previously.[8,17] The cis disposition of these ligands allows π-back-bonding between the filled d_{xy} (taking z as the direction along W=O) and the π^* CO orbitals. The mutual cis arrangement of the oxo, carbonyl, and halide ligands is also dictated by the facial coordination mode of the $HB(Me_2pz)_3^-$ ligand in these complexes. We believe the steric protection offered to the WO(CO)X fragment by the $HB(Me_2pz)_3^-$ ligand enhances the kinetic stability of the $\{HB(Me_2pz)_3\}WO(CO)X$ complexes. We note that further oxidation of the complexes to the more thermodynamically stable *cis*-dioxotungsten(VI) complexes $\{HB(Me_2pz)_3\}WO_2X$ does take place, and indeed, the susceptibility of the bromo complex to this reaction has made it difficult to isolate pure $\{HB(Me_2pz)_3\}WO(CO)Br$. The mechanism of the reaction, which appears to proceed via an isolable as yet uncharacterized dicarbonyl intermediate, is of great interest and is under further study.

Preliminary studies of the reactivity of 1 have revealed that the phenylnitrene complex $\{HB(Me_2pz)_3\}W(NPh)(CO)I$[18] is formed upon reaction with aniline (eq 3). The CO frequency of 1930 cm^{-1} indicates that greater electron density is available for back-bonding in the nitrene complex than in the oxo analogue (ν_{CO} = 1975 cm^{-1}) as was found by Mayer and co-workers.[8] NMR reveals the carbonyl carbon at 278.7 ppm with $^1J_{WC}$ = 178 Hz while the ipso carbon of the nitrene phenyl group displays two-bond coupling to tungsten ($^2J_{WC}$ = 35 Hz). Similar two-bond coupling has been reported for related cationic nitrenes with phenyl and *tert*-butyl substituents.[19]

$$\{HB(Me_2pz)_3\}WO(CO)I + PhNH_2 \rightarrow \{HB(Me_2pz)_3\}W(NPh)(CO)I \quad (3)$$

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Supplementary Material Available: Tables giving a summary of the crystal data and details of the X-ray data collection, atomic fractional coordinates, thermal parameters, and complete interatomic distances and angles and a drawing of 1 showing the complete atomic labeling (7 pages); a list of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(18) Synthesis of $\{HB(Me_2pz)_3\}W(NPh)(CO)I$: A solution of $\{HB(Me_2pz)_3\}W(CO)(O)I$ (1.00 g, 1.53 mmol) in aniline (50 mL) was heated to 80 °C for 4 h, and the color changed from red-brown to brown. The solvent was removed under reduced pressure. The residue was recrystallized from $CH_2Cl_2/MeOH$ three times to yield dark brown crystals (0.57 g, 46%). IR (KBr, cm^{-1}): ν(CO) 1930. ^1H NMR (CD_2Cl_2): δ 7.40 (m, 3 H, C_6H_5), 7.25 (m, 2 H, C_6H_5), 6.12, 6.01, and 5.80 [1:1:1, 3 H, *CH* of $HB(Me_2pz)_3$], 2.56, 2.55, 2.53, 2.50, 2.36, and 2.29 [3:3:3:3:3:3, 18 H, CH_3 of $HB(Me_2pz)_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 278.7 ($^1J_{WC}$ = 178 Hz, *C*O), 158.1 ($2J_{WC}$ = 35 Hz, *C* ipso), 154.3, 154.2, 153.5, 146.4, 146.3, and 146.0 (*C*CH_3), 129.7, 126.6, and 125.1 (C_6H_5), 108.4, 107.9, and 107.3 (*C*H_3), 18.0, 17.5, 16.3, 13.0, 12.72, and 12.68 (C*C*H_3). Anal. Calcd for $WBN_7C_{22}H_{27}OI \cdot CH_2Cl_2$: C, 34.02; H, 3.60. Found. C, 34.27; H, 3.76.

