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The Structure and Solid-State Reactivity of a New Polymorph of Tetrakis(4-vinylpyridine)diisothiocyanatocobalt(II)

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The crystal structure of $Co(NCS)_2[4\text{-vinylpyridine}]_4$ *has been determined by X-ray diffraction methods. The complex crystallizes in space group* Pbca, *with* $a = 32.293(15)$ Å, $b = 11.416(6)$ Å, $c = 17.033(10)$ Å, *and* $Z = 8$. *Full-matrix least-squares refinement of positional and thermal parameters for all atoms (H atoms fixed at calculated positions), with 1458 reflections* ($F > 3.92\ \sigma(F)$) *led to* $R = 0.075$ *and* $R_w = 0.079$. *The* trans-*octahedral complex consists of four vinylpyridine ligands, arranged in a propeller-shape, and two isothiocyanate ligands. Powder diffraction of* $Co(NCS)_2(4\text{-vinylpyridine})_2$ *indicates an isometric cell, with* $a = 13.77$ Å. *The analogous Ni(II) complexes are isomorphous with the Co(II) complexes, suggesting that the yellow–green complex* $Ni(NCS)_2(4\text{-vpy})_2$, *previously thought to be polymeric, is in fact tetrahedral.*

Introduction

In organic solid-state polymerization reactions, the constraints imposed by the crystal lattice may promote the formation of highly oriented, crystalline product [1]. Single crystals of an organic monomer contain a basic repeat unit, *e.g.*, a carbon–carbon multiple bond, which is an inherent part of the reactant. In transition metal solid-state chemistry, the use of complexes with polyfunctional ligands may allow a close analogy to be drawn to the organic species. For example, we have shown that square-planar nickel(II) complexes of tris (2-cyanoethyl)phosphine polymerize in the solid state to produce polymer crystals with 'single crystal' diffraction properties [2], and also undergo polymorphic transitions [3]. We have endeavored to extend our study of such processes to metal complexes with other polyfunctional ligands.

It has been demonstrated that cobalt(II) and nickel(II) complexes of 4-vinylpyridine undergo a series of interesting solid-state reactions [4, 5], and also have the ability to act as preferential clathrates [6]. The reactivity of these complexes, *i.e.*

$$\text{M (substituted pyridine)}_4X_2 \xrightarrow[\Delta]{-2py} \text{M(substituted pyridine)}_2X_2,$$

where X = halogen or pseudohalogen group, is initially similar to that of the analogous pyridine, lutidine, picoline and quinoline complexes [7]. Dichlorobis(4-vinylpyridine)cobalt(II) exists in two forms: an α, low density, blue form [8] and a β, high density, violet form [9]. The α form is tetrahedrally coordinated while the β form is octahedrally coordinated *via* bridging chlorine atoms. Upon heating, the vinyl groups of the α form polymerize. However, the vinyl groups in the β form do not polymerize; rather, the β form undergoes a solid-state reaction to produce the α form.

Extensive differential scanning calorimetry and optical microscopic studies have been carried out on the solid-state reaction of $Co(4\text{-vinylpyridine})_4(NCS)_2$ [5]. In an attempt to comment on the molecular mechanism of the transformation $Co(4\text{-vpy})_4(NCS)_2 \xrightarrow{\Delta} Co(4\text{-vpy})_2 + 2(4\text{-vpy})$ we synthesized a previously uncharacterized polymorph of $Co(4\text{-vpy})_4(NCS)_2$. The present work is a study of the preparation and molecular structure of that material and its decomposition reaction in the solid state.

Experimental

Stoichiometric amounts of $Co(NCS)_2$ (Alfa/Ventron) and 4-vinylpyridine (Aldrich) are mixed in absolute ethanol; red crystals form upon standing for ten hours. $Co(NCS)_2(4\text{-vinylpyridine})_2$ can be obtained by prolonged heating (~6 h) of the red crystals at 115 °C, upon which they become blue. The analogous nickel complexes (which are iso-

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TABLE I. Data for the X-ray Diffraction Study of Tetrakis(4-vinylpyridine)diisothiocyanatocobalt(II).

