Inorganica Chimica Acta, *83* (1984) 55–64

Crystal Structures of Na[M(1,3-PDTA)]·3H_2O (M = Cr, Rh; 1,3-PDTA = 1,3-propanediaminetetraacetate), and the Absolute Configuration of the $(-)_D$-Isomer of the Rh Complex

R. HERAK*, G. SRDANOV

Laboratory of Solid State Physics and Radiation Chemistry, 'Boris Kidrič' Institute, 11001 Belgrade, P.O. Box 522, Yugoslavia

M. I. DJURAN, D. J. RADANOVIĆ

Institute of Chemistry, Faculty of Science, 'Svetozar Marković' University, 34000 Kragujevac, Yugoslavia

and M. BRUVO

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, 41001 Zagreb, P.O. Box 153, Yugoslavia

Received May 21, 1983

In order to clarify the relation between the absolute configuration and circular dichroism, and to investigate the influence of the size of metal ion on the strain in chelate rings of M(1,3-PDTA) complexes (M = Co, Cr, Rh; 1,3-PDTA = 1,3-propanediaminetetraacetate), X-ray crystal structure analysis of Na[Cr(1,3-PDTA)]·3H_2O and $(-)_D$Na[Rh(1,3-PDTA)]·3H_2O were performed. The crystals of the two compounds are isomorphous and belong to the orthorhombic system, space group $P2_12_12_1$, Z = 4, with cell dimensions a *= 16.514(5),* b *= 8.809(2),* c *= 11.429(3) Å and* a *= 16.511(13),* b *= 8.836(13),* c *= 11.431(7) Å for chromium and rhodium complex, respectively. The structures were determined on the basis of 1699 and 2928 diffractometer data points, and were refined by least squares methods to R 0.053 and 0.025 for chromium and rhodium complexes respectively. Crystal structures consist of the complex and of the sodium ions and molecules of water. In the complex anion, the metal ion is coordinated octahedrally by a sexidentate 1,3-PDTA ligand. The six-membered 1,3-propanediamine chelate T ring in both compounds takes a twist-boat δ conformation. Two equatorially-disposed glycinate G rings have an envelope λ conformation and two out-of-plane R rings are relatively flat. The absolute configuration of the Rh complex is Λ. The absolute configuration of the Cr complex, a crystal selected by chance from the optically-inactive complex, is also Λ. The ring strains were determined and compared with those in related Co(III) complexes.*

Introduction

Complexes structurally related to $[Co(EDTA)]^-$ (EDTA = ethylenediaminetetraacetate) are of special interest in the study of factors contributing to their optical activity. Recently, many M(III) EDTA-type complexes (M = Co, Cr, Rh) in which the strain in the chelate ring system was varied, have been studied in order to determine the influence of various structural changes in the ligand on the rotational strength of the d–d transition [1, 4–9].

It has been found that:

– X-ray crystal structure analysis of $[Co(EDTA)]^-$ shows that the ligand acts as sexidentate, forming five five-membered chelate rings. The diamine backbone (E) and two relatively strained glycinate (G) rings line in equatorial plane, the other two, axially disposed glycinate (R) rings, are almost planar and are less strained.

– Increasing ionic radius (Co < Cr < Rh) reduces the tendency of the metal ions to form sexidentate complexes with EDTA: Cr(III) forms complexes where EDTA acts as sexi-, as well as quinquedentate ligand, while Rh only has complexes with quinquedentate EDTA.

– In $[Co(1,3\text{-}PDTA)]^-$, the sexidentate ligand forms two G and R glycinate rings and one six-membered diamine (T) ring [2]. Such a chelate ring system is less strained, than sexidentate EDTA.

– Some spectroscopic investigations indicate that 1,3-PDTA acts as sexidentate in complexes with Cr(III) [10] and Rh(III) [11]. However, it has

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*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Summary of Experimental Data.

	$Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$	$Na[Rh(1,3\text{-}PDTA)]\cdot 3H_2O$
Molecular formula	$CrNaN_2O_{11}C_{11}H_2O$	$RhNaN_2O_{11}C_{11}H_2O$
Formula weight	431.270	482.179
a, Å	16.514(5)	16.511(13)
b, Å	8.809(2)	8.836(13)
c, Å	11.429(3)	11.431(7)
V, Å^3	1662.5	1668
Z	4	4
D_m, g cm^{-3} (by flotation)	1.716	1.910
D_c, g cm^{-3}	1.724	1.921
Space group	$P2_12_12_1$	$P2_12_12_1$
Linear absorption coefficient μ(Mo-K$_\alpha$), mm^{-1}	0.8165	1.0939
Crystal dimensions, mm	0.20 × 0.20 × 0.15	0.18 × 0.17 × 0.15
Diffractometer	Syntex P$\bar{1}$	Philips PW 11000
Radiation	Mo-K$_\alpha$	Mo-K$_\alpha$
Monochromator	graphite	graphite
2θ range, degrees	2–30	2–33
Scan type	$\omega-2\theta$	$\theta-2\theta$
Standards	320 (every 30 refl.)	302, 320, 04$\bar{2}$ (every 2 hours)
Number of data	1696 ($I > 2\sigma(I)$)	2928 ($I > 3\sigma(I)$)
Number of variables	168	235
Transition coef.	–	0.83–0.87
Extinction coef.	–	4.097×10^{-6}
R	0.053	0.025
R_w	0.058	0.032
R for enantiomer	0.061	0.028
R_w for enantiomer	0.073	0.035

been observed that CD peak in the region of the first absorption band of the Rh(III) complexes is reversed in sign compared to the related complexes of Co(III) of the same absolute configuration [12].

