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The Crystal Structures of Two Polymorphs of Dichlorobis(pyridine)cobalt(II)

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Crystal structures have been determined for two polymorphs of dichlorobis(pyridine)cobalt(II) which are related *via* a reversible solid-state phase transformation at about 150 K. Above this temperature, the well known α-form is more stable and below it, the previously unknown γ-form occurs. Crystal data are: α-form (294 K) $a=34{\cdot}486$ (3), $b=17{\cdot}408$ (2), $c=3{\cdot}6635$ (6) Å, $\gamma=90{\cdot}121$ (6)°, $Z=8$, monoclinic $C2/b$ (c unique); γ-form (89 K) $a=17{\cdot}437$ (13), $b=8{\cdot}408$ (2), $c=3{\cdot}593$ (7) Å, $\beta=90{\cdot}05$ (5)°, $Z=2$, monoclinic $P2_1/n$ (b unique). Intensity data for the α-form were collected by the equi-inclination Weissenberg technique and for the γ-form by the general inclination Weissenberg method. The structures were refined by full-matrix least-squares calculations. The R values for α- and γ-forms based on 886 and 368 reflexions were 11·4 and 9·8% respectively. Both crystal structures contain polymeric chains linked by cobalt–chlorine bridging bonds leading to an octahedral environment for the cobalt atoms. The two crystal structures represent two modes of packing of the pyridine rings within the framework formed by the cobalt–chlorine chains.

Introduction

Dichlorobis(pyridine)cobalt(II), $CoCl_2(C_6H_5N)_2$, (hereinafter COPYCL) exhibits three polymorphs within the temperature range 89 to 400 K. The violet or α-form was first prepared by Reitzenstein (1894) by reacting pyridine with a solution of cobalt chloride in ethanol and allowing crystals to grow at room temperature. Hantzsch (1927) prepared blue crystals of a second polymorph, β-COPYCL, by crystallization from a hot ethanolic solution of COPYCL. From magnetic data, Mellor & Coryell (1938) assigned a polymeric octahedrally coordinated structure to α-COPYCL, and a monomeric tetrahedrally coordinated structure to β-COPYCL. These conclusions were later supported by the crystallographic work of Dunitz (1957), Ferroni & Bondi (1958), and Porai-Koshits, Atovmayan & Tischenko (1960).

Recently, the existence of a third, low-temperature, polymorph has been demonstrated by magnetic anisotropy and preliminary crystallographic studies carried out on α-COPYCL at 150 K (Bentley, 1968; Bentley, Gerloch, Lewis & Quested, 1971; Thomas, 1969). We now report a re-examination of the crystal structure of α-COPYCL together with the crystal structure determination of the new low-temperature polymorph which we designate γ-COPYCL. Observations on the reversible solid-state phase transformation occurring between the α- and γ-forms at about 150 K are discussed in the following paper (Clarke & Milledge, 1975).

Crystal structure analysis of α-COPYCL at 294K

The crystal structure of α-COPYCL has previously been determined independently by Dunitz (1957) and Ferroni & Bondi (1958). These authors reached broadly the same conclusions, but differed in detail as discussed by Ferroni & Bondi. However, both analyses were directed toward the demonstration of octahedral coordination in the complex rather than the derivation of an accurate crystal structure and hence the crystal structure of α-COPYCL was redetermined during the present study in order to allow meaningful comparisons to be made between the α- and γ-forms. The redetermination of the α-COPYCL structure also allowed the examination of criticisms made by Dornberger-Schiff (1965, 1966) of the earlier crystallographic work on this compound.

Collection and processing of intensity data

Violet-pink needle crystals of α-COPYCL were grown from a saturated ethanolic solution of COPYCL at room temperature under anhydrous conditions to avoid decomposition (Gill & Nyholm, 1961). The crystals were dichroic, and yielded biaxial interference figures. Preliminary oscillation and Weissenberg photo-

Table 1. *Crystal data for α-COPYCL*

	a (Å)	b (Å)	c (Å)	γ (°)
Dunitz (1957)	34·42	17·38	3·66	90·0
Ferroni & Bondi (1958)	34·44	17·36	3·66	90·0 (1)
Zannetti & Serra (1966)	34·40	17·40	3·66	90·0
This work* (294 K)	34·486 (3)	17·408 (2)	3·6635 (6)	90·121 (6)

$D_o=1{\cdot}75$ (1) g cm^{-3}; $D_c=1{\cdot}75$ g cm^{-3}; $Z=8$

Systematic absences

hkl: $h+k=2n+1$; $hk0$: $h,k=2n+1$; $h00$: $h\neq 4n$; $0k0$: $k\neq 4n$;

Space group $C2/b$ (c unique)

* From a least-squares fit to 18 Bragg angles measured by a back-reflexion method.

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graphs confirmed the unit cell and space group found by previous workers (Table 1).

Dunitz (1957) has reported twinning in α-COPYCL, the occurrence of which he has ascribed to the para-orthorhombic nature of the crystals (Dunitz, 1964). Such twinning was said to produce anomalous orthorhombic Laue symmetry in many of the crystals examined by Dunitz, and indeed similar observations were made in the present study. However, careful inspection of all oscillation and Weissenberg photographs taken during the present work of about 20 crystals of α-COPYCL with Cu *K*α, Co *K*α, and Cr *K*α radiations revealed the previously unrecorded existence of an unusual triplet reflexion replacing the normal α_1–α_2 doublet at high Bragg angles. This triplet reflexion was interpreted (*cf.* Ubbelohde & Woodward, 1946) as arising from the partial overlap of two α_1–α_2 doublets produced by twinning of the crystal across either (100) or (010). In either case, non-equivalent reciprocal lattice points from the twins are superimposed, but a triplet reflexion, rather than two completely superimposed doublets or a quartet, arises only for a particular, non-orthogonal, value of the monoclinic angle γ. Examination of Laue photographs of α-COPYCL indicated (Clarke, 1973) that the twinning probably occurred by reflexion across (100). Hence the triplet reflexions consisted of $\alpha_1^{\bar{h}kl}$, $\{\alpha_2^{\bar{h}kl}$ and $\alpha_1^{hkl}\}$, and α_2^{hkl}.

Despite the superposition of non-equivalent reciprocal lattice points, diffraction intensities corresponding to a single crystal may be derived from the experimental intensities provided that the sizes of the twins are unequal, and their relative size can be estimated (see Lonsdale, Milledge & Pant, 1965). The appropriate mathematical relationship is:

$$I_{hkl}=(P_{hkl}-fP_{\bar{h}kl})/(1-f^2) \qquad (1)$$

where I_{hkl} is the single-crystal intensity of reflexion *hkl*, *P* denotes the measured twinned intensity indexed relative to the larger twin, and *f* is the ratio of the size of the smaller twin to the larger. In the case of α-COPYCL, the value of *f* was derived by the method of least squares through comparison of visually estimated intensities of the separated α_1 reflexions comprising the high-angle triplets.

Intensity data were collected by the equi-inclination Weissenberg technique using two twinned crystals. Full details of the photographs taken are given in Table 2. The reflexions were indexed relative to the larger twin, and the intensities were measured on the Joyce–Deeley flying-spot microdensitometer. Equation (1) was then applied to derive single-crystal intensities from the twinned data. Where one of the pair of values P_{hkl} and P_{hkl} was classed as unobserved, the other value was taken as the single-crystal intensity. Since each of the pairs of intensities was measured on the same photograph, the relative scale of the data was of no consequence during the detwinning operation. The detwinned data were corrected for the Lorentz–polarization effect, and an approximate absorption correction was applied assuming the crystal envelope to be a cylinder (Table 2). In this manner, detwinned intensities were derived for 886 observed reflexions.

Table 2. *Data collection for α-COPYCL at* 294 K

Layer	Crystal	Factor *f* in equation (1)	Cylinder radius for absorption correction
*hk*0	*A*	0·29	0·0075 cm
*hk*1			
*hk*2			
*hk*3	*B*	0·67	0·012 cm

Co *K*α radiation, $\lambda=1{\cdot}7902$ Å; $\mu=98{\cdot}5$ cm^{-1}
Crystal faces {100}, {010}, {001}
Crystal dimensions: A 0·010 × 0·020 × 0·040 cm
B 0·019 × 0·030 × 0·035 cm
Crystal rotation axis: *c*

The data were placed on approximately the same relative scale by comparison with intensities measured from a Weissenberg photograph of the *h*0*l* zone. Intensities in this zone are independent of twinning since the superposed reciprocal lattice points are symmetry equivalent.

