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The Crystal and Molecular Structure of an Isomer of Chloro(RS-1,2-diaminopropane)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II)

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The crystal structure of B-chloro(RS-1,2-diaminopropane)(diethylenetriamine)cobalt(III) tetrachlorozincate(II) (one of the seven isolated isomers) has been determined from three-dimensional X-ray data collected by counter methods at room temperature.

The crystals are monoclinic: space group C_s^4*–Cc, with four molecules in a unit cell of dimensions* a = *9.744(2),* b = *13.263(3),* c = *13.955(2) Å, β = 95.26(1)°. Observed and calculated densities are 1.79 and 1.77 g cm*$^{-3}$*. A final value of the conventional R-factor (on F) of 0.037 was obtained from the 1331 reflections having* $F^2 \geqslant 3\sigma(F^2)$*.*

The structure consists of the complex cation and discrete tetrachlorozincate(II) anions. The complex cation contains the cobalt atom surrounded by one chlorine atom and five nitrogen atoms in an approximately octahedral configuration. In this isomer, the three nitrogen atoms of the diethylenetriamine ligand are in a plane with the nitrogen atom of the 1,2-diaminopropane which is adjacent to the methyl substituted carbon atom. The other end of the 1,2-diaminopropane ligand is trans *to the chlorine atom. The orientation about the secondary nitrogen group of the coordinated diethylenetriamine ligand is such that the NH proton is remote from the coordinated chlorine atom.*

The isolated five-membered ring has the δ configuration with the methyl group in the axial orientation while the tetrachlorozincate(II) anion has a slightly distorted tetrahedral configuration.

Introduction

Of the four geometric configurations possible for $CoCl(en)(dien)^{2+}$ [1], (Figure 1), three have been characterised by single crystal X-ray analysis [2–4]. These are the *a, bc, def-*(π)- [2], *a, bc, def-*(ω)- [3, 4] and (H↓)-*a, bf, cde-*(κ)-$CoCl(en)(dien)^{2+}$ [2], isomers corresponding to I, II and IIIb respectively of Figure 1 [5].

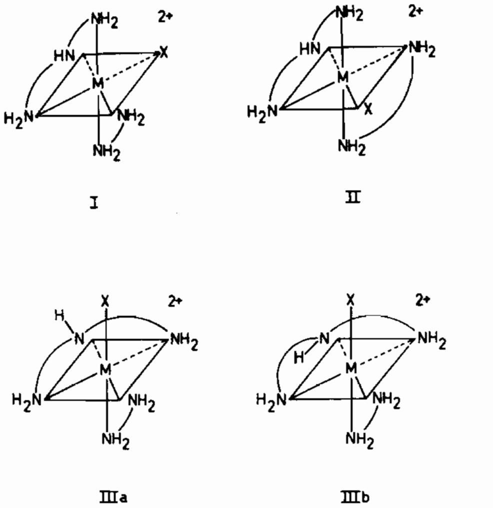

Figure 1. Possible geometric isomers for the $CoCl(en)(dien)^{2+}$ cation.

The introduction of an unsymmetric diamine such as (RS)-1,2-diaminopropane [6, 7] or N-methyl-1,3-diaminopropane [6, 8] almost doubles the number of potential geometric conformations, because of the alternate modes of diamine coordination. Thus, configuration I (Figure 1) could have the *a, bc, def-* or the *a, cb, def-*$CoCl(RS\text{-}pn)(dien)^{2+}$ ligand arrangement.

Using the synthetic methods established for the ethylenediamine system [9], Gainsford [6, 7] has isolated seven infrared and crystallographically distinct isomers of $[CoCl(RS\text{-}pn)(dien)]ZnCl_4$. This paper reports the single crystal X-ray structure analysis of one of these seven isomers [10].

