# The Phenomenon of Conglomerate Crystallization. Part 34.[1] Crystal Structures of the Conglomerate $(-)_{599}$-$K[\mathit{cis}\text{-}\alpha\text{-}\Lambda(\delta\lambda\delta)\text{-}Co(edda)(NO_2)_2]$ and of the Racemate $K[\mathit{cis}\text{-}\alpha\text{-}\Lambda(\delta\lambda\delta)\text{-}Co(edda)(NO_2)_2]\cdot H_2O$ (edda = ethylenediamine-*N,N'*-diacetate)†

**Ivan Bernal,**[*,a] **James Cetrullo,**[a] **Jozef Myrczek,**[a] **Jiwen Cai**[a] **and William T. Jordan**[b]
[a] *Chemistry Department, University of Houston, Houston, TX, USA*
[b] *Department of Chemistry, Pacific University, 2043 College Way, Forest Grove, OR, USA*

A racemic solution of $K[\mathit{cis}\text{-}\alpha\text{-}Co(edda)(NO_2)_2]$ **1** (edda = ethylenediamine-*N,N'*-diacetate) was found to crystallize as a conglomerate in the enantiomorphic, orthorhombic space group $P2_12_12_1$. An acidified solution of it produced racemic crystals of $K[\mathit{cis}\text{-}\alpha\text{-}Co(edda)(NO_2)_2]\cdot H_2O$ **2**, space group $P\bar{1}$, as well as conglomerate crystals of **1**. Their crystal structures and the absolute configuration of **1** were determined. In both species the anions form infinite strings which are linked to one another by the potassium cations (and/or waters, where relevant, **2**). With **1** the helical strings are homochiral, while with **2** pairs of spiral strings have opposite helical chirality, as expected from the fact that they are related to one another by an inversion centre.

Conglomerate crystallization is defined as the phenomenon whereby a solution of racemates produces a mechanical mixture of enantiomorphic, homochiral, crystals, *e.g.* each individual crystal contains, exclusively, a single enantiomer or diastereoisomer. Although few in number so far, there are examples in the literature of racemic pairs crystallizing as the asymmetric unit of enantiomorphic crystals, *e.g.* $[Co(en)_3]_2[Pb_2Cl_9]Cl\cdot 3H_2O$ (en = ethane-1,2-diamine)[2] which crystallizes in space group $P2_1$, $Z = 2$ (or four cations in the unit cell). The asymmetric unit of this substance consists of pairs of $\Delta(\lambda\lambda\delta)$ and $\Lambda(\delta\delta\lambda)$ cations which are related to one another by a non-crystallographic, pseudo-inversion centre; thus, the fact that a substance crystallizes in an enantiomorphic space group does not guarantee its contents are homochiral if the number of molecules in the unit cell is an even multiple of the number of symmetry positions in that space group. Such is the case in $[Co(en)_3]_2[Pb_2Cl_9]Cl\cdot 3H_2O$. In those cases in which the asymmetric unit is an odd integer, greater than one, its contents are either a homochiral set or an unbalanced mixture of enantiomers. Examples of the latter situation were reported by Albano *et al.*[3] who studied a series of compounds of Rh, Ir and Cu crystallizing with three molecules in the asymmetric unit, two of which were of the same chirality while the third was enantiomeric to both members of the pair.

The crystal structures of $NH_4[Co(edta)]\cdot 2H_2O$ (edta = ethylenediaminetetraacetate),[4] $K[Co(edta)]\cdot 2H_2O$,[4] $Rb[Co(edta)]\cdot 2H_2O$[4] (space group $P2_12_12_1$ for all three), $K[Mn(edta)]\cdot 2H_2O$[5] (space group $P2_12_12_1$), $K[Al(edta)]\cdot 2H_2O$[6] (space group $P2_12_12_1$), $Na_2[Mg(edta)(H_2O)]\cdot 5H_2O$[7] (space group $C2$), $K[Co(pdta)]\cdot 2H_2O$ (pdta = propylenediaminetetraacetate)[8] (space group $B22_12$), $Na_2[(edta)W(\mu\text{-}OH)_2W(edta)]$[9] (space group $P2_1$), $Rb_2H_2edta\cdot 2H_2O$[10] (space group $P2_1$), $[Co(NH_3)_6][Na(edta)]\cdot 3.5H_2O$[11] (space group $P2_1$), $[\{Sn_2(edta)\}_n]\cdot 2nH_2O$[12] (space group $P1$), $Na[Cu(nta)]\cdot H_2O$ (nta = nitrilotriacetate)[13] (space group $P2_12_12_1$), $Li[Ca(nta)]\cdot 3H_2O$[14] (space group $P2_12_12_1$) and of $Na[Ca(nta)]\cdot H_2O$[15] (space group $P2_13$) have been determined previously. In every case, the optically active crystals used in the structural study were the result of conglomerate crystallization and such a large number of 'accidents' suggests that these aminecarboxylates have a marked tendency to crystallize in this way. Also, that if systematic studies of this phenomenon were to be carried out, one might find an even larger number of cases of conglomerate crystallization among compounds of this class.

As a result of such observations, we began a systematic study of metal derivatives of the aminecarboxylates with the view of ascertaining what molecular fragments of these compounds are necessary for the substance to crystallize as a conglomerate. We noted for example, that (*a*) changing $NH_4^+$ for $K^+$ or for $Rb^+$ seems not to affect the outcome in salts of $[Co(edta)]^-$, (*b*) the potassium salts $K[M(edta)]\cdot 2H_2O$ (M = Co, Mn or Al) are isomorphous and isostructural (space group $P2_12_12_1$), (*c*) comparison of K[Co(edta)] and K[Co(pdta)] demonstrates that one can change the central ring from five- to six-membered and still observe conglomerate crystallization. Thus, the aminecarboxylate system seems to be extremely flexible while, consistently, producing mechanical mixtures of homochiral crystals.

