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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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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the Li—O lengths of 2.064 (9) and 2.112 (4) Å found for the five-coordinate Li in [Li(dme)₂]Br (Rogers & Atwood, 1983, unpublished results).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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Experimental. Red, multifaceted crystals obtained by vacuum sublimation at 351 K. Crystal $0.5 \times 0.5 \times 0.5$ mm. Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$. Lattice parameters from refinement of setting angles of 15 reflections with $30^\circ \leq 2\theta \leq 35^\circ$. Systematic absences $h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$. Nonstandard setting chosen to avoid highly obtuse β angle. Intensities measured for 4224 independent reflections ($h, k, \pm l$) with $2\theta \leq 55^\circ$. Three standard reflections (021, 021, 141) measured after every 100 data; no statistically significant variations. Scan rate $4-16^\circ \text{ min}^{-1}$; scan range -1.1° in 2θ from $K\alpha_1$ to $+1.2^\circ$ from $K\alpha_2$. Backgrounds evaluated from 96 step peak profile. No absorption correction. Total of 2498 observed reflections with $I > 3\sigma(I)$. Structure solved by difference Fourier methods with Pd at origin. Least-squares refinement on F ; weights as defined by Corfield, Doedens & Ibers (1967) with $p = 0.05$. Atomic scattering factors, including anomalous-dispersion corrections, from *International Tables for X-ray Crystallography* (1974). H atoms included in fixed idealized positions; orientations of methyl groups obtained from difference Fourier map. Final refinement included 232 variable parameters; largest shift in final cycle 0.24σ . Final values of $R = 0.045$, $R_w = 0.064$, $S = 2.05$. Maximum peak height on final difference Fourier map $1.2 e \text{ \AA}^{-3}$ in vicinity of CF_3 group. All computations carried out with local version of *UCLA Crystallographic Program Package* (Strouse, 1981).

Magnetic susceptibility data were measured between 6–300 K by use of an SHE superconducting SQUID magnetometer at a field strength of 1 T. The data were corrected for the magnetization of the sample holder. Pascal's constants were used to estimate the correction for sample diamagnetism. The effective magnetic moments per radical were calculated by the relation $\mu_{\text{eff}} = 2.00 (\chi_m T)^{1/2}$.

Discussion. Final atomic parameters for all nonhydrogen atoms are tabulated in Table 1.* Intramolecular bond distances and angles are listed in Tables 2 and 3, respectively.

The crystal structure of $\text{Pd}(\text{F}_6\text{acac})_2(\text{tmpCN})_2$ comprises alternating layers, perpendicular to the b axis, of bis(hexafluoroacetylacetonato)palladium(II) and 3-cyano-2,2,5,5-tetramethyl-2,5-dihydropyrrolyl-1-oxyl molecules. A view of the contents of one unit cell is shown in Fig. 1. Intermolecular contacts show no evidence for specific interactions between the two co-crystallized species. The shortest interlayer contact

* Lists of structure factors, anisotropic thermal parameters, H-atom positions, distances and angles in CF_3 groups, magnetic susceptibility data, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39608 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for $\text{Pd}(\text{F}_6\text{acac})_2(\text{tmpCN})_2$

$U_{\text{eq}} = \frac{1}{3}$ of the trace of the diagonalized U matrix.

