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Synthesis, X-ray structural characterization and pyrolysis studies of heterobi- and trimetallic molecular complexes

Mazhar Hamid^a, Muhammad Mazhar^{*b}, Zainudin Arifin^b and Kieran C. Molloy^c**Keywords:** Polynuclear complexes, Synthesis, Characterization, Heterobi-, trimetallic.

Heterobi- and -trimetallic complexes $[\text{NiTl}(\text{acac})_2(\text{dmae})]_2$ (**1**) Single crystal X-ray analysis of both complexes show that and $[\text{Ba}(\text{acac})(\text{OH}_2)\text{Ni}_2(\text{acac})_4\text{Tl}(\text{dmae})_2]$ (**2**), (acac= they crystallize in a monoclinic crystal system with space acetylacetonate, dmae= N, N-dimethyl aminoethanolate) have group $P2_1/c$. TGA studies of the complexes indicate that been synthesized by a simple reaction of Ni(II) acetylacetonate, complex (**1**) is a suitable precursor for the preparation of Tl(I) acetylacetonate and dmaeH for (**1**) and Ni(II) composite $\text{NiO}/\text{Tl}_2\text{O}_3$ while complex (**2**) yields an acetylacetonate, Tl(I) acetylacetonate, Ba metal and dmaeH for unstable composite $\text{NiO}/\text{Tl}_2\text{O}_3/\text{BaO}$ which on exposure to (**2**) in toluene to obtain crystalline products which were air is converted to $\text{NiO}/\text{Tl}_2\text{O}_3/\text{BaCO}_3$ by the absorption of characterizes by physicochemical and spectroscopic methods. atmospheric carbon dioxide.

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Introduction

Recently, considerable attention has been focused on the synthesis of heterometallic complexes in which different metal centers are bonded through bridging donor atoms such as O, N, and S. Such molecular complexes provide a direct route to the synthesis of multi-metallic ceramic composites for high-tech industrial applications. For the synthesis of these complexes, the choice of proper ligands plays an important role. In this regard, several bi- and tridentate

ligands such as amino alcohols, acetylacetone, acetate and fluoroacetate, have been used to form molecular species such as $[\text{CuCoZn}_2(\text{Dea})_3\text{Cl}_3(\text{HOMe})] \cdot \text{MeOH}$, $[\text{CuCoZn}(\text{Me}_2\text{Ea})_4(\text{NCS})_2(\text{OAc})]^{1-1}$ (H_2Dea is diethanolamine and $\text{HMe}_2\text{Ea} = 2$ -(dimethylamino)ethanol), $[\text{Cu}_2\text{CoPbCl}_4(\text{L})_4]_2$ and $[\text{Cu}_2\text{CoCd}_2\text{Cl}_6(\text{L})_4(\text{HOMe})_2]^{[2]}$ ($\text{L} = 2$ -dimethylamino)ethanolate).

As far as thallium heterometallic chemistry is concerned, a few examples of its complexes with transition metals such as gold and titanium have been reported in the past.^[3,4,5] For example, an Au(I)-Tl(I) complex was prepared by the reaction of $\text{M}[\text{AuR}_2]$ with a Tl(I) salt to yield $[\text{Au}_2\text{Tl}_2\text{R}_4] \cdot (\text{CH}_3)_2\text{CO}$, (where M = alkali metal or Bu_4N ; R = C_6H_5 , C_6Cl_5)^[3] and a variety of double alkoxides with different stoichiometries of thallium and titanium has been reported.^[4] The unusual properties of thallium complexes^[6,7] attributed to the relativistic disturbance of the $6s^2$ electrons provided the background of our interest in the synthesis of

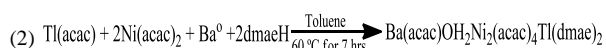
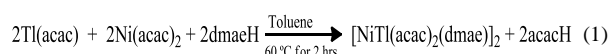
its bimetallic complex with nickel and its successful use as a template for a more complex extended trimetallic geometry. The introduction of barium (s-block) into the Ni/Tl framework of complex **(1)** is of particular interest in order to study the ‘one pot’ syntheses of these precursors.