Finally, some time ago, we studied the crystallization behaviour of $\mathit{cis}\text{-}\alpha\text{-}[Co(trien)(NO_2)_2]X$ (trien = triethylenetetramine, X = Cl or I) both of which were found[16] to crystallize as conglomerates (space group $P2_12_12_1$). The cobalt moiety in the *cis*-α-trien derivatives resembles $[Co(edta)]^-$ in that the central ring is, basically, an en ring and the two arms protruding from each of the amines are also five-membered rings, with the entire ensemble in the *cis*-α configuration. Thus, it occurred to us that the compound $K[\mathit{cis}\text{-}\alpha\text{-}Co(edda)(NO_2)_2]$ **1** (edda = ethylenediamine-*N,N'*-diacetate) may also crystallize as a conglomerate if the two basal plane glycinate rings in $K[Co(edta)]\cdot 2H_2O$ can be substituted by two $NO_2^-$ anions, which somewhat resemble in their stereochemistry the $CO_2^-$ functional group. In this report we relate the results of our observations of the crystallization behaviour of **1**, carried out with crystals obtained from unresolved material; also, we report the crystal structure of the monohydrate of **1**, $K[Co(edda)(NO_2)_2]\cdot H_2O$ **2**, which is a racemate.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

## Experimental

*Synthesis and Crystallization.*—The salt K[*cis*-α-Co(edda)($NO_2$)$_2$] **1** was prepared according to the procedure of Jordan and Douglas[17] who suggested that the K[*cis*-α-Λ(δλδ)-Co(edda)($NO_2$)$_2$] enantiomer is characterized by the following CD bands: $\Delta\varepsilon_{599}$ −0.17, $\Delta\varepsilon_{496}$ +2.50 and $\Delta\varepsilon_{413}$ −0.73 l g$^{-1}$ cm$^{-1}$. Crystals were obtained by slow evaporation of a water solution of the racemate standing at ambient (*ca.* 18 °C) temperature.

In the past we have prepared oxalato complexes by displacement of two $NO_2$ ligands by oxalic acid.[18] Consequently, we decided to replace the *cis*-dinitro pair of **1** by oxalate in order to ascertain its crystallization behaviour. The first batch of crystals obtained was the starting material. Therefore, the solution was acidified with HCl and the crystals obtained were a mixture of unreacted **1** as well as crystals of **2**. The two are readily differentiated since crystals of **1** are red-brown and brick-shaped, whereas those of **2** are thin orange plates.

*Crystal-structure Determinations of Complexes* **1** *and* **2**.—The crystal of complex **1** used in the structure determination was selected randomly from material prepared according to Jordan and Douglas.[17] The crystal of **2** was taken from those deposited during the synthesis described above. Alignment, space-group determination, and data collection and processing were carried out as described in standard sources.[19-22]

A summary of the data collection and processing parameters is given in Table 1.

*Data collection and treatment.* For both compounds, data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a TEXRAY-230 modification[19] of the SDP-PLUS software package.[20] The crystal was centred with 25 data obtained in the 18 ⩽ 2θ ⩽ 25° range. Examination of the cell constants and Niggli matrix[21] showed it to crystallize in a primitive, orthorhombic lattice, the systematic absences of which showed it to belong to the space group $P2_12_12_1$. An identical procedure was followed for **2**, which crystallizes in the centrosymmetric space group $P\bar{1}$. The intensity data sets were corrected for absorption using empirical curves derived from ψ scans[19,20] of six reflections. The scattering curves were taken from Cromer and Waber's compilation.[22] The structures were solved from Patterson maps, using the Co atom as the heavy atom. The hydrogens of the anions were added at idealized positions (C–H = N–H 0.95 Å, fixed $B$ = 5.0 Å$^2$). Heavy atoms were refined anisotropically until convergence, at this point the hydrogens of the waters of crystallization of **2** were found in difference maps and added as fixed contributions ($B$ = 5.0 Å$^2$). At the end of the refinement of **1** the values of the $R(F)$ and $R'(F)$ factors were computed for the two possible enantiomorphic configurations of the cobalt anion. The results were as follows: $R(F)$ and $R'(F)$ for the original (+ + +) coordinates were 0.0384 and 0.0422, respectively. For its enantiomorph (− − −) the values were 0.0227 and 0.0275. Thus, the coordinates of the latter were assumed correct, and this defined the absolute configuration of the anion for our data collection crystal. For **2**, $R(F_o)$ = 0.0800 and $R'(F_o)$ = 0.0858, where $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R'(F_o) = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$. The latter high residuals are due to the nature of the crystal, which was a small, very thin plate which produced only 961 usable data. Nonetheless, it was of sufficiently high quality that we were able to locate experimentally the hydrogen atoms of the water of crystallization.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Fig. 1 gives a labelled view of the anion of complex **1** and its environment, while Fig. 2 depicts the packing of the ions in the unit cell. Fig. 3 gives a labelled view of the asymmetric unit of **2** and Fig. 4 depicts the packing of the ions and the water of crystallization present in the unit cell. Final values of the fractional coordinates are given in Tables 2 and 3, bond lengths and angles in Tables 4 and 5 for **1** and **2**, respectively.

