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The Crystal Structure of (−)$_{589}$-Dinitrobis(ethylenediamine)cobalt(III) (+)$_{589}$-Bis(malonato)ethylenediaminecobaltate(III)

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The crystal structure of (−)$_{589}$-[Co(NO$_2$)$_2$en$_2$] (+)$_{589}$-[Co mal$_2$ en] has been investigated by the X-ray method. Crystal data: triclinic, space group $P1$; $a=10.58(2)$Å, $b=7.98(1)$Å, $c=7.99(1)$Å, $\alpha=122.8(2)°$, $\beta=105.3(2)°$, $\gamma=74.6(2)°$; $Z=1$. The crystal structure was determined by the Fourier technique and was refined by the least-squares method to an R factor of 0.101. The Δ configuration has been assigned to both the complex cation and anion, (−)$_{589}$-[Co(NO$_2$)$_2$en$_2$]$^+$ and (+)$_{589}$-[Co mal$_2$en]$^-$. The two Co-mal chelate rings are nearly planar. The O–Co–O angle in this ring is 96°, slightly larger than the N–Co–N angle observed in the cobalt(III)-trimethylenediamine chelate ring. All the ethylenediamine ligands in the two complex ions have the *ob*-conformation.

The absolute configuration of (−)$_{589}$-[Co mal$_2$en]$^-$ (mal=malonate ion) was studied by Douglas and his co-workers[1] by means of the ORD and CD spectra. They identified the lowest frequency CD peak with a positive sign as the A component by referring to the ORD and CD spectra of (+)$_{589}$-[Co ox$_2$en]$^-$ and (−)$_{546}$-[Co EDTA]$^-$; thus, they assigned the Λ configuration to (−)$_{589}$-[Co mal$_2$en]$^-$ on the basis of Mason's empirical rule.[2]

Recently, Judkins and Royer[3] measured the CD spectrum of $\Delta(+)_{589}$-[Co tn$_3$]$^{3+}$ in a signle crystal, showed that the relative positions of the E_a and A_2 bands in this complex are reversed as compared with those found in $\Delta(-)_{589}$-[Co en$_3$]$^{3+}$, and concluded that the sign of the Cotton effect should change when the coordination angle (θ) in the chelate ring goes from less than to greater than 90°, as had been predicted by Piper.[4] If such is the case with the Δtris(malonato)-cobalt(III) (possibly $\theta>90°$; this complex has not yet been prepared) and the Δtris(oxalato)coablt(III) complexes, the CD signs of their E_a components will be the opposite of each other. On the other hand, the rotational strength of the A component, $R(A)$, of the bis-complex seems to have a sign reflecting that of the R (E_a) of the parent tris-complex.[5] Therefore, the sign of the A component of $\Lambda(-)_{589}$-[Co mal$_2$en]$^-$ should be the reverse of that of $\Lambda(+)_{589}$[Co ox$_2$en]$^-$. These circumstances were not taken into account by Douglas *et al.* in making the assignment of the absolute configuration of (−)$_{589}$-[Co mal$_2$en]$^-$. In order to re-examine and determine its configuration directly,

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[1] B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

[2] S. F. Mason, *Quart. Rev.*, **17**, 20 (1963).

[3] R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

[4] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

[5] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

we carried out a crystal-structure analysis of $(-)_{589}$-$[Co(NO_2)_2en_2](+)_{589}$-$[Co\ mal_2en]$.

Experimental

The complex compound, $(-)_{589}$-$[Co(NO_2)_2en_2]$ $(+)_{589}$-$[Co\ mal_2en]$, was prepared following the method of Dwyer *et al.*[6]; subsequent recrystallization from an aqueous solution yielded brown crystals suitable for X-ray work. Using Cu*Kα* radiation, the unit-cell dimensions were determined from higher angle reflections of Weissenberg photographs, on which aluminum powder diffraction lines were superimposed for calibration. Oscillation and Weissenberg photographs did not show any special symmetry or systematic absences, indicating that the space group is $P1$ or $P\bar{1}$. Only the former is, however, consistent with the optical activity of the specimen. The crystal data are as follows:

Triclinic
$a=10.58(0.02)$Å
$b=7.98(0.01)$Å
$c=7.99(0.01)$Å
$\alpha=122.8(0.2)°$
$\beta=105.3(0.2)°$
$\gamma=74.6(0.2)°$
Space group $P1$
$Z=1$ $(D_m=1.81,\ D_c=1.82\ \text{g cm}^{-3})$
$\mu=35.9\ \text{cm}^{-1}$ for Ni*Kα*

Multiple-film, equi-inclination Weissenberg photographs were taken about the c (0 to 4th layers) and a axes (0 to 3rd layers) using Ni*Kα* radiation. The intensities of 1442 independent reflections were estimated visually with the standard calibrated scales, but 71 of these were too weak to be measured: therefore, their intensities were assumed to be zero. The intensities were corrected for the usual L_p factor and spot shape,[7] but not for absorption. The crystal specimen used for the data collection had dimensions of 0.1×0.04×0.4 mm.

Determination of the Crystal Structure

The positions of the two cobalt atoms were readily determined from the three-dimensional Patterson map. Their positional and thermal parameters were refined by the least-squares method. At this stage, the R factor was 0.411. The two nitro groups and one malonate ligand were found on the Fourier map phased by the two heavy atoms (Co_1 and Co_2). Then, the parameters of the 15 atoms thus obtained were refined and the structure factors were computed by their use. The subseuqent Fourier synthesis of the electron density showed the locations of all the remaining atoms. The five cycles of the least-squares refinement with an individual isotropic temperature factor reduced the R value to 0.101 for 1371 observed reflections. The weighting scheme employed was:

$$w=0.3 \quad \text{for } F_0<3.8$$
$$w=1.0 \quad \text{for } 3.8\leq F_0\leq 25.9$$
$$w=25.9/F_0 \quad \text{for } F_0>25.9$$

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[8] The real part of the anomalous disperison correction for Co was taken into account.[9] A subsequent refinement, in which anisotropic vibrations were permitted to the two cobalt atoms, improved neither the R factor nor the e.s.d.'s of the parameters. A difference synthesis computed at this stage did not show peaks corresponding to any of the hydrogen atoms. The final atomic coordinates, the temperature factors, and their e.s.d.'s are given in Table 1. The observed and calculated structure factors are preserved by the Chemical Society of Japan.[10]

Table 1. Atomic parameters and their e.s.d.'s[a]

Atom	x/a	y/b	z/c	B
Co_1	0.0	0.0	0.0	2.06(6)
O_1	−0.177(1)	0.074(2)	−0.095(2)	2.2(3)
O_2	0.057(1)	0.248(2)	0.098(2)	2.4(3)
O_3	−0.059(1)	0.100(2)	0.248(2)	2.3(3)
O_4	0.178(1)	−0.096(2)	0.078(2)	2.5(3)
O_5	−0.356(1)	0.295(2)	−0.079(2)	2.4(3)
O_6	0.041(1)	0.543(2)	0.124(2)	2.5(3)
O_7	−0.046(2)	0.118(2)	0.536(2)	3.5(3)
O_8	0.355(2)	−0.082(2)	0.294(2)	2.8(3)
C_1	−0.233(2)	0.257(3)	−0.055(3)	2.2(3)
C_2	−0.157(3)	0.418(4)	0.019(4)	5.1(6)
C_3	−0.010(2)	0.401(3)	0.080(3)	2.9(4)
C_4	0.008(2)	0.079(4)	0.399(4)	3.4(4)
C_5	0.147(3)	0.008(4)	0.411(4)	5.4(7)
C_6	0.230(2)	−0.052(3)	0.255(3)	2.7(4)
C_7	0.006(3)	−0.418(4)	−0.293(4)	4.2(5)
C_8	−0.003(2)	−0.305(3)	−0.406(4)	3.3(4)
N_1	−0.053(2)	−0.262(3)	−0.111(3)	3.2(4)
N_2	0.053(2)	−0.114(4)	−0.259(3)	2.3(3)
Co_2	0.5000(4)	0.3613(6)	0.3624(6)	2.24(6)
N_3	0.640(2)	0.151(3)	0.204(3)	2.5(3)
N_4	0.531(2)	0.210(2)	0.499(3)	2.2(3)
N_5	0.362(2)	0.198(3)	0.155(3)	3.3(4)
N_6	0.470(2)	0.501(3)	0.210(3)	2.7(3)
N_7	0.367(2)	0.552(3)	0.529(3)	2.4(3)
N_8	0.635(2)	0.525(2)	0.556(3)	2.2(3)
C_9	0.655(3)	−0.030(4)	0.221(4)	4.2(5)
C_{10}	0.648(2)	0.050(3)	0.446(3)	2.9(4)
C_{11}	0.345(2)	0.226(4)	−0.022(4)	3.3(4)
C_{12}	0.352(2)	0.449(4)	0.048(4)	3.5(4)
O_9	0.295(2)	0.491(3)	0.571(3)	3.9(3)
O_{10}	0.351(2)	0.735(2)	0.581(3)	3.8(3)
O_{11}	0.651(2)	0.584(3)	0.730(3)	4.2(4)
O_{12}	0.705(2)	0.573(3)	0.490(3)	4.1(4)