– The changes in the net rotational strength in CD spectra of M(EDTA)-type complexes are attributed to differences in the strains of the chelate ring systems [13].

In order to clarify the relation between the absolute configuration and circular dichroism and to investigate the influence of the size of the metal ion on strain in chelate rings of M(1,3-PDTA) complexes, an X-ray crystal structure investigation of $Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$ and $(-)_{589}$-$Na[Rh(1,3\text{-}PDTA)]\cdot 3H_2O$ was carried out.

Experimental

The crystals of $Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$ were prepared according to the method described by Weyh and Hamm [10], by heating the solution of the equimolar mixture of Cr(III) and ligand at 70 °C for 12 hours. The compound was characterized by electronic absorption and IR spectra.

Preliminary rotation and Weissenberg data showed the reddish-violet crystals to be orthorhombic, with systematic absences h00 for h odd, 0k0 for k odd and 00l for l odd, which uniquely defined the space group as $P2_12_12_1$. Crystal data and the X-ray data collection are given in Table I.

The structure was solved by a routine application of the heavy atom method and the atomic parameters refined by full matrix least-squares calculations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2$. After the refinement of the positional and thermal parameters (anisotropic for chromium, sodium and carbonyl and water oxygen atoms, isotropic for the others) almost all the hydrogen atoms, including those belonging to molecules of water, were located in a difference Fourier map. The hydrogen atoms from the complex ion were included in the structure factor calculations at calculated, fixed positions, with the fixed temperature factors.

TABLE II. Final Positional Parameters (×10^4 and ×10^5 for nonhydrogen atoms in Cr complex and Rh complex, respectively, ×10^3 for hydrogen atoms).

	Na[Cr(1,3-PDTA)]·3H$_2$O			Na[Rh(1,3-PDTA)]·3H$_2$O		
	x	y	z	x	y	z
M	2529.3(6)	2624(1)	12840.0(8)	25298(1)	25946(2)	12532(2)
Na	148.1(10)	3479.5(33)	4430.3(25)	1348(8)	34642(17)	44306(13)
O(1)	1723(3)	1025(5)	1465(4)	17102(14)	9519(25)	14857(21)
O(2)	1979(3)	3831(5)	2485(4)	19878(13)	38671(27)	25178(19)
O(3)	3316(3)	4213(6)	978(4)	33461(12)	42474(25)	10248(22)
O(4)	3310(3)	1519(5)	2275(4)	32956(14)	14022(27)	23222(20)
O(5)	1323(3)	−1283(6)	906(5)	13604(16)	−13436(29)	8941(26)
O(6)	828(3)	5019(6)	2878(5)	8259(16)	50351(27)	28750(25)
O(7)	3476(3)	6574(6)	325(5)	34819(15)	65370(28)	3473(26)
O(8)	4345(3)	−66(7)	2213(5)	43440(19)	−1518(38)	22348(29)
O(W1)	4996(3)	4266(8)	604(5)	50092(15)	42687(35)	5711(25)
O(W2)	4591(4)	3070(7)	4024(5)	45668(17)	30926(34)	40452(26)
O(W3)	466(4)	1466(8)	3177(5)	4633(16)	14554(33)	31857(26)
N(1)	2971(3)	1220(6)	−14(4)	29981(15)	12152(28)	9(23)
N(2)	1799(3)	3901(6)	197(6)	18075(15)	38750(30)	2094(21)
C(1)	3069(4)	2007(8)	−1159(6)	30833(21)	20128(37)	−11440(28)
C(2)	2265(4)	2615(8)	−1700(6)	22923(22)	26020(28)	−16852(27)
C(3)	1576(4)	3091(8)	−897(6)	15841(19)	30736(36)	−8916(28)
C(4)	1054(4)	4165(8)	921(6)	10613(18)	41287(38)	9276(29)
C(5)	1287(4)	4386(9)	2186(6)	12924(18)	43894(34)	22022(28)
C(6)	3826(4)	701(8)	1735(6)	38297(21)	6377(40)	17559(31)
C(7)	3800(4)	778(8)	407(6)	38232(20)	7924(43)	4389(31)
C(8)	2439(5)	−166(7)	−103(6)	24687(27)	−1698(30)	−855(28)
C(9)	1778(4)	−190(8)	818(6)	17967(19)	−2290(36)	8226(31)
C(10)	2206(4)	5400(7)	−29(5)	22249(19)	53580(35)	−124(32)
C(11)	3071(4)	5450(8)	447(6)	30789(19)	54392(36)	4870(30)
H(1)	333	121	−178	336	123	−176
H(2)	348	295	−106	349	297	−101
H(3)	203	173	−226	207	172	−225
H(4)	242	359	−223	245	359	−219
H(5)	124	209	−66	125	205	−66
H(6)	119	385	−139	118	380	−139
H(7)	65	320	84	67	314	87
H(8)	75	517	61	73	510	60
H(9)	395	−33	7	401	−26	4
H(10)	424	160	11	425	167	18
H(11)	281	−117	0	284	−116	15
H(12)	216	−18	−96	219	−19	−95
H(13)	223	560	−96	225	553	−95
H(14)	186	629	38	187	625	38
HW(1)	522(7)	455(16)	121(10)	525	450	124
HW(2)	455(6)	436(14)	68(10)	450	405	75
HW(3)	433(7)	284(14)	378(11)	427	278	364
HW(4)	495(6)	366(13)	368(10)	500	350	357
HW(5)	86(6)	103(12)	274(11)	95	119	277
HW(6)	22(7)	140(15)	265(11)	12	98	273

