through S normal to (020). Since they are over 2 Å from the sulphur atom they are not likely to result from spurious thermal motion of this atom. The peak heights are very similar, though not related by symmetry, and are 0·5 e.A^{-3} ($\varrho_o-\varrho_c$) and 3·3 e.A^{-3} (ϱ_o). The standard deviation of the electron density as defined by

$$\sigma(\varrho)=\frac{2}{V}\sum_{q}||F_o|-|F_c||^2$$

will be overestimated (Lipson & Cochran, 1966) and in this case evaluates to 0·35 e.A^{-3}. There are several peaks of density 0·5 e.A^{-3} in the difference map but only the two in question are related either to each other or to spurious peaks in ϱ_o.

Covalent bonds are associated with a bonding density located between the bound atoms and in this respect the geometry of the spurious Fourier peaks is consistent with such a concept. Salmond (1968) has discussed the valence shell expansion of sulphur in certain heterocyclic compounds. The valence shell of sulphur ($3s^23p^4$) has d atomic orbitals available and excitation into the $3s^13p^33d^2$ state generates a set of six equivalent octahedral orbitals. It is not suggested that there are six equivalent orbitals in this case but the geometry of the octohedral arrangement is consistent with the geometry of the contacts and the covalent bond at the S atom. Two of the four orbitals in the xy plane may participate in the S=C(4) bond and the two orbitals in the $\pm z$ directions may be active in the contact.

It is not valid to argue the influence of other crystal field forces in explaining these contacts. There are configurations of the complex relative to the screw axis which require no overlap of van der Waals radii, and therefore a genuine minimum must exist in the interaction potential function for S and C(2) in this structure.

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The Crystal Structure and Absolute Configuration of $(+)_{589}$-*cis*-Dinitrobis$[(-)_{589}$-1,2-propylenediamine$]$cobalt(III) chloride

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The crystal structure of $(+)_{589}$-*cis*-dinitrobis$[(-)_{589}$-1,2-propylenediamine$]$cobalt(III) chloride has been determined by three-dimensional X-ray methods and refined by full-matrix least-squares procedures. The structure consists of simple chloride ions and complex octahedral cations in which the two *cis* nitro groups are planar and the propylenediamine chelate rings have the λ conformation. The methyl groups of the two chelate rings occupy *trans* positions. There is some evidence for intra-ionic hydrogen bonding. The absolute configuration of the complex cation was determined from the known absolute configuration of $(-)_{589}$-1,2-propylenediamine and was confirmed by the Bijvoet method.

Introduction

The determinations of the crystal structure and of the absolute configuration of $(+)_{589}$-*cis*-dinitrobis$[(-)_{589}$-1,2-propylenediamine$]$cobalt(III) chloride were undertaken in order to confirm the assignment of the absolute configuration of the cation that was predicted from a comparison of its circular dichroism (C.D.) spectrum with that of the $(+)_{589}$-tris(ethylenediamine)cobalt(III) ion, whose absolute configuration is known (Saito, Nakatsu, Shiro & Kuroya 1955, 1957). An account of this study and a preliminary report on the crystal structure of the compound have already been given in a previous communication (Barclay, Goldschmied, Stephenson & Sargeson, 1966).

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Crystal data

$(+)_{589}$-*cis*-Dinitrobis[$(-)_{589}$-1,2-propylenediamine]cobalt(III) chloride crystallizes in thin, needle-shaped, transparent, amber-coloured crystals, elongated along [100]. The unit-cell parameters were measured from Weissenberg photographs taken with unfiltered Co $K\alpha$ radiation and from [$h0l$] precession photographs taken with Zr-filtered Mo $K\alpha$ radiation.

The density of the crystals was measured by flotation in a mixture of 1,2-dibromoethane and benzene. The crystal data are as follows:

$$\mathrm{CoC_6H_{20}N_6O_4Cl},\ M=334{\cdot}7,\ F(000)=696\ .$$

Orthorhombic, space group $P2_12_12_1$ (from systematic absences)

$$a=6{\cdot}46,\ b=9{\cdot}62,\ c=22{\cdot}36\ \text{Å},\ U=1390\ \text{Å}^3$$
$$D_m=1{\cdot}60\ \text{g.cm}^{-3},\ D_x=1{\cdot}60\ \text{g.cm}^{-3},\ Z=4\ .$$

Experimental

Intensity data for the structure determination were collected from single-crystal equi-inclination Weissenberg photographs, taken by rotation about [100] ($h=0,1,2,3$) using unfiltered Co $K\alpha$ radiation and from single-crystal [$h0l$] precession photographs, using Zr-filtered Mo $K\alpha$ radiation. The intensity data for the anomalous dispersion study were obtained from single-crystal [$1kl$]–[$3kl$] Weissenberg photographs, taken with Ni-filtered Cu $K\alpha$ radiation. In order to lessen the effects of background blackening due to the copious emission of fluorescent radiation in this study, the intensity data were collected from an extremely small crystal (approximate dimensions: 0·05 mm diameter, 0·5–1 mm long); this necessitated very long exposure times, particularly in view of the heavy absorption occurring at such close proximity to the cobalt K-absorption edge. Exposure times were 200–400 hours.

The intensities on Weissenberg photographs were estimated visually, using a calibrated intensity strip which had been prepared from a suitable reflexion using the same crystal from which the data had been collected. An 'Optica Milano' photometer was used to estimate the intensities on precession photographs. Internal interlayer correlation of the 800 independent observed reflexions was effected, using the $h0l$ data from the precession photographs. Subsequently a Wilson plot provided improved estimates for the scale factors of the five zones, as well as a first estimate of an overall isotropic temperature factor. No corrections were made for absorption or extinction effects.

The structure determination and refinement

The structure was solved by the 'heavy atom' Fourier method. The positions of the two heavy atoms (Co and $\mathrm{Cl^-}$) and also that of one of the nitrogen atoms were found from a three-dimensional Patterson synthesis and those of the other 'light' atoms were found from a series of F_{obs} and difference Fourier syntheses.

An F_{calc} synthesis was used to help identify the diffraction ripples in the electron-density distribution that were present because of the relative scarcity of high-angle data.

The structure was partially refined from these Fourier syntheses and the refinement was completed by full-matrix, least-squares refinement using unit weights.

Isotropic temperature factors, scale factors and positional parameters were varied separately in three different cycles and then two cycles in which all these parameters were allowed to vary simultaneously led to convergence with a final R of 0·12.

The atomic scattering factors used were the 'mean atomic scattering factors from self-consistent and variational wave functions' tabulated in *International Tables for X-ray Crystallography* (1962). 'In phase' corrections allowing for anomalous dispersion were applied to the scattering factors of cobalt and chlorine, using Hönl's (1933*a*, *b*) formula. The numerical values of the corrections were interpolated from the tables given by James (1954).