a) e.s.d.'s in parentheses

The absolute configurations of the complex ions

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[6] F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 1285 (1961).

[7] D. C. Philips, *Acta Crystallogr.*, **7**, 746 (1954).

[8] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), pp. 202, 214.

[9] R. W. James, "The Optical Principles of the Diffraction of X-rays," G. Bell & Sons, London (1948), p. 608.

[10] The complete data of the F_o-F_c table are kept as Document No. 7206 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and remittimg, in advance, ¥200 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

Table 2. Calculated and observed intensities

$h\ k\ l$	$F_c^2(hkl)$	Obsd.	$\bar{h}\ \bar{k}\ \bar{l}$	$F_c^2(\bar{h}\bar{k}\bar{l})$
$\bar{1}$ 2 0	576	>	1 $\bar{2}$ 0	196
$\bar{2}$ 2 0	81	<	2 $\bar{2}$ 0	169
$\bar{1}$ 5 0	225	>	1 $\bar{5}$ 0	121
2 2 0	144	>	$\bar{2}$ $\bar{2}$ 0	9
4 1 0	169	>	$\bar{4}$ $\bar{1}$ 0	49
1 3 0	484	>	$\bar{1}$ $\bar{3}$ 0	361
7 1 0	484	<	$\bar{7}$ $\bar{1}$ 0	784
7 2 0	676	<	$\bar{7}$ $\bar{2}$ 0	841
0 3 0	81	<	0 $\bar{3}$ 0	361
$\bar{2}$ 3 0	256	>	2 $\bar{3}$ 0	9
$\bar{1}$ 4 0	25	<	1 $\bar{4}$ 0	169
0 6 0	256	>	0 $\bar{6}$ 0	64

were determined by using the anomalous dispersion effects of the cobalt atoms for Cu*Kα* radiation. The right-handed coordinate system was used in the indexing of the Weissenberg photographs throughout the present work. The intensities of the *hk*0 reflections were compared with those of $\bar{h}\bar{k}0$ on Weissenberg photographs around the *c* axis. The inequality relationships which were observed for some Bijvoet pairs are shown in Table 2. In this table the calculated intensities which were obtained by the use of the atomic coordinates shown in Table 1 are also listed. The values of $\Delta f'_{Co}$ and $\Delta f''_{Co}$ were taken from the International Tables for X-ray Crystallography.[8] A comparison of the observed inequality relationships with the calculated ones indicates that the set of the atomic coordinates shown in Table 1 represents the absolute structure of the crystal.

Results and Discussion

Projections of the crystal structure of an symmetric unit along the *c* and *b* axes are presented in Figs. 1 and 2 respectively. The crystal is composed of $(-)_{589}$-[Co$(NO_2)_2en_2$]$^+$ and $(+)_{589}$-[Co mal_2en]$^-$ ions, which are linked to each other by hydrogen bonds. In order to confirm the hydrogen bonds which exist between the amine groups of the coordinated ethylenediamine ligands and the oxygen atoms of the malonate ions, the positions of the hydrogen atoms were computed on the assumption that the $>NH_2$ groups have the tetrahedral geometry and the N–H bond distance is 1.03 Å.[11] The hydrogen bonds are summarized in Table 3. In the $(-)_{589}$-[Co$(NO_2)_2en_2$]$^+$ cation, all of the H(NH_2)'s of the ethylenediamine ligands participate in the hydrogen bonding. The N_4–H···O_8 and N_6–H···O_5 bonds seem to be stronger than the other six bonds. In the $(+)_{589}$-[Co mal_2en]$^-$ anion, only one hydrogen atom of the individual NH_2 group takes part in the hydrogen bonding; these N–H···O bonds are as strong as the N_4–H···O_8 and N_6–H···O_5 bonds.