The complex Na[Rh(1,3-PDTA)] was prepared using the 'sealed-tube' technique employed by Dwyer and Garvan [14]. Crystals of the three-hydrate of the complex were crystallized from water after removing species with higher charge. The pure complex was obtained by recrystallization from water, resolved and characterized on the basis of PMR, ^{13}C NMR, IR, electronic absorption and CD spectra [11, 12].

The crystals of $(-)_{589}$-Na[Rh(1,3-PDTA)]·3H$_2$O are yellow plates with pinacoids and domes. A summary of the experimental data is given in Table I. Dur-

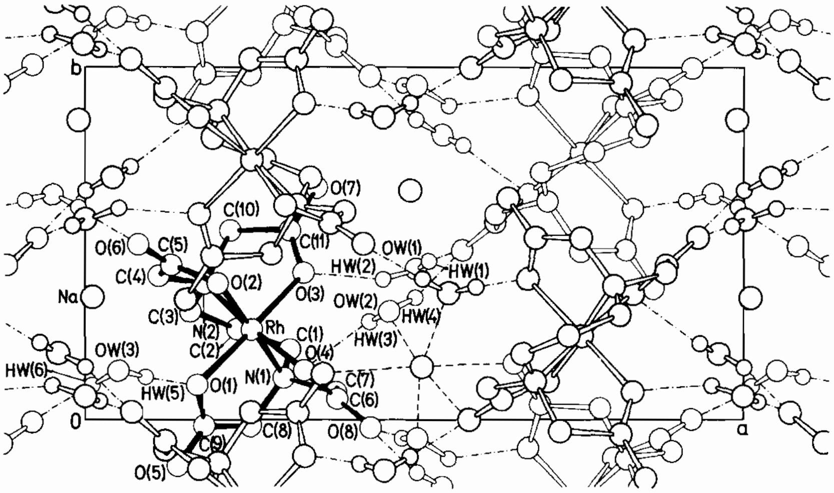

Fig. 1. Crystal structure of $(-)_D$-Na[Rh(1,3-pdta)]$\cdot 3H_2O$ projected along the *c*-axis. The broken lines represent the coordination sphere of Na ions. Hydrogen bonds are shown by dotted lines. Hydrogen atoms of the complex ion are omitted for clarity.

ing the collection of the data it was observed that the intensity of three standard reflexions, checked after every 2 hours, showed a slight loss of intensity with time. A linear correction corresponding to overall decomposition of 2.3% was applied to the data.

Since the cell parameters and the space group strongly suggest that the complex is isomorphous with chromium analogue, initial values for atomic coordinates were taken from the structure of the chromium compound. All hydrogen atoms were located in the difference Fourier map. Hydrogen atoms of the complex ion were included in structure factor calculations at calculated, fixed positions, with temperature factors fixed at B = 3.5. The positional and isotropic thermal parameters of water hydrogen atoms were also fixed during the refinement. An examination of calculated and observed structure factors after the refinement of positional and anisotropic thermal parameters of non-hydrogen atoms with the contribution of hydrogen atoms (R = 0.030) showed that several, strong, low angle reflexions have a large negative ΔF, indicating the presence of secondary extinctions. Hence, a secondary extinction correction was applied to all data. The function minimized by full-matrix least-squares was $\Sigma w(F_o - F_c/ZACH)^2$, where $1 = 1/\sigma^2$, $ZACH = \{c\beta I + [1 + (c\beta I)^2]\}^{1/2}$, β is Zachariasen's angulary dependent function, c is the extinction coefficient and I is the observed intensity. R factor after such refinement was reduced to 0.025.

The absolute configuration for both compounds was determined by anomalous scattering techniques, including the correction terms f' and f'' for chromium and rhodium atoms. The enantiomeric structures were refined separately. The R and R_w values are given in Table I. To confirm the results, a limited set of data for the rhodium compound was collected using CuK_α radiation which gives a stronger effect of anomalous dispersion. The observed structure amplitudes of a number of Bijvoet pairs were compared with calculated values. The comparison certainly confirmed the chosen absolute structure. The final positional and thermal parameters for both compounds and their associated estimated standard deviations are listed in Tables II and III.

Values for atomic scattering factors and anomalous terms were taken from International Tables for X-ray Crystallography [15]. The main computer programs used on the CDC-3600 computer were Zalkin's FORDAP Fourier program, Ibers' and Doeden's NUCLS least-squares program, and GEOM, molecular geometry and standard deviations, written by K. W. Muir and P. Mallinson.

