

Insights into crystallization mechanism: a synchrotron study of polymorphism in a cobalt acetate cluster compound

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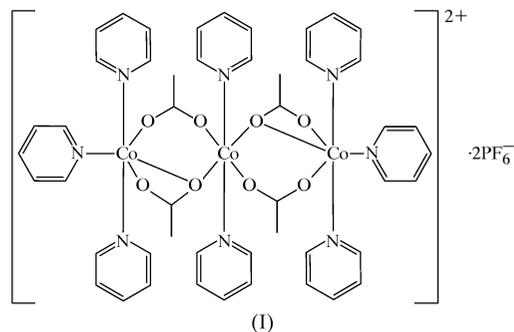
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The structure of the title compound, di- μ_3 -acetato- $1\kappa^2O, O':2\kappa O'; 2\kappa O:3\kappa^2O, O'$ -di- μ_2 -acetato- $1\kappa O:2\kappa O'; 2\kappa O:3\kappa O'$ -octapyridyl- $1\kappa^3N, 2\kappa^2N, 3\kappa^3N$ -tricobalt(II) bis(hexafluorophosphate), $[\text{Co}_3(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_5\text{H}_5\text{N})_8](\text{PF}_6)_2$, consists of divalent multinuclear cations in which three Co^{II} ions are bridged by four μ_2 -acetate groups. The Co^{II} ions are arranged in an approximately linear manner. The bridging acetates adopt two distinct coordination geometries: one pair bridges *via* a single O atom and the other pair employs both O atoms. The coordination octahedron around each Co^{II} ion is completed by three pyridine molecules for the two outer Co^{II} ions and by two for the inner ion. Charge is balanced by two PF_6^- anions. Single-crystal synchrotron X-ray studies indicate the existence of two polymorphs, both triclinic, which are distinguished primarily by differences in the relative orientations of the multinuclear cations, which in form 1 are tilted with respect to each other, but in form 2 are co-parallel as a result of the central Co atom lying on an inversion centre. The results of the structural studies allow an insight into the crystallization mechanism and resultant polymorphism. They suggest that a (bidentate carboxyl) $\text{C}-\text{O}\cdots\text{H}-\text{C}(\text{pyridine})$ interaction exists in solution. For form 1, crystallized from pyridine, the interaction is not structure determining, as it is satisfied by interactions between solvent and solute. For form 2, crystallized from CH_2Cl_2 , the interaction is between a bound acetate carboxyl group on one cation and a bound pyridine on another and is thus structure directing.

