Conformations of Malonate Chelate Rings: the Crystal and Molecular Structure of Sodium $(+)_{546}$Ethylenediaminebis(malonato)cobaltate(III) Dihydrate

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The crystal structure of $Na(+)_{546}[Co(mal)_2(en)],2H_2O$ has been determined by the heavy-atom method from photographic data. Crystals are orthorhombic, space group $P2_12_12_1$, with $a = 13.46(2)$, $b = 14.24(2)$ $c = 7.344(10)$ Å, and $Z = 4$. Refinement by full-matrix least-squares gave R 0.05 for 838 observed reflections. The absolute configuration of the complex ion is Δ, in agreement with correlations from c.d. spectra. The tris-bidentate complex has an approximate two-fold axis with the two malonate ligands adopting boat conformations and folding towards each other while the ethylenediamine ligand is skewed oblique rather than parallel to the pseudo-three-fold axis of the anion. This result confirms the prediction that chair conformations are energetically unfavoured for malonate complexes and suggests the nature of the conformation interconversions shown by solution n.m.r. studies.

THE absolute configuration of $(-)_{589}[Co(mal)_2(en)]^-$ (mal = malonate, en = ethylenediamine) was predicted to be Λ from its c.d. and o.r.d. spectra.[1] A preliminary communication [2] of the X-ray study of $Na(+)_{589}[Co(mal)_2(en)],2H_2O$ and of the diastereoisomer $(-)_{589}[Co(NO_2)_2(en)_2]$ $(+)_{589}[Co(mal)_2(en)]$[3,4] has confirmed this prediction. The conformations of the malonate chelate rings in these structures differ considerably. Proton n.m.r. studies [5-7] have been unable to assign satisfactorily the conformations of malonate complexes in solution. The X-ray studies appear relevant to this problem and in view of the paucity of structural data for malonate co-ordination the results for the sodium salt are now presented.

EXPERIMENTAL

Recrystallisation from aqueous solution of a sample of $Na(+)_{546}[Co(mal)_2(en)],2H_2O$ gave red-violet prisms, the majority of which exhibited {1,1,1} bevels at one end of the needle axis and were badly twinned; the faces parallel to the needle axis were of the form {1,1,0}. Space-group and unit-cell parameters were determined from calibrated precession and Weissenberg photographs.

Crystal Data.—$C_8H_{16}CoNaN_2O_{10}$, $M = 382.1$, Orthorhombic, $a = 13.46(2)$, $b = 14.24(2)$, $c = 7.344(10)$ Å, $U = 1\,408(5)$ Å^3, $D_m = 1.78(2)$, $Z = 4$, $D_c = 1.80$, $F(000) = 728$. Space group $P2_12_12_1$ (No. 19). Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 13.3 cm^{-1}.

The crystal used for data collection with Mo-K_α radiation (Zr-filter) was a rectangular prism, 0.10 × 0.10 × 0.40 mm, mounted along the needle axis (c). Integrated photographic intensities were recorded for reciprocal layers $h0$—$2l$ and 0—$2kl$ with a precession camera taking multiple exposures. Layers $hk0$—7 were recorded with an integrating Weissenberg equi-inclation camera employing multiple films. The layer $hk1$ (non-integrated) was recorded for determination of the absolute configuration with Cu-K_α ($\lambda = 1.5418$ Å) radiation. This layer was visually estimated against a calibrated intensity strip and the integrated intensities measured with a Nonius II microdensitometer.

Data were corrected and brought to a common scale as described previously.[8] Absorption corrections were not applied. A total of 1 060 unique reflections was obtained, of which only the 838 reflections above background were used in the refinement.

Structure Analysis.—A Patterson synthesis yielded the cobalt position which was used by the heavy-atom procedure to locate all non-hydrogen atoms excluding the water molecules. The latter were found in difference maps obtained after full-matrix least-squares refinement of the other atoms. Refinement, employing anisotropic thermal parameters for the two metal atoms, converged with a conventional R factor (on F) of 0.069. The distribution of $w\Delta^2$ [w is the reflection weight = $1/\sigma^2(F_o)$, and $\Delta = |F_o| - |F_c|$, averaged in ranges of $|F_o|$] *vs.* $|F_o|$ was fitted to a Cruickshank-type weighting scheme [9] of the form: $\sigma(F_o) = (a + |F_o| + b|F_o|^2)^{\frac{1}{2}}$ with $a = 1.35$ and $b = 0.016$. This procedure was adopted since the weights assigned during data reduction gave an increasing trend of $w\Delta^2$ *vs.* $|F_o|$. There was no evidence for a secondary extinction effect.