(A) Crystal Data at 20(1) °C

Crystal system: orthorhombic
Space group: *Pbca* [D_{2h}^{15}; No. 61]

a = 32.293(15) A
b = 11.416(6) A
c = 17.033(6) A
V = 6279.3 A^3

$Z = 8$
crystal size: 0.25 × 0.08 × 0.06 mm
(elongated along b)
formula wt. = 595.69
ρ(calcd) = 1.260 g-cm^{-3}
ρ(obsd)^a = 1.28(1) g-cm^{-3}
μ = 7.3 cm^{-1} (MoKα)

Cell constant determination: 6 pairs of ±(hkl) and refined 2θ, ω, χ values in the range $23 < |2\theta| < 24°$ (λ (MoK$\bar{\alpha}$) 0.71073 A)

(B) Measurement of Intensity Data

Radiaton: MoKα
Reflections measured: –h, +k, +l (to 2θ = 42°)
Scan type, speed: ω, variable, 1.95–3.91°/min
Scan range: 1° with a 1° displacement in ω for background from Kα position: background time/scan time = 0.5
No. of reflections measured: 3899 total; 3259 in unique set
Standard reflections: $\bar{2}20$, $\bar{1}\bar{2}4$, $\bar{2}\bar{9}\bar{1}$, showed a 19% decrease with time; two linear, time dependent corrections were applied
Automatic recentering after every 1000 reflections
Absorption correction: empirical

(C) Treatment of Intensity Data^b

Data reduction: intensities as before [10]; esd's of $|F_o|$ values calcd by method of finite differences, after Churchill *et al.*^{c}
Statistical information: $R_s = 0.051$ ($I > 1.96\sigma(I)$)

(D) Refinement^d, with 1458 Data for which $F > 3.92\sigma(F)$

Weighting of reflections: $w = [\sigma^2(|F_o|) + (p|F_o|)^2]^{-1}$; p = 0.030
Isotropic refinement, all nonhydrogen atoms: $R = 0.106$; $R_w = 0.115$
Anisotropic refinement fo Co, S(1), S(2), isotropic refinement of the remaining nonhydrogen atoms, fixed contributions from the hydrogen atoms: $R = 0.075$; $R_w = 0.079$
Structure factor calcn, all 3259 data: $R = 0.190$; $R_w = 0.092$
Standard deviation of an obsvn of unit weight (SDU): 1.5120
Final difference Fourier map: random peaks ⩽ 0.48 e/A^3

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[a] Measured by flotation in C_2H_5OH–$CHCl_3$. [b] $R_s = \Sigma\sigma(|F_o|)/\Sigma|F_o|$. [c] M. R. Churchill, R. A. Lashewycz and F. J. Rotella, *Inorg. Chem., 16,* 265 (1977). [d] $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$. SDU = $\{\Sigma w[|F_o|-|F_c|]^2/(m-n)\}^{1/2}$ where m (=1458) is the number of observations and n (=172) is the number of parameters.

morphous) can be formed similarly; a color change from blue to yellow-green is noted.

Collection and Reduction of Diffraction Data

Preliminary Weissenberg (h0l, hll) photographs showed the symmetry and characteristic absences 0kl, k = 2n + 1, h0l, l = 2n + 1; hk0, h = 2n + 1 of the space group *Pbca.* A crystal was mounted on a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Most operations were carried out as described previously [10]; other operations are described below. Details of the structure analysis, in outline form, are presented in Table I.

Solution and Refinement

The analysis was performed on a Syntex XTL structure determination system [11]. The analytical scattering factors of Cromer and Waber were used [12a]; real and imaginary components of anomalous scattering were included in the calculations for all nonhydrogen atoms [12b]. The cobalt atom position was found from a three-dimensional Patterson map. Subsequent difference Fourier syntheses and structure factor calculations revealed the remaining atomic positional parameters.

