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Synthesis, characterization and investigation of the thermal behaviour of six novel polynuclear cobalt and copper complexes for potential application in MOCVD

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New tetranuclear complexes of copper and cobalt have been prepared under ambient conditions from corresponding metal acetates in acetone, using triethanolamine and diethanolamine as the ligands. The complexes have been characterized by infrared spectroscopy, mass spectroscopy, elemental analysis and thermal analysis. The mass spectra of the complexes show that the complexes retain the acetate moiety in their structures. Simultaneous thermogravimetric and differential thermal analysis (TGA–DTA) reveal that the complexes are solids that sublime over the temperature range 50–100 °C, under atmospheric pressure. The TGA–DTA curves reveal that the complexes retain carbon at temperatures as high as 500 °C. The presence of carbon is known to limit the mobility of growth species for oxides, restricting them to nanometersized crystals. Thus, the complexes have potential applications as precursors in the growth of nanostructured metal oxide thin films under specific CVD conditions. Because of their low sublimability, the complexes are prospective candidates as precursors for low-temperature growth of multilayer oxide thin films where the thickness of individual layers needs to be controlled at nanometer level and for introducing dopants at low concentrations by MOCVD technique. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: polynuclear complexes; thermal studies; precursor; MOCVD; nanostructured metal oxides

INTRODUCTION

The study of polynuclear metal complexes is one of the most active areas in coordination chemistry. These compounds constitute common ground for two areas of current interest, viz., molecular magnetism and metal sites in biology. Triethanolamine ($teaH_3$) has attracted much interest in metal coordination chemistry. Metal triethanolamine complexes have covered most of the metals in the periodic table,[1] including the elements of groups 1–5, transition metals and lanthanides, for various purposes such as biological activity of enzymes,[2] supramolecular chemistry[3] and low-temperature MOCVD.[4] Although triethanolamine as a tetradentate ligand has been extensively used to prepare mononuclear metal complexes with a variety of monomeric tricyclic structures, its suitability as a coordinating ligand in the synthesis of polynuclear metal complexes has not been extensively investigated. Polynuclear metal triethanolamines reported to date contain several structure types, such as dimeric metalatranes for Ba[5] and Ti,[6–8] trimeric metalatranes for Sn,[9] tetranuclear complexes for Al[10] and Cu,[11] metallo-crownethers for Fe[3] and extended structures for alkali metal complexes.[5] Reports on polynuclear complexes containing diethanolamine as the bridging ligand are even fewer in number.[12,13]

MOCVD (metalorganic chemical vapour deposition) is a well-known technique for growth of thin films of metals and metal oxides in industry as well as in the research laboratory. In this process, the metalorganic precursor plays a crucial role in controlling the micro/nanostructure and the properties of the resultant material. Thus, there is considerable interest in the convenient synthesis of precursors for the formation of materials via the sol–gel and low temperature MOCVD techniques. The features desirable in a metalorganic complex for its application as precursor in a MOCVD process are: low toxicity,

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ease of synthesis, non-pyrophoricity and low temperature volatility. So far, the precursors used in the MOCVD of thin films of various metal oxides have been metalorganic complexes containing ligands with one/two binding sites per ligand,[14] e.g. various β-diketonates and alkoxides. Although conventional metal alkoxides of the type $M(OR)_x$ have been widely studied as MOCVD precursors, far less emphasis has thus far been placed on compounds of the type derived from polyfunctional alcohols or aminoalcohols. Such aminoalcohols, e.g. triethanolamine and diethanolamine, form robust tricyclic or bicyclic structures that are easily solvated and may, in many cases, be sublimed or distilled at relatively low temperatures.[15] Because the coordination number per ligand for ligands of this type is more than two, the resulting complexes have extra stability due to chelation. As a result, their synthesis requires conditions less stringent than those needed for alkoxides; indeed, synthesis may often be carried out under ambient conditions in aqueous media (e.g. the synthesis of several triethanolamine complexes of early transition metals).[16] Another advantage is that the ligands are commercially available and are relatively inexpensive. In addition, triethanolamine is a biologically compatible ligand, which potentially renders the corresponding metalorganic complexes less toxic. Thus, the use of such complexes as the precursor in MOCVD can make the state-of-the-art MOCVD processes more environmentally friendly. The use of triethanolamine complexes of transitions metals is industrially more viable in terms of the low cost involved in their synthesis, low toxicity and long shelf-life. In this context, our objective has been to synthesize complexes containing triethanolamine and diethanolamine of transition metals such as cobalt and copper, and to investigate their applicability in MOCVD processes as a novel class of precursors.

EXPERIMENTAL

Synthesis

The syntheses of all metal complexes were carried out under ambient atmosphere. AR-grade reagents were used as received, without further purification.

Preparation of $Cu_4(deaH)(dea)(oAc)_5\cdot(CH_3)_2CO$ (C-1)

A 5 g (25.04 mmol) aliquot of $Cu(OAc)_2\cdot H_2O$ was mixed with 240 ml acetone. The mixture was stirred for 5–10 min for partial dissolution of copper acetate in acetone. A 2.5 ml (26.07 mmol) aliquot of diethanolamine was added into this mixture drop-by-drop through a pipette over a duration of ~20 min. Upon stirring, a green-blue precipitate started to appear. This reaction mixture was magnetically stirred for 5 h under ambient conditions, which yielded a light green precipitate in a blue solution. The solution was decanted, and the light green precipitate obtained was then suction-filtered, washed several times with acetone, and dried over tissue paper.

Preparation of $Cu_4(dea)_2(OAc)_4\cdot(C_2H_5)_2O$ (C-2)

A 1.00 g (5 mmol) aliquot of $Cu(OAc)_2\cdot H_2O$ was taken in a 250 ml round-bottomed flask, to which 30 ml of acetone were added, followed by a few minutes of shaking. To this mixture, 30 ml of diethyl ether were added, followed by shaking for another few minutes. The green-coloured solution turned light blue. Into this, 0.5 ml (5.21 mmol) of diethanolamine was added dropwise. The reaction mixture was shaken and 10 ml acetone were added to it to facilitate the dissolution of copper acetate. On stirring for 5–10 min, a light blue-coloured precipitate appeared. This reaction mixture was magnetically stirred for 5 h. On filtration, a blue-green-coloured precipitate was obtained. It was washed with acetone and dried over tissue paper in air.

Preparation of $Cu_4(teaH)(teaH_2)(OAc)_5\cdot(CH_3)_2CO$ (C-3)

A 10 g (50 mmol) aliquot of $Cu(OAc)_2\cdot H_2O$ was mixed with 300 ml of acetone. Into this, 6.5 ml (48.9 mmol) of triethanolamine were added. Immediately, a copious amount of a sky-blue precipitate appeared. The reaction mixture was magnetically stirred for 3 h, and then ultrasonicated for 2 h for completion of the reaction. The light-blue precipitate so obtained was suction-filtered, washed several times with acetone and dried over tissue paper.