Experimental

The deep red crystals of B-chloro(RS-1,2-diaminopropane)(diethylenetriamine)cobalt(III) tetrachlorozincate show monoclinic symmetry with systematic absences for h k l, h + l = 2n + 1 and for h 0 l, l = 2n

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+ 1 establishing the space group as either Cc or C_2/c The density measured by floatation in CH_3I/CH_3Br was consistent with the presence of 4 molecules in the unit cell and thus indicated the non-centrosymmetric space group

A small crystal was mounted with the unique b axial direction parallel to the phi goniometer axis and was used for all measurements Precise cell parameters and diffractometer orientation matrix [11] were determined by a least squares fit of the setting angles of 12 widely dispersed reflections ($80° < 2\theta < 98°$) carefully centred using CuKα radiation

Cell Data [*12*]

$ZnCoCl_5C_7N_5H_{23}$, mol wt = 478 6 daltons, monoclinic, a = 9 744(2) Å, b = 13 263(3) Å, c = 13 955(2) Å, β = 95 26(1)°, V = 1795 9 Å^3, space group Cc, d_m (by floatation) = 1 79 g cm^{-3}, Z = 4, d_c = 1 770 g cm^{-3}, $\bar{\lambda}$CuKα = 1 5418 Å, μ(CuKα) = 164 5 cm^{-1}, F(000) = 968$\bar{e}$

Data (reflection forms +h −k ±l, $3° < 2\theta < 126°$) were collected on a Picker FACSI automated four circle diffractometer with graphite monochromated (monochromator 2θ = 26 50°) copper Kα radiation using the θ–2θ scan technique Each reflection was scanned (2°/min) from 0 85° below the position of the α_1 peak to 0 85° beyond that of the α_2 maximum Stationary background counts were taken for 10 seconds at either end of the scan range Three large axial reflections were measured every one hundred data but only statistical variations in their intensities were recorded over the period of the data collection

The reflection data were corrected for Lorentz, polarisation and absorption [13] effects (absorption factors varied between 0 275 and 0 555) and intensities less than three standard deviations were removed After sorting and averaging equivalent forms 1331 significant data remained

The unsharpened Patterson yielded the locations of the zinc and cobalt, and the succeeding heavy atom phased Fourier maps provided the remaining non hydrogen atoms Refinement was by full matrix least squares minimisation of $\Sigma\ \omega(|F_o| - |F_c|)^2$ where the individual weights $\omega^{1/2}$ had the form

$$([(\sigma(I)/Lp)^2 + (\rho|F_o|^2)^2]/2|F_o|)^{-1/2}$$

where $\sigma(I)$ is the standard deviation of the intensity, Lp the appropriate Lorentz and polarisation correction and ρ(0 045) is an instrumental "uncertainty" constant Neutral atom scattering factors were taken from the compilation by Cromer and Waber [14] and the anomalous dispersion corrections for zinc and cobalt were taken from Cromer [15] All hydrogens apart form those on the methyl carbon C(7) were positioned by calculation (C–H 0 95 Å, N–H 0 87 Å) [16] and entered into the structure factor calculation with isotropic temperature factors set equal to 1 1 times the equivalent B value of the parent atom These parameters were not refined When refinement had all but ceased the hydrogens were repositioned and the non hydrogen atom parameters were again refined to convergence The final R value ($= \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$) was 0 036 while the weighted R value ($= [\Sigma\ \omega(|F_o| - |F_c|)^2/\Sigma\ \omega|F_o|^2]^{1/2}$) was 0 054 All calculated shifts were less than 0 01 times their estimated standard deviation and the estimated error in an observation of unit weight [$= \Sigma\ \omega(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 1 41 Inspection of the weighting analysis showed no systematic dependence on either F_o or sin θ/λ

The final difference map showed several maxima as large as 0 5$\bar{e}$ and all associated with the heavy atoms, indicating perhaps the need for a secondary extinction correction No maxima could be found in locations reasonable for methyl hydrogens

The final refined atom parameters are presented in Table I and a listing of the final observed and calculated structure factors is available [17] Bond lengths and angles are in Table II, together with those intermolecular approaches less than 3 7 Å

Results

The structure of the cation is shown in Figure 2 [18] Like the isomorphous κ isomer of chloro(ethylenediamine)(diethylenetriamine)cobalt(III) tetrachlorozincate(II) [2], the dien chelate assumes a meridional configuration with the proton on the secondary nitrogen being directed away from the chlorine The chlorine is *trans* to N(1) of the 1,2-diaminopropane moiety (the nitrogen attached to the C(1) atom) while the methyl group on C(2) is axial to the five-membered ring in the δ configuration [19] Thus, the cation can be represented as the (H↓)-*a, fb, cde*-CoCl(RS-pn)(dien)$^{2+}$ isomer [5]