Here we report the synthesis and X-ray characterization of the hitherto unknown heterobi- and -trimetallic complexes $[\text{Ni}(\text{acac})_2\text{Tl}(\text{dmae})]_2$ **(1)** and $[\text{Ba}(\text{acac})(\text{OH}_2)\text{Ni}_2(\text{acac})_4\text{Tl}(\text{dmae})_2]$ **(2)** for their possible applications in the preparation of composite ceramic materials.

Results and Discussion

Synthesis:

Coordination complexes $[\text{Ni}(\text{acac})_2\text{Tl}(\text{dmae})]_2$ **(1)** and $\text{Ba}(\text{acac})(\text{OH}_2)\text{Ni}_2(\text{acac})_4\text{Tl}(\text{dmae})_2$, **(2)**, were prepared in 70% and 75% yield respectively, by simple mixing of stoichiometric quantities of reactants as shown in equation 1 and 2, respectively.



The use of dmae with its terminal tertiary amino function reduces the risk of oligomerization via multiple oxo or hydroxy bridges and thus is able to stabilize relatively low weight multinuclear molecular compounds that can be isolated and purified.^[8,9] Both of these complexes are paramagnetic, stable under normal conditions, soluble in common hydrocarbon solvents and thus are potential

candidates for the formation of composite ceramic materials in an open atmosphere.^[10,11]

The ORTEP drawings of the complexes are shown in Figure 1 and the crystal data and refinement parameters are tabulated in Table 1. The structure of **(1)**, $[\text{NiTl}(\text{acac})_2(\text{dmae})]_2$, can be considered as a composite of two $[\text{Ni}(\text{acac})_2(\text{dmae})]^-$ anions with two Tl^+ cations while that of **(2)**, $[\text{Ba}(\text{acac})(\text{OH}_2)\text{Ni}_2(\text{acac})_4\text{Tl}(\text{dmae})_2]$, as a combination of also two $[\text{Ni}(\text{acac})_2(\text{dmae})]^-$ anions, but not with two but one Tl^+ cation and instead, one additional $\text{Ba}(\text{acac})(\text{OH}_2)^+$ cation. In **(1)** the octahedral $[\text{Ni}(\text{acac})_2(\text{dmae})]^-$ anion acts as monodentate ligand towards both Tl-atoms via a μ_2 -oxygen atom of its dmae ligand (Figure 1). In complex **(2)**, the Tl^+ is also coordinated by two dmae O-atoms from the two $[\text{Ni}(\text{acac})_2(\text{dmae})]^-$ anions. Towards the $\text{Ba}(\text{acac})(\text{OH}_2)^+$ unit, the complex nickel anions act as a tridentate ligand *via* two μ_2 -O atoms (one from each acac ligand) and the dmae μ_3 -O that also coordinates to the Tl-atom as shown in Figure 1.

The overall geometry of the $[\text{Ni}(\text{acac})(\text{dmae})]^-$ moiety remains comparable to that of the neutral $\text{Ni}(\text{acac})_2(\text{dmaeH})$ ^[12] molecule with only small variations in bond distances and angles around the central Ni-atom. A comparison of data of both the complexes shows that the nickel to donor atom (N, O) bond lengths of the chelated N,N-dimethylaminoethanolato anion slightly decrease in all the $\text{Ni}(\text{acac})_2(\text{dmae})^-$ subunits compared with that in the neutral complex. The Ni-N distances [2.129(2), 2.116(2), 2.141(2)Å] in the complex are less than in $\text{Ni}(\text{acac})_2(\text{dmaeH})$ (2.169Å)^[12] and [cis-

$\text{NiCl}_2(\text{HOCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2$]¹³ (2.142(9), 2.148(9)Å) which incorporate neutral aminoalcohol ligands. The Ni–O(dmae) bond lengths [2.058(19), 2.0495(17), 2.0576(17)Å] in both cases are comparable to the average Ni–O(acac) bond lengths but less than in $\text{Ni}(\text{acac})_2(\text{dmaeH})$ [2.111Å] and in the adduct [*cis*- $\text{NiCl}_2(\text{HOCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2$] [Ni–O: 2.171(7), 2.147(8)Å].