Preparation of $Cu_4(teaH)_2(OAc)_3(OH)\cdot 2(CH_3)_2$ CO (C-4)

A 1.00 g (5 mmol) aliquot of $Cu(OAc)_2\cdot H_2O$ was mixed with 10 ml of distilled water. Into this mixture, 40 ml of acetone were added. Immediately, a copious bluish-green precipitate appeared. Into this, 0.65 ml (4.89 mmol) of triethanolamine were added, whereupon the reaction mixture turned immediately into a dark blue solution. The reaction mixture was magnetically stirred for 24 h. A dark-blue solution was obtained. On evaporation of the solvent, dark blue dendritic crystals were obtained after 10 days. The crystals were washed with acetone to remove any excess ligand, and dried over tissue paper in air. A turquoise–blue crystalline precipitate was obtained.

Preparation of $Co_4(teaH)_2(teaH_2)_2(OAc)_2\cdot 2(CH_3)_2CO$ (C-5)

A 5 g (20 mmol) aliquot of $Co(OAc)_2\cdot 4H_2O$ was mixed with 240 ml of acetone. Into this suspension, 3 ml (22.6 mmol) of triethanolamine were added slowly, dropwise. A copious amount of a pink precipitate appeared immediately. The reaction mixture was then ultrasonicated for 30 min, and subsequently stirred magnetically for 6 h. The pink precipitate obtained was then suction-filtered, washed several times with acetone, and dried over tissue paper.

Preparation of $Co_4(dea)(deaH_2)_2(OAc)_6 \cdot 3H_2O$ (C-6)

A 5 g (20 mmol) aliquot of $Co(OAc)_2 \cdot 4H_2O$ was mixed with 230 ml acetone. Into this slurry, 3 ml (31.2 mmol) of diethanolamine were added dropwise through a pipette. The reaction mixture was then magnetically stirred for 9 h. A light violet precipitate was obtained. The precipitate was then suction filtered, washed with acetone and then dried over tissue paper.

Physical and chemical characterizations

The complexes were purified by vacuum sublimation wherever applicable, at room temperature, before they were characterized. IR spectra of the complexes were recorded using a Perkin Elmer 781 FTIR spectrometer. Mass spectra of the complexes were obtained on a Micromass QTOF mass spectrometer in the electrospray (ES) positive ion mode, with methanol as the matrix. Simultaneous thermogravimetric and differential thermal analyses (TGA–DTA) of the complexes were obtained on a TA Instruments (model STDQ 600) thermal analyser under nitrogen flow at atmospheric pressure, and a heating rate of 10 °C/min. Melting points were determined with a Buchi B-540 melting point apparatus. Elemental (CHN) analysis was performed on a Carlo Erba Strumentazione analyser (model 1106).

RESULTS AND DISCUSSION

Synthesis and general properties

Whitmire *et al.* reported[11] the formation of tetrameric $[Cu(teaH)]_4$ using $Cu(OH)_2$ as starting metal salt in aqueous media, but their synthesis procedure is too elaborate. Moreover, during the removal of solvent (H_2O), the product decomposes due to heating. We have used acetone as either the solvent or the dispersion medium for the starting metal acetate. This ensures better yield of the product without any decomposition. All the products were obtained on pot using a simple bench-top method. In case of cobalt complexes, ultrasonication was found to be more useful and convenient than stirring as, unlike copper acetate, cobalt acetate is insoluble in acetone. In the reaction between the metal acetates and the ligands, triethanolamine or the diethanolaamine displaces the water molecules and acetates in form of acetic acid from the metal acetates. The reaction pathways are given by equations (1)–(4).

$$2deaH_2 + 4Cu(OAC)_2.H_2O + Solv \longrightarrow Cu_4(dea)(deaH_{0(1)})(OAc)_{4(5)}.Solv + 4H_2O + 4(3)CH_3COOH \quad (1)$$

$$2teaH_3 + 4Cu(OAC)_2.H_2O + nSolv. \longrightarrow Cu_4(teaH)(teaH_{1(2)})(OAc)_{3(5)}\ (OH)_{1(0)}.nSolv + 3(4)H_2O + 5(3)CH_3COOH \quad (2)$$

$$4teaH_3 + 4Co(OAc)_2.4H_2O + 2Solv \longrightarrow Co_4(teaH)_2(teaH_2)_2(OAc)_2 \cdot 2Solv + 16H_2O + 6CH_3COOH \quad (3)$$

$$3deaH_2 + 4Co(OAc)_2.4H_2O + Solv \longrightarrow Co_4(dea)(deaH_2)_2(OAc)_6 \cdot 3H_2O + 13H_2O + 2CH_3COOH \quad (4)$$

In case of the complex $Cu_4(dea)_2(OAc)_4 \cdot (C_2H_5)_2O$, the reaction between the copper acetate and $deaH_2$ is more profound in the presence of dithyl ether in acetone. The overall dielectric constant of the mixed solvent system, comprising acetone and diethyl ether, can be calculated from the simple equation, $\varepsilon_m = \varphi_1\varepsilon_1 + \varphi_2\varepsilon_2$; where ε_m, ε_1 and ε_2 are the dielectric constants of the mixture and solvent 1 and solvent 2, respectively, and φ_1 and φ_2 are the volume (weight or mole) fractions of solvent 1 and solvent 2. The calculated value of dielectric constant of the mixed solvent system, comprising acetone and diethyl ether, is 13.6, whereas the dielectric constant of acetone is 20.7. Therefore, upon addition of diethylether to acetone, there is an overall reduction of dielectric constant and the polarity of the solvent. Polar solvent decreases the stability of hydrogen bonded network. In a more nonpolar solvent, the molecule is stabilized by enhanced hydrogen bonding, thus re-protonation is prevented. The characteristic general properties of the complexes are shown in Table 1.

Table 1. Characteristics of the complexes

Complex	Yield (%) as prepared	M.P. (°C)	Colour and physical state	Analysis (%): found (calcd) M (Cu/Co)	C	H	N
C-1 [$C_{21}H_{40}N_2O_{15}Cu_4$]	100	132.5	Light green solid	31.5 (31.0)	31.0 (31.0)	4.97 (4.92)	3.46 (3.44)
C-2 [$C_{20}H_{40}N_2O_{13}Cu_4$]	86	124	Blue green solid	33 (32.8)	31.12 (31.20)	5.19 (5.20)	3.59 (3.60)
C-3 [$C_{24}H_{48}N_2O_{15}Cu_4$]	100	170	Light blue solid	28.5 (28.0)	33.0 (33.3)	5.57 (5.33)	3.11 (3.11)
C-4 [$C_{24}H_{48}N_2O_{15}Cu_4$]	55	169	Dark blue solid	29.8 (29.4)	33.38 (33.64)	5.67 (5.60)	3.14 (3.27)
C-5 [$C_{34}H_{72}N_4O_{18}Co_4$]	100	160	Pink solid	22.6 (22.3)	38.49 (38.5)	6.66 (6.61)	5.28 (5.29)
C-6 [$C_{24}H_{55}N_3O_{21}Co_4$]	80	145	Light violet solid	25.2 (25.0)	30.53 (30.50)	5.81 (5.82)	4.45 (4.44)