Comment

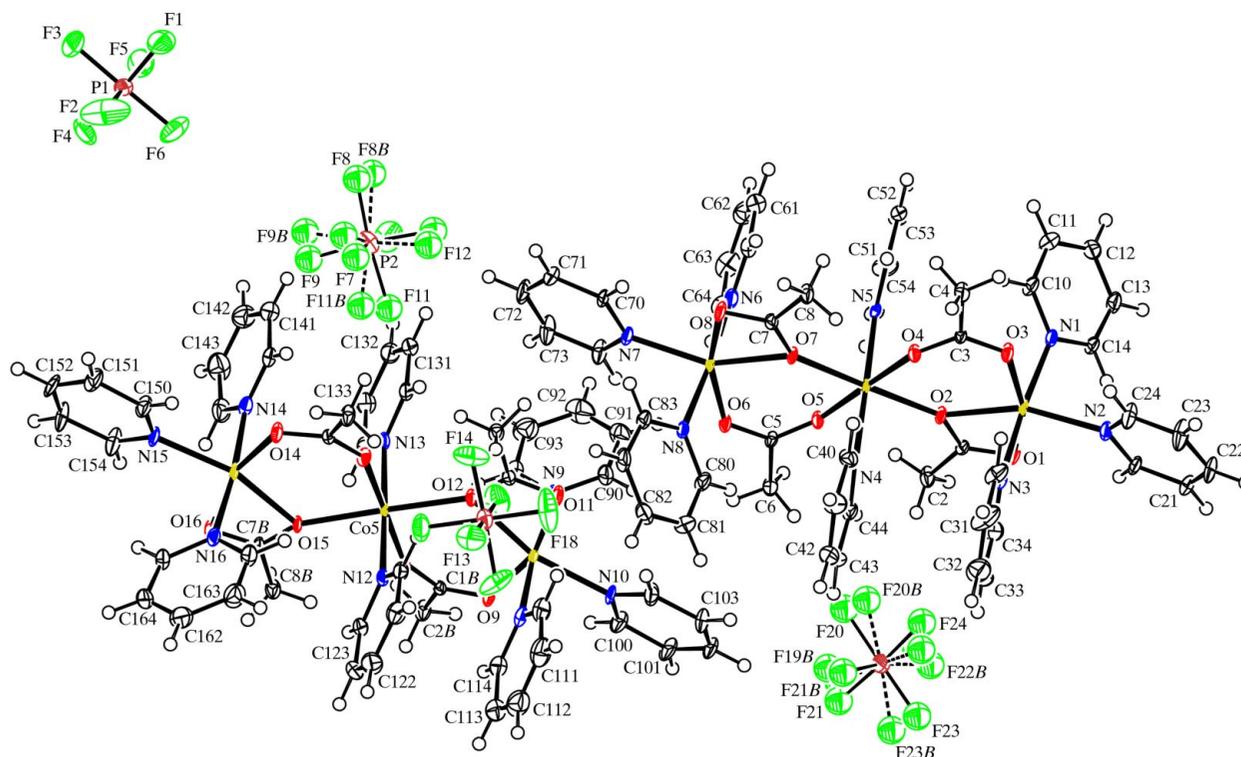
Multinuclear transition metal complexes have been intensively studied over a number of years, with interest driven by structural similarities to active sites in biological systems (Hagen *et al.*, 1993), fundamental magnetism studies (Chudnovsky, 1996) and possible use as supramolecular building blocks (Yaghi *et al.*, 2003). During the course of investigations

into possible complexes formed by Co^{II} , pyridine and acetate derivatives, the title compound, (I), was isolated as two polymorphs (Figs. 1 and 2). Examination of the refined crystal structures allows postulation of a crystal nucleation mechanism which is consistent both with the synthetic conditions and the existence of the two polymorphic forms.



Both polymorphs adopt the space group $P\bar{1}$, form 1 with $Z = 4$ and form 2 with $Z = 1$. The cations in both forms adopt essentially identical molecular structures and are formed by three Co^{II} ions arranged in an approximately linear manner. The cations possess an approximate (form 1) or an exact (form 2) crystallographic centre of symmetry located at the central Co^{II} ion. For octahedral coordination about Co^{II} , there are 18 coordination sites available for the ligands. The three Co^{II} ions are linked by four bridging acetate groups, which adopt two distinct coordination modes. One pair of acetates bridges in a *syn-syn* manner, with each O atom coordinated to a single Co^{II} ion, thus occupying a total of four coordination sites. The other pair of acetates adopts a *syn-anti* configuration, with one O atom acting as a μ_2 -bridge and the other coordinated to a single Co^{II} ion. This pair of acetates therefore occupies a total of six coordination sites. The coordination modes adopted by the acetate groups lead to the central Co^{II} ion being surrounded by four O atoms, arranged in an approximately square-planar manner; for form 2, the O—Co—O angles deviate from 90° by $1.56(15)^\circ$. The terminal Co^{II} ions are surrounded by three O atoms, which are not regularly spaced; for form 2, the O4—Co2—O3 angle is $60.7(1)^\circ$, whereas O2—Co2—O3 is $101.4(1)^\circ$. The remaining eight available metal-coordination sites are occupied by pyridines, two of which bind along the molecular axis and six of which bind perpendicular to the molecular axis. The lack of an exact molecular centre of symmetry in form 1 is manifested primarily in the lengths of the *trans* bonds about the central Co^{II} ion, Co2—O2 and Co2—O7 (formed by the acetate μ_2 -O atom), which are $2.154(2)$ and $2.134(2)$ Å, respectively; each pair of bond lengths is identical by symmetry in form 2. In form 1, half of the PF_6^- groups exhibit a significant degree of rotational disorder about the central P atom; the occupancies, constrained to sum to unity, refined to $0.565(5):0.435(5)$ and $0.600(4):0.400(4)$ for the major and minor components of P2 and P4, respectively. However, in form 2 there is no evidence in difference Fourier maps for disorder of the PF_6^- units.

