

the high-temperature phases cannot recover complete order at room temperature.

The description of the phases derived by the interpretation of X-ray measurements is in full agreement with the results obtained from spectroscopic (Mlik, Daoud & Couzi, 1980) and nuclear quadrupole resonance measurements. In Walther (1982) the observed angles of 50° between consecutive field-gradient directions in the *ab* plane are equal to the angles of the two N—H...Cl directions attached to the disordered Cl octahedra locked on the origin. This independent observation based on spectroscopic measurements fully confirms the model of disorder and the structures proposed in this article.

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Reversible Thermal Phase Transition in Crystalline (β -Cyanoethyl)bis(dimethylglyoximato)(4-methylpyridine)cobalt(III)

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Abstract

A reversible single crystal–single crystal thermal phase transition has been observed for the crystalline (β -cyanoethyl)bis(dimethylglyoximato)(4-methylpyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $C_{17}H_{25}CoN_6O_4$, [$Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_6H_7N)$]. The transition occurred at 357.5 K when the crystal was warmed but the reverse transition was observed at 327.6 K. Differential scanning calorimetry measurement revealed that the heat of transition was 4.1 kJ mol⁻¹. The crystal structures below and above the transition were determined by X-rays. Low-temperature phase (I): $T = 298$ K, $M_r = 436.36$, monoclinic, $P2_1/a$, $a = 30.979$ (9), $b = 9.0379$ (8), $c = 17.043$ (5) Å, $\beta = 124.07$ (2) $^\circ$, $V = 3953$ (2) Å³, $Z = 8$, $D_x = 1.467$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 9.43$ cm⁻¹, $F(000) = 1824$; high-temperature phase (II): $T = 363$ K, monoclinic, $P2_1/a$, $a = 32.03$ (5), $b = 8.902$ (3), $c = 8.83$ (1) Å, $\beta =$

126.02 (5) $^\circ$, $V = 2035$ (5) Å³, $Z = 4$, $D_x = 1.425$ g cm⁻³. The structures of (I) and (II) were solved by direct methods and refined by full-matrix least squares. The final *R* values were 0.059 and 0.083 for 5782 and 2208 observed reflections, respectively. Two crystallographically independent molecules in (I) are approximately related by a half-translation along the *c* axis except for the β -cyanoethyl groups. After the transition from (I) to (II), the conformations of the β -cyanoethyl groups of the two molecules became the same and the cell dimensions of the *c* axis reduced to half. The mechanism of the transition without degradation of the crystallinity is discussed comparing the cavities for the β -cyanoethyl groups before and after the transition.

Introduction

It has been found that the β -cyanoethyl group ($-CH_2-CH_2CN$) bonded to the Co atom is transformed to the α -cyanoethyl group [$-CH(CH_3)CN$] in the bis(di-

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Table 1. *Final atomic coordinates* ($\times 10^5$ for Co; $\times 10^4$ for C, N and O) and equivalent isotropic thermal parameters, B_{eq} (\AA^2), for non-H atoms for the low-temperature phase

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij}(\mathbf{a}_i, \mathbf{a}_j).$$

