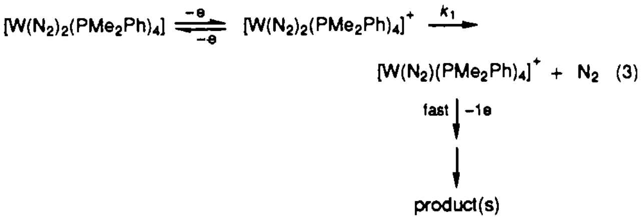
of Mo and W has been determined previously by a double-potential-step method.[7] For the cis and trans monodentate phosphine complexes studied here, the rate-determining loss of N_2 from the 17e cation is followed by fast one-electron oxidation chemistry (eq 3). We therefore determined k_1 by a single-potential-step



$$[\mathrm{W(N_2)_2(PMe_2Ph)_4}] \underset{-e}{\overset{-e}{\rightleftharpoons}} [\mathrm{W(N_2)_2(PMe_2Ph)_4}]^+ \xrightarrow{k_1} [\mathrm{W(N_2)(PMe_2Ph)_4}]^+ + \mathrm{N_2} \quad (3)$$

$$[\mathrm{W(N_2)(PMe_2Ph)_4}]^+ \xrightarrow{\text{fast}\ \ -1e} \text{product(s)}$$

method.[20] The value of k_1 for N_2 loss from the cis cation was estimated to be 2.7 (±0.5) s^{-1} and for the trans cation to be 0.51 (±0.04) s^{-1} at 298 K. The rate of N_2 loss from the cis cation is ca. 5 orders of magnitude faster than for the neutral complex, and the corresponding difference for the trans isomer is at least 8 orders of magnitude. Whereas the trans effect appears to dominate the relative lability of N_2 in the metal(0) isomers, the difference in relative rates of N_2 loss from the isomers in the +1 oxidation state is considerably less dramatic (ca. a factor of 5). In the higher oxidation state the ligand arrangement appears less important in determining the lability of the N_2 ligand.

The temperature dependence of the rate constants was determined in order to calculate activation parameters. The $\Delta H^{\ddagger}$ (kJ mol^{-1}) and $\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}) values (with estimated errors in parentheses) for *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ are 98 (14) and +51 (51), and 109 (8) and +38 (24).[7] The corresponding values for *cis*-$[W(N_2)_2(PMe_2Ph)_4]^+$ and *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$ are 79 (10) and 228 (35), and 89 (4) and 246 (13), respectively. The large positive entropy of activation change for the step involving N_2 loss from *cis*- and *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$, which is significantly greater than the corresponding values obtained for neutral bis(dinitrogen) complexes, suggests a productlike transition state with extensive $W-N_2$ bond weakening.

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Registry No. *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, 28915-53-9; *trans*-$[W(N_2)_2(PMe_2Ph)_4]$, 139405-90-6; $[WCl_4(PMe_2Ph)_2]$, 30411-60-0; WCl_6, 13283-01-7; *trans*-$[W(N_2)_2(PMe_2Ph)_4]^+$, 139348-54-2; *cis*-$[W(N_2)_2(PMe_2Ph)_4]^+$, 139405-91-7.

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[20] The rate constants (k_1) were determined using the following expression: $n_{app} = 2 - \exp(-k_1t)$ (see ref 21).

[21] See for example: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 11.

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Coordination Polymers of Tetracyanoethylene with Metal Hexafluoroacetylacetonates: Formation and X-ray Crystal Structures

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Introduction

Tetracyanoethylene has been observed to react with metal complexes to form charge-transfer adducts,[1,2] alkene carbon bonded complexes,[3,4] and nitrile nitrogen donor complexes.[5,6] Neutral and reduced forms of TCNE ($TCNE^-$, $TCNE^{2-}$) can also potentially use nitrile coordination to bridge metal centers in forming coordination polymers. $[Co(acacen)_2{\cdot}TCNE]_x$[5a] and $[Sn(acac)_2{\cdot}TCNE]_x$[5b] are possible examples for this general type of coordination polymer, but structural characterization is lacking. This paper reports the formation and X-ray structure determinations for metal hexafluoroacetylacetonate complexes of TCNE, $[M(hfacac)_2{\cdot}TCNE]_x$, which occur as linear-chain coordination

