

LIQUID COMPOUNDS FOR CVD OF ALKALINE EARTH METALS

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ABSTRACT

The first room-temperature liquid compounds useful for the CVD of alkaline earth metal-containing oxides were prepared by reacting metal (Mg, Ca, Sr, and Ba) beta-diketonates with novel polyamine ligands. The compounds are monomeric and can be completely flash-vaporized without leaving any non-volatile residue detectable at the parts-per-million level. A stable, solvent-free liquid mixture was formed by mixing new liquid barium, strontium and titanium compounds. CVD experiments using direct liquid injection of this liquid mixture deposited films of barium strontium titanate. This approach should also be applicable to the deposition of many other multicomponent oxides containing alkaline earth metals: ferroelectrics (strontium bismuth tantalate), metallic conductors (strontium vanadium oxide, lanthanum strontium cobalt oxide), phosphors (calcium tungstate), non-linear optical materials (beta-barium borate), magnetic oxides (barium ferrite), colossal magnetoresistive materials (lanthanum strontium manganese oxide), high T_c superconductors (yttrium barium copper oxide, bismuth calcium strontium copper oxide) and microwave dielectrics (barium magnesium tantalate).

INTRODUCTION

Chemical vapor deposition (CVD) is a versatile method for preparing solid materials in the form of films, powders and fibers. Successful use of CVD requires reliable sources of reactant vapors, which are most easily generated from liquids. Solids are less convenient as sources of vapors, for a variety of reasons. Solids often have low vapor pressures, and the kinetics of vaporization of solids is usually slow. The surface area from which solids evaporate changes as a function of time, providing a non-reproducible vapor flux. Decomposition products and impurities can segregate on the surface of a solid, further degrading their reproducibility as vapor sources. In fact, most practical applications of CVD use liquid sources, rather than solids.

Solid sources can also be dissolved in a liquid solvent, and the liquid solution can subsequently be flash-vaporized. This approach, however, introduces large amounts of solvent vapors into the CVD reactor. The solvent vapors can introduce impurities, such as carbon, into the deposited material. Hazards, such as flammability or toxicity, may be introduced by adding solvents. Solvents also increase the effort needed to dispose of waste from the process.

Alkaline earth metals are essential components of many important materials, such as those listed in the abstract. Unfortunately, volatile liquid compounds have not been available for the alkaline earth metals, so CVD of these materials has had to rely on inconvenient solid sources.¹ A room-temperature liquid barium compound was reported,² but it has been found to be non-volatile. Numerous low-melting solid barium compounds have been prepared, but all reported compounds are solid at room temperature.^{1,3} Liquid mixtures of certain alkaline earth compounds have been made, and can be flash vaporized as CVD precursors.⁴ While these mixtures are useful, it would be easier to purify and analyze pure liquid alkaline earth compounds.

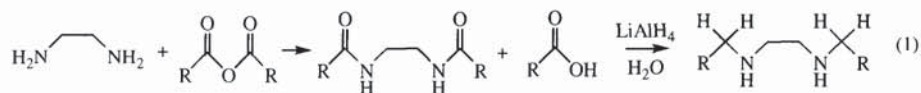
The first pure liquid barium compounds were reported recently.⁵ They are barium beta-diketonates bound to N,N',N''-trialkyldiethylenetriamines. When the alkyl chains are more than

four carbons long, the resulting barium compounds are liquid at room temperature. These liquid compounds were successfully flash-vaporized as vapor sources for CVD of barium-containing materials, such as barium titanate.

In the present paper, similar liquid compounds are reported for strontium, calcium and magnesium, and methods for their synthesis are given. These beta-diketonates bound to partially alkylated polyamines are liquid at room temperature and monomeric in hydrocarbon solution. One of the strontium compounds crystallized just below room temperature. It was found to be monomeric by X-ray crystallography, with four oxygen atoms and three nitrogen atoms bound to each strontium atom. All of the new compounds can be flash-vaporized as CVD precursors. Some of the magnesium compounds can even be distilled intact at low pressures, although the barium, strontium and calcium compounds dissociate into metal β -diketonate and polyamine under slow distillation. As an example, barium strontium titanate films were prepared by CVD using some of the new liquid compounds as precursors.