Hydrogen atom co-ordinates (other than for the water molecules) were calculated (C–H 1.02, N–H 0.95 Å) assuming tetrahedral angles at carbon and nitrogen. Refinement was continued to convergence (shifts $<0.1\sigma$) giving R 0.050 with fixed hydrogen atom contributions (98 variables). The absolute configuration was verified in two ways. Firstly the sign of the imaginary component of scattering by cobalt ($\Delta f''_{Co}$ 1.06, for Mo-K_α[10]) was reversed and refinement again converged at R 0.054 suggesting the former (Δ) configuration of the complex ion. Secondly, calculation of structure amplitudes for the 38 pairs of Cu-K_α Weissenberg data ($h \pm kl$, $\Delta f''_{Co} = 3.95$, for Cu-K_α[10]) gave agreement in the Δ configuration for all but the weakest pair of intensities.†

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† Observed and calculated structure amplitudes (×10) are listed in Supplementary Publication No. SUP 21434 (4 pp., 1 microfiche). Unreliable and unobservable reflections were excluded from least-squares and are denoted E and U respectively.

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Scattering factors used were taken from ref. 11. Computer programs used are listed in ref. 8. Final least-squares parameters are given in Table 1.

TABLE 1

Positional ($\times 10^4$) and thermal parameters for $Na(+)_{546}\Delta[Co(malonate)_2(ethylenediamine)],2H_2O$

Atom	x	y	z	$B/Å^2$
Co	−970(03)	1 642(03)	815(05)	*
Na	−3 538(08)	1 681(09)	−2 504(14)	*
O(1)	−2 299(14)	1 449(13)	1 017(25)	1.41(32)
O(2)	−1 341(14)	1 790(14)	3 282(24)	1.48(34)
O(3)	345(14)	1 931(13)	1 546(23)	1.16(33)
O(4)	−769(14)	326(13)	1 001(27)	1.85(37)
O(5)	49(17)	−941(16)	1 737(27)	2.24(40)
O(6)	1 609(19)	1 760(19)	3 354(32)	3.52(51)
O(7)	−3 789(15)	854(15)	270(28)	2.18(43)
O(8)	−2 206(15)	1 374(14)	5 667(31)	2.35(39)
O(9)	−2 128(21)	4 104(20)	4 403(39)	4.64(60)
O(10)	−3 391(30)	4 258(29)	1 420(54)	7.88(105)
N(1)	−1 176(19)	2 960(18)	386(32)	2.14(53)
N(2)	−520(18)	1 573(19)	−1 673(29)	1.82(41)
C(1)	−1 005(29)	3 167(24)	−1 549(43)	2.90(63)
C(2)	−237(27)	2 519(25)	−2 319(46)	2.86(67)
C(3)	−2 083(19)	1 337(18)	4 003(38)	1.34(45)
C(4)	−2 782(21)	742(20)	2 922(36)	1.25(46)
C(5)	−2 955(20)	1 039(18)	968(37)	1.32(44)
C(6)	−93(25)	−73(22)	1 876(37)	1.84(55)
C(7)	496(24)	468(23)	3 218(41)	1.94(55)
C(8)	872(25)	1 427(20)	2 674(39)	2.14(55)
N(1)H(1)	−1 839	3 123	701	3.0
N(1)H(2)	−726	3 314	1 109	3.0
N(2)H(1)	−1 040	1 334	−2 415	3.0
N(2)H(2)	39	1 167	−1 743	3.0
C(1)H(1)	−1 654	3 085	−2 249	4.0
C(1)H(2)	−765	3 843	−1 679	4.0
C(2)H(1)	−243	2 541	−3 706	4.0
C(2)H(2)	452	2 693	−1 853	4.0
C(4)H(1)	−2 508	75	2 907	4.0
C(4)H(2)	−3 453	747	3 571	4.0
C(7)H(1)	1 103	69	3 541	4.0
C(7)H(2)	65	553	4 346	4.0

* Anisotropic thermal parameters ($\times 10^5$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	140(16)	107(14)	410(81)	−23(20)	−55(31)	0(30)
Na	215(65)	305(63)	792(21)	22(71)	88(84)	149(103)