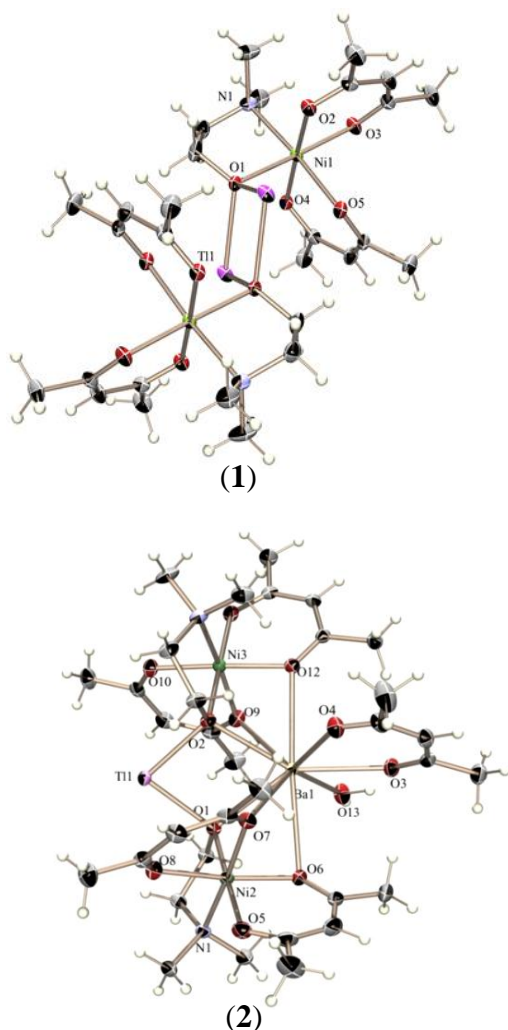


Figure 1: ORTEP drawing of complex (1), $[\text{Ni}(\text{acac})_2\text{Tl}(\text{dmaeH})_2]_2$ and complex (2) $\text{Ba}(\text{acac})(\text{OH}_2)\text{Ni}_2(\text{acac})_4\text{Tl}(\text{dmae})_2$. Ellipsoids are drawn at the 50% probability level.

The coordination environment around the nickel ion is octahedral, with a *cis, cis, cis*-orientation of the three ligands.

The donor nitrogen atoms orient themselves *trans* to the μ_2 -O of each bidentate acac ligand in complex (2). The Ni–O(acac) bond lengths lie in the range 2.014(18)–2.053(17)Å

Table 1: Crystal data and structure refinement parameters for complexes (1) and (2)

Empirical formula	$\text{C}_{28}\text{H}_{48}\text{N}_2\text{Ni}_2\text{O}_{10}\text{Tl}_2$	$\text{C}_{33}\text{H}_{57}\text{N}_2\text{Ba}_1\text{Ni}_2\text{O}_{13}\text{Tl}_1$
Formula weight	1098.84	1148.94
Solvent	Toluene	Toluene
Crystal habit, color	Block, blue	Block, green
Temperature	100(2) K	100(2) K
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	$a = 9.0965(9)\text{Å}$, $b = 20.133(2)\text{Å}$, $c = 10.568(1)\text{Å}$, $\beta = 110.023(2)^\circ$	$a = 11.7960(6)\text{Å}$, $b = 13.8395(7)\text{Å}$, $c = 27.4032(13)\text{Å}$, $\beta = 100.499(1)^\circ$
Volume	$1818.3(3)\text{Å}^3$	$4398.7(4)\text{Å}^3$
Z	2	4
Density (calculated)	2.007 mg/m^3	1.735 mg/m^3
Absorption coefficient	9.905 mm^{-1}	5.435 mm^{-1}
$F(000)$	1056	2264
θ range for data collection	2.02 to 30.56°	1.65 to 28.28°
Reflections collected	21283	38305
Independent reflections	5538	10818
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.070 and 0.041	0.17 and 0.1210
Data / restraints / parameters	5538 / 0 / 205	10818 / 2 / 489
Goodness-of-fit on F^2	1.065	1.054
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0233$, $wR2 = 0.0579$	$R1 = 0.0228$, $wR2 = 0.0564$
R indices (all data)	$R1 = 0.0256$, $wR2 = 0.0579$	$R1 = 0.0281$, $wR2 = 0.0694$
Largest diff. peak and hole	2.529 and $-1.129\text{ e} \times \text{Å}^{-3}$	0.726 and $-0.386\text{ e} \times \text{Å}^{-3}$
Crystal size (mm)	$0.38 \times 0.33 \times 0.27$	$0.50 \times 0.33 \times 0.33$
θ range for data collection	2.02 to 30.56°	1.65 to 28.28°
Index ranges	$-12 \leq h \leq 12$ $-28 \leq k \leq 28$ $-15 \leq l \leq 15$	$-15 \leq h \leq 15$ $-18 \leq k \leq 17$ $-36 \leq l \leq 36$