Table 1. *Atomic parameters and standard deviations*

	x/a	y/b	z/c	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Co	0·0915	0·0351	0·0873	2·12 Å^2	0·0048 Å	0·0036 Å	0·0032 Å	0·08 Å^2
Cl	−0·3877	0·0425	0·2213	5·21	0·0096	0·0077	0·0065	0·17
N(1)	0·1021	0·1121	0·0102	3·24	0·027	0·019	0·017	0·39
N(2)	0·0729	−0·0521	0·1688	3·42	0·027	0·020	0·017	0·41
N(3)	−0·0913	0·1843	0·1166	3·27	0·026	0·020	0·018	0·41
N(4)	0·2662	−0·1206	0·0650	3·18	0·024	0·021	0·018	0·42
N(5)	0·3264	0·1531	0·1105	2·67	0·023	0·019	0·019	0·43
N(6)	−0·1487	−0·0671	0·0621	3·73	0·028	0·021	0·019	0·48
C(1)	−0·0808	0·4149	0·1687	4·71	0·039	0·027	0·025	0·62
C(2)	0·1500	−0·2016	0·1611	3·68	0·032	0·026	0·024	0·56
C(3)	0·0410	0·2767	0·1558	3·25	0·031	0·024	0·023	0·53
C(4)	0·3270	−0·1985	0·1212	3·98	0·034	0·027	0·026	0·63
C(5)	0·2514	0·2931	0·1231	4·18	0·034	0·027	0·026	0·62
C(6)	0·4022	−0·3434	0·1000	5·54	0·041	0·030	0·028	0·70
O(1)	0·0132	0·2192	−0·0037	4·64	0·021	0·019	0·019	0·45
O(2)	−0·3193	−0·0037	0·0549	5·15	0·023	0·020	0·018	0·49
O(3)	0·2177	0·0600	−0·0279	4·55	0·022	0·018	0·017	0·43
O(4)	−0·1387	−0·1876	0·0478	5·05	0·024	0·020	0·018	0·46

A difference synthesis computed from the structure factors based on the refined model showed only one peak representing a residual density of more than 1 e.Å^{-3}; its value was 1·3 e.Å^{-3} and its position coincided with that of a diffraction ripple associated with the chloride ion observed on the F_{calc} map.