The form of the thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

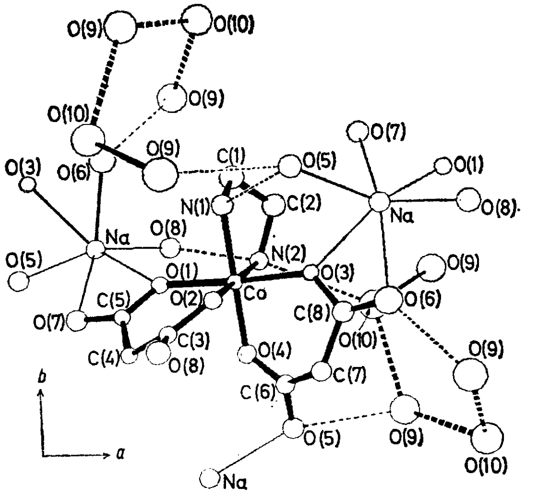

FIGURE 1 The complex anion environment of the $Na(+)_{546}$-$[Co(mal)_2(en)],2H_2O$ structure. Hydrogen bonds are shown as broken lines

RESULTS AND DISCUSSION

The Structure.—The immediate environment of the complex anion is shown in Figure 1 as a projection slightly tilted from the *ab* plane. Molecular geometry is given in Table 2, and Table 3 lists sodium ion contacts and possible hydrogen bonds. The complex has an approximate two-fold axis passing through the cobalt and the centre of the ethylenediamine ring and relates the

TABLE 2

Bond distances and angles

(*a*) Distance (Å)

Co–O(1)	1.90(2)	O(5)–C(6)	1.26(4)
Co–O(2)	1.89(2)	O(6)–C(8)	1.21(4)
Co–O(3)	1.90(2)	Mean O–C	1.240(12)
Co–O(4)	1.90(2)	C(3)–C(4)	1.50(4)
Mean Co–O	1.897(6)	C(4)–C(5)	1.51(4)
O(1)–C(5)	1.27(3)	C(6)–C(7)	1.48(4)
O(2)–C(3)	1.30(3)	C(7)–C(8)	1.51(4)
O(3)–C(8)	1.31(3)	Mean C–C	1.500(18)
O(4)–C(6)	1.25(4)	Co–N(1)	1.92(3)
Mean O–C	1.281(13)	Co–N(2)	1.93(2)
O(7)–C(5)	1.26(3)	Mean Co–N	1.925(18)
O(8)–C(3)	1.24(4)	C(1)–C(2)	1.50(5)

(*b*) Angles (°)

O(1)–Co–O(2)	93.6(8)	O(3)–C(8)–C(7)	119.0(28)
O(3)–Co–O(4)	93.5(8)	O(6)–C(8)–C(7)	121.4(29)
Co–O(1)–C(5)	123.5(17)	O(4)–C(6)–O(5)	121.1(29)
Co–O(2)–C(3)	122.5(17)	O(4)–C(6)–C(7)	119.7(29)
Co–O(3)–C(8)	124.6(19)	O(5)–C(6)–C(7)	119.0(29)
Co–O(4)–C(6)	126.1(20)	C(3)–C(4)–C(5)	116.2(25)
O(2)–C(3)–O(8)	118.9(25)	C(6)–C(7)–C(8)	118.2(26)
O(2)–C(3)–C(4)	123.3(25)	N(1)–Co–N(2)	86.6(11)
O(8)–C(3)–C(4)	117.8(25)	Co–N(1)–C(1)	109.4(20)
O(1)–C(5)–O(7)	119.5(25)	Co–N(2)–C(2)	109.8(20)
O(1)–C(5)–C(4)	123.0(24)	N(1)–C(1)–C(2)	110.5(29)
O(7)–C(5)–C(4)	117.6(23)	N(2)–C(2)–C(1)	105.3(29)
O(3)–C(8)–O(6)	119.5(28)		

TABLE 3

Close contacts

(*a*) With the sodium ion, <2.6 Å

	Distance/Å
Na · · · O(8^{I})	2·282(24)
Na · · · O(5^{II})	2.358(25)
Na · · · O(3^{VI})	2.581(22)
Na · · · O(6^{VI})	2.314(30)
Na · · · O(1)	2.513(21)
Na · · · O(7)	2.377(22)

(*b*) Possible hydrogen bonds (A–H · · · B); distances (Å), angles (°)