	x	y	z	B_{eq}
Co(A)	12936 (2)	30385 (6)	29596 (4)	2.2
N(1A)	1531 (1)	1077 (4)	3337 (3)	3.2
N(2A)	1628 (1)	2781 (4)	2325 (3)	2.8
N(3A)	1071 (1)	5012 (4)	2605 (3)	2.6
N(4A)	979 (1)	3290 (4)	3624 (3)	3.0
O(1A)	1454 (2)	310 (4)	3928 (3)	4.6
O(2A)	1667 (1)	3866 (4)	1808 (3)	3.7
O(3A)	1165 (1)	5784 (3)	2044 (2)	3.2
O(4A)	966 (2)	2215 (4)	4162 (3)	4.6
C(1A)	1775 (2)	483 (5)	3009 (4)	3.6
C(2A)	1834 (2)	1494 (5)	2391 (4)	3.4
C(3A)	815 (2)	5580 (5)	2921 (3)	2.7
C(4A)	763 (2)	4559 (6)	3532 (3)	3.4
C(5A)	1987 (3)	-1050 (6)	3217 (4)	5.1
C(6A)	2102 (2)	1060 (7)	1923 (5)	4.9
C(7A)	615 (3)	7125 (7)	2723 (5)	5.0
C(8A)	501 (3)	4967 (9)	4026 (5)	5.7
N(5A)	599 (1)	2287 (4)	1797 (2)	2.5
C(9A)	351 (2)	1119 (5)	1868 (3)	3.1
C(10A)	-125 (2)	611 (6)	1115 (4)	3.5
C(11A)	-364 (2)	1300 (5)	244 (3)	3.1
C(12A)	-113 (2)	2506 (6)	169 (3)	3.5
C(13A)	362 (2)	2953 (5)	947 (3)	3.0
C(17A)	-893 (2)	810 (8)	-595 (4)	5.0
C(14A)	1979 (2)	3630 (5)	4135 (3)	3.1
C(15A)	2119 (2)	5265 (5)	4358 (4)	3.4
C(16A)	1907 (2)	5985 (5)	4839 (4)	3.9
N(6A)	1756 (2)	6576 (6)	5229 (4)	6.1
Co(B)	13989 (2)	29290 (6)	79055 (4)	2.5
N(1B)	1644 (1)	972 (4)	8179 (3)	2.8
N(2B)	1667 (1)	2811 (4)	7147 (3)	2.9
N(3B)	1162 (2)	4909 (4)	7650 (3)	3.4
N(4B)	1152 (2)	3045 (4)	8694 (3)	3.3
O(1B)	1613 (1)	100 (4)	8788 (2)	3.7
O(2B)	1672 (2)	3972 (4)	6644 (3)	4.4
O(3B)	1198 (2)	5762 (4)	7046 (3)	4.8
O(4B)	1181 (2)	1883 (4)	9238 (3)	4.5
C(1B)	1841 (2)	453 (5)	7732 (3)	3.0
C(2B)	1853 (2)	1545 (5)	7116 (3)	3.0
C(3B)	964 (2)	5396 (5)	8102 (4)	3.8
C(4B)	962 (2)	4284 (6)	8716 (4)	3.8
C(5B)	2054 (2)	-1080 (6)	7855 (4)	4.5
C(6B)	2081 (2)	1240 (7)	6552 (4)	4.4
C(7B)	765 (3)	6933 (7)	7994 (7)	6.3
C(8B)	754 (3)	4558 (9)	9320 (5)	5.8
N(5B)	682 (1)	2187 (4)	6792 (3)	2.6
C(9B)	435 (2)	1075 (5)	6902 (3)	3.2
C(10B)	-55 (2)	612 (5)	6184 (4)	3.4
C(11B)	-314 (2)	1284 (5)	5304 (4)	3.4
C(12B)	-50 (2)	2404 (6)	5185 (4)	3.7
C(13B)	442 (2)	2828 (5)	5942 (3)	3.2
C(17B)	-858 (2)	866 (8)	4520 (4)	5.2
C(14B)	2083 (2)	3787 (6)	8964 (4)	3.9
C(15B)	2535 (2)	2744 (7)	9637 (4)	4.8
C(16B)	2836 (2)	2191 (7)	9265 (5)	5.4
N(6B)	3079 (2)	1815 (8)	9010 (5)	8.2

Table 2. *Final atomic coordinates* ($\times 10^5$ for Co; $\times 10^4$ for C, N and O) and equivalent isotropic thermal parameters, B_{eq} (\AA^2), for non-H atoms for the high-temperature phase