Table 2. *Observed and calculated structure factors*

H	K	L	|FO|	|FC|
0	0	4	71	67
0	0	6	61	62
0	0	8	8	7
0	0	10	33	32
0	0	12	34	39
0	0	14	23	14
0	0	16	37	29
0	0	18	23	29
0	0	20	13	10
0	0	22	16	10
0	0	24	16	16
0	0	28	14	14
0	0	30	6	8
0	1	1	41	47
0	1	2	170	173
0	1	4	90	85
0	1	5	16	27
0	1	6	59	59
0	1	7	67	58
0	1	8	101	107
0	1	9	75	89
0	1	10	36	35
0	1	11	39	30
0	1	12	39	36
0	1	13	15	13
0	1	14	34	32
0	1	22	11	9
0	1	23	7	5
0	1	24	19	19
0	2	0	64	84
0	2	1	5	5
0	2	2	8	6
0	2	3	15	16
0	2	4	44	49
0	2	5	8	6
0	2	6	85	99
0	2	7	118	109
0	2	8	82	88
0	2	9	39	37
0	2	10	12	16
0	2	11	54	53
0	2	12	38	39
0	2	13	21	25
0	2	14	11	20
0	2	15	27	28
0	2	16	49	47
0	2	17	5	5
0	2	18	21	23
0	2	19	7	11
0	2	20	15	15
0	2	21	9	8
0	2	22	22	24
0	2	23	11	9
0	3	1	34	33
0	3	2	43	39
0	3	3	14	5
0	3	4	5	6
0	3	5	15	9
0	3	6	34	27
0	3	7	47	38
0	3	8	77	70
0	3	9	55	43
0	3	10	40	41
0	3	11	6	12
0	3	12	20	17
0	3	13	13	11
0	3	14	50	48
0	3	15	38	33
0	3	16	19	20
0	3	17	32	33
0	3	18	15	16
0	3	19	12	14
0	3	20	19	24
0	3	22	8	10
0	3	23	16	18
0	4	0	64	60
0	4	1	36	44
0	4	2	16	6
0	4	3	7	3
0	4	4	4	5
0	4	5	26	28
0	4	6	24	22
0	4	7	39	37
0	4	8	16	11
0	4	9	21	25
0	4	10	10	5
0	4	11	7	6
0	4	12	14	18
0	4	14	16	15
0	4	15	49	44
0	4	16	28	26
0	4	17	5	5
0	4	18	11	11
0	4	19	14	16
0	4	21	19	20
0	4	22	15	17
0	5	1	60	59
0	5	2	50	46
0	5	3	8	4
0	5	4	18	17
0	5	5	12	8
0	5	7	50	52
0	5	8	20	16
0	5	9	29	27
0	5	10	11	6
0	5	11	15	16
0	5	12	8	4
0	5	13	37	37
0	5	14	7	7
0	5	15	22	16
0	5	16	14	12
0	5	17	33	35
0	5	18	11	13
0	5	19	11	12
0	5	20	9	11
0	5	21	7	9
0	6	0	21	16
0	6	1	14	18
0	6	2	12	8
0	6	4	32	30
0	6	5	43	40
0	6	6	40	39
0	6	7	49	50
0	6	8	5	4
0	6	9	58	58
0	6	10	11	11
0	6	11	5	8
0	6	12	14	12
0	6	14	14	11
0	6	15	32	32
0	6	19	10	15
0	7	1	27	27
0	7	3	11	11
0	7	5	44	39
0	7	7	50	50
0	7	8	14	10
0	7	9	31	31
0	7	10	7	9
0	7	11	9	12
0	7	13	15	15
0	7	15	8	8
0	7	16	6	3
0	7	17	21	20
0	8	0	33	32
0	8	1	43	44
0	8	2	4	7
0	6	3	40	35
0	8	4	13	10
0	8	5	4	7
0	8	7	31	29
0	8	9	23	24
0	8	12	5	5
0	8	13	10	12
0	8	14	8	7
0	8	15	15	19
0	8	16	6	8
0	9	1	23	22
0	9	2	18	19
0	9	4	6	6
0	9	5	15	17
0	9	6	4	6
0	9	7	21	23
0	9	8	11	15
0	9	9	5	8
0	9	11	7	10
0	9	13	8	13
0	10	0	8	13
0	10	1	8	9
0	10	3	8	10
0	10	5	13	13
0	10	6	13	17
0	10	7	3	4
0	10	8	3	5
0	10	9	5	13
1	0	1	40	49
1	0	2	72	74
1	0	3	98	114
1	0	4	18	8
1	0	5	37	40
1	0	6	114	128
1	0	7	25	29
1	0	8	35	43
1	0	9	46	38
1	0	10	49	45
1	0	11	49	56
1	0	12	37	36
1	0	13	48	52
1	0	14	25	28
1	0	15	23	21
1	0	16	20	18
1	0	17	10	5
1	0	19	25	20
1	0	23	8	8
1	0	31	6	6
1	0	25	22	18
1	0	26	19	13
1	0	27	18	14
1	1	3	35	41
1	1	4	39	43
1	1	5	68	76
1	1	6	51	54
1	1	7	12	7
1	1	8	21	18
1	1	9	10	9
1	1	10	33	35
1	1	11	77	76
1	1	12	51	54
1	1	13	17	19
1	1	14	20	18
1	1	15	6	8
1	1	16	15	18
1	1	17	26	26
1	1	18	29	28
1	1	19	15	16
1	1	21	13	13
1	1	22	7	1
1	1	23	12	14
1	1	24	10	10
1	2	0	29	21
1	2	1	46	47
1	2	2	70	70
1	2	3	81	94
1	2	4	25	26
1	2	5	14	10
1	2	6	25	27
1	2	7	32	31
1	2	8	47	39
1	2	9	58	58
1	2	10	57	59
1	2	11	32	29
1	2	12	21	27
1	2	13	50	51
1	2	14	26	22
1	2	15	20	23
1	2	16	18	18
1	2	17	20	23
1	2	18	22	24
1	2	19	18	18
1	2	20	17	22
1	2	21	13	17
1	2	22	6	7
1	2	24	5	8
1	3	0	10	10
1	3	1	28	19
1	3	2	26	24
1	3	3	43	41
1	3	4	61	55
1	3	5	63	61
1	3	6	18	14
1	3	7	38	34
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1	3	9	37	32
1	3	10	35	34
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1	3	14	24	25
1	3	15	10	11
1	3	16	25	24
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1	3	18	28	27
1	3	19	18	20
1	3	20	17	16
1	3	21	10	5
1	3	22	9	11
1	3	23	5	7
1	4	1	63	51
1	4	2	53	46
1	4	3	52	46
1	4	4	38	37
1	4	5	39	39
1	4	6	54	49
1	4	7	27	32
1	4	8	22	19
1	4	9	27	31
1	4	10	23	19
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1	4	12	30	29
1	4	13	21	22
1	4	14	14	17
1	4	15	15	12
1	4	16	21	23
1	4	17	12	11
1	4	18	28	31
1	4	19	22	23
1	4	20	21	20
1	4	22	8	13
1	5	0	29	29
1	5	1	26	25
1	5	2	29	26
1	5	3	44	45
1	5	4	43	44
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1	5	6	25	26
1	5	7	24	21
1	5	8	18	17
1	5	9	36	33
1	5	10	35	37
1	5	11	32	33
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1	5	16	20	18
1	5	17	15	14
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1	5	19	13	13
1	5	20	16	20
1	5	21	3	4
1	6	0	15	13
1	6	1	22	20
1	6	2	44	41
1	6	3	44	36
1	6	4	37	32
1	6	5	31	26
1	6	6	48	39
1	6	7	31	32
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1	6	12	21	23
1	6	14	13	10
1	6	17	16	17
1	6	18	21	23
1	6	19	10	11
1	7	1	12	12
1	7	2	21	19
1	7	3	42	37
1	7	4	38	37
1	7	5	18	13
1	7	6	34	29
1	7	7	11	8
1	7	8	31	30
1	7	9	26	23
1	7	10	19	20
1	7	11	18	15
1	7	12	14	16
1	7	14	8	10
1	7	15	5	5
1	7	16	14	14
1	7	17	7	9
1	7	18	3	7
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1	8	2	12	10
1	8	3	20	18
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1	8	5	31	31
1	8	6	24	24
1	8	8	16	17
1	8	11	16	16
1	8	12	19	20
1	8	15	5	7
1	8	16	8	13
1	9	1	12	11
1	9	2	12	13
1	9	3	17	18
1	9	4	23	24
1	9	5	18	18
1	9	7	11	11
1	9	8	9	9
1	9	9	15	16
1	9	10	14	18
1	10	0	14	15
1	10	2	13	15
1	10	3	9	11
1	10	4	7	9
1	10	5	7	7
1	10	6	8	11
1	10	8	6	8
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2	0	2	22	30
2	0	3	7	8
2	0	4	16	2
2	0	5	49	55
2	0	6	27	28
2	0	7	51	44
2	0	8	19	15
2	0	9	24	21
2	0	10	36	40
2	0	11	40	38
2	0	12	57	58
2	0	13	74	77
2	0	14	11	13
2	0	15	26	23
2	0	16	20	23
2	0	17	41	43
2	0	19	9	12
2	0	20	10	7
2	0	21	5	8
2	0	22	12	15
2	0	23	24	27
2	0	29	15	12
2	1	0	38	52
2	1	1	82	100
2	1	2	50	45
2	1	3	14	14
2	1	4	40	37
2	1	5	29	32
2	1	6	23	26
2	1	7	26	24
2	1	8	24	17
2	1	9	56	56
2	1	10	9	9
2	1	11	16	18
2	1	12	20	23
2	1	13	42	42
2	1	14	36	36
2	1	15	56	56
2	1	16	12	14
2	1	17	18	15
2	1	18	7	9
2	1	19	9	12
2	1	20	15	16
2	1	21	22	25
2	1	22	14	16
2	1	23	6	7
2	2	0	15	5
2	2	1	90	95
2	2	2	46	39
2	2	3	49	45
2	2	4	52	56
2	2	5	70	57
2	2	6	72	63
2	2	7	77	71
2	2	8	19	20
2	2	9	41	45
2	2	10	19	18
2	2	11	16	10
2	2	12	22	23
2	2	13	12	12
2	2	14	12	14
2	2	15	22	21
2	2	16	22	19
2	2	17	22	19
2	2	18	7	8
2	2	19	8	9
2	2	20	9	12
2	2	21	4	6
2	2	22	7	8
2	2	23	17	22
2	3	0	66	68
2	3	1	71	72
2	3	2	36	42
2	3	3	61	58
2	3	4	27	22
2	3	5	57	50
2	3	6	57	54
2	3	7	60	56
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2	3	9	30	29
2	3	10	31	31
2	3	11	7	5
2	3	12	11	15
2	3	13	11	7
2	3	14	33	33
2	3	15	16	12
2	3	16	21	19
2	3	17	10	13
2	3	18	7	11
2	3	19	8	7
2	3	20	5	6
2	3	21	14	16
2	3	22	11	11
2	4	0	24	29
2	4	1	56	51
2	4	2	67	66
2	4	3	34	32
2	4	4	20	14
2	4	5	44	49
2	4	6	12	12
2	4	7	43	43
2	4	8	62	64
2	4	9	8	9
2	4	10	15	14
2	4	11	9	12
2	4	12	22	18
2	4	13	20	19
2	4	14	34	36
2	4	15	31	27
2	4	16	8	10
2	4	17	14	11
2	4	18	6	7
2	4	19	7	10
2	5	0	64	66
2	5	1	17	15
2	5	2	13	10
2	5	3	15	13
2	5	4	10	13
2	5	5	25	27
2	5	6	53	57
2	5	7	16	13
2	5	8	21	20
2	5	9	31	31
2	5	10	25	28
2	5	11	24	24
2	5	12	9	9
2	5	13	14	14
2	5	14	14	15
2	5	15	14	17
2	5	16	19	23
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2	5	18	5	9
2	5	19	9	10
2	5	20	5	7
2	6	0	10	7
2	6	1	16	14
2	6	2	37	35
2	6	3	25	20
2	6	4	35	32
2	6	6	14	14
2	6	7	33	26
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2	6	10	8	5
2	6	11	15	14
2	6	12	7	5
2	6	13	15	14
2	6	14	14	15
2	6	16	4	8
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2	7	0	37	38
2	7	2	8	7
2	7	3	19	17
2	7	4	11	12
2	7	5	20	20
2	7	6	42	43
2	7	7	11	13
2	7	8	18	16
2	7	9	7	8
2	7	10	16	15
2	7	11	6	6
2	7	12	5	11
2	7	13	6	7
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2	7	17	5	10
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2	8	1	10	10
2	8	2	16	17
2	8	3	16	12
2	8	4	10	10
2	8	5	6	8
2	8	6	10	10
2	8	7	5	6
2	8	8	19	26
2	8	9	8	9
2	8	10	8	11
2	8	11	8	8
2	8	12	7	8
2	8	13	10	12
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2	8	15	8	15
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2	9	1	9	11
2	9	2	8	10
2	9	4	8	10
2	9	5	5	6
2	9	6	12	16
2	9	7	11	12
2	9	9	9	10
2	9	10	10	14
2	9	11	4	6
2	10	0	7	7
2	10	1	5	8
2	10	2	8	13
2	10	3	5	9
2	10	4	6	11
2	10	5	3	6
3	0	1	24	29
3	0	2	30	30
3	0	3	6	6
3	0	4	31	48
3	0	5	8	6
3	0	6	11	16
3	0	7	19	18
3	0	8	7	5
3	0	9	8	10
3	0	10	45	52
3	0	11	19	20
3	0	12	34	39
3	0	13	12	9
3	0	14	53	57
3	0	16	26	28
3	0	17	17	10
3	0	18	20	20
3	0	19	8	9
3	0	20	24	28
3	0	22	3	1
3	0	26	17	17
3	1	0	29	28
3	1	1	20	18
3	1	2	38	37
3	1	3	20	23
3	1	4	51	52
3	1	5	30	34
3	1	6	18	15
3	1	7	26	24
3	1	8	25	21
3	1	9	23	17
3	1	10	25	29
3	1	11	24	23
3	1	12	60	64
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3	1	14	7	5
3	1	15	14	14
3	1	16	17	17
3	1	17	14	13
3	1	18	27	27
3	1	19	13	12
3	1	20	11	6
3	1	21	5	3
3	1	22	10	16
3	2	0	22	20
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3	2	3	24	26
3	2	4	75	66
3	2	5	43	41
3	2	6	27	24
3	2	7	34	32
3	2	8	16	18
3	2	9	14	14
3	2	10	30	26
3	2	11	31	29
3	2	12	34	31
3	2	13	17	16
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3	2	15	10	9
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3	2	22	4	9
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3	3	2	32	34
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3	3	4	51	56
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3	3	6	48	47
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3	3	8	25	26
3	3	9	32	28
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3	3	13	19	16
3	3	14	13	11
3	3	15	13	12
3	3	16	12	10
3	3	17	19	20
3	3	18	13	16
3	3	19	12	13
3	3	20	5	6
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3	4	0	19	14
3	4	1	27	21
3	4	2	42	43
3	4	3	13	9
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3	4	9	16	9
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3	4	11	38	38
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3	4	16	6	7
3	4	17	14	15
3	4	18	7	7
3	4	19	6	6
3	4	20	8	12
3	5	0	8	8
3	5	1	9	10
3	5	2	17	15
3	5	3	57	58
3	5	4	15	14
3	5	5	9	10
3	5	6	31	31
3	5	7	30	27
3	5	8	16	13
3	5	9	33	28
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3	5	14	6	5
3	5	15	12	17
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3	7	4	10	10
3	7	5	12	12
3	7	6	15	12
3	7	7	12	12
3	7	9	26	27
3	7	10	6	7
3	7	11	11	11
3	7	12	7	6
3	7	13	19	18
3	7	15	9	13
3	8	0	6	3
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3	9	8	7	12
4	0	0	64	72
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4	0	4	15	16
4	0	5	31	27
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4	0	7	20	22
4	0	8	11	13
4	0	9	14	17
4	0	10	18	18
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4	0	12	14	12
4	0	13	27	24
4	0	16	24	24
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4	0	23	13	10
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7	0	16	9	11
7	0	20	7	8
8	0	1	16	12
8	0	7	11	12
8	0	5	14	8
8	0	11	7	8
9	0	2	7	5
9	0	3	5	6
9	0	4	5	8