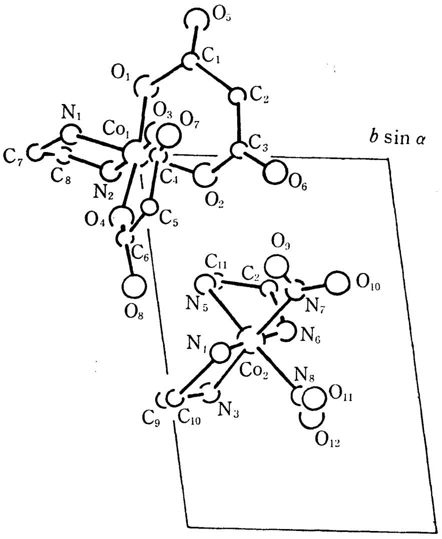

Fig. 1. The structure in an asymmetric unit, viewed along the *c* axis.

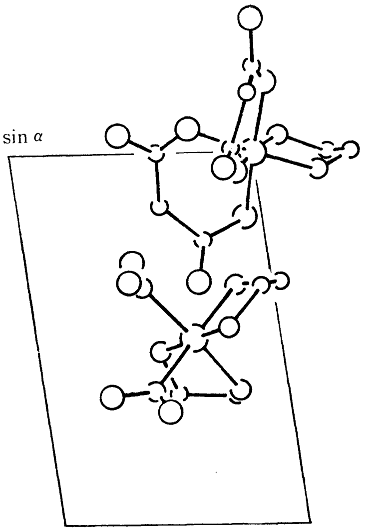

Fig. 2. Projection of the unit cell contents along the *b* axis.

Table 3. Possible hydrogen bonds with N···O distances less than 3.20Å

N	O	N···O	H···O	Angle around H
N_1 (1)	O_6 (5)	2.88Å	1.88Å	153°
N_2 (1)	O_7 (6)	2.93	1.92	166
N_3 (1)	O_5 (2)	3.05	2.34	125
N_3 (1)	O_3 (2)	3.05	2.19	140
N_4 (1)	O_5 (3)	3.02	2.18	137
N_4 (1)	O_8 (1)	2.85	1.92	149
N_5 (1)	O_8 (1)	3.01	2.34	122
N_5 (1)	O_2 (1)	3.09	2.24	139
N_6 (1)	O_8 (4)	2.98	2.15	136
N_6 (1)	O_5 (2)	2.82	1.89	148

(1) x, y, z (2) $1+x, y, z$ (3) $1+x, y, 1+z$ (4) $x, 1+y, z$ (5) $x, -1+y, z$ (6) $x, y, -1+z$

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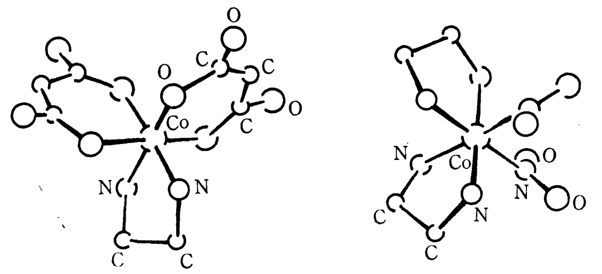
[11] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

The perspectives of $(-)_{589}$-$[\mathrm{Co(NO_2)_2en_2}]^+$ and $(+)_{589}$-$[\mathrm{Co\ mal_2en}]^-$ are depicted in Fig. 3. It has been elucidated by the present work that both the complex ions have the same configuration, *i.e.*, *Δ*.[12]



$(+)_{589}$-$[\mathrm{Co\ mal_2en}]^-$ $(-)_{589}$-$[\mathrm{Co(NO_2)_2en_2}]^+$

Fig. 3. The absolute configurations of the complex ions.