Results and Discussion

The crystal structures of the two isomorphous compounds consist of the Na^+ cations, complex anions and molecules of water, joined together by electrostratic forces and hydrogen bonds. A projection of the structure of Na[Rh(1,3-PDTA)]$\cdot 3H_2O$ down the *c*-axis with numbering scheme of the atoms is shown in Fig. 1. The complex anions lie in layers parallel to the plane (010), at x ~ ¼, ¾. Sodium ions and molecules of water are arranged between these layers.

Sodium ions are surrounded by six oxygen atoms, three from water molecules and three from carboxylato groups belonging to three different complex ions. The coordination polyhedron of sodium may be described as distorted octahedron. The average

TABLE III. Final Thermal Parameters with Their e.s.d.s. The anisotropic temperature parameters ($\times 10^4$) are expressed in the form: $\exp(-\Sigma_i\Sigma_j\beta_{ij}h_ih_j)$.

	Na[Cr(1,3-PDTA)] · 3H$_2$O						Na[Rh(1,3-PDTA)] · 3H$_2$O					
	β_{11}/B (Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}/B (Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M	12.2(3)	43.8(10)	25.8(5)	0.1(7)	1.9(4)	−1.8(8)	11.42(6)	41.7(2)	23.5(1)	−0.2(1)	0.9(1)	−2.0(1)
Na	21(1)	83(4)	46(2)	3(2)	2(1)	−9(3)	22.5(5)	75(1)	52(1)	1(1)	2(1)	−6(1)
O(1)	2.03(8)						17.5(7)	54(2)	45(2)	−5(1)	7(1)	0(2)
O(2)	1.93(8)						17.8(8)	74(3)	31(2)	8(1)	0(1)	−14(2)
O(3)	2.03(8)						13.4(7)	56(2)	53(2)	−3(1)	−1(1)	1(2)
O(4)	2.16(9)						19.1(8)	76(3)	31(2)	10(1)	−3(1)	1(2)
O(5)	28(2)	72(6)	78(5)	−20(3)	−4(3)	−6(5)	24.0(9)	60(3)	78(3)	−13(1)	−1(1)	−6(2)
O(6)	21(2)	83(7)	52(5)	9(3)	13(2)	2(5)	20.8(9)	89(3)	46(2)	13(1)	8(1)	−3(2)
O(7)	26(2)	63(7)	67(5)	−16(3)	1(3)	0(5)	21.1(9)	60(3)	80(3)	−9(1)	19(1)	2(2)
O(8)	33(2)	180(10)	54(5)	42(4)	−17(3)	−10(6)	32(1)	167(5)	57(3)	42(2)	−11(1)	−16(3)
O(W1)	18(2)	126(9)	62(5)	3(4)	−10(3)	0(6)	18.9(9)	121(4)	61(2)	6(2)	−5(1)	7(2)
O(W2)	35(3)	109(9)	62(5)	−12(4)	−1(3)	17(6)	31(1)	121(4)	60(2)	−12(2)	4(1)	8(3)
O(W3)	24(2)	115(8)	67(5)	−7(4)	9(3)	24(6)	25(1)	108(4)	65(2)	−15(2)	13(1)	−23(3)
N(1)	1.56(9)						16.0(8)	50(3)	27(2)	1(1)	4(1)	−4(2)
N(2)	1.54(9)						12.4(7)	53(3)	28(2)	−2(1)	0(1)	−2(2)
C(1)	2.3(1)						25(1)	76(4)	28(2)	−1(2)	9(1)	1(2)
C(2)	2.4(1)						29(1)	80(4)	25(2)	0(2)	0(1)	−3(2)
C(3)	2.0(1)						20(1)	70(4)	30(2)	−6(2)	−8(1)	−7(2)
C(4)	1.7(1)						13(1)	76(4)	35(2)	3(2)	2(1)	1(2)
C(5)	1.8(1)						16(1)	52(3)	36(2)	1(1)	6(1)	0(2)
C(6)	2.2(1)						18(1)	73(4)	42(2)	7(2)	−1(1)	−10(2)
C(7)	2.2(1)						15(1)	86(4)	43(2)	10(2)	4(1)	−9(3)
C(8)	2.1(1)						27(1)	46(2)	34(2)	−4(2)	2(2)	−7(2)
C(9)	1.9(1)						16(1)	53(3)	41(2)	−1(2)	−4(1)	4(2)
C(10)	1.7(1)						18(1)	46(3)	39(2)	−6(1)	−1(1)	2(2)
C(11)	1.7(1)						16(1)	53(3)	43(2)	−2(1)	4(1)	−9(2)
H(1)	3.5						3.5					
H(2)	3.5						3.5					
H(3)	3.5						3.5					
H(4)	3.5						3.5					
H(5)	3.0						3.5					
H(6)	3.0						3.5					
H(7)	2.5						3.5					
H(8)	2.5						3.5					
H(9)	3.5						3.5					
H(10)	3.5						3.5					
H(11)	3.0						3.5					
H(12)	3.0						3.5					
H(13)	3.0						3.5					
H(14)	3.0						3.5					
HW(1)	4.0						4.0					
HW(2)	4.0						4.0					
HW(3)	4.5						4.0					
HW(4)	4.5						4.0					
HW(5)	4.0						4.0					
HW(6)	4.0						4.0					

TABLE IV. Selected Bond Distances in the Crystal Structures of Na[Cr(1,3-PDTA)]·3H_2O and (–)-Na[Rh(1,3-PDTA)]·3H_2O (Å), with standard Deviations in Parentheses.