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All the complexes were found to be very soluble in polar protic solvents such as water and methanol, and sparingly soluble in ethanol. The complexes are completely insoluble in nonpolar or polar solvents. In polar solvents such as dichloromethane, the copper complexes tend to decompose into a green oily mass, i.e. into copper acetate and the corresponding ligand. The complexes were found to be hygroscopic, upon prolonged (more than 24 h) exposure to moisture and, in solutions containing water, decompose occurred within 2–3 months under ambient conditions, into a brownish-coloured residue—that of the corresponding metal oxides. Further, during our attempts to grow single crystals, some of these complexes, e.g. copper–diethanolamine, react with the solvent molecules and leave a brown residue in the crystallisation vessel. Another problem encountered during the crystallization process is that the complexes, being solids that sublime at rather low temperatures (50–100 °C at atmospheric pressure), evaporate along with the solvents such as ethanol and methanol, and thus leave a oily mass on the side of the crystallization vessel. Such residue was found to adhere to the side of the vessel for the copper–triethanolamine complex, even at a temperature as low as 4 °C, when the crystallization solvent was methanol. Some of the complexes, e.g. copper–diethanolamine, were found to sublime at room temperature, when the round-bottom flask containing the complex was connected directly to a pump.

IR spectroscopy

The broad band at $\sim 3400\ \mathrm{cm^{-1}}$ can be attributed to the hydrogen-bonded OH group of the triethanolamine or diethanolamine for the complexes C-3, C-4, C-5 and C-6. For C-6, the broad band at $3410\ \mathrm{cm^{-1}}$ is due to intermolecular hydrogen bonding because of presence of coordinating H_2O and ($deaH_2$) ligand. For the complexes, C-1 and C-2, the bands around 3400 and $3200\ \mathrm{cm^{-1}}$ are strong and sharp, which corresponds to N–H stretching of $deaH_2$ ligand. The shoulder observed at $3171\ \mathrm{cm^{-1}}$ for the complex C-2 is Fermi resonance band with over tone of band at $1628\ \mathrm{cm^{-1}}$, i.e. N-H bend. IR spectra of the copper complexes do not show any band around $1700\ \mathrm{cm^{-1}}$; this indicates that there is no nonbridging (bonded to only one atom) C=O group in the molecule. On the contrary, both the cobalt complexes show bands at 1723 and $1706\ \mathrm{cm^{-1}}$, which indicates the presence of free (non-bridging) C=O bonds in these two complexes. These results are consistent with the structure of the parent acetates, as the acetates are bridging between two copper atoms in copper acetate, while they are free in cobalt acetate. The characteristic IR frequency and their assignments are presented in Table 2.

For the copper complex $Cu_4(teaH)(teaH_2)(OAc)_5{\cdot}(CH_3)_2CO$, the very broad O–H bands, centered at 3402 and $3208\ \mathrm{cm^{-1}}$, respectively, correspond to the hydrogen-bonded tetramer. The O–H bands extend into C–H absorption bands between 2962 and $2845\ \mathrm{cm^{-1}}$. A similar broadening of O–H bands was observed in the IR spectrum of the complex, $Cu_4(teaH)_2(OAc)_3(OH){\cdot}2CH_3COCH_3$. Three bands around $3400\ \mathrm{cm^{-1}}$ were observed, which correspond to O–H of hydroxide, metal-bonded O–H and hydrogen-bonded O–H of the triethanolamine complex. However, for this complex, the O–H bands are separated from bands which correspond to C–H stretching, observed at 2962, 2874 and $2845\ \mathrm{cm^{-1}}$.

The strong bands observed at 1049, 1086, 1085, 1069 and $1051\ \mathrm{cm^{-1}}$ are due to the C–O stretching frequencies of primary ROH group, as shown in Table 2. The bands between 1560 and $1580\ \mathrm{cm^{-1}}$ are due to hydrogen-bonded C=O stretching frequencies, which are similar to C=O bands observed for enols. This suggests that the carbonyl of acetate moiety and OH of the $teaH_3$ or $deaH_2$ are engaged in hydrogen bonding in the complexes. The unconjugated C–N linkages of the ligands $deaH_2$ or $teaH_3$ give medium to week bands ($1250–1020\ \mathrm{cm^{-1}}$) due to C–N stretching vibrations. The strong bands observed between 1419 and $1446\ \mathrm{cm^{-1}}$ are due to C–H bending corresponding to methylene group of the ligands; those observed between $1332–1388\ \mathrm{cm^{-1}}$ are due to C–H bend of the methyl group of the acetate moiety.

Mass spectral analysis

Mass spectra of the all the complexes show two predominant features. Firstly, various m/z peaks associated with fragments containing coordinating ligand such as acetone or diethyl ether and, secondly, protonation of the fragmented species including the ligands. Such protonation of fragmented moieties are observed when mass spectra of complexes are recorded in positive ion electrospray mode.[17] Since oxygen is more electronegative than nitrogen, protonation occurs at the nitrogen of secondary or tertiary amine to form species that contains the fragment $N^+H_2(CH_2CH_2OH)_2$, i.e. $H^+(deaH_2)$ or $N^+H(CH_2CH_2OH)_3$. In all the cases, the solvent methanol was found to be coordinated in the fragments. Figures 1 and 2 show the experimental and calculated mass spectra of different fragments for the complex C-1, respectively. The calculated m/z values tabulated in Table 3 correspond to the Cu-63 isotope. The m/z values and the isotope distribution pattern obtained from the experimental mass spectra of all the complexes match well with that of the calculated ones (see supplementary material).

For the complex $Cu_4(deaH)(dea)(oAc)_5{\cdot}(CH_3)_2CO$, the peak at $m/z = 803$ corresponds to the moiety $Cu_4(dea)(deaH)(OAc)_4(CH_3)_2CO(CH_3OH)(H_2O)$. In this moiety, both the copper atoms are in the +2 oxidation state. The mass spectrum shows a small peak at $m/z = 833$, which corresponds to the moiety $HCu_4(dea)(deaH)(OAc)_5(CH_3)_2CO(H_2O)$ as the nearest match to the molecular ion peak. The peak at $m/z = 564$, corresponds to the moiety $Cu_3(dea)_2(OAc)(CH_3)_2CO(CH_3OH)(H_2O)$.