The final positional and isotropic thermal parameters are listed in Table 1 and the structure amplitudes calculated from these parameters are tabulated in Table 2, where they are compared with the corresponding observed values; both $|F_{\text{obs}}|$ and $|F_{\text{calc}}|$ are expressed on an absolute scale.

The determination of the absolute configuration of the cation

The absolute configuration of the cation could be deduced from the known absolute configuration of the $(-)_{589}$-1,2-propylenediamine ligand (Saito & Iwasaki, 1962), but it was also determined independently by the Bijvoet absorption edge technique (Bijvoet, 1949, 1954, 1955; van Bommel, 1953; Peerdeman, 1956; Peerdeman & Bijvoet, 1956; Peerdeman, van Bommel & Bijvoet, 1951 *a, b;* Trommel & Bijvoet, 1954).

Cu $K\alpha$ radiation was chosen to take the photographs, since its wavelength (1·54 Å) is slightly shorter than that of the cobalt K-absorption edge (1·61 Å); under these conditions anomalous scattering will occur from the electrons of the cobalt atom.

As the model from which the atomic coordinates were taken had been based on a right-handed system of axes in real space, a right-handed system had to be used also in reciprocal space to index the photographs. The relative intensities of several pairs of hkl and $h\bar{k}l$ reflexions ($h=1,2,3$) were estimated visually, the readings being taken independently by two different persons. In the space group $P2_12_12_1$, $|F_{\bar{h}\bar{k}\bar{l}}|=|F_{h\bar{k}l}|$, even under con-, ditions of anomalous scattering.

The computation of $|F_{hkl}|^2$ and $|F_{h\bar{k}l}|^2$ under conditions of anomalous scattering were made using the atomic coordinates of a model corresponding to the Δ enantiomer, *i.e.* the isomer whose configuration is enantiomorphously related to that of $(+)_{589}$-$[\mathrm{Co(en)_3}]^{3+}$. The configuration of the 1,2-propylenediamine (pn) ligand on this model is identical with that of $(-)_{589}$-pn, that is, it has the R configuration.

