

The Bis[di(2-aminoethyl)sulfide]cobalt(III) Ion. Existence of only the Unsymmetrical-facial Geometric Isomer and Its Optical Resolution.

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Bis[di(2-aminoethyl)sulfide]cobalt(III) was prepared by a variety of methods. The products from all preparations were the same geometric isomer exclusively, as established by Sephadex ion-exchange chromatography and NMR spectra. From comparisons of CD spectra with the spectra of the isomers of the analogous $[\text{Co}(\text{dien})_2]^{3+}$ system, the resolved complex $(-)_D\text{-}[\text{Co}(\text{daes})_2]^{3+}$ was assigned the *unsymmetrical-facial* geometry, and it probably has the absolute configuration Δ . It racemises rapidly on charcoal (complete within 10 min at 20 °C). The observed ion-association effects and the NMR spectrum are also consistent with the geometry being *u-facial*. The two other possible geometric isomers, *s-facial* and *meridional* could not be detected. Some sulfur-sulfur interaction is possible, and this might confer rigidity on the chelate ring conformations and thus account for the multiple NH_2 resonances observed in the ^1H NMR spectrum.

A number of metal complexes of various thioether ligands are known. When the thioether donor atom bridges two chelate rings, there exists the possibility of two coordination modes, *facial* and *meridional*, for the tridentate moiety. Although there have been several detailed studies over recent years of the stereochemistry associated with coordination of flexible multidentate linear thia-amine ligands, a *meridional* topology of five-membered chelate rings about donor sulfur has not yet been demonstrated in any complex. By comparison, such *meridional* coordination appears to be

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common at coordinated secondary amine sites.

It was the purpose of this work to attempt to establish the *meridional* coordination mode for donor sulfur coupling five-membered chelate rings in the complex system $[\text{Co}(\text{daes})_2]^{3+}$ where daes represents the tridentate ligand di(2-aminoethyl) sulfide, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}_2$.

The investigation reported here of the complex system $[\text{Co}(\text{daes})_2]^{3+}$ was prompted by our recent studies on the closely analogous bis(diethylenetriamine)cobalt(III) complex system.^{1,2} Both these systems can potentially exist in three topological forms designated *s-fac*, *u-fac* and *mer* and shown in Fig. 1. In addition the *u-fac* and *mer* forms are dissymmetric and can exist in optical forms. All these isomeric forms of $[\text{Co}(\text{dien})_2]^{3+}$ (*dien* = diethylenetriamine) have been isolated and characterized.^{1,2}

The three geometric isomers of $[\text{Co}(\text{dien})_2]^{3+}$ coexist at equilibrium, and each separate iso-

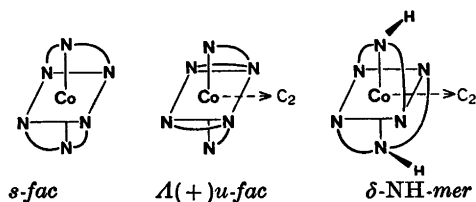


Fig. 1. The geometric isomers of $[\text{Co}(\text{dien})_2]^{3+}$. The possible isomers of $[\text{Co}(\text{daes})_2]^{3+}$ are analogous to those above, with S replacing NH. The nomenclature is elaborated in Ref. 1.

mer isomerizes slowly to the same equilibrium mixture under similar conditions. The equilibrium proportions in aqueous solution at 18 °C and with singly charged anions (halide, nitrate, perchlorate) are *mer:u-fac:s-fac* = 65:27:8, so that the *meridional* topology of coordinated dien is clearly preferred over the *facial* arrangements.^{1,2}

The difference between the three isomers of [Co(dien)₂]³⁺ or those of [Co(daes)₂]³⁺ (Fig. 1) can be broadly defined in terms of the planar or angular stereochemistry about the secondary nitrogen or thioether donor atoms,⁴ but the description of donor atom bond angles as *angular* or *planar* (corresponding to the descriptions of topology as *facial* or *meridional*) does not necessarily make these angles key angles in determining relative isomer stabilities. It has been appreciated for some time that any strain arising from departures of bond angles about the metal and donor atoms from their natural octahedral and tetrahedral values should be alleviated by a "levelling-out" process over all the bond angles of the structure.⁴ More recently it has been realized from energy minimization calculation that the energetics of a molecular system is a function of *all* its degrees of freedom (bond angles, bond lengths, non-bonded interactions and bond torsions),⁵ and it follows therefore that the separation of any one structural parameter as contributing more or less to the energetics is not valid.

Full energy minimization calculations for each of the [Co(dien)₂]³⁺ isomers have indicated that in the energy minimized structures the C–N–C bond angles do not differ greatly over the three isomers, and that the energies associated with the departures of these angles from tetrahedral (at most ~5° for the *mer* isomer) are relatively minor contributions to the total energies.⁵

The isomeric distribution in [Co(daes)₂]³⁺ was of some interest therefore, and on the basis of the above results for [Co(dien)₂]³⁺ there seemed reasonable likelihood of being able to obtain the *mer* isomer of [Co(daes)₂]³⁺ having a donor sulfur in a pseudo-planar arrangement. The immediate aim of the present work therefore was to prepare [Co(daes)₂]³⁺ by various methods and to isolate, characterize and identify the geometric isomers present.

