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36. TRICYANOMETALATE BUILDING BLOCKS AND ORGANO METALLIC CYANIDE CAGES

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Tricyanometalate complexes are useful building blocks for the construction of molecular cage compounds and coordination solids. One class of tricyanometalates that has proved especially useful are those with the formula \( \text{MC}\left(\text{CN}_3\right)_2 \), where \( \text{M}^{2+} \) is a cation that limits the degree of polymerization and facilitates the formation of molecular cages. The tricyanides of the monocyclopentadienyl containing transition series metals were not well studied until the early 1970s. Parson and Dinner reported the preparation of \( \text{K}_{12}\text{(Cl}\left(\text{CN}_3\right)_2\text{)} \) and \( \text{K}_4\text{(CH}_3\text{CN}_3)_2\text{)} \) via the reaction of cyanide with \( \text{CO}_2 \). We have obtained the former compound using a

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slightly modified procedure and have been able to convert it to the organic solvent soluble \( \text{K}_{18}\text{(crown-6)}\text{)} \) salt. The related tricyanides \( \text{Cr(CN}_3\text{)}^2\text{)}, \( \text{Fe(CN}_3\text{)}^2\text{)} \), and \( \text{Cu(CN}_3\text{)}^2\text{)} \) are readily prepared from commercially available \( \text{Cu(CN}_3\text{)}^2\text{)} \) and the tricyanides \( \text{Fe(CN}_3\text{)}^2\text{)} \) can be obtained from the photolysis of \( \text{Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \). If these, \( \text{Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \) and \( \text{Cr(C}^5\text{)CN}_3\text{)}^2\text{)} \) are useful in the synthesis of molecular cages. Of particular note in the condensation between \( \text{Cu(C}^3\text{)CN}_3\text{)}^2\text{)} \) and \( \text{Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \) to give a molecular cube of formula \( \text{[Cu(C}^3\text{)CN}_3\text{)}^2\text{)(Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \) or a molecular bowl of formula \( \text{[Cu(C}^3\text{)CN}_3\text{)}^2\text{)(Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \), depending on the stoichiometric ratio of the reagents used.

**Caution.** Because of the toxic nature of cyanide, special care should be exercised in these preparations. We make amyl nitrite available in the laboratory as an antidote to acute cyanide poisoning. Organic soluble salts of cyanide (and potentially cyanometalates) are especially hazardous contact poisons because they are transported intravenously through the skin.

A. TETRAETHYLAMMONIUM TRICYANOPENTAMETHYL CYPEN DADENYL[PHENATETRAHI DRATED] MONOHYDRATE, [NE\(_4\)]\(_2\)[Cr(CN\(_3\))\(_2\)] \( \cdot \) H\(_2\)O

\( [\text{Cr(C}^3\text{)CN}_3\text{)}^2\text{)} + 6\text{KCN} + 2\text{Na}_2\text{SiO}_3 + 2\text{Na}_2\text{[Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \cdot 6\text{H}_2\text{O} + 6\text{KCl} \)

**Procedure.** A 250-mL round-bottomed flask containing a stirring bar is covered with aluminum foil (to exclude light) and then charged with 0.30 g (0.485 mmol) of \( \text{Cr(C}^3\text{)CN}_3\text{)}^2\) and 50 mL of H\(_2\)O. To the resulting slurry, 0.359 g (1.94 mmol) of AgNO\(_3\) is added. Over the course of 40 min, the color of the solution becomes yellow and a white precipitate of AgCl appears. The slurry is filtered through Celite. To the filtered solution of \( \text{Cr(C}^3\text{)H}_2\text{O}_3\text{)}^2\) is added 0.284 g (4.36 mmol) of KCN. This solution is allowed to stir overnight. The resulting colorless solution is treated with 0.161 g (0.503 mmol) of Et\(_2\)O. After a further 20 min, the solvent is evaporated. The pale yellow solid residue is extracted into 30 mL of CH\(_3\)Cl, and the solution is filtered through a medium-porosity frit to remove a white solid consisting of KCN, KNO\(_3\), and K\(_2\)CO\(_3\). The product, \( \text{K}_2\text{[Cr(C}^3\text{)CN}_3\text{)}^2\text{)} \) is precipitated by the addition of 50 mL Et\(_2\)O to the filtered extract. The precipitate is collected by filtration, washed with 10 mL of Et\(_2\)O, and dried under vacuum. Yield: 0.450 g (93%).

