

O(13) very much displaced from the ideal positions. O(1), the furan oxygen, takes no part in coordination.

In (II), Fig. 3, each anion links four Ca atoms to give chains Ca(2)'...Ca(2)...Ca(1)...Ca(2)'', cross-linked by Ca(1)...Ca(1)', where the mid-point of Ca(2)...Ca(2)' [3.965 (1) Å] is the origin and the mid-point of Ca(1)...Ca(1)' is 0.5,0,0.5. O(27) and O(27)'' link Ca(2) and Ca(2)' and O(28) links Ca(1) and Ca(2) but Ca(1) and Ca(1)' are only connected across the anion from O(21), the furan oxygen, to O(33). Each Ca atom is eight-coordinate and of irregular geometry including three water molecules. Bond lengths and angles are given in Table 6.* The water molecules O(10) and

O(11) take part in the extensive network of hydrogen bonds.

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* Table 6 has been deposited.

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Tris(1,2-dimethoxyethane)lithium μ -Chloro- μ -oxo-bis[chloro(pentamethylcyclopentadienyl)(1-pyrrolyl)zirconate(IV)] Dimethoxyethane Solvate, [Li(C₄H₁₀O₂)₃][Zr₂Cl₃O(C₄H₄N)₂(C₁₀H₁₅)₂].C₄H₁₀O₂

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Abstract. $M_r = 1074.9$, monoclinic, $C2/c$, $a = 12.203$ (3), $b = 30.853$ (9), $c = 15.194$ (4) Å, $\beta = 106.82$ (4)°, $V = 5475$ Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 5.67$ cm⁻¹, $T = 293$ K, $F(000) = 2248$; $R = 0.082$ for the 1850 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Zr–O length is short, 1.910 (6) Å, while the Zr–Cl(bridge) distance is long, 2.665 (4) Å, especially compared to the Zr–Cl(terminal) distance of 2.472 (4) Å. The angles at the bridge are Zr–O–Zr = 132.5 (8)° and Zr–Cl–Zr = 82.0 (2)°. Both the cation and the anion reside on crystallographic twofold axes. An uncoordinated dimethoxyethane (dme) lies highly disordered about a twofold axis.

Introduction. The pyrrolyl anion, $\bar{N}C_4H_4$, is isoelectronic with the cyclopentadienyl anion, but the chemistry of the former is not nearly so well developed as that of the latter. In the course of our investigations of pyrrolyl complexes of the early transition metals, we have noted an interesting competitive effect: $\bar{N}C_4H_4$ is able

reversibly to displace \bar{C}_5H_5 in some instances. For example, the reaction of $(\eta^5-C_5H_5)_2ZrCl_2$ with $NaNc_4H_4$ in H_4 furan‡ leads to the formation of the expected $(\eta^5-C_5H_5)_2Zr(Nc_4H_4)_2$ upon extraction with toluene. However, it has been demonstrated that $[Na(H_4furan)_6]_2[Zr(Nc_4H_4)_6]$ is formed as an intermediate (Bynum, Hunter, Rogers & Atwood, 1980). This allows the inference of an unexpected lability of the cyclopentadienyl rings. In order to learn of the range of this behavior, the reaction of $(C_5Me_5)_2ZrCl_2$ with $NaNc_4H_4$ was undertaken in dme.

Experimental. Straw-colored crystal, air-sensitive. Specimen, 0.20 × 0.25 × 0.30 mm sealed under N₂ in a glass capillary. CAD-4 diffractometer; unit-cell parameters refined from Bragg angles of 24 reflections, 2θ 25–30°, space group $C2/c$ or Cc from systematic absences, shown to be $C2/c$ by successful refinement; 4474 reflections measured in the quadrant $h = -14$ to 14, $k = 0$ to 34, $l = 0$ to 17, $\theta - 2\theta$ scan (0.80° + 0.20° tan θ), net count of 4000 obtained if scan time of less than 240 s required, 2° < 2 θ < 50°; three standard reflections every 200 reflections, only

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‡ Tetrahydrofuran.

