

Notes

Correlation Between Structure and Circular Dichroism. Structure and Absolute Configuration of the (-) Isomer of Lithium (Ethylenediamine-*N,N'*-diacetato-*N,N'*-di-3-propionato)rhodate(III) Pentahydrate†

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In order to determine the geometrical isomerism and absolute configuration of the ion $(-)[\text{Rh}(\text{eddda})]^-$ (eddda = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) and to correlate the structure with the c.d. spectrum, the *X*-ray crystal structure analysis of the title compound was carried out. The bright yellow crystals are orthorhombic, space group $P2_12_12_1$, with $a = 11.609(2)$, $b = 13.309(1)$, $c = 12.603(2)$ Å, and $Z = 4$. The structure was refined on the basis of 2 883 intensities by full-matrix least-squares methods on a SEL 32/27 minicomputer. The refinement terminated at $R = 0.016$, $R_w = 0.020$. The structure of this complex is isomorphous with the chromium analogue and comprises the complex anion, lithium ions, and molecules of water. The five-membered glycinate rings are *trans* and the absolute configuration of the complex is Λ . The *trans*(O_5)- $(-)[\text{Rh}(\text{eddda})]^-$ ion has a negative sign for the lowest energy $E(D_{4h})$ c.d. peak and the assignment of the absolute configuration would be reversed, based on a correlation with $[\text{Co}(\text{edta})]^-$ (edta = ethylenediaminetetra-acetate) type complexes. The average metal-ligand distances are as follows: Rh-N 2.022(2), Rh-O(eq) 2.045(2), Rh-O(ax) 2.007(2) Å. Interbond angles deviate from +4.1 to -5.1° from the ideal octahedral geometry.

Complexes with ligands structurally similar to edta (edta = ethylenediaminetetra-acetate), but with longer carboxylate chains, are of interest in the study of the effects of the size of the chelate rings and their arrangement around the central metal ion on chiroptical properties of the complexes. The ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate (eddda) ligands on sixidentate co-ordination form three five- and two six-membered rings. Three geometrical isomers are possible, which differ in the number (2, 1, or 0) of six-membered rings in the equatorial, girdle plane: *trans*(O_5), *trans*(O_5O_6), and *trans*(O_6). The c.d. spectra of $[\text{M}(\text{eddda})]^-$ ($\text{M} = \text{Co}$ or Cr) complexes have been considered in terms of the C_2 symmetry. Tentative assignment of the configuration has been made for the (-) isomer on the basis of a positive lowest energy $A(C_2)$ peak^{1,2} and confirmed by the *X*-ray analysis of *trans*(O_5)- $(-)\text{Li}[\text{Cr}(\text{eddda})]\cdot 5\text{H}_2\text{O}$.³ However, it has been observed recently that Λ isomers of $[\text{Rh}(1,3\text{-pdta})]^-$ (1,3-pdta = propane-1,3-diaminetetra-acetate) and $[\text{Rh}(\text{SS-edds})]^-$ (SS-edds = SS-ethylenediamine-*N,N'*-disuccinate) have a negative sign for the lowest energy $E(D_{4h})$ c.d. peak.⁴⁻⁶ The Λ absolute configuration of *trans*(O_5)- $(-)[\text{Rh}(\text{eddda})]^-$ was tentatively assigned by comparison of the c.d. spectrum to that of the (+) isomer of the *trans*(O_5) Rh^{III} complex containing a stereospecific SS-edds ligand.⁴ Both complexes have a negative c.d. peak in the lowest energy spin-allowed region which suggests a Δ absolute

configuration by analogy to $[\text{M}(\text{eddda})]^-$ ($\text{M} = \text{Co}$ or Cr) and many other Co^{III} edta-type complexes. Thus, the evidence for the absolute configuration of these complexes derived from their optical properties is ambiguous. Therefore, an *X*-ray crystal structure analysis of the title compound was carried out.

Experimental

Preparation of the Complex.—The complex was prepared by the procedure described in ref. 4 and characterized by electronic absorption and c.d. spectra.

Crystal Data.— $\text{Li}[\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_8\text{Rh}]\cdot 5\text{H}_2\text{O}$, $M = 516.2$, orthorhombic, $a = 11.609(2)$, $b = 13.309(1)$, $c = 12.603(2)$ Å, $U = 1947.2$ Å³, $Z = 4$, $D_c = 1769$ g cm⁻³, $F(000) = 1056$, space group $P2_12_12_1$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 5.2$ cm⁻¹.