For the complex $Cu_4(dea)_2(OAc)_4{\cdot}(C_2H_5)_2O$, several peaks reveal the presence of $(C_2H_5)_2O$ as the coordinating ligand. The peak at $m/z = 819$ corresponds to the moiety $HCu_4(dea)_2(OAc)_4(CH_3OH)(H_2O)_5$ as the nearest match to the molecular ion peak. For the complex, $Cu_4(teaH)(teaH_2)(OAc)_5{\cdot}(CH_3)_2CO$, the nearest match to

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Table 2. IR spectra of the complexes, Band position, cm^{-1}

C-1	C-2	C-3	C-4	C-5	C-6
3425s (νN–H)	3425s (νN–H)	3402m (νO–H)	3424m (νO–H)	3438s (νO–H)	3410s (νO–H)
3267m (νN–H)	3267m (νN–H)	3208m (νO–H)	2962w (νC–H)	3070w (νC–H)	2911m (νC–H)
2943m (νC–H)	3171m, sh	2962m (νC–H)	2874w (νC–H)	2902w (νC–H)	2871m (νC–H)
2877m (νC–H)	2944m (νC–H)	2914m (νC–H)	2845w (νC–H)	2852m	1706m (νC=O)
1628s	2878m (νC–H)	2875m (νC–H)	1568s	2726w (νC–H)	1580s
1560s	1628s	1568s	(νOH...O=C)	2608w	(νOH...O=C)
(νOH...O=C)	(N–Hbend)	(νOH...O=C)	1490w	1723m (νC=O)	1419s
1428s	1560s	1446s	1446s	1578s	(C–H bend)
(C–H bend)	1428s	(C–H bend)	(C–H bend)	(νOH...O=C)	1222w
1347w	(C–H bend)	1389s	1388s	1556m	1151w νC–N
1296w	1361w	1332s	1332s	1474w	1086m
1198w	1345w	1266m	1299w	1458w	1051m (νC–O)
1122w νC–N	1296w	1140m	1265w	1416s	1023m
1089m	1235w	1086s (νC–O)	1245w	(C–H bend)	984m
1075m	1198w	1062m	1140m	1384w	941w
1049m (νC–O)	1119m νC–N	1024m	1085s (νC–O)	1371w	900w
1012m	1090m	1001m	1062m	1345w	861w
925w	1075m	902m	1024m	1247m	786w
891w	1049s (νC–O)	867m	1001m	1145w	674m
869w	1012s	750w	914w	1069s(νC–O)	657m
686m	925w	681m	902m	1043m	635w
626m	870w	619m	867m	1024m	618w
	685m	552m	750w	917w	566w
	626w	520m	680m	889m	529w
	591w		619m	870w	504w
	543w		551m	753w	474w
	521w		517w	658w	437w
	445w		449w	643w	428w
			420w	607w	419w
				565w	406w
				444w	
				428w	
				416w	

Table 3. Main metal containing fragments for C-1

m/z	Fragment
303	$Cu_2(OAc)_3$
333	$HCu_2(dea)_2$
454	$Cu_3(dea)_2(OAc)$
469	$Cu_3(dea)(OAc)_3$
562	$Cu_3(dea)(OAc)(CH_3)_2CO(CH_3OH)(H_2O)$
635	$Cu_4(dea)_2(OAc)_3$
665	$Cu_4(CH_2CH_2O)_3(CH_2CH_2OH)(OAc)_4$
831	$HCu_4(dea)(deaH)(OAc)_5(CH_3)_2CO(H_2O)$

molecular ion peak was observed at $m/z = 808$, which corresponds to the fragment, $HCu_4(teaH)_2(OAc)_3(CH_3OH)_2(H_2O)$. Peaks at $m/z = 544$ and 633 reveal the presence of acetone as the coordinating ligand. The mass spectra of the complex $Cu_4(teaH)_2(OAc)_3(OH)\cdot 2CH_3COCH_3$ shows a peak at $m/z = 694$, which corresponds to the fragment $HCu_4(tea)(OAc)_3(CH_3)_2CO(CH_3)_2CO$, and a peak at $m/z = 665$, which corresponds to the fragment $Cu_4(teaH)_2(OAc)(CH_3)_2CO$.

For the cobalt–triethanolamine complex, $Co_4(teaH)_2(teaH_2)_2(OAc)_2\cdot 2(CH_3)_2CO$, the nearest match to the molecular ion peak was observed at $m/z = 1000$, which corresponds to the fragment $HCo_4(teaH)_4(OAc)(CH_3)_2CO(CH_3)_2CO$. The peak at $m/z = 254$ reveals that the two acetates are located on the same cobalt atom in this molecule. The peaks at $m/z = 254$ and 321 reveal that at least one of the acetone ligands binds to the cobalt bonded to the two acetate. The peak at $m/z = 649$ suggests that two triethanolamine ligands are bonded to the same cobalt atom. For the complex $Co_4(dea)(deaH_2)_2(OAc)_6\cdot 3H_2O$, the nearest match to molecular ion peak appears at $m/z = 916$, which corresponds to the fragment, $Co_4(dea)(deaH_2)_2(OAc)_5\cdot 4H_2O$.

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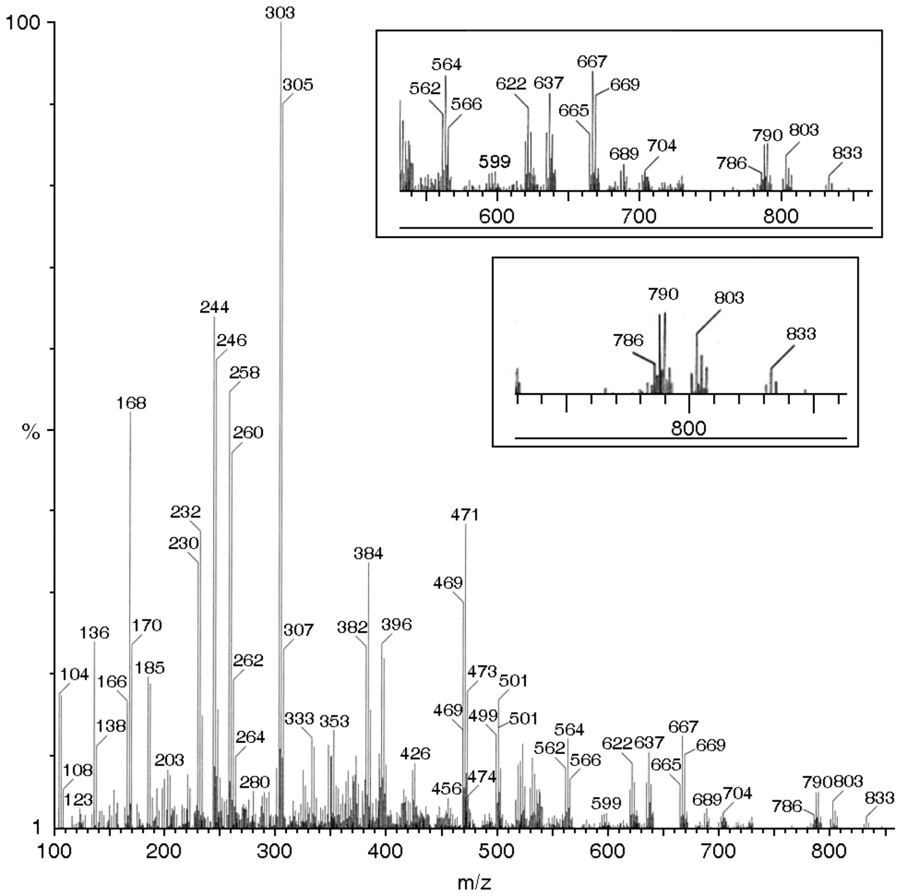

Figure 1. Mass spectra of C-1.

The most probable molecular structures of the complexes

On the basis of the experimental results given above, and by analogy with previously isolated tetra nuclear cobalt diethanolamine complex,[18] copper triethanolamine complex[11] and the crystals structure of parent copper acetate[16] and cobalt acetate,[20] the most probable structures of the complexes are presented in Fig. 3. Since syntheses were carried out in coordinating solvents such as acetone and diethyl ether, it can be anticipated that the metal centre will most likely saturate their coordination sphere in these complexes.