The effects of anomalous scattering are not altogether negligible for atoms of high atomic number, even when their absorption edge occurs at a wavelength well above that of the incident radiation. Dispersion corrections were therefore applied for the chloride ion, as well as for the cobalt atom.

The values used for the real and imaginary dispersion corrections to the atomic scattering factors of these two atoms were the mean values of those calculated from Hönl's formula and those published by Dauben & Templeton (1955), *i.e.*

$$\text{for Co}: \Delta f'_K=-2{\cdot}6,\quad \Delta f''_K=3.6$$

$$\text{for Cl}^-: \Delta f'_K=+0{\cdot}33,\ \Delta f''_K=0{\cdot}81$$

A comparison of the observed values of the intensities and the calculated values of the squares of the structure amplitudes for some of these pairs of reflexions confirmed the absolute configuration of the cation to be Δ as indicated by the correct configuration of the $(-)_{589}$-pn ligand on the Δ model (Table 3.) There were no reflexions in which the enantiomorphous configuration was indicated.

Table 3. *Determination of the absolute configuration of the cation*

			Calculated for the △ enantiomer corrected for anomalous scattering by Co and Cl⁻		Observed
h	k	l	$\lvert F_{hkl}\rvert^2$	$\lvert F_{\bar{h}\bar{k}\bar{l}}\rvert^2$	$I_{hkl} \lesseqgtr I_{h\bar{k}l}$
1	1	7	5	177	<
1	1	8	429	202	>
1	2	5	34	199	<
1	3	1	722	130	>
1	3	2	389	836	<
1	3	12	1230	788	>
1	5	2	1144	352	>
1	9	9	95	481	<
2	1	3	38	540	<
2	2	2	1124	2058	<
2	2	5	2663	3811	<
2	6	9	189	620	<
3	1	2	1760	1009	>
3	1	6	66	648	<
3	3	9	1231	450	>
3	4	2	2067	1568	>

Description of the structure

The structure is essentially ionic consisting of complex cations and chloride ions; these are arranged in layers parallel to (001), in such a way that each layer consists of pairs of like ions, separated from the next such layer by a layer containing pairs of oppositely charged ions. Within each layer, like ions are separated from each other by the operation of screw axes.

The coordinates of the cobalt atom and the chloride ion are very nearly related by:

$$(x_1,y_1,z_1) \text{ and } [(\tfrac{1}{2}+x_1),y_1,z_2]$$

so that each chloride ion is approximately equi-distant from two cobalt atoms and *vice versa*.

The atomic packing in the crystals, in the (100) and (010) projections of the unit cell is shown in Figs. 1 and 2. The shape of the cation can best be seen from Fig. 3. Table 4 gives the interatomic distances and bond angles between atoms in the cation.

The cobalt atom is surrounded by six nitrogen atoms situated at the corners of a slightly distorted octahedron. On the whole the Co–N distances are in good agreement with values ranging from 1·90–2·02 Å, obtained for other cobalt complexes with nitrogen donor ligands, but the mean value of 1·90 Å of the distances between the cobalt and nitro group nitrogen atoms is slightly, but significantly, less than the mean value of 1·97 Å of the four Co–N distances to the amine nitrogen atoms. Evidence for the existence of intra-ionic hydrogen bonding is provided by four non-bonded O–N distances between 2·7 and 2·8 Å [Table 4(*b*)], whose value is significantly lower than the sum of the van der Waals radii for these two atoms.

The distortion of the N–Co–N bond angles from their ideal octahedral values of 90° is due to the formation of the five-membered chelate rings. The values obtained for the angle in the two propylenediamine rings of *cis*-$(+)_{589}$-[Co-$(-)_{589}$-$pn_2(NO_2)_2$]Cl are 87·4 and 86·9° respectively. Corey & Sneen (1955) showed that in a cobalt-ethylenediamine ring with the following 'normal' dimensions:

$$\text{C–C}=1{\cdot}54,\ \text{C–N}=1{\cdot}47,\ \text{Co–N}=2{\cdot}00\ \text{Å}$$

$$\text{Co–N–C}=\text{N–C–C}=109{\cdot}5^\circ\ ,$$

the N–Co–N angle would be 86·2°.

The propylenediamine molecules assume *gauche* configurations on chelation. The ring conformation is λ with the methyl groups of the $(-)_{589}$pn ligands in equatorial positions. The puckering of the ring is such that while the cobalt atom lies within the least-squares mean plane through the five ring atoms, the nitrogen and carbon atoms are situated alternately above and below this mean plane; the displacement of the carbon atoms from this plane is approximately twice as great as that of the nitrogen atoms and it is approximately equal in magnitude for the two adjacent carbon atoms, so that the mid-points of the C–C bonds lie within the mean plane. The dihedral angles between the planes defined by the C–C and C–N bonds are 53 and 52° respectively. These values compare well with the corresponding value of 51° in Δ [Co$(-)_{589}$pn$_3$]Br$_3$ (Iwasaki & Saito, 1966) and the mean value of 55° in

$$trans\text{-}[\text{Co}(-)_{589}\text{pn}_2\text{Cl}_2]\text{Cl}.\text{HCl}.2\text{H}_2\text{O}$$

(Saito & Iwasaki, 1962).

The two nitro groups which occupy *cis* positions are both coplanar with the cobalt atom and perpendicular to each other, the dihedral angle between them being 91°. None of the four atoms: Co, N, O, O is significantly

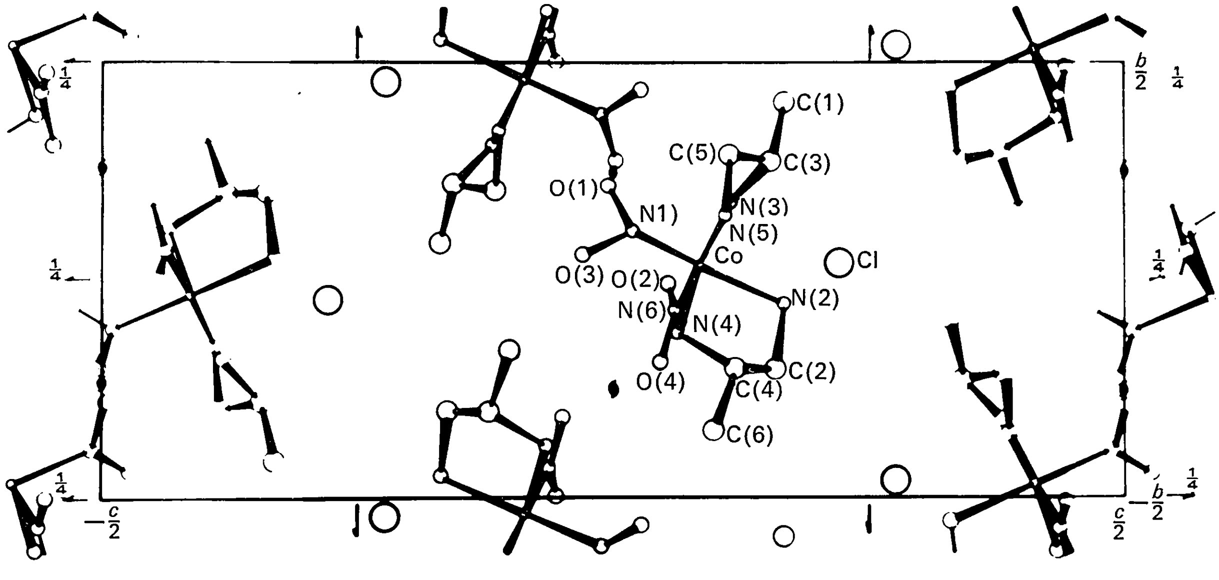


Fig. 1. (100) projection of the unit cell of *cis* $(+)_{589}$[Co$(-)_{589}$pn$_2$(NO$_2$)$_2$]Cl.