The absolute configuration of $(+)_{589}$-$[\mathrm{Co\ mal_2en}]^-$ is consistent with the assignment made by Douglas *et al.*[1] Their spectral assignment of the *A* transition is possibly correct. On the other hand, if Piper's model is also applicable in the case of the tris(malonato)-coablt(III) complex,[4] the sign of the rotational strength, *R*(*A*), of $\Delta(+)_{589}$-$[\mathrm{Co\ mal_2en}]^-$ should be reversed to that of $\Delta(-)_{589}$-$[\mathrm{Co\ ox_2en}]^-$, as has already been stated. Douglas *et al.* gave the negative sign to the rotational strengths of the *A* components of these two complexes. Therefore, their assignment of the *A* component is not entirely satisfactory.

The *Δ* configuration of $(-)_{589}$-$[\mathrm{Co\ (NO_2)_2en_2}]^+$ established in the present work has already been assigned by some workers on the basis of the CD[5,13,14] and ORD[15] data. It is possible that the sign of the major CD peak in the first-absorption-band region is to be regarded as a diagnostic of the absolute configuration of the dissymmetric *cis*-$[\mathrm{CoL_2en_2}]$ complexes (the ligands, L, are unidentate).[5,16,17]

The bond distances and angles in the complex ions are listed in Table 4. The approximate symmetry of $(-)_{589}$-$[\mathrm{Co(NO_2)_2en_2}]^+$ and $(+)_{589}$-$[\mathrm{Co\ mal_2en}]^-$ is C_2. All the ethylenediamine molecules in both com-

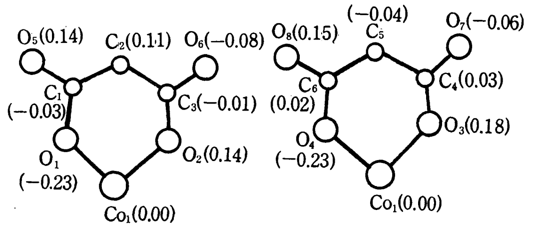


Fig. 4. Projection of the Co–mal six-membered chelate rings.
mal: malonate ion
Deviations of the atoms from the mean planes are given in parentheses.

Table 4. The bond lengths and bond angles in the complex ions
Their e.s.d.'s are given in parentheses