On the final cycles of least-squares refinement, only the Co and S were assigned anisotropic temperature factors; H atoms were fixed at calculated positions (r_{C-H} = 0.95 Å) with temperature factors one unit higher than that of the carbon atom to which they were bonded. At convergence, [$\Delta/\sigma_{max} \leqslant 0.31$], a weighting scheme analysis revealed no systematic dependence of $w[|F_o|-|F_c|]^2$ on $|F_o|$, ($\sin\theta/\lambda$), parity of indices, or sequence number. Table II lists thepositional and isotropic temperature factors for all atoms.

TABLE II. Atomic Coordinates and Isotropic Temperature Factors.[a]

Atom	X	Y	Z	UISO
CO	0.133079(63)	0.07132(15)	−0.05968(11)	0.0571(12)
S(1)	0.19088(17)	0.20270(36)	−0.30521(27)	0.0978(37)
S(2)	0.09133(19)	−0.11660(46)	0.18030(34)	0.1350(49)
N(1)	0.15567(37)	0.13940(95)	−0.16592(74)	0.0694(37)
N(2)	0.10908(34)	0.0029(10)	0.04180(69)	0.0653(36)
N(3)	0.16006(39)	−0.09966(96)	−0.08951(67)	0.0702(39)
N(4)	0.10583(36)	0.2406(10)	−0.03372(74)	0.0680(37)
N(5)	0.07777(40)	0.01386(97)	−0.12270(73)	0.0735(38)
N(6)	0.18946(33)	0.11585(86)	0.00009(64)	0.0528(32)
C(1)	0.17051(43)	0.1667(11)	−0.22583(88)	0.0569(43)
C(2)	0.10230(46)	−0.0497(13)	0.09709(94)	0.0714(48)
C(3)	0.14087(47)	−0.1999(13)	−0.07128(87)	0.0778(49)
C(4)	0.15378(55)	−0.3096(14)	−0.10178(98)	0.0886(55)
C(5)	0.18592(51)	−0.3135(13)	−0.15382(94)	0.0762(50)
C(6)	0.20669(48)	−0.2133(13)	−0.16972(86)	0.0774(50)
C(7)	0.19364(49)	−0.1089(12)	−0.13628(88)	0.0684(46)
C(8)	0.20330(75)	−0.4276(22)	−0.1966(14)	0.1482(87)
C(9)	0.1876(10)	−0.5086(27)	−0.1908(17)	0.223(14)
C(10)	0.08916(54)	0.3070(15)	−0.0893(10)	0.0973(61)
C(11)	0.07136(55)	0.4191(16)	−0.0739(11)	0.1073(59)
C(12)	0.07292(52)	0.4628(13)	−0.0035(11)	0.0852(54)
C(13)	0.09123(55)	0.3980(14)	0.0515(11)	0.0946(56)
C(14)	0.10765(46)	0.2872(12)	0.03597(93)	0.0696(48)
C(15)	0.05687(73)	0.5886(20)	0.0239(14)	0.1452(85)
C(16)	0.03742(91)	0.6451(24)	−0.0186(17)	0.194(12)
C(17)	0.03927(55)	0.0179(13)	−0.09119(87)	0.0801(50)
C(18)	0.00662(54)	−0.0470(14)	−0.1190(11)	0.0928(56)
C(19)	0.01015(55)	−0.1156(13)	−0.18535(97)	0.0829(53)
C(20)	0.04784(54)	−0.1163(12)	−0.22022(86)	0.0725(48)
C(21)	0.08006(48)	−0.0519(13)	−0.19041(91)	0.0754(48)
C(22)	−0.03083(78)	−0.1867(21)	−0.2089(14)	0.1494(88)
C(23)	−0.02311(92)	−0.2665(26)	−0.2371(19)	0.217(14)
C(24)	0.21178(46)	0.2102(12)	−0.01604(83)	0.0630(43)
C(25)	0.24899(47)	0.2373(12)	0.01530(83)	0.0626(41)
C(26)	0.26733(45)	0.1648(12)	0.06738(87)	0.0660(44)
C(27)	0.24453(46)	0.0632(12)	0.08552(78)	0.0691(43)
C(28)	0.20645(42)	0.0433(10)	0.05195(82)	0.0567(40)
C(29)	0.30733(57)	0.1895(14)	0.1049(10)	0.0895(56)
C(30)	0.32971(60)	0.1240(16)	0.1445(12)	0.1179(70)