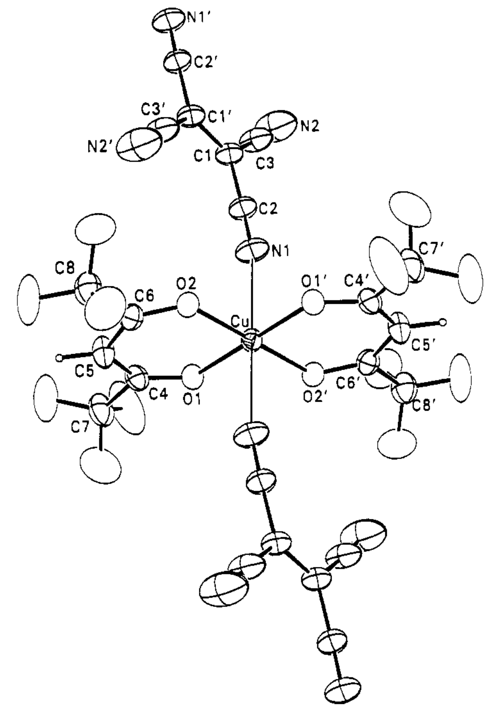

Figure 1. ORTEP view of the unit molecular structure of the coordination polymer $[Cu(hfacac)_2{\cdot}TCNE]_x$ showing the atom numbering and thermal motion ellipsoids (30%) for the non-hydrogen atoms. The molecular structure of $[Co(hfacac)_2{\cdot}TCNE]_x$ is essentially identical except for the M–NC axial ligand distance. The Cu–NC distance (2.563 Å) is significantly longer than the Co–NC distance (2.209 Å).

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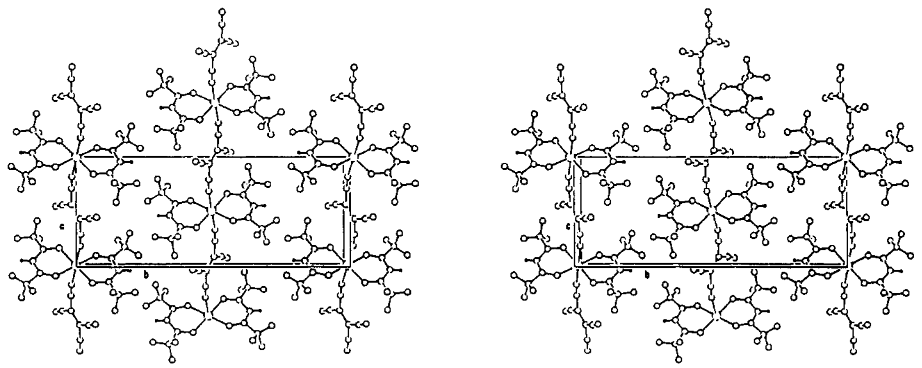

Figure 2. Stereoview of the unit cell of $[Cu(hfacac)_2{\cdot}TCNE]_x$ viewed perpendicular to the *bc* plane. The unit cell of $[Co(hfacac)_2{\cdot}TCNE]_x$ is essentially identical.

Table I. Selected Internuclear Distances (Å) and Angles (deg) for $[M(hfacac)_2{\cdot}TCNE]_x$ (M = Cu(II), Co(II))

$[Cu(hfacac)_2{\cdot}TCNE]_x$				$[Co(hfacac)_2{\cdot}TCNE]_x$			
Cu–O1	1.940 (2)	O1–Cu–O1′	180.0 (0)	Co–O1	2.045 (2)	O1–Co–O1′	180.0 (0)
Cu–O2	1.950 (2)	O2–Cu–O2′	180.0 (0)	Co–O2	2.024 (2)	O2–Co–O2′	180.0 (0)
Cu–N1	2.563 (3)	O1–Cu–O2	92.6 (1)	Co–N1	2.208 (2)	O1–Co–O2	89.5 (1)
		N1–Cu–N1′	180.0 (0)			N1–Co–N1′	180.0 (0)
C1–C1′	1.352 (5)	Cu–N1–C2	164.7 (3)	C1–C1′	1.349 (4)	Co–N1–C2	168.8 (2)
C1–C2	1.443 (4)	N1–C2–C1	176.8 (4)	C1–C2	1.441 (4)	N1–C2–C1	174.7 (3)
C1–C3	1.421 (5)	C2–C1–C1′	120.2 (3)	C1–C3	1.427 (4)	C2–C1–C1′	119.7 (3)
C2–N1	1.119 (4)	C2–C1–C3	119.4 (3)	C2–N1	1.130 (4)	C2–C1–C3	119.6 (3)
C3–N2	1.133 (6)	C1–C3–N2	176.8 (4)	C3–N2	1.131 (5)	C1–C3–N2	175.1 (3)

polymers with N-bonded bridging TCNE units.