$\mathrm{Co_1-O_1}$	1.89(2) Å	$\mathrm{O_1-Co_1-O_2}$	96(1)°	$\mathrm{Co_2-N_3}$	2.00(2) Å	$\mathrm{N_3-Co_2-N_4}$	85(1)°
$\mathrm{Co_1-O_2}$	1.90(2)	$\mathrm{O_3-Co_1-O_4}$	96(1)	$\mathrm{Co_2-N_4}$	1.95(2)	$\mathrm{N_5-Co_2-N_6}$	86(1)
$\mathrm{Co_1-O_3}$	1.91(2)	$\mathrm{Co_1-O_1-C_1}$	126(2)	$\mathrm{Co_2-N_5}$	1.99(3)	$\mathrm{Co_2-N_3-C_9}$	109(2)
$\mathrm{Co_1-O_4}$	1.91(2)	$\mathrm{Co_1-O_2-C_3}$	128(2)	$\mathrm{Co_2-N_6}$	1.98(2)	$\mathrm{Co_2-N_4-C_{10}}$	113(2)
$\mathrm{Co_1-N_1}$	1.96(2)	$\mathrm{Co_1-O_3-C_4}$	127(2)	$\mathrm{Co_2-N_7}$	1.93(2)	$\mathrm{Co_2-N_5-C_{11}}$	107(2)
$\mathrm{Co_1-N_2}$	1.93(2)	$\mathrm{Co_1-O_4-C_6}$	125(2)	$\mathrm{Co_2-N_8}$	1.95(2)	$\mathrm{Co_2-N_6-C_{12}}$	113(2)
$\mathrm{O_1-C_1}$	1.31(3)	$\mathrm{O_1-C_1-C_2}$	123(2)	$\mathrm{N_3-C_9}$	1.49(4)	$\mathrm{N_3-C_9-C_{10}}$	106(2)
$\mathrm{O_2-C_3}$	1.30(3)	$\mathrm{O_2-C_3-C_2}$	121(3)	$\mathrm{N_4-C_{10}}$	1.48(3)	$\mathrm{N_4-C_{10}-C_9}$	106(2)
$\mathrm{O_3-C_4}$	1.30(3)	$\mathrm{O_3-C_4-C_5}$	122(3)	$\mathrm{N_5-C_{11}}$	1.51(4)	$\mathrm{N_5-C_{11}-C_{12}}$	112(3)
$\mathrm{O_4-C_6}$	1.26(3)	$\mathrm{O_4-C_6-C_5}$	121(3)	$\mathrm{N_6-C_{12}}$	1.51(4)	$\mathrm{N_6-C_{12}-C_{11}}$	103(2)
$\mathrm{C_1-O_5}$	1.24(3)	$\mathrm{C_1-C_2-C_3}$	124(3)	$\mathrm{C_9-C_{10}}$	1.57(4)	$\mathrm{O_9-N_7-O_{10}}$	121(2)
$\mathrm{C_3-O_6}$	1.22(3)	$\mathrm{C_4-C_5-C_6}$	125(3)	$\mathrm{C_{11}-C_{12}}$	1.57(4)	$\mathrm{O_{11}-N_8-O_{12}}$	119(2)
$\mathrm{C_4-O_7}$	1.22(3)	$\mathrm{O_1-C_1-O_5}$	119(2)	$\mathrm{N_7-O_9}$	1.20(3)	$\mathrm{N_7-Co_2-N_8}$	90(1)
$\mathrm{C_6-O_8}$	1.27(3)	$\mathrm{O_2-C_3-O_6}$	122(3)	$\mathrm{N_7-O_{10}}$	1.26(3)		
$\mathrm{C_1-C_2}$	1.46(4)	$\mathrm{O_3-C_4-O_7}$	121(3)	$\mathrm{N_8-O_{11}}$	1.18(3)		
$\mathrm{C_2-C_3}$	1.50(5)	$\mathrm{O_4-C_6-O_8}$	118(3)	$\mathrm{N_8-O_{12}}$	1.25(3)		
$\mathrm{C_4-C_5}$	1.43(5)	$\mathrm{C_2-C_1-O_5}$	119(3)				
$\mathrm{C_5-C_6}$	1.51(5)	$\mathrm{O_6-C_3-C_2}$	117(3)				
$\mathrm{N_1-C_7}$	1.47(4)	$\mathrm{C_5-C_4-O_7}$	117(3)				
$\mathrm{N_2-C_8}$	1.49(4)	$\mathrm{C_5-C_6-O_8}$	120(3)				
$\mathrm{C_7-C_8}$	1.56(4)	$\mathrm{N_1-Co_1-N_2}$	86(1)				
		$\mathrm{Co_1-N_1-C_7}$	112(2)				
		$\mathrm{Co_1-N_2-C_8}$	110(2)				
		$\mathrm{N_1-C_7-C_8}$	103(3)				
		$\mathrm{N_2-C_8-C_7}$	108(2)				

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13) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1965**, 1368.

14) G. A. Barclay, E. Goldschmied, N. E. Stephenson, and A. M. Sargeson, *Chem. Commun.*, **1966**, 540.

15) T. E. McDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1968).

16) K. Matsumoto, S. Ooi, and H. Kuroya, This Bulletin, **43**, 3801 (1970).

17) K. Matsumoto, S. Ooi, and H. Kuroya, *ibid.*, **44**, 2721 (1971).

plexes are of the *ob*-conformation. The role of the hydrogen bonding in $(-)_{589}$-[Co$(NO_2)_2$en$_2$]$^+$ may be important in stabilizing the unstable *ob-ob* conformer.[11] The two Co-mal chelate rings are approximately planar (Fig. 4). The maximum deviation of the atom from mean plane is 0.23 Å. The presence of N–H···O hydrogen bonds seems to be significant in the formation of the nearly planar Co-mal chelate rings.[12] The average O–Co–O angle is 96°, slightly larger than the N–Co–N angle (94°) found in $(-)_{589}$-[Co tn$_3$]$^{3+}$.[18] The C–C–C angle (125°) is far from the tetrahedral angle, indicating that there is much strain in this bond angle. The C–O (coordinated to the Co atom) distances in the carboxyl groups are likely to be slightly larger than in the uncoordinated C–O bonds.

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