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Communications

A Liquid MOCVD Precursor for Thin Films of CdO

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Many of the electronic and optical properties[1] of CdO are originated by its nonstoichiometric composition which, in turn, strongly depends on the synthetic procedure adopted. In fact, the presence of cadmium interstitials, Cd^+ ions, or oxygen vacancies gives rise to donor states whose carrier concentration ranges from semiconductors to degenerate metallic conductors.[2,3] Many studies have been reported for preparation of thin films of CdO.[1,3−10] Recently, we reported on metal organic chemical vapor deposition (MOCVD) of CdO using the cadmium 1,1,1,5,5,5,-hexafluoro-2,4-pentanedionate dihydrate complex, $Cd(C_5F_6HO_2)_2 \cdot 2H_2O$, hereafter $Cd(hfa)_2 \cdot 2H_2O$, as a precursor.[2] Moreover, another study regarding MOCVD of CdO using the volatile $Cd(hfa)_2 \cdot$ *N*,*N*,*N*′,*N*′-tetramethylethylenediamine has also been published.[8] Both these studies, to date, represent the few examples of MOCVD of CdO.[2,8]

In this perspective, MOCVD from liquid precursors certainly represents a considerable improvement because of the accurate reproducibility associated with constant evaporation (hence constant mass-transport) rates for given source temperatures.[11] Therefore, in the present communication we report on the novel $Cd(C_5F_6HO_2)_2 \cdot CH_3OCH_2CH_2OCH_3$ liquid adduct which has proven to be a well-suited precursor for MOCVD of CdO films.

Cadmium-containing compounds are exceedingly toxic and, therefore, care was taken during all sample manipulations.

The $Cd(C_5F_6HO_2)_2 \cdot CH_3OCH_2CH_2OCH_3$ adduct, hereafter $Cd(hfa)_2 \cdot$monoglyme, was synthesized by adding, under vigorous stirring, 0.642 g (0.005 mol) of CdO, 1.41 mL (0.01 mol) of H-hfa, and 0.52 mL of monoglyme (0.005 mol) to 40 mL of CH_2Cl_2. After a few minutes of stirring, the suspension became clear. A colorless oil was obtained after evaporation of the CH_2Cl_2 solvent. A white powder was obtained after the addition of the oil to 30 mL of pentane. Colorless, transparent crystals resulted by dissolving the oil in 90 mL of hexane and leaving the solution to concentrate to room temperature; yield: 99%. Melting point (mp) of the crude product: 72−73 °C. (Elemental analysis for $CdC_{14}H_{12}F_{12}O_6$.

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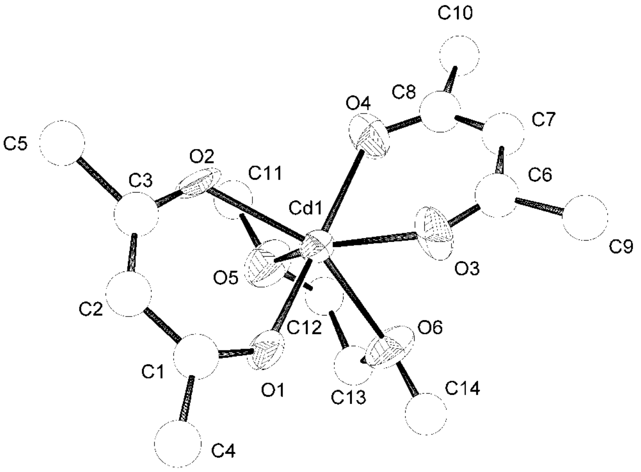


Figure 1. ORTEP drawing of Cd(hfa)$_2$·monoglyme (thermal ellipsoid probability 50%).

Calcd: C, 27.27; H, 1.95. Found: C, 26.94; H, 1.82%). Fast atom bombardment mass spectra (FAB-MS using 3-nitrobenzyl alcohol, $O_2NC_6H_4CH_2OH$ = 3NBA, as a matrix and cesium as bombarding atoms (35 kV)), (*m*/*z* fragments; M = Cd(hfa)$_2$·monoglyme): 493 $(M-CH_3-COCHCF_3)^+$, 311 $(M-\text{monoglyme}-COCHCF_3-CF_3-2F)^+$, 292 $(M-OCH_3-\text{hfa}-F-CF_3)^+$.[11] The most intense peak at 493 *m*/*z* (100%) corresponds to the fragment $[Cd(hfa)COCF_3{\cdot}OCH_2CH_2OCH_3]^+$. Infrared transmittance spectra: IR (Nujol; ν/cm^{-1}): 3561 (b), 3308 (b), 1647 (s), 1596 (w), 1563 (s), 1530 (s), 1497 (s), 1342 (vw), 1258 (s), 1223 (m), 1191 (m), 1154 (s), 1088 (m), 1060 (m), 1027 (w), 947 (vw), 872 (vw), 853 (m), 830 (w), 797 (s), 768 (w), 740 (m), 722 (m), 670 (s). ^1H NMR ($CDCl_3$): δ 6.04 (s, 2H of the hfa ligands); 3.72 (s, 4H of methylenic groups of monoglyme), 3.51 (s, 6H of the two methyl groups of monoglyme).[11]