In terms of crystal packing, for both polymorphs the cations and anions adopt an arrangement in which layers are formed in the *ab* plane. It should be noted that a description of the

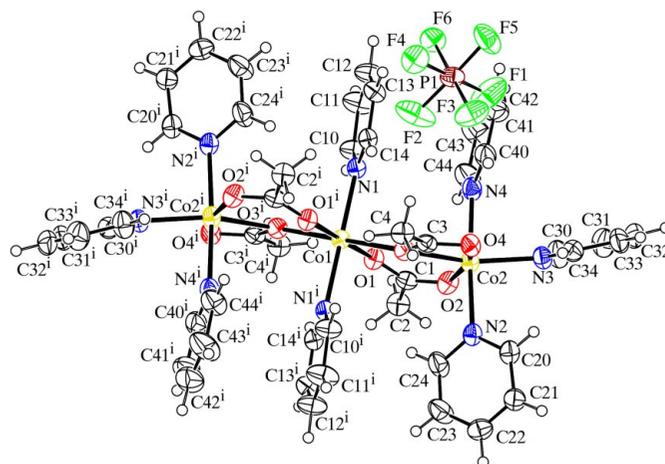

Figure 1

The molecular structure of form 1 of compound (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Both disorder components of the PF_6^- ions are shown.

structure as layered is for convenience and does not reflect the presence of any obvious specific intralayer interactions. The two forms are very similar. In fact, viewed along $[100]$ and $[\bar{1}00]$, the two structures may practically be superimposed (Fig. 3*a* and 3*b*). However, when the two forms are viewed in a projection achieved by rotating by 90° about the normal to 001, a significant difference becomes clear. In form 2, the layers are formed by cations which have $\text{Co}\cdots\text{Co}\cdots\text{Co}$ molecular axes co-parallel (Fig. 3*d*). However, in form 1 the two distinct trimers are not arranged with their axes co-parallel (Fig. 3*c*).

The only notable non-ionic interaction in either polymorph is the short $\text{C}-\text{O}\cdots\text{H}-\text{C}$ distance (carboxyl-pyridine) of 2.56 Å between cations in form 2 (Fig. 4). This can be compared with the sum of the van der Waals radii (2.72 Å; Bondi, 1964; Rowland & Taylor, 1996) and the average of the intramolecular $\text{C}-\text{O}\cdots\text{H}-\text{C}$ (pyridine) distances (2.62 Å). Thus, in form 2 the intermolecular $\text{C}-\text{O}\cdots\text{H}-\text{C}$ distance is 0.15 Å shorter than the sum of the van der Waals radii, and 0.03 Å shorter than the corresponding mean intramolecular distance. The equivalent distance in form 1 is 3.13 Å, which is 0.41 Å greater than sum of the van der Waals radii and 0.54 Å longer than the corresponding distance in form 2. These short $\text{C}-\text{O}\cdots\text{H}-\text{C}$ interactions in form 2 form a linear network of cations which runs along the a axis. Given the generally accepted correlation between intermolecular distance and interaction strength, it seems reasonable that this interaction has the potential to be chemically important and structure directing.

The presence of this short contact in form 2 and its absence in form 1 are consistent with a crystal nucleation mechanism in which the intermolecular $\text{C}-\text{O}\cdots\text{H}-\text{C}$ interaction occurs between a bridging acetate of one cation and pyridine. For form 1, crystallized from pyridine, the interaction is between the cations and the solvent molecules, whereas for form 2, crystallized from CH_2Cl_2 , the interaction is between a bound pyridine on one cation and a bridging acetate on a neighbouring cation, and is thus structure-directing.


