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Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02254

# A Sterically Crowded Organopentacyanocobaltate: Single-Crystal X-ray Structure Determination and Reactivity Study of $K_6[(NC)_5CoC(COOCH_3)=C(COOCH_3)Co(CN)_5]\cdot 6H_2O$

KAREN D. GRANDE, AMANDA J. KUNIN, LOUIS S. STUHL,* and BRUCE M. FOXMAN*

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An X-ray diffraction study of hexapotassium [$\mu$-1,2-bis(methoxycarbonyl)-1,2-ethenediyl]decakis(cyano-*C*)dicobaltate (K-**1**), a product of the reaction of dimethyl acetylenedicarboxylate with $Co(CN)_5^{3-}$, has demonstrated that the molecular anion is an extremely crowded trans-ethylene derivative. Crystal data: triclinic, $P\bar{1}$; $a = 9.242$ (3), $b = 9.842$ (3), $c = 10.014$ (3) Å; $\alpha = 79.01$ (3), $\beta = 70.33$ (3), $\gamma = 68.64$ (3)°; $Z = 1$; $R = 0.031$ for 2969 reflections. Compound K-**1** is characterized by major steric interactions leading to orthogonality between the ethylene plane and carbomethoxy substituent and to an extremely long Co–C bond (2.076 (2) Å). Although ($\sigma$-vinyl)cobalt cyanides have been postulated as intermediates in the cobalt-catalyzed cyanation of vinyl halides, compound K-**1** does not display reactivity appropriate to a model for such catalysis intermediates. Implications for the mechanism of this catalysis are discussed.

## Introduction

The reactions of organic compounds with cobalt cyanide complexes have been the subject of extensive study.[1a] The formation and reactivity of complexes $RCo(CN)_5^{3-}$, R = alkyl, have been of interest because of their possible relationship to vitamin $B_{12}$ chemistry.[1b] More recently, a cobalt cyanide system has been shown to be an effective catalyst for the displacement by cyanide of halide in vinyl halides.[2] Surprisingly, no organocobalt cyanides have heretofore been structurally characterized via single-crystal X-ray diffraction techniques. We surmised that this may have in part been a consequence of the limited stability and difficulty in isolation and purification of many of these compounds. The compound $K_6[(NC)_5CoC(CO_2Me)=C(CO_2Me)Co(CN)_5]$ (K-**1**), first reported by Kaska,[3] appears to be the most stable of the family of compounds resulting from the reaction of acetylene[4] or certain substituted alkynes[3] with $Co(CN)_5^{3-}$. In particular, this compound is one of the very few organocobalt cyanide complexes to have been reported as a stable, analytically pure solid; it has also been the subject of a detailed vibrational analysis.[5]

Thus, we were attracted to this compound as a subject for further structural and chemical study. Although it is to be expected that the molecule will be sterically congested, the nature and severity of the distortions arising from the crowding are *not* predictable. Further, while steric crowding might be expected to hinder the approach of reactants, it may well provide a driving force for reaction.[6] Finally, the thermal reactivity of the molecule is worthy of comment, particularly within the context of mechanistic proposals for the cobalt-catalyzed cyanation of vinyl halides.[2b]

## Experimental Section

All chemicals were reagent grade and were used as received except as otherwise indicated. Dimethyl acetylenedicarboxylate (Aldrich) from freshly opened bottles was of sufficient purity for use; material showing discoloration from prolonged storage was purified by distillation before use. Infrared spectra were recorded on a Perkin-Elmer 567 instrument and were calibrated with polystyrene. Proton NMR spectra were recorded on a Perkin-Elmer R32 spectrometer. Spectra taken in $D_2O$ as solvent used $CH_3CN$ as internal reference ($\delta$ 2.00).