Structure solution and refinement

Dornberger-Schiff (1964) pointed out the possibility of a second solution to the crystal structure of α-COPYCL in addition to that proposed originally by Dunitz. The relation between the two structures is summarized in Table 3. In Dunitz's structure, which has space group *C*2/*b* (*c* unique), there are two crystallographically independent molecules with cobalt atoms sited on twofold axes at $(0,\frac{1}{4},z)$ and $(\frac{1}{4},0,z)$, and the *b* glide planes occur at $z=0$ and $\frac{1}{2}$. The structure therefore contains alternating, geometrically and crystallographically non-equivalent layers of molecules parallel to (100). Dornberger-Schiff's structure is a generalization of this along the *z* direction such that the projection of both structures on (001) is the same. In Dornberger-Schiff's structure, which has space group *C*2 (*c* unique), there are four crystallographically independent molecules with cobalt atoms sited on twofold axes at $(0,\frac{1}{4},z)$, $(0,\frac{3}{4},z)$, $(\frac{1}{4},0,z)$, and $(\frac{1}{4},\frac{1}{2},z)$. Molecules with the same *x* coordinate are related by a pseudo *b* glide plane occuring at $z=0$ for layers at $x=0$ and $\frac{1}{2}$, and $z=A\neq 0$ for layers at $x=\frac{1}{4}$ and $\frac{3}{4}$. The value of the parameter *A* is such that the two types of layer in the structure are geometrically, but not crystallographically, equivalent. The α-COPYCL structure then falls into the category of OD-structures defined by Dornberger-Schiff (1956) and Dornberger-Schiff & Grell-Niemann (1961).

Solution of the α-COPYCL structure using the two models discussed above is thereby reduced to the determination from the three-dimensional Patterson map of the values of the parameters (Table 3) z_1 and z_2 for Dunitz's structure, and *A* and *z*, for Dornberger-Schiff's structure. The correct structure corresponding to each of the two models was selected from the possible

Table 3. *Coordinates for the cobalt atoms in α-COPYCL after Dunitz* (1957) *and Dornberger-Schiff* (1964)

Dunitz
(space group $C2/b$)

$$(0,0,0)+,\ \text{and}\ (\tfrac{1}{2},\tfrac{1}{2},0)+$$
$$(0,\tfrac{1}{4},z_1),\ (0,\tfrac{3}{4},-z_1),\ (\tfrac{1}{4},0,z_2),\ (\tfrac{3}{4},0,-z_2)$$
$$z_1\neq z_2$$

Dornberger–Schiff
(space group $C2$)

$$(0,0,0)+,\ \text{and}\ (\tfrac{1}{2},\tfrac{1}{2},09)+$$
$$(0,\tfrac{1}{4},z_1),\ (0,\tfrac{3}{4},-z_1),\ (\tfrac{1}{4},0,A+z_2),\ (\tfrac{3}{4},0,A-z_2)$$
$$z_1=z_2,\ 0<A<1$$

Patterson solution

Dunitz	$z_1=0\cdot1,\ z_2=0\cdot4$
Dornberger–Schiff	$z_1=0\cdot1,\ A=0\cdot5$

giving, for both models

$$(0,0,0)+,\ \text{and}\ (\tfrac{1}{2},\tfrac{1}{2},0)+$$
$$(0,\tfrac{1}{4},0\cdot1),\ (0,\tfrac{3}{4},-0\cdot1),\ (\tfrac{1}{4},0,-0\cdot4),\ (\tfrac{3}{4},0,0\cdot4)$$

solutions to the Patterson function with the aid of structure-factor calculations giving $z_1=0\cdot1$, $z_2=-0\cdot4$, and $A=0\cdot5$, $z_1=0\cdot1$ respectively. Coordinates for the chlorine atoms were derived from the Patterson function, and those of the light atoms by Fourier methods. It is of interest to note that the two models initially give the same solution to the structure.

Full-matrix least-squares refinement was carried out for each of the two interpretations of the α-COPYCL structure. Because of the extremely high correlation coefficients, refinement of the structure proposed by Dornberger-Schiff could only be accomplished by imposing the restriction that parameters of atoms related by the pseudo *b*-glide plane were not refined simultaneously.

Refinement of Dornberger-Schiff's structure destroyed the geometrical equivalence of the two types of layer, and the spatial distribution of the heavy atoms approached that originally proposed by Dunitz. In addition, the light atoms were shifted to positions corresponding to chemically unreasonable geometries for the pyridine rings. The interpretation of the structure of α-COPYCL proposed by Dornberger-Schiff was therefore rejected since it was not in accord with experimental observation.

The initial R value for the structure corresponding to Dunitz's interpretation was 23%. Refinement of atomic coordinates, layer-line scale factors, and eventually isotropic temperature factors reduced the R value to 11·8%. At this stage, the heavy atoms were assigned anisotropic temperature factors, and their scattering factors were modified to include anomalous dispersion terms which were calculated for Co $K\alpha$ radiation as described by Cromer (1965). The values of $\Delta f'$ and $\Delta f''$ were for cobalt $-2\cdot23$ and $0\cdot75$ and for chlorine 0·35 and 0·93 respectively. Hydrogen atoms were added to the structure in calculated positions, and further refinement of coordinates and temperature factors for the non-hydrogen atoms reduced R to the final value of 11·4%. The structure factors were given unit weight throughout the refinement, and the function minimized was therefore $|\sum(|F_o|-|F_c|)^2|$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Table 4. *Fractional coordinates and U tensors* ($\times 10^4$) *for α-COPYCL at* 294 K

(*a*) Cobalt and chlorine. The anisotropic temperature factor takes the form $\exp\,[-2\pi^2(h^2a^{*2}U_{11}\ldots+2hka^*b^*U_{12}\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(*A*)	0·0	0·25	0·15965	205	179	191	−10	0	0
Cl(*A*)	0·03694	0·18497	0·65286	223	256	213	30	−20	4
Co(*B*)	0·25	0·0	−0·44307	229	212	83	38	0	0
Cl(*B*)	0·21279	−0·06497	0·05751	224	270	227	−40	8	16

(*b*) Pyridine rings

	Layer *A*				Layer *B*			
	x	y	z	U_{iso}	x	y	z	U_{iso}
C(1)	0·0786	0·3288	0·1224	232	0·3281	−0·0771	−0·5092	391
C(2)	0·1072	0·3840	0·0729	328	0·3567	−0·1351	−0·5092	356
C(3)	0·0943	0·4611	0·1282	430	0·3468	−0·2090	−0·4202	512
C(4)	0·0577	0·4772	0·1391	490	0·3091	−0·2239	−0·3678	287
C(5)	0·0311	0·4155	0·1884	291	0·2820	−0·1645	−0·3615	231
N	0·0420	0·3384	0·1349	261	0·2920	−0·0931	−0·4304	278
H(1)	0·088	0·269	0·072		0·338	−0·020	−0·558	
H(2)	0·139	0·372	0·048		0·387	−0·119	−0·557	
H(3)	0·116	0·509	0·110		0·367	−0·259	−0·421	
H(4)	0·048	0·535	0·188		0·298	−0·281	−0·301	
H(5)	0·000	0·427	0·208		0·252	−0·178	−0·309	

For hydrogen, $U_{\text{iso}}=0\cdot038$ Å^2

Standard deviations for coordinates

	x	y	z
Co	–	–	0·0014
Cl	0·00013	0·00027	0·0016
N	0·00045	0·00090	0·0060
C	0·0005–0·0007	0·0010–0·0014	0·007–0·009

Final atomic parameters for α-COPYCL are given in Table 4, bond lengths and angles (Busing, Martin & Levy, 1964) in Table 5, coordination angles about the cobalt atoms in Table 6, and observed and calculated structure factors in Table 7. A diagram of the crystal structure is given in Fig. 1. In the remainder of this paper, the crystallographically non-equivalent alternating layers in the α-COPYCL structure will be designated type *A* at $x=0$ and $\frac{1}{2}$, and type *B* at $x=\frac{1}{4}$ and $\frac{3}{4}$.