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Linear Trimeric and Monomeric Octahedral Vanadium(II) Diphenylacetate Complexes

The ability of carboxylate anions to work as bridging three-center chelating ligands is an attractive feature of this class of molecules widely employed for the assemblage of di-[1] and polymetallic units.[2] The most useful characteristics of carboxylate anions as ligands can be summarized in the ability (i) to easily form dimers via bridging interactions of the two oxygen donor atoms, each binding one of the two metal centers,[1] (ii) to accommodate an enormous range of M-M distances (from very short[3] to considerably long nonbonding distances),[4] and (iii) to establish efficient magnetic couplings between two metal centers.[5] Thus, structural investigations on transition-metal carboxylates may be helpful for understanding the nature of the M-M interaction.

Among low-valent early transition metals, vanadium(II) carboxylates are especially interesting because of some attractive performances expected or reported for these species, including dinitrogen fixation[6] and formation of short V-V triple bonds.[7] Early theoretical work has predicted the stability of dimeric vanadium(II) carboxylate with a V-V bonding distance of ca. 2.2 Å.[7c] Although initial attempts to prepare vanadium(II) carboxylates have been hampered by the apparent tendency of vanadium(II) to abstract oxygen from the $-COO^-$ group to form a mixed-valence $[V_3O]$ core,[8] an encouraging result describing the preparation of cationic $[V_2(CF_3COO)_2Cl(THF)_6]^+$ has been recently reported.[9] However, no neutral vanadium(II) carboxylates have been reported to date. In this paper, we wish to report the preparation and characterization of the first linear trimeric vanadium(II) carboxylates, together with their facile cleavage.

In a standard experiment, a solution of $VCl_2(TMEDA)_2$[10,11]

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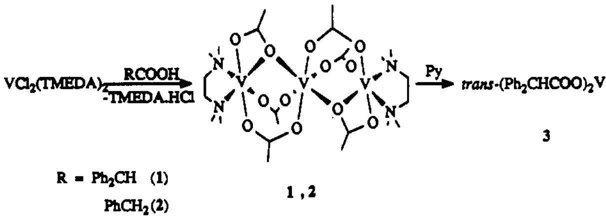
Scheme I



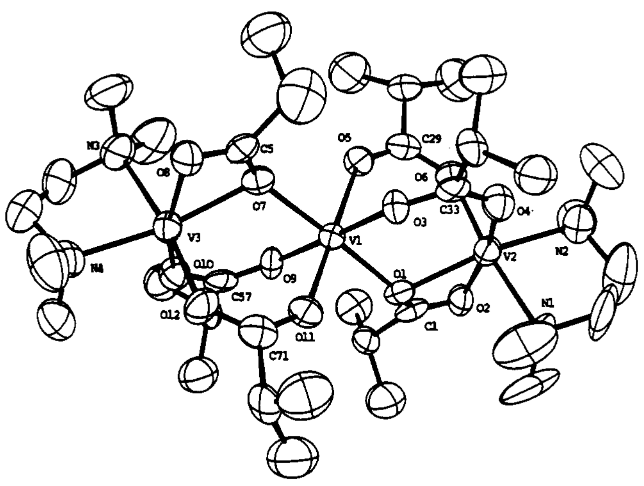


Figure 1. ORTEP drawing of **1**, showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): V1··V2 = 3.555 (7), V1··V3 = 3.549 (7) (7), V2–N2 = 2.198 (9), V1–O1 = 2.195 (7), V2–O1 = 2.163 (7), V1–O3 = 2.112 (7), V2–O4 = 2.085 (7); O1–V1–O7 = 176.7 (3), O3–V1–O9 = 178.4 (3), O1–V1–O3 = 93.3 (3), O3–V1–O5 = 88.7 (3).