[a] Standard deviations in the least significant digit appear in parentheses in this and subsequent tables. For atoms refined anisotropically, $U_{iso} = U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Supplementary Data Available

Tables of anisotropic thermal parameters, H atom coordinates, and observed *vs.* calculated structure factors are available on request from the Editor or the authors.

Results and Discussion

The molecular structure of the octahedral complex is depicted in Fig. 1. The Co–N(isothiocyanate) bond lengths, 2.100(13) Å and 2.049(12) Å, are comparable to the 2.086(7) Å bond length found in the low-density form of $Co(NCS)_2(4\text{-vinylpyridine})_4$, reportedly an 'unsolvated' or desorbed clathrate complex [13]. The Co–N–C–(isothiocyanate linkage) angles, however, 173.0(11)° and 166.4(12)°, are nearer to linearity than those in the desorbed form (161.4(7)°). The geometrical arrangement of the vinylpyridine rings with respect to one another and to the plane defined by the four N(pyridine) atoms is comparable to that found in the desorbed form, nickel 4-methylpyridine complexes [14], and other tetrakis (pyridine or substituted pyridine) complexes [15]. The vinylpyridine rings are arranged in a staggered 'propeller' configuration. The rings *trans* to

TABLE III. Selected Bond Lengths (Å) and Angles (deg).

Co–N(1)	2.100(13) Å	Co–N(1)–C(1)	173.0(11)°
N(1)–C(1)	1.17(2)	N(1)–C(1)–S(1)	179.2(13)
C(1)–S(1)	1.56(2)	Co–N(2)–C(2)	166.4(12)
Co–N(2)	2.049(12)	N(2)–C(2)–S(2)	175.6(14)
N(2)–C(2)	1.14(2)	N(1)–Co–N(2)	177.8(5)
C(2)–S(2)	1.65(2)	N(3)–Co–N(4)	178.3(4)
Co–N(3)	2.197(11)	N(5)–Co–N(6)	175.8(4)
Co–N(4)	2.169(12)	C(5)–C(8)–C(9)	120.1(26)
Co–N(5)	2.185(13)	C(12)–C(15)–C(16)	119.6(23)
Co–N(6)	2.147(11)	C(19)–C(22)–C(23)	110.8(25)
C(5)–C(8)	1.60(3)	C(26)–C(29)–C(30)	129.3(17)
C(8)–C(9)	1.06(4)		
C(12)–C(15)	1.60(3)		
C(15)–C(16)	1.16(4)		
C(19)–C(22)	1.60(3)		
C(22)–C(23)	1.06(4)		
C(26)–C(29)	1.47(2)		
C(29)–C(30)	1.24(3)		

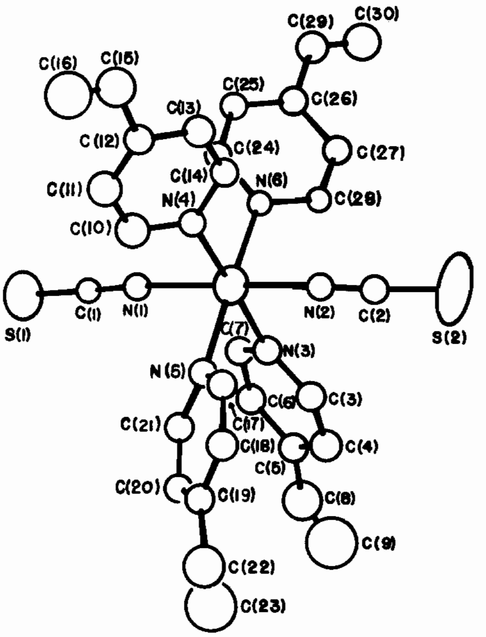

Fig. 1. Molecular structure of the complex.