Since the publication of the pioneering work of Weakliem and Hoard[4] on the crystal structures of [Co(edta)]$^-$ anions, it has been known that the four glycinate chains experience different degrees of strain depending on whether they are binding the two positions axial to the N–N vector or lie in the equatorial plane. The former are less strained, as demonstrated by the smaller N–C–C–O torsional angles (−9.8 and 8.0°, as opposed to values of −20.0 and −13.2° for the other two). This is not surprising in view of the fact that the $CH_2$ carbons of the axial chains lie in the equatorial position of the four-bonded N atoms, whereas the other set occupy the axial positions, thus the strain.

**Table 1** Summary of data collection and processing parameters for complexes **1** and **2**[a]

| | **1** | **2** |
|---|---|---|
| Molecular formula | $C_6H_{10}CoKN_4O_8$ | $C_6H_{12}CoKN_4O_9$ |
| $M$ | 364.20 | 382.22 |
| Symmetry | Orthorhombic | Triclinic |
| Space group | $P2_12_12_1$ | $P\bar{1}$ (no. 2) |
| $a$/Å | 8.361(1) | 7.261(3) |
| $b$/Å | 10.348(2) | 9.816(6) |
| $c$/Å | 14.076(1) | 10.372(3) |
| α/° | | 107.82(4) |
| β/° | | 104.91(3) |
| γ/° | | 103.70(5) |
| $U$/Å$^3$ | 1217.88 | 640.39 |
| $F$(000) | 736 | 378 |
| $D_c$/g cm$^{-3}$ | 1.986 | 1.982 |
| μ/cm$^{-1}$ | 17.912 | 17.131 |
| Transmission coefficients | 0.9484–0.9998 | 0.3696–0.9938 |
| Scan width, Δθ | 1.00 + 0.35tanθ | 0.95 + 0.35tanθ |
| Total data collected | 2048 | 1685 |
| Data used in refinement | 1745[b] | 961[c] |

[a] Details in common: $Z$ = 4; Mo-Kα radiation (λ = 0.710 73 Å); data collection range 4 ⩽ 2θ ⩽ 60°; weighting scheme $w = 1/\sigma(F_o)^2$. [b] The differences between this number and the total is due to subtraction of 303 data which either were systematically absent (but collected for verification of space group), standards or did not meet the criterion $I \geqslant 3\sigma(I)$. [c] The difference between this number and the total is due to subtraction of 724 data which either were symmetry related, standards or did not meet the criterion $I \geqslant 3\sigma(I)$.

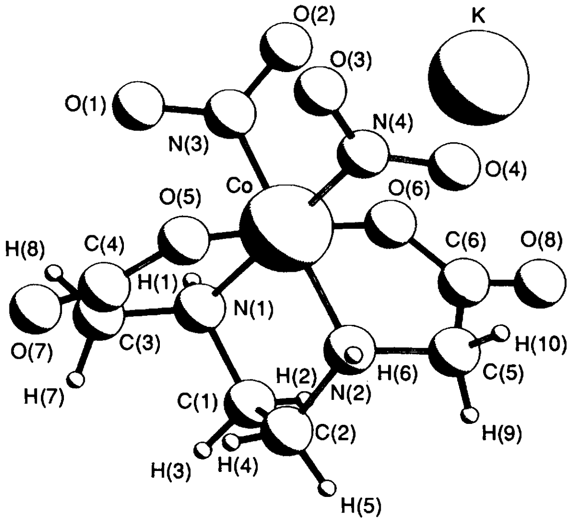

**Fig. 1** Contents of the symmetric unit of complex **1**. The K$^+$ ions were placed at that symmetry position which allows their closest contacts to the cobaltate anions

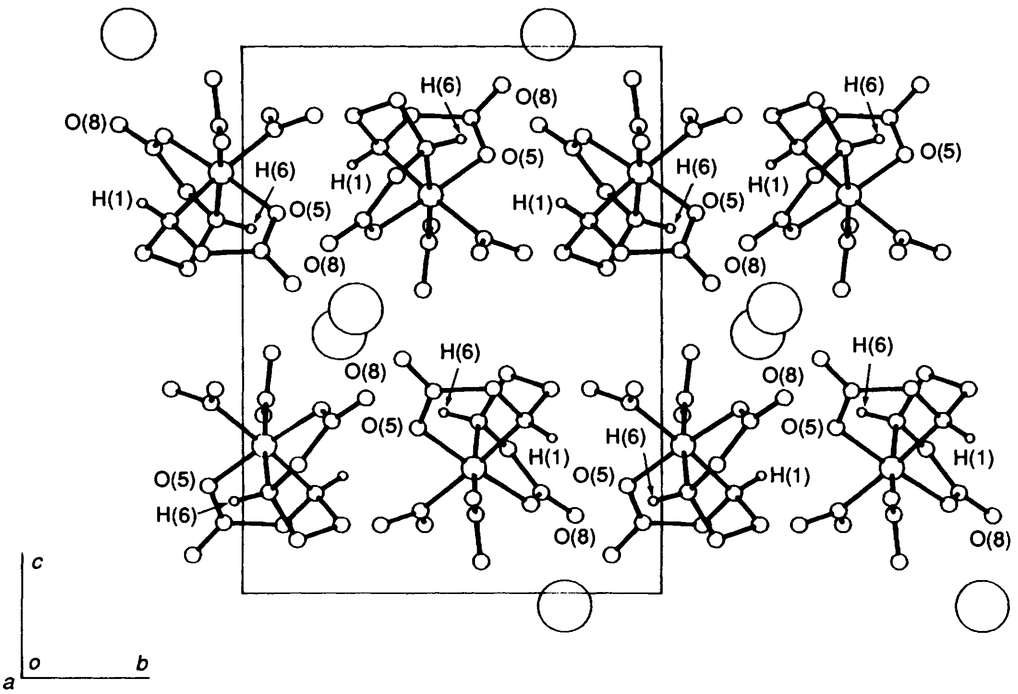

Fig. 2 A simplified packing diagram of $(-)_{599}$-K[*cis*-α-Λ(δλδ)-Co(edda)$(NO_2)_2$] **1** in which only one layer of molecules along the *a* direction is shown for clarity and to avoid obscuring the hydrogen-bonding scheme linking the anions of adjacent spiral strings. Hydrogens of $CH_2$ fragments are also omitted for clarity