and are identical to the average value of 2.015Å found in $[\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2]$ ¹⁴ and $\text{Ni}(\text{acac})_2\text{dmaeH}$ (2.013(4)–2.2045(3)Å). The Ni–O(acac) bond lengths are slightly longer than the Ni–O bond lengths of the terminal acac

ligands in $[\text{Ni}(\text{acac})_2]_3$ [1.93(3)–2.00(3)Å]^[15] and in $[\text{Ni}(\text{acac})_2(\text{py})]_2$ (1.968(17), 2.008(14)Å)^[16] but are close to the Ni–O bond lengths of the terminal acac group in $[\text{Ni}(\text{acac})_2(\text{pip})]_2$ (2.050(10), 2.033(10)Å).^[15] It has previously been observed^[17] that the mean Ni–O(acac) bond length in the octahedral Ni–acetylacetonate complexes $[\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{acac})_2]_3$ (2.01(7) and 2.015(1)Å) are significantly longer than the Ni–O bonds in the tetrahedral complex $[\text{Ni}(\text{thd})_2]$ (thd=2,2,6,6-tetramethylheptane-3,5-dionate) (1.836(5)Å)^[15] and the present work confirms this trend. In complex (1), the bite angles of the acac ligands are close to 90° [O(2)—Ni(1)—O(3) = 90.97(7)° and O(4)—Ni(1)—O(5) = 89.13(7)°] which is a usual feature of such complexes. The O—Ni—N, bite angle of the dmae ligand is significantly less [84.56(8)°] than that of acac due to the five membered ring strain, but it is still more than the bite angles of the dmaeH ligands in $[\text{cis-NiCl}_2(\text{HOCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ [80.1(3)° and 78.5(3)°] and comparable to that in $[\text{Ni}(\text{acac})_2\text{dmaeH}]$ [(83.31(14)°)].

Table 2: Selected bond distances and angles for complex (1)

Bond Distances (Å)			
O(1)—Tl(1)#1	2.4385(18)	Ni(1)—O(4)	2.0368(18)
O(1)—Tl(1)	2.4834(18)	Ni(1)—O(5)	2.0517(18)
Ni(1)—O(3)	2.0138(18)	Ni(1)—O(1)	2.0579(19)
Ni(1)—O(2)	2.0319(17)	N(1)—Ni(1)	2.129(2)
Bond Angles (°)			
Tl(1)#1—O(1)—Tl(1)	102.70(6)	O(3)—Ni(1)—O(2)	90.97(7)
Ni(1)—O(1)—Tl(1)	107.98(7)	O(4)—Ni(1)—O(5)	89.13(7)
Ni(1)—O(1)—Tl(1)#1	99.71(7)	O(5)—Ni(1)—O(1)	91.41(7)
O(1)—Ni(1)—N(1)	84.56(8)		

Symmetry code #1: -x+1, -y+2, -z+2

In complex (2), the axial/equatorial [83.73(7) - 93.50(7)°] and some axial/axial [173.20(7), 174.51(7)°] O–Ni–O bond angles show significant deviations from 90° and 180° respectively while the other set of axial/axial O–Ni–O angles

[179.52(7), 178.44(8)°] are close to 180° in both $[\text{Ni}(\text{acac})_2(\text{dmae})]^-$ anionic units. The axial/axial O–Ni–N bond angles 170.28(8)° and 176.28(8)° in complex (2) are less than 180° but still larger than in $\text{Ni}(\text{acac})_2\text{dmaeH}$ 169.9(13)° (Table 3). The O–Ni–N, bite angles of the dmae ligand [83.73(7)°, 85.90(7)°] are significantly smaller and are comparable to the bite angles of the dmaeH ligands in $[\text{cis-NiCl}_2(\text{HOCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ [80.1(3)° and 78.5(3)°] and $[\text{Ni}(\text{acac})_2\text{dmaeH}]$ [(83.31(14)°)].