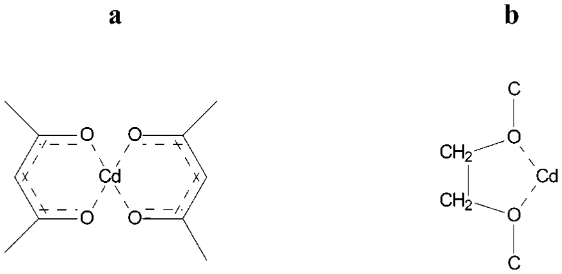
The solid-state structure of Cd(hfa)$_2$·monoglyme was determined by using single-crystal X-ray diffraction. Experimental conditions and refinement information were similar to those already reported.[12−16] The cadmium cation results as hexacoordinated by the four oxygen atoms of the two hfa ligands and by the two oxygen atoms of the monoglyme molecule (Figure 1). The dihedral angles around the bonds O5−C12, C12−C13, and C13−O6 are −180(2)°, −56(2)°, and 179(2)°, respectively. These torsion angles imply a trans−gauche−trans geometric conformation of the monoglyme molecule. The gauche torsional angle around the middle bond of the ether is an obvious consequence of the coordination pattern around the cadmium cation. As expected for the two different ligands, there are two sets of Cd⋯O distances (Table 1). Thus, the Cd⋯O bonds involving the hfa anions are shorter [2.19(1)−2.24(1) Å] than those involving the oxygen atoms of the monoglyme molecule [2.34(1) Å]. Related solid-state structures were retrieved from the Cambridge Structural Database (CSD)[17] to compare the present Cd⋯O distances with those of analogous complexes (see Table 2 sketch **a**−**b**) for the searched fragments. Results are summarized as follows:

Table 1. Selected Bond Distances (Å) and Angles (deg) of Cd(hfa)$_2$·Monoglyme

Cd(1)−O(1)	2.19(1)	O(1)−Cd(1)−O(4)	167.2(4)
Cd(1)−O(4)	2.20(1)	O(1)−Cd(1)−O(3)	92.4(4)
Cd(1)−O(3)	2.24(1)	O(4)−Cd(1)−O(3)	79.2(4)
Cd(1)−O(2)	2.23(1)	O(1)−Cd(1)−O(2)	81.8(3)
Cd(1)−O(5)	2.34(1)	O(4)−Cd(1)−O(2)	93.8(4)
Cd(1)−O(6)	2.34(1)	O(3)−Cd(1)−O(2)	119.1(4)
		O(1)−Cd(1)−O(5)	107.3(4)
		O(4)−Cd(1)−O(5)	84.7(4)
		O(3)−Cd(1)−O(5)	146.8(3)
		O(2)−Cd(1)−O(5)	90.6(4)
		O(1)−Cd(1)−O(6)	85.8(4)
		O(4)−Cd(1)−O(6)	102.7(4)
		O(3)−Cd(1)−O(6)	84.3(4)
		O(2)−Cd(1)−O(6)	153.9(4)
		O(5)−Cd(1)−O(6)	71.2(4)

Table 2. Results of the CSD Analysis on the Sketched Fragments

	distance range (Å)	mean value (Å)	number of refcodes (fragments)
Cd⋯O$_a$	2.220−2.325	2.262	7 (12)
Cd⋯O$_b$	2.438−2.734	2.513	8 (15)



--: any kind of bond

(i) The Cd⋯O$_{hfa}$ distances found in Cd(hfa)$_2$·monoglyme are in agreement with those found in other cadmium complexes with acetylacetonate (acac) and hfa ligands (Table 2).[2,18]

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(12) Cell parameters and intensity data for Cd(hfa)$_2$·monoglyme were obtained on a Nonius CAD4 diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects; an absorption correction was applied once the structure was solved by using the Walker and Stuart method.[13] The structure was solved using the SIR-97[14] program and subsequently refined by the full-matrix least-squares program SHELX-97.[15] The hydrogen atoms were introduced in calculated positions and their coordinates refined in agreement with those of the linked atoms [the overall temperature factor converged to 0.11(3) Å^2]. The cadmium, the fluorine, and the oxygen atoms were refined anisotropically, while the carbon atoms were refined isotropically to improve the data/parameters ratio. Fluorine atoms are in disordered positions and show, as expected, a rather large anisotropic factor.