Figure 2

The molecular structure of form 2 of compound (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Form 1 has a slightly lower volume per formula unit than form 2 [1375.98 (13) versus 1379.3 (8) Å³], and thus packing considerations suggest that form 1 has the lower lattice energy, although the difference may be slight. Furthermore, the disorder in the PF₆⁻ groups suggests that form 1 should also be favoured on entropic grounds. That form 2 has been isolated despite the apparent greater stability of form 1 in

terms of both lattice energy and lattice entropy is consistent with our argument above that the pyridine-H···O—C interaction is of some importance in stabilizing this form, both kinetically in the crystallization of both forms, and thermodynamically in the stability of form 2.

In conclusion, structural studies of the two polymorphic forms of (I) have provided an insight into the crystal nucleation mechanism for this compound and the reason for the existence of two polymorphs.

Experimental

A solution of Co(OAc)₂·4H₂O (0.5 g), pyridine (10 ml) and acetic anhydride (5 ml) were warmed to 323 K and stirred for approximately 4 h. Two molar equivalents of NH₄PF₆ were added, and a pink solid was precipitated on addition of excess hexane. Pink transparent crystals of form 1 of (I) were grown by slow cooling of a saturated solution in pyridine. Crystals of form 2 of (I) were obtained by recrystallization from dichloromethane. The crystals are air-stable for several months.

Compound (I), polymorph 1

Crystal data

[Co₃(C₂H₃O₂)₄(C₅H₅N)₈](PF₆)₂
M_r = 1335.71
 Triclinic, *P* $\bar{1}$
a = 10.7354 (6) Å
b = 22.1257 (12) Å
c = 23.6103 (13) Å
 α = 99.380 (1)°
 β = 95.008 (1)°
 γ = 92.238 (1)°
V = 5503.9 (5) Å³
Z = 4

D_x = 1.612 Mg m⁻³
 Synchrotron radiation
 λ = 0.84610 Å
 Cell parameters from 38731 reflections
 θ = 3.6–31.6°
 μ = 1.05 mm⁻¹
T = 120 (2) K
 Plate, pink
 0.25 × 0.1 × 0.05 mm

Data collection

Bruker D8 diffractometer
 ω rotation scans with narrow frames
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
*T*_{min} = 0.463, *T*_{max} = 0.949
 38731 measured reflections
 21108 independent reflections

17966 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.030
 θ _{max} = 31.6°
h = 0 → 13
k = -27 → 27
l = -29 → 28

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.056
wR(*F*²) = 0.152
S = 1.05
 21108 reflections
 1432 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 8.495P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.48 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.46 \text{ e \AA}^{-3}$

Compound (I), polymorph 2

Crystal data

[Co₃(C₂H₃O₂)₄(C₅H₅N)₈](PF₆)₂
M_r = 1335.71
 Triclinic, *P* $\bar{1}$
a = 10.688 (4) Å
b = 11.839 (4) Å
c = 12.480 (4) Å
 α = 98.149 (5)°
 β = 103.605 (5)°
 γ = 111.722 (5)°
V = 1379.3 (8) Å³
Z = 1

D_x = 1.608 Mg m⁻³
 Synchrotron radiation
 λ = 0.67110 Å
 Cell parameters from 3499 reflections
 θ = 3.0–26.9°
 μ = 1.05 mm⁻¹
T = 120 (2) K
 Needle, pink
 0.1 × 0.02 × 0.02 mm