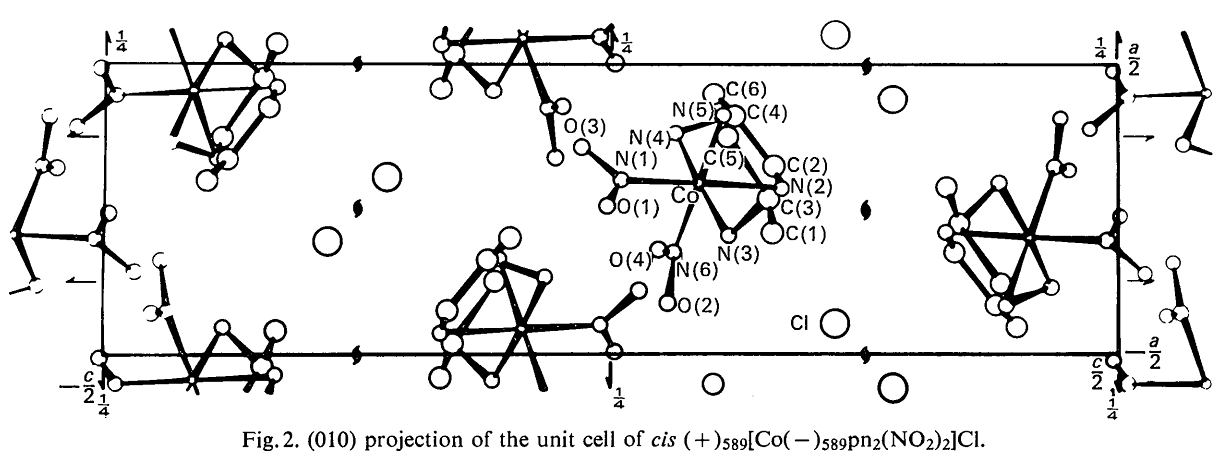


Fig. 2. (010) projection of the unit cell of *cis* $(+)_{589}$[Co$(-)_{589}$pn$_2$(NO$_2$)$_2$]Cl.

displaced from the least-squares mean plane through them, in either of the two nitro groups. The four oxygen atoms are coplanar, forming a somewhat distorted rectangle.

There is an approximate twofold axis of symmetry through the cation.

Table 5 lists some of the shorter distances between atoms in adjacent ions. There does not appear to be any appreciable inter-ionic N–O or N–Cl$^-$ hydrogen-bond-like interaction. The nearest inter-ionic N–O approaches (2·9–3·0 Å) are significantly longer than the 2·7–2·8 Å found for four inter-ionic N–O distances between amine nitrogen atoms and the oxygen atoms of the nitro groups.

Discussion

The results of the determinations of the structure and absolute configuration of (+)$_{589}$-*cis*-dinitrobis[(−)$_{589}$-propylenediamine]cobalt(III) chloride bear out all the predictions regarding the most likely configuration of the cation, both from the point of view of the stereospecifically most stable arrangement as well as from the point of view that the Δ absolute configuration and the λ ring conformation of the propylenediamine rings are those which would be predicted from the C.D. spectrum of the ion.

According to Corey & Bailar (1959), propylenediamine rings favour a ring conformation in which the methyl groups occupy equatorial positions, which, in the case of (−)$_{589}$pn, is the λ conformation and since tris(chelate) and bis-isomers of *cis* chelate complexes with λ rings favour the Δ absolute configuration, it follows that Δ complexes with λ rings are most favoured with (−)$_{589}$pn ligands.

The fact that the configuration of the cation is enantiomorphously related to that of Λ(+)$_{589}$[Co en$_3$]$^{3+}$ can also be deduced from a comparison of the signs of the C.D. bands associated with the first ligand field band, if the single C.D. band in the spectrum of (+)$_{589}$[Co(−)$_{589}$pn$_2$(NO$_2$)$_2$]$^+$ occurring in its wavelength region is interpreted as an unresolved composite due to the transitions $^1A_1 \rightarrow {}^1A_2$ (E_a), $^1A_1 \rightarrow {}^1B_2$ E_a) and $^1A_1 \rightarrow {}^1B_1$ (A_2). Its sign is that of the principal $^1A_1 \rightarrow {}^1A_2$ C.D. band and is diagnostic of configuration (McCaffery, Mason & Norman, 1965*a*). Since it is negative, while the corresponding $^1A_1 \rightarrow {}^1E_a$ band of (+)$_{589}$[Co en$_3$]$^{3+}$ has a positive Cotton effect (Barclay *et al.*, 1966), the two ions must have enantiomorphously related configurations. The charge transfer band, occurring at approximately 240 mμ has a positive Cotton effect which, according to McCaffery *et al.* (1965*b*), is indicative of λ rings.

Table 4. *Interatomic distances and bond angles in the cation*

(*a*) Bond lengths

		σ
Co—N(1)	1·88 Å	0·019 Å
Co—N(2)	2·01	0·020
Co—N(3)	1·97	0·023
Co—N(4)	1·94	0·023
Co—N(5)	1·96	0·023
Co—N(6)	1·92	0·027
N(2)–C(2)	1·53	0·032
N(3)–C(3)	1·51	0·032
N(4)–C(4)	1·52	0·032
N(5)–C(5)	1·46	0·033
C(1)–C(3)	1·57	0·038
C(2)–C(4)	1·45	0·039
C(3)–C(5)	1·55	0·040
C(4)–C(6)	1·55	0·039
N(1)–O(1)	1·22	0·025
N(1)–O(3)	1·24	0·026
N(6)–O(2)	1·27	0·029
N(6)–O(4)	1·20	0·026