Table 5. *Interatomic distances* (Å) *and angles* (°) *for α-COPYCL*

(*a*) Distances

	Type *A*	Type *B*
N—C(1)	1·28 (2)	1·30 (3)
N—C(5)	1·41 (2)	1·31 (2)
C(1)–C(2)	1·39 (3)	1·41 (3)
C(2)–C(3)	1·43 (3)	1·37 (3)
C(3)–C(4)	1·29 (3)	1·34 (3)
C(4)–C(5)	1·42 (3)	1·39 (3)
Co—N	2·112 (16)	2·178 (16)
Co—Cl	2·485 (7)	2·506 (7)
Co—Cl$^{\mathrm{i}}$	2·521 (7)	2·503 (7)
Cl—Cl$^{\mathrm{i}}$	3·664	3·664
Cl—Cl$^{\mathrm{ii}}$	3·412 (9)	–
Cl—Cl$^{\mathrm{iii}}$	–	3·417 (9)

Symmetry operators

i $(x,y,z-1)$; ii $(\bar{x},\frac{1}{2}-y,z)$; iii $(\frac{1}{2}-x,\bar{y},z)$

(*b*) Angles

	Type *A*	Type *B*
Co—N—C(1)	126 (1)	118 (1)
Co—N—C(5)	120 (1)	122 (1)
N—C(1)–C(2)	128 (2)	121 (2)
N—C(5)–C(4)	122 (2)	122 (2)
C(1)–C(2)–C(3)	114 (2)	120 (2)
C(2)–C(3)–C(4)	121 (2)	117 (2)
C(3)–C(4)–C(5)	118 (2)	121 (2)
C(5)–N—C(1)	113 (2)	120 (2)

Least-squares planes of pyridine rings relative to crystal axes.

Type *A* $4{\cdot}035x-0{\cdot}633y+3{\cdot}636z=0{\cdot}494$

Type *B* $5{\cdot}813x+2{\cdot}761y+3{\cdot}564z=-0{\cdot}104$

Angle (°) between plane of pyridine rings and (001)

Type *A* 7·8 (1·8) Type *B* 14·0 (1·2)

Angle (°) between *b* axis and Co–N bond

Type *A* 43·3 (4) Type *B* 41·8 (4)

Table 6. *Coordination angles* (°) *about cobalt in α-COPYCL*

Type *A*		Type *B*	
N—Co–Cl	90·7 (5)	N—Co–Cl$^{\mathrm{iv}}$	90·6 (5)
N—Co–Cl$^{\mathrm{i}}$	87·1 (5)	N—Co–Cl$^{\mathrm{v}}$	88·8 (5)
N—Co–Cl$^{\mathrm{ii}}$	92·9 (5)	N—Co–Cl$^{\mathrm{i}}$	91·2 (5)
N—Co–Cl$^{\mathrm{iii}}$	89·3 (5)	N—Co–Cl	89·4 (5)
Cl—Co–Cl$^{\mathrm{ii}}$	86·7 (3)	Cl$^{\mathrm{i}}$—Co–Cl$^{\mathrm{iv}}$	86·1 (3)
Cl—Co–Cl$^{\mathrm{i}}$	94·1 (2)	Cl—Co–Cl$^{\mathrm{i}}$	94·0 (2)
Cl$^{\mathrm{i}}$—Co–Cl$^{\mathrm{iii}}$	85·1 (3)	Cl—Co–Cl$^{\mathrm{v}}$	85·9 (3)
Cl—Co–Cl$^{\mathrm{iii}}$	179·2 (3)	Cl—Co–Cl$^{\mathrm{iv}}$	179·9 (3)
N—Co–Co$^{\mathrm{i}}$	87·5 (6)	N—Co–Co$^{\mathrm{vi}}$	88·8 (6)
C(3)–Co–Co$^{\mathrm{i}}$	88·4 (3)	C(3)–Co–Co$^{\mathrm{vi}}$	89·0 (4)

Symmetry operators

i	$(x, y, z-1)$;	ii	$(\bar{x},\frac{1}{2}-y, z)$
iii	$(\bar{x},\frac{1}{2}-y,z-1)$;	iv	$(\frac{1}{2}-x,\bar{y},z-1)$
v	$(\frac{1}{2}-x, \bar{y},z)$;	vi	$(x,y,z+1)$

The accuracy of the α-COPYCL structure

The geometry of the pyridine rings, especially that of type *A*, is only of moderate accuracy (Table 5). In particular, the bond lengths N(*A*)–C(1*A*) and C(3*A*)–C(4*A*), and bond angles C(1*A*)–C(2*A*)–C(3*A*) and C(5*A*)–N(*A*)–C(1*A*) are too small, and the angles Co(*A*)–N(*A*)–C(1*A*) and N(*A*)–C(1*A*)–C(2*A*) are too large. It is therefore of interest to examine the effects on the accuracy of the final structure of using a twinned crystal for data collection.

There are two ways in which the reliability of the detwinned structure factors, and hence of the final structure, could be reduced relative to single-crystal structure factors. Firstly, the detwinning operation itself increases the random error of the resultant

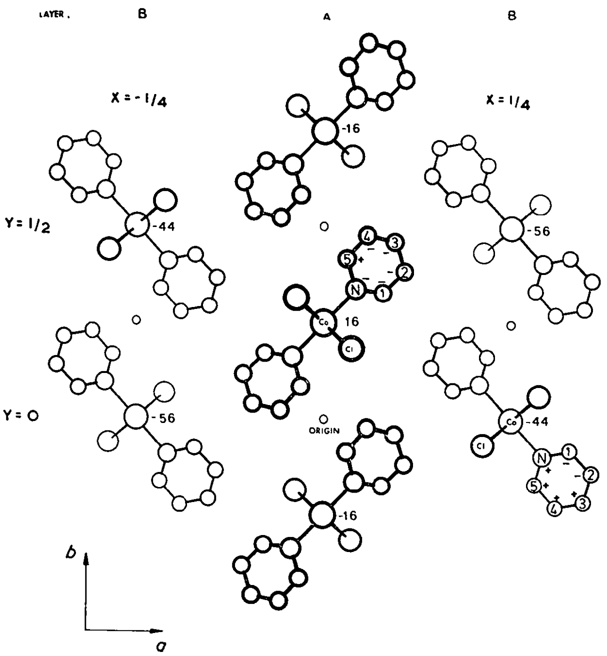

Fig. 1. The crystal structure of α-COPYCL projected on the (001) plane. 100*z* for cobalt is given and the + and − signs indicate the *z* coordinate of the light atoms relative to cobalt.

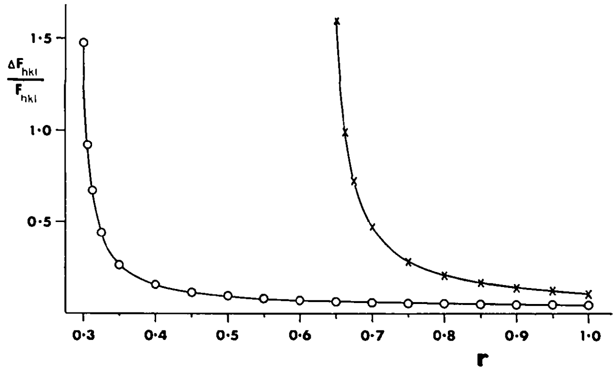

Fig. 2. The variation of $\Delta F_{hkl}/F_{hkl}$ with intensity ratio *r* for two values of the twin ratio *f*. o–o, $f=0{\cdot}29$; x–x, $f=0{\cdot}67$.

structure factors, and secondly, systematic errors are produced by any inaccuracy in the experimental value of the factor f used in equation (1). This section of the paper is devoted to an assessment of the importance of these two factors.

The random error associated with each structure factor may be derived as follows from the error in the measured intensities. The error in the value of I_{hkl} derived from equation (1) is given by

$$\Delta I_{hkl}=\frac{(\Delta P_{hkl}+f\Delta P_{\bar{h}\bar{k}l})}{(1-f^2)} \qquad (2)$$

where the quantity I can lie within the range $I\pm\Delta I$. Inspection of the experimental measurements of P_{hkl} showed that, except for measurements close to the threshold level, the value of ΔP_{hkl} could be approximated by the general relationship

$$\Delta P_{hkl}=eP_{hkl} \qquad (3)$$

where e is a fractional quantity. Substitution of equation (3) into equation (2) followed by combination of equations (1) and (2) gives the relationship

$$\frac{\Delta I_{hkl}}{I_{hkl}}=\frac{e(r+f)}{(r-f)} \qquad (4)$$

where $r=P_{hkl}/P_{\bar{h}\bar{k}l}$, the ratio of the measured intensities related by twinning. In addition, it is easily shown that