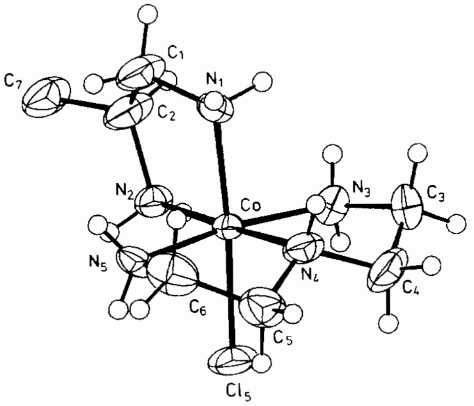

Figure 2 A general view of the B-CoCl(RS-pn)(dien)$^{2+}$ cation showing the atom numbering scheme

TABLE I. Positional and Thermal Parameters for B-[CoCl(RS-pn)(dien)]ZnCl$_4$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	1.0000	1.0094(1)	1.0000	0.0092(1)	0.0036(1)	0.0042(1)	−0.0000(1)	0.0004(1)	−0.0005(1)
Cl(1)	1.1691(2)	1.1038(1)	1.0303(2)	0.0108(2)	0.0038(1)	0.0061(1)	+0.0001(1)	−0.0014(1)	−0.0011(1)
Cl(2)	1.0433(3)	0.9966(2)	0.3430(2)	0.0182(4)	0.0051(1)	0.0045(1)	−0.0037(2)	0.0027(2)	−0.0014(1)
Cl(3)	0.7977(2)	1.0896(2)	1.0136(2)	0.0096(2)	0.0066(1)	0.0048(1)	+0.0022(2)	−0.0006(1)	−0.0003(1)
Cl(4)	0.9970(3)	0.3433(2)	1.0574(2)	0.0118(2)	0.0041(1)	0.0053(1)	−0.0001(1)	0.0013(1)	+0.0004(1)
Co	1.4375(2)	0.3245(1)	1.2615(1)	0.0053(1)	0.0021(1)	0.0036(1)	−0.0003(1)	0.0005(1)	−0.0003(1)
Cl(5)	1.4845(3)	0.9817(1)	1.3161(2)	0.0116(3)	0.0031(1)	0.0078(2)	−0.0022(1)	0.0020(2)	−0.0018(1)
N(1)	1.3789(6)	0.6375(4)	1.2231(4)	0.0074(7)	0.0026(3)	0.0037(3)	+0.0005(4)	0.0013(4)	+0.0002(3)
N(2)	1.2903(7)	0.8202(5)	1.3460(5)	0.0070(7)	0.0031(4)	0.0048(4)	−0.0007(4)	0.0018(4)	−0.0008(3)
N(3)	1.5734(6)	0.7748(5)	1.3597(5)	0.0064(6)	0.0050(4)	0.0035(3)	−0.0005(4)	0.0002(4)	+0.0001(3)
N(4)	1.5347(7)	0.3241(5)	1.1759(5)	0.0082(7)	0.0034(4)	0.0049(4)	−0.0015(4)	0.0017(5)	−0.0001(3)
N(5)	1.3228(7)	0.8865(5)	1.1620(5)	0.0099(8)	0.0026(3)	0.0047(4)	+0.0009(4)	−0.0002(4)	+0.0012(3)
C(1)	1.2333(9)	0.6693(7)	1.2539(8)	0.0096(10)	0.0047(6)	0.0103(8)	−0.0027(6)	0.0054(7)	−0.0030(6)
C(2)	1.2156(9)	0.7222(7)	1.3412(3)	0.0097(11)	0.0051(6)	0.0099(8)	−0.0032(7)	0.0047(7)	−0.0031(6)
C(3)	1.7105(8)	0.7534(7)	1.3134(7)	0.0061(8)	0.0056(6)	0.0073(6)	+0.0016(6)	0.0004(6)	−0.0000(5)
C(4)	1.7181(9)	0.3289(3)	1.2342(8)	0.0062(8)	0.0070(7)	0.0085(7)	−0.0026(6)	0.0016(6)	−0.0015(6)
C(5)	1.5552(10)	0.9015(7)	1.1009(7)	0.0119(11)	0.0048(6)	0.0065(6)	−0.0000(7)	0.0024(7)	+0.0013(5)
C(6)	1.4040(11)	0.8857(7)	1.0657(7)	0.0164(14)	0.0056(6)	0.0041(5)	+0.0006(8)	0.0000(7)	+0.0016(4)
C(7)	1.0711(10)	0.7300(3)	1.3669(9)	0.0094(10)	0.0056(6)	0.0108(9)	−0.0023(6)	0.0051(8)	−0.0025(6)
H(14)[a,b]	1.595	0.768	1.138						

[a] On N(4). [b] B = 3.4.