(*b*) Short N–O distances signifying possible intra-ionic hydrogen bonds

N(3)–O(1)	2·79 Å	0·030 Å
N(3)–O(2)	2·71	0·031
N(4)–O(3)	2·73	0·028
N(4)–O(4)	2·72	0·036

(*c*) Bond angles

		σ
N(1)–Co—N(2)	178°	1·0°
N(3)–Co—N(4)	175	0·8
N(5)–Co—N(6)	175	1·0
N(1)–Co—N(3)	92	0·9
N(1)–Co—N(4)	93	0·9
N(1)–Co—N(5)	89	0·9
N(1)–Co—N(6)	88	1·0
N(2)–Co—N(3)	88	0·9
N(2)–Co—N(4)	87	0·9
N(2)–Co—N(5)	93	0·9
N(2)–Co—N(6)	90	0·9
N(3)–Co—N(5)	87	1·0
N(3)–Co—N(6)	89	1·1
N(4)–Co—N(5)	94	1·0
N(4)–Co—N(6)	90	1·1
Co—N(2)–C(2)	106	1·3
Co—N(3)–C(3)	106	1·8
Co—N(4)–C(4)	109	1·5
Co—N(5)–C(5)	109	1·9
N(2)–C(2)–C(4)	108	2·2
N(3)–C(3)–C(1)	109	2·3
N(3)–C(3)–C(5)	106	2·0
N(4)–C(4)–C(2)	109	2·4
N(4)–C(4)–C(6)	106	2·1
N(5)–C(5)–C(3)	107	2·2
C(1)–C(3)–C(5)	116	2·2
C(2)–C(4)–C(6)	115	2·5
Co—N(1)–O(1)	123	1·8
Co—N(1)–O(3)	120	1·7
Co—N(6)–O(2)	120	1·7
Co—N(6)–O(4)	122	2·6
O(1)–N(1)–O(3)	117	1·9
O(4)–N(6)–O(6)	118	2·8

Within the limits of experimental error the stereochemistry of the 1,2-propylenediamine rings, as found in $\Delta[\mathrm{Co}(-)_{589}\mathrm{pn}_3]^{3+}$, *trans*-$[\mathrm{Co}(-)_{589}\mathrm{pn}_2\mathrm{Cl}_2]^+$ and *cis*-$\Delta[\mathrm{Co}(-)_{589}\mathrm{pn}_2(\mathrm{NO}_2)_2]^+$ may be said to be identical. The only difference lies in the positions of these ligands relative to each other and to the equatorial plane of the cation. Whereas in $\Delta[\mathrm{Co}(-)_{589}\mathrm{pn}_3]^{3+}$ the methyl groups occupy *cis* positions, thus preserving (exact) trigonal symmetry (space group $P6_3$, with the cobalt atom on the threefold axis), they occupy *trans* positions in the two bis(propylenediamine) complexes, thus maintaining approximate twofold symmetry. In all three cases the maximum attainable symmetry is thus at least approximately achieved, resulting in the maximum possible spatial separation of the methyl groups. According to Jaeger & Bijkerk (1937) this represents the most favoured arrangement.

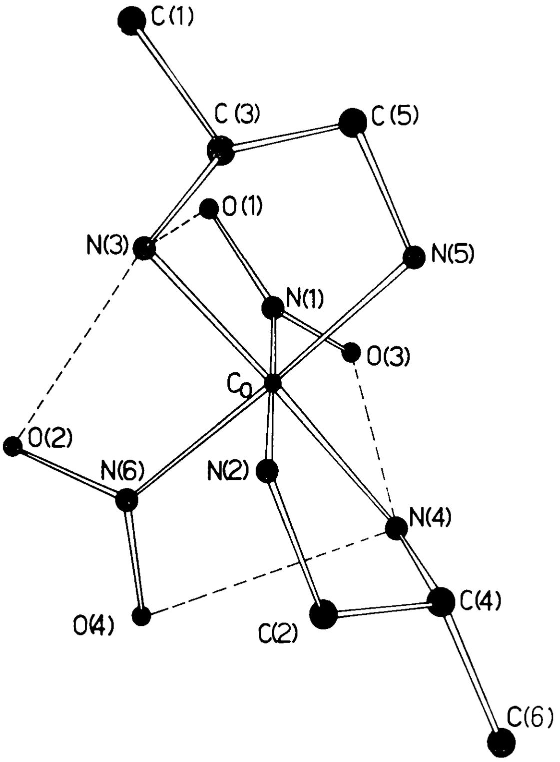
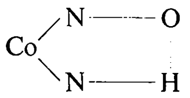


Fig. 3. The complex ion *cis*$(+)_{589}[\mathrm{Co}(-)_{589}\mathrm{pn}_2(\mathrm{NO}_2)_2]^+$.

The most surprising result of the structure determination was the closeness of the approach of the oxygen atoms to one or other of two *trans* nitrogen atoms [N(3) and N(4)] on either side of the equatorial plane, as shown in Fig. 4. If, on the basis of these short interatomic distances intra-ionic hydrogen bonds between nitrogen and oxygen atoms are envisaged, the result would be the formation of four approximately planar five-membered, hydrogen-bonded, chelate rings,



consisting of two mutually perpendicular pairs of coplanar rings. Broadly speaking, each of these two planes also embraces the mean plane through one of the propylenediamine rings and the complex ion as a whole experiences the sixfold chelation shown schematically in Fig. 5. The hydrogen bonds so formed would, of course, not be linear.

It should be noted that a necessary requirement for the close approach of the hydrogen atoms on N(3) and N(4) to the oxygen atoms of the nitro groups and also for the near-planarity of the resultant hydrogen-bonded chelate rings is that, in the Δ complex, the propylenediamine rings should have the λ conformation; this is due to the orientations imposed on the N–H bonds on N(3) and N(4), by the orientations of the N(3)–C(3) and N(4)–C(4) bonds respectively, which result from the λ conformation of the propylenediamine rings.

As can be seen from Table 6, the N(3)–Co–N(4) axis is much more nearly coplanar with one of the nitro groups than with the other, and the same is also true for the nitrogen atoms *trans* with respect to the nitro groups.

An attempt was made to investigate the extent and nature of the hydrogen bonding in this compound by infrared spectroscopy, but no conclusive evidence could be obtained from it. Owing to the insolubility of the ionic material in non-polar solvents, infrared measurements in solution could not be carried out and the solid

Table 5. *Interionic distances*

(Atom *A* is in asymmetric unit *xyz*)

Distance *A–B*	Asymmetric unit of atom *B*			Length	σ	Sum of van der Waals radii*
N(4)–O(2)	$(1+x)$	y	z	2·91 Å	0·035 Å	2·9 Å
N(5)–O(1)	$(\frac{1}{2}+x)$	$(\frac{1}{2}-y)$	$\bar{z}$	2·94	0·030	
N(5)–O(2)	$(1+x)$	y	z	3·01	0·032	
N(5)–Cl⁻	$(1+x)$	y	z	3·27	0·025	3·3
N(3)–Cl⁻	x	y	z	3·32	0·025	
N(2)–Cl⁻	x	y	z	3·33	0·030	
C(5)–O(1)	$(\frac{1}{2}+x)$	$(\frac{1}{2}-y)$	$\bar{z}$	3·16	0·037	3·4
C(5)–C(6)	x	$(1+y)$	$\bar{z}$	3·67	0·044	4·0

* Van der Waals radii were taken from Pauling (1960) *i.e.* O = 1·40; N = 1·5; Cl = 1·80; CH_3, CH_2 = 2·0 Å.

state spectrum in the 3μ region proved inconclusive, since the N–H stretching bands were poorly resolved.