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij}(\mathbf{a}_i, \mathbf{a}_j).$$

	x	y	z	B_{eq}
Co	13159 (4)	30193 (11)	59185 (13)	3.8
N(1)	1570 (3)	1029 (8)	6513 (10)	5.5
N(2)	1616 (3)	2919 (7)	4608 (10)	5.5
N(3)	1087 (3)	5000 (9)	5410 (9)	4.6
N(4)	1029 (3)	3125 (10)	7292 (10)	5.0
O(1)	1520 (3)	157 (7)	7641 (9)	7.5
O(2)	1605 (3)	4112 (10)	3635 (10)	8.2
O(3)	1128 (4)	5918 (9)	4287 (13)	7.5
O(4)	1058 (4)	1953 (12)	8305 (11)	7.5
C(1)	1792 (3)	536 (11)	5791 (16)	6.6
C(2)	1816 (3)	1627 (15)	4656 (15)	6.8
C(3)	870 (3)	5504 (10)	6139 (13)	5.5
C(4)	850 (4)	4386 (11)	7310 (13)	5.7
C(5)	2017 (6)	-1002 (15)	6164 (23)	10.8
C(6)	2061 (6)	1427 (24)	3641 (25)	11.7
C(7)	670 (6)	7078 (12)	5837 (27)	9.7
C(8)	647 (7)	4659 (20)	8445 (23)	9.9
N(5)	619 (2)	2288 (7)	3594 (8)	3.4
C(9)	369 (3)	1129 (9)	3700 (10)	4.3
C(10)	-105 (3)	633 (9)	2197 (12)	4.7
C(11)	-343 (3)	1315 (10)	482 (10)	4.6
C(12)	-85 (3)	2494 (10)	370 (11)	4.6
C(13)	388 (3)	2907 (8)	1913 (11)	4.1
C(17)	-878 (3)	856 (14)	-1189 (15)	7.2
C(14)	1971 (3)	3715 (14)	8312 (14)	7.5
C(15)	2414 (4)	4246 (14)	8306 (19)	9.6
C(16)	2744 (4)	2965 (14)	8541 (17)	8.8
N(6)	3020 (4)	2179 (15)	8573 (20)	11.7

Table 3. *Selected bond distances* (\AA), *angles* ($^\circ$) and *torsional angles* ($^\circ$)

	298 K (A)	298 K (B)	363 K
Co-N(1)	1.889 (5)	1.878 (4)	1.891 (9)
Co-N(2)	1.886 (5)	1.892 (4)	1.892 (9)
Co-N(3)	1.886 (4)	1.890 (5)	1.860 (8)
Co-N(4)	1.876 (4)	1.884 (5)	1.907 (8)
Co-N(5)	2.059 (4)	2.065 (4)	2.057 (7)
Co-C(14)	2.010 (6)	2.015 (7)	2.009 (13)
N(1)-Co-N(2)	81.1 (2)	81.1 (2)	80.5 (4)
N(1)-Co-N(4)	98.3 (2)	98.3 (2)	99.1 (4)
N(1)-Co-N(5)	90.9 (2)	90.0 (2)	91.0 (3)
N(1)-Co-C(14)	85.3 (2)	93.7 (2)	89.1 (5)
N(2)-Co-N(3)	98.8 (2)	99.2 (2)	99.6 (4)
N(3)-Co-N(4)	81.8 (2)	81.4 (2)	80.7 (4)
N(2)-Co-C(14)-C(15)	-96.4 (5)	84.4 (5)	-13.0 (11)
Co-C(14)-C(15)-C(16)	-83.7 (6)	-81.2 (7)	86.4 (14)
N(2)-Co-N(5)-C(9)	-123.0 (4)	-130.2 (4)	-128.7 (7)

single-crystal form. The crystal-structure analyses before and after the transition using one crystal revealed that the transition was followed by a conformational change of the β -cyanoethyl group (cn group). The opposite transition was observed upon cooling, the single-crystal form being retained. Such a reversible single crystal-single crystal phase transition with a conformational change is very rare, although a reversible monomer-dimer transformation of the cobalt complex crystal has been reported (Miller, Brill, Rheingold & Fultz, 1983).