TABLE II. Bond Lengths and Angles for B-[CoCl(RS-pn)(dien)] $ZnCl_4$ and κ-[CoCl(en)(dien)] $ZnCl_4$.

(a) Bond Lengths (Å)

	B-isomer	κ-isomer[a]
Zn–Cl(1)	2.284(2)	2.284(4)
Zn–Cl(2)	2.275(2)	2.272(5)
Zn–Cl(3)	2.263(2)	2.256(5)
Zn–Cl(4)	2.283(2)	2.279(4)
Co–Cl(5)	2.252(2)	2.268(4)
Co–N(1)	1.965(6)	1.96(1)
Co–N(2)	1.939(6)	1.95(1)
Co–N(3)	1.962(6)	1.98(1)
Co–N(4)	1.948(7)	1.93(1)
Co–N(5)	1.986(6)	1.97(1)
N(1)–C(1)	1.49(1)	1.48(2)
C(1)–C(2)	1.44(1)	1.44(3)
C(2)–N(2)	1.49(1)	1.49(2)
C(2)–C(7)	1.49(1)	
N(3)–C(3)	1.52(1)	1.49(2)
C(3)–C(4)	1.50(1)	1.53(2)
C(4)–N(4)	1.47(1)	1.49(2)
N(4)–C(5)	1.47(1)	1.45(2)
C(5)–C(6)	1.52(1)	1.51(3)
C(6)–N(5)	1.50(1)	1.47(2)

(b) Bond Angles (°)

Cl(1)–Zn–Cl(2)	109.11(9)	108.8(2)
Cl(1)–Zn–Cl(3)	107.17(9)	107.3(2)
Cl(1)–Zn–Cl(4)	111.82(9)	111.0(2)
Cl(2)–Zn–Cl(3)	110.81(10)	110.5(2)
Cl(2)–Zn–Cl(4)	106.14(9)	107.8(2)
Cl(3)–Zn–Cl(4)	111.81(10)	111.5(2)
Cl(5)–Co–N(1)	173.5(2)	172.5(4)
Cl(5)–Co–N(2)	87.7(2)	87.7(4)
Cl(5)–Co–N(3)	88.1(2)	88.4(4)
Cl(5)–Co–N(4)	94.1(2)	94.8(4)
Cl(5)–Co–N(5)	87.7(2)	88.2(4)
N(1)–Co–N(2)	85.7(3)	85.1(5)
N(1)–Co–N(3)	92.7(3)	94.1(5)
N(1)–Co–N(4)	92.4(3)	92.4(5)
N(1)–Co–N(5)	92.5(3)	90.5(3)
N(2)–Co–N(3)	94.3(3)	94.3(5)
N(2)–Co–N(4)	178.1(3)	177.5(5)
N(2)–Co–N(5)	94.8(3)	95.4(5)
N(3)–Co–N(4)	85.4(3)	85.6(6)
N(3)–Co–N(5)	169.8(3)	169.6(5)
N(4)–Co–N(5)	85.6(3)	84.9(5)
Co–N(1)–C(1)	108.8(5)	108.1(9)
N(1)–C(1)–C(2)	112.4(7)	109(1)
C(1)–C(2)–N(2)	110.5(8)	108(1)
C(1)–C(2)–C(7)	117.4(8)	
N(2)–C(2)–C(7)	113.5(8)	
Co–N(2)–C(2)	112.6(5)	111(1)

TABLE II. Continued

Co–N(3)–C(3)	109.4(5)	109.6(9)
N(3)–C(3)–C(4)	106.8(7)	108(1)
C(3)–C(4)–N(4)	106.2(7)	105(1)
Co–N(4)–C(4)	108.9(6)	110.4(9)
Co–N(4)–C(5)	109.0(5)	110(1)
C(4)–N(4)–C(5)	117.8(7)	118(1)
N(4)–C(5)–C(6)	104.7(7)	105(1)
C(5)–C(6)–N(5)	107.8(7)	107(1)
Co–N(5)–C(6)	108.3(5)	109(1)

