	m	4.236	4.234
3 2 0				mw	4.205	4.209	mw	4.187	4.186
3 1 1	w	4.040	4.037	w	4.079	4.079	mw	4.058	4.057
0 0 2	w	4.006	4.002	w	4.020	4.018	mw	4.008	4.007
0 1 2				mw	3.895	3.896	w	3.885	3.886
1 0 2							w	3.869	3.867
1 4 0	m	3.829	3.829	mw	3.844	3.845	w	3.838	3.837
2 3 1	mw	3.782	3.782	mw	3.806	3.805	w	3.792	3.792
3 3 0	w	3.595	3.592						
4 1 0	w	3.575	3.575	mw	3.622	3.621			
2 0 2				mw	3.535	3.535			
1 4 1	vw	3.456	3.454	mw	3.469	3.469	mw	3.461	3.461
2 1 2	vw	3.433	3.430	mw	3.449	3.451	mw	3.440	3.439
4 0 1	mw	3.336	3.336	vw	3.375	3.375	w	3.354	3.354
4 1 1				w	3.301	3.301			
2 2 2	m	3.213	3.213	vw	3.230	3.231	w	3.220	3.220
2 4 1				vw	3.214	3.216	w	3.205	3.207
1 3 2	m	3.119	3.118				w	3.122	3.124

Refined unit cell dimensions assuming orthorhombic unit cell (Å)		
<i>a</i> = 14.656(4)	<i>a</i> = 14.873(4)	<i>a</i> = 14.774(4)
<i>b</i> = 15.834(6)	<i>b</i> = 15.932(6)	<i>b</i> = 15.893(5)
<i>c</i> = 7.986(3)	<i>c</i> = 8.036(3)	<i>c</i> = 8.014(2)

Racemic and optically active *u-fac*[Co(daes)₂]Cl₃·2H₂O crystallize in the same chiral space group *P*₂₁₂₁. The compound thus exhibits the phenomenon of spontaneous resolution, and large single crystals having the required optical rotations of the fully resolved complex have been obtained from solutions of the racemate. The crude product of [Rh(daes)₂]Cl₃·2H₂O behaves similarly.

When $\Delta(-)_D$ -[Co(daes)₂]Cl₃·2H₂O and $(+)_D$ -[Rh(daes)₂]Cl₃·2H₂O are co-recrystallized crystals are obtained which contain both [Co(daes)₂]³⁺ and [Rh(daes)₂]³⁺. However, when $\Delta(-)_D$ -[Co(daes)₂]-

Cl₃·2H₂O and $(+)_D$ -[Rh(daes)₂]Cl₃·2H₂O are co-recrystallized only red crystals of the cobalt complex and white crystals of the rhodium complex are formed. These experiments prove conclusively that $(+)_D$ -*u-fac*[Rh(daes)₂]³⁺ has the Δ absolute configuration.

When small amounts of the rhodium complex are used the effect is hard to appreciate with the naked eye since twinned crystals may occur. However, under a microscope the difference between the two co-recrystallizations is easily recognized. X-Ray powder photographs provide conclusive proof even

when small amounts are used: Table 1 lists the observed d-spacings for the pure cobalt and rhodium complexes as well as those for the mixed salt $\{\Delta(-)_D\text{-}[\text{Co}(\text{daes})_2], \Delta(+)_D\text{-}[\text{Rh}(\text{daes})_2]\}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ prepared from solution A (see Experimental). Crystals obtained from solution B, containing $\Lambda(+)_D\text{-}[\text{Co}(\text{daes})_2]^{3+}$ and $\Delta(+)_D\text{-}[\text{Rh}(\text{daes})_2]^{3+}$, gave X-ray powder photographs which exhibit all the lines observed for both of the pure complexes and no extra lines. The powder photographs of crystals obtained from solution A were indexed and refined assuming an orthorhombic unit cell. The unit cell parameters for the solid mixture lie between those for the pure cobalt and rhodium complexes.

The method for correlating absolute configurations presented above is limited to cases in which the racemate crystallizes in a chiral space group. However, when this condition is fulfilled the method has an appealing simplicity because the experiment can often be performed without the use of sophisticated apparatus.

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