$$\frac{\Delta I_{hkl}}{I_{hkl}}=\frac{2\Delta F_{hkl}}{F_{hkl}} \qquad (5)$$

Table 7. 100F_o and 100F_c for α-COPYCL at 294 K

L= 0

K	H	FOBS	FCALC
-18	2	7790	8821
-18	4	5027	5373
-18	6	6240	7307
-18	8	5887	6158
-16	0	8458	10024
-16	4	9319	9238
-16	8	6079	6760
-14	2	17780	16738
-14	4	11260	9822
-14	8	9783	9646
-14	10	3183	4280
-14	20	6856	6859
-14	22	6823	6993
-12	0	16554	14747
-12	4	17201	16136
-12	6	12696	11116
-12	10	11054	8865
-12	18	8222	9062
-12	22	8879	9421
-12	24	11231	10476
-12	28	7068	7402
-10	2	7449	6237
-10	4	8588	5707
-10	6	8383	6818
-10	8	4270	4464
-10	10	15095	13878
-10	14	16070	16326
-10	16	9301	8136
-10	18	10385	10296
-10	22	6668	8519
-10	32	4306	3962
-8	0	5891	4889
-8	2	8510	6901
-8	6	3307	3530
-8	8	18644	20501
-8	10	9700	8365
-8	12	19500	20996
-8	16	20636	22444
-8	20	11962	12841
-8	26	4910	4695
-6	2	5335	4400
-6	4	5357	5369
-6	6	21890	21211
-6	10	28233	29107
-6	12	6830	6810
-6	14	19233	19477
-6	16	8564	8953
-6	18	13161	13451
-6	20	7450	6899
-6	24	6499	6624
-6	30	4964	4084
-6	32	5394	6116
-6	34	7595	7646
-4	0	8329	6497
-4	2	13895	12601
-4	4	19146	15093
-4	6	18536	19250
-4	8	11084	10943
-4	10	18049	19233
-4	12	20564	20463
-4	16	17391	17742
-4	18	13618	13334
-4	20	11276	12164
-4	22	6070	7010
-4	24	6660	6072
-4	26	6398	6325
-4	32	8676	8790
-4	34	9610	9536
-4	36	4036	4314
-2	2	26043	26191
-2	4	13584	12235
-2	6	23559	23747
-2	8	12690	15640
-2	10	4171	3813
-2	12	3207	1676
-2	14	6097	5375
-2	18	5674	2791
-2	22	13180	13949
-2	26	19906	20792
-2	30	7702	9056
-2	36	5757	5134
0	12	9539	10479
0	16	10603	8826
0	20	13165	14037
0	24	18366	19178
0	28	23431	20716
0	32	10255	8991
2	2	26742	26761
2	4	13394	12507
2	6	23585	24234
2	8	16187	16249
2	10	5883	4232
2	12	3940	2314
2	14	4974	4675
2	18	3884	2482
2	22	14382	14437
2	26	19305	19731
2	36	6488	5774
4	2	15814	13775
4	4	17929	13680
4	6	20839	19114
4	8	11380	10804
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2	22	4597	5123
2	24	3506	3906
3	3	5222	4990
3	5	7179	7338
3	9	5973	8154
3	13	5265	6085
3	17	2017	2081
3	19	4203	1594
3	21	3810	766
3	23	3826	3520
3	25	1627	1437
4	0	3949	4213
4	2	4191	2642
4	4	6644	5601
4	6	8116	8646
4	8	5651	4205
4	10	3048	1712
4	12	5108	4330
4	14	2531	2802
4	16	4752	5566
4	20	4521	5378
4	20	4521	5378
4	22	7128	6976
4	24	2726	4158
5	1	6011	6985
5	3	5252	6176
5	5	6904	8040
5	7	4855	4470
5	9	5642	6118
5	11	4859	5048
5	15	1728	193
5	17	3266	1458
5	23	4075	2103
6	0	4227	3165
6	2	6951	5269
6	6	7556	5995
6	8	2389	1444
6	16	2284	508
6	18	5554	4173
6	20	4084	3312
6	22	3795	3844
7	1	6117	6278
7	3	5987	4911
7	5	6991	7089
7	7	3707	2405
8	0	9562	9904
8	2	4987	4239
8	4	9223	9219
8	6	4505	3810
8	8	3364	2515
8	18	1455	1020
8	20	3801	4928
9	1	2741	3333
9	3	5823	5676
9	5	2822	795
9	9	1975	1192
9	11	2430	2430
9	17	2844	3218
10	0	2147	2804
10	2	7574	8954
10	4	4918	5995
10	6	5792	6058
10	8	4602	5481
10	10	3400	4363
11	1	4494	3692
11	3	2239	476
11	5	3685	2258
11	7	2972	2027
11	9	1443	1669
11	11	1369	544
12	0	3817	3841
12	2	3683	4902
12	4	4422	5557
12	6	5166	5705
12	8	3676	4608
12	10	2824	3759
13	3	1029	1349

where F_{hkl} is the detwinned structure factor for reflexion hkl. Combining equations (4) and (5), the desired result is obtained

$$\frac{\Delta F_{hkl}}{F_{hkl}} = \frac{e(r+f)}{2(r-f)}\,. \tag{6}$$

The variation of $\Delta F_{hkl}/F_{hkl}$ as a function of r is shown in Fig. 2 for the particular value $e=0{\cdot}05$ which was in accord with the measured intensity data. The value of $\Delta F_{hkl}/F_{hkl}$ increases rapidly when $P_{hkl}/P_{\bar{h}kl}$ approaches the value of f, and therefore the accuracy of the smaller value of the pair of structure factors F_{hkl} and $F_{\bar{h}kl}$ diminishes relative to the single-crystal case ($f=0$) when P_{hkl} and $P_{\bar{h}kl}$ are unequal, but the accuracy of the larger structure factor of the pair may be almost unchanged.

In order to assess the effect of random error on the final structure, least-squares refinement was carried out using only those structure factors where $\Delta F_{hkl}/F_{hkl}$ calculated from equation (6) was less than an arbitrary limit of 0·125. This limit removed 140 structure factors from the data set of 886 reflexions, and the immediate result was to lower the R value to 9·4%. However, the atomic parameters did not change appreciably on refinement, and therefore the magnification of random error during the detwinned operation did not have a significant effect on the final structure for α-COPYCL. Values of $\Delta F_{hkl}/F_{hkl}$ calculated from equation (6) could, of course, be used to construct a weighting function for the data during structure refinement, but we have not attempted this since our interest lay in eliminating the effect on the final structure of the least accurate intensity measurements.

The effect on the final structure of a possibly inaccurate value of the factor f used in equation (1) was estimated by employing extreme values of this factor to produce data sets which were under and over corrected for twinning. For this purpose, reflexions with $l \leq 2$ were processed with equation (1) using values of $f=0{\cdot}0$, 0·29, and 0·50, the intermediate value being that determined experimentally. Least-squares refinement of the atomic coordinates and isotropic temperature factors for α-COPYCL was carried out using each of these three data sets leading to R values of 15·8, 12·0 and 12·8% respectively. The only significant differences between the three structures derived in this manner concerned the geometry of the pyridine rings which is given for all three structures in Table 8. For both the under and over corrected data, the pyridine ring geometry is slightly more distorted than for the correctly detwinned data, but there is no radical difference between the structures derived from the three data sets. It would appear, therefore, that the geometry of the pyridine rings in the α-COPYCL structure is partially dependent on the value of the detwinning constant f, but that the possible error in the experimentally determined value is too small to produce any serious effect on the structure.

Table 8. *Pyridine ring geometries for α-COPYCL obtained through the use of various values of twin size ratio, f, for data with* $1 \leq 2$

(*a*) Bond lengths (Å)

	$f=0{\cdot}0$		$f=0{\cdot}29$		$f=0{\cdot}50$	
	A	*B*	*A*	*B*	*A*	*B*
N——C(1)	1·31	1·32	1·28	1·33	1·30	1·24
C(1)–C(2)	1·39	1·43	1·41	1·42	1·39	1·44
C(2)–C(3)	1·37	1·42	1·43	1·38	1·44	1·41
C(3)–C(4)	1·29	1·36	1·32	1·37	1·25	1·27
C(4)–C(5)	1·40	1·36	1·43	1·40	1·42	1·43
C(5)–N	1·50	1·45	1·43	1·31	1·45	1·35

(*b*) Bond angles (°)

	$f=0{\cdot}0$		$f=0{\cdot}29$		$f=0{\cdot}50$	
	A	*B*	*A*	*B*	*A*	*B*
C(1)–N——C(5)	119	119	114	120	116	120
N——C(1)–C(2)	126	123	128	120	127	124
C(1)–C(2)–C(3)	116	117	114	120	114	116
C(2)–C(3)–C(4)	121	117	121	117	122	117
C(3)–C(4)–C(5)	122	126	118	120	121	124
C(4)–C(5)–N	113	116	121	122	118	117

Clarke (1973) has shown by examination of diffuse scattering and difference Fourier syntheses that there is no appreciable disorder in the crystal structure of α-COPYCL, and we are therefore forced to conclude that the distortions of the pyridine rings in the crystal structure are due to a combination of errors arising from the intensity measurements, the approximate absorption correction and the detwinning process.