	x	y	z	$U_{\text{eq}}(\text{\AA}^2 \times 10^4)$
Pd	0.0	0.0	0.0	464
O(1)	0.1824 (3)	-0.0311 (2)	-0.0501 (2)	571
O(2)	-0.1497 (3)	-0.0045 (1)	-0.1769 (3)	558
O(3)	-0.5630 (4)	0.3085 (2)	-0.3743 (3)	791
N(1)	-0.4572 (4)	0.2634 (2)	-0.3237 (3)	564
N(2)	0.0051 (6)	0.1358 (3)	-0.3086 (7)	1270
C(1)	0.1716 (5)	-0.0449 (2)	-0.1661 (4)	526
C(2)	0.0407 (5)	-0.0418 (2)	-0.2750 (4)	562
C(3)	-0.1062 (5)	-0.0222 (2)	-0.2713 (3)	502
C(4)	0.3293 (6)	-0.0655 (3)	-0.1813 (4)	688
C(5)	-0.2469 (6)	-0.0229 (3)	-0.3972 (4)	667
C(6)	-0.4547 (5)	0.2211 (2)	-0.2102 (4)	558
C(7)	-0.3107 (5)	0.1783 (2)	-0.1943 (4)	598
C(8)	-0.2438 (4)	0.1931 (2)	-0.2833 (4)	540
C(9)	-0.3303 (4)	0.2482 (2)	-0.3779 (3)	515
C(10)	-0.4394 (6)	0.2689 (3)	-0.0949 (5)	786
C(11)	-0.6049 (6)	0.1781 (3)	-0.2406 (6)	859
C(12)	-0.1035 (6)	0.1611 (2)	-0.2948 (6)	778
C(13)	-0.2316 (7)	0.3136 (2)	-0.3755 (5)	796
C(14)	-0.3967 (6)	0.2201 (3)	-0.5152 (4)	813
F(1)	0.4095 (6)	-0.0123 (2)	-0.1886 (7)	1486
F(2)	0.4135 (4)	-0.1016 (3)	-0.0838 (4)	1461
F(3)	0.3149 (5)	-0.1016 (3)	-0.2854 (9)	1387
F(4)	-0.1999 (5)	-0.0319 (4)	-0.5005 (3)	1553
F(5)	-0.3395 (5)	-0.0739 (2)	-0.3998 (4)	1483
F(6)	-0.3247 (5)	0.0331 (2)	-0.4160 (4)	1341

Table 2. Bond distances (\AA)

(a) $\text{Pd}(\text{F}_6\text{acac})_2$ molecule*			
Pd—O(1)	1.968 (3)	C(1)—C(2)	1.381 (6)
Pd—O(2)	1.975 (3)	C(2)—C(3)	1.378 (6)
O(1)—C(1)	1.267 (4)	C(1)—C(4)	1.521 (6)
O(2)—C(3)	1.258 (5)	C(3)—C(5)	1.542 (6)
(b) tmpCN molecule			
N(1)—O(3)	1.269 (4)	C(7)—C(8)	1.322 (6)
N(1)—C(6)	1.475 (5)	C(8)—C(9)	1.508 (5)
N(1)—C(9)	1.465 (5)	C(8)—C(12)	1.436 (6)
C(6)—C(7)	1.488 (6)	C(9)—C(13)	1.526 (6)
C(6)—C(10)	1.528 (6)	C(9)—C(14)	1.527 (6)
C(6)—C(11)	1.519 (6)	C(12)—N(2)	1.136 (6)

* Distances within the CF_3 groups are deposited with the supplementary material.

Table 3. Bond angles ($^\circ$)

(a) $\text{Pd}(\text{F}_6\text{acac})_2$ molecule*			
O(1)—Pd—O(2)	94.5 (1)	C(2)—C(1)—C(4)	118.5 (4)
Pd—O(1)—C(1)	122.2 (3)	C(1)—C(2)—C(3)	122.8 (4)
Pd—O(2)—C(3)	121.7 (3)	O(2)—C(3)—C(2)	129.9 (4)
O(1)—C(1)—C(4)	112.5 (4)	C(2)—C(3)—C(5)	119.1 (4)
O(1)—C(1)—C(2)	128.9 (4)	O(2)—C(3)—C(5)	111.0 (4)
(b) tmpCN molecule			
O(3)—N(1)—C(6)	123.4 (3)	C(7)—C(8)—C(9)	113.6 (4)
O(3)—N(1)—C(9)	121.5 (3)	C(7)—C(8)—C(12)	125.7 (4)
C(6)—N(1)—C(9)	115.0 (3)	C(9)—C(8)—C(12)	120.7 (4)
N(1)—C(6)—C(7)	100.6 (3)	N(1)—C(9)—C(8)	99.0 (3)
N(1)—C(6)—C(10)	109.8 (3)	N(1)—C(9)—C(13)	110.3 (3)
N(1)—C(6)—C(11)	109.7 (4)	N(1)—C(9)—C(14)	111.0 (3)
C(7)—C(6)—C(10)	112.6 (4)	C(8)—C(9)—C(13)	113.2 (4)
C(7)—C(6)—C(11)	113.5 (4)	C(8)—C(9)—C(14)	112.5 (4)
C(10)—C(6)—C(11)	110.3 (4)	C(13)—C(9)—C(14)	110.4 (4)
C(6)—C(7)—C(8)	111.8 (4)	N(2)—C(12)—C(8)	177.6 (7)

* Angles within the CF_3 groups are deposited with the supplementary material.

involving nonhydrogen atoms is one of length 3.047 (5) Å between the nitroxyl oxygen atom O(3) and C(2), a carbon atom in the chelate ring. The closest approach of O(3) to the Pd atom is 4.016 Å. In view of the structure of this material, it is surprising that it could be sublimed without decomposition.