*The checkers' yield was 73-79%.
Properties

The product is a colorless crystalline solid. It is air stable both as a solid and in solutions. It is soluble in polar solvents such as water, acetonitrile, and acetonitrile as well as CH$_2$Cl$_2$ and is insoluble in ether and benzene. The $^1$H NMR spectrum (CD$_2$Cl) exhibits a triplet at $\delta$ 3.18 (3H, CH$_3$CH$_2$), a singlet at $\delta$ 1.86 (36H, 15H, and a signal at $\delta$ 1.20 (11H, CH$_2$CH$_2$). The $^1$H NMR spectrum in CDCl$_3$ is similar to $\delta$ 3.38 [5H, (CH$_3$CH$_2$)$_2$] a singlet at $\delta$ 1.19 (18H, (CH$_3$)$_2$C$\equiv$CCH$_2$), and a triplet at $\delta$ 1.34 (12H, (CH$_3$)$_2$C$\equiv$CCH$_2$). The $^1$H NMR spectrum in CD$_2$CN is similar, with signals at $\delta$ 3.15, 1.95, and 1.20, respectively. The cyanide region in the infrared spectrum of the solid (KBr pellet) shows a typical two-band pattern at 2107 and 2123 cm$^{-1}$.

B. TETRAETHYLMAMMONIUM TRICYANO (PENTAMETEYLICYCLOPENTADIENYL)REDACTE(III) MONOHYDROXY, [NEt$_4$] [C$_6$H$_5$C$_3$N$_4$] $\cdot$ H$_2$O

Procedure

A 250-mL round-bottomed flask containing a stirring bar is charged with 0.300 g (0.377 mmol) of (C$_6$H$_5$C$_3$N$_4$) and 100 mL of H$_2$O. To this slurry is added 6.150 g (2.30 mmol) of KCN. The resulting mixture is heated to reflux for 3 h under N$_2$ to give a clear, colorless solution. To the solution is added 0.150 g (0.900 mmol) of Et$_3$O, and then the solvent is removed under vacuum. The pale yellow solid residue is extracted with 50 mL of CH$_2$Cl$_2$ and the volume of the resulting colorless solution is reduced under vacuum to ~5 mL. The product, [NEt$_4$][C$_6$H$_5$C$_3$N$_4$] $\cdot$ H$_2$O, is precipitated by the addition of 50 mL of Et$_2$O. The precipitate is collected by filtration, washed with 10 mL of Et$_2$O, and dried under vacuum. Yield: 0.295 g (73%).

Anal. Calc. for C$_6$H$_5$N$_4$: C, 55.53; H, 6.75; N, 10.12. Found: C, 55.65; H, 6.60; N, 10.22.

The checkers' yield was 85-87%.

C. (18-CROWN-6) POTASSIUM TRICYANO (CYPENTADENDRINYL) COBALATE(III), [K[18-CROWN-6][C$_6$H$_5$C$_3$N$_4$]Co$_2$]

$\text{Co}$$_2$[C$_6$H$_5$C$_3$N$_4$] + I$_2$ → $\text{Co}$$_2$[C$_6$H$_5$C$_3$N$_4$] + CO

$\text{Co}$$_2$[C$_6$H$_5$C$_3$N$_4$] + KCN → $\text{K}$[C$_6$H$_5$C$_3$N$_4$] + CO + 2K

$\text{K}$[C$_6$H$_5$C$_3$N$_4$] + 18-crown-6 → $\text{K}$[18-crown-6][C$_6$H$_5$C$_3$N$_4$]

Procedure

Caution. The procedure involves the formation of gases CO and should be conducted in a well-ventilated hood.