Results and Discussion

Anhydrous $M(hfacac)_2$ (M = Co, Cu) and TCNE were sublimed in a heated reaction tube such that they mixed in the vapor phase. Lustrous black films appeared on the surface of the reaction tube in the hotter zone (100–300 °C), and transparent crystals grew in the cooler zone (30–50 °C).[7] The relative yield of crystals increases where the temperature of the reaction tube is below 100 °C. The green and orange crystals that respectively result from reactions of TCNE with $Cu(hfacac)_2$ and $Co(hfacac)_2$ were studied by IR spectroscopy and single-crystal X-ray diffraction. X-ray structure determinations revealed the presence of coordination polymers based on 1:1 stoichiometry ($M(hfacac)_2{\cdot}TCNE$). Trans nitrile donor sites of TCNE are used in bridging metal centers to form "linear"-chain polymer structures. The structures are illustrated by ORTEP and unit cell drawings in Figures 1 and 2, and the pertinent bond angles and distances are listed in Table I.

The central C–C bond distances for coordinated TCNE in the $[Cu(hfacac)_2{\cdot}TCNE]_x$ (1.352 Å) and $[Co(hfacac)_2{\cdot}TCNE]_x$ (1.349 Å) are only slightly changed from that in crystalline TCNE (1.339 Å).[8] This is clear evidence that these coordination polymers contain neutral TCNE and M^{2+} units. When TCNE oxidizes the metal center to form species containing $TCNE^-$ or $TCNE^{2-}$, the central C–C distance increases substantially (C–C ~ 1.4–1.5 Å).[2b,c] The C–CN and C–N distances which respectively shorten and elongate when TCNE is reduced are also found to be virtually unchanged from those in neutral TCNE (Table I). The only structural feature that is significantly different in the set of coordination polymers is that the Cu–NC distance (2.563 Å) is substantially longer than the Co–NC distance (2.209 Å), as expected for six-coordinate d^9 and d^7 complexes,[9] respectively.

Tetracyanoethylene manifests diverse reactivity and bonding modes with metal complexes. Numerous examples of structurally characterized alkene π complexes[4] and charge-transfer complexes and salts[2] containing $TCNE^-$ and $TCNE^{2-}$ are available. Relatively few structures have been reported for nitrile-bonded TCNE complexes,[6] and none are currently available for complexes with bridging TCNE units. Both $[Co(acacen)_2{\cdot}TCNE]_x$ and $[Sn(acac)_2{\cdot}TCNE]_x$ have been proposed to contain TCNE units that bridge metal centers by nitrile coordination on the basis of IR spectra and elemental analysis[5a,6] but were not structurally characterized by X-ray diffraction.

$M(hfacac)_2{\cdot}TCNE$ (M = Cu, Co) are apparently the only structurally characterized complexes where TCNE nitrile coordination is used to bridge metal centers in producing coordination polymers.

Experimental Section

Synthesis of Metal Hexafluoroacetylacetonate Complexes, $M(hfacac)_2$. (a). $Cu(hfacac)_2$. Copper nitrate trihydrate (10 mmol) was dissolved in water (50 mL); to this were added, with mixing, hexafluoroacetylacetone (20 mmol) and sodium acetate (20 mmol) in water (20 mL). The green needles which precipitated were filtered off and dried in air; the product was further purified by sublimation; mp 134–136 °C (lit.[10] mp 134–136 °C). The anhydrous complex was prepared by placing the dihydrate in a vacuum desiccator over phosphorus pentoxide, where the color gradually changes from green to purple; mp 95–98 °C (lit.[11] mp 95–98 °C).