The crystal structure of γ-COPYCL at 89K

Crystallographic studies on γ-COPYCL were carried out using the low-temperature X-ray camera described by Thomas (1972). Considerable difficulty was experienced in obtaining undamaged crystals of γ-COPYCL suitable for X-ray work because of the unusually violent, self-induced, agitation of the α-COPYCL crystals which occurred whilst the crystals passed through the low-temperature phase transition to the γ-form at about 150 K. Nevertheless, one undamaged crystal was eventually obtained by cooling very slowly in the region of the transition.

The triplet reflexions, characteristic of twinning in α-COPYCL, did not appear in any of the oscillation or Weissenberg photographs taken of γ-COPYCL indicating that the unit cell-angle γ had become exactly 90°. Indeed, there were no extra maxima in the diffraction pattern of γ-COPYCL which might have indicated twinning of the crystal, and the γ-COPYCL crystals therefore had complete single-crystal character, although they were derived from twinned material. [A similar observation was made for Rochelle salt by Ubbelohde & Woodward (1946)].

γ-COPYCL crystals are monoclinic with space group $P2_1/n$ (second setting, b unique), $Z=2$, and $D_c=1{\cdot}82$ g cm^{-3}. The unit cell was chosen to correspond closely to that of α-COPYCL, and the unit-cell parameters, derived by least-squares calculations from

11 Bragg angles measured by a back-reflexion technique with Cu $K\alpha$ radiation are $a = 17{\cdot}437$ (13), $b = 8{\cdot}408$ (2), $c = 3{\cdot}593$ (7) Å, $\beta = 90{\cdot}05$ (5)°. γ-COPYCL is therefore isomorphous with dichlorobis(pyridine)copper(II), a structure previously examined by Dunitz (1957), who pointed out the similarity to the structure of α-COPYCL. In fact the unit cell of γ-COPYCL is of similar shape to that of α-COPYCL, but the a and b axes are halved in length in the low-temperature form, and the unique axis of the monoclinic cell is b instead of c.

Collection of intensity data at 89 K

The limitations of the low-temperature X-ray camera (Thomas, 1972) suggest the inclined-beam oscillation method (Milledge, 1963) as the most convenient for data collection. In this case, the method was usefully modified by taking 40° oscillation photographs of a crystal mounted about the c axis with the Weissenberg motion in operation but without the layer-line screens. Data from adjacent layers did not overlap on the film because of the large gap between layer lines, and the separation of the reflexions produced by the Weissenberg motion greatly facilitated indexing.

Unfortunately, the construction of the cryostat in which the crystal was mounted did not allow the recording of data with $l = -3$, but all of the available data in the range $-2 \leq l \leq 0$ were collected using unfiltered Cu $K\alpha$ radiation and a beam inclination angle of 20·75°. Certain portions of the reciprocal sphere could not be explored since the cryostat of the low-temperature camera is supported by three struts arranged with trigonal symmetry about the camera rotation axis (see Thomas, 1972). Each of these struts subtends an angular obstruction of 30° at the crystal, and together they obscure one quarter of reciprocal space. The unobscured volume of reciprocal space is thus divided into three equal portions which may be explored using three non-overlapping oscillation ranges of 90°, chosen so that the direct X-ray beam sweeps across the gap between two adjacent struts. In this investigation, these 90° ranges were further subdivided into three 40° oscillation ranges overlapped by 15°. Nine such 40° oscillation photographs were needed to explore the available portion of reciprocal space, each photograph being taken with a three-film pack.

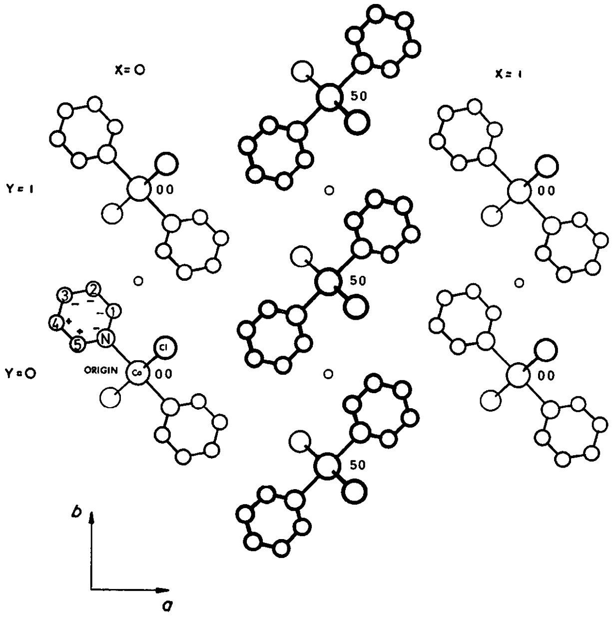

Fig. 3. The crystal structure of γ-COPYCL projected on the (001) plane. $100z$ for cobalt is given, and the + and − signs indicate the z coordinate of the light atoms relative to cobalt.

The reflexions were indexed by comparing the photographs with computer generated replicas, and the intensities were measured on the Joyce–Deeley flying-spot microdensitometer. Least-squares scaling of the three 40° oscillation photographs in each 90° range was achieved by comparison of the same reflexions measured on overlapping photographs. This operation yielded three batches of data corresponding to the three unique 90° ranges. Lorentz–polarization and absorption corrections were then applied. The absorption correction was calculated by the method of Busing & Levy (1957) using the measured dimensions of the crystal envelope. The crystal used was bounded by faces of the type {100}, {010}, and {001}, and had dimensions $0{\cdot}0171 \times 0{\cdot}0341 \times 0{\cdot}0900$ cm with μ(Cu $K\alpha$) $= 162{\cdot}6$ cm^{-1}. The remaining three batches of data were merged into one final set of unique data by least-squares comparison of the corrected intensities of equivalent reflexions. This unique set of data was not placed on a common relative scale because it was not possible to estimate scale factors between the three layer lines.

Structure solution and refinement

With only two molecules in the unit cell, and space group $P2_1/n$, the COPYCL units in γ-COPYCL must be sited on the centres of symmetry at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The γ-COPYCL structure, therefore, was easily derived by Patterson and Fourier methods. Full-matrix least-squares refinement of layer-line scale factors, coordinates, and isotropic temperature factors reduced R from the initial value of 32% to 11·2% after four cycles. Hydrogen atoms were added in calculated positions, and the scattering factors of the heavy atoms were modified to include anomalous dispersion terms (*International Tables for X-ray Crystallography*, 1962). Further refinement of coordinates and isotropic temperature factors of the non-hydrogen atoms followed by refinement of anisotropic temperature factors for cobalt and chlorine reduced R to the final value of 9·6% for the 368 unique observed reflexions. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The function minimized was $\sum\omega(|F_o| - |F_c|)^2$ with $\omega = 1$ for all data.

Table 9. *Fractional coordinates and U-tensors* ($\times 10^4$) *for γ-COPYCL at* 89 K

(*a*) Cobalt and chlorine. The anisotropic temperature factor takes the form $\exp[-2\pi^2(h^2a^{*2}U_{11}\ldots+2hka^*b^*U_{12}\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0·0	0·0	0·0	73	36	41	−4	29	19
Cl	0·07178	0·13623	0·48657	81	33	91	−30	10	−29

(*b*) Pyridine ring

	x	y	z	$U_{\rm iso}$		x	y	z
N	−0·0855	0·1850	−0·0208	82				
C(1)	−0·0651	0·3350	−0·0868	219	H(1)	−0·005	0·359	−0·139
C(2)	−0·1193	0·4535	−0·1277	173	H(2)	−0·104	0·577	−0·172
C(3)	−0·1948	0·4163	−0·0620	164	H(3)	−0·237	0·512	−0·073
C(4)	−0·2155	0·2646	0·0150	140	H(4)	−0·273	0·239	0·057
C(5)	−0·1595	0·1525	0·0350	115	H(5)	−0·173	0·030	0·086

For hydrogen, $U_{\rm iso}=0{\cdot}028$ Å^2.

Standard deviations for coordinates

	x	y	z
Cl	0·00022	0·00046	0·0017
N	0·0008	0·0017	0·0062
C	0·0010–0·0012	0·0023–0·0026	0·0075–0·0083

Final parameters for the γ-COPYCL structure are given in Table 9, bond lengths and angles in Table 10 (Busing, Martin & Levy, 1964), coordination angles about the cobalt in Table 11, and observed and calculated structure factors in Table 12. The crystal structure of γ-COPYCL projected onto the (001) plane is shown in Fig. 3.