Table 1. Atom coordinates and U_{eq} values
$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Zr	0.1374 (1)	0.13504 (5)	0.23623 (9)	0.049
Cl(1)	0.0000	0.2002 (2)	0.2500	0.060
Cl(2)	0.2827 (3)	0.1843 (1)	0.3333 (3)	0.069
O(1)	0.0000	0.1101 (4)	0.2500	0.053
N	0.239 (1)	0.0816 (4)	0.3179 (9)	0.069
C(1)	0.351 (1)	0.0810 (6)	0.360 (1)	0.076
C(2)	0.377 (2)	0.0389 (7)	0.396 (1)	0.090
C(3)	0.277 (2)	0.0133 (7)	0.373 (2)	0.118
C(4)	0.191 (1)	0.0398 (5)	0.323 (1)	0.076
C(5)	0.241 (1)	0.1499 (6)	0.115 (1)	0.069
C(6)	0.218 (2)	0.1051 (6)	0.112 (1)	0.074
C(7)	0.102 (2)	0.0998 (6)	0.082 (1)	0.081
C(8)	0.051 (1)	0.1402 (7)	0.0668 (9)	0.076
C(9)	0.137 (2)	0.1724 (6)	0.086 (1)	0.074
C(10)	0.363 (2)	0.1720 (8)	0.142 (1)	0.123
C(11)	0.313 (2)	0.0699 (7)	0.135 (1)	0.156
C(12)	0.042 (3)	0.0552 (7)	0.068 (2)	0.173
C(13)	0.074 (1)	0.1496 (9)	0.031 (1)	0.138
C(14)	0.122 (2)	0.2222 (6)	0.071 (1)	0.114
Li	0.0000	0.373 (1)	0.2500	5.2 (8)*
O(2)	0.041 (1)	0.3613 (4)	0.3721 (8)	7.0 (3)
O(3)	0.135 (1)	0.3285 (4)	0.3253 (8)	7.4 (3)
O(4)	0.114 (1)	0.4268 (4)	0.2881 (8)	7.2 (3)
C(15)	0.118 (2)	0.3900 (7)	0.403 (1)	8.7 (5)
C(16)	0.044 (2)	0.3385 (7)	0.441 (1)	9.0 (5)
C(17)	0.109 (1)	0.3086 (6)	0.401 (1)	7.0 (4)
C(18)	0.212 (2)	0.3022 (6)	0.291 (1)	7.2 (4)
C(19)	0.226 (2)	0.4281 (6)	0.353 (1)	8.6 (5)
C(20)	0.052 (2)	0.4659 (7)	0.290 (1)	8.7 (5)
O(5)	0.5497	0.3668	0.3176	15.7
C(21)	0.5220	0.4169	0.2826	15.7
C(22)	0.4462	0.3253	0.1766	15.7
C(23)	0.5216	0.3211	0.2242	15.7
C(24)	0.5456	0.4078	0.3218	15.7

* Atoms of the cation were refined with isotropic $B(=8\pi^2U^2)$, B given here.

statistical variations noted; absorption correction not applied since minimum and maximum transmission factors were 0.87 and 0.90, respectively. Structure solved by direct methods and refined by full-matrix least squares on F ; H atoms not located; non-hydrogen atoms of the anion refined with anisotropic thermal parameters; 1850 reflections with $F_o^2 > 3\sigma(F_o^2)$, 202 variables refined, $R = 0.082$, $R_w = 0.083$, $S = 0.63$, $(\Delta/\sigma)_{\max} = 0.05$; unit weights; peaks and troughs of ca 1 e \AA^{-3} near the disordered molecule of solvation; scattering factors from Cromer & Waber (1965); scattering for all atoms corrected for the real and imaginary components of anomalous dispersion (Cromer & Liberman, 1970); other mathematical and computational details are given elsewhere (Holton, Lappert, Ballard, Pearce, Atwood & Hunter, 1979).

Discussion. The final positional and equivalent isotropic thermal parameters are listed in Table 1* and a view of

* Anisotropic thermal parameters and a listing of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39607 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the anion of the title compound is exhibited in Fig. 1. The anion, which resides on a crystallographic twofold axis, possesses several interesting features. The Zr—O bond length at 1.910 (6) Å is quite short. It may be compared with values of 1.945 (3) Å in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2\text{O}$ (Hunter, Hrcir, Bynum, Penttila & Atwood, 1983), and 1.966 (5) Å in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr(SPh)}]_2\text{O}$ (Petersen, 1979), molecules which possess Zr—O—Zr linkages which are near linear, angle = 169–180°. The Zr—O length may also be compared with the 1.970 (4) Å bond length in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W=C(H)OZr(H)(}\eta^5\text{-C}_5\text{Me}_5)_2$ (Wolczanski, Threlkel & Santarsiero, 1983). The angle at the O atom, 132.5 (8)°, is the most acute yet reported for a Zr—O—metal situation, and may be compared with 142.5° in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrO}]_3$ (Fachinetti, Floriani, Chiesi-Villa & Guastini, 1979).

The Zr—Cl(terminal) bond length, 2.472 (4) Å, agrees well with the 2.441 (10) Å value in $[(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)]_2\text{ZrCl}_2$ (Saldarriaga-Molina, Clearfield & Bernal, 1974) and the 2.435 (4) Å standard in $(\eta^5\text{-C}_5\text{H}_4\text{CMe}_3)_2\text{ZrCl}[\text{CH}(\text{SiMe}_3)_2]$ and in $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{ZrCl}[\text{CH}(\text{SiMe}_3)_2]$ (Lappert, Riley, Yarow, Atwood, Hunter & Zaworotko, 1981), and is substantially shorter than the Zr—Cl(bridge) length, 2.665 (4) Å. The bridge angle at the Cl is sharp at 82.0 (2)°.