**Preparation of $K_6[(NC)_5CoC(CO_2Me)=C(CO_2Me)Co(CN)_5]\cdot 6H_2O$.** Hexapotassium [$\mu$-1,2-bis(methoxycarbonyl)-1,2-ethenediyl]decakis(cyano-*C*)dicobaltate (K-**1**) was prepared by a modification of the literature procedure[3] for the dihydrate. This modification yields the desired product as a hexahydrate. A deoxygenated solution of 40 mL of distilled water and 2.38 g (10.0 mmol) of $CoCl_2\cdot 6H_2O$ was syringed into a deoxygenated solution of 3.6 g (55 mmol) of KCN in 30 mL of $H_2O$, which was cooled in an ice bath. The resultant green solution was stirred for 7 min after which a solution of 0.61 mL (5.0 mmol) of dimethyl acetylenedicarboxylate in 2 mL of deoxygenated methanol was added. The solution rapidly became orange. It was stirred for 4 min, and then 200 mL of deoxygenated 95% ethanol was added via a double-ended needle cannula, with stirring. The solution became cloudy and darkened. A brown oil and some lighter crystals separated. The mixture was stored at 0 °C overnight, resulting in crystallization of the oil. The crude product was isolated by filtration as yellow and yellow-orange crystals. Purification was accomplished by dissolving the crude product in 10 mL of water and adding methanol until crystallization began (about 11 mL). The cloudy solution was then chilled in a refrigerator. Bright yellow crystals were isolated by filtration; yield 3.0 g (70%). Additional crops of crystals were significantly less pure. The infrared spectrum was in good agreement with that in the literature.[5] NMR ($D_2O$): $\delta$ 3.7.

**Conversion of K-1 to a PPN Salt (PPN-1).** A solution of 1.8 g (3.1 mmol) of bis(triphenylphosphine)nitrogen(1+) chloride (Strem Chemical Co.) (henceforth referred to as $PPN^+Cl^-$) in 280 mL of warm water was prepared. A solution of 0.4 g (0.5 mmol) of $K_6[(NC)_5CoC(CO_2Me)=C(CO_2Me)Co(CN)_5]\cdot 6H_2O$ in 10 mL of water was added dropwise with stirring to the cooled $PPN^+Cl^-$ solution. The reaction mixture immediately became cloudy, and a light yellow precipitate formed. The mixture was allowed to stand 30 min and was then filtered. The yellow microcrystalline product was washed with water and then anhydrous diethyl ether; yield 1.5 g (77%). NMR ($CD_3CN$): $\delta$ 3.7 (s, 1 H), 7.6 (m, 30 H). IR, $cm^{-1}$ (KBr pellet): 3450, 3060, 2110, 1660, 1590, 1440.

**X-ray Structure Determination.** Crystals of the title complex were grown by slow crystallization from $MeOH-H_2O$ mixtures at -25 °C. Most operations on the Syntex $P2_1$ diffractometer and XTL Structure Determination System were carried out as described previously;[6,7] other operations are described below. Essential details of the structure analysis, in outline form, are given in Table I. All hydrogen atoms were located and refined except for one H atom bonded to the water oxygen atom O(3), which appeared to be involved in a 50:50 (%) disorder. Contributions from this H atom were not included in the structure factor calculations. Atomic coordinates are listed in Table II.

## Results and Discussion

**Crystal and Molecular Structure.** The molecular structure of the complex anion is shown in Figure 1; bond lengths and

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**Table I.** Data for the X-ray Diffraction Study of $K_6[(NC)_5CoC(COOCH_3)=C(COOCH_3)Co(CN)_5]\cdot 6H_2O$

(A) Crystal Data at 21 (1) °C

cryst system: triclinic
space group: $P\bar{1}$ ($C_i^1$; No. 2)[a]
$a = 9.242$ (3) Å
$b = 9.842$ (3) Å
$c = 10.014$ (3) Å
$\alpha = 79.01$ (3)°
$\beta = 70.33$ (3)°
$\gamma = 68.64$ (3)°
$V = 796.4$ Å$^3$
$Z = 1$
cryst size: 0.13 × 0.13 × 0.42 mm
fw: 862.9
$\rho_{calcd} = 1.799$ g cm$^{-3}$
$\rho_{obsd} = 1.78$ (1) g cm$^{-3}$
$\mu = 19.1$ cm$^{-1}$ (Mo K$\alpha$)

cell constant determination: 12 pairs of $\pm(hkl)$ and refined $2\theta$, $\omega$, and $\chi$ values in the range $33 < |2\theta| < 43°$ ($\lambda$(Mo K$\bar{\alpha}$) = 0.710 73 Å)