Table 3: Selected geometric parameters of complex (2)

Bond Distances (Å)			
Ba(1)—O(4)	2.6787(19)	N(1)—Ni(2)	2.116(2)
Ba(1)—O(2)	2.6998(17)	N(2)—Ni(1)	2.141(2)
Ba(1)—O(3)	2.7106(18)	Ni(1)—O(10)	2.0203(18)
Ba(1)—O(1)	2.7539(16)	Ni(1)—O(9)	2.0307(18)
Ba(1)—O(13)	2.8041(19)	Ni(1)—O(12)	2.0350(17)
Ba(1)—O(7)	2.8217(17)	Ni(1)—O(2)	2.0495(17)
Ba(1)—O(12)	2.8348(17)	Ni(1)—O(11)	2.0495(18)
Ba(1)—O(9)	2.9065(17)	Ni(2)—O(5)	2.0182(18)
Ba(1)—O(6)	2.9442(17)	Ni(2)—O(6)	2.0423(18)
Ba(1)—Tl(1)	4.0195(2)	Ni(2)—O(8)	2.0512(18)
O(1)—Tl(1)	2.4105(17)	Ni(2)—O(7)	2.0528(17)
O(2)—Tl(1)	2.4269(17)	Ni(2)—O(1)	2.0576(17)
Bond Angles (°)			
Ni(2)—O(1)—Ba(1)	92.72(6)	Ni(2)—O(6)—Ba(1)	87.70(6)
Tl(1)—O(1)—Ba(1)	102.01(6)	Ni(2)—O(7)—Ba(1)	90.89(6)
Ni(1)—O(2)—Tl(1)	113.32(7)	Ni(1)—O(9)—Ba(1)	89.60(6)
Ni(1)—O(2)—Ba(1)	95.19(6)	Ni(1)—O(12)—Ba(1)	91.55(6)
Tl(1)—O(2)—Ba(1)	103.13(6)	O(1)—Tl(1)—Ba(1)	42.08(4)
Ni(2)—O(1)—Tl(1)	107.93(7)	O(2)—Tl(1)—Ba(1)	40.85(4)

Thallium (I) coordination is based on a quite different type of metal–ligand interaction: Owing to the relativistically contracted valence shell and the low electrical charge, the Tl^+ cation is intermediate in character between standard hard and soft cations and has an affinity for both hard and soft donor atoms, such as oxygen and sulfur, or chloride and iodide.^[18] The thallium ions in (1) and (2) have attained their usual behaviour by coordinating with only two oxygen atoms and they have the expected angular geometry^[19,20] with O—Tl—O angles of 77.30(7)° in (1) and 82.89(5)° in

(2), which are both larger than previously reported values [48.97(11)°, 74.73(13)°] of wedge-like angles.^[19] This angular geometry of Tl as seen in compound (1) and (2) results from the presence of stereochemically active lone pair and is often found in Tl-complexes.^[19,20]

The Tl-O bond distances in (1) and (2) are identical and found to be 2.438(18) and 2.483(18) Å and 2.411(2) and 2.427(2) Å respectively. The oxygen atom of the aminoalcohols is bridging in a μ_2 fashion in (1) and μ_3 in (2) due to additional coordination towards the barium ion. In this way the oxygen and metal (Tl/Tl or Tl/Ba) atoms in both (1) and (2) occupy the vertices of a square plane M_2O_2 oxo-metal core (Figure 2).