SYNTHESIS OF NEW LIQUID PRECURSORS

Dialkylethylenediamines were prepared by the following reaction:



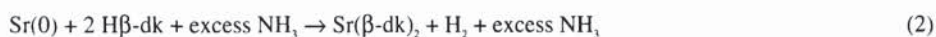
Synthesis of N,N'-dihexylethylenediamine (dheda): In a 500-mL flask, ethylenediamine (7.79 mL, 120 mmol) was dissolved in 150 mL of tetrahydrofuran (THF). To this solution, hexanoic anhydride (59.44 mL, 260 mmol) was added dropwise over 40 minutes with vigorous stirring, the solution becoming extremely turbid. The reaction was then refluxed at 78°C for 4 hours. Excess anhydride was quenched by the addition of 0.2 mL of distilled water, and the volatiles, including the byproduct hexanoic acid, were removed *in vacuo*. The resulting solid amide was washed into a Buchner funnel (under air) with 2 x 25 mL hexane and pressed dry. In a separate 500-mL flask, lithium aluminum hydride (11.5 g, 300 mmol) was suspended in 150 mL of diethylether and cooled to 0°C. The previously synthesized solid powdered amide was added slowly with evolution of H₂ gas. The rate of addition of amide should be kept low enough so that the generation of foam is controlled. The mixture was then refluxed at 37°C overnight. The resulting mixture was then cooled to 0°C and quenched as follows: 1) Water (11.6 g, 640 mmol) was added dropwise with vigorous stirring. 2) With the mixture becoming increasingly turbid, a 15% w/w aqueous solution of sodium hydroxide (11.6 g) was added dropwise with vigorous stirring. Hexane was added in amounts sufficient to prevent the mixture from becoming too solid to stir. 3) Water (34.8 g, 1.93 mol) was again added and the mixture became easier to stir. This solution was filtered and the filtrate was stirred with magnesium sulfate overnight. This mixture was filtered and the volatiles were removed *in vacuo*, resulting in a clear colorless dihexylethylenediamine (dheda). The dheda was subsequently distilled at 84-90°C at 90 mTorr (15.5 g, 58% yield). NMR: ¹H in C₆D₆ (2.62 ppm, 4 H, singlet), (2.52 ppm, 4 H, triplet), (1.42 ppm, 4 H, triplet of triplets), (1.26 ppm, 12 H, multiplet), (0.88 ppm, 6 H, triplet).

In a similar manner, the other alkylpolyamines in Table I were prepared from commercially available chemicals.

Table I. Alkylpolyamines, abbreviations and vapor pressures

Amine	Formula	Abbr	Vapor P. °C/mTorr
N,N'-dihexylethylenediamine	$(\text{CH}_3(\text{CH}_2)_5\text{NHCH}_2)_2$	dheda	90/90
N,N'-dibutylethylenediamine	$(\text{CH}_3(\text{CH}_2)_3\text{NHCH}_2)_2$	dbeda	92/100
N,N',N''-triethyldiethylenetriamine	$(\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_3$	tedeta	111/25
N,N',N''-triethyltriethylenetriamine	$(\text{CH}_3(\text{CH}_2)_4\text{NHCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2)_4\text{CH}_3$	tadeta	116/25
N,N',N''-trihexyldiethylenetriamine	$(\text{CH}_3(\text{CH}_2)_4\text{NHCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2)_4\text{CH}_3$	thdeta	145/40

Synthesis of the metal beta-diketonates (β -dk) followed one of three general syntheses, depending on the metal in question. For strontium, activation of the metal surface with ammonia increased the rate of reaction (Equation 2):



Periodic charging of the solution with NH_3 was necessary to achieve complete reaction.

If the resulting amine adduct of the metal beta-diketonate is a liquid, synthesis can be done neat with moderate heat using a 1:1 stoichiometry. This holds true for calcium and magnesium as well:



The liquid amine and product act as solvents for the reaction. If the amine adduct is solid, it is necessary to add a small amount of solvent to facilitate the reaction.