	Na[Cr(1,3-PDTA)]·3H_2O	Na[Rh(1,3-PDTA)]·3H_2O
M–O(1)	1.949(5)	2.002(2)
M–O(2)	1.960(5)	2.038(2)
M–O(3)	1.941(5)	2.004(2)
M–O(4)	1.973(5)	2.050(2)
M–N(1)	2.065(6)	2.033(3)
M–N(2)	2.065(5)	2.031(3)
N(1)–C(1)	1.490(9)	1.493(4)
C(1)–C(2)	1.559(9)	1.536(5)
C(2)–C(3)	1.521(10)	1.537(5)
C(3)–N(2)	1.486(8)	1.490(4)
O(1)–C(9)	1.304(8)	1.298(4)
C(9)–O(5)	1.225(9)	1.223(4)
C(9)–C(8)	1.517(10)	1.520(5)
C(8)–N(1)	1.508(9)	1.507(4)
O(2)–C(5)	1.289(8)	1.289(4)
C(5)–O(6)	1.229(9)	1.229(4)
C(5)–C(4)	1.509(10)	1.524(5)
C(4)–N(2)	1.501(8)	1.497(4)
O(3)–C(11)	1.311(9)	1.297(4)
C(11)–O(7)	1.203(9)	1.187(4)
C(11)–C(10)	1.529(9)	1.523(5)
C(10)–N(2)	1.504(8)	1.502(4)
O(4)–C(6)	1.275(8)	1.286(4)
C(6)–O(8)	1.220(9)	1.228(5)
C(6)–C(7)	1.520(10)	1.512(5)
C(7)–N(1)	1.502(8)	1.499(4)
Na–O(5)	2.468(5)	2.502(3)
Na–O(6)	2.499(5)	2.528(3)
Na–O(7)	2.492(5)	2.513(3)
Na–O(W1)	2.408(5)	2.402(3)
Na–O(W2)	2.415(5)	2.410(3)
Na–O(W3)	2.339(5)	2.339(3)

TABLE V. Selected Bond Angles in the Crystal Structures of Na[Cr(1,3-PDTA)]·3H_2O and Na[Rh(1,3-PDTA)]·3H_2O.

	Na[Cr(1,3-pdta)]·3H_2O	Na[Rh(1,3-pdta)]·3H_2O
O(1)–M–O(2)	90.0(2)	90.5(1)
O(1)–M–O(3)	175.7(2)	179.7(1)
O(1)–M–O(4)	91.7(2)	88.0(1)
O(1)–M–N(1)	83.4(2)	85.2(1)
O(1)–M–N(2)	93.4(2)	94.9(1)
O(2)–M–O(3)	92.7(2)	89.2(1)
O(2)–M–O(4)	99.7(2)	97.6(1)
O(2)–M–N(1)	172.8(2)	175.6(1)
O(2)–M–N(2)	81.7(2)	81.5(1)
O(3)–M–O(4)	91.2(2)	92.1(1)
O(3)–M–N(1)	93.8(2)	95.1(1)
O(3)–M–N(2)	83.7(2)	85.0(1)
O(4)–M–N(1)	83.5(2)	82.9(1)
O(4)–M–N(2)	174.8(2)	177.0(1)
N(1)–M–N(2)	95.8(2)	98.3(1)
M–N(1)–C(1)	113.0(4)	111.7(2)
N(1)–C(1)–C(2)	114.6(5)	115.6(3)
C(1)–C(2)–C(3)	119.5(6)	120.1(3)
C(2)–C(3)–N(2)	117.0(5)	116.0(3)
C(3)–N(2)–M	112.9(4)	112.1(2)
M–O(1)–C(9)	119.0(4)	115.5(2)
O(1)–C(9)–C(8)	115.6(6)	116.8(3)
O(1)–C(9)–O(5)	123.8(6)	122.9(3)
O(5)–C(9)–C(8)	120.6(6)	120.2(3)
C(9)–C(8)–N(1)	112.6(5)	114.0(2)
C(8)–N(1)–M	109.1(4)	108.2(2)
M–O(2)–C(5)	115.5(4)	113.0(2)
O(2)–C(5)–C(4)	115.5(6)	115.9(3)
O(2)–C(5)–O(6)	123.2(6)	123.3(3)
O(6)–C(5)–C(4)	121.2(6)	120.8(3)
C(5)–C(4)–N(2)	109.8(5)	109.9(2)
C(4)–N(2)–M	103.4(4)	104.2(2)
M–O(3)–C(11)	118.4(4)	115.1(1)
O(3)–C(11)–O(7)	124.5(6)	122.5(3)
O(7)–C(11)–C(10)	120.1(6)	120.5(3)
O(3)–C(11)–C(10)	115.4(6)	117.0(3)
C(11)–C(10)–N(2)	112.4(5)	113.7(3)
C(10)–N(2)–M	108.7(3)	108.4(2)
M–O(4)–C(6)	116.0(4)	113.1(2)
O(4)–C(6)–O(8)	124.4(6)	123.3(3)
O(8)–C(6)–C(7)	119.4(6)	120.0(3)
O(4)–C(6)–C(7)	116.1(6)	116.7(3)
C(6)–C(7)–N(1)	110.9(5)	111.2(3)
C(7)–N(1)–M	104.3(4)	105.1(2)
C(1)–N(1)–C(8)	112.4(5)	112.3(2)
C(7)–N(1)–C(8)	110.0(5)	110.3(3)
C(3)–N(2)–C(10)	112.8(4)	112.7(2)
C(10)–N(2)–C(4)	109.0(5)	109.8(2)
C(7)–N(1)–C(1)	107.6(5)	109.0(3)
C(4)–N(2)–C(3)	109.6(5)	109.3(2)