Measurements, Structure Determination, and Refinement.—An extremely small crystal, of excellent quality, was used on an Enraf-Nonius CAD4 diffractometer, with graphite-monochromatized Mo- K_α radiation. Cell parameters were determined from the setting angles of 25 reflections ($\theta = 14.5\text{--}17.3^\circ$); intensity data were collected for $2 < \theta < 30^\circ$ using an ω/θ scan, with a scan width of 0.70° . Two intensity standards were taken every 2 h; intensity variations were random (less than 3%) and three orientation standards were taken every 200 data reflections. The integrated intensities, I , and their standard deviations, $\sigma(I)$, were derived as described elsewhere,⁷ using a q value of 0.04. Corrections for Lorentz and polarization effects were applied, but not for absorption; 3 507 data were collected

† Supplementary data available (No. SUP 56109, 10 pp.); thermal parameters, bond lengths and angles involving H atoms, H-bonding parameters, packing diagram. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Atomic fractional co-ordinates for (-)Li[Rh(eddda)]·5H₂O with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Rh	-0.143 95(1)	0.129 38(1)	0.071 58(1)	Li	-0.179 8(4)	0.219 0(3)	-0.384 5(3)
O(1)	-0.219 84(13)	0.142 59(12)	-0.074 13(12)	H(1)	-0.017(4)	0.353(3)	-0.346(3)
O(2)	-0.232 05(16)	0.179 76(16)	-0.242 92(13)	H(2)	-0.057(3)	0.349(2)	-0.457(3)
O(3)	-0.299 83(13)	0.081 26(13)	0.127 68(12)	H(3)	-0.042(3)	0.097(3)	-0.429(3)
O(4)	-0.442 50(16)	0.087 54(17)	0.239 88(16)	H(4)	-0.133(4)	0.053(3)	-0.434(4)
O(5)	-0.094 48(15)	-0.013 04(11)	0.043 57(13)	H(5)	-0.331(4)	0.315(4)	-0.501(4)
O(6)	0.000 67(18)	-0.139 27(13)	0.117 40(15)	H(6)	-0.363(3)	0.233(3)	-0.448(3)
O(7)	-0.186 15(14)	0.272 94(12)	0.099 46(13)	H(7)	0.169(5)	0.051(4)	-0.371(4)
O(8)	-0.128 61(17)	0.429 04(12)	0.072 98(17)	H(8)	0.138(3)	0.027(3)	-0.452(3)
O(9)	-0.075 55(18)	0.337 04(17)	-0.397 16(16)	H(9)	-0.188(3)	0.447(3)	-0.298(3)
O(10)	-0.102 49(21)	0.102 15(15)	-0.442 09(17)	H(10)	-0.261(4)	0.524(3)	-0.332(3)
O(11)	-0.314 62(20)	0.262 15(19)	-0.459 03(20)	H(21)	-0.023(3)	0.138(2)	-0.236(2)
O(12)	0.137 48(24)	0.073 86(16)	-0.414 33(21)	H(22)	-0.030(4)	0.241(4)	-0.180(3)
O(13)	-0.221 52(22)	0.490 00(20)	-0.272 69(21)	H(31)	0.047(3)	0.074(3)	-0.071(3)
N(1)	0.007 73(16)	0.186 38(14)	0.020 00(15)	H(32)	0.116 1(21)	0.167 2(19)	-0.107 5(19)
N(2)	-0.068 72(16)	0.109 98(13)	0.214 60(15)	H(41)	0.116 8(19)	0.082 7(17)	0.087 2(18)
C(1)	-0.173 05(20)	0.164 93(17)	-0.162 85(17)	H(42)	0.171 0(26)	0.188 3(21)	0.095 1(22)
C(2)	-0.043 68(22)	0.175 66(25)	-0.174 92(21)	H(51)	0.092 5(27)	0.137 9(23)	0.261 8(24)
C(3)	0.037 65(20)	0.145 41(20)	-0.086 76(19)	H(52)	0.029 8(28)	0.235 4(23)	0.227 9(25)
C(4)	0.095 12(20)	0.152 31(19)	0.100 35(19)	H(61)	-0.097 2(22)	0.147 2(20)	0.369 9(22)
C(5)	0.044 60(22)	0.164 99(20)	0.209 23(21)	H(62)	-0.148 6(27)	0.223 2(22)	0.285 4(22)
C(6)	-0.139 87(26)	0.152 54(18)	0.302 60(17)	H(71)	-0.255 8(27)	0.043 1(24)	0.338 4(24)
C(7)	-0.257 96(24)	0.105 27(22)	0.315 78(19)	H(72)	-0.291 3(29)	0.131 6(25)	0.365 3(26)
C(8)	-0.338 11(19)	0.093 11(16)	0.221 96(18)	H(101)	0.011(3)	-0.008(3)	0.263(3)
C(9)	-0.045 31(21)	-0.055 69(17)	0.122 92(20)	H(102)	-0.114 1(22)	-0.030 8(20)	0.270 1(22)
C(10)	-0.049 60(24)	-0.000 75(19)	0.227 78(20)	H(121)	0.003 3(25)	0.321 5(19)	-0.045 6(21)
C(11)	-0.112 60(20)	0.337 44(16)	0.066 34(21)	H(122)	0.061 1(22)	0.330 1(19)	0.054 8(21)
C(12)	-0.001 01(23)	0.299 34(18)	0.019 58(22)				