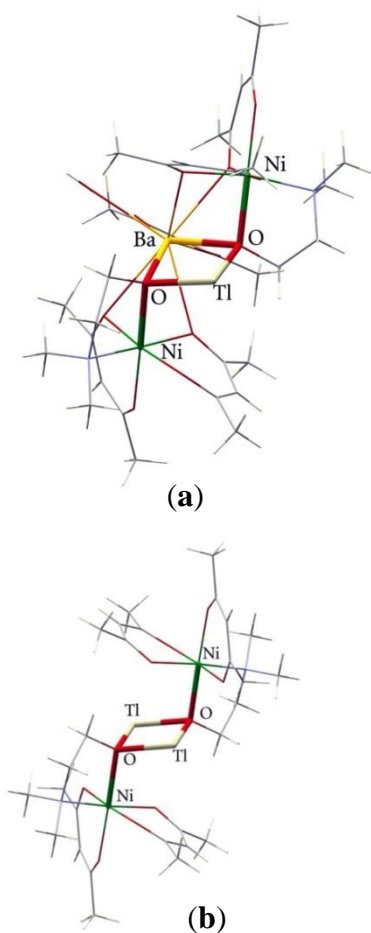


Figure 2: Depictions of complexes (1) and (2) showing the highlighted structural similarities between the core templates.

The coordination environment of the barium ion in (2) is multifaceted and less regular. Two equivalent $[\text{Ni}(\text{acac})_2\text{dmae}]^-$ units contribute one μ_2 -oxygen each from both acac ligands and one μ_3 -oxygen from the alcoholate in coordinating Ba-atom. The large coordination sphere of Ba is further satisfied by a bidentate acac ligand and a coordinated water molecule, thus giving the barium cation a coordination number of nine with a BaO_9 ligation set (Figure 3c).

The Ba-O(acac) bond lengths of independently coordinated acac group of complex (2) [$\text{Ba}(1)\text{-O}(4) = 2.6787(19)$, $\text{Ba}(1)\text{-O}(3) = 2.7106(18)$ Å] are similar to the average value of 2.690 Å in $\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})$.^[21] The Ba-O bonds involving the four μ_2 -O [O6, O7, O9, O12] of the bridging acac moieties [2.8217(17), 2.8348(17), 2.9065(17), 2.9442(17) Å], are longer and weaker but still comparable to the similar bridging lengths [2.770(2), 2.917(2) Å] in $\text{Ba}_2\text{Co}(\text{acac})_4(\text{dmae})_3(\text{dmaeH})$.

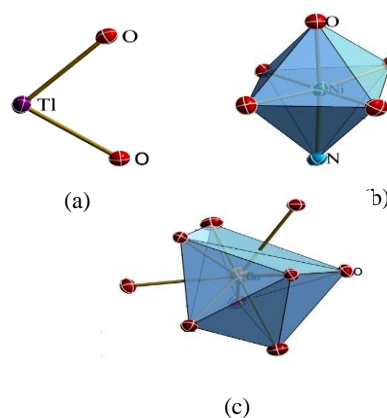


Figure 3: General patterns of coordination spheres of (a) Tl (angular), (b) Ni1, Ni2 (octahedral) and (c) Ba (irregular) in complexes (1) and (2).

Both dmae ligands behave in a similar manner, chelating Ni (through O, N) with further bridging to both Ba and Tl via a μ_3 -O atom. In this way single O-atom is involved in simultaneous bridging to three different metals. The remaining four acac groups are bidentate with respect to nickel but have an additional bridging bond to barium through one of the two oxygen centers. The “bite” angles [87.43(7) - 90.95(8)°] of these four acac groups are close to 90°, but are slightly smaller than the average bite angle of 92.4° in [Ni(acac)₂(H₂O)₂]; the fifth acac, coordinated to Ba, has a much reduced bite angle [64.88(5)°] due to the high coordination number of barium, but it compares well with those observed in Ba₂Co(acac)₄(dmae)₃(dmaeH) (CN = 8) [64.17(8) - 66.45(7)°].

Thermal behaviour:

The thermogram of complex (1) (Fig.4), shows at least three steps of weight loss. The first step that occurs in the temperature range of 100-194°C where only 9% of the complex is degraded while in second step a weight loss of 21% is indicated by a sharp dip from 197°C to 243°C. Finally, the third weight loss step starts at 243°C and is completed at 298°C producing a stable residual mass of 53.5% against 55.2% as expected for the formation of {Tl₂O₃ + 2NiO} from the complex (1). Complex (2) undergoes a weight loss of approximately 4.7% at 102°C-

167°C, while a major weight loss occurs at the temperature range of 167-301°C. At 301°C, a stable residual mass of approximately 45.3% is obtained which is in good agreement with theoretical value of 46.22% for the composite of composition 2NiO, 1/2Tl₂O₃ and BaO.