(c) Intermolecular Distances[b]

Cl(1)–N(4)	3.343(7)	3.27(1)	x	y	z[c]
Cl(1)–N(5)	3.357(6)	3.39(1)	x – ½	y – ½	z
Cl(1)–N(2)		3.39(1)			
Cl(1)–C(4)	3.679(10)		x	y	z
Cl(2)–N(1)	3.292(6)	3.30(1)	x	–y – 1	½ + z
Cl(2)–N(2)	3.417(7)	3.30(1)	x – ½	–y – ½	½ + z
Cl(2)–N(3)	3.622(7)		x	–y – 1	½ + z
Cl(2)–C(7)	3.649(11)		x – ½	–y – ½	½ + z
Cl(3)–N(1)	3.230(7)	3.21(1)	x	y	z
Cl(3)–N(3)	3.401(7)	3.32(1)	x + ½	–y – ½	½ + z
Cl(3)–C(1)	3.613(11)		x	y	z
Cl(3)–C(3)	3.525(10)		x + ½	–y – ½	½ + z
Cl(4)–N(3)	3.363(7)	3.32(1)	x	–y – 1	½ + z
Cl(4)–N(5)	3.363(7)	3.34(1)	x – ½	y – ½	z
Cl(5)–C(1)	3.668(9)		x – ½	y + ½	z
Cl(5)–C(7)	3.457(10)		x – ½	y + ½	z
C(3)–C(7)	3.538(13)		x – 1	y	z
C(6)–C(7)	3.679(15)		x – ½	–y – ½	½ + z

[a] Data for the κ-isomer from Ref. 2. [b] Intermolecular distances <3.7 Å for the B-isomer and <3.5 Å for the κ-isomer [2]. [c] To move atom 2 into contact with atom 1, for the B-(RS)-pn complex.

Bond lengths (Table II) have estimated standard deviations of about 0.006 Å for Co–N distances and 0.013 Å for light atom–light atom interactions while bond angles have estimated errors of between 0.3° and 0.8°. Most bond lengths and bond angles have values which are within 3σ of the values found previously [2] for the isomorphous κ-ethylene diamine complex. The Co–Cl(5) distance is found shortened to 2.252(2) Å as compared with 2.268(4) Å found for the κ isomer and is much nearer the value of 2.249 Å reported for the π complex [2]. The other major differences are to be found in the diaminopropane chelate ring which is found considerably flattened when compared with the en ring of the κ complex. The torsion angle [21] about the C(1)–C(2) bond has been reduce from –45(2)° in the κ complex to –34(1)° in the present study and this is accompanied by changes of about 3σ in the angles at C(1) and N(2). At C(2) the endocyclic angle remains close to the tetrahedral value at 110.5(8)° while the two exocyclic angles that the C(7)–C(2) bond makes with C(1)–C(2) and N(2)–C(2) are

117.4(8)° and 113.5(8)° respectively indicating again the tendency for this diaminopropane chelate ring to flatten.

This ring distortion is predicted on the basis of strain energy minimisation calculations where the methyl group with (R) absolute configuration at C(2) in the axial orientation on a δ chelate ring is expected to tilt away from the *a* position to alleviate non-bonded interactions [21, 22].

Zinc–chlorine bonds within the tetrachlorozincate anion vary between 2.263(2) Å and 2.284(2) Å and again compare very closely with those found in the isomorphous structure. Interbond angles are also very similar with only minor differences from the tetrahedral.

Anion–cation interactions (<3.7 Å) between chlorine and nitrogen are also listed in Table II and vary between 3.230(7) Å and 3.417(7) Å. While most of these presumed Cl–N hydrogen bonds are similar in length to those also found in the isomorphous κ complex it should be noted that the interaction Cl(1)–N(2) (3.39 Å) which occurs in the κ(en) isomer is not present in the present study. Nitrogen(2) is thus H bonded to only one chlorine, whereas all others (apart from N(4)) are bonded to two and it is presumably this which has given rise to the shortest Co–N(2) bond length (1.939(6) Å).