(B) Measurement of Intensity Data[b]

radiation: Mo K$\alpha$, graphite monochromator
reflcns measd: $-h, \pm k, \pm l$ (to $2\theta = 55°$)
scan type, speed: $\theta$-$2\theta$, 1.95-3.91°/min
scan range: symmetrical, $[1.8 + \Delta(\alpha_2-\alpha_1)]°$
no. of reflcns measd: 4010 total; 3624 in unique set
std reflcns: $\bar{3}1\bar{1}$, $\bar{2}4\bar{2}$, $\bar{1}1\bar{6}$; period 50; variation $\leq 3\sigma(I)$ for each
abs cor: empirical; transmission factors 0.838-1.000
statistical information: $R_s = 0.019$; $R_{av} = 0.016$ (mainly $0kl$ reflections)

(C) Solution and Refinement,[c] with 2969 Data for Which $F > 3.92\sigma(F)$

soln: Patterson and difference-Fourier, routine
weighting of reflcns: as before,[8] $p = 0.035$
refinement (by full-matrix least squares): anisotropic temperature factors for Co, K, O, N, C atoms; isotropic temperature factors for H atoms (see text); $R = 0.031$, $R_w = 0.043$, SDU = 0.98
structure factor calcn (all 3624 unique data): $R = 0.045$, $R_w = 0.046$
final diff map: five peaks 0.3-0.58 e/Å$^3$ in vicinity of K, N(3), O(4); other peaks random, <0.3 e/Å$^3$
weighting scheme anal.: no systematic dependence on magnitude of $|F_o|$, $(\sin\theta)/\lambda$, or indices

[a] Unit cell parameters of the corresponding Delaunay reduced cell: $a = 10.771$, $b = 9.842$, $c = 10.014$ Å; $\alpha = 100.99$, $\beta = 96.58$, $\gamma = 126.96°$. [b] $R_s = \Sigma(|F_o|)/\Sigma|F_o|$; $R_{av} = \Sigma(||I - I_{av}||)/\Sigma|I|$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; SDU $= [\Sigma w(|F_o| - |F_c|)^2/(m - n)]$, where $m$ (=2969) is the number of observations and $n$ (=231) is the number of parameters.

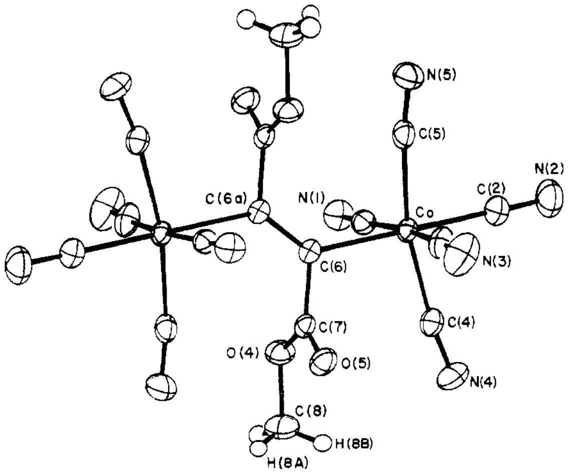

**Figure 1.** Perspective view of the molecular anion, showing the labeling scheme and 50% probability ellipsoids for atoms refined anisotropically (H atoms plotted at 10% probability).

**Table II.** Atomic Coordinates[a] for $K_6[(NC)_5CoC(COOCH_3)=C(COOCH_3)Co(CN)_5]\cdot 6H_2O$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Co | 0.11532 (4) | 0.18167 (3) | 0.31269 (3) |
| K(1) | 0.50318 (9) | 0.77630 (8) | 0.08551 (7) |
| K(2) | 0.22635 (8) | 0.54936 (7) | 0.36085 (8) |
| K(3) | 0.18789 (8) | 0.05088 (9) | 0.77722 (7) |
| O(1) | 0.7978 (4) | 0.6910 (3) | 0.1637 (4) |
| O(2) | 0.5343 (3) | 0.4825 (3) | 0.2032 (3) |
| O(3) | 0.2586 (4) | 0.7071 (3) | 0.0316 (4) |
| O(4) | 0.3064 (2) | −0.0977 (2) | 0.5238 (2) |
| O(5) | 0.2860 (2) | −0.2004 (2) | 0.3525 (2) |
| N(1) | 0.1280 (3) | 0.3074 (3) | 0.5614 (3) |
| N(2) | 0.1849 (4) | 0.4423 (3) | 0.1100 (3) |
| N(3) | 0.1094 (4) | 0.0231 (4) | 0.0833 (3) |
| N(4) | 0.4842 (3) | 0.0480 (3) | 0.2034 (3) |
| N(5) | −0.2273 (3) | 0.3927 (3) | 0.3519 (3) |
| C(1) | 0.1248 (3) | 0.2576 (3) | 0.4686 (3) |
| C(2) | 0.1584 (3) | 0.3438 (3) | 0.1846 (3) |
| C(3) | 0.1064 (3) | 0.0865 (3) | 0.1698 (3) |
| C(4) | 0.3456 (3) | 0.0920 (3) | 0.2523 (3) |
| C(5) | −0.1041 (3) | 0.3034 (3) | 0.3419 (3) |
| C(6) | 0.0684 (3) | 0.0086 (3) | 0.4546 (2) |
| C(7) | 0.2265 (3) | −0.1083 (3) | 0.4379 (2) |
| C(8) | 0.4719 (4) | −0.1973 (4) | 0.5007 (4) |
| H(1A) | 0.813 (8) | 0.653 (7) | 0.227 (7) |
| H(1B) | 0.842 (6) | 0.652 (5) | 0.114 (5) |
| H(2A) | 0.581 (6) | 0.430 (6) | 0.141 (6) |
| H(2B) | 0.587 (6) | 0.473 (5) | 0.248 (5) |
| H(3A) | 0.179 (5) | 0.749 (5) | 0.069 (5) |
| H(8A) | 0.477 (5) | −0.302 (5) | 0.503 (4) |
| H(8B) | 0.525 (5) | −0.202 (5) | 0.407 (5) |
| H(8C) | 0.500 (6) | −0.184 (5) | 0.574 (5) |