The synthesis of Co$_2$[C$_6$H$_5$C$_3$N$_4$] is performed by using a modification of literature methods. A 25-mL round-bottomed flask containing a stirring bar is charged with 0.400 g (1.7 mmol) of Co$_2$[C$_6$H$_5$C$_3$N$_4$] and 50 mL of MeOH to give a yellow solution. Then 4.20 g (7.0 mmol) of Na$_2$CO$_3$ is added to the stirred solution until the pH reaches 7.0. The solution is heated under reflux for 3 hours. The precipitate is filtered, washed with 10 mL of Et$_2$O, and dried under vacuum. Yield: 0.350 g (95%).

$\text{K}$[18-crown-6][C$_6$H$_5$C$_3$N$_4$] + 18-crown-6 → $\text{K}$[18-crown-6][C$_6$H$_5$C$_3$N$_4$]

Under a nitrogen atmosphere, a solution of 2.41 g (37 mmol) of KCN in 20 mL of MeOH is added to a solution of 5.0 g (32 mmol) of Co$_2$[C$_6$H$_5$C$_3$N$_4$] in 20 mL of MeOH, and the resulting solution is filtered under reflux for 3 days. The reaction mixture is allowed to cool, and then it is filtered in air. The filtrate is evaporated to dryness and the residue is washed with 100 mL of MeCN in 50 mL portions until the washings contain no KCl (as indicated by the failure to obtain a
precipitate on addition of Et₂O to the washing. The solid K[CaCO(CN)₅] is washed with two 10-mL portions of Et₂O and dried under vacuum for 2 h. Yield: 1.16 g (42%).

Then 1.16 g (4.81 mmol) of K[CaCO(CN)₅] is suspended in a solution containing 1.28 g (4.84 mmol) of 18-crown-6 in 250 mL of MeCN, and the suspension is stirred for 3 h. During this time the K[CaCO(CN)₅] dissolves to give a golden yellow solution. The solution is filtered to remove a small quantity of an insoluble brown impurity, and then the solvent is reduced in volume to ~100 mL under vacuum. Addition of 150 mL of Et₂O precipitates the product as yellow microcrystals. The product is collected by filtration, washed with two 10-mL portions of Et₂O, and finally dried under vacuum for 1 h. Yield: 2.31 g (91% from K[CaCO(CN)₅]; 33% overall).[^2]

Anal. Calcd. for C₂₅H₂₆CaC₇N₀₂₀: C, 41.52; H, 5.78; N, 8.31. Found: C, 47.50; H, 5.82; N, 8.36.

**Properties**

The compound is a golden yellow microcrystalline solid. It is stable in air both as a solid and in solution. It is soluble in water, methanol, and acetone, and is insoluble in ether and hexanes. The ¹H NMR spectrum (CD₃CN) shows two singlets at δ 3.56 (24H, [K₂C₇H₂₀O₃]) and 5.23 (5H, CH₂CO). The infrared spectrum of the solid (KBr) shows a single band in the cyanide region at 2119 cm⁻¹.

**D. DODECACYANOTETRASIS (CYCLOPENTADIENYL) COBALT(III) TETRASIS(PENTAMETHYLCYCLOPENTADIENYLHYDRODIUM(III)) TETRASIS (HEXAFLUOROPHOSPHATE), [C₅(C₇H₂₀O₃)][C₅Rh₂(PF₆)₄]**

4 [K(18-crown-6)][C₅(C₇H₂₀O₃)] + 4 [C₅Rh₂(NCMe₃)₂][PF₆]₂ → [C₅(C₇H₂₀O₃)][C₅Rh₂(PF₆)₄] + 4 [K(18-crown-6)][PF₆]

**Procedure**

A solution of 50 mg (0.10 mmol) of [K(18-crown-6)][C₅(C₇H₂₀O₃)] in 15 mL of MeCN is added dropwise to a stirred solution of 65 mg (0.1 mmol) of [C₅Rh₂(NCMe₃)₂][PF₆]₂ in 15 mL of MeCN. The resulting solution is allowed to stand for 36 h, and then the product is precipitated as a yellow powder by addition of 100 mL of Et₂O. The product is collected by filtration, washed with two 10-mL portions of Et₂O, and dried under vacuum for 1 h. Yield: 58% (99%).

**References**


[^2]: The checkers' yield was 88-90% and 25-30% overall.