A	B	H	A · · · B	Angle at H
N(2)	O(8^{I})	N(2)H(1)	3.007(32)	157
N(2)	O(10^{IV})	N(2)H(2)	3.105(47)	149
N(1)	O(5^{VII})	N(1)H(2)	3.035(34)	163
O(9)	O(10)		2.781(49)	
O(9)	O(10^{III})		2.851(51)	
O(9)	O(6^{V})		2.670(40)	
O(9)	O(5^{VII})		2.920(36)	
O(10)	O(3^{VI})		3.241(44)	

Roman numerals indicate symmetry transformations as follows:

I $x, y, -1 + z$
II $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$
III $-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
IV $\frac{1}{2} + x, \frac{1}{2} - y, -z$
V $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
VI $-\frac{1}{2} + x, \frac{1}{2} - y, -z$
VII $-x, \frac{1}{2} + y, \frac{1}{2} - z$

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[11] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

two malonate rings which have boat conformations and fold towards each other. There is extensive hydrogen bonding involving the two water molecules and the hydrogens of the amino-groups. The water molecules form a right-handed hydrogen-bonded spiral around the 2_1 screw axis parallel to c; the hydrogen atoms of the water molecules were not located in the final difference map. The sodium ion makes six close contacts with malonate oxygens, but none with the water molecules.

The carboxy-groups [C(5), O(7), O(1), and C(8), O(3), and O(6)] behave as bidentate ligands for sodium and its co-ordination is completed by two *exo*-carboxy-oxygens. The range of Na–O distances (2.28—2.58 Å) is as expected for six-co-ordinate sodium.[12]

In the anion the chemically equivalent Co–O, N–C, and C–C(malonate) bond lengths agree to better than 1σ of an individual bond length. Mean Co–O [1.897(6) Å] and Co–N [1.925(20) Å] bond lengths are in good agreement with those for the similar chromophore in ammonium ethylenediaminetetra-acetatocobaltate(III) [1.900(15) and 1.925(5) Å].[13] The Co–N bond length is shorter than those normally found with cobalt ethylenediamine complexes such as $[Co(en)_3]Cl_3,H_2O$, 1.974(7) Å.[14] Shortened Co^{III}–N(amino) distances in the range 1.901(6)—1.929(7) Å are also evident in cobalt(III) aspartate complexes[15] which also have the *cis*-$(N_2)O_4Co$ chromophore. In the ethylenediaminetetra-acetate complex, it could be argued that the short distance arises from the concerted attachment of the multidentate complex, though it would more properly now seem to be a property of the *cis*-$(N_2)O_4Co$ grouping. In the structure of $(+)_{589}[Co(mal)_2(en)](-)_{589}$-$[Co(NO_2)_2(en)_2]$, the Co–N(en) distances of the anion average 1.935(20) and those of the cation 1.98(2) Å. The bond lengths in the anion do not differ significantly from those listed in Table 2. The bond angles, however, show a notable difference in the malonate C–C–C values. The diastereoisomer has values averaging 125(3)°, *cf.* 117(2)° for the sodium salt, and the difference reflects the more flattened conformation of the malonate rings in the former structure.

The ethylenediamine ring has the same oblique (*ob*) conformation in both complexes; this particular conformation has now been observed in several other complexes and the detailed conformation seems to depend on the hydrogen bonding and van der Waals interactions.[16,17]

The Malonate Chelate Rings.—From the evidence of the structures of three complexes, the chelated malonate ring has a high degree of conformational flexibility. In the structure[2,18] of $\Delta[Co\{(-)1,2\text{-diaminopropane}\}_3]\Delta[Cr(malonate)_3],3H_2O$ the malonate rings are equivalent, by symmetry, and have envelope conformations in which only the methylene group is significantly displaced from the chelate ring plane [Figure 2(a)].

In the diastereoisomer $(+)_{546}[Co(mal)_2(en)](-)_{589}[Co(NO_2)_2(en)_2]$ both rings are described as having an approximately planar conformation. The largest deviation from the mean plane of the malonate chelate ring is the 0.23 Å of a ligating oxygen atom and the pattern for both rings suggests a distortion towards a skew-boat conformation [Figure 2(b)]. The skew angle between the O–Co–O and C–C–C planes is estimated at only 8 and 9° for the two rings. For the sodium salt, the cobalt and methylene carbons [C(4) and C(7)] depart very significantly from the plane of the other four ring atoms (Table 4) to give boat conformations [Figure 2(c)]. The two rings are folded towards each other almost as far as van der Waals contacts between the two rings permit. Thus the methylene hydrogen C(4)H(2) has a contact with O(4) of 2.75 Å, and C(7)H(2) is 2.70 Å from O(2). These values are just larger than the sum of the van der Waals radii (2.6 Å).[19]