Bulk oxide composite materials were obtained by the thermal decomposition of complexes (1) and (2) at 400°C for four hours at a heating rate of 1°C/min in a ceramic crucible placed inside a temperature programmed tube furnace. The powder obtained from complex (1) was analysed using SEM/EDX and X-ray powder diffraction, while the powder obtained from complex (2) was subjected to SEM, EDS, XPS, AES and XRD analysis.

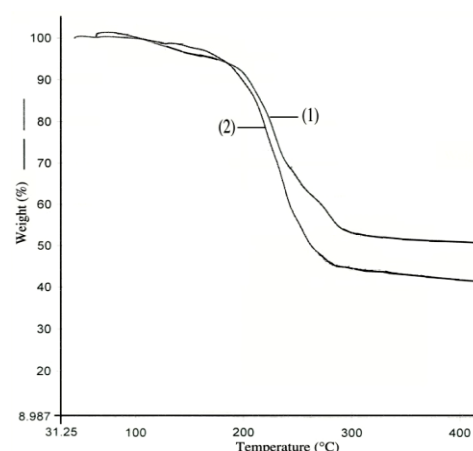
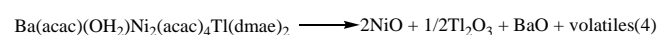


Figure 4: Thermogravimetric curves showing loss in weight with increase in temperature for complex (1) and (2) under an atmosphere of flowing nitrogen gas (25ml/min.) at a heating rate of 10°C/min.



The XRD powder patterns of the decomposed product

from (1) matches well with a mixture of oxide species, Tl_2O_3 in the form of avicennite^[22] and NiO.^[23] The metallic composition obtained by EDX analysis shows the elemental ratio of Ni : Tl as 1: 0.97, close to their proportion in the precursor complex suggesting that the quantitative decomposition leads to the NiO/ Tl_2O_3 composite.

The powder X-ray diffraction pattern of composite material obtained from the pyrolysis of complex (2) shows the presence of three phases NiO, Tl_2O_3 and $BaCO_3$, that are matched with the standard ICDD cards (Nickel Oxide, 44-1159), (Avicennite, 33-1404) and (Witherite, 45-1471) respectively. (Pl. See supporting informations)

The presence of different phases, elemental ratio and their distribution in the residue from complex (2) was studied by using XRPD and SEM/EDS analysis. The data of point by point EDS analysis collected show the presence of Ba, Tl, Ni and oxygen at different locations. XRPD indicates the presence of NiO and Tl_2O_3 phases while barium oxide being unstable in open atmospheric conditions has been converted to barium carbonate due to absorption of atmospheric carbon dioxide. The presence of $BaCO_3$ in the residue has been further characterised by FT-IR and Auger electron spectroscopy. FT-IR studies show absorptions at 693, 856 and 1462 cm^{-1} due to in-plane and out-plane CO_3^{2-} bending and asymmetric C-O stretching vibrations respectively as reported earlier.^[24] AES data at etching level of 10, 50 and 100 nm show the presence of carbon, oxygen, nickel, barium and thallium with slight variation in atomic concentrations. The average atomic concentration in bulk

powder sample was found to be C_{1s} 23.85, O_{1s} 51.06, N_{2p} 16.82, Ba_{3d} 5.64 and Tl_{4f} 2.65%.

The analytical studies carried out on the residues obtained from thermal decomposition of complexes (1) and (2) at 300°C under inert atmosphere of nitrogen and in an open atmosphere indicate that complex (1) decomposes under both atmospheres to give a composite of composition NiO/ Tl_2O_3 whereas complex (2) decomposes under an inert atmosphere of nitrogen gas to give a composite material of composition NiO/ Tl_2O_3 / BaO and in an open atmosphere to yield a composite of composition NiO/ Tl_2O_3 / $BaCO_3$.