(b) $Co(hfacac)_2$. Cobaltous chloride hexahydrate (10 mmol) and hexafluoroacetylacetonate (20 mmol) in water (50 mL) were treated with 0.1 N sodium hydroxide solution (20 mmol). The dihydrate product precipitated as a yellow/orange powder; mp 173–174 °C (lit.[12] mp

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(7) Our initial efforts in this research were concerned with the development of a novel approach to the synthesis of polymer films from the gas-phase-initiated polymerization of organic tetracyano derivatives. Films of the Cu(II) derivative produced from reaction with tetracyanobenzene have a mirrorlike metallic luster and two probe conductivities in the range 10–50 S cm^{-1} (298 K). However, these materials were not well characterized. (See for example: Naraba, T.; et al. *Jpn. J. Appl. Phys.* **1965**, *4* (12), 977. Wöhrle, D.; et al. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 975 and references therein.)

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Table II. Crystallographic Data for [M(hfacac)$_2$·TCNE]$_x$

	[Cu(hfacac)$_2$·TCNE]$_x$	[Co(hfacac)$_2$·TCNE]$_x$
formula	$CuC_{16}H_2N_4O_4F_{12}$	$CoC_{16}H_2N_4O_4F_{12}$
fw	605.74	601.13
cryst class	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	2	2
a, Å	6.069 (2)	5.784 (2)
b, Å	20.203 (5)	21.084 (4)
c, Å	8.732 (1)	8.358 (2)
β, deg	90.53 (2)	91.45 (2)
V, Å^3	1070.6 (7)	1019.1 (8)
μ, cm^{-1}	11.53	9.78
ρ_{calc}, g/cm^3	1.879	1.959
T, °C	24	24
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
R_1 (=R[13])	0.034	0.038
R_2 (=R_w[13])	0.041	0.047

172–174 °C). The anhydrous complex, Co(hfacac)$_2$, is obtained as a fine brown powder by the procedure described for anhydrous Cu(hfacac)$_2$.

[Cu(hfacac)$_2$·TCNE]$_x$. TCNE (30 mg, 23.4 mmol) and anhydrous copper hexafluoroacetylacetonate, Cu(hfacac)$_2$ (56 mg, 11.7 mmol), were placed in a thick-walled glass vessel, and the tube was evacuated on the vacuum line prior to sealing. A significant temperature gradient along the reaction vessel was arranged by allowing half of the tube to protrude outside the heating oven. Lustrous polymeric films and an insoluble black amorphous polymer powder residue remained in the heated area of the tube.[13] Green crystals of [Cu(hfacac)$_2$·TCNE]$_x$ were formed in the cooler regions of the tube. In the melting point apparatus, the green crystals failed to actually melt but instead were transformed to a black amorphous powder at 162 °C. [Cu(hfacac)$_2$·TCNE]$_x$ was characterized by IR spectroscopy (ν_{CN} = 2262, 2252, 2220 cm^{-1}) and by single-crystal X-ray diffraction studies.

[Co(hfacac)$_2$·TCNE]$_x$. Orange crystals of [Co(hfacac)$_2$·TCNE]$_x$ were prepared from TCNE and anhydrous Co(hfacac)$_2$ and characterized in the manner outlined above (ν_{CN} = 2258, 2228, 2214 cm^{-1}).

X-ray Structure Determinations of [M(hfacac)$_2$·TCNE]$_x$. Both compounds crystallize in the monoclinic space group $P2_1/c$ (systematic absences: $0k0$, k = odd; $h0l$, l = odd) with $Z = 2$. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) over the range $4 \leq 2\theta \leq 55°$ using the ω–2θ scan technique. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was performed. Reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement (Table II).

The structures were solved by standard heavy-atom Patterson techniques followed by weighted Fourier syntheses. Hydrogen atoms were found from difference Fourier maps calculated after anisotropic refinement. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Nonhydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