[a] Estimated standard deviations in the least significant digits appear in parentheses in this and subsequent tables.

**Table III.** Selected Bond Lengths (Å) and Angles (deg) in the $[(NC)_5CoC(COOCH_3)C(COOCH_3)Co(CN)_5]^{6-}$ Ion[a]

| | | | |
|---|---|---|---|
| Co-C(1) | 1.895 (3) | C(6)-C(6a)′ | 1.333 (5) |
| Co-C(2) | 1.921 (3) | C(6)-C(7) | 1.473 (4) |
| Co-C(3) | 1.892 (3) | C(7)-O(4) | 1.347 (3) |
| Co-C(4) | 1.909 (3) | C(7)-O(5) | 1.213 (3) |
| Co-C(5) | 1.897 (3) | C(8)-O(4) | 1.452 (4) |
| Co-C(6) | 2.076 (2) | | |
| C(1)-Co-C(3) | 173.7 (1) | Co-C(5)-N(5) | 170.2 (3) |
| C(2)-Co-C(4) | 84.4 (1) | Co-C(6)-C(6a) | 132.2 (2) |
| C(2)-Co-C(5) | 83.2 (1) | Co-C(6)-C(7) | 122.0 (2) |
| C(4)-Co-C(5) | 167.5 (1) | C(6a)-C(6)-C(7) | 105.7 (2) |
| C(4)-Co-C(6) | 95.7 (1) | C(6)-C(7)-O(4) | 112.2 (2) |
| C(5)-Co-C(6) | 96.7 (1) | C(6)-C(7)-O(5) | 125.6 (2) |
| Co-C(3)-N(3) | 176.1 (3) | O(4)-C(7)-O(5) | 122.0 (2) |
| Co-C(4)-N(4) | 172.8 (3) | | |

[a] Other distances and angles, whose values lie very near expected values, are to be found in supplementary tables.

**Table IV.** Important Intramolecular Nonbonded Contacts (Å)[a] for the $[(CN)_5CoC(COOCH_3)C(COOCH_3)Co(CN)_5]^{6-}$ Ion

| | | | |
|---|---|---|---|
| N(4)-O(4) | 3.39 | N(5)-O(4)′ | 3.17 |
| N(4)-O(5) | 3.41 | N(5)-O(5)′ | 3.19 |
| N(4)-C(7) | 3.33 | N(5)-C(7)′ | 3.16 |
| C(3)-C(7) | 3.26 | N(5)-C(8)′ | 3.29 |
| C(4)-O(4) | 2.98 | C(5)-O(4)′ | 3.07 |
| C(4)-O(5) | 3.05 | C(5)-O(5)′ | 3.13 |
| C(4)-C(7) | 2.71 | C(5)-C(7)′ | 2.85 |

[a] "Primes" indicate that the contact is between atoms in the centrosymmetrically related "halves" of the molecule.

angles are given in Table III. The conformation of the anion, which is characterized by a Co-C(6)-C(6a)-Co torsion angle of 180° (Figure 1), is reminiscent of the decacyano($\mu$-dioxygen)cobaltate(III) complexes.[8,9] In this case, however, the presence of a bulky substituent, $-CO_2Me$, on the vinyl carbon atom leads to unusual conformational effects as well as bond length and angle deformations.