in THF was treated with neat carboxylic acid at room temperature (Scheme I). The color turned rapidly reddish brown, and after elimination of the TMEDA·HCl salt, light brown analytically pure crystals of $V_3(RCOO)_6(TMEDA)_2$ [R = Ph_2CH (**1**), $PhCH_2$ (**2**)], were obtained by crystallization from toluene at −30 °C.[12]

The trimeric structure of **1** has been demonstrated by an X-ray diffraction analysis.[13] The molecule is composed of three slightly distorted octahedral vanadium atoms forming an almost linear V_3 core [V2–V1–V3 = 177.34°] (Figure 1). Two coplanar TMEDA molecules are attached to each of the two external vanadium atoms, forming V–N distances [V2–N1 = 2.198 (9) Å] that compare quite well with those of other V(II)–TMEDA complexes.[10,11] The linkage between the three vanadium atoms is obtained by six bridging carboxylates. Four carboxylates work as conventional three-center chelating ligands adopting the classical syn–syn arrangement with each oxygen donor atom bonding one metal center.[14] The V–O distances formed with the terminal and central vanadium atoms are rather similar (ranging from 2.063 to 2.112 Å) and compare well with those observed in $[V_2Cl(CF_3COO)_2]^+$.[9] The angles subtended at the central carbon atom by the two oxygen atoms in each –COO group slightly deviate from the normal angles expected for sp^2 carbon atoms [ranging from 125.1 to 127.6°]. The remaining two carboxylic groups adopted a "tridentate" bonding mode with one oxygen attached to the terminal vanadium [V2–O2 = 2.151 (8) Å, V3–O8 = 2.160 (7) Å] and the second oxygen which bridges two metal centers [V1–O1 = 2.195 (7) Å, V2–O1 = 2.163 (7) Å]. As a result of the two considerably different bonding modes, the angles subtended at the carbon atoms by the two donor oxygen atoms are significantly narrower [O1–C1–O2 = 117.9 (9)°, O7–C43–O8 = 119.7°]. The geometry around the tricoordinated bridging oxygen is pyramidal, forming normal tetrahedral angles [V1–O1–V2 = 109.0 (3)°, V1–O7–V3 = 113.9 (3)°].

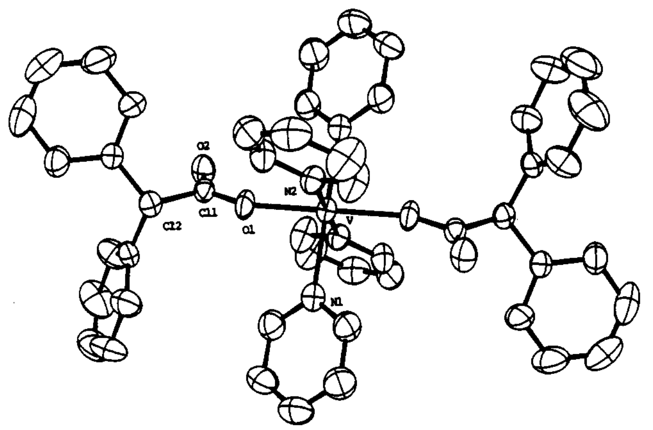


Figure 2. ORTEP drawing of **3**, showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): V–O1 = 2.087 (2), V–N1 = 2.220 (3), V–N2 = 2.208 (3); N1–V1–O1 = 88.28 (9), N1–V1–N2 = 91.66 (10), N2–V1–O1 = 87.62 (10).

Although the acetate ligand in complex **1** does not allow the formation of a V–V multiple bond [V1··V2 = 3.555 Å, V1··V3 = 3.549 Å], nevertheless it does provide an efficient electronic coupling between the three metal centers. The magnetic moment of the trimer is in fact lower than expected for a high-spin d^3 V(II) (μ_{eff} = 5.45 μ_B per trimer), probably as a result of an efficient ligand-mediated superexchange operated by the three bridging oxygen donor atoms. It is noteworthy that the normal high-spin configuration with three unpaired electrons per vanadium atom has been observed in the dimeric $[V_2Cl(CF_3COO)_2(THF)_6]^+$, having only a slightly longer value of the V··V nonbonding distance.[9] This suggests that the nature of the bridging ligand and the positioning of the bridging donor atoms around the transition metal, as determined by steric factors or geometry optimization, may be responsible, rather than the M–M distance, for the efficiency of the magnetic couplings.