Table 2. Selected bond distances (Å) with standard deviations for (-)Li[Rh(eddda)]·5H₂O; some relevant corresponding values for (-)Li[Cr(eddda)]·5H₂O are given in square brackets

Rh-O(1)	2.044(2) [1.96(1)]	O(5)-C(9)	1.284(3) [1.26(2)]	N(2)-C(5)	1.507(4) [1.53(2)]
Rh-O(3)	2.046(2) [1.97(1)]	O(6)-C(9)	1.236(3) [1.26(2)]	N(2)-C(6)	1.494(4) [1.52(2)]
Rh-O(5)	2.012(2) [1.95(1)]	O(7)-C(11)	1.281(3) [1.26(2)]	N(2)-C(10)	1.500(4) [1.49(2)]
Rh-O(7)	2.003(2) [1.96(1)]	O(8)-C(11)	1.236(3) [1.25(2)]	C(1)-C(2)	1.516(4) [1.55(2)]
Rh-N(1)	2.025(2) [2.10(1)]	O(9)-Li	1.989(5)	C(2)-C(3)	1.513(4) [1.51(2)]
Rh-N(2)	2.019(2) [2.07(1)]	O(10)-Li	1.937(5)	C(4)-C(5)	1.502(4) [1.50(2)]
O(1)-C(1)	1.278(3) [1.28(2)]	O(11)-Li	1.913(5)	C(6)-C(7)	1.517(5) [1.55(2)]
O(2)-C(1)	1.235(3) [1.26(2)]	N(1)-C(3)	1.493(4) [1.50(2)]	C(7)-C(8)	1.513(4) [1.52(2)]
O(2)-Li	1.956(5)	N(1)-C(4)	1.503(4) [1.54(2)]	C(9)-C(10)	1.511(4) [1.53(2)]
O(3)-C(8)	1.278(3) [1.30(2)]	N(1)-C(12)	1.507(4) [1.44(2)]	C(11)-C(12)	1.511(4) [1.54(2)]
O(4)-C(8)	1.235(3) [1.24(2)]				

of which there were 2883 independent reflections with $I > 3\sigma(I)$. Initial values for atomic co-ordinates were taken from the structure of the chromium analogue,³ atomic parameters were refined by full-matrix least-squares methods using two large blocks of parameters; H atoms from a difference map were refined isotropically. Complex neutral-atom scattering factors were taken from ref. 8. To test the validity of the chosen absolute configuration of the structural model, a polarity factor (η)⁹ was refined, 367 variables in total: $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.016$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.020$, $w = 1/\sigma^2$; with an alternative enantiomorph $R = 0.021$, $R_w = 0.029$; an R -factor ratio test¹⁰ gave $R' = R^\Delta/R^\Lambda = 1.338$, $R_w' = R_w^\Delta/R_w^\Lambda = 1.441$, $\eta = 1.08$ [$1 + |\eta|\sigma(\eta) = 53.0$], with the final difference map clean. Computers used were SEL 32/27 (GX, Glasgow X-ray crystallographic system of programs developed by Drs. C. J. Gilmore, P. R. Mallinson, K. W. Muir, and D. N. J. White) and CDC-3600 (programs GEOM, written by Drs. K. W. Muir and P. R. Mallinson, and RING, written by Dr. L. K. Parkanyi).