The centrosymmetric $Pd(F_6acac)_2$ moiety has a structure essentially the same as that recently reported for this species in its pure crystalline form (Siedle, Newmark & Pignolet, 1983). The present results, however, are of substantially higher precision than those for the pure solid. In that structure, a few rather large variations in chemically equivalent bond distances were observed; however, we find all such sets of distances to be equal within experimental error. The OCCCO grouping of the chelate ring is planar within 0.002 Å and the metal atom is displaced from this plane by only 0.018 Å. The thermal ellipsoids and atom numbering for the $Pd(F_6acac)_2$ molecule are displayed in Fig. 2.

The structure of the tmpCN radical is identical in all significant respects to that recently reported for weakly coordinated tmpCN in a bis(hexafluoroacetylacetonato)copper(II) complex (Dickman & Doedens, 1983). The atoms of the five-membered ring, the cyano group, and the nitroxyl O atom are coplanar. Although the structure of free tmpCN is not known, closely related nitroxyl radicals with five-membered rings display very similar structural features to those observed here, most notably planar N atoms and an N—O distance of *ca* 1.27 Å (Boeyens & Kruger, 1970; Turley & Boer, 1972). Fig. 3 illustrates the atom labeling and the thermal ellipsoids for the tmpCN molecule.

The structural and magnetic (see below) results for $Pd(F_6acac)_2(tmpCN)_2$ leave no room for doubt that this material contains neutral $Pd(F_6acac)_2$ and tmpCN species. There is no evidence for any sort of specific intermolecular interaction. A similar situation involving a palladium β -diketonate 'adduct' was observed for the tetrathiafulvalene derivative (TTF) $Pd(acac)_2$ (Siedle, Kistenmacher, Metzger, Kuo, Van Duyne & Cape, 1980). Although the TTF and tmpCN derivatives both crystallize in the same space group with the Pd atom at the origin of the unit cell, their overall crystal-packing arrangements are quite different. In the tmpCN derivative, the planar core of the $Pd(F_6acac)_2$ molecule is nearly perpendicular to the *b* axis, leaving room for the interleaved layers of tmpCN molecules. On the other hand, in (TTF) $Pd(acac)_2$, one of the Pd—O bonds is approximately parallel to *b* and the TTF molecules are situated in channels perpendicular to the symmetry axis.

The observed magnetic susceptibilities and corresponding effective magnetic moments are included with the supplementary material. The reciprocal susceptibility *vs* temperature curve is essentially linear from

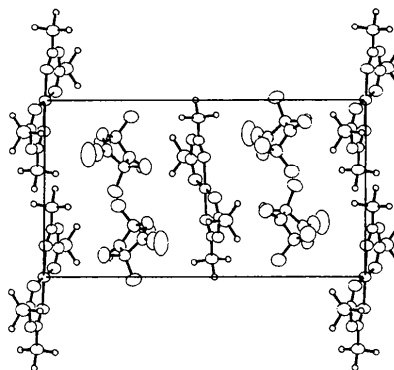


Fig. 1. The contents of one unit cell of $Pd(F_6acac)_2(tmpCN)_2$. The projection is down the *a* axis. The *b* direction is horizontal, and the origin is in the lower right corner. For clarity, H atoms have been omitted and F atoms have been given artificially small thermal parameters.

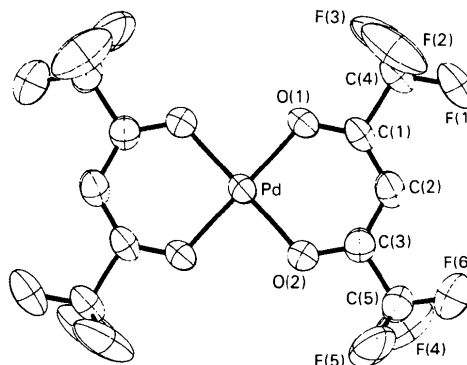


Fig. 2. Thermal ellipsoids (50% probability) and atom numbering for the $Pd(F_6acac)_2$ molecule in $Pd(F_6acac)_2(tmpCN)_2$. H atoms have been omitted for clarity.