Some metal complexes of daes coordinated in a tridentate manner have been isolated previously. The cobalt(III) complexes [Co(daes)₂]Cl₃, [Co(daes) (dien)]Cl₃ and [Co(daes)Cl₂] were reported recently by Hori⁶ but the isomeric compositions were not investigated. For [Pt(daes)Cl₂]Cl only one of the two possible isomers could be detected but its structure was not established,⁷ and [Ni(daes)₂]X₂ was suggested to consist at least largely of the *s-fac* isomer from the tetragonal splitting observed in the electronic spectrum.⁸ Thus the detailed coordination behaviour of daes is essentially unknown.

EXPERIMENTAL

Instrumentation. Absorption spectra, circular dichroism spectra, and optical rotations, were measured on a Cary 14 spectrophotometer, a Roussel-Jouan Dicrograph model II, and a Perkin-Elmer 141 polarimeter, respectively. ORD curves were measured on a Perkin-Elmer 141 MC polarimeter. ¹H NMR spectra were measured on Varian A-60A and Bruker JX-90 NMR spectrometers.

Preparation of daes. The diamine was prepared by modification of literature methods.^{9–11} Hydrogen sulfide (about 55 g, J. T. Baker Chemical Co., New Jersey, 98.5 % pure) was bubbled in a slow stream (2 h) through a stirred solution of ethylenimine monomer (93 g, Koch-Light Laboratories Ltd., England) in methanol (100 ml, Analar) in a flask cooled in an ice bath. The solvent was removed on a rotary evaporator, and some 2-aminoethylthiol by-product also sublimed off. The crude product was distilled under pressure when more 2-aminoethylthiol was removed first, and the required diamine was then collected separately. Yield: 73 g (56 %). The diamine was redistilled, b.p. 124–126 °C/17 mmHg (uncorr.), and comparisons of ¹H NMR spectra in D₂O indicated that it was free of the monomer by-product.

Preparation of daes.2HCl. HCl (59 ml of 11.3 M) in ethanol was added to a stirred solution of daes (40.0 g) in ethanol cooled in an ice bath. The solution was concentrated on a rotary evaporator, and the product crystallized on standing in a refrigerator. The hygroscopic product was filtered off, washed with ethanol, and dried in a vacuum desiccator. Yield: 57.0 g (88 %). M.p. 123–124 °C. (Found: C 24.8; H 7.3; N 14.3; Cl 36.7; S 16.9. Calc. for C₄H₁₄N₂Cl₂S: C 24.9; H 7.3; N 14.5; Cl 36.7; S 16.6).

Preparations of the [Co(daes)₂]³⁺ complex. *Method A, aerial oxidation.* To a solution of CoCl₂·6H₂O (2.38 g, 0.01 mol) in water (300

ml), a solution of daes.2HCl (4.25 g) and LiOH.H₂O (1.39 g) in water was added. Powdered charcoal (1 g) was added, and the solution was aerated for 40 h. The charcoal was filtered from the red-orange solution. After reserving a small sample for Sephadex chromatography, the solution was diluted three-fold, and absorbed on a short column of Bio-Rex 70 weak acid cation exchange resin (analytical grade, 50–100 mesh) in the Li⁺ form. After washing the column with water, the complex was eluted with 0.1 M HBr. Evaporation of the effluent solution to dryness in a rotary evaporator gave orange-red crystals of crude [Co(daes)₂]₂·Br₂·H₂O. Yield after standing in a hygrostat: 5.51 g (98 %).

Method B, aerial oxidation with added phosphate. To CoCl₂·6H₂O (2.38 g) in water (500 ml) was added Na₃PO₄·12H₂O (19 g). Charcoal (1 g) was added to the mixture followed by daes (2.41 g) and HCl (10 ml of 1 M). After aeration (40 h) the charcoal was removed leaving a dark orange-brown solution of pH~11. This solution contained a substantial proportion of polynuclear complex species which remained as a grey-green band at the column head during passage of the [Co(daes)₂]₂³⁺ product down a column of SP-Sephadex C-25 with sodium (+)-antimonyl tartrate solution. The presence of polymeric material precluded isolation of the required complex by the weak acid cation exchange procedure as in method A, and isolation of product was not pursued.

Method C, from [Co(NH₃)₆]Cl₂. This was similar to the method used by Hori.¹³ A mixture of [Co(NH₃)₆]Cl₂ (2.68 g, 0.01 mol), daes.2HCl (4.2 g), LiOH.H₂O (1.85 g) and powdered charcoal (0.5 g) in water (80 ml) was warmed over a steam bath for 2 h, when evolution of ammonia had ceased. The solution was diluted and the charcoal was filtered off. A small volume was reserved for Sephadex chromatography. The product was obtained as the bromide salt using Bio-Rex 70 cation exchange resin as in method A. A small amount of some brownish-green product, probably [Co(daes)Cl₂] obtained on evaporation of the effluent solution was extracted with warm ethanol. The orange crystals of [Co(daes)₂]₂·Br₂·H₂O were filtered off from the ethanol solution, washed with 96 % ethanol, air-dried, then treated in a hygrostat. Yield: 4.70 g (85 %).