Severe steric effects in the molecule are minimized primarily via torsion about the C(6)-C(7) bond. Thus, the planes C(6a)-C(6)-C(7) and C(6)-C(7)-O(5) are nearly orthogonal (91.7°). Relief of strain is also achieved by large deformations

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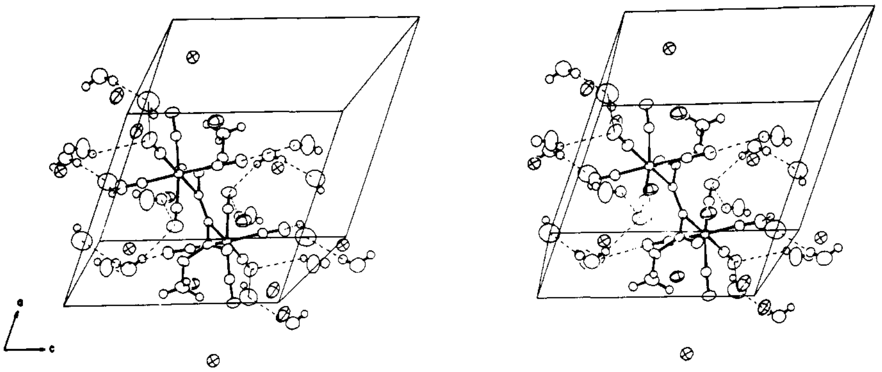

**Figure 2.** Stereoview of the unit cell contents. Hydrogen bonds are indicated by dashed lines, and potassium ions are shown as ellipsoids with boundary ellipses and principal axes. In this view the *c* axis runs from $-^1/_2$ to $+^1/_2$.

in the Co–C(4)–N(4) (172.8 (3)°) and Co–C(5)–N(5) (170.2 (3)°) angles. As indicated in Table IV, nonbonded contacts between the 4- and 5-cyano groups and the $\alpha$- and $\beta$-ester functionalities are nearly equalized as a consequence of these deformations. However, there would appear to be considerable steric strain remaining in this molecule; most of the contacts in Table IV are at distances much less than the sum of the corresponding van der Waals radii and are shorter than those observed in $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\sigma\text{-}C(CO_2Et){=}CMe_2)$.[10] There, nonbonded interactions led to near-orthogonality of the olefin and $-CO_2Et$ planes (78.5°). In the present case the crowding is much greater, since *one* $-Co(CN)_5$ unit interacts strongly with *both* $-CO_2Me$ moieties.

The $Co–C_{vinyl}$ bond length, 2.076 (2) Å, is considerably longer than that found in other structures; cf. 1.968–1.971 (13)[11] and 1.966 (6)[12] Å in (vinyl)(py)Co(dmg)$_2$ complexes. This lengthening could presumably arise from a combination of steric strain, trans effects, and/or the $\sigma$-electron-withdrawing effect of the ester moiety. In a series of elegant experiments,[13,14] Marzilli, Randaccio, and co-workers have shown that, as the steric requirements of both ligands $L_1$ (=alkyl) and $L_2$ (=N or P ligand) in $(L_1)(L_2)Co(dmg)_2$ complexes are increased, the $Co–C_{alkyl}$ distance increases markedly, e.g., from 1.998 (7) Å where $L_1 = CH_3$, $L_2$ = py to 2.22 (2) Å where $L_1 = (CH_3)_2CH$, $L_2 = PPh_3$. These observations, as well as the known instability of cobaloximes containing secondary alkyl groups,[15] correlate well with quantitative studies of structural and kinetic steric effects in $M(NH_2R)_5Cl^{2+}$ (M = Co, Cr) complexes.[6,16,17] Long Co–N distances were observed in $Co(NH_2CH_3)_5Cl^{2+}$.[6] However, much relief of steric strain could be achieved in that case via Co–N–C bond angle deformations (there is no analogy in the constrained cobaloxime system). In the alkylamine complexes a similar lack of stability of isopropylamine and secondary amine complexes was noted and discussed.[6] It would appear that, owing to the extremely small size of Co(III), its complexes are rather susceptible to the bond length and angle distortions of the type discussed here.[18] We propose that the present case is a further example of the impact of severe steric effects on Co–C bond lengths and that steric effects are a major contribution to this lengthening. Although no individual distortion in the molecule lies outside unprecedented ranges, the observed *set* of nonbonded contacts and torsional and angular deformations characterizes a rather sterically crowded molecule.