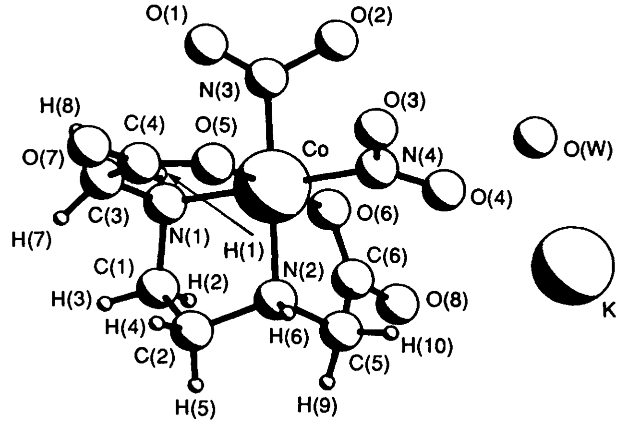

Fig. 3 Contents of the asymmetric unit of complex **2**. The $K^+$ ions and waters of crystallization were placed at that symmetry position which allows the closest contacts between them and the cobaltate anions

Given the above facts, one would expect that the stereochemically most stable isomer of complex **1** would be the *cis*-α one in which the two carboxylato-O ligands are *trans* to each other. This is indeed the case, as shown in Figs. 1 and 2, where the $NO_2$ ligands lie in the equatorial plane with the amine N ligand atoms; they can be viewed as taking up the positions formerly occupied by the two most strained chains of a [Co(edta)]$^-$ anion, thereby relieving conformational strain. The Co–N(amine) distances are 1.984(2) and 1.975(2) Å and the Co–O distances are 1.886(1) and 1.885(1) Å, values which are close to those found [1.906(3), 1.909(3), 1.911(3) and 1.914(3) Å] in recent structure determinations of amine acetates, such as K[Co(pddadp)]·$2H_2O$ (pddadp = propane-1,3-diamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate).[23] The Co–N($NO_2$) distances are 1.913(2) and 1.916(2) Å, close to those we found for Λ-*cis*-α-[Co(trien)$(NO_2)_2$]Cl·$H_2O$[16] [1.914(4) and 1.926(4) Å]. Thus, the geometrical parameters characterizing the anions in **1** and **2** are sensible and similar to one another, as well as being consistent with those of substances containing related fragments.

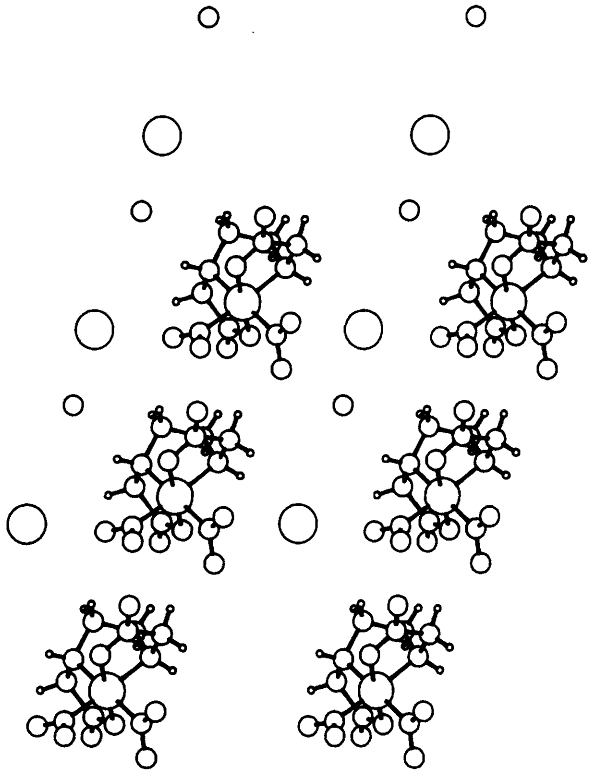

Fig. 4 A simplified packing diagram of K[*cis*-α-Λ(δλδ)-Co(edda)-$(NO_2)_2$]·$H_2O$ **2** in which only one layer of molecules along the *c* direction (*a* runs from left to right) is shown for clarity and to avoid obscuring the hydrogen-bonding scheme linking the anions of adjacent spiral strings

*Conglomerate Crystallization*.—Regarding the conglomerate crystallization mode of compound **1**, Fig. 2 shows that the amine hydrogens form hydrogen bonds with the carboxylate and $NO_2$ oxygens of adjacent anions, see Table 4. The