Experimental

The title complex was synthesized in the same way as reported previously (Ohgo, Takeuchi, Natori,

methylglyoximate), cobaloxime, complexes when the powdered sample is exposed to visible light (Ohgo & Takeuchi, 1985). Several crystals with different base ligands were prepared to examine the relationship between the structure and the reactivity (Uchida, Ohashi, Sasada & Ohgo, 1985; Uchida, Ohashi & Sasada, 1986; Uchida, Danno, Sasada & Ohashi, 1987).

When the crystal of (β -cyanoethyl)(4-methylpyridine)cobaloxime was warmed to about 360 K to examine the reactivity at high temperatures, a phase transition was found to occur without destroying the

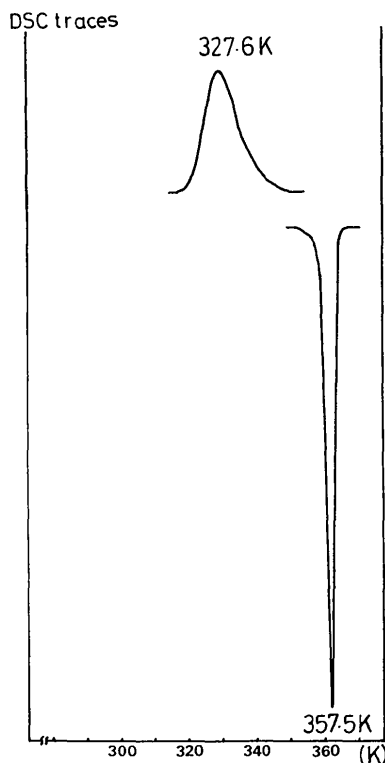
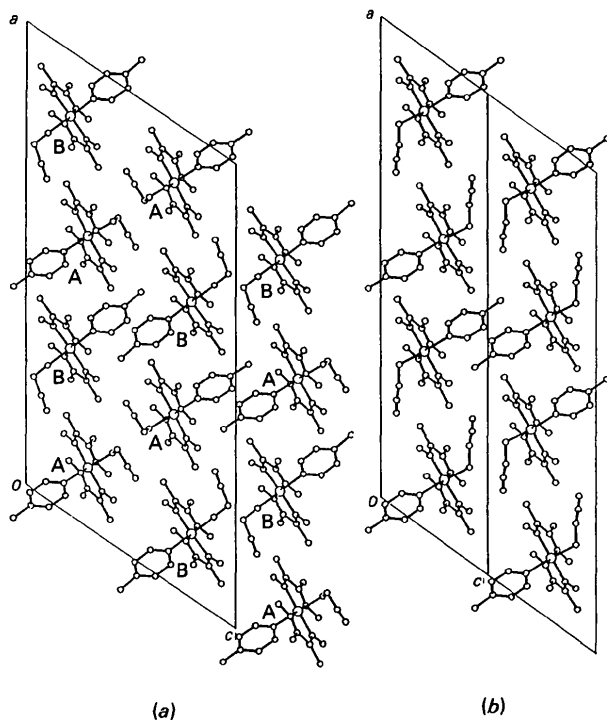


Fig. 1. DSC diagram of the phase transition.

Fig. 2. Crystal structures of (a) low-temperature phase and (b) high-temperature phase, viewed along the *b* axis.

Yoshimura, Ohashi & Sasada, 1981). Low-temperature-phase crystals were obtained from a methanol solution.

Low-temperature phase (I)

Orange rod-like crystals. Preliminary unit-cell dimensions and space group determined from photographs; systematic absences $h = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$. Crystal size $0.3 \times 0.3 \times 0.5$ mm, Rigaku AFC-4 diffractometer; Mo $K\alpha$ monochromated by