The $\sigma$-vinyl group is normally expected to show a pronounced structural trans effect;[19] however, in the present case the presence of steric effects as well as competition with the high $\pi$ acidity of the $-CN^-$ ligand has reduced the effect greatly. The Co–C(2) distance, 1.921 (3) Å, is significantly longer than the Co–cis-carbon atom distances, but the absolute magnitude of the difference ranges only from 0.012 to 0.029 (4) Å.[20] The C═C distance, 1.333 (5) Å, and other bond distances and angles in the molecule lie within normal ranges (Table III).

The crystal structure consists of individual anions interconnected by $K^+$ ions as well as hydrogen bonding via the three independent water molecules (Figure 2). It is probable that the crystal structure and perhaps the molecular anion itself owe their stability to this well-defined, highly ordered (cf. disordered $K_5[Co_2(CN)_{10}O_2]\cdot H_2O^8$) packing arrangement.

Previous workers have reported **K-1** as being a pentahydrate,[5] a dihydrate,[3] and an anhydrous compound.[5] The crystal that was examined in this study was washed with diethyl ether and air-dried. The diffraction study and density measurements on several crystals show unambiguously that **K-1** as isolated from solution is a hexahydrate.

**Solution Chemistry and Reactivity of the Complex.** Compound **K-1** was prepared in good yield via the literature synthesis.[3] It was isolated as air-stable yellow crystals soluble in water and aqueous–organic mixtures containing a high percentage of water but insoluble in all pure organic solvents examined, including acetonitrile, dimethylformamide, tetrahydrofuran, nitromethane, sulfolane, and alcohols. It is stable as a solid for at least 1 year when stored in a desiccator. In order to facilitate study of its reactions with organic reagents, several attempts were made to synthesize salts of the anion

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(20) The observation that the Co–C(2) distance is the longest cobalt to cyanide carbon atom distance in the molecule certainly suggests that there is a small structural trans effect exerted by the vinyl group on the cyanide ligand. This is in agreement with the postulate that, in Co(III) complexes $CH_2{=}CH^-$ is expected to exhibit a greater trans effect than $CN^-$ on the basis of the amount of negative charge donated via the $\sigma$ bond.[21] The $\sigma$-withdrawing influence of the ester moiety, enhanced by its orthogonality to the vinyl group, would tend to reduce the difference between $CN^-$ and $C(CO_2Me){=}C(CO_2Me)$.

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of **K-1** containing organic cations. Curiously, the replacement of KCN by tetraalkylammonium cyanide in the synthesis of **K-1** gave none of the desired product in either aqueous or acetonitrile solvent. Cation metathesis reactions with $R_4NBF_4$ gave complex mixtures of incompletely exchanged salts.[22]

Success was achieved by precipitation of $([(C_6H_5)_3P]_2N)_6[(NC)_5CoC(CO_2Me){=}C(CO_2Me)Co(CN)_5]$ (**PPN-1**) from aqueous solution using bis(triphenylphosphine)nitrogen(1+) chloride ($PPN^+Cl^-$). Surprisingly, **PPN-1** proved to be far less stable thermally than **K-1** both as a solid and in solution. It also proved impossible to completely dry **PPN-1** without significant decomposition.

The reaction chemistry of **1** proved to be quite limited. Nucleophiles such as $CN^-$ and $OH^-$ reacted only with the ester functionalities of **1**; no evidence was observed for conjugate addition products. The double bond of **1** also proved inert to Diels–Alder dienes.[23]