**Table 2** Positional parameters and their estimated standard deviations (e.s.d.s) for complex **1**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| K | 0.726 54(8) | 0.730 32(7) | 1.022 88(5) |
| Co | 0.801 80(5) | 0.948 71(4) | 0.770 71(3) |
| O(1) | 1.118 3(3) | 0.950 6(3) | 0.826 8(2) |
| O(2) | 0.956 5(3) | 0.930 5(3) | 0.942 7(2) |
| O(3) | 0.780 6(3) | 1.171 0(2) | 0.875 6(2) |
| O(4) | 0.561 8(3) | 1.065 8(3) | 0.875 2(2) |
| O(5) | 0.891 3(3) | 1.082 2(2) | 0.696 6(2) |
| O(6) | 0.703 9(3) | 0.812 2(2) | 0.837 6(2) |
| O(7) | 1.039 6(3) | 1.119 2(3) | 0.569 0(2) |
| O(8) | 0.477 3(3) | 0.706 2(2) | 0.858 5(2) |
| N(1) | 0.910 0(3) | 0.827 0(3) | 0.682 7(2) |
| N(2) | 0.615 1(3) | 0.937 4(3) | 0.685 1(2) |
| N(3) | 0.979 2(3) | 0.944 2(3) | 0.856 5(2) |
| N(4) | 0.702 0(3) | 1.076 1(2) | 0.849 7(2) |
| C(1) | 0.782 3(4) | 0.764 7(3) | 0.624 6(2) |
| C(2) | 0.666 7(4) | 0.869 4(3) | 0.596 7(2) |
| C(3) | 1.023 5(4) | 0.902 6(3) | 0.623 9(3) |
| C(4) | 0.984 4(4) | 1.045 2(3) | 0.628 6(2) |
| C(5) | 0.486 8(4) | 0.866 9(3) | 0.735 7(3) |
| C(6) | 0.558 3(4) | 0.788 0(3) | 0.816 0(2) |

**Table 3** Positional parameters and their e.s.d.s for complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Co | 0.1505(3) | 0.2415(3) | 0.2460(3) |
| K | 0.0086(7) | −0.2481(6) | 0.3755(5) |
| O(1) | −0.032(2) | 0.453(2) | 0.264(2) |
| O(2) | −0.082(2) | 0.339(2) | 0.404(1) |
| O(3) | −0.195(2) | 0.011(2) | 0.187(2) |
| O(4) | 0.044(2) | 0.037(2) | 0.377(2) |
| O(5) | −0.023(2) | 0.171(2) | 0.054(1) |
| O(6) | 0.334(2) | 0.312(1) | 0.441(1) |
| O(7) | −0.084(2) | 0.239(2) | −0.133(1) |
| O(8) | 0.586(2) | 0.268(2) | 0.575(2) |
| N(1) | 0.312(2) | 0.405(2) | 0.212(2) |
| N(2) | 0.326(2) | 0.126(2) | 0.189(1) |
| N(3) | −0.006(2) | 0.360(2) | 0.307(2) |
| N(4) | −0.018(2) | 0.073(2) | 0.273(2) |
| C(1) | 0.506(2) | 0.380(2) | 0.212(2) |
| C(2) | 0.453(2) | 0.213(2) | 0.127(2) |
| C(3) | 0.199(2) | 0.403(3) | 0.074(2) |
| C(4) | 0.017(2) | 0.257(2) | −0.009(2) |
| C(5) | 0.440(2) | 0.113(2) | 0.317(2) |
| C(6) | 0.458(2) | 0.243(2) | 0.450(2) |
| O(W) | −0.382(1) | −0.268(1) | 0.2209(9) |

**Table 4** Bond distances (Å) and angles (°) for complex **1**

| | | | |
|---|---|---|---|
| Co–O(5) | 1.886(1) | O(6)–C(6) | 1.280(2) |
| Co–O(6) | 1.885(1) | O(7)–C(4) | 1.226(2) |
| Co–N(1) | 1.984(2) | O(8)–C(6) | 1.238(2) |
| Co–N(2) | 1.975(2) | N(1)–C(1) | 1.491(3) |
| Co–N(3) | 1.913(2) | N(1)–C(3) | 1.483(3) |
| Co–N(4) | 1.916(2) | N(2)–C(2) | 1.493(2) |
| O(1)–N(3) | 1.238(2) | N(2)–C(5) | 1.480(3) |
| O(2)–N(3) | 1.236(2) | C(1)–C(2) | 1.505(3) |
| O(3)–N(4) | 1.236(2) | C(3)–C(4) | 1.513(3) |
| O(4)–N(4) | 1.230(2) | C(5)–C(6) | 1.517(3) |
| O(5)–C(4) | 1.292(2) | | |
| O(5)–Co–O(6) | 176.14(7) | Co–N(2)–C(2) | 107.9(1) |
| O(5)–Co–N(1) | 86.48(6) | Co–N(2)–C(5) | 108.0(1) |
| O(5)–Co–N(2) | 91.13(6) | C(2)–N(2)–C(5) | 112.2(2) |
| O(5)–Co–N(3) | 93.41(7) | Co–N(3)–O(1) | 120.9(1) |
| O(5)–Co–N(4) | 89.44(6) | Co–N(3)–O(2) | 120.2(1) |
| O(6)–Co–N(1) | 91.96(6) | O(1)–N(3)–O(2) | 118.8(2) |
| O(6)–Co–N(2) | 85.25(7) | Co–N(4)–O(3) | 119.1(2) |
| O(6)–Co–N(3) | 90.16(7) | Co–N(4)–O(4) | 121.6(2) |
| O(6)–Co–N(4) | 92.08(6) | O(3)–N(4)–O(4) | 119.3(2) |
| N(1)–Co–N(2) | 86.70(7) | N(1)–C(1)–C(2) | 107.0(2) |
| N(1)–Co–N(3) | 91.42(7) | N(2)–C(2)–C(1) | 107.9(2) |
| N(1)–Co–N(4) | 175.89(7) | N(1)–C(3)–C(4) | 110.6(2) |
| N(2)–Co–N(3) | 174.97(7) | O(5)–C(4)–O(7) | 123.3(2) |
| N(2)–Co–N(4) | 92.90(7) | O(5)–C(4)–C(3) | 116.8(2) |
| N(3)–Co–N(4) | 89.31(8) | O(7)–C(4)–C(3) | 119.8(2) |
| Co–O(5)–C(4) | 115.6(1) | N(2)–C(5)–C(6) | 109.8(2) |
| Co–O(6)–C(6) | 116.2(1) | O(6)–C(6)–O(8) | 122.6(2) |
| Co–N(1)–C(1) | 106.9(1) | O(6)–C(6)–C(5) | 116.5(2) |
| Co–N(1)–C(3) | 107.8(1) | O(8)–C(6)–C(5) | 120.9(2) |
| C(1)–N(1)–C(3) | 112.3(2) | | |