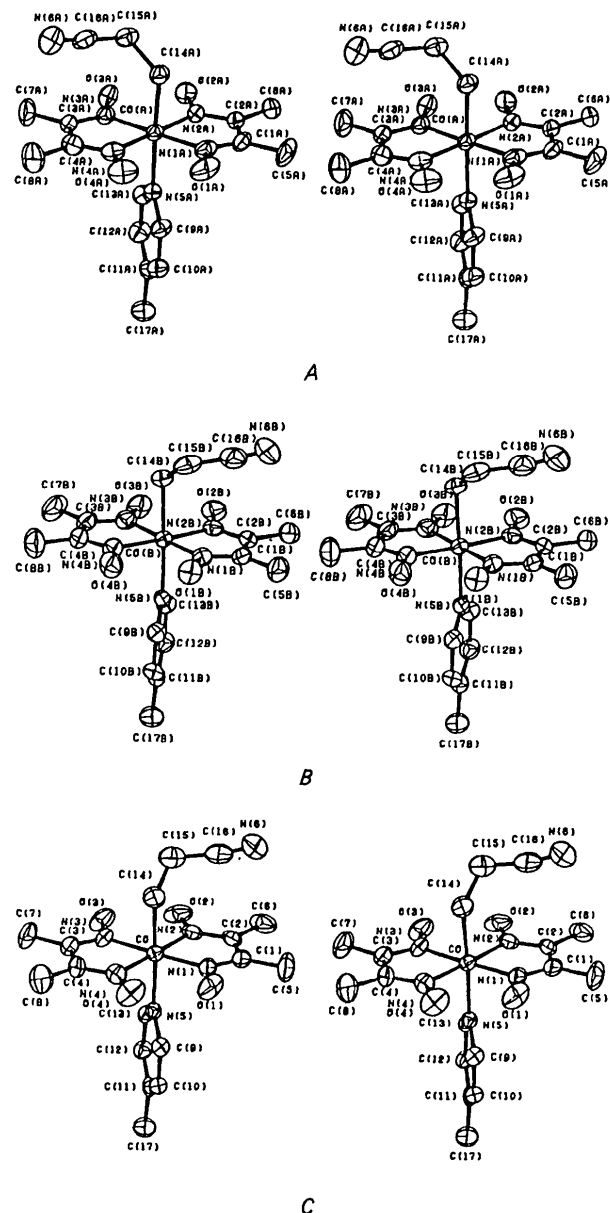


Fig. 3. Molecular structures of A and B of the low-temperature phase and C of the high-temperature phase. Thermal ellipsoids of 50 and 30% probability levels for low and high temperatures, respectively.

graphite, unit-cell dimensions from 2θ values of 15 reflections in the range $20 < 2\theta < 29^\circ$. Intensities measured up to $2\theta = 50^\circ$, range of hkl -36 to 30, 0 to 10 and 0 to 19, $\omega/2\theta$ scan mode, scan rate $4^\circ (\theta) \text{ min}^{-1}$, scan width $(1.0 + 0.35 \tan\theta)^\circ$, stationary background counts accumulated for 5 s before and after each scan. 6900 independent reflections, of which 5782 with $|F_o| > 3\sigma(|F_o|)$ used for structure determination. No absorption corrections. No intensity variation of standard reflections.

Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976). Positions of

all H atoms except those of methyl groups obtained from a difference map. Positions of H atoms of methyl groups refined as a rigid body in which C-H was 1.00 \AA and H-C-H a tetrahedral angle. Anisotropic and isotropic thermal parameters for the non-H atoms and H atoms, respectively. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(|F_o|)^2 + 0.009267(|F_o|)^2]^{-1}$; $(\Delta/\sigma)_{\text{max}} = 0.5$; $\Delta\rho_{\text{max}} = 0.4 \text{ e \AA}^{-3}$; $R = 0.059$ and $wR = 0.102$ for 5782 reflections, $S = 1.005$. The atomic parameters for the non-H atoms are given in Table 1.

High-temperature phase (II)

The same crystal as used for the structure analysis of the low-temperature phase was kept at $363 \pm 1 \text{ K}$ by use of the hot-air flow method. Space group determined from three-dimensional intensities measured with the diffractometer. Unit-cell dimensions from 2θ values of 15 reflections in the range $19 < 2\theta < 27^\circ$. Intensities measured up to $2\theta = 45^\circ$, range of hkl -34 to 27, 0 to 9 and 0 to 9, 2678 reflections, of which 2208 with $|F_o| > 3\sigma(|F_o|)$ used for structure determination.