In another preparation by this method the solution left after removing the charcoal was concentrated to a small volume and the product crystallized on addition of ethanol. The orange crystals of [Co(daes)₂]₂Cl₂·2H₂O were filtered off, washed with 96 % ethanol and ether, and air-dried. Yield: 3.84 g (87 % calculated as dihydrate).

Isolation of complex as the perchlorate salt was carried out from another batch using a column of SP-Sephadex C-25 cation exchange

resin. The product was passed down the column as a single band using 0.5 M NaClO₄ solution.

Method D, from trans-[Co(py)₄]Cl₂]Cl₂·6H₂O in methanol solvent. trans-[Co(py)₄]Cl₂]Cl₂·6H₂O¹³ (2.95 g, 0.005 mol) was dissolved in methanol (80 ml, Analar) by warming. A solution of daes (1.35 g) in methanol (20 ml) was added dropwise to the above stirred solution, when a greyish precipitate commenced to settle out immediately. The solution was heated to boiling over a steam bath when the suspended solid became orange, and the solution was then evaporated to dryness on a rotary evaporator. The resulting orange solid was dissolved in water, and the solution was filtered and made up to 500 ml. After reserving a small sample (3 ml) for Sephadex chromatography, the solution was applied to a column of Bio-Rex 70 cation exchange resin. The complex was recovered as bromide (as in method A) and some purplish-grey by-products were retained on the resin.

In another preparation by this method, the crude [Co(daes)₂]₂·2H₂O was filtered off from the methanol solution after cooling, washed with ethanol and ether, and air-dried. Yield: 2.05 g (93 % calculated as dihydrate).

Method E, from trans-Co(py)₄]Cl₂]Cl₂·6H₂O in pyridine solvent. This was carried out in a similar manner to that in method D. On evaporation to dryness the solid was greenish-yellow, but formed a red-brown solution in water. Some solution was reserved for Sephadex chromatography, and [Co(daes)₂]₂·Br₂·H₂O was isolated as in method D. More by-products were apparent from this method than in the methanol preparation, but these were essentially retained on the BioRex 70 resin and in the ethanol. Yield: 2.12 g (76 % calculated as monohydrate).

Method F, from Na₃[Co(CO₃)₂]·3H₂O. To an ice-cold stirred slurry of Na₃[Co(CO₃)₂]·3H₂O¹³ (3.62 g, 0.01 mol) in water (30 ml) was added daes.2HCl (3.86 g) and HCl (20 ml of 1 M). The mixture was warmed over a steam bath (30 min) and gradually became red-brown, and the solution was filtered. A sample was chromatographed on Sephadex with 0.3 M sodium (+)-antimonyl tartrate eluent and produced two bands. A carmine band ran just ahead of the single yellow-orange band of [Co(daes)₂]₂³⁺ so that it was probably a 3+ charged complex. Its visible absorption spectrum did not correspond with that expected for a [Co(daes)₂]₂³⁺ complex.

The [Co(daes)₂]₂³⁺ product was isolated by the weak acid cation exchange procedure as in method A, but it could not be completely separated from the carmine complex by this procedure. Evaporation of the 0.1 M HBr effluent solution gave a solid containing two compounds. Water then dissolved the orange [Co(daes)₂]₂·Br₂ and left an insoluble green powder which was removed. Its analysis

(Table 1) was consistent with $[\text{Co}(\text{daes})\text{Br}_3]$. Yield of $[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot \text{H}_2\text{O}$: 4.93 g (88 %).

Sephadex chromatographic analysis of complex products from preparations. The solutions in all the above preparations were made sufficiently dilute to retain all the complex products in solution. A suitable aliquot of each product solution (~ 0.02 g of product complex) was applied to a column (60×1.8 cm) of SP-Sephadex C-25 cation exchange resin in the Na^+ form, washed with water and chromatographed with 0.3 M sodium (+)-antimonyl tartrate solution. From each preparation the same single yellow-orange band corresponding to a 3+ charged ion was obtained. This single $[\text{Co}(\text{daes})_2]^{3+}$ band was eluted from the column and collected in a number of 10 ml fractions. The CD spectra recorded for all fractions from all preparations were of the same form with opposite maxima at 512 and 457 nm, but changed sign over each set of fractions demonstrating a partial optical resolution within the band.

For some runs, optical densities at the maximum 485 nm were also measured for the fractions. Using $\epsilon_{485} = 215$ the values of $\Delta\epsilon_{512}$ could be calculated, and the values of $\Delta\epsilon_{512}$ so obtained for the fractions in order from preparative method A were: ~ -5.3 , -3.4 , -2.6 , -1.5 , 0 , $+1.0$, $+2.1$, $+2.6$, $+3.0$, $+3.4$, $\sim +3.7$.

From most preparations, small amounts of by-products were also evident during the above chromatography procedures.