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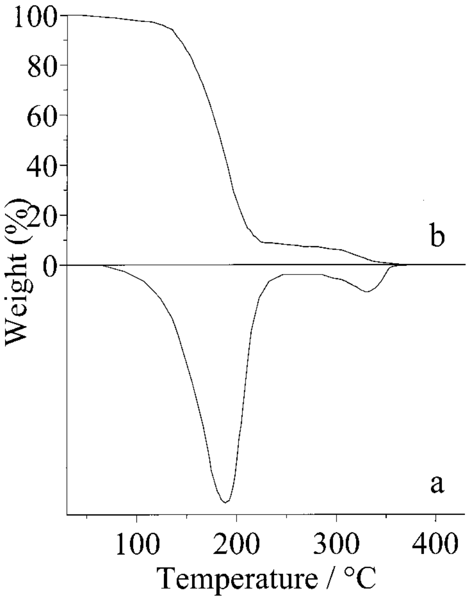

Figure 2. DTG (a) and TG (b) of $Cd(hfa)_2\cdot$monoglyme.

(ii) The $Cd\cdots O_{monoglyme}$ distances appear shorter than those of Cd complexes with other noncyclic ethers (Table 2).[19,20]

The Cd center adopts a distorted octahedral geometry with an arrangement of the two hfa ligands similar to that observed in other Cd β-diketonates.[2,18,21] Finally, the present geometry is very similar [RMS value 0.34 Å, calculated as stated in ref 21] to that of the $Cd(hfa)_2\cdot 2H_2O$ complex,[2] where the two oxygen atoms of the water molecules are replaced by those of the monoglyme ligand.

The thermal behavior of the $Cd(hfa)_2\cdot$monoglyme was investigated by thermal gravimetric analysis (TGA), under atmospheric prepurified nitrogen, using a 2 °C/min heating rate in the 10−400 °C range.[11] Results show a 93.4% mass loss at 189.2 °C (Figure 2). Moreover, the remaining mass is lost quantitatively in a second step at 330.8 °C. The behavior above 300 °C is probably consistent with some dissociation of the remaining precursor in two fragments: $Cd(hfa)_2$ and monoglyme.

MOCVD experiments were performed in a horizontal, low-pressure, hot-wall reactor,[2,11] using the present, as-synthesized, melted $Cd(hfa)_2\cdot$monoglyme adduct as a liquid Cd source. Fused SiO_2 (quartz) was used as a substrate. Pure Ar (70−100 sccm) and O_2 (100−400 sccm) were used as carrier and reaction gases, respectively. The total pressure was kept in the 2−6 Torr range. Evaporation rates of the source precursor, suited for MOCVD experiments (4.3 mg/min), were found in the 100−110 °C range. The substrate temperature was maintained in the 320−400 °C range and the deposition time was 120 min.

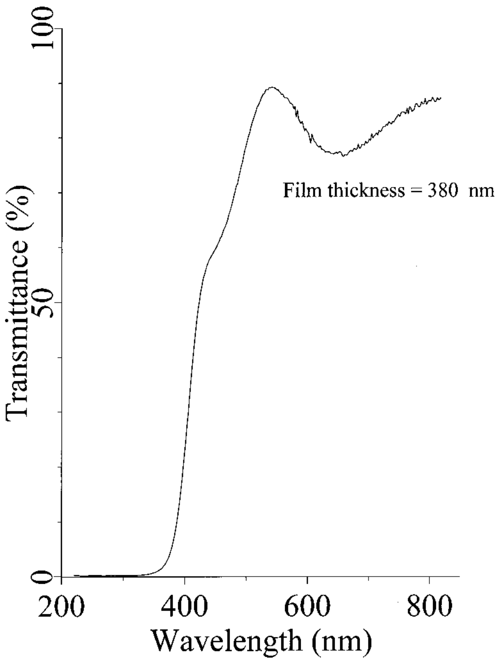

Figure 3. UV−visible transmission spectrum for a representative CdO thin film on SiO_2 substrate obtained using 400 sccm O_2 flow rate.