Discussion of the crystal structures of α- and γ-COPYCL

The crystal structures of both α- and γ-COPYCL contain polymeric chains of molecules linked by Co–Cl bridging bonds. These chains run parallel to the *c* axis of the unit cell. The Co atom is surrounded by a

Table 10. *Interatomic distances* (Å) *and angles* (°) *for γ-COPYCL*

Distances		Angles	
N—C(1)	1·33 (3)	Co—N—C(1)	120 (1)
N—C(5)	1·33 (2)	Co—N—C(5)	121 (1)
C(1)-C(2)	1·38 (5)	N—C(1)-C(2)	121 (2)
C(2)-C(3)	1·37 (3)	N—C(5)-C(4)	123 (2)
C(3)-C(4)	1·35 (3)	C(1)-C(2)-C(3)	118 (2)
C(4)-C(5)	1·36 (2)	C(2)-C(3)-C(4)	120 (2)
Co—N	2·156 (14)	C(3)-C(4)-C(5)	118 (2)
Co—Cl	2·435 (5)	C(5)-N—C(1)	119 (2)
Co—Cl$^{\rm i}$	2·507 (5)		
Cl—Cl$^{\rm ii}$	3·593		
Cl—Cl$^{\rm iii}$	3·395 (7)		

Symmetry operators

i $(\bar{x},\bar{y},\bar{z})$; ii $(x,y,z-1)$; iii $(\bar{x},\bar{y},1-z)$

Least-squares plane of pyridine ring relative to crystal axes.

$$1{\cdot}804x+1{\cdot}561y+3{\cdot}510z=0{\cdot}071$$

Angle (°) between plane of pyridine ring and (001): 11·0 (1·0)

Angle (°) between *b* axis and Co–N bond: 43·8 (4).

Table 11. *Coordination angles* (°) *about cobalt in γ-COPYCL*

N$^{\rm i}$—Co-Cl$^{\rm ii}$	90·5 (5)
N$^{\rm i}$—Co-Cl	87·7 (5)
N$^{\rm i}$—Co-Cl$^{\rm i}$	92·3 (5)
N$^{\rm i}$—Co-Cl$^{\rm iii}$	89·5 (5)
Cl$^{\rm iii}$—Co-Cl	86·7 (1)
Cl$^{\rm ii}$—Co-Cl	93·3 (1)
N$^{\rm i}$—Co-Co$^{\rm iv}$	88·0 (6)
C(3$^{\rm i}$)-Co-Co$^{\rm iv}$	87·4 (3)

Symmetry operators

i $(\bar{x},\bar{y},\bar{z})$; ii $(x,y,z-1)$

iii $(\bar{x},\bar{y},1-z)$; iv $(x,y,1+z)$

Table 12. $100F_o$ *and* $100F_c$ *for γ-COPYCL at* 89 K

K	H	FOBS	FCALC
L= -2			
0	18	985	1263
1	1	4663	4027
1	2	1038	807
1	3	1840	2588
1	4	1611	2465
1	15	2972	3207
1	16	1858	1763
1	17	1480	1309
1	18	1932	1861
2	1	1003	596
2	2	3584	3636
2	3	2973	3304
2	4	2840	2581
2	5	2080	2566
2	8	3065	3159
2	9	2258	2532
2	10	2687	2940
2	11	1083	1679
2	16	2318	2233
2	17	2581	2427
2	18	1168	1536
2	19	1053	1317
3	2	1521	1119
3	3	3453	3512
3	4	2278	1862
3	5	5831	5922
3	7	5538	5766
3	8	1782	1777
3	9	4040	3783
3	11	783	882
3	12	1337	2192
3	17	2004	2132
3	19	2985	3005
4	4	4420	4406
4	6	4645	4016
4	8	5850	5243
4	9	1481	1087
4	10	3090	3002
4	18	2446	2464
5	1	2208	2260
5	2	2313	2333
5	3	1901	1797
5	4	3122	2595
5	5	2691	2712
5	6	1683	802
5	7	3527	3168
5	8	3090	2871
5	9	2185	2103
5	10	2127	1689
5	11	3067	2673
5	12	1271	792
6	2	3564	3535
6	3	2980	3135
6	4	1730	1667
6	5	1416	1703
6	9	2493	2035
6	11	2420	2348
6	12	2878	3151
7	1	4231	4284
7	3	1898	1132
7	4	1965	2216
7	10	1375	1537
7	11	3178	3082
8	2	2297	1707
8	3	1464	1794
8	4	1179	1315
8	5	1415	1685
L= -1			
0	19	3574	3835
0	21	2988	3020
1	3	4623	5165
1	4	4991	4668
1	5	3774	4000
1	6	6541	7068
1	8	5418	5710
1	9	3891	4104
1	10	2268	2219
1	17	1368	1502
1	18	2060	2065
1	19	1494	1586
1	20	2861	2700
2	1	4106	4260
2	2	3966	4535
2	3	3327	3627
2	4	4493	4334
2	5	2741	2703
2	7	4111	4021
2	8	1250	1613
2	9	3223	3189
2	10	4335	4162
2	11	3200	3413
2	12	2283	2607
2	17	2202	2629
2	18	1420	1709
2	19	1401	1249
2	21	1491	1514
3	1	511	953
3	2	6020	5796
3	3	3229	3414
3	4	4693	4525
3	9	1849	1818
3	10	1532	1590
3	11	1433	1281
3	12	2951	2636
3	17	2132	1853
4	1	5265	5802
4	2	3361	3373
4	3	4214	3997
4	4	1118	1067
4	7	1834	1341
4	8	1386	1348
4	9	2977	2764
4	10	2407	2052
4	11	3203	2741
4	13	3805	4504
5	2	3561	3957
5	3	4503	3859
5	4	1622	1561
5	5	2418	2039
5	6	1494	1417
5	9	2778	1995
5	10	3507	2949
5	11	5261	4573
5	12	3943	3817
5	14	2921	2726
6	1	2386	2316
6	2	2960	2744
6	3	3139	3180
6	4	1938	2188
6	5	2635	2375
6	7	4105	3634
6	10	2205	1933
6	11	1946	1753
6	12	1821	1557
6	13	1975	1937
6	17	1464	1339
7	3	1633	1139
7	4	2632	2764
7	6	5886	5495
7	8	4304	4024
7	10	2860	2607
8	1	1417	1511
8	2	1997	2003
8	3	1990	1358
8	5	4732	4502
8	7	4642	4586
8	9	3056	3063
8	10	1801	1647
9	3	2300	2122
9	4	1511	1851
9	5	1804	1776
9	6	1737	1729
L= 0			
-8	0	3705	3596
-6	0	4496	4762
-4	0	1150	1343
0	8	2912	2443
0	10	3727	3651
0	12	4627	5115
0	14	6323	6420
0	16	3337	3404
0	18	955	1301
1	2	3466	3002
1	4	4565	4430
1	5	1899	1602
1	7	1667	1558
1	10	2045	1575
1	11	4343	3948
1	12	1243	1238
1	13	5792	5963
1	15	2805	2656
1	16	1613	883
1	17	1277	1447
1	18	1913	2211
2	1	3500	3212
2	2	4006	3516
2	3	4316	4839
2	4	2939	2994
2	5	4342	5260
2	6	5159	5965
2	8	5306	5337
2	9	3709	3471
2	10	3262	3277
2	11	1852	1848
2	12	1613	1490
2	13	2749	2755
2	16	3228	3025
2	17	3227	3505
2	18	1865	1620
2	19	2158	2236
2	20	1960	1913
3	1	1673	1558
3	3	5127	5130
3	4	3398	3612
3	5	6953	7546
3	6	1523	1647
3	7	5480	5596
3	8	2308	2042
3	9	4511	4503
3	10	1933	1675
3	11	1642	1248
3	12	2262	2140
3	14	987	1209
3	16	993	1440
3	17	2004	1976
3	19	3178	2876
4	1	1745	1593
4	4	5420	5126
4	5	2509	2406
4	6	5790	5562
4	8	6893	6905
4	10	4405	3843
4	11	1767	1387
4	13	2238	1353
4	18	2573	2495
5	1	2368	2528
5	2	2513	2276
5	3	2489	2199
5	4	2193	1849
5	5	3378	3004
5	6	1639	1447
5	7	4185	3678
5	8	2845	2361
5	9	3604	3144
5	11	3660	3098
5	16	1483	1725
6	2	5008	5234
6	3	3429	3329
6	4	1730	1328
6	5	3491	3118
6	9	3442	2943
6	11	3267	3039
6	12	4776	4239
6	14	2553	3022
6	16	1260	1974
7	1	4720	5347
7	2	2161	2167
7	3	1376	1547
7	4	2397	2447
7	5	1578	1485
7	10	2035	1568
7	11	2066	2291
7	13	3006	3522
8	2	2915	2857
8	3	2921	2537
8	4	2698	2324
8	5	836	1764
8	12	1999	2590
9	3	2408	2293
9	4	3255	3023
9	6	1700	1420
9	7	1187	1480
9	8	1516	1700
L= 1			
-5	0	4694	5407
-3	0	5325	5614
-1	0	2221	1514
0	5	6145	6133
0	7	5830	5775
0	9	6362	6109
0	11	2207	2361
0	19	2183	2948
1	3	4794	5528
1	4	3253	3728
1	5	3960	3527
1	6	6012	6118
1	8	5555	5404
1	9	3932	3834
1	10	2966	2942
1	11	3299	2841
1	12	3064	2859
1	13	1712	1534
1	15	2726	2465
1	17	2286	1768
1	18	2350	2272
2	1	2784	2445
2	2	4433	3940
2	5	3835	4067
2	7	5035	4891
2	9	2678	2424
2	10	4157	3935
2	11	2308	1855
2	12	2909	2506
2	13	1084	1281
2	14	2130	1718
2	15	2787	2862
2	16	1619	1385
2	17	2840	2679
2	18	1471	1425
2	19	863	985
3	1	1897	1619
3	2	6252	6543
3	8	1449	1037
3	10	2733	2110
3	11	1518	1493
3	12	3514	3064
3	14	4632	4523
3	16	3898	4026
3	17	2162	2148
3	18	1771	1637
4	1	5579	6224
4	2	2767	2421
4	3	4083	4335
4	9	1857	1549
4	15	4193	4085
4	17	2074	2250
5	2	3488	3819
5	3	4724	5225
5	4	1815	2171
5	16	1880	1856
5	17	1751	1798
6	1	2135	2496
6	2	2748	2572
6	3	2186	2178
6	12	1724	2492
6	13	2502	2317
6	16	1493	1568
8	7	4396	4254
8	9	2319	3005
9	8	1340	1975
L= 2			
-6	0	3035	3732
-3	0	1242	1320
0	6	712	854
0	8	1250	1069
0	10	2038	1868
0	12	4272	3715
0	14	6755	6277
0	16	2073	2281
1	3	3745	4538
1	4	2758	3181
1	6	1526	1339
1	10	1883	1682
1	11	3084	2944
1	13	3977	3733
1	15	2171	2063
1	17	2050	2057
2	1	1626	1908
2	5	3796	3729
2	6	4473	4442
2	8	3000	3317
2	9	2377	2579
2	10	1711	1504
2	11	2510	1946
2	12	1422	1272
2	13	2576	2498
2	16	2140	2302
2	17	2951	3053
2	18	1038	1110
3	7	3267	3954
3	9	4859	4521
3	10	1698	1557
3	11	2476	2044
3	17	639	1387
4	8	5079	4832
4	10	3463	3073
4	18	1574	1759
5	1	1119	1553
5	16	984	1507
6	0	3759	3732
6	3	2696	3243
6	11	1462	2148
6	12	3429	3593
6	14	2253	2165
7	1	4267	4527
7	10	1403	1616
7	11	1173	954
7	13	2764	3139
8	11	1266	1583
9	4	3040	3045
9	7	1307	1286