The trimeric aggregation of **1** is rather weak, since simple reaction with pyridine cleaves the linear trimer forming the monomeric $(R_2CHCOO)_2V(py)_4$ (**3**) (Scheme I).[15]

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(12) $VCl_2(TMEDA)_2$ (2.65 g, 7.5 mmol) in THF (70 mL) was treated with neat diphenylacetic acid (3.17 g, 15.0 mmol) at room temperature. The color turned rapidly reddish brown upon boiling, and the mixture was stirred for 12 h. The TMEDA·HCl salt was filtered out from a boiling solution, and light brown, analytically pure crystals of $V_3(RCOO)_6(TMEDA)_2$·2toluene [R = Ph_2CH (**1**), $PhCH_2$ (**2**)] (3.46 g, 2.1 mmol) separated upon evaporation and crystallization from toluene at −30 °C. IR [KBr, Nujol mull, cm^{-1}]: 1600 (s), 1545 (m), 1490 (w), 1390 (s), 1290 (w), 1260 (w), 1170 (w), 1130 (w), 1080 (m), 1040 (m), 1035 (m), 950 (m), 795 (s), 740 (s), 730 (s), 695 (s), 640 (s), 560 (m), 490 (w), 465 (m). Anal Calcd (found) for $C_{110}H_{104}N_4O_{12}V_3$: C, 72.32 (72.31); H, 5.74 (5.65); N, 3.07 (2.99); V, 8.37 (8.29). μ_{eff} = 5.45 μ_B at room temperature.

(13) Crystal data for $C_{110}H_{104}N_4O_{12}V_3$ (**1**) at room temperature: monoclinic, space group $P2_1/n$ with a = 15.142 (7) Å, b = 26.543 (6) Å, c = 24.775 (22) Å, β = 101.78 (5)°, V = 9748 (10) Å^3, Z = 4, d_{calcd} = 1.245 g cm^{-3}, μ = 1.27 mm^{-1}. Of 10018 unique reflections collected by using Cu (λ = 1.540 56 Å) radiation ($2\theta_{max}$ = 100°), 6783 with $I > 2.5\sigma(I)$ were used in the final refinement. The highest residual peak in the final difference Fourier map was 0.960 e/Å^3. All non-hydrogen atoms were anisotropically refined, except the carbon atoms of the phenyl rings and the two disordered molecules of toluene. This disorder, together with the poor quality of the data set, is probably responsible for preventing the convergence to lower residuals (R = 0.103; R_w = 0.089). Hydrogen atoms were introduced at calculated positions and refined with one common thermal parameter.

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(15) The addition of pyridine (5 mL) to a solution of $V_3(Ph_2COO)_6(TMEDA)_2·2C_7H_8$ (2.27 g, 1.31 mmol) in THF (50 mL) turned the solution deep purple. The resulting solution was boiled and evaporated to dryness. The solid residue was crystallized from THF (10 mL) containing 1 mL of pyridine. Black crystals of **3** precipitated upon standing at room temperature (1.76 g, 2.65 mmol, 67%). IR [KBr, Nujol mull, cm^{-1}]: 1610 (s), 1595 (m), 1495 (w), 1480 (m), 1450 (s), 1415 (s), 1375 (m), 1370 (s), 1345 (s), 1270 (m), 1220 (m), 1175 (m), 1150 (m), 1070 (m), 1040 (m), 1035 (m), 1005 (w), 950 (w), 880 (w), 850 (w), 775 (m), 760 (m), 735 (m), 710 (s), 700 (s), 695 (s), 645 (s), 625 (m), 565 (m), 475 (w), 445 (m). Anal Calcd (found) for $C_{48}H_{42}N_4O_4V$: C, 72.32 (72.19); H, 5.74 (5.66); N, 3.07 (3.00); V, 8.37 (8.33). μ_{eff} = 3.73 μ_B at room temperature.