The use of 0.3 M NaClO_4 , 0.1 M Na_3PO_4 and 0.3 M sodium (+)-D-tartrate solutions as eluents likewise produced only a single $[\text{Co}(\text{daes})_2]^{3+}$ band.

Recrystallization and analyses of complexes. The chloride, bromide and perchlorate salts of $[\text{Co}(\text{daes})_2]^{3+}$ had high solubilities in water. The chloride and bromide salts were recrystallized from 50 % aqueous methanol (10 g complex in 40 ml) by gradually adding ethanol while stirring. After standing at 6 °C overnight, the orange crystals were filtered off, washed with 96 % ethanol, air-dried, and then left in a hygostat of 45 weight-% H_2SO_4 (50 % relative humidity approximating to normal room conditions) over 1 day.

All the salts showed variable water content dependent on the mode of drying, so that treatment in a hygostat was employed to give reproducible analyses (Table 1). Thermogravimetric analyses showed that removal of hydrate water commenced at low temperatures (e.g. 35 °C at a slow heating rate, 2 °C per min) indicating loosely bound hydrate water reminiscent of $[\text{Co}(\text{en})_3]^{3+}$ salts.¹⁴

Resolution of $[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. To a boiling, stirred solution of $[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (4.42 g, 0.01 mol) in water (25 ml), solid sodium (+)-D-arsenyl tartrate (4.10 g, 0.016 mol) was added and dissolved. Crystallization commenced shortly after the solution was left to cool to

room temperature and after 2 h in an ice bath $(-)_\text{D}$ - $[\text{Co}(\text{daes})_2](+)_\text{D}$ - $[\text{AsO}(\text{tart})]_3 \cdot \text{H}_2\text{O}$ were filtered off, washed with cold water and methanol, and air-dried. Yield: 3.9 g (80 % of one optical form). This diastereoisomer had specific rotations $[\alpha]_D^{25}$ of -224 , $+162$, $+401^\circ$ at the mercury wavelengths 546, 436, 364 nm, respectively. The diastereoisomer was recrystallized by dissolution in hot water (~ 200 ml), filtration and concentration to ~ 50 ml. After seeding, the mixture was left to crystallize in an ice bath for 1 h, and the fine plates were filtered off, washed with ice-water, 96 % ethanol, and air-dried. After four recrystallizations the specific rotations (0.1 % solution, 1 dm tube) had become constant at $[\alpha]_{589}^{25} -129^\circ$; $[\alpha]_{578}^{25} -170^\circ$; $[\alpha]_{546}^{25} -345^\circ$; $[\alpha]_{436}^{25} +237^\circ$; $[\alpha]_{364}^{25} +596^\circ$. Analyses of recrystallized compounds are listed in Table 1.

The recrystallized diastereoisomer was converted into fine orange needles of $(-)_\text{D}$ - $[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ using Bio-Rex cation exchanger. The specific rotations (0.04 % solution, 1 dm tube), which were unchanged on recrystallization, were $[\alpha]_{589}^{25} -256^\circ$; $[\alpha]_{578}^{25} -359^\circ$; $[\alpha]_{546}^{25} -735^\circ$; $[\alpha]_{436}^{25} +501^\circ$; $[\alpha]_{364}^{25} +1620^\circ$.

After removing the diastereoisomer, the filtrate containing $(+)_\text{D}$ - $[\text{Co}(\text{daes})_2]^{3+}$ was heated to near boiling and further (+)-sodium arsenyl tartrate (4.0 g, 0.0156 mol) was added. After filtration 10 ml 96 % ethanol was added to the warm solution and the mixture was allowed to cool to room temperature. 5.7 g (5.4 mmol ~ 110 % of the $(+)_\text{D}$ -stereoisomer) $(+)_\text{D}$ - $[\text{Co}(\text{daes})_2](-)_\text{D}$ - $[\text{AsO}(\text{tart})]_3$ precipitated. This diastereoisomer had specific rotations $[\alpha]_D^{25}$ of 127, -46 and -890° at the mercury lines 546, 436, 364 nm, respectively. The diastereoisomer was recrystallized three times. The last recrystallization did not change the specific rotations: $[\alpha]_{578}^{25} 164^\circ$; $[\alpha]_{546}^{25} 301^\circ$; $[\alpha]_{436}^{25} -153^\circ$; $[\alpha]_{364}^{25} -579^\circ$. $(+)_\text{D}$ - $[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$ was obtained analogously to the antipode and with the same optical purity.

The racemic bromide monohydrate could be resolved in an analogous manner to that above.

RESULTS AND DISCUSSION

In seeking the three possible geometric isomers of $[\text{Co}(\text{daes})_2]^{3+}$ the complex was prepared by a number of different methods as described above.

Preparation of the complex by the dimethyl sulfoxide oxidative procedure¹⁵ was unsuccessful; no reaction was apparent when solutions of CoCl_2 and $2(\text{daes} \cdot 2\text{HCl}) + 3\text{LiOH}$ in dimethyl sulfoxide were mixed and warmed.

Table 1. Analytical data for $[\text{Co}(\text{daes})_2]^{3+}$ complexes prepared.