The final atomic co-ordinates are listed in Table 1.

Results and Discussion

The crystal structure of (-)Li[Rh(eddda)]·5H₂O consists of Li⁺ and [Rh(eddda)]⁻ ions and molecules of water, held together by electrostatic forces and hydrogen bonds. The compound is isostructural with the chromium analogue, (-)Li[Cr(eddda)]·5H₂O.³ A perspective drawing of the asymmetric unit and atom numbering is given in the Figure. Selected interatomic distances and angles are listed in Tables 2 and 3. Some relevant corresponding data observed for Li[Cr(eddda)]·5H₂O³ are given for comparison in square brackets.

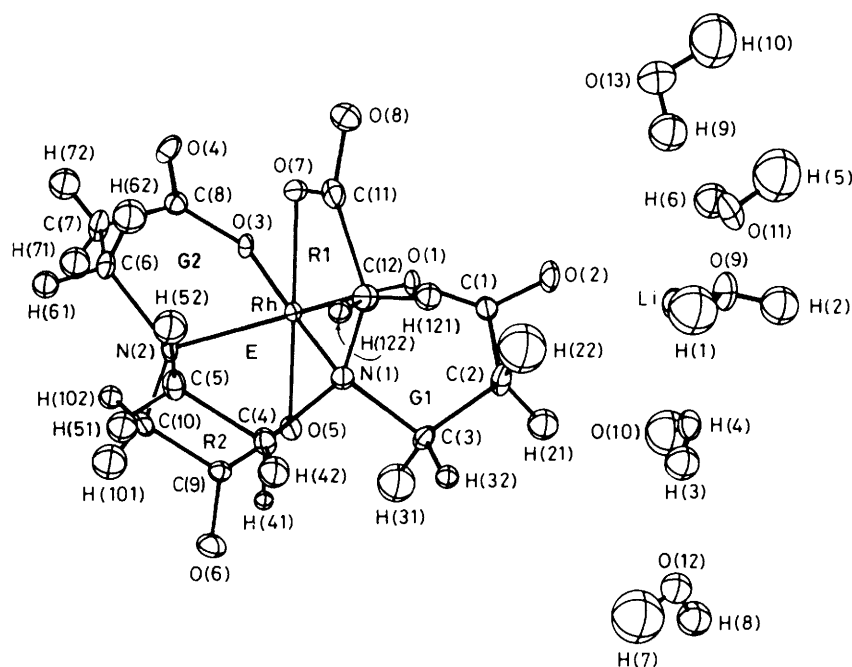
The lithium ion is tetrahedrally co-ordinated by four oxygen atoms. The Li-O distances, in the range 1.913(5)–1.989(5) Å, and the O-Li-O angles, 102.8(3)–118.2(3)°, are unexceptional.

In the complex anion, the rhodium ion is co-ordinated octahedrally by two nitrogen and four oxygen atoms from a sixidentate eddda ligand. The arrangement of chelate rings is *trans*(O₅). The absolute configuration of the complex is Λ .

The rhodium(III)-ligand bond lengths are very similar to the corresponding ones observed in the crystal structure of the ion [Rh(1,3-pdta)]⁻⁶ and to a great extent in [Rh(H₂O)(Hedta)]¹¹

Table 3. Selected bond angles ($^{\circ}$) with standard deviations for $(-)\text{Li}[\text{Rh}(\text{eddda})]\cdot 5\text{H}_2\text{O}$; some relevant corresponding values for $(-)\text{Li}[\text{Cr}(\text{eddda})]\cdot 5\text{H}_2\text{O}$ are given in square brackets