one another are nearly orthogonal (N(3) ring 108° to N(4) ring; N(5) ring 94° to N(6) ring). There are no intermolecular contacts less than the sum of the corresponding van der Waals radii, either in the present crystal structure or in that of the low-density polymorph [13]. However, as might be expected, the intermolecular contacts are shorter and more numerous in the high-density polymorph. Table III lists other pertinent bond lengths and angles.

TABLE IV. Powder Pattern of $Co(NCS)_2(4\text{-vinylpyridine})_2$.

Number	Intensity	hkl
1	95	220
2	50	222
3	60	400
4	70	422
5	50	432, 520
6	100	600, 442
7	40	730
8	80	650, 643
9	20	820, 644
10	20	664
11	20	864, 1004
12	20	880
13	20	884, 1200
14	20	888

Thermal decomposition of $Co(4\text{-}vpy)_4(NCS)_2$

Agnew and Brown [5] have reported that one can generate $Co(4\text{-vpy})_2(NCS)_2$ by the liberation of 4-vinylpyridine from the analogous tetrakis-(4-vinylpyridine) complex. The former complex is blue, and is similar to other tetrahedral Co(substituted pyridine)$_2$X$_2$ complexes. We note that the decomposition produces polycrystalline $Co(4\text{-vpy})_2(NCS)_2$, and all diffraction lines from the powder pattern of $Co(4\text{-vpy})_2(NCS)_2$ can be indexed to an isometric system [16] with a = 13.77 Å (see Table IV). The density of this presumably tetrahedral complex, 1.46(1) g cm^{-3} (measured by neutral bouyancy in chloroform-hexane), indicates six molecules per unit cell. This high-symmetry crystal structure need not be disordered; for example, Co(4-vpy)$_2$(NCS)$_2$, with $Z = 6$ in space group *P23*, could occupy any of the sites 6f through 6i [17]. Studies in this laboratory of the thermal decomposition of Ni(4-vpy)$_4$(NCS)$_2$ (isomorphous with Co(4-vpy)$_4$(NCS)$_2$) indicate that the Ni(4-vpy)$_2$(NCS)$_2$ product is also cubic, with a = 13.77 Å. Thus, the polymeric octahedral structure proposed for Ni(4-vpy)$_2$(NCS)$_2$ [4] based on the C–N stretching frequency, and magnetic susceptibility measurements, is inconsistent with our X-ray data.

For Ni(4-vpy)$_2$(NCS)$_2$, the infrared spectrum of the yellow–green material produced by decomposition of Ni(4-vpy)$_4$(NCS)$_2$ is nearly identical to the published spectrum for the green solution-prepared product [4]. In view of this, and considering the similar thermal behavior as well as the isomorphism between analogous Ni and Co complexes, it appears likely that Ni(vpy)$_2$(NCS)$_2$ is tetrahedral.

Polymorphism and Reactivity of Co(4-vpy)$_4$(NCS)$_2$

As mentioned above, there are at least two polymorphic forms of the title complex. We have studied the orthorhombic form, space group *Pbca*, with a = 32.293, b = 11.416 and c =17.033 Å; the tetragonal form [13], space group $I4_1/a$, has a = 17.05 and c = 25.79 Å. While the near-equality of the 17 Å axes in the two polymorphs might suggest a spatial relationship, we have been unable to discover it. This is consistent with the large disparity in crystal densities ($\rho_{\mathrm{orth}} = 1.26$, ρ_{tetr} 1.05 g cm^{-3}). These structural differences suggested to us that a comparative study of the thermal loss of two vinylpyridine ligands would be worthwhile. Unfortunately, we were unable to prepare the low-density form of the complex by the literature syntheses or alternative methods. All efforts produced only the orthorhombic form of the crystals.

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