The structure of **3**, as demonstrated by X-ray analysis,[16] showed the unit cell composed of discrete monomeric units with two carboxylate groups occupying the axial positions of the ideal octahedron centered on vanadium [O1–V–N1 = 88.28 (9)°, O1–V–N2 = 87.6 (1)°, N1–V–N2 = 91.6 (1)°] (Figure 2). The nitrogen atoms of the four pyridine molecules occupy the equatorial plane forming V–N distances [V–N1 = 2.220 (3) Å] comparable to those of $VCl_2(py)_4$.[17] The two carboxylate ligands work as a simple monodentate group forming V–O distances [V–O1 = 2.087 (2) Å], which fall in the range of those formed by the bridging carboxylates in complex **1**.

Acknowledgment. This work has been supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) is gratefully acknowledged for providing a visiting scholarship (J.J.H.E.). We are indebted to Dr. W. Armstrong (U. C. Berkley) for making us aware of his unpublished results.

Supplementary Material Available: A full ORTEP drawing for **1** and labeling schemes for **1** and **3**, listings of crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **3**, and listings of least-squares planes and dihedral angles for **3** (27 pages); listings of observed and calculated structure factors for **1** and **3** (69 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for $C_{48}H_{42}N_4O_4V$ (**3**) at room temperature: monoclinic, space group $P2_1/n$ with $a = 9.999$ (2) Å, $b = 18.333$ (7) Å, $c = 11.500$ (1) Å, $\beta = 105.53$ (1)°, $V = 2031.1$ (9) Å^3, $Z = 2$, $d_{calcd} = 1.291$ g cm^{-3}, $\mu = 0.26$ mm^{-1}. Of 3009 unique reflections collected by using Mo ($\lambda = 0.709\,30$ Å) radiation ($2\theta_{max} = 46.9°$), 1933 with $I > 2.5\sigma(I)$ were used in the final refinement. $R = 0.045$ ($R_w = 0.017$) for 316 parameters. The highest residual peak in the final difference Fourier map was 0.200 e/Å^3.

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Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: The First Organic Superconductor Containing a Polymeric Copper Cyanide Anion

Recently we have reported the organic superconductors with the highest superconducting transition temperatures (T_c) at ambient pressure, viz., κ-(ET)$_2$Cu[N(CN)$_2$]Br ($T_c = 11.6$ K inductively),[1] as well as at a slight elevated pressure, viz., κ-(ET)$_2$Cu[N(CN)$_2$]Cl ($T_c = 12.8$ K at 0.3 kbar, inductively),[2] where ET (or BEDT-TTF) is bis(ethylenedithio)tetrathiafulvalene. These record-high T_c's clearly established the κ-type structural family as the most prominent group of ET-based superconductors. The κ-structural type is characterized by *conducting* organic layers, sandwiched between essentially *insulating* anion layers, of face-to-face dimers of ET donor molecules, which themselves are rotated by about 90° with respect to neighboring dimers. Furthermore, the long axes of all ET molecules are inclined ca. 30° with respect to the layer normal. Thus, the ET molecule layers have a rectangular intralayer repeat unit of typically 9 Å × 13 Å for κ-phases. However, not all κ-phase salts are isostructural, as they differ in the relative arrangement of the layers and in the symmetry of the anion (the organic layers are always virtually centrosymmetric, even if not so required by the space group symmetry). κ-(ET)$_2$Cu[N(CN)$_2$]X (X = Cl, Br) and the nonsuperconducting iodide analogue[3,4] are orthorhombic two-layer systems, whereas κ-(ET)$_2$Cu(NCS)$_2$ ($T_c = 10.4$ K),[5] κ-(ET)$_2$Ag(CN)$_2$·H$_2$O ($T_c = 5.0$ K),[6] and κ-(ET)$_2$I$_3$ ($T_c = 3.6$ K)[7] are monoclinic single-layer systems.