O(3)-Rh-O(1)	87.5(1)	[92.8(4)]	C(4)-N(1)-Rh	104.9(2)	O(2)-C(1)-O(1)	121.1(3)
O(7)-Rh-O(1)	88.3(1)	[91.9(4)]	C(5)-N(2)-Rh	106.0(2)	O(9)-Li-O(2)	118.2(3)
N(2)-Rh-O(1)	177.6(1)	[175.0(4)]	C(10)-N(2)-Rh	106.8(2)	O(11)-Li-O(2)	105.9(3)
O(5)-Rh-O(3)	91.0(1)	[93.1(4)]	C(2)-C(1)-O(1)	122.0(3)	C(7)-C(8)-O(3)	121.7(3)
N(1)-Rh-O(3)	176.1(1)	[173.0(4)]	C(2)-C(1)-O(2)	116.9(3)	O(6)-C(9)-O(5)	123.1(3)
C(8)-O(3)-Rh	126.2(2)		O(10)-Li-O(2)	105.7(3)	C(10)-C(9)-O(6)	119.9(3)
N(1)-Rh-O(5)	92.8(1)	[92.7(4)]	O(4)-C(8)-O(3)	120.2(3)	C(12)-C(11)-O(7)	118.3(2)
C(9)-O(5)-Rh	114.0(2)		C(7)-C(8)-O(4)	117.8(3)	O(10)-Li-O(9)	108.8(3)
N(2)-Rh-O(7)	94.1(1)	[92.1(4)]	C(10)-C(9)-O(5)	116.9(3)	C(4)-N(1)-C(3)	109.9(2)
N(2)-Rh-N(1)	87.6(1)	[86.5(5)]	O(8)-C(11)-O(7)	122.6(3)	C(2)-C(3)-N(1)	114.8(3)
O(5)-Rh-O(1)	92.7(1)	[92.6(4)]	C(12)-O(11)-O(8)	119.1(3)	C(5)-C(4)-N(1)	108.5(2)
N(1)-Rh-O(1)	93.1(1)	[91.0(4)]	O(11)-Li-O(9)	102.8(3)	C(6)-N(2)-C(5)	109.4(2)
C(1)-O(1)-Rh	128.5(2)		O(11)-Li-O(10)	115.9(3)	C(4)-C(5)-N(2)	109.1(3)
O(7)-Rh-O(3)	91.2(1)	[92.3(4)]	C(12)-N(1)-C(3)	112.1(2)	C(10)-N(2)-C(6)	111.8(2)
N(2)-Rh-O(3)	92.0(1)	[90.1(5)]	C(12)-N(1)-C(4)	110.4(2)	C(9)-C(10)-N(2)	112.6(2)
O(7)-Rh-O(5)	177.6(1)	[172.8(4)]	C(11)-C(12)-N(1)	113.0(2)	C(8)-C(7)-C(6)	120.9(3)
N(2)-Rh-O(5)	85.0(1)	[83.2(4)]	C(10)-N(2)-C(5)	110.7(2)	C(7)-C(6)-N(2)	115.1(2)
N(1)-Rh-O(7)	84.9(1)	[81.6(4)]	C(12)-N(1)-Rh	108.4(2)	C(3)-C(2)-C(1)	121.3(3)
C(11)-O(7)-Rh	114.8(2)		C(6)-N(2)-Rh	112.0(2)		
C(3)-N(1)-Rh	110.8(2)					

**Figure.** Perspective view of $(-)\text{Li}[\text{Rh}(\text{eddda})]\cdot 5\text{H}_2\text{O}$ showing the atom-numbering scheme

The Rh-O bonds lying in the equatorial plane are on average 0.038 Å shorter than the axial ones, which is often found in the edta type complexes.^{11,12} The Rh-N bond lengths are within the range of values found for the Rh-O distances and therefore shorter than would be expected on the basis of the covalent radii of oxygen and nitrogen. In the crystal structure of the ion $[\text{Cr}(\text{eddda})]^{-}$, for example, oxygen atoms are statistically equidistant from the chromium ion and Cr-N bonds are on average 0.12 Å longer than the Cr-O distances. The shortening of the Rh-N bonds could be considered to demonstrate a greater affinity of rhodium for nitrogen than for oxygen. However, in some complexes of cobalt(III) with ligands structurally related to edta, shortening of the Co-N bond lengths was also observed.¹³⁻¹⁶