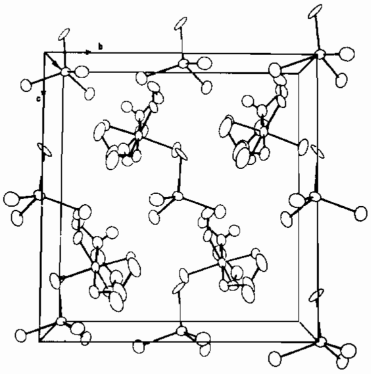

Figure 3. The packing of the ions in B-[CoCl(RS-pn)(dien)]-ZnCl$_4$ as viewed down the *a*-axis.

Figure 3 shows the packing of the anions and cations within the unit cell. This is essentially the same as that for the κ complex apart from the methyl group C(7) which inserts into a gap between the tetrachlorozincates. The closest approach of this group to the other atoms in the cell is to Cl(5) at ½ + x y– ½ z (3.46(1) Å) and C(4) at 1 + x y z (3.55(1) Å). Clearly, those small differences which are found between the κ complex and this structure are the result of the very minor accommodations which were necessary to fit the methyl group C(7) into the crystal lattice of the κ complex.

Chemical Implications

A number of Co(III)–dien structures have now been determined with the dien in the meridional configuration, *viz.*, *a, bf, cde*-κ-CoCl(en)(dien)$^{2+}$ [2], *a, fb, cde*-B-CoCl(RS-pn)(dien)$^{2+}$, *a, bcd, ef*-Co(NH$_3$)(dien)(ox)$^{+}$ [23], *a, bf, cde*-K-CoCl(NH$_3$)$_2$(dien)$^{2+}$ [24], and Co$_2$(en)$_2$(dien)$_2$O$_2^{4+}$ [25]. If the *a* and *f* positions of the complex are different, there are two possible orientations for the sec NH proton. In all cases so far, this NH proton is adjacent to an –NH$_2$ or NH$_3$ group, rather than the Cl or O atom in the other axial position. The reasons for this preference are not clear at the moment, but if this observation can be extended generally, it will be of considerable use in the assignment of the sec NH proton position, as the meridional dien configuration can often be established by infrared spectroscopy [26, 27].

The seven [CoCl(RS-pn)(dien)] ZnCl$_4$ isomers isolated by Gainsford [6] can be arranged into two non-interconvertible groups. It had been assumed that these groups arose by virtue of the two alternate modes of coordination of the unsymmetrical diamine [28] but, until this study, the orientation of the diamine in a particular group was unknown. The establishment of the *fb*-pn coordination in the B isomer now allows the assignment of the *bf*-pn coordination to the related G-isomer [6, 7] and in particular, the *a, bc, dfe*-CoCl(RS-pn)(dien)$^{2+}$ to the configuration of the H-isomer [29]. This H-isomer is isomorphous with the only [CrCl(RS-pn)(dien)] ZnCl$_4$ complex so far isolated [30] and thus the Cr(III) complex also has the *a, bc, dfe*-chloro(RS-1,2-diaminopropane)(diethylenetriamine) configuration (Figure 1, II).

Acknowledgements

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ligands are coordinated stepwise from one end and in the order of the alphabetical letters. For asymmetric ligands, the donor site with the lowest number according to the conventional Organic Nomenclature practice, is given the first letter. The recommended nomenclature systems do not distinguish between the alternative positions for the NH proton of the secondary amine group in the symmetric tridentate ligand. The system adopted here is to use (H↑) or (H↓) for this proton if it is adjacent to, or remote from the coordinated chlorine atom.

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10 As each isomer was characterised, it was given an arbitrary alphabetical letter. The B-[CoCl(RS-pn)(dien)]-ZnCl$_4$ form [6, 7] is the isomer described here.

11 The Busing and Levy programs for four-circle diffractometers *Acta Crystallogr., 22,* 457 (1967) were used for all phase of diffractometer control and data collection.

12 Here and throughout the crystallography sections, the uncertainties given in parentheses are estimated standard deviations in the least significant digits quoted.

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18 The atom numbering scheme is the same as that used for the (H↓)-*a, bf, cde*-(κ)-CoCl(en)(dien)$^{2+}$ isomer [2], apart from the C(7) methyl carbon atom.

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22 The absolute configuration of the 1,2-diaminopropane ligand shown in Figure 2, is (S). Of the four molecules in the unit cell, two are (R) and two are (S) at the asymmetric carbon atom (Figure 3).

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