Copper acetate has a dimeric structure in the solid state where the acetate moiety acts as the bridging ligand between the two copper atoms, with two water molecules located at the axial position. In the reaction between copper acetate and triethanolamine in the presence of acetone, it is likely that triethanolamine will displace the axial water molecule and one of the bridging acetate moieties, thereby acting as the bridging ligand between two dimeric units of the copper acetate. We have carried out single crystal X-ray diffraction study of the product obtained from the complex C-1 in a solution of methanol and dichoromethane. The complex was dissolved in such mixture of solvent in an attempt to recrystallise the complex. Single crystal X-ray diffraction study, however, unexpectedly reveals the structure that correspond to exactly the structure of copper acetate. The retention of original dimeric structure of copper acetate in the molecule is supported by such study. The labile diethanolamine ligand is slowly replaced by reverse reaction with water and subsequently the complex, C-1 reverts back to the dimeric copper acetate.

For the complex, C-1 [Fig. 3(a)], the peak at $m/z = 333$ in the mass spectra is clearly indicative of presence of the puckered ring structures formed by the two diethanolamine ligands on the adjacent copper atoms (Cu3 and Cu4) that originate from dimeric copper acetate, i.e. one $Cu_2(OAc)_4$ unit. In this structure, bridging acetate in manner, which is very similar to structure of parent copper acetate, links the copper toms. The peak at $m/z = 303$, corresponding to the fragment $[Cu_2(OAc)_3]^+$ [the fragment that contains Cu1 and Cu2, Fig. 3(a)], provides further evidence for this structure.

The complex C-2 has a structure similar to that of C-1, as shown in Fig. 3(b). The peak at $m/z = 438$ (see Fig. 1, Supplementary Material) is indicative of the structural feature of the two diethanolamine moieties being located at adjacent copper atoms that originated from same the $Cu_2(OAc)_4$ dimeric unit. For the complex, C-3, the peaks at $m/z = 392$ and

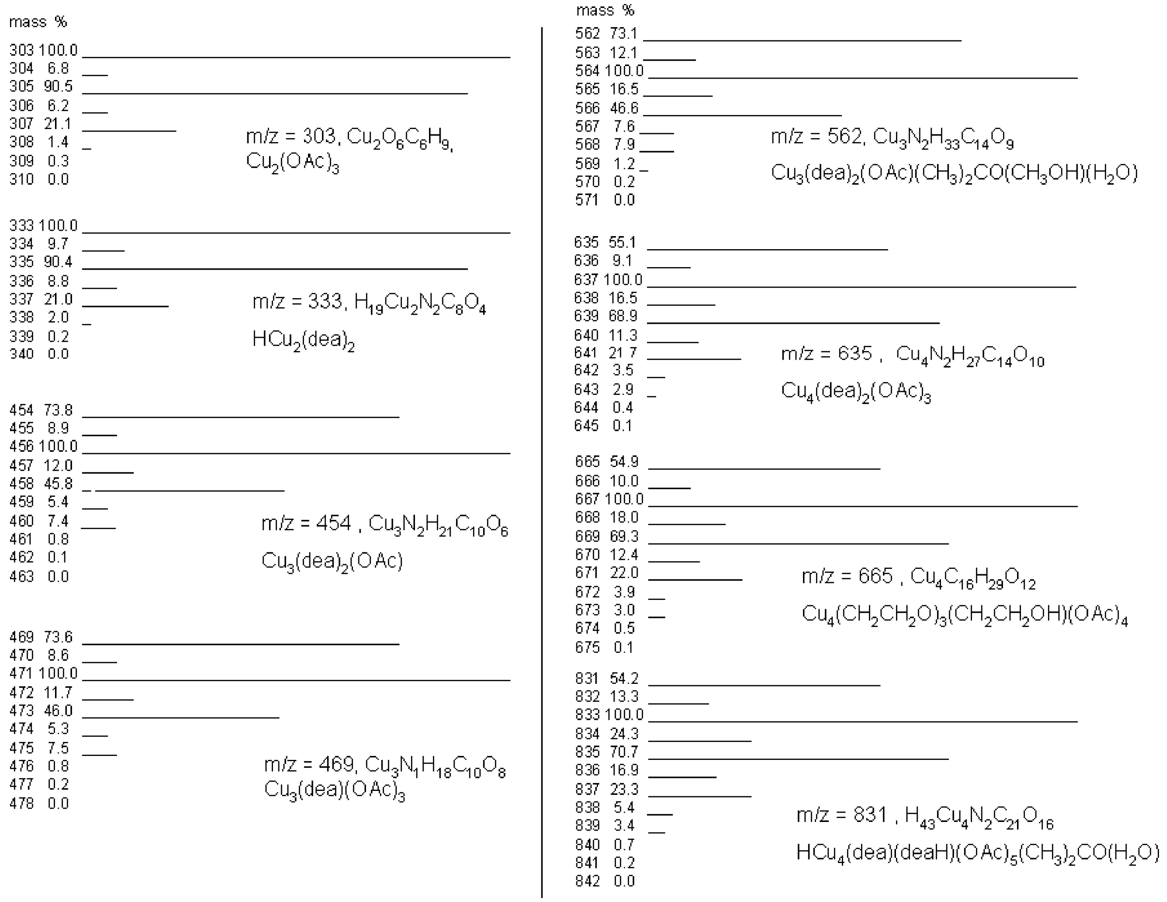

Figure 2. Calculated mass spectra of the complex C-1.

421 reveal the presence of two triethanolamine on the adjacent copper atoms. The peak at $m/z = 544$ for the fragment $[Cu_3(OAc)_5](CH_3)_2CO$ provides additional evidence for the proposed structure. Similarly for the complex C-4, the presence of two triethanolamines on adjacent copper atoms is revealed by the peak at $m/z = 544$.

It is evident from the peak at $m/z = 421$ that the two acetones coordinate with the same Cu atom in this complex. The structure of cobalt acetate is monomeric with cobalt atoms surrounded octahedrally by four water molecules and by two oxygen atoms, which belong to two different acetate groups. In this structure, the carbonyl oxygens of the acetate and hydrogens of water molecules are engaged in hydrogen bonding.

For the complex C-5 [Fig. 3(e)], the peaks at m/z 254 and 649, (Fig. 7, Supplementary material) indicate that the two triethanolamine ligands bind to the same cobalt atom. For the complex C-6 [Fig. 3(f)], two out of the three diethanolamine ligands are located on the same cobalt atom as evidenced by the peak at $m/z = 267$ in the mass spectra.

Thermal properties

The sublimation of the complexes was revealed by weight loss recorded in TGA over the temperature range of 52–100 °C, accompanied by a simultaneous plateau region in the DTA pattern, or a broad endothermic dip in the DTA curve.[21] TGA–DTA curves of all the complexes showed decompositions in steps, revealed by weight loss in TGA, accompanied by an exothermic peak in the DTA. Melting points of the complexes were characterized by sharp endothermic dips appearing in the DTA patterns of the complexes between 100 and 200 °C.