Na–O distances are 2.437 and 2.449 Å in chromium and rhodium complex, respectively. The interbond angles have a mean deviation from the ideal values of 7.0° in chromium, and 7.5° in rhodium octahedron. These values are within the range reported for NaO_6 polyhedra [24].

In the complex anion, the metal ion is coordinated octahedrally by two nitrogen and four oxygen atoms from a sexidentate 1,3-PDTA ligand. In both complexes, the six-membered 1,3-propanediamine chelate ring T takes a twist boat δ conformation, provided that the helicity is defined by the line connecting the two nitrogen atoms and the line connecting the methylene carbon atoms which are directly attached to the nitrogen atoms. Equatorial glycinato G rings have an envelope λ conformation, while the two axial R rings are relatively flat. The absolute configuration of the rhodium complex ion, as well as that of Na[Cr(1,3-PDTA)]·3H_2O, a crystal selected by chance from the optically-inactive complex, is Λ. This is in accordance with the predictions based on consideration of the Dreiding model, namely that the

TABLE VI. Comparison of Selected Bond Angles (°) and Bond Angle Sums in Chelate Rings.

Angle	Ideal	[Cr(1,3-PDTA)]$^-$	[Rh(2,3-PDTA)]$^-$	[Co(1,3-PDTA)]$^-$	[Co(HPDTA)]$^-$
O_{G_1}–M–O_{G_2}	90	99.7(2)	97.6(1)	92.6(3)	89.8(4)
O_{G_1}–M–N(1)	90	83.5(2)	82.9(1)	84.3(3)	84.7(4)
O_{G_2}–M–N(2)	90	81.7(2)	81.5(1)	84.3(3)	86.7(5)
O_{R_1}–M–N(1)	90	83.4(2)	85.2(1)	87.9(3)	87.0(4)
O_{R_2}–M–N(2)	90	83.7(2)	85.0(1)	87.9(3)	83.4(4)
N(1)–M–N(2)	90	95.8(2)	98.3(1)	99.0(3)	98.8(5)
M–O_{G_1}–C	120	115.9(4)	113.1(2)	114.8(6)	111.0(9)
M–O_{G_2}–C	120	115.5(4)	113.0(2)	114.8(6)	114.2(9)
M–O_{R_1}–C	120	119.0(4)	115.5(2)	116.6(6)	114.8(8)
M–O_{R_2}–C	120	118.4(4)	115.1(2)	116.6(6)	114.5(8)
C_{G_1}–N(1)–C_{R_1}	109.5	110.0(5)	110.3(3)	110.0(8)	110.3(10)
C_T–N(1)–C_{R_1}	109.5	112.4(5)	112.4(2)	112.9(8)	111.8(12)
C_T–N(1)–C_{G_1}	109.5	107.6(5)	109.0(2)	108.8(6)	108.7(10)
C_{G_2}–N(2)–C_{R_2}	109.5	109.0(5)	109.8(2)	110.0(8)	108.7(11)
C_T–N(2)–C_{R_2}	109.5	112.8(4)	112.7(2)	112.9(8)	113.1(11)
C_T–N(2)–C_{G_2}	109.5	109.6(5)	109.3(2)	108.8(6)	108.6(10)
M–N(1)–C_{R_1}	109.5	109.1(4)	108.2(2)	108.1(5)	109.4(8)
M–N(1)–C_{G_1}	109.5	104.3(4)	105.1(2)	103.9(8)	103.7(8)
M–N(1)–C_T	109.5	113.0(4)	111.7(2)	112.7(7)	112.8(8)
M–N(2)–C_{R_2}	109.5	108.7(3)	108.4(2)	108.1(5)	107.4(8)
M–N(2)–C_{G_2}	109.5	103.4(4)	104.2(2)	103.9(5)	104.0(9)
M–N(2)–C_T	109.5	112.9(4)	112.1(2)	112.7(7)	114.3(8)
Ring					
R_1	538.4	539.7	539.7	539.5	537.2
R_2	538.4	538.6	539.2	539.5	535.8
G_1	538.4	530.8	529.0	526.5	522.3
G_2	538.4	525.9	524.5	526.5	526.1
T	637.3	672.8	673.8	673.8	674.3

absolute configuration of the complex is determined by the helicity of the T ring [1].