Complex ^a	C		H		N		S		Halogen		Molar ratio $\text{H}_2\text{O}:\text{Co}$ ^b
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot \text{H}_2\text{O}$	17.2	17.0	4.7	4.6	10.1	10.1	11.5	11.3	43.0	43.2	1.1
$[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$	21.7	21.5	6.4	6.4	12.7	12.6	14.5	14.4	24.1	24.3	2.3
$[\text{Co}(\text{daes})_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	15.6	15.7	4.3	4.1	9.1	9.1	10.4	10.6	17.3	16.7	1.0
$[\text{Co}(\text{daes})\text{Br}_3]$	11.5	11.7	2.9	3.0	6.7	6.9	7.7	7.7	57.2	56.2	
$(-)_\text{D}-[\text{Co}(\text{daes})_2]-$ $(+)_\text{D}-(\text{AsOC}_4\text{H}_4\text{O}_6)_3 \cdot \text{H}_2\text{O}$	23.2	23.1	3.7	3.6	5.4	5.4	6.2	6.5			^c
$(-)_\text{D}-[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$	16.7	16.4	4.9	4.8	9.7	9.6	11.2	11.6	41.7	41.7	2.1
$(+)_\text{D}-[\text{Co}(\text{daes})_2]-$ $(+)_\text{D}-(\text{AsOC}_4\text{H}_4\text{O}_6)_3 \cdot \text{H}_2\text{O}$	23.2	23.8	3.7	3.5	5.4	5.5					
$(+)_\text{D}-[\text{Co}(\text{daes})_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$	16.7	16.5	4.9	4.8	9.7	9.7	11.2	11.5	41.7	41.4	
$(+)_\text{D}-[\text{Co}(\text{daes})_2]-$ $(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	15.6	15.8	4.3	4.3	9.1	9.2	10.4	10.5	17.3	17.0	

^a $\text{daes} = \text{C}_4\text{H}_{12}\text{N}_2\text{S}$. ^b By thermogravimetric analysis. ^c Uncertain due to decomposition.

The preparations with charcoal would be expected to give equilibrium mixtures of the geometric isomers, whereas different isomer distributions might be expected from the other methods. Moreover, isomer proportions can be modified by changes of solvent,³ and different isomers can be the main products isolated from reactions under such different conditions.¹⁶

The product from all the above preparations appeared to be a single geometric isomer, however, and two approaches were used to check this.

Samples of the product solutions from all the preparations were separately chromatographed on columns of SP-Sephadex C-25

cation exchange resin using 0.3 M sodium $(+)_\text{D}$ -antimonyl tartrate as eluent. In each case only a single yellow-orange band was obtained, and this was eluted and collected totally in a number of fractions. The optical activity showed a regular change over all the fractions, with $\Delta\epsilon_{\text{max},513}$ of early fractions negative, the $(-)_\text{D}$ optical isomer, and of later fractions positive. These observations are consistent with the band on Sephadex containing a single geometric isomer which is partially optically resolved within the band during the elution with $(+)_\text{D}$ -antimonyl tartrate. This separation of optical isomers provides substantial evidence that only one geometric isomer

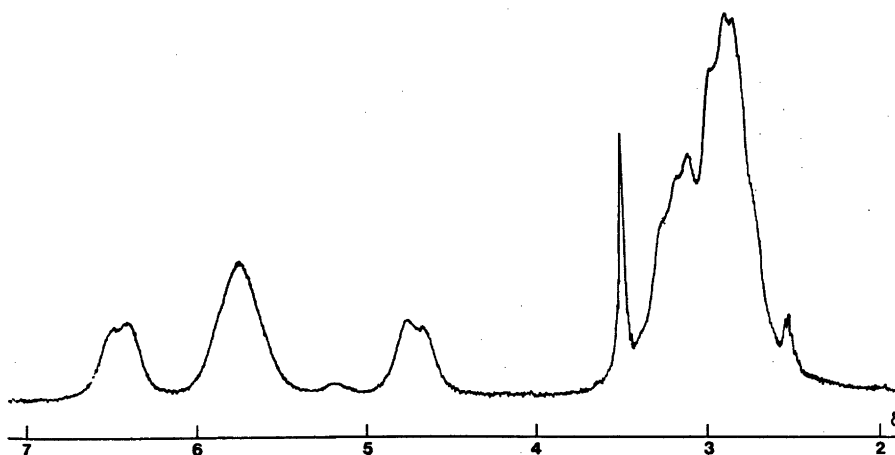


Fig. 2. 90 MHz ^1H NMR spectrum of $u\text{-fac-}[\text{Co}(\text{daes})_2]^{3+}$ in $\text{DMSO-}d_6$ with tetramethylsilane as internal reference.

was present in all these preparative mixtures, as a chromatographic procedure which can separate optical isomers would be expected to discriminate even more readily between geometric isomers if more than one of these were present.¹

The second approach was to isolate the $[\text{Co}(\text{daes})_2]^{3+}$ products from the various preparations in the maximum possible yields and to compare their ^1H NMR spectra. The product complex from each preparative method was isolated almost quantitatively as $[\text{Co}(\text{daes})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ using a weak acid cation exchange resin procedure, and all these products had identical ^1H NMR spectra (Fig. 2). The three geometric isomers of $[\text{Co}(\text{daes})_2]^{3+}$ should have substantially different ^1H NMR spectra, as do the isomers of $[\text{Co}(\text{dien})_2]^{3+}$,^{1,2} so that any second isomer of $[\text{Co}(\text{daes})_2]^{3+}$ has been beyond the limits of detection from NMR variations.