Synthesis of Sr(tod)₂: Metallic strontium (1.82 g, 21 mmol) and 2,2,6,6-tetramethyloctane-3,5-dione (Htod) (8.23 g, 42 mmol) were mixed; gas started evolving immediately from the surface of the metal. To this, 75 mL of THF was added and NH_3 gas was bubbled into the solution for 1 minute. The reaction became very vigorous and was allowed to stir for 2 hours, with periodic charging of the solution with NH_3 to maintain the metal activation. The NH_3 was removed *in vacuo* and the solution was filtered to remove a small amount of suspended powder. The volatiles were removed *in vacuo*, leaving a waxy white solid. This solid was pumped at 60°C for 3 hours to remove completely the THF from the Sr(tod)₂ (6.5 g, 65% yield). ¹H NMR (in CDCl_3): (5.57 ppm, 2 H, broad singlet), (1.42 ppm, 4 H, quartet), (1.05 ppm, 18 H, singlet), (1.01 ppm, 12 H, singlet), (0.72 ppm, 6 H, triplet).

Synthesis of Sr(tod)₂·thdeta: In a 10-mL flask, Sr(tod)₂ (1.16 g, 2.4 mmol) and N,N',N''-trihexyldiethylenetriamine (0.849 g, 2.4 mmol) were mixed in 5 mL of benzene. The solution was stirred for a few minutes until the solid dissolved. The resulting solution of Sr(tod)₂·thdeta was stirred under vacuum at 50°C for 3 hours to remove the benzene.

The strontium beta-diketonates in the Table II were synthesized in a similar manner. For n-alkyl groups larger than methyl, the alkylamine adducts are liquids at room temperature. The melting points and viscosities of these compounds decrease with increasing numbers of torsion angles (listed in columns 2-4) around C-C single bonds that rotate alkyl groups with less symmetry than a methyl or a t-butyl group, including angles on both the β -diketones (column 2) and the amine or other neutral adduct (column 3). We observe that the melting points and viscosities generally decrease with increasing numbers of torsion angles.

The molecular masses of these new compounds were determined by cryoscopy in *p*-xylene solution. Their "molecular complexities," defined as the ratio of the cryoscopic molecular mass to the theoretical monomeric value, do not differ significantly from unity.

Table II. Strontium beta-diketonate compounds

Metal	β -diketone (angles)	Adduct (angles)	Torsion Angles	Melting Point (°C)	Viscosity (centipoise)	Molecular Complexity
Sr	thd(0)	Hthd(0)	0	200	solid	3
Sr	thd(0)	pmdeta(0)	0	129	solid	
Sr	tod(4)	none(0)	4	>20	solid	
Sr	tod(4)	tedeta(3)	7	~20	>10 ⁴	0.94
Sr	thd(0)	tadeta(12)	12	~20	2008	0.99
Sr	thd(0)	thdeta(15)	15	<20	1030	1.01
Sr	tod(4)	tadeta(12)	16	<20	638	0.83
Sr	tod(4)	thdeta(15)	19	<20	489	0.89

(Hthd = 2,2,6,6-tetramethylheptane-3,5-dione; pmdeta = N,N,N',N'',N'''-pentamethyldiethylentriamine)

After several weeks just below room temperature, one batch (out of four) of Sr(thd)₂·tadeta partially crystallized. An X-ray analysis of a crystal showed three independent and inequivalent monomeric molecules, one of which is depicted in Figure 1. The other two molecular units show a similar 7-coordinate strontium center, but differ in the torsion angles of the three pentyl chains attached to the three nitrogens. Cryoscopy showed that the amine-complexed materials are also monomeric in *p*-xylene solution, in contrast to the trimeric nature of [Sr(thd)₂]₃·Hthd.⁶

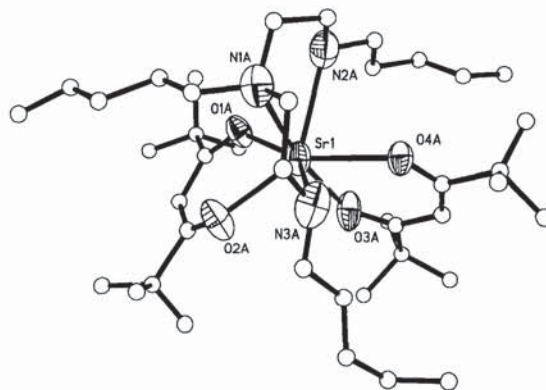


Figure 1. Molecular structure of Sr(thd)₂·tadeta

In the case of Ca(β -dk)₂, activation of the metal could be accomplished by ethanol (equation 4), which generates a calcium ethoxide intermediate *in situ*. The ethanol is regenerated when the β -diketonate is formed:



Synthesis of Ca(3hd)₂: In a 100-mL round bottom, Ca shot (0.70 g, 17.5 mmol), 2,2,6-trimethylheptane-3,5-dione (H3hd) (6.0 g, 35.0 mmol) and ethanol (3.24 g, 70.3 mmol) were combined in 30 mL of tetrahydrofuran (thf) and refluxed overnight. A very small amount of dark suspended powder was filtered off. The volatiles were removed *in vacuo* from the clear filtrate. The white solid was then dried at 50°C for 3 hours under vacuum, resulting in 5.40 g of Ca(3hd)₂ (81% yield). ¹H NMR (in d₂-pyridine): (5.74 ppm, 2 H, singlet), (2.49 ppm, 2 H, septet), (1.21 ppm, 18 H, singlet), (1.15 ppm, 12 H, doublet)

Synthesis of Ca(3hd)₂-dheda: In a 5-dram vial, Ca(3hd)₂ (1.00g, 2.6 mmol) was combined with N,N'-dihexylethylenediamine (dheda) (0.60 g, 2.6 mmol) and heated to 45°C. Clear, liquid Ca(3hd)₂-dheda formed quantitatively. ¹H NMR (in d₂-pyridine): (5.71 ppm, 2 H, singlet), (2.77 ppm, 4 H, singlet), (2.66 ppm, 4 H, multiplet), (2.49 ppm, 2 H, septet), (1.52 ppm, 2 H, multiplet), (1.51 ppm, 4 H, broad triplet of triplets buried under a multiplet), (1.23 ppm, 18 H, singlet), (1.15 ppm, 12 H, doublet), (1.1-1.4 ppm, 8 H, broad multiplet), (0.83 ppm, 6 H, broad triplet). In a similar manner, the calcium compounds in Table III were synthesized.

Table III. Calcium beta-diketonate compounds

Metal	β-diketone (angles)	Amine (angles)	Torsion Angles	Melting Point (°C)	Viscosity (centipoise)	Molecular Complexity
Ca	thd(0)	dheda(10)	10	>20	solid	1.21
Ca	tod(4)	dheda(10)	14	>20	solid	0.93
Ca	thd(0)	thdeta(15)	15	<20	270	1.03
Ca	tod(4)	thdeta(15)	19	<20	214	0.85
Ca	3hd(2)	dheda(10)	12	<20	135	0.93
Ca	3hd(2)	thdeta(15)	17	<20	78	1.02

(H3hd = 2,2,6-trimethylheptane-3,5-dione)

As in the strontium case, reaction with a trialkyldiethylenetriamine caused the solid calcium β-diketonates to become liquids. However, the dialkylethylenediamines gave either liquids or solids, depending upon number of torsion angles (Table III). The β-diketonate ligand “3hd” gave the lowest viscosities. All of these calcium compounds were successfully flash-vaporized.

Synthesis of volatile liquid magnesium compounds

Magnesium compounds were formed by the reaction of magnesium ethoxide with the appropriate β-diketone.



Synthesis of Mg(thd)₂: In a 100-mL round bottom, Mg(OEt)₂ was suspended in dimethoxyethane (DME) and a DME solution of 2,2,6,6-tetramethylheptane-3,5-dione (Hthd) was added. The solution was refluxed at 90°C overnight. The resulting cloudy solution was evacuated leaving a solid which was then taken up in 50 mL of THF. A small amount of solid was filtered off and the volatiles were again removed leaving 5.6 g of white Mg(thd)₂ (82% yield). ¹H NMR (in d₂-pyridine): (5.75 ppm, 2 H, singlet), (1.23 ppm, 36 H, singlet).

Synthesis of Mg(thd)₂-dheda: In a 10-mL flask, Mg(thd)₂ (3.80 g, 97.0 mmol) and theda (2.22 g, 97.0 mmol) were mixed without solvent. After slight warming, clear, slightly yellow liquid Mg(thd)₂-dheda was formed. This material was distilled at 72°C at 27 mTorr (4.03g, 67% yield). NMR: ¹H in C₆D₆ (5.76, 2 H, singlet), (2.58 ppm, 4 H, broad singlet), (2.41 ppm, 4 H, broad multiplet), (1.46 ppm, broad singlet, 2 H), (1.40-1.10 ppm, 16 H, broad multiplets buried under a singlet), (1.26 ppm, 36 H, singlet), (0.90 ppm, 6 H, triplet). In a similar manner, the other magnesium compounds in Table IV were prepared.