Selected hydrogen bonds *

| | | | |
|---|---|---|---|
| O(8) ··· H(6) | 2.00 | N($2^{I}$)–H(6) ··· O(8) | 170.5 |
| O(5) ··· H(1) | 2.52 | N($1^{II}$)–H(1) ··· O(5) | 176.9 |
| O(3) ··· H(1) | 2.63 | N($1^{II}$)–H(1) ··· O(3) | 115.5 |

* No e.s.d.s are shown since hydrogen atoms were not refined. Symmetry-related positions: I $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; II $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$. Numbers in parentheses are e.s.d.s in the least significant digits.

intermolecular hydrogen bonds in question are: for carboxylate, O(8) ··· H(6) 2.00 and O(5) ··· H(1) 2.52; for $NO_2$, O(3) ··· H(1) 2.63 Å. For the carboxylate bonds, the N–H ··· O angles are close to the ideal 180° (see Table 4), indicating these are fairly substantial; in the case of the nitro ligand, N–H ··· O 115.5°, which is characteristic of much weaker bonds. Nonetheless, a three-point attachment is formed between pairs of anions which is reminiscent of the enzymatic three-point attachment model proposed as the origin of chiral recognition. Thus, it seems that for this molecule conglomerate crystallization is the result of the formation of stable spiral strings, the links of which are defined by three-point attachments on either side of a given anion, and running along the *b* axis, as is readily observed in Fig. 2. These strings are, in turn, stitched together by the potassium cations, which are bonded to carboxylic and nitro oxygens, such that strings of the same chirality give rise to a preferred mode of crystallization; that is, the Gibbs free energy must favour the formation of crystals with homochiral strings. Similar remarks can be made about the packing of many of the compounds listed in the Introduction which pack in space groups in which the metal aminecarboxylate moiety forms sturdy, hydrogen-bonded, homochiral, spiral strings which are stitched together in the lattice by the agency of the counter ion, and by waters of hydration, where relevant.

We have previously encountered such a pattern of spiral-string formation in the oxalato series $[Co(en)_2(C_2O_4)]X{\cdot}nH_2O$ (X = Cl, $n = 4$; Br, $n = 1$; I, $n = 0$)[18] in which conglomerate crystallization seems to be caused by the formation of spiral strings of cations held together by strong O ··· $H_2N$ hydrogen bonds in which the oxalato ligand binds, in a bidentate fashion, a pair of $NH_2$ hydrogens of an adjacent cation. Since the process can be repeated indefinitely, these spiral strings are a polymer extending as a single strand throughout the length of the crystal. Scaled models show these hydrogen bonds are more effective when adjacent cations are twisted with respect to one another so as to expose the hydrogens to the non-bonded pairs of the terminal oxygens of oxalate. The formation of the first pair begins the spiral twist. Moreover, we know that these interactions persist in solution since deuterium exchange of the $NH_2$ hydrogens of these oxalato ions is slow, suggesting steric hindrance to exchange access by the $D_2O$ molecules.[24] We have recently measured (by $^1H$ NMR spectroscopy) the approximate rate of exchange of amineoxalato complexes of $Co^{III}$ and found it to require 3 d for complete exchange.*

We, therefore, suggest that we are witnessing a common

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* For example, one can observe the amine $^1H$ NMR signals of the cation $[Co(MeHNCH_2CH_2NH_2)_2(C_2O_4)]^+$ for many hours. Complete disappearance of these signals take up to 3 d. For the structure of this cation see ref. 25.