Structure solved by direct methods, refined by full-matrix least squares. Positions of all H atoms except those of methyl groups obtained from a difference map. Positions of H atoms of methyl groups refined in the same manner as described above. Anisotropic and isotropic thermal parameters for the non-H atoms and H atoms, respectively. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(|F_o|)^2 + 0.002847(|F_o|)^2]^{-1}$; $(\Delta/\sigma)_{\text{max}} = 0.2$; $\Delta\rho_{\text{max}} = 0.8 \text{ e \AA}^{-3}$; $R = 0.083$ and $wR = 0.100$ for 2208 reflections, $S = 1.358$. The high R value may be caused by slight decomposition of the crystal and some disordering of the molecules in the process of the phase transition. The

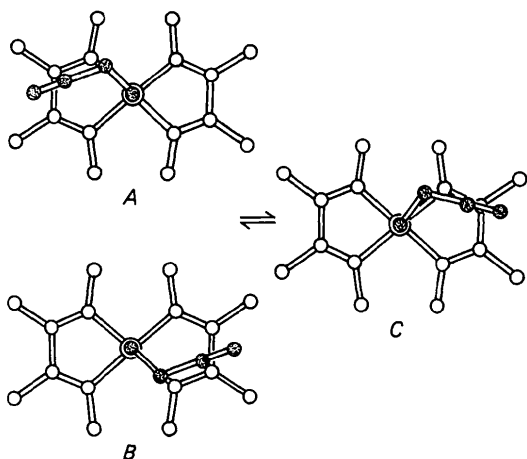


Fig. 4. Conformations of the cn groups of the *A*, *B* and *C* molecules, viewed along the normal to the cobaloxime plane.

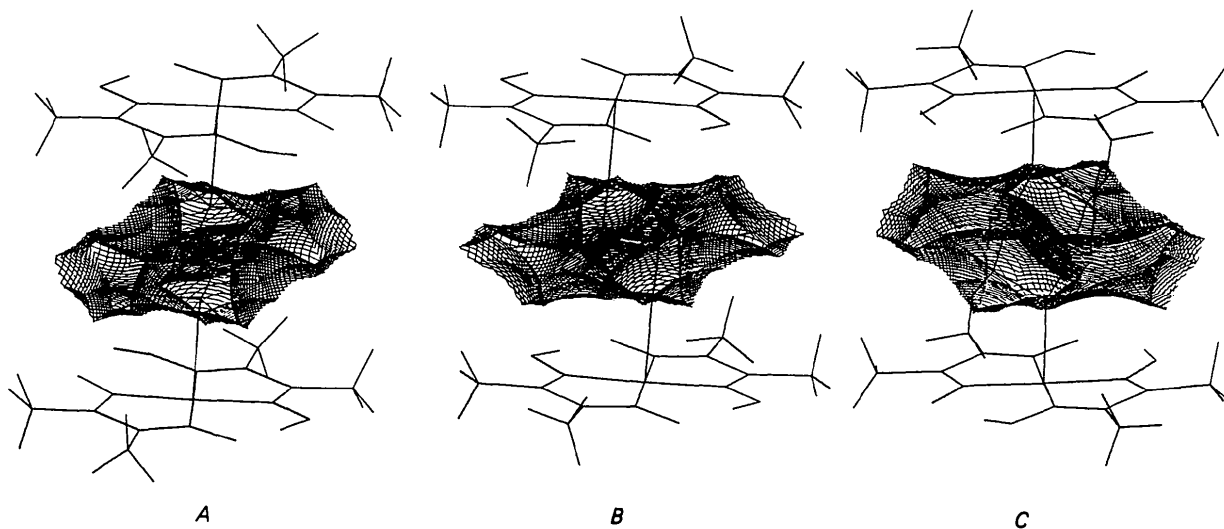


Fig. 5. Cavities for the *A*, *B* and *C* cn groups. Each cavity is drawn for two cn groups along the 2, axis. Contours are drawn in sections separated by 0.1 \AA .

atomic parameters for non-H atoms are given in Table 2.*

The crystal was cooled to room temperature and the intensity data were collected. Essentially the same structure as that of the low-temperature phase was obtained. However, several small peaks less than $1.0 \text{ e } \text{\AA}^{-3}$ were found in the neighborhood of the *cn* group in the difference map.