For the complex $Cu_4(deaH)(dea)(oAc)_5{\cdot}(CH_3)_2CO$, Fig. 4(a) shows the simultaneous TGA–DTA pattern of the complex. The stepwise weight loss of ~2% within a temperature range 55–90 °C illustrates a moderate volatility over this relatively low temperature range. The weight loss in small steps at 57, 65 and 90 °C is due to the sublimation of the complex. Even at temperatures as high as 500 °C, the decomposition of the complexes is not complete. This is revealed by the gradual changes of slope, which appear between 400 and 590 °C in the TGA patterns. For this complex, the weight loss is about 2.5% within the range 400–590 °C. This suggests that, in the given range of temperature and under an inert nitrogen atmosphere, the complex retains carbon and other organic species to a certain extent.

For the complex, $Cu_4(dea)_2(OAc)_4{\cdot}(C_2H_5)_2O$, the small step in the TGA curve at about 52 °C [Fig. 4(b)] may be attributed

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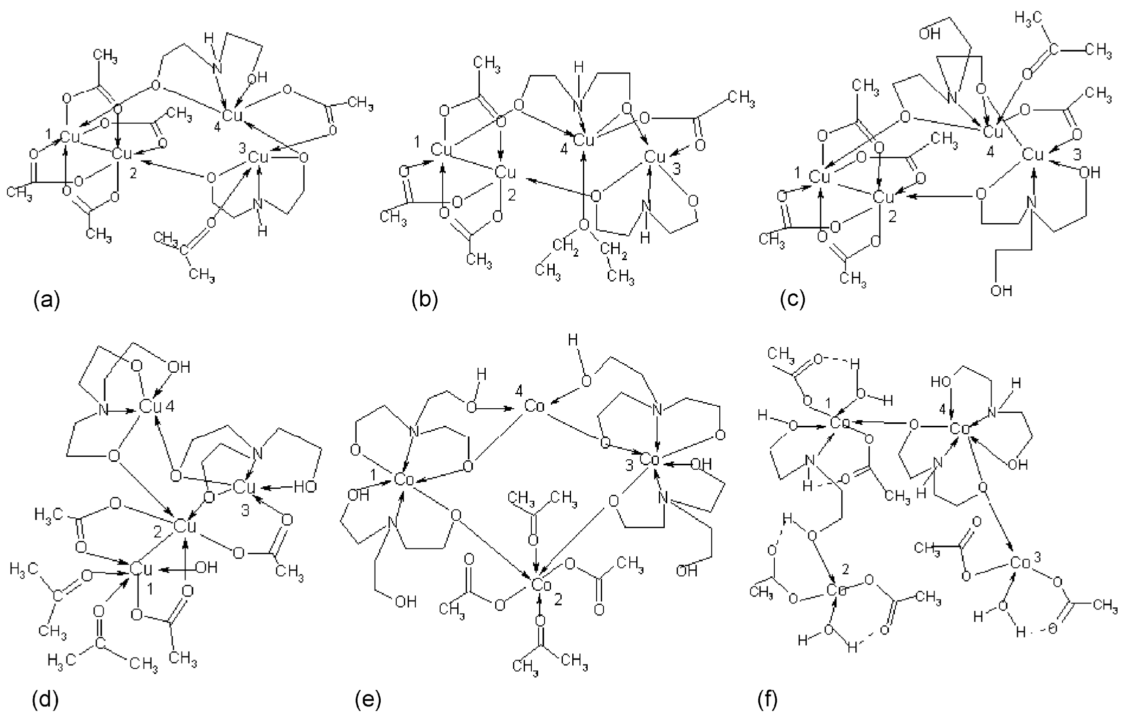

Figure 3. Most probable structures of the complexes, (a) C1; (b) C-2; (c) C-3; (d) C-4; (e) C-5; (f) C-6.

to the sublimibility of the complex. The melting temperature of the complex was revealed by a sharp endothermic dip at about 130 °C in the DTA curve. The endothermic dip at 130 °C extended into another relatively broader endothermic dip centered at about 143 °C; this can be attributed to vapourization of the molten mass of the complex.

For the complex $Cu_4(teaH)(teaH_2)(OAc)_5{\cdot}(CH_3)_2CO$, there was a gradual weight loss, along with an exothermic peak, centered at 76 °C [Fig. 4(c)], in the DTA curve. The weight loss up to 110 °C was ~1.8%, corresponding to the loss of one molecule of water, eventually resulting from the intramolecular reaction between the hydroxyl (g) groups of two triethanolamine ligands. The melting temperature for this complex was characterized by a sharp endothermic dip in the DTA pattern, centred at about 170 °C.

For the complex $Cu_4(teaH)_2(OAc)_3(OH){\cdot}2CH_3COCH_3$ the weight loss up to 100 °C was negligible (0.15%), which can be attributed to loss of residual solvents [Fig. 4(d)]. The melting temperature of this complex was revealed by the sharp endothermic dip centered at about 169 °C. For this complex, no measurable weight loss due to sublimation was observed in the TGA–DTA pattern.

For the complex $Co_4(teaH)_2(teaH_2)_2(OAc)_2{\cdot}2(CH_3)_2CO$, the three small steps at 55, 64 and 74 °C were due to the stepwise sublimation of the complex [Fig. 4(e)]. The weight loss between 80 and 140 °C was about 6%, which corresponds to loss of one molecule of acetone. This is manifested by the sharp and rather symmetric endothermic dip at about 109 °C. The second sharp endothermic dip at 160 °C was attributed to the melting of the complex. Two broad endothermic dips centered at 213 and 268 °C were due to the vapourization of the molten mass of the solid.

For the cobalt–diethanolamine complex, the first very broad endothermic dip in the DTA curve, centered at about 57 °C, was due to the sublimation of the complex [Fig. 4(f)]. This was accompanied by a gradual weight loss of about 2% as the temperature was raised to 100 °C. The second sharp endothermic dip observed at around 145 °C was due to the melting of the complex. The weight loss in the temperature range 100–145 °C was 4.2%, which corresponds to the removal of two molecules of water from the complex. The endothermic dip for the melting and that for removal of two molecules of water are superimposed in the DTA curve in this region. The weight loss between 160–223 °C was about 2%, and was accompanied by a sharp endothermic dip at about 190 °C, caused by the loss of the remaining water molecule from the complex. The multi-step decomposition, observed at various temperatures up to 600 °C, may be attributed to the diverse nature of metal–ligand bonding present in this molecule.

The simultaneous TGA–DTA of the complexes reveal that the complexes C-1, C-2, C-5 and C-6 are volatile within the temperature 52–100 °C, whereas the complexes C-3 and C-4 are not volatile within the same temperature range. Isothermal TGA were carried out for the aforementioned four complexes, namely C-1, C-2, C-5 and C-6, at an Ar flow rate of 100 ml/min for duration of 160 min at atmospheric pressure. The isothermal TGA data of the complexes are presented in Fig. 5.