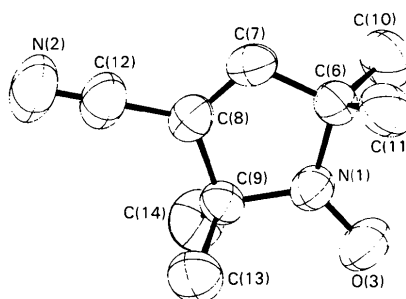


Fig. 3. Thermal ellipsoids (50% probability) and atom numbering for the tmpCN molecule in $Pd(F_6acac)_2(tmpCN)_2$. H atoms have been omitted for clarity.

20–300 K, with an average μ_{eff} per radical of 1.743 (8) BM.* Below 20 K the moment increases slightly, reaching a maximum value of 1.805 BM at 6 K, the lowest temperature investigated. The equation of the least-squares straight line for the 20–300 K data is $1/\chi = 1.3003 (17) T + 1.43 (18)$ or in standard Curie–Weiss form $\chi = 0.7691 (11)/[T + 1.10 (14)]$. Thus the results closely approach those expected for a single free spin on each nitroxyl radical.

In view of the relatively large separation between radical centers, it is not surprising that the magnetic data from 20–300 K show no evidence for interaction between the free spins of the nitroxyl radicals. The small increase in μ_{eff} below 20 K could be indicative of the onset of some sort of magnetic ordering, but a more thorough magnetic study would be needed to establish this point. The layered packing illustrated in Fig. 1 could very well give rise to one- or two-dimensional magnetic ordering at low temperatures.

This is the second instance in which the tmpCN radical has combined with a transition-metal complex to yield a material of well-defined stoichiometry containing no direct metal–nitroxyl interaction. With $\text{Cu}(\text{F}_6\text{acac})_2$, in the presence of small amounts of water,

* 1 BM (Bohr magneton) $\equiv 0.927 \times 10^{-23}$ Am²; 1 e.m.u. $\equiv 4\pi \times 10^{-6}$ SI unit.

a product with a linear chain structure was obtained (Dickman & Doedens, 1983). The nitroxyl O atom of the tmpCN ligand was hydrogen bonded to a coordinated water molecule and very weakly bound to copper through its nitrile N atom. When water was rigorously excluded, no new product could be isolated. Thus, no complex of tmpCN containing a metal–nitroxyl covalent bond has yet been prepared.

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Structure of Calcium Hydrogen Triacetate Monohydrate, $\text{CaH}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$

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Abstract. $M_r = 236.24$, triclinic, $P\bar{1}$, $a = 6.858 (1)$, $b = 12.281 (2)$, $c = 12.520 (3) \text{ \AA}$, $\alpha = 83.86 (2)$, $\beta = 91.62 (2)$, $\gamma = 87.09 (2)^\circ$, $U = 1046.5 (3) \text{ \AA}^3$, $Z = 4$, $D_x = 1.499 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 5.9 \text{ cm}^{-1}$, $T = 295 \text{ K}$, $F(000) = 496$, $R = 0.046$ for 2551 observed reflections with $I > 2.5\sigma(I)$. The structure consists of infinite multiple O-bridged double-stranded Ca chains running in the **a** direction that are cross linked in the **b** and **c** directions *via* hydrogen bonds.

Introduction. The acid salt $\text{CaH}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ was crystallized in an attempt to prepare the neutral salt $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. Its existence has been reported previously by Walter-Levy & Perrier (1958) who studied the ternary system $\text{CaO}-\text{Ac}_2\text{O}-\text{H}_2\text{O}$ at 298 K. Acid salts of monocarboxylic acids are not rare; for a review see Speakman (1972). The structure of the neutral salt $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ has been published previously (Klop, Schouten, van der Sluis & Spek, 1984). The study of the crystal structures of the calcium acetates is considered to be relevant for the understanding of the incongruently saturating behaviour of the double salt $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$ (Klop, Duisenberg & Spek, 1983).

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