The pyrrolyl ligand is bonded in a head-on fashion with the Zr—N—centroid(pyrrolyl) angle of 174°. The Zr—N length of 2.21 (1) Å compares favorably with the related value of 2.169 (3) Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^1\text{-NC}_4\text{H}_4)_2$ (Bynum, Hunter, Rogers & Atwood, 1980) and 2.23 (2) Å in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^1\text{-NC}_4\text{H}_2\text{Me}_2)_2$ (Bynum, Zhang, Hunter & Atwood, 1984).

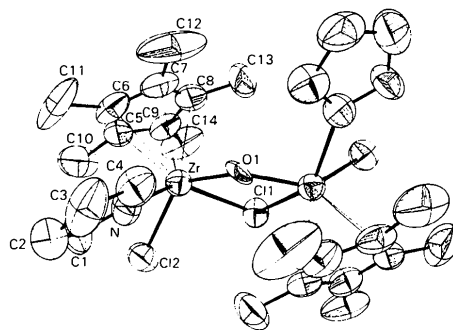


Fig. 1. Structure of the $[(\mu\text{-O})(\mu\text{-Cl})\{(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}(\eta^1\text{-NC}_4\text{H}_4)\text{(Cl)}\}_2]^-$ anion. The crystallographic twofold axis passes through both the bridging atoms. Important bond angles include: Cl(1)—Zr—Cl(2) = 81.3 (1), Cl(1)—Zr—N = 141.3 (3), Cl(1)—Zr—O = 72.2 (4), Cl(1)—Zr—centroid = 108.4, Cl(2)—Zr—N = 86.3 (4), Cl(2)—Zr—O = 133.0 (2), Cl(2)—Zr—centroid = 110.9, N—Zr—O = 90.3 (5), N—Zr—centroid = 110.3, O—Zr—centroid = 114.2°.

The \bar{C}_5 Me₅ ring shows η^5 -coordination: the Zr—C lengths range from 2.49 (1) to 2.57 (2) Å. The bond lengths and angles within the ligands themselves are normal (Bynum, Hunter, Rogers & Atwood, 1980).

The two independent Li—O lengths, 2.09 (1) and 2.20 (3) Å, have large e.s.d.'s associated with them due to the high thermal motion of the cation. However, the distances are long when compared to the Li—O lengths of 2.064 (9) and 2.112 (4) Å found for the five-coordinate Li in [Li(dme)₂]Br (Rogers & Atwood, 1983, unpublished results).

An uncoordinated dme molecule was found highly disordered about a crystallographic twofold axis. Refinement of the parameters of this moiety could not be carried out, and the non-hydrogen atoms were included with fixed contributions. The rather high R value resulted from this difficulty.

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Co-crystallized Bis(hexafluoroacetylacetonato)palladium(II) and 3-Cyano-2,2,5,5-tetramethyl-2,5-dihydropyrrolyl-1-oxyl, C₁₀H₂F₁₂O₄Pd.2C₉H₁₃N₂O

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Abstract. $M_r = 850.9$, monoclinic, $P2_1/n$, $a = 8.932$ (3), $b = 19.139$ (7), $c = 10.928$ (3) Å, $\beta = 108.42$ (3)°, $V = 1772$ (1) Å³, $Z = 2$, $D_x = 1.595$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.62$ mm⁻¹, $F(000) = 852$, $T = 296$ K, final $R = 0.045$ for 2498 observed reflections. The co-crystallized species are arranged in alternating layers perpendicular to the b axis, with only van der Waals type interactions between layers. Magnetic susceptibility data (6–300 K) are consistent with the presence of one free spin on each nitroxyl radical.

Introduction. Several complexes in which a transition-metal ion is directly bound to a nitroxyl group have recently been prepared and characterized by crystal structure analyses (Anderson & Kuechler, 1980; Dickman & Doedens, 1983; Porter, Dickman & Doedens, 1983; Dickman, 1983). These molecules constitute a relatively rare example of a series of metal

complexes containing a coordinated free-radical ligand which retains its radical character. They also show other interesting features, including unusual metal-ligand binding geometries and various types of magnetic behavior. One factor which favors formation of a metal–nitroxyl bond is a strongly Lewis acidic metal center. Most frequently this has been achieved by the presence of electron-withdrawing groups on other ligands. The nature of the nitroxyl ligand is also a factor, though this has not been thoroughly investigated.

The title compound was prepared in the course of exploratory studies designed to define the conditions under which a transition-metal–nitroxyl bond will be formed. From bis(hexafluoroacetylacetonato)-palladium(II) [Pd(F₆acac)₂] and 3-cyano-2,2,5,5-tetramethyl-2,5-dihydropyrrolyl-1-oxyl (tmpCN) in pentane a compound of stoichiometry Pd(F₆acac)₂(tmpCN)₂ was obtained in good yield. A crystal structure analysis was performed to establish the mode of binding of the tmpCN in this material.

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