**Comments on the Mechanism of Cobalt-Catalyzed Cyanation.** Our attention was initially drawn to **K-1** because of its potential for modeling the ($\sigma$-vinyl)cobalt cyanide complexes proposed to be intermediates in the cobalt-catalyzed cyanation of vinyl halides.[3] Wilkinson et al.[4] have reported that the unsubstituted analogue of **K-1** derived from acetylene and $Co(CN)_5^{3-}$ decomposes in solution to an uncharacterized organic nitrile. Since this was the only known example of a characterized organocobalt cyanide undergoing thermal decomposition to a nitrile product, a key step in the mechanism proposed for the aforementioned cobalt-catalyzed cyanation, the thermal reactivity of **K-1** was of great interest. Both **K-1** and **PPN-1** decompose in solution at moderate temperatures. The decomposition mixtures were examined by NMR and infrared spectroscopy and found to be quite complex, with no evidence for significant amounts of nitriles in the mixture.[24] An alternate mechanistic hypothesis for the nitrile formation step of the cobalt-catalyzed reaction would be a bimolecular reaction between the ($\sigma$-vinyl)cobalt cyanide intermediate and some other cyanide-containing species in the reaction mixture. To test the feasibility of this idea, **K-1** was exposed to the catalytic mixture; it proved to be unreactive and could be recovered in good yield.[25]

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**Registry No.** K-1·6H$_2$O, 85439-49-2; PPN-1, 85439-51-6.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, nonessential bond lengths and angles, hydrogen bonds, angles subtended at potassium ions, and observed and calculated structure factors and Figure 3, showing the coordination geometry of the potassium ions (18 pages). Ordering information is given on any current masthead page.

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[22] With a substantial excess of tetraalkylammonium ion in the solution $(R_4N)_6[(NC)_5CoC(COOMe){=}C(COOMe)Co(CN)_5]$ could be isolated but in unsatisfactory yield.

[23] Iodine has been reported to effect cobalt–carbon bond cleavage of **K-1** rather than addition to the double bond.[3] Another electrophile, benzyl bromide, was found to be unreactive with **K-1**. Cyclopentadiene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene were chosen as sterically unencumbered representative Diels–Alder substrates with extreme electronic qualities, electron rich vs. electron poor. No reaction was observed with either.

[24] Attempts to extract organic products from aqueous solutions of decomposed **K-1** were unsuccessful.

[25] Hydrogenolysis and hydrogenation products are observed as byproducts of the $\beta$-bromostyrene cyanation reaction.[2a] However, compound **K-1** was found to be inert to $NaBH_4$ and also to the Funabiki cyanation reaction mixture (sans $\beta$-bromostyrene).

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Contribution from the School of Chemistry,
The University of New South Wales, Kensington, NSW 2033, Australia

# Cadmium Thiolates. Tetrahedral $CdS_4$ and Dodecahedral $CdS_4O_4$ Coordination in *catena*-Bis(carbethoxymethanethiolato)cadmium(II)

IAN G. DANCE,* MARCIA L. SCUDDER, and RODNEY SECOMB

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Crystals of $Cd(SCH_2COOCH_2CH_3)_2$ from ethanol solution contain $[Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$ linear chains, along which cadmium atoms of two different coordination stereochemistries alternate. Cadmium atoms are separated by 344 pm and bridged by two thiolate functions. At each cadmium atom the primary coordination is $(\mu\text{-SR})_4$: additional, secondary, coordination at one cadmium atom is by four carbonyl oxygen atoms (Cd1–S = 262 pm, Cd1–O = 288 pm) in stereochemistry idealized as dodecahedral, and at the other cadmium the secondary carbonyl oxygen coordination is very weak (Cd2–S = 253 pm, Cd2–O = 323 pm) in tetracapped-tetrahedral stereochemistry. Crystal data: $CdS_2C_8H_{14}O_4$, space group $I4_1/acd$, $a = 1937.1$ (3) pm, $c = 1376.4$ (3) pm, $Z = 16$, $d_{obsd} = 1.81$ (2) g cm$^{-3}$, $d_{calcd} = 1.80$ g cm$^{-3}$, 509 observed reflections, Cu K$\alpha$, $R = 0.055$.

A variety of structure types have been found for cadmium complexes in which the coordination is exclusively or predominantly by the thiolate function. Observed molecular structures range in size from $[Cd(SPh)_4]^{2-}$[1] through $[Cd_4(SR)_{10}]^{2-}$[2] to $[ICd_8(SCH_2CH_2OH)_{12}]^{3+}$,[3] $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$,[4] and $[S_4Cd_{10}(SPh)_{16}]^{4-}$,[5] while one-dimensional nonmolecularity occurs in $\{Cd[SCH(CH_2CH_2)_2NHCH_3]_2^{2+}\}_\infty$[6] and two-dimensional nonmolecularity occurs in $[Cd(SCH_2CH_2OH)_2]_\infty$.[7]

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