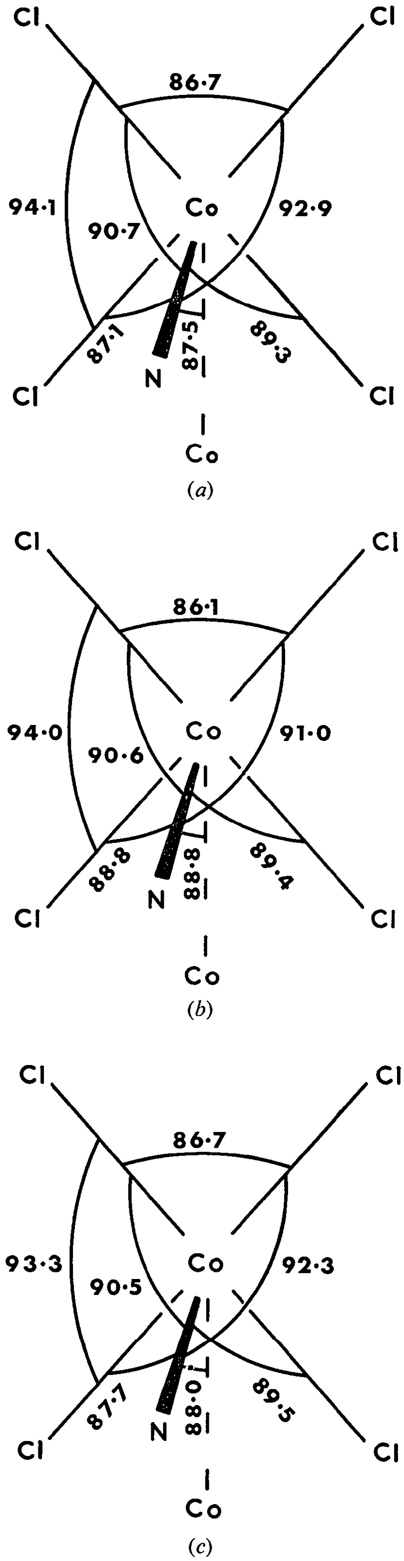

Fig. 4. Cobalt coordination angles in the three crystallographically independent polymeric chains of COPYCL. (a) α-COPYCL, type *A*; (b) α-COPYCL, type *B*; (c) γ-COPYCL.

tetragonally distorted octahedron whose corners are defined by two N and four Cl atoms (Fig. 4). In both structures, the Co–N bond distances are close to 2·15 Å (Tables 5 and 10), and the Co and the surrounding Cl atoms are coplanar. The Co–Cl distances in α-COPYCL are all equal (2·50 Å, Table 5) within experimental error, but two of these bonds are shorter in the γ-form (2·43 Å, Table 10) with two remaining the same. Two of the Cl atoms have therefore moved closer to the Co as a result of the phase transformation and the contraction of these Co–Cl bonds is presumably the cause of the decrease in the length of the *c* axis by 0·07 Å during the transition to γ-COPYCL.

The basic unit of the coordination sphere about the Co atom (Fig. 4, Tables 6 and 11) is the same within experimental error in all three of the molecular environments found in the α- and γ-COPYCL structures as shown by the coordination angles about Co. The only variation is the position of the second N atom, not shown in Fig. 4, which is dictated by the crystallographic symmetry at the Co atom. In α-COPYCL, where the Co is situated on a twofold axis, symmetry produces a bend of 2 × 2·5° or 2 × 1·2° (Fig. 4) in the N–Co–N line, but this line is straight in the γ-form where the Co atom is centrosymmetric. A comparison of the three coordination geometries in Fig. 4 suggests that these represent a preferred position of the N atom with respect to the plane of the Co and Cl atoms and the Co–Cl bonds, the only variation being one of enantiomorph.

In both α- and γ-COPYCL, the Co–N bonds and the Co–C(3) lines make acute angles with the *c* axis (Tables 6 and 11). Whether this acute angle is bounded by $+c$ or $-c$ is determined by intermolecular contacts to the terminal atoms, C(3) and H(3), of the pyridine rings. These terminal atoms are directed between the *ortho* and *meta* C atoms of the pyridine rings in the adjacent layer in the structure (Figs. 1 and 3), and in three dimensions are sandwiched between two neighbouring pyridine rings, one unit-cell translation apart along **c**, which are at higher and lower *z* coordinate than the occluded terminal atoms. The direction of the Co–N bond and Co–C(3) line is, in all cases, that which tends to equalize the intermolecular contact distances between atoms C(3) and H(3) and the *ortho* and *meta* C and H atoms of the pyridine rings at higher and lower *z* coordinate in the adjacent layer (Table 13).