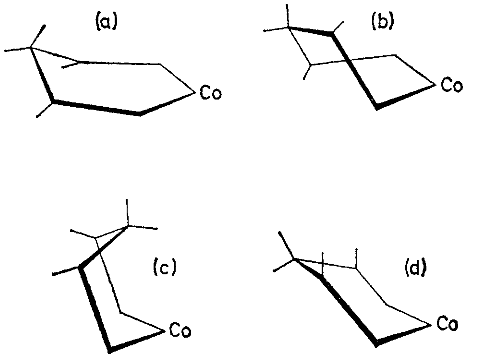

FIGURE 2 Malonate ring conformations: (a) envelope, (b) skew boat, (c) boat, and (d) chair

TABLE 4

Equations of least-squares planes in the form $lX + mY + nZ + p = 0$ where X,Y,Z are orthogonal (Å) co-ordinates. Deviations (Å) of relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): O(1), O(2), C(3), C(5)	0.4993	−0.8610	0.0967	3.3263
[Co 0.603, O(1) 0.003, O(2) −0.003, C(3) 0.003, C(4) 0.339, C(5) −0.003, O(7) −0.285, O(8) −0.245]				
Plane (2): O(3), O(4), C(6), C(8)	0.5759	−0.1892	−0.7953	1.2111
[Co −0.459, O(3) 0.055, O(4) −0.058, C(6) 0.062, C(7) −0.409, C(8) −0.059, O(5) 0.025, O(6) 0.489]				
Plane (3): Co, N(1), N(2)	−0.9350	−0.1889	−0.3001	−0.6002
[C(1) 0.155, C(2) −0.468]				

The *exo*-cyclic oxygens O(7) and O(8) are nearly equally displaced from their ring plane (1), but the corresponding

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[12] 'International Tables for Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, p. 258.

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oxygens [O(5) and O(6)] of the other ring differ by nearly 0.5 Å in their displacement from their plane (2). These differences must reflect the conformational mobility of the rings in allowing the oxygens to maximise their interactions with water and sodium. An alternative description of the ring conformations is given (Table 5) by the torsion angles about the ring bonds. The differences discussed are here reflected in the torsion angles of the C–C bonds. Those for ligand (1) are equivalent while those for ligand 2 differ by 13°. No estimates for the potential barriers of rotation about the bonds of malonate derivatives are available. However the low three-fold barrier for CH_3–CO_2H [$V = 0.48\ (1 - \cos 3\phi)$ kcal mol^{-1}] [20] is indicative that these must be similarly low. Several n.m.r. studies [5-7] of mono- and bis-malonate complexes have been reported. Consideration of lone-pair with lone-pair interactions on the oxygens and with other atoms led to the conclusion that skew and boat conformations should be energetically favoured over a chair conformation [5] [Figure 2(d)]. Experimentally, the n.m.r. results for $[Co(mal)(en)_2]^+$ and $[Co(mal)_2(en)]^-$ show rapid interconversion between conformers. The data for the latter ion are most satisfactorily interpreted with a two-fold axis in the complex inter-relating equivalent malonate conformations.[5] The structures of both salts of this ion have close to two-fold symmetry and it would be reasonable to suggest that these represent points on the conformational interconversion. The extreme points of the interconversion would thus be boat forms folding towards each other (represented by the sodium salt) and folding away from each other (no model structure). The intermediate point would be represented by the flattened skew boats of the $[Co(NO_2)_2(en)_2]^+$ salt. The prediction that chair forms are energetically unfavoured, not proven in the n.m.r. studies, is well supported by these two structures.

TABLE 5

Torsion angles (°) in the chelate rings

Malonate ligand (1)		Ligand (2)		Ethylenediamine	
Bond	Angle	Bond	Angle	Bond	Angle
Co–O(1)	33(2)	Co–O(3)	32(2)	Co–N(1)	6(2)
O(1)–C(5)	6(4)	O(3)–C(8)	11(4)	N(1)–C(1)	31(4)
C(5)–C(4)	31(4)	C(8)–C(7)	32(4)	C(1)–C(2)	46(4)
C(4)–C(3)	30(4)	C(7)–C(6)	45(4)	C(2)–N(2)	40(3)
C(3)–O(2)	7(4)	C(6)–O(4)	14(4)	N(2)–Co	20(2)
O(2)–Co	34(2)	O(4)–Co	19(2)		

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