**Table 5** Bond distances (Å) and angles (°) for complex **2**

| | | | |
|---|---|---|---|
| Co–O(5) | 1.869(6) | O(6)–C(6) | 1.254(10) |
| Co–O(6) | 1.914(5) | O(7)–C(4) | 1.24(2) |
| Co–N(1) | 1.946(8) | O(8)–C(6) | 1.297(10) |
| Co–N(2) | 1.973(5) | N(1)–C(1) | 1.484(8) |
| Co–N(3) | 1.888(6) | N(1)–C(3) | 1.441(13) |
| Co–N(4) | 1.952(10) | N(2)–C(2) | 1.505(12) |
| O(1)–N(3) | 1.16(2) | N(2)–C(5) | 1.431(13) |
| O(2)–N(3) | 1.31(2) | C(1)–C(2) | 1.506(10) |
| O(3)–N(4) | 1.238(8) | C(3)–C(4) | 1.523(10) |
| O(4)–N(4) | 1.25(2) | C(5)–C(6) | 1.514(7) |
| O(5)–C(4) | 1.25(2) | | |
| O(5)–Co–O(6) | 178.4(2) | Co–N(2)–C(2) | 106.9(5) |
| O(5)–Co–N(1) | 87.3(3) | Co–N(2)–C(5) | 106.6(4) |
| O(5)–Co–N(2) | 92.1(2) | C(2)–N(2)–C(5) | 114.3(5) |
| O(5)–Co–N(3) | 90.1(4) | Co–N(3)–O(1) | 122.0(1) |
| O(5)–Co–N(4) | 90.5(3) | Co–N(3)–O(2) | 119.0(1) |
| O(6)–Co–N(1) | 92.0(3) | O(1)–N(3)–O(2) | 119.0(8) |
| O(6)–Co–N(2) | 86.5(2) | Co–N(4)–O(3) | 116.9(9) |
| O(6)–Co–N(3) | 91.4(4) | Co–N(4)–O(4) | 122.1(6) |
| O(6)–Co–N(4) | 90.1(3) | O(3)–N(4)–O(4) | 121.0(1) |
| N(1)–Co–N(2) | 87.3(3) | N(1)–C(1)–C(2) | 106.2(5) |
| N(1)–Co–N(3) | 91.0(4) | N(2)–C(2)–C(1) | 108.3(5) |
| N(1)–Co–N(4) | 177.8(3) | N(1)–C(3)–C(4) | 111.0(1) |
| N(2)–Co–N(3) | 177.2(2) | O(5)–C(4)–O(7) | 126.1(8) |
| N(2)–Co–N(4) | 92.4(3) | O(5)–C(4)–C(3) | 118.0(1) |
| N(3)–Co–N(4) | 89.4(4) | O(7)–C(4)–C(3) | 116.0(1) |
| Co–O(5)–C(4) | 114.5(5) | N(2)–C(5)–C(6) | 109.5(8) |
| Co–O(6)–C(6) | 111.6(4) | O(6)–C(6)–O(8) | 120.2(5) |
| Co–N(1)–C(1) | 108.2(7) | O(6)–C(6)–C(5) | 119.6(7) |
| Co–N(1)–C(3) | 108.1(5) | O(8)–C(6)–C(5) | 119.6(8) |
| C(1)–N(1)–C(3) | 111.4(6) | | |

Selected hydrogen bonds*

| | | | |
|---|---|---|---|
| O(1) ··· H(1) | 2.58 | N(1)–H(1) ··· O(1) | 93.3 |
| O(5) ··· H(6) | 2.15 | N(2$^{\text{I}}$)–H(6) ··· O(5) | 78.9 |
| O(8) ··· H(1) | 2.13 | N(1$^{\text{II}}$)–H(1) ··· O(8) | 171.5 |

* No e.s.d.s are shown since hydrogen atoms were not refined. Symmetry-related positions: I $-x, -y, -z$; II $1 - x, 1 - y, 1 - z$. Numbers in parentheses are e.s.d.s in the least significant digits.

origin for the seemingly frequent occurrence of conglomerate crystallization in metal aminecarboxylates; namely, they are stereochemically rigid ions with a high tendency to associate in spiral strings which are polymeric in nature and, thus, resemble a polypeptide. These spiral strings are formed either by (*a*) hydrogen bonds which directly link each cation to two adjacent ones or (*b*) anions are linked by the agency of the counter ions (and/or waters of crystallization). In both types, adjacent strings are linked to one another by the counter ions (and/or waters of crystallization), as was the case with complexes **1** and **2**, which illustrate the (*a*) mode of string formation and of interstring linking. Illustrations of the formation of type (*b*) strings are the diamine tetracarboxylates[4–6,8] for which intra-string attachments through hydrogen bonds are impossible, due to the lack of NH hydrogens; here, the anions are linked to one another by the cations and the waters of crystallization, both of which are bonded to the carboxylate oxygens.

In a racemic solution both types of spirals are formed, left- and right-handed, since a racemate is equally composed of Λ and Δ moieties. Thus, both types of spirals must form; however, since many of the substances under current scrutiny crystallize as homochiral crystals, the obvious conclusion is that, in conglomerate crystallization, the stitching together of the spiral strings by the counter ions (and the waters, if present) must lead to more negative free energies of crystallization when they segregate into enantiomorphic lattices. In the case of racemic crystallization the opposite must be true. An interesting example of the role the cation plays in this is provided by the observation that $[\text{NH}_4][\text{Co(edta)}]\cdot 2\text{H}_2\text{O}$,[4] $\text{K}[\text{Co(edta)}]\cdot 2\text{H}_2\text{O}$[4] and $\text{Rb}[\text{Co(edta)}]\cdot 2\text{H}_2\text{O}$[4] crystallize in space group $P2_12_12_1$; however, the sodium salt crystallizes in the polar, but not enantiomorphic, space group $Pna2_1$ the cell contents of which must be heterochiral due to the presence of the two glide planes.

Compounds **1** and **2** are an interesting pair since they differ in composition only by the presence of a water of crystallization. Moreover, both form the required spiral strings mentioned in the above paragraph. Yet, the addition of the extra water is all it takes to disrupt the selective linking, by lone potassium cations, of spiral strings of equal spiral helicity. The water must, therefore, be responsible for the selection of a racemic crystallization mode which is quite extraordinary since the constituent anions of a given string are homochiral while those of the adjacent ones are their enantiomorphs, both from the standpoint of individual anions and of the helical chirality of the string (see Figs. 2 and 4).

## Conclusion

First, we must remark that the formation of helical strings in these systems is not caused by lattice forces of space groups containing screw axes since complex **2** contains the said spirals and crystallizes in a space group devoid of such symmetry elements. Unlike **1** which crystallizes with homochiral helices, in a space group containing two-fold screw axes, **2** contains helical spirals of both chiralities, as expected from the centrosymmetric nature of the space group $P\bar{1}$ (no. 2), an observation in accord with the above statement that helical spirals of both chiralities should be present in solutions of racemates of this type.