X-ray diffraction (XRD) measurements of as-deposited films provide evidence of cubic CdO crystallites.[2] Only the (200) reflection (θ = 38.30) was observed, thus pointing to highly textured CdO.[2] This behavior was found highly repetitive using the mentioned deposition parameters. The deposited films are yellow and transparent and Figure 3 shows their UV−visible spectrum. The absorption edge is at $\lambda = 384$ nm (films deposited using $O_2 = 400$ sccm) and a 90% transmittance value is evident in the visible range.[8,22−27] The thickness of prototypical films, evaluated from UV−visible data,[2] is 380 nm ($O_2 = 400$ sccm) for 120-min experiments. The associated CdO growth rate is 32 Å/min. Similar transmittance and growth rates have already been reported for CdO films.[2,28]

X-ray photoelectron spectra (XPS) were measured with a PHI 5600 Multi Technique System (base pressure of the main chamber 3×10^{-10} Torr).[2,11] The Cd 3d features consist of the main $3d_{5/2}$ and $3d_{3/2}$ spin−orbit components at 404.6 and 411.4 eV, respectively.[2,29] It has been reported that atomically clean CdO surfaces,

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(20) The eight systems, found in the CSD show $Cd\cdots O_{ether}$ distances in the range 2.438−2.734 Å, while in our complex the two bond distances are 2.34(1) Å.

(21) Six of the seven structures, retrieved in the Cambridge Structural Database, show a disposition of the acac derivatives similar to that observed in $Cd(hfa)_2\cdot$monoglyme, being the maximum root-mean-square (RMS) value, calculated using all the atoms in sketch **a** of Table 2, 0.54 Å (for the compound [*cis*-bis(1,3-diphenylpropane-1,3-dionato)dipyridinecadmium(II)] reported in ref 18f).

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exposed a few minutes in air, give the characteristic double XPS O 1s peak, due to the presence of hydroxide species.[2,29] In fact, two O 1s peaks are presently evident at 529.2 and 531.9 eV. In addition, very weak features (at 285.0 and 289.0 eV) due to surface carbon contaminant (2−3 at. %) almost ubiquitous in similarly MOCVD fabricated materials were observed.[2,11] No XPS fluorine signals were detected. Moreover, energy-dispersive X-ray (EDX) data point to the absence of any carbon or fluorine in the bulk of the films. Accordingly, XPS depth profiles, obtained eroding CdO films with Ar^+-ion sputter etching (4 kV, beam current 1.0 μA), do not show evidence of any bulk carbon and fluorine contaminants. Note that, after 1 min of sputtering, only the 529.2 eV O 1s component remains evident because of the removal of surface hydroxide species. Resistivity values of the as-deposited CdO films are $\leq 6 \times 10^{-4}$ Ω·cm, thus indicating conducting films.[2,25,29] In particular, lower resistivity values were observed for films deposited using low (100 sccm) oxygen flow rates. In CdO the electronic conduction is promoted by the presence of cadmium interstitials or oxygen vacancies which act as n-type defects and produce donor states in the bulk band gap. Therefore, synthesis under more oxidizing condition yields less defective, thus lower conducting, compounds.[2,23,26−28]

In conclusion, a novel $Cd(hfa)_2$·monoglyme adduct was prepared and characterized by elemental analysis, X-ray single-crystal analysis, mass and NMR spectra, thermal measurements, and IR transmittance spectroscopy. Mild heating (73 °C) resulted in a thermally stable, liquid compound which, in turn, can be easily evaporated. Deposition experiments, in a low-pressure horizontal hot-wall reactor, on SiO_2 substrates, resulted in CdO films. XRD measurements provided evidence that they consist of cubic, (100)-oriented crystals. UV−vis spectra showed that the transmittance of as-deposited films in the visible region is about 90%, better than that observed in CdO films obtained using the simple $Cd(hfa)_2 \cdot 2H_2O$ precursor.[2] Finally, resistivity values were lower than those observed for CdO films obtained using the simple $Cd(hfa)_2 \cdot 2H_2O$ precursor.[2] The difference between the $Cd(hfa)_2$·monoglyme adduct and that re-ported in ref 8b is due to the different donor ligand attached to the Cd center. Nevertheless, our low-melting $Cd(hfa)_2$·monoglyme allows MOCVD from liquid precursors, which certainly represents a considerable improvement due to the accurate reproducibility associated with constant evaporation rates for given source temperatures.

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