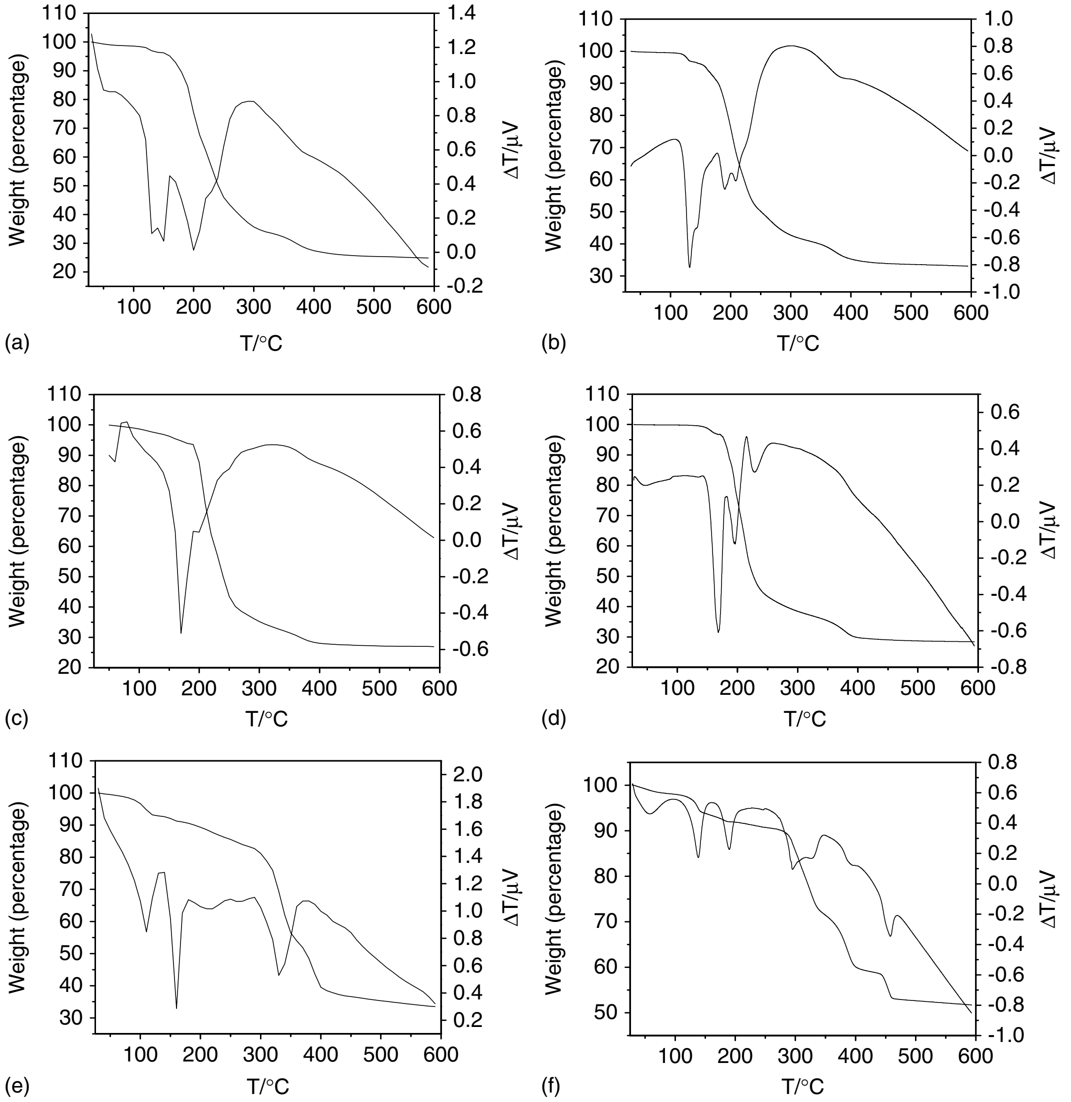

Figure 4. Simultaneous TGA–DTA of the complexes under nitrogen flow at atmospheric pressure.

The graphs reveal that, at extremely low sublimation regime (where the total weight loss was ~1%), the sublimation follows a multi step mechanism. It is likely that, as the sublimation rate increases, the steps come close enough to result in an almost straight line, as observed for the complex C-5. The observation that the sublimation follows a multi-step mechanism at low sublimation regime could be understood from a molecular level perspective of sublimation process through cluster formation. Since the sublimed molecules are in equilibrium with the adsorbed species at atmospheric pressure, the observed weight oscillates for a certain period of time; as a result, darkening of the steps was observed [Fig. 5(b) and (d)]. Under reduced pressure (1–10 Torr for low-pressure CVD), such equilibrium between the sublimed and adsorbed species was disturbed (as the sublimed species were constantly removed under vaccum, the equilibrium shifted towards the right); as a result the isothermal weight loss at reduced pressure should be significantly larger than what was observed at atmospheric pressure.

The thickness of resultant films obtained by using such complexes as precursors depends on many factors, such as growth temperature and pressure in a low pressure MOCVD process. Typically using such polynuclear complexes, for example, for the complex $Cu_4(deaH)(dea)(OAc)_5 \cdot (CH_3)_2CO$, as the precursor, film with thickness of ~1 μm could be obtained by low-pressure (1–5 Torr) MOCVD for a deposition duration of about 1 h, at a temperature of 350 °C, which gives a typical growth rate of about 16 nm/min. Upon increasing the growth temperature, the extent of carbon in the film decreases; thus, relatively pure oxide film as thin as 159 nm could be obtained with a growth rate of 2.6 nm/min for a deposition duration of 1 h at a growth temperature of 430 °C. By using conventional precursor such as copper acetylacetonate for growth of oxides at temperatures around 430 °C using