The isolated complex was resolved into optical isomers using sodium (+)_D-arsenyl tartrate. Through recrystallization of the diastereoisomer to maximum rotation, optically pure (-)_D- $[\text{Co}(\text{daes})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was obtained whose ^1H NMR spectrum (Fig. 2) was identical to those of the crude products from all preparations. This reinforces the above evidence for the existence of only one geometric isomer.

Absorption and CD spectra, and assignment of the isomer as *u-fac*. The resolution of the complex excludes the centrosymmetric *s-fac* isomer (symmetry C_{2h}) but does not distinguish the dissymmetric isomers *u-fac* and *mer* which both have C_2 symmetry. However, several lines of evidence, particularly the CD spectrum, indicate that it is *u-facial*.

The absorption, ORD and CD spectra of the (-)_D-isomer of the resolved complex are shown in Fig. 3 and data are listed in Table 2. The visible absorption spectrum exhibits a maximum at 485 nm ($20\,600\text{ cm}^{-1}$, $\epsilon=215$) with a band half-width $\bar{\nu}_1$ of 3200 cm^{-1} . The corresponding low energy band of *u-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ has maximum at 468 nm ($21\,400\text{ cm}^{-1}$, $\epsilon=96$) and $\bar{\nu}_1$ 3400 cm^{-1} .¹ There are no signs of splitting in these bands, and the second octahedral absorption bands (at 359 nm for $[\text{Co}(\text{daes})_2]^{3+}$, 338 nm for *u-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ are apparent single transitions

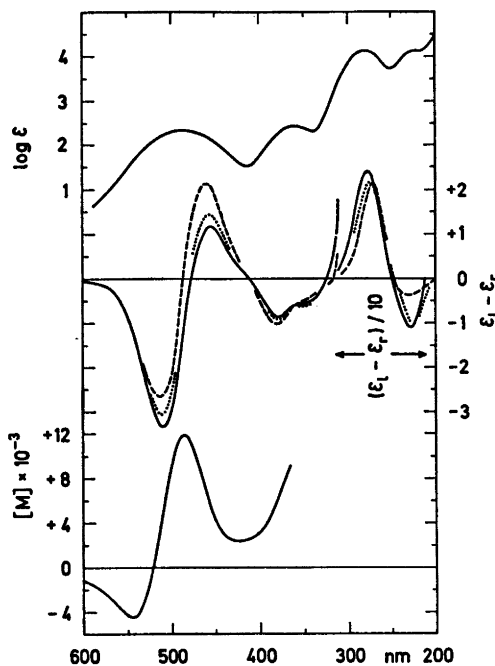


Fig. 3. The absorption, CD and ORD spectra of (-)_D-*u-fac*- $[\text{Co}(\text{daes})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ in water (approx. 10^{-3} M solution), and the CD in 0.2 M Na_2SeO_3 (---) and in 0.2 M Na_2SO_4 (...).

also. The circular dichroism spectrum of the $[\text{Co}(\text{daes})_2]^{3+}$ isomer shows two components under the first absorption band with an energy separation of 2400 cm^{-1} . For *u-fac*- $[\text{Co}(\text{dien})_2]^{3+}$ a similar pattern has been found with an energy separation of 2500 cm^{-1} between the two CD components.^{3,17} These data indicate that daes lies somewhat lower in the spectrochemical series than dien. From the relative positions of the first ligand field bands in the absorption spectra of $[\text{Co}(\text{daes})_2]^{3+}$ (Fig. 3) and $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_2]^{3+}$ and *cis*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$,¹⁸ we deduce that daes lies between H_2O and NH_3 (and near dien) in the spectrochemical series in accord with some previous proposals.^{3,19,20}

On the basis of all these spectral comparisons, the visible spectra of the three possible geometric isomers of $[\text{Co}(\text{daes})_2]^{3+}$ might be expected to exhibit maxima at similar energies, so that the positions of bands and the degree of splitting may not distinguish between these arrangements.

Table 2. Electronic band maxima for $(-)_D$ -[Co(daes)₂]Br₃·2H₂O in water.