The constancy of the Co coordination geometry, and the observed invariance, within experimental error, of the directions of the crystallographic axes relative to the crystal morphology enables the directions of the Co–N bond and the *b* axis of the unit cell to be used as reference axes to compare the crystal structures of α- and γ-COPYCL. In α-COPYCL, the angle between the Co–N bond and the *b* axis is 43·3° for type *A* layers and 41·8° for type *B* layers whilst in γ-COPYCL it is 43·8°. The polymeric chains in the type *B* layers of α-COPYCL have therefore rotated about the *c* axis of

Table 13. *Intermolecular contacts* (Å) *for α- and γ-COPYCL*

(*a*) Between pyridine rings

α-COPYCL

C(3A)–C(1B^{i})	3·64	C(3B^{iii})–C(1A)	3·86
C(3A)–C(1B^{ii})	4·03	C(3B^{iii})–C(1A^{iv})	3·71
C(3A)–C(2B^{i})	3·74	C(3B^{iii})–C(2A)	3·88
C(3A)–C(2B^{ii})	4·13	C(3B^{iii})–C(2A^{iv})	3·91
H(3A)–H(1B^{i})	2·3	H(3B^{iii})–H(1A)	2·4
H(3A)–H(1B^{ii})	2·6	H(3B^{iii})–H(1A^{iv})	2·4
H(3A)–H(2B^{i})	2·5	H(3B^{iii})–H(2A)	2·6
H(3A)–H(2B^{ii})	2·8	H(3B^{iii})–H(2A^{iv})	2·8
C(4A)–C(5A^{v})	3·79	C(4B)–C(5B^{vi})	3·82
C(4A)–C(4A^{v})	4·19	C(4B)–C(4B^{vi})	4·28
C(5A)–C(5A^{v})	3·90	C(5B)–C(5B^{vi})	3·84
H(4A)–H(5A^{v})	2·3	H(4B)–H(5B^{vi})	2·3
H(4A)–H(4A^{v})	3·8	H(4B)–H(4B^{vi})	3·8
H(5A)–H(5A^{v})	3·0	H(5B)–H(5B^{vi})	2·9

γ-COPYCL

C(3^{vii})–C(5^{viii})	3·64	C(1)–C(2^{v})	3·76
C(3^{vii})–C(5^{ix})	3·74	C(2)–C(2^{v})	4·33
C(3^{vii})–C(4^{viii})	3·70	C(1)–C(1^{v})	3·64
C(3^{vii})–C(4^{ix})	3·86	H(1)–H(2^{v})	2·6
H(3^{vii})–H(5^{viii})	2·4	H(2)–H(2^{v})	4·0
H(3^{vii})–H(5^{ix})	2·3	H(1)–H(1^{v})	2·6
H(3^{vii})–H(4^{viii})	2·6		
H(3^{vii})–H(4^{ix})	2·7		

(*b*) Contacts to chlorine atoms

α-COPYCL

Cl(A)–C(5A^{x})	5·62	Cl(B)–C(5B^{xi})	5·36
Cl(A)–C(2B^{iii})	5·69	Cl(B)–C(2A^{xii})	4·92
Cl(A)–C(3B^{iii})	5·63	Cl(B)–C(3A^{xii})	5·09
Cl(A)–H(5A^{x})	5·6	Cl(B)–H(5B^{xi})	5·4
Cl(A)–H(2B^{iii})	5·3	Cl(B)–H(2A^{xii})	4·3
Cl(A)–H(3B^{iii})	5·3	Cl(B)–H(3A^{xii})	4·7

γ-COPYCL

Cl–C(1^{xiii})	4·94	Cl–H(1^{xiii})	5·0
Cl–C(4^{xiv})	5·16	Cl–H(4^{xiv})	4·4
Cl–C(3^{xiv})	5·57	Cl–H(3^{xiv})	5·2

Symmetry operators

i	$(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z})$;	ii	$(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}-1)$
iii	$(\frac{1}{2}-x, \bar{y}, z)$;	iv	$(x, y, z-1)$
v	$(\bar{x}, 1-y, \bar{z})$;	vi	$(\frac{1}{2}-x, \frac{1}{2}-y, 1-z)$
vii	$(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$;	viii	$(\bar{x}, \bar{y}, \bar{z})$
ix	$(\bar{x}, \bar{y}, 1-z)$;	x	$(x, y-\frac{1}{2}, \bar{z})$
xi	$(\frac{1}{2}-x, \bar{y}-\frac{1}{2}, \bar{z}-1)$;	xii	$(x, y-\frac{1}{2}, 1-z)$
xiii	$(\bar{x}, 1-y, 1-z)$;	xiv	$(\frac{1}{2}+x, \bar{y}-\frac{1}{2}, \frac{1}{2}+z)$

the unit cell by 2·0° on transformation to γ-COPYCL. It is this rotation which allows the *a* axis of the unit cell to expand by 0·388 Å from 34·486 Å to 2 × 17·437 Å whilst the *b* axis contracts by 0·592 Å from 17·408 Å to 2 × 8·408 Å as the crystal transforms from α- to γ-COPYCL. A molecular rotation of this kind for *all* the polymeric chains in α-COPYCL was previously predicted by approximate calculations based on magnetic anisotropy data (Bentley *et al.*, 1971).

A fundamental difference between the crystal structures of α- and γ-COPYCL concerns the arrangement of the pyridine rings about Co (Fig. 5). This arrangement is determined by the symmetry of the Co atom and thus in α-COPYCL the planes of the pyridine rings are twofold related, whilst in γ-COPYCL these planes are parallel. Consequently, half of the pyridine rings in α-COPYCL undergo a rotation about the Co–N bond on transformation to γ-COPYCL.

The degree of rotation of the pyridine rings about the Co–N bond can be represented by the angle between the plane of the pyridine ring and the (001) plane, and is determined in both structures by intermolecular contacts between the closest centrosymmetrically related pyridine rings in the same layer.

The fact that the *b*-glide related Co atoms in α-COPYCL have different *z* coordinates uniquely determines the direction of rotation of the pyridine rings about the Co–N bond, and the angle between the ring plane and (001) is such that the closest centrosymmetrically related *ortho* and *meta* C and H atoms are in van der Waals contact (Table 13). The non-equivalence of the adjacent layers in α-COPYCL means that the pyridine rings in these layers are inclined to (001) to different extents, and the inclination is least where the difference in *z* coordinates of the *b*-glide related Co atoms is greatest. The observed angles of inclination are for layer $A \pm 7{\cdot}8°$ ($\Delta z = 0{\cdot}32$) and for layer $B \pm 14{\cdot}0°$ ($\Delta z = 0{\cdot}12$). For γ-COPYCL, the direction of rotation of the pyridine rings about the Co–N bond is not uniquely determined by the relative *z* coordinate of adjacent Co atoms in each layer since this quantity is zero. However, once a direction of rotation is chosen, packing considerations would reproduce it

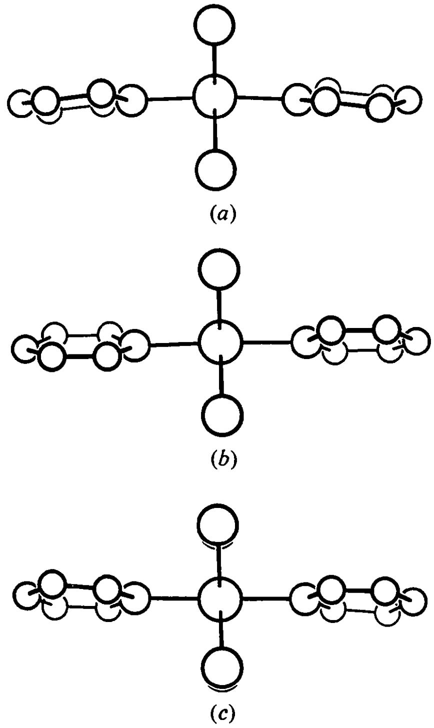

Fig. 5. Portions of the polymeric chains in the COPYCL structures viewed along the plane of the cobalt and chlorine atoms. (*a*) α-COPYCL, type *A*; (*b*) α-COPYCL, type *B*; (*c*) γ-COPYCL.

throughout the structure, and the observed magnitude of the inclination of the ring to (001), 11·0°, is again such that the closest centrosymmetrically related pyridine rings within each layer are in van der Waals contact (Table 13).

By far the greatest difference between the α- and γ-COPYCL structures concerns the distribution of the Co atoms along the *z* direction. The crystallographically independent layers in the α-COPYCL structure, which are approximately related by the non-crystallographic symmetry operation $(\frac{1}{4}+x,\frac{1}{4}-y,z-0{\cdot}6)$, become related by a crystallographic *n*-glide plane in the γ-form, and in addition the unit-cell axes *a* and *b* are halved in length. Therefore the Co atoms of types *A* and *B* which occur at $z=\pm0{\cdot}16$ and $\pm0{\cdot}44$ respectively in α-COPYCL move along *z* to $z=0{\cdot}0$ and $\pm0{\cdot}5$ during the transformation to γ-COPYCL (Figs. 1 and 3) with the remaining atoms in the polymeric chains moving by the same amount. Neglecting the small difference in the length of the *c* axis in the two forms, these changes are equivalent to a *z* shift of 0·58 Å in type *A* layers and 0·22 Å in type *B*.

Despite this considerable movement, and the reorientation of the pyridine rings, the van der Waals contact distances of α-COPYCL are maintained as such for γ-COPYCL, a typical result for a displacive phase transformation (Buerger, 1951). Indeed none of the intermolecular contacts involving only C or H atoms differs by more than 0·37 Å between the two crystal structures. [A full list of such contacts is given by Clarke (1973)]. In contrast, the intermolecular contacts between Cl and C or H atoms differ by up to 0·9 Å. The major changes of this type are given in Table 13. It would therefore appear that the packing in both structures is controlled by the interactions between C and H atoms since it is this type of interaction that remains largely unaltered by the phase transformation.

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