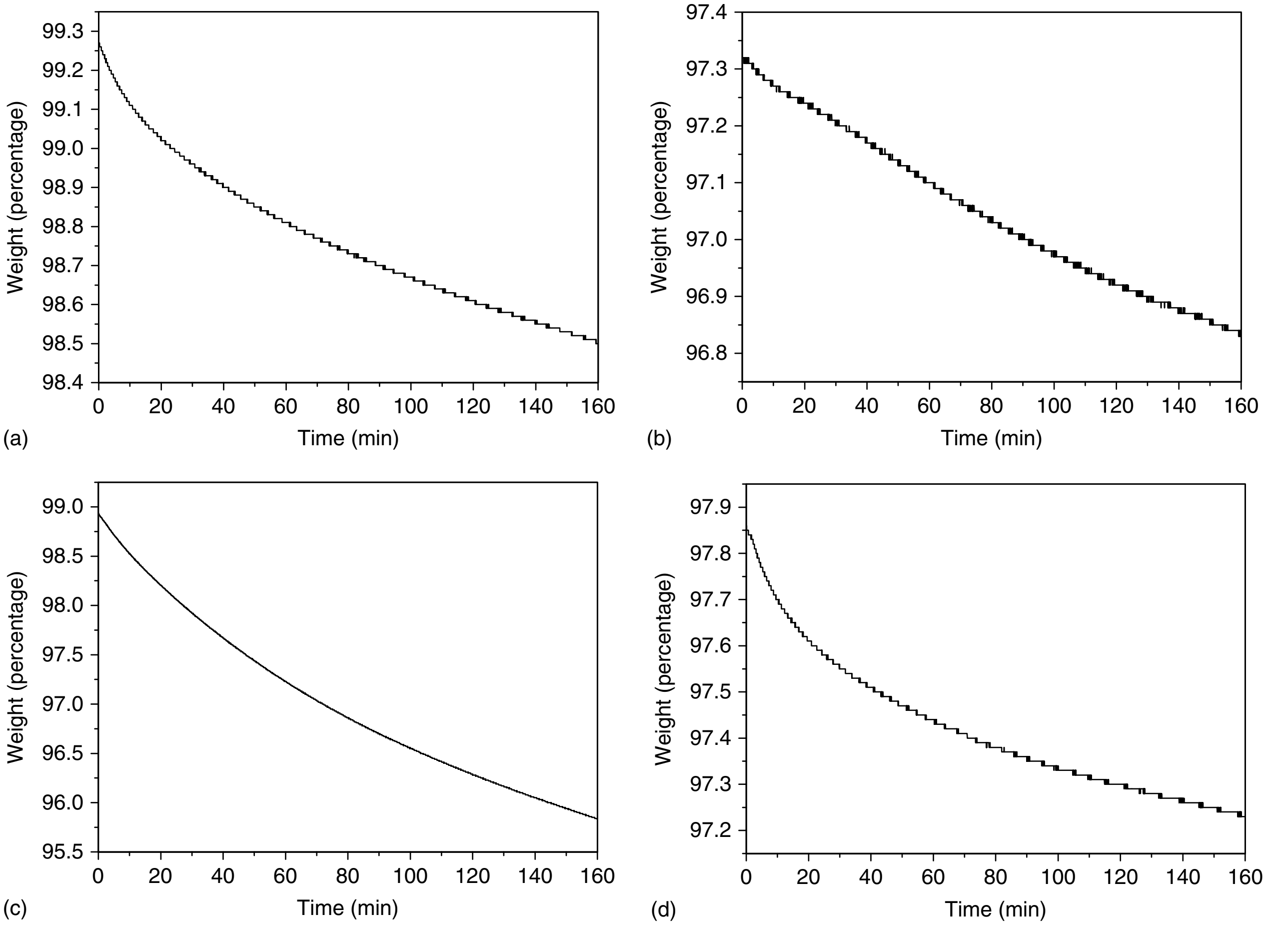

Figure 5. Isothermal TGA of the complexes at atmospheric pressure: (a) C-1, $T = 93\,°C$; (b) C-2, $T = 52\,°C$; (c) C-5, $T = 63\,°C$; (d) C-6, $T = 57\,°C$.

LPCVD, the typical growth rate can be 10–15 nm/min. Thus by informed variation of CVD parameters, the thickness of the films could be controlled at nanometers using such polynuclear complexes as precursor.

The simultaneous TGA–DTA curve reveals that the complexes retain carbon at temperatures at high as 500 °C. The presence of carbon is known to limit the mobility of growth species for oxides, restricting them to nanometersized crystals.[22] Thus, the complexes have potential applications in the growth of nanostructured metal oxides thin films under specific CVD conditions.

Comment on low temperature volatility and molecular structure

Thermal studies on the complexes show that they are sublimable solids at relatively low temperatures of 52–80 °C. The IR spectra of the complexes reveal intermolecular hydrogen bonding through the hydroxyl O–H group of the triethanolamine and diethanolamine ligand. The sublimation (volatility) of these complexes may be correlated with two factors, in terms of their structure: the intermolecular van der Waals interaction and to presence/absence of the intermolecular hydrogen bonding. Of these, the absence of intermolecular hydrogen bonding contributes to lowering the temperature of sublimation to below 100 °C. The two copper triethanolamine complexes do not show any appreciable sublimation, which could be due to the presence of intermolecular hydrogen bonding through the hydroxyl group of triethanolamine ligand. It is possible that the different functional groups of monomers within the tertrameric unit are oriented in such a way as to prevent the intramolecular hydrogen bonding taking place. In other words, the most stable conformation of these molecules probably determines whether a molecule sublimes or not.

Advantages of polynuclear complexes as MOCVD precursor over other state of art precursor and future outlook

An ideal precursor for MOCVD should fulfil many criteria in addition to volatility; these are low toxicity, stability, ease of synthesis, ease of handling, non-pyrophoricity, and low cost involved in the synthesis. While the state

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of art precursors for MOCVD, namely metal beta diketonates and alkoxides of monofunctional alcohols, have considerable volatility, these suffer from the drawbacks of having high toxicity, relatively high cost involved in synthesis, and tedious and time-consuming synthesis methodology.

The polynuclear complexes investigated in the present study, on the other hand, fulfil many criteria to be considered as ideal precursors for MOCVD because of their ease of preparation, ease of handling without glove box, low cost involved in synthesis, low toxicity (due to presence of biologically compatible ligands such as triethanolamine), nonpyrophoricity and low to moderate sublimability. In their syntheses, from metal acetates, the reactions leads to water as the by-product, which is an aspect of environmentally friendly chemistry. The complexes sublime at low temperatures, which renders the overall MOCVD process cost-effective. Owing to retention of carbon even at high temperature, such complexes lead to nanostuctured metal oxide particles, through carbon-induced restriction of grain growth. While the relatively low sublimability of such complexes may appear to be a drawback for considering these complexes as suitable precursors for MOCVD, it has certain advantages. Because of the low vapour pressure of such complexes even at low reactor pressure, such complexes can potentially be the ideal precursors for the growth of multilayer oxide thin films, where the thickness of individual layer needs to be controlled at nanometer or even at angstrom level.

The current state-of-the-art thin film deposition techniques such as molecular beam epitaxy and atomic layer deposition (ALD) allow one to grow such thin film structures where thickness of individual layers could be controlled typically below 100 nm for specific device requirement. Using polynuclear complexes as precursors, such growth may be possible using MOCVD technique in future.

In addition, for a similar reason, such precursors can be used for introducing dopants at low concentration into films. The high sublimability of state-of-the-art complexes is often a drawback against introducing dopants using MOCVD technique.

Because of inherent high metal stoichiometries per molecule, polynucelar complexes, investigated in the present study, are capable of forming one unit cell of crystals from one individual molecule. Such growth may lead to unusual crystalline phases, not obtainable using mononuclear complexes. In other words, molecular structure-directed crystal growth might be possible using these complexes as precursors. We are currently investigating the possibility of such growth using these complexes as precursors.

CONCLUSIONS

Novel polynuclear complexes of cobalt and copper with the polyfunctional aminoalkohals such as triethanolamine and diethanolamine have been synthesized in moderate to high yield, using a simple bench-top technique, under ambient atmosphere. The complexes can be easily handled in air without the need for a glove box. The complexes were characterized by infrared spectroscopy, elemental analysis, mass spectroscopy and thermogravimetry. Simultaneous TGA–DTA study of the complexes reveals that the complexes are volatile at temperatures from 50–100 °C. Hence, these complexes are promising candidates as a novel class of precursors in the low-pressure MOCVD process for the growth of thin films.

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