The stereochemistries of [Cr(1,3-PDTA)]$^-$ and [Rh(1,3-PDTA)]$^-$ closely resemble one another and that of [Co(1,3-PDTA)]$^-$ (Tables IV and V). The crystal packings are also very similar, although the cobalt complex has a rigorous C_2 symmetry and crystallizes with two molecules of water. Some differences, however, are noticeable.

The bond lengths Cr–O and Cr–N are typical for chromium amino acidato and diamine complexes. The largest deviation of octahedral geometry in bond angles is associated with the angle O(2)–Cr–O(4) of 99.7°, which is considerably greater than the corresponding value of 92.6° in [Co(1,3-PDTA)]$^-$ and close to the value of 104.0° found in Co(EDTA) anion. Lengths of the twelve edges of the octahedron vary from 2.632 to 3.063 Å.

In coordination polyhedrons of Rh, Rh–O bond lengths lying in the plane of nitrogen ligators are significantly longer (mean value 0.04 Å) than the bonds axial to this plane. This phenomenon has been already noticed in a number of EDTA-type complexes [14, 24] but which in [Cr(1,3-PDTA)]$^-$ is not pronounced. The Rh–N bond lengths in [Rh(1,3-PDTA)]$^-$ are in the range of the values found in related compounds [16, 17]. However, Rh–N distances do not exceed the Rh–O bond lengths, as one would expect on the basis of covalent radii of N and O. Geue and Snow [19] have noticed a distinct contraction of Co–N distances in strained CoN_2O_4 and $CoN_2O_2S_2$ chromophores, the strain being relieved by formation of six-membered rings or by the presence of other substituents. On the basis of such a discussion it could be supposed that the presence of a larger metal ion causes the contraction of M–N bond lengths, even in compounds with six-membered rings. Such a tendency is not observed in the geometry of [Cr(1,3-PDTA)]$^-$ ions.

TABLE VII. Conformation of Chelate Rings.

		Five-membered rings Puckering parameters			Torsion O–C–C–N	Angles (°) τ
		p.a. (Å)	ϕ(M) (°)	Conformation*		
[Cr(1,3-PDTA)]$^-$	R_1	0.046	264.0	T	5.9(8)	4.1
	R_2	0.126	175.4	E	−0.7(8)	9.0
	G_1	0.335	141.9	E	−25.5(8)	22.0
	G_2	0.431	154.0	T	−22.2(8)	26.2
[Rh(1,3-PDTA)]$^-$	R_1	0.048	289.5	E	5.9(4)	4.0
	R_2	0.099	180.0	E	0.6(4)	6.0
	G_1	0.366	145.1	E	−26.0(4)	23.8
	G_2	0.456	155.2	T	−22.4(4)	27.7
[Co(1,3-PDTA)]$^-$	R	0.069	186.5	E	1.4(14)	4.5
	G	0.411	149.1	E,T	−24.6(15)	25.9
[Co(HPDTA)]$^-$	R_1	0.179	140.8	E	−13.4(13)	12.1
	R_2	0.178	260.3	E	23.0(17)	15.9
	G_1	0.478	161.2	T	−36.4(16)	29.1
	G_2	0.380	127.9	T	−16.5(17)	27.2
			Six-membered rings			
		p.a. (Å)	ϕ(M) (°)	θ (°)		τ
[Cr(1,3-PDTA)]$^-$		0.728	263.9	92.1		44.2
[Rh(1,3-PDTA)]$^-$		0.725	264.2	91.3		44.0
[Co(1,3-PDTA)]$^-$		0.718	270.9	90.0		43.6
[Co(PHDTA)]$^-$		0.723	279.9	90.7		43.2

*E = envelope, T = puckered (twisted).

An analysis of bond angles in rhodium-coordination polyhedrons shows that the largest deviation from an ideal octahedral geometry is associated with the N(1)–Rh–N(2) angle, as was found in Co(1,3-PDTA). Twelve edges of the octahedron vary in the range from 2.655 to 3.075 Å.

Interatomic distances and angles within the 1,3-PDTA ligand are normal in both compounds (Tables IV and V). The carboxylato groups have all the characteristics of the coordinated group in amino carboxylato complexes, *i.e.* they are planar, the C=O bond length is shorter than that of C–O, and the angles C_α–C–O < C_α–C=O < O=C–O.

It has been suggested that the sum of bond angles could be used as an estimate of the ring strain (the ideal bond angle sum of 338.4°, allowing five-membered rings to be nearly planar) and that the primary reason for the G ring strain is the angular strain around the coordinated nitrogen [4]. Selected bond angles and sums of the bond angles of chelate rings in the investigated complexes compared with the values for [Co(1,3-PDTA)]$^-$ [2] and [Co(HPDTA)]$^-$ (HPDTA = 2-hydroxy-1,3-PDTA) [3] are given in Table VI. The analysis of the data shows that R rings, as usual, are less strained than the G rings. The distortion of nitrogen tetrahedra is almost the same in all [M(1,3-PDTA)]$^-$ complexes. The difference in the distortion of the O–M–N and M–O–C angles is noticeable but the correlation of the distortion with ionic radius is not obvious. There is a significant difference between the sum of bond angles in the two G rings in the chromium and rhodium complexes, indicating that the G_1 ring is less, and the G_2 ring more, strained than are the symmetry-equivalent G rings in cobalt compounds. This difference comes from different distortions of the O–M–N, O–C–C and C–C–N angles. The latter two angles are more liable to the influence of intermolecular contacts, which are different for carbonyl oxygens O(8) and O(7) in G_1 and G_2 respectively.