In our attempt to synthesize new κ-phase superconductors, we have concentrated on ET salts with complex anions composed of Cu(I) or Ag(I) metal ions and pseudohalide anions. The Cu$^+$–CN$^-$ system is an obvious candidate, but synthesis attempts in the past starting from anhydrous (n-Bu)$_4$NCu(CN)$_2$[8] failed to yield any characterizable product. However, the "targeted anion approach", by use of a *preformed* anion as found in KCu$_2$(CN)$_3$·H$_2$O, and the presence of trace amounts of water, led to the discovery of the first copper–cyanide containing superconductor, κ-(ET)$_2$Cu$_2$(CN)$_3$, whose synthesis, crystal structure, superconducting properties, and band electronic structure we describe herein.

Synthesis. The title compound was synthesized by two different electrocrystallization routes: In method 1 we used a solution of 8.5 mg of ET (Strem Chemical Co., Inc.), 17.1 mg of CuCN (8 equiv), 12.3 mg of KCN (8 equiv), and 18-crown-6 (~8 equiv) in a solvent mixture containing 1,1,2-trichloroethane (TCE), 9.9% (vol) absolute ethanol, and 0.1% (vol) water, whereas method 2 started from a solution of 8 mg of ET, 41.3 mg of KCu$_2$(CN)$_3$·H$_2$O[9] (8 equiv) containing the "preformed" anion (vide infra), and 18-crown-6 (~8 equiv) in TCE and 10% (vol) absolute ethanol. In the absence of small amounts of water, either deliberately mixed into the solution or as crystal water in the case of KCu$_2$(CN)$_3$·H$_2$O, no characterizable product was formed. The electrocrystallization cells were prepared inside a glovebox, and crystal growth on a Pt anode at a current density of 0.1–0.2 μA cm^{-2} was carried out for about 30 days. The product (black rhomboid-shaped platelets) appears to be a single phase, as judged by visual inspection and the room-temperature ESR line width, $\Delta H_{pp} \approx 60$ G, of several crystal specimens.

Crystal Structure. All crystals examined to date were twinned. However, a small crystal containing a single crystal domain of at least two-thirds of the crystal volume, as estimated from X-ray diffraction photographs, was used for a structure determination.[10] Since the twinning law could not be determined, all reflections

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(10) X-ray data were collected on a Syntex P2$_1$ diffractometer, and the monoclinic unit cell data (space group P2$_1$/c, $Z = 2$) are as follows (298 K): $a = 16.117$ (5) Å, $b = 8.5858$ (9) Å, $c = 13.397$ (3) Å, $\beta = 113.42$ (2)°, $V = 1701.2$ (7) Å^3. A total of 4696 diffraction data were collected (ω scans, 1.2°, 1.5–6° min^{-1}) in the range $4° \leq 2\theta \leq 50°$ (all h, $k \geq -1$, $l \geq -2$). A total of 43 reflections were eliminated a priori as severely affected by twinning, and the remainder were corrected for absorption ($\mu = 22.25$ cm^{-1}, $T_{min} = 0.679$, $T_{max} = 0.957$) and averaged ($R_{av} = 0.046$) to 2964 unique, allowed reflections. The structure was solved by direct methods, with 188 variables refined by full-matrix least-squares methods to 2043 observed reflections ($F_o > 4\sigma$), with $R(F) = 0.118$, $R_w(F) = 0.116$, and GOF = 4.02. The programs used in the analysis of the diffraction data were modified versions of: Strouse, C. *UCLA Crystallographic Program Package*; University of California: Los Angeles, CA, 1986.

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