Secondly, we have investigated the crystallization behaviour of compounds of the *cis*-α-$[\text{Co(trien)}(\text{NO}_2)_2]\text{X}\cdot\text{H}_2\text{O}$ (X = Cl[16] or I[26]), *cis*-$[\text{Co(en)}_2(\text{NO}_2)_2]\text{X}$ (X = Cl,[16] Br[27] or I[28]), $[\text{Co(en)}_2(\text{C}_2\text{O}_4)]\text{X}\cdot n\text{H}_2\text{O}$ (X = Cl, $n = 4$; Br, $n = 1$; or I, $n = 0$),[23] all of which crystallize as conglomerates. It is our experience with these series that the exact same pattern of hydrogen-bonded attachments is formed between their cations, leading to the formation of polymeric, spiral strings resembling helical polypeptides. In the case of **1** the three-point attachments between adjacent cations are reminiscent of the chiral recognition, three-point attachment, such as is postulated in enzymatic catalysis. The reader is directed to the original papers for details of the crystallization patterns observed in the above-mentioned systems.[16,26–28]

As a result of our recognition of common features prevailing in the crystallization of conglomerates we have examined thus far, we concluded that there appear to be three required ingredients for such a crystallization mode to prevail.

(1) Rigidity of molecules (or ions) needs to be achieved, if not already there. Both, the *cis*-dinitro series, *cis*-α-$[\text{Co(trien)}(\text{NO}_2)_2]\text{X}\cdot\text{H}_2\text{O}$ (X = Cl[16] or I[26]) and *cis*-$[\text{Co(en)}_2(\text{NO}_2)_2]\text{X}$ (X = Cl[16], Br[27] or I[28]), achieve this by strong intramolecular hydrogen bonds between $\text{NO}_2$ oxygens and axial $\text{NH}_2$ hydrogens. We have shown that, if these hydrogen bonds are interfered with, racemate(heterochiral) crystals are obtained.[16,26–28] A simple way of introducing such interference is the use of powerful hydrogen-bonding anions, such as $\text{NO}_2^-$ and $\text{NO}_3^-$, both of which cause *cis*-$[\text{Co(en)}_2(\text{NO}_2)_2]\text{X}$ (X = $\text{NO}_2$ or $\text{NO}_3$) to crystallize as racemates.[29] The current compound **1**, as well as all those aminecarboxylates listed in the Introduction, are rigid enough that intramolecular interactions are probably a minor factor in the selection of a crystallization pathway. The same comments apply to the members of the series $[\text{Co(en)}_2(\text{C}_2\text{O}_4)]\text{X}\cdot n\text{H}_2\text{O}$ (X = Cl, $n = 4$; Br, $n = 1$; or I, $n = 0$) that crystallize as conglomerates and are rigid enough as such.[18]

(2) String formation in solution and in the solid state. This seems to be an essential ingredient for all compounds thus far mentioned to crystallize as conglomerates and, if interfered with, results in racemates. We demonstrated this by comparison of the crystallization behaviour of the three series: *cis*-α-$[\text{Co(trien)}(\text{NO}_2)_2]\text{X}\cdot\text{H}_2\text{O}$ (X = Cl[16] or I[26]), *cis*-$[\text{Co(en)}_2(\text{NO}_2)_2]\text{X}$ (X = Cl,[16] Br[27] or I[28]), and $[\text{Co(en)}_2(\text{C}_2\text{O}_4)]\text{X}\cdot$

$n$H$_2$O (X = Cl, $n$ = 4; Br, $n$ = 1; or I, $n$ = 0),[18] all of which crystallize with polymeric, infinite, spiral strings. Also, in order to test the importance of this phenomenon to the crystallization pathway, we prepared the series [Co(tn)$_2$(C$_2$O$_4$)]X·H$_2$O (tn = 1,3-diaminopropane; X = Cl, Br or I)[30] which we knew, from models, to be incapable of forming spiral strings due to steric hindrance at the site of the necessary hydrogen bonds. Such an expectation was found correct, since, unlike their bis(ethylenediamine) analogues, the compounds [Co(tn)$_2$(C$_2$O$_4$)]X crystallize as racemates.[30] We know that association takes place in solution since, as mentioned above, deuterium exchange in the oxalato series is retarded,[24] suggesting that the associated ions slow down exchange of amine hydrogens due to hydrogen-bonded interactions in fluid media.

(3) Interactions between strings. These can be of two types (*a*) direct interactions between strings, as in the two halves of a zipper, or protein strands, examples of which are the structures of *mer*-[Co(NH$_3$)$_3$(NO$_2$)$_3$] (space group $P2_12_12_1$)[31] and of *fac*-[Co(NH$_3$)$_3$(NO$_2$)$_3$] (space group $P2_12_12_1$)[32] and (*b*) when counter ions (and/or waters of crystallization, where relevant) are present, as is the case of **1** and of the diamine tetracarboxylates discussed above and, in such cases, the strings are joined by the agency of the cations (and/or the waters of crystallization). In both cases the linkages must have a clear preference for joining strings of the same chirality; if not, either heterochiral crystals are obtained or one obtains both conglomerates and racemates. An example of clear preference for heterochiral string formation is the case of [Co(en)$_2$(C$_2$O$_4$)]PF$_6$ which crystallizes as a racemate, unlike the chloride and bromide which crystallize as conglomerates.[18] An example of an ambiguous crystallization behaviour is [Co(en)$_2$(C$_2$O$_4$)]I, which crystallizes as both a racemate and a conglomerate. This latter result has been confirmed by phase-diagram studies of the system.[33] We have preliminary crystallographic data on the optically active and the racemic crystals, both of which are of poor quality; however, to the extent that we have found both types of crystals in the same crystallization batch,[18,27] our results are in accord with those of Yamanari and co-workers.[33]

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