Table III. Refined Positional Parameters of Selected Atoms for [Cu(hfacac)$_2$·TCNE]$_x$

atom	x	y	z	B_{eq},[a] Å^2
Cu	0.5000 (0)	0.5000 (0)	0.5000 (0)	3.229 (9)
O1	0.3345 (3)	0.4264 (1)	0.4142 (2)	3.78 (4)
O2	0.6611 (3)	0.4428 (1)	0.6418 (2)	3.63 (4)
C1	−0.0396 (5)	0.5162 (2)	0.9379 (4)	4.21 (7)
C2	0.0877 (5)	0.5189 (2)	0.7992 (4)	4.28 (7)
C3	−0.2468 (7)	0.5488 (2)	0.9433 (4)	5.9 (1)
N1	0.1939 (5)	0.5196 (2)	0.6952 (3)	5.36 (7)
N2	−0.4124 (7)	0.5741 (2)	0.9548 (5)	9.6 (1)
C4	0.3701 (5)	0.3671 (2)	0.4451 (4)	3.88 (7)
C5	0.5207 (6)	0.3413 (2)	0.5476 (4)	4.74 (8)
C6	0.6533 (5)	0.3810 (2)	0.6379 (4)	3.85 (7)

[a] $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$.

Table IV. Refined Positional Parameters of Selected Atoms for [Co(hfacac)$_2$·TCNE]$_x$

atom	x	y	z	B_{eq},[a] Å^2
Co	0.5000 (0)	0.5000 (0)	0.5000 (0)	2.185 (8)
O1	0.6737 (3)	0.57527 (8)	0.4128 (2)	2.77 (4)
O2	0.3341 (3)	0.55925 (8)	0.6532 (2)	2.76 (4)
C1	1.0385 (5)	0.4844 (1)	0.9354 (3)	2.96 (5)
C2	0.8999 (5)	0.4834 (1)	0.7897 (3)	2.88 (5)
C3	1.2565 (5)	0.4527 (2)	0.9414 (4)	3.65 (6)
N1	0.7781 (4)	0.4848 (1)	0.6818 (3)	3.05 (5)
N2	1.4305 (5)	0.4288 (2)	0.9573 (4)	5.57 (8)
C4	0.6239 (5)	0.6320 (1)	0.4369 (3)	2.90 (5)
C5	0.4625 (6)	0.6560 (1)	0.5407 (4)	3.77 (6)
C6	0.3348 (5)	0.6185 (1)	0.6421 (3)	2.98 (5)

[a] $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$.

In each compound, the metal atom was found to lie on a crystallographic center of symmetry ($^1/_2$, $^1/_2$, $^1/_2$) and the midpoint of the carbon–carbon double bond in TCNE also lies on a crystallographic symmetry center ($^1/_2$, 0, 1). In both compounds, the CF_3 groups exhibited rotational disorder. In the Cu compound, both crystallographically independent CF_3 groups were disordered in a 70:30 ratio, while in the Co compound, only one of the two crystallographically independent CF_3 groups was disordered, in a 60:40 ratio. The refined positional parameters for selected atoms are found in Table III and IV.

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Registry No. Cu(hfacac)$_2$, 14781-45-4; Co(hfacac)$_2$, 19648-83-0; [Cu(hfacac)$_2$·TCNE]$_x$, 139070-93-2; [Co(hfacac)$_2$·TCNE]$_x$, 139070-95-4.

Supplementary Material Available: Tables giving structure determination summaries, refined atomic coordinates (with esd's), refined thermal parameters, bond distances, and bond angles for both compounds (11 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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(12) Attempts to study the black polymeric powders were hindered by its complete insolubility in all organic solvents and even concentrated sulfuric acid. Our observations concerning this poorly characterized polymer are consistent with those reported in previous studies on solid-state reactions between organic tetracyano compounds and metals or metal halides. In particular, diffuse-reflectance infrared spectroscopy has illustrated the disappearance of absorptions due to free –CN groups (at 2220 cm^{-1}) with increased reaction temperature and times and also the corresponding appearance of broad bands covering the region 1260–1380 cm^{-1}, which have been attributed to the phthalocyanine/porphyrazine structure. (See, for example: Wöhrle, D.; et al. *Makromol. Chem.* **1985**, *186*, 2209. Lin, J.; Dudek, L. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1579–1597 and references therein.)

(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

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A Simple, Efficient Route to a μ_6-Oxo-Centered Hexanuclear Iron(III) Alkoxide Complex: Preparation and Structure of $Na_2Fe_6O(OCH_3)_{18}{\cdot}6CH_3OH$

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We recently reported the structure of a μ_6-oxo-centered, hexanuclear Fe(III) complex with six entities of fully deprotonated, facially coordinated tris(hydroxymethyl)ethane (THME) entities as chelating ligands.[2] However, the formation of this complex

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