When dihexylethylenediamine (“dheda”) was used, all of the Mg(β-dk)₂ adducts became liquids. Only in the case where the β-diketonate was symmetrical (tetramethylheptanedione, “thd”) and the alkyl group had a small number of torsion angles (dibutylethylenediamine, “dbeda”) was a solid formed. The smallest β-diketonate, 3hd, formed the lowest viscosity liquids, as in the case of calcium. Some of these magnesium compounds were successfully distilled under the conditions listed in Table IV, while others dissociated into amine vapor and the magnesium β-diketonate during slow distillation. All of these liquid magnesium compounds can be flash vaporized without measurable residue.

Table IV. Magnesium beta-diketonate compounds

Metal	β-diketonate (angles)	Amine (angles)	Torsion Angles	Melting Point (°C)	Viscosity centipoise	Molecular Complexity	Vapor Pressure °C/mTorr
Mg	thd(0)	dbeda(6)	6	>20	solid	1.03	
Mg	tod(4)	dbeda(6)	8	<20	381	0.94	dissoc.
Mg	thd(0)	dheda(10)	10	<20	113	0.89	72/27
Mg	tod(4)	dheda(10)	12	<20	110	1.03	158/27
Mg	3hd(2)	dbeda(6)	8	<20	54	0.95	dissoc.
Mg	3hd(2)	dheda(10)	12	<20	48	1.13	123/31

CVD EXPERIMENTS

The liquids were mixed with mesitylene to lower their viscosity below 5 centipoise so that they could be nebulized into tiny droplets (about 20 microns in diameter) by a high-frequency (1.4 MHz) ultrasonic system.⁴ The resulting fogs were entrained in a flow of oxygen gas into a tube furnace at 400 °C with silicon substrates placed on the bottom of the tube. Films of magnesium oxide and barium, strontium or calcium carbonates were deposited.

A stable liquid mixture was formed from Ba(tod)₂-thdeta, Sr(tod)₂-thdeta and Ti(OnBu)₂(tod)₂, and used for CVD of films of barium strontium titanate. The three metals had molar ratios of Ba:Sr:Ti equal to 1.6:1.8:1 in the liquid. A film 120 nm thick was deposited in 5 minutes on a substrate at 500 °C using nitrogen carrier gas, followed by 1 hour of annealing in oxygen to eliminate residual carbon from the film. The ratio of metals in the film, as determined by fitting the Rutherford Backscattering Spectrum (RBS) in Figure 2, was Ba:Sr:Ti equal to 0.5:0.4:1. No carbon was observed by RBS in the annealed film.

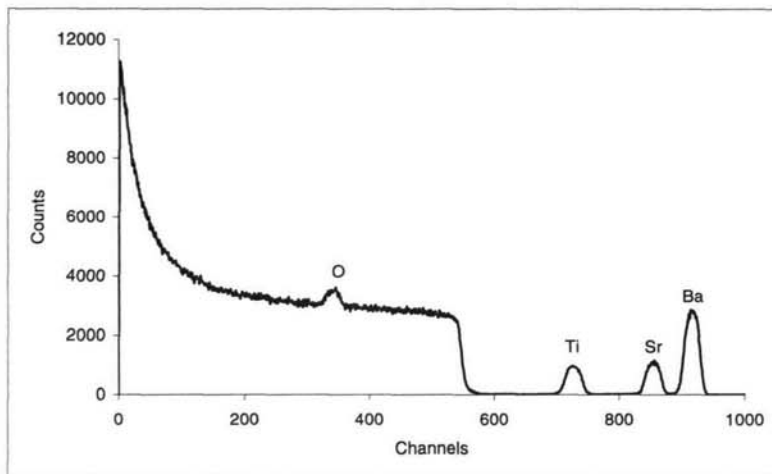


Figure 2. RBS Spectrum of a CVD Barium Strontium Titanate Film

CONCLUSIONS

The first volatile liquid compounds of magnesium, calcium, strontium and barium have been synthesized. They are monomeric, with chelating β -diketone and polyamine ligands. Their viscosities and melting points decrease with increasing numbers of C-C torsion angles that affect the molecular shape. They can be flash vaporized without residue, and some of the magnesium compounds can be distilled intact under vacuum. These liquids were used in CVD of films of alkaline earth metal oxides and carbonates, and barium strontium titanate.

ACKNOWLEDGMENTS

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