Unpolarised absorption λ (nm)	ϵ	Circular dichroism λ	$(\epsilon_1 - \epsilon_2)$	CD in 0.2 M Na ₂ SeO ₃ λ	$(\epsilon_1 - \epsilon_2)$	Optical rotary dispersion λ	[M]
485	215	512	-3.35	515	-2.68	545	-4 420 (trough)
		457	+1.18	461	+2.15	521	0
		379	-0.88	381	-1.04	461	+11 980 (peak)
359	274	~340	~-0.55	~340	inflexion	425	+2 430 (trough)
		279	14 000	276	+24.3	271	+21.1
224	14 500	227	-11.3	232	-3.8		

The CD spectrum of $(-)_D$ -[Co(daes)₂]³⁺ shows a close correspondence to that of $(-)_D$ -*u-fac*-[Co(dien)₂]³⁺ over the ligand field and charge-transfer regions, in respect of both the relative positions of the component CD bands and their sign.²¹ In particular both complexes show lower-energy negative and higher-energy positive components under the ¹A_{1g}→¹T_{1g} absorption band (parent O_h), a negative component in the region of the ¹A_{1g}→¹T_{2g} band (two negative components are shown here for $(-)_D$ -[Co(daes)₂]³⁺; two similarly-signed components may merely be less well resolved in the $(-)_D$ -*u-fac*-[Co(dien)₂]³⁺ complex), and lower-energy positive and higher-energy negative components in the charge-transfer region. There is also a correspondence in the relative magnitudes of the component bands within each complex, although $\Delta\epsilon$ for the bands of $(-)_D$ -[Co(daes)₂]³⁺ are larger than for the corresponding component bands of $(-)_D$ -*u-fac*-[Co(dien)₂]³⁺ by factors of about two or three. The effect of added selenite is to diminish and enhance, respectively, the lower- and higher-energy components of the ¹A_{1g}→¹T_{1g} bands in both complexes (Fig. 3).

The CD of $(-)_D$ -[Co(daes)₂]³⁺ thus differs from that expected for a *mer* structure in each of the three respects mentioned, the high intensity of the charge-transfer components ($\Delta\epsilon = +24, -11$) being particularly noteworthy. The close correspondence of the spectrum with that of $(-)_D$ -*u-fac*-[Co(dien)₂]³⁺ and the similar effects of selenite thus allow the present structure to be assigned as *u-facial*. On this basis also $(-)_D$ -*u-fac*-[Co(daes)₂]³⁺

probably has the same absolute configuration as $(-)_D$ -*u-fac*-[Co(dien)₂]³⁺, which has been assigned previously as Δ .^{3,17,21}

ORD spectrum and optical stability of the complex. The Cotton effect which crosses zero at 521 nm is clearly associated mainly with the negative CD transition at 512 nm (Fig. 3). The positive section of the ORD will have contributions also from positive tails of component anomalies associated with the positive CD transitions at 457 nm and in the ultraviolet, so that the peak is very large.

The resolved complex has a high optical stability. The optical rotations (mercury lines) of a solution in water had not decreased measurably after 30 h at 50 °C. On the other hand addition of charcoal caused complete loss of activity within 10 min at 20 °C. After removal of the charcoal, this racemized solution gave the same single yellow-orange chromatography band when eluted down a Sephadex column using sodium (+)_D-antimonyl tartrate.

These features are similar to the properties of (+)_D-[Co(en)₃]³⁺, and the rapid racemization on charcoal indicates the facility of bond rearrangement, albeit possibly in a Co(II) intermediate.²² There would seem to be no mechanistic barrier therefore to the formation of the other two geometric isomers accompanying racemization of $(-)_D$ -*u-fac*-[Co(daes)₂]³⁺, and the fact that there has been no evidence throughout this work for the existence of the *s-fac* and *mer* isomers must indicate their relatively low thermodynamic stabilities.

The effect of phosphate in preparations of amine complexes. The equilibrium geometric

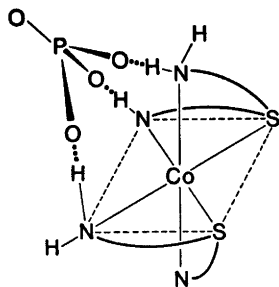


Fig. 4. The proposed ion-pair between *u-fac*-[Co(daes)₂]³⁺ and PO₄³⁻.

isomer proportions of [Co(dien)₂]³⁺, *mer:u-fac*:*s-fac* = 65:28:7 under "normal" conditions, are considerably modified by the presence of phosphate to become 12:29:59.² This enhanced proportion of the *s-fac* isomer at the expense of *mer* has been ascribed to the differential specific associations between the PO₄³⁻ anion and the three isomeric cations, with the interaction magnitudes being in the order *s-fac* > *u-fac* > *mer*. In the [Co(daes)₂]³⁺ system, *only* the *u-fac* isomer has three amine donor groups suitably disposed to permit hydrogen bonding with three oxygens of a tetrahedral oxyanion in the manner previously proposed² (Fig. 4). On this rationale the order of the

magnitudes of interactions of [Co(daes)₂]³⁺ with PO₄³⁻ should thus be *u-fac* ≫ *s-fac* ~ *mer*.

It would be expected that if the other two isomers were present, their separation from *u-fac*-[Co(daes)₂]³⁺ should be effected readily on Sephadex by ion-associating eluents such as Na₃PO₄. The single [Co(daes)₂]³⁺ chromatographic band always obtained, under all chromatography conditions and from all preparations (including particularly the aerial oxidation preparation carried out in 0.1 M Na₃PO₄ solution), is then consistent with the *u-facial* isomer being the exclusive product.