Atomic scattering factors including the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The calculation was carried out on a FACOM-HITAC system computer at this Institute.

DSC measurement

The enthalpy change of the phase transition was measured on a Rigaku L-DSC differential scanning calorimeter with an air atmosphere, temperature range 273 to 373 K and heating or cooling rate 10 K min^{-1} . Fig. 1 shows the heating and cooling scan. A single endotherm or exotherm was observed in increasing or decreasing temperature, respectively. Indium metal was used for calibration.

Results and discussion

Structure of phase (I)

Fig. 2(a) shows the crystal structure at 298 K viewed along the *b* axis. Except for the *cn* group, two independent molecules, *A* and *B*, are related by a half-translation along the *c* axis. The *cn* groups of *A* and *B* molecules, *A* and *B* *cn* groups, are connected by 2_1 axes at $Z=0$ and $Z=\frac{1}{2}$, respectively, to form ribbons along the *b* axis, and the two ribbons are arranged alternatively along the *c* axis. The ribbons are surrounded by the rigid cobaloxime and 4-methylpyridine moieties. There are no unusually short contacts between the molecules.

Fig. 3 shows the structures of *A* and *B* molecules with the numbering of the atoms. Selected bond distances, bond angles and torsional angles are listed in Table 3. There is no significant difference in the structures of *A* and *B* molecules except for the torsional angle around the Co—C bond. The conformation of the *B* *cn* group can be obtained if the *A* *cn* group is rotated by 180° around the Co—C bond.

Structure of phase (II)

The crystal structure of 363 K viewed along the *b* axis is drawn in Fig. 2(b). As the result of con-

formational change of the *cn* groups in (I), *A* and *B* molecules become the same and are related by a crystallographic translation along the *c* axis. Then the length of *c* becomes a half.

Fig. 3 also shows the molecular structure of phase (II) with the numbering of the atoms (*C* molecule). Bond distances and angles are in fair agreement with those of *A* and *B* molecules. The torsional angles around the Co—C(14) and C(14)—C(15) bonds vary significantly before and after the phase transition. Fig. 4 shows the conformations of the *cn* groups of *A*, *B* and *C* molecules viewed along the normal to their cobaloxime planes. The *A* and *B* *cn* groups are related to *C* by mirror planes through the short and long axes of the cobaloxime plane, respectively.

Comparison of the cavities

In order to explain the conformational change of the *cn* groups with retention of the crystallinity, the cavities for the *A*, *B* and *C* *cn* groups (*A*, *B* and *C* cavities) were calculated. Fig. 5 shows the three cavities. Since the *cn* groups are connected by a 2_1 axis in each crystal structure, the cavity for the two *cn* groups along the 2_1 axis is given for each case. The volumes of the *A*, *B* and *C* cavities were calculated to be 24.41 , 37.20 and 39.53 \AA^3 , respectively. At the phase transition, the *A* and *B* cavities would be greater and the *C* cavity may be smaller than the above values. The cavity for the α -cyanoethyl group in crystalline [(*R*)- α -cyanoethyl]-piperidine)cobaloxime increased in volume by 2.5 \AA^3 when the temperature was raised from 293 to 333 K (Danno, 1986). This means that the cavity for two *cn* groups may increase or decrease by 5 \AA^3 in the temperature change of 40 K. Therefore, the average volume of the *A* and *B* cavities would become the same as the volume of the *C* cavity at the transition point. This would cause the phase change without degradation of the crystallinity. The structure analyses of both phases at the same temperature are in progress.