The interbond angles in the rhodium co-ordination polyhedron deviate from ideal octahedral geometry from $+4.1(1)$ to $-5.1(1)^{\circ}$. Twelve edges of the octahedron vary in the range 2.720(2)—2.954(2) Å. The r.m.s. deviations of the atoms from three least-squares planes based on the rhodium and six ligating atoms are 0.045, 0.023, and 0.005 Å, respectively. The corresponding values for the Cr^{III} co-ordination polyhedron in the structure of $\text{Li}[\text{Cr}(\text{eddda})]\cdot 5\text{H}_2\text{O}$ are $+3.0(4)$ to $-8.4(4)^{\circ}$; 2.655(15)—2.932(15) Å, and 0.082, 0.035, and 0.029 Å; this indicates that, in spite of the larger ionic radius, the Rh^{III} octahedron is less distorted than that of Cr^{III} .³

The geometries of eddda ligands in the crystal structures of $[\text{Rh}(\text{eddda})]^{-}$ and $[\text{Cr}(\text{eddda})]^{-}$ are essentially the same. Some differences which occur in bond lengths, especially of

Table 4. Conformation of chelate rings; values in square brackets are corresponding data for (-)[Cr(eddda)]⁻

Ring	Puckering parameters			Torsion angles (°)		Bond-angles sum (°)
	Puckering amplitude (Å)	θ_i	φ_i	Around C-C bond	$\bar{\tau}^*$	
R1	0.085 [0.119]	175.0 [191.2]		-0.4 [3.8]	5.1 [8.0]	538.8 [538.7]
R2	0.221 [0.214]	126.6 [132.1]		-22.8 [-19.8]	16.5 [15.1]	534.9 [535.8]
E	0.447 [0.487]	263.4 [262.6]		54.2 [58.8]	36.1 [38.9]	516.1 [547.9]
G1	0.533 [0.580]	99.4 [95.9]	127.2 [124.8]		38.2 [40.5]	687.2 [684.7]
G2	0.516 [0.534]	118.3 [114.0]	148.9 [151.8]		42.8 [44.8]	687.9 [685.4]

* $\bar{\tau}$ = Root mean square torsion angle.

carboxylate groups, could be attributed to different levels of accuracy of the two structure analyses.

The conformations of the chelate rings and ring strains, expressed by puckering parameters¹⁷ and sum of the bond angles,¹⁸ respectively, in [Rh(eddda)]⁻ and [Cr(eddda)]⁻ ions are given in Table 4. The analysis of the conformational parameters shows that one of the glycinate rings lying out of the plane of the diamine ring (R1) is relatively flat. The other (R2) shows a significant deviation from planarity; it is puckered and has a λ conformation. The diamine ring (E) is also puckered and has a δ conformation. The conformation of the two six-membered rings lying in the plane of the diamine ring (G1 and G2) is close to half-chair and λ , provided that the helicity is defined by the line connecting ligating nitrogen and hydrogen atoms and the line connecting methylene carbon atoms which are directly attached to the ligating atoms. The comparison between conformational parameters of chelate rings in [Rh(eddda)]⁻ and those in the chromium analogue shows that there is no marked difference between the data for the two compounds.

In conclusion, this work confirms our previous observation that the analogy to the Co^{III}(edta) type complexes could not be used for the assignment of the absolute configurations on the basis of the c.d. spectra. Comparison of the structural data for [Rh(eddda)]⁻ and [Cr(eddda)]⁻ does not reveal a significant difference to which a rather dramatic difference in sign and shape of their c.d. spectra could be attributed. The greatest difference occurs in metal-ligand bond lengths, the Rh-N bonds exhibiting a contraction. Two interbond angles (O_{G1} -Rh- O_{G2} and O_{G1} -Rh- O_{R2}) have changed from greater than 90° to less than 90°, but these angles are not subtended by the ligand atoms, whose change is considered to profoundly affect the energies of electronic states. Finally, the ring strains, according to the deviations from planarity and sum of the bond angles, are almost the same in both compounds. It could be that the strain in chelate rings is manifested by the contraction of the Rh-N bond lengths, as Geue and Snow¹⁶ have suggested for the strained CoN₂O₄ and CoN₂O₂S₂ chromophores. However,

the observed Cr-N distances in crystal structures of the ions [Cr(eddda)]⁻³ and [Cr(1,3-pdta)]⁻⁶ do not favour such an assumption. Apparently, more experimental data on the X-ray crystal structures and absolute configurations of Rh^{III} complexes with edta type ligands, and circular dichroism measurements on single crystals are needed to give an insight into factors which are dominant in determining the shape and sign of the c.d. spectra of these complexes.

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