The pronounced effect of selenite on the CD spectrum (Fig. 3) demonstrates significant ion-association, so that this effect provides additional evidence for the *u-facial* geometry.

¹H NMR spectra. ¹H NMR spectra were studied at both 60 and 90 MHz, and some chemical shift data are given in Table 3.

The isolated [Co(daes)₂]³⁺ products (and various fractions from some recrystallizations) all had essentially identical ¹H NMR spectra in dimethyl sulfoxide-*d*₆, showing three broad NH₂ signals integrating in the ratio 1:2:1, and the same CH₂ characteristics. The region of the CH₂ protons was complicated but showed little distinct fine structure.

The CH₂ region was essentially invariant with the different anions used (Br⁻, Cl⁻,

Table 3. Chemical shifts δ of *u-fac*-[Co(daes)₂]³⁺ in dimethyl sulphoxide-*d*₆ (ppm downfield from internal TMS).

Complex	CH ₂ ^a	NH ₂	NH ₂	NH ₂	NH ₂
[Co(daes) ₂]Br ₃ (90 MHz)	2.87, 2.91, 3.00, 3.12 3.19, 3.27	4.67, 4.77 ^b (1) (1)	5.17 (weak)	5.76 (4)	6.41, 6.49 (1) (1)
[Co(daes) ₂]Br ₃ (60 MHz)	2.92, 3.15	4.68, 4.83		5.70, 5.82	6.33, 6.50
[Co(daes) ₂]Br ₃ + added LiCl (60 MHz)	2.88, 3.17	5.27, 5.40 ^b (1) (1)	5.70 (2)	6.30 (2)	6.73, 6.87 (1) (1)
[Co(daes) ₂]Cl ₃ (90 MHz)	2.87, 2.99, 3.15	5.36, 5.46 ^b (1) (1)	5.84 (2)	6.26 (2)	6.90, 6.96 (1) (1)
[Co(daes) ₂]Cl ₃ (60 MHz)	2.92, 3.15	5.32, 5.48		5.97, 6.08	6.77, 6.87
[Co(daes) ₂]Cl ₃ in D ₂ O/D ₂ SO ₄ (60 MHz)	3.07, 3.25, 3.43	~ 4.5 ^c		5.2	5.8
[Co(daes) ₂](ClO ₄) ₃ (90 MHz)	2.91, 3.10, 3.20	4.04, 4.17	4.71 (weak)	5.10, 5.21	5.56, 5.64
<i>u-fac</i> -[Co(dien) ₂]I ₃ (60 MHz) ^d	2.7–3.0	4.68 (2)	5.08 (2)	6.40 (1) (>NH)	
<i>u-fac</i> -[Co(4-methyldien) ₂]- Br ₃ (60 MHz)	2.6–3.1 (CH ₃ at 2.79)	5.00 (1)	5.30 (1)		

^a Peak positions above complex background. ^b Figures in parentheses are relative peak areas. ^c Obscured by HOD peak. ^d From Ref. 3.

ClO_4^-), but the NH_2 resonances showed a considerable anion dependence.

With $[\text{Co}(\text{daes})_2]\text{Br}_3$ in $\text{DMSO}-d_6$ at 60 MHz, each of the three NH_2 signals seems split into doublets. At 90 MHz a fourth very weak NH_2 signal at δ 5.17 was observed, and the major signal now appears as a single resonance at δ 5.76 (Fig. 2). Spin-decoupling indicated that the weak NH_2 resonance at δ 5.17 is coupled to the NH_2 resonances at $\delta \sim 4.7$ (doublet) and at 5.76 but is not coupled to the NH_2 resonances at $\delta \sim 6.4$.

The NH_2 pattern for the perchlorate is similar, although it has shifted upfield from the bromide situation. The chloride salt shows four distinct NH_2 signals (intensity ratio 1:1:1:1), downfield from those of the bromide, and the NH_2 signals at highest and lowest fields show similar splitting to the signals at corresponding positions in the other salts.

This variation in the NH_2 resonances is indicative of differential ion-association effects, and when LiCl was added to the tube of $[\text{Co}(\text{daes})_2]\text{Br}_3$ the resulting NH_2 pattern was similar to that of the chloride salt. However, INDOR and tickling experiments also indicate that smaller fractions than 1/8 of the total number of an equivalent N-bound protons are distinguishable. This observation may point to slow (by the NMR time scale) conformational interconversions. Computer simulation (LAOCOON II) seems to exclude that these effects arise from the coupling within the six protons of a given chelate ring.

We expect to clarify this point in the near future when better equipment is placed at our disposal.

It is noted that the NH_2 splitting is considerably greater in the present complex than in the *u-fac* and *mer* isomers of $[\text{Co}(\text{dien})_2]^{3+}$ and of $[\text{Co}(4\text{-methyl dien})_2]^{3+}$ where only two NH_2 resonances are observed in each instance (Table 3).^{3,23} This may reflect the larger difference between *equatorial vs. axial* character expected for the substituents on the ring atoms of the $[\text{Co}(\text{daes})_2]^{3+}$ rings which are expanded relative to the rings of $[\text{Co}(\text{dien})_2]^{3+}$.

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