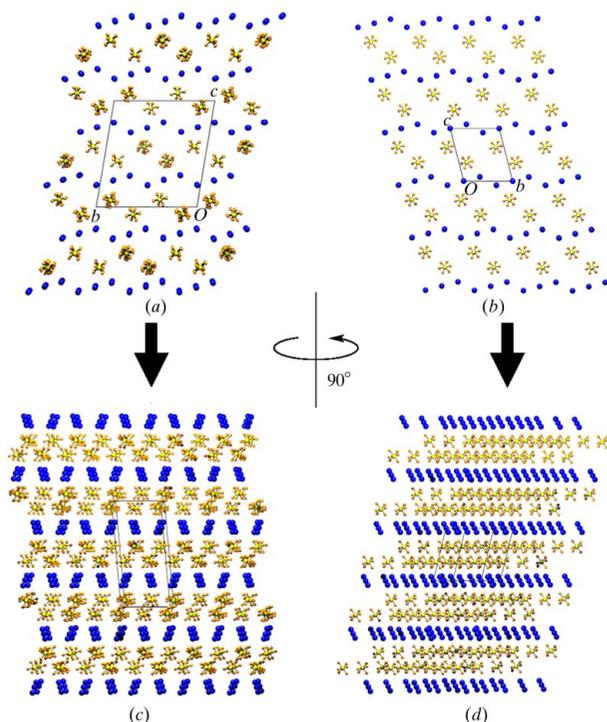


Figure 3 Packing diagrams (PLATON; Spek, 2003) of the two polymorphic forms of (I). (a) Projection view of form 1 along 100, (b) projection view of form 2 along 100, (c) projection view of form 1 rotated 90° about the normal to 001 and (d) projection of form 2 rotated 90° to the 001 normal.

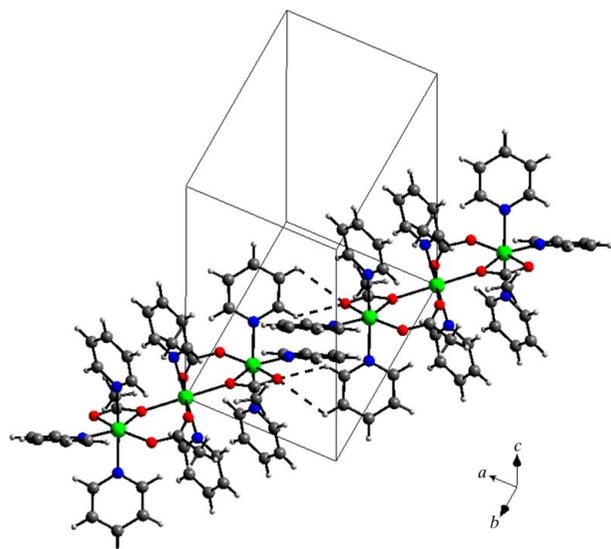


Figure 4 Intermolecular interactions in form 2 of (I); these are absent in form 1 (PLATON; Spek, 2003).

Data collection

Bruker D8 diffractometer	3897 reflections with $I > 2\sigma(I)$
ω rotation scans with narrow frames	$R_{\text{int}} = 0.052$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$\theta_{\text{max}} = 24.8^\circ$
$T_{\text{min}} = 0.207$, $T_{\text{max}} = 1$	$h = -13 \rightarrow 13$
11698 measured reflections	$k = -14 \rightarrow 14$
5565 independent reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1413P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.072$	$+ 0.0662P]$
$wR(F^2) = 0.214$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} < 0.001$
5565 reflections	$\Delta\rho_{\text{max}} = 1.29 \text{ e } \text{\AA}^{-3}$
369 parameters	$\Delta\rho_{\text{min}} = -0.84 \text{ e } \text{\AA}^{-3}$
H-atom parameters constrained	

Pyridine H atoms were placed in idealized positions, with C–H = 0.93 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl H atom were also placed in idealized positions, with C–H = 0.96 Å, and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. For form 2, the highest difference peak is located 1.04 Å from atom H2B and the deepest hole is 0.82 Å from atom Co1. A number of difference peaks with density greater than $1 \text{ e } \text{\AA}^{-3}$ were present and are due to the quality of the crystal employed, which was the best available.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Version 1.64; Farrugia, 1999) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1176). Services for accessing these data are described at the back of the journal.

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