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* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and structure factors for phases (I) and (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44614 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Electron Density in the Spin Crossover Complex *trans*-[N,N'-Ethylenebis(salicylideneaminato)]bis(imidazole)iron(III) Perchlorate

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Abstract

The title compound, [Fe(salen)(imd)₂]ClO₄, [Fe(C₁₆H₁₄N₂O₂)(C₃H₄N₂)₂]ClO₄, has an orthorhombic structure, *P*2₁2₁2₁ with *Z* = 4, *a* = 15.411 (7), *b* = 13.328 (7), *c* = 11.149 (4) Å at 120 K, and *a* = 15.556 (6), *b* = 13.495 (6), *c* = 11.468 (4) Å at 295 K, λ(Mo *K*α) = 0.71069 Å, *M_r* = 557.77, *F*(000) = 287. Over that temperature range the magnetic moment increases sharply from 2.1 to 5.5 Bohr magnetons. The Fe atom coordinates in a slightly distorted octahedron with four N and two O ligands. The plane of one imidazole group bisects two N–Fe–O angles. The other is approximately coplanar with Fe–N and Fe–O vectors. The average length of the Fe–N bonds increases by 0.16 Å during that transition. Atomic charges derived from the electron difference density indicate that roughly 0.5 electrons are transferred to the Fe/ligand system in the spin transition. The changes in the topography of the density from low to room temperature are related to the increases in bond lengths, but are inconsistent with a model for the electron density derived from 3*d* states alone. The maxima are tetrahedrally disposed, and oriented so as to reduce interaction with the ligating N and O atoms. The idealized form of the low-temperature difference density is consistent with that expected for *both* imidazole rings oriented in the bisecting position, and at right angles to each other. This would favour interaction between the lone-pair 3*d* electrons and four imidazole H atoms.

Introduction

Changes in spin state induce marked changes in the structural geometries of crystalline materials. Reversible temperature-dependent spin transitions are favourable for study, because of the simple relationship between the structures of the low- and high-temperature forms. It may be difficult to characterize the states

Table 1. *Crystal data and refinement details*

	120 K	295 K
<i>V</i> (Å ³)	2290 (2)	2407 (2)
<i>D_x</i> (Mg m ⁻³)	1.617	1.538
<i>μ</i> (mm ⁻¹)	0.826	0.786
<i>N</i> measured	25572	17599
<i>N</i> unique	7215	4866
<i>h, k, l</i> range	0 ~ <i>h</i> ~ 27, 0 ~ <i>k</i> ~ 23, 0 ~ <i>l</i> ~ 19	0 ~ <i>h</i> ~ 23, 0 ~ <i>k</i> ~ 20, 0 ~ <i>l</i> ~ 17
(sinθ)/λ (Å ⁻¹)	< 0.883	< 0.856
<i>R_{int}</i>	0.025	0.026
<i>R</i>	0.071	0.074
<i>wR</i>	0.042	0.042
<i>S</i>	1.51 (1)	2.14 (2)
1/σ _{max}	0.01	0.01

involved from structural geometry alone, and in principle measurement of the difference density by diffraction experiments should help in identifying the states involved in the transition. However, spin crossover complexes are labile because of their structural instability, and it is difficult to achieve the accuracy desired in the diffraction data.

The magnetic properties of the spin crossover complex [Fe(salen)(imd)₂]ClO₄ were determined by Kennedy, McGrath, Murray, Skelton & White (1987), who also determined crystal structures below (120 K) and above (295 K) the transition. The system is a useful model for studying spin equilibrium in heme proteins. The quality of the diffraction data indicated that, with care, the standards required for a charge density study of modest quality might be achieved.

Experimental

The data sets measured by Kennedy, McGrath, Murray, Skelton & White (1987) were scrutinized and carefully extended. Crystal irregularly shaped with (10 $\bar{1}$), (12 $\bar{1}$), (011), (101), (1 $\bar{2}$ 0), (2 $\bar{0}$ 1), (1 $\bar{2}$ 1), (02 $\bar{1}$) faces at distances of 0.11, 0.17, 0.10, 0.14, 0.148, 0.11, 0.10 and 0.30 mm respectively from a common centre. Data measured on a Syntex *P*₂ diffractometer