The fact that the Co–NO_2 bonds are slightly, but significantly, shorter than the Co–NH_2 bonds may be due to d_π–p_π bonding from the Co^{III} d_ε electrons to the non-hybridized p-orbital of the nitrogen atoms. Such π bonding is favoured by coplanarity of the nitro-groups with the N(3)–Co–N(4) axis, which is approximately found here. A similar shortening of the Co–NO_2 bond length has not been observed in cobalt(III)nitroammines (Tanito, Saito & Kuroya, 1952, 1953; Bokii & Gilinskaya, 1953), but the extent of the Co→NO_2 π-bonding might be expected to be somewhat greater in the case of a propylenediamine complex because of the slightly greater donor power of the diamine ligand. The intra-ionic hydrogen bonding between the oxygen atoms and hydrogen atoms from the NH_2 groups on N(3) and N(4) will also result in a tendency to push the nitro groups closer to the N(3)–Co–N(4) axis, with a consequent lowering of the cobalt–nitro group nitrogen distance. It is interesting to note that a similar shortening of the Co–NO_2 bond length has been observed in the recently reported structure of (−)D-*cis*-β-dinitro-(L-3,8-dimethyltriethylenetetramine)cobalt(III) ion (Saito, 1969; Ito, Marumo & Saito, 1969), which is structurally very similar to the cation under discussion here.

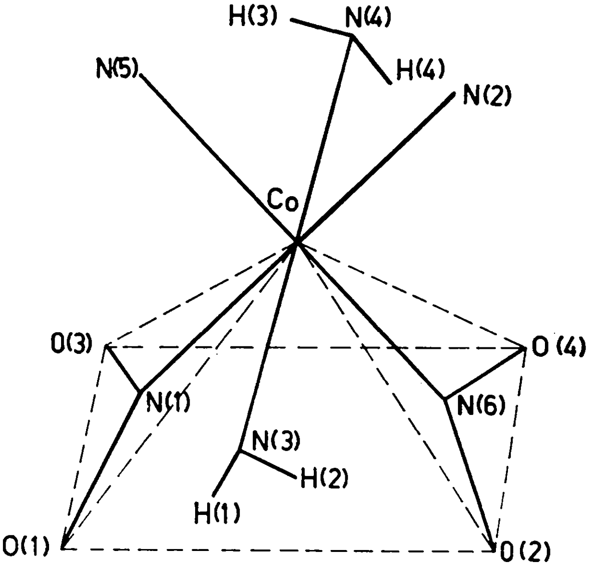


Fig. 4. The nitro groups and their environment.

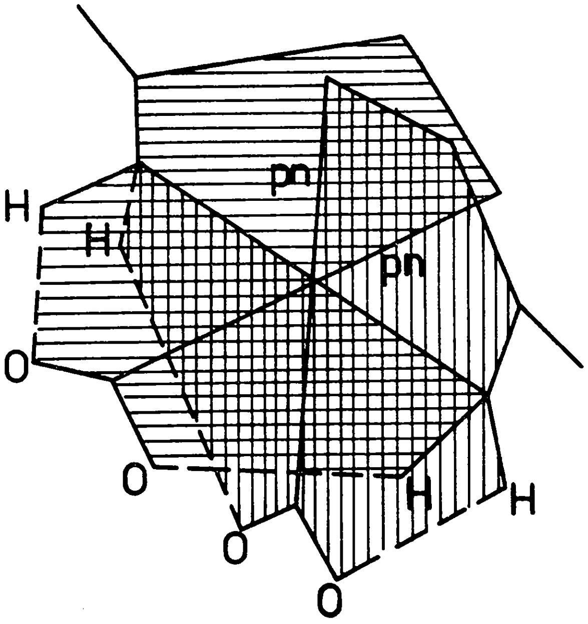


Fig. 5. A schematic representation of the chelation in the cation.

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Table 6. *The planes through the nitro groups and their environment*

	(NO_2) (1)		(NO_2) (2)	
Least-squares plane of best fit through the atoms:	Co, N(1), O(1), O(3)		Co, N(6), O(4), O(2)	
Perpendicular equation to the plane, referred to the orthogonal crystallographic axes:	$0.772X+0.562Y+0.295Z=1.215$		$-0.224X-0.233Y+0.946Z=1.645$	
Displacement of atoms from the plane:				
(i) the *trans* nitrogen atom	N(2)	−0·02 Å	N(5)	−0·12 Å
(ii) the N(3)–Co–N(4) axis	N(3) N(4)	+0·10 −0·11	N(4) N(3)	−0·39 +0·54
Dihedral angle between this plane and:				
(i) the mean plane through the pn ring containing the *trans* nitrogen atom	6°		23°	
(ii) the mean plane through the other nitro group	91°			

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Structure Cristalline de $BaC_2O_4.H_2C_2O_4.2H_2O$

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The crystal structure of $BaC_2O_4.H_2C_2O_4.2H_2O$ has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $C2/c$, with $a=14{,}45$, $b=5{,}40$, $c=12{,}45$ Å and $\beta=116°$. The final R value for 630 reflexions is 0·108. The structure consists of chains of oxalic acid molecules held together by hydrogen bonds. These chains form layers which are parallel to the (001) plane and packed together by means of O–Ba–O bonds. The molecule of water is very weakly bonded. This explains the dehydration curve, and at a higher temperature, the decomposition of this salt with formation of oxalic acid.

Introduction

La détermination de la structure du sel hydraté de formule $BaH_2(C_2O_4)_2.2H_2O$ fut entreprise dans le but d'expliquer, grâce à la connaissance des distances interatomiques et de la cohésion de l'édifice cristallin, son comportement thermique exposé ci-après.

L'étude de la dissociation de cet oxalate effectuée en thermobalance MacBain, sous pression de vapeur d'eau contrôlée, révèle tout d'abord la présence d'eau 'non stoechiométrique' en ce sens qu'une fraction quelconque de mole x, par mole de sel, peut être éliminée puis réintégrée dans le réseau. On aboutit donc en deshydratant le sel initial par élévation de température à une infinité d'hydrates, de formule $BaH_2(C_2O_4)_2.(2-x)H_2O$, stables dans des conditions de pression et de température précisées par l'expérience. Aucune modification de la position des raies de diffraction X caractérisant ces oxalates ne fut observée au moins en première approximation par rapport à celles fournies par l'oxalate initial.

Bien que le comportement thermique de ce sel rappelle celui des zéolites, tous les critères d'identification ne sont pas satisfaits, entre autres le domaine d'existence pression–température du système divariant, for-