Concerning the structure of [Co(HPDTA)]$^-$ it is obvious that the presence of OH groups, as a substituent and strong hydrogen bond which the group forms with the oxygen atom of the R ring from the neighbouring complex unit, causes additional strain in chelate rings.

TABLE VIII. Hydrogen Bond Lengths (Å) and Angles (°).

D–H····A	$Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$				$Na[Rh(1,3\text{-}PDTA)]\cdot 3H_2O$			
	D···A	D–H	H···A	∢D–H···A	D···A	D–H	H···A	∢D–H···A
O(W1)–HW(1)···O(8^1)	2.808	0.83	1.96	170	2.774	0.888	1.891	172.5
O(W1)–HW(2)···O(3)	2.785	0.74	2.07	170	2.795	0.886	1.939	161.7
O(W2)–HW(3)···O(4)	3.215	0.56	2.67	167	3.243	0.729	2.578	173.4
O(W2)–HW(4)···O(8^1)	2.790	0.88	1.91	173	2.790	0.969	1.854	161.6
O(W3)–HW(5)···O(1)	2.879	0.91	2.04	154	2.866	0.960	1.947	159.4
O(W3)–HW(6)···O(6^2)	2.765	0.73	2.20	166	2.752	0.870	1.908	163.1

Symmetry code:

1) 1 – x ½ + y ½ – z
2) –x ½ – y ½ – z

The bond angle sums for T rings are almost the same in all [M(1,3-PDTA)]⁻ complexes and are significantly greater than the ideal value.

The conformation of chelate rings, expressed by puckering parameters [20], torsion angle around the C–C bond and the root mean square torsion angle τ, is given in Table VII. Comparing these data for R and G rings in chromium and rhodium complexes it can be seen that chelate rings in the rhodium complex, with the exception of the R_2 ring, are more puckered than are the corresponding ones in the chromium compound. However, in [Co(1,3-PDTA)]⁻, the puckering amplitudes are between the values found in G and R rings for [Cr(1,3-PDTA)]⁻ and [Rh(1,3-PDTA)], while in [Co(HPDTA)]⁻ they are much greater.

Puckering parameters for six-membered T rings show that all investigated complexes have twist-boat conformation and similar puckering amplitude.

The intermolecular hydrogen bonding scheme is shown in Fig. 1. The distances and angles involving hydrogen bonds are given in Table VIII. Each molecule of water connects by hydrogen bonds two complex ions belonging to adjacent layers. Each complex ion is involved in five hydrogen bonds with surrounding molecules of water. In this way, all the oxygen atoms from the complex ion, except O(2), are included in intermolecular interactions. Carbonyl oxygens from the axial glycinate R rings are in the coordination sphere of sodium ion, the oxygen atom O(6) belonging to the equatorial G_1 ring is involved in electrostatic interaction with sodium and also in hydrogen bond with O(W3), while O(8) from G_2 ring is acceptor for two hydrogen bonds with water molecules O(W1) and O(W3). The carboxyl oxygen atom O(4) belonging to the G_2 chelate ring has an intermolecular contact with O(W2) slightly greater than 3.2 Å, which appears to be the weakest hydrogen bond in the structure.

Conclusions

The results of the X-ray crystal structure determinations performed in this work show that the $(-)_D$-[Rh(1,3-PDTA)]⁻ ion has Λ absolute configuration, the same as found for $(-)_D$-[Co(1,3-PDTA)]⁻ [2]. However, the CD peak in the lowest-energy spin-allowed region of this complex has the negative sign, opposite to $(-)_D$-[Co(1,3-PDTA)]⁻ and many other sexidentate complexes of Co(III) and Cr(III) with EDTA-type ligands [6–8, 21–23]. The same has been found for $(-)_D$-*trans*(O_5)-[Rh(EDDDA)]⁻ ion (EDDDA = ethylenediamine-N,N′-diacetato-N,N′-di-3-propionate) [17]. Therefore, the analogy to Co(III) EDTA-type complexes could not be used for the assignment of the absolute configuration of Rh(III) complexes on the basis of CD spectra. The empirical correlation of the Rh(III) complex with the CD spectrum with stereospecific *S,S*-EDDS ligands (*S,S*-EDDS = *S,S*-ethylenediamine-N,N′-disuccinate ion) seems to be justified [9, 12].

The analysis of the ring strains and conformations of chelate rings in M(1,3-PDTA) complexes (M = Co, Cr, Rh) indicates that the ring strains are not simply related to the size of the metal ion. Besides, the differences are too small to account for the large difference between the CD curves of [Co(1,3-PDTA)]⁻ and [Rh(1,3-PDTA)]⁻.

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