Conclusions

The molecular complexes $[NiTl(acac)_2(dmae)]_2$, (1) and $[Ba(acac)(OH_2)Ni_2(acac)_4Tl(dmae)_2]$ (2), are synthesized in a 'one step' reaction of the appropriate reagents in N,N-dimethylaminoalcohol that not only acts as a bridging ligand but also oxidizes barium metal as found in (2). The characterization of both the complexes by m.p., elemental analysis, FT-IR and single crystal X-ray analysis confirms the formation of heterobi- and heterotrimetallic molecular species. Single crystal X-ray structural analysis of the complexes shows angular coordination geometry around thallium and an octahedral geometry around nickel. The insertion of barium in the prefabricated heterobimetallic complex provides an excellent route to the synthesis of extended architecture of heterotrimetallic complex in a direct reaction. Thermogravimetric analyses of the complexes prove them to be easily decomposable species at 300°C in an open atmosphere to yield composite materials

of composition NiO/Tl₂O₃ from complex (1) and NiO/Tl₂O₃/BaCO₃ from complex (2) respectively.

Experimental Section

All syntheses were carried out in a controlled atmosphere of argon gas using standard Schlenk tube and glove box techniques. Analytical grade toluene was purchased from FRIENDEMANN SCHMIDT and freshly dried and redistilled over sodium/benzophenone before use.

N,N-dimethylaminoethanol was purchased from Merck and dried over anhydrous sodium carbonate. Ni(II)acetylacetonate, Tl(I) acetylacetonate and Ba(0) metal were the products of Fluka chemicals and used as such. Melting points were recorded on a Mitamura Riken Kogyo (MT-D) apparatus and are reported as such. Elemental analysis was performed using CHN Analyzer LECO model CHNS-932. Fourier transform IR (FT-IR) spectra were recorded as KBr disks with Spectrum-1000 spectrometer from Perkin-Elmer. Magnetic measurements were made using a commercial model BHV-50 vibrating sample magnetometer, Perkin Denshi Co. (Ltd.), Japan.

Single crystal diffraction data of complex (1) and (2) were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo-K α radiation with omega scan technique. The unit cells were determined using SAINT+^[25] and the data were corrected for absorption using SADABS in SAINT+.^[25] The structures were solved by direct methods and refined by full matrix least squares against F² with all reflections using SHELXTL.^[25,26] Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were

refined anisotropically. Water hydrogen atoms in complex (2) were localized in the difference density Fourier map and have been restraint to have an O-H bond length of 0.9Å within a standard deviation of 0.02. All other hydrogen atoms were placed in calculated positions. All hydrogen atoms were refined with an isotropic displacement parameter 1.5 times (methyl, water) or 1.2 times (all others) that of the adjacent carbon or oxygen atom.

Controlled thermal analyses of the complexes were investigated using a Perkin Elmer Thermogravimetric Analyzer TGA-7 with computer interface. The measurements were carried out in an alumina crucible under an atmosphere of flowing nitrogen gas (25ml/min.), using a heating rate of 10°C/min.

Metallic elemental ratios for the ceramic residue from complex (1) were measured on an Inca-200 EDX analyzer from Oxford Instruments, U.K. The SEM/EDS analysis of the residue from (2) was performed by scanning electron microscope marketed by TOPCON (ISI DS-130), Inc. of Paramus, NJ. EDS data in the form of spectra and elemental distribution maps were collected from the sample using a Si(Li) crystal detector manufactured by Gresham Scientific Instruments Ltd. of Buckinghamshire, UK, coupled to a multichannel analyzer interface manufactured by 4pi Analysis, Inc., that is resident in an Apple Macintosh® G4 workstation. The data were quantified using Revolution® software from 4pi Analysis, Inc., and the results are tabulated along with identifiers for each sample area evaluated.

The XPS spectra of the bulk surface were obtained by XPS surface analysis system Model DS800 manufactured by Kratos Analytical Plc of Manchester, UK. The XPS spectra were collected using a magnesium K α X-ray source, 80eV pass energy and 0.75eV steps for each sample survey spectrum. The obtained spectra were plotted and used to generate estimates of the atomic and weight concentrations of the elements indicated by the peaks present in the spectral data. High-resolution spectra were collected for the major elements detected to study their chemical bonding structures. These were obtained at pass energy of 40eV and in 0.1eV steps. The high-resolution data were then peak fitted, plotted and tabulated to illustrate the chemical species present for each major element detected.

The AES spectra were obtained at the surface and etched at 10nm, 50nm, and 100nm using a Model 660 scanning Auger surface analysis system manufactured by Physical Electronics USA of Chanhassen, MN. FT-IR data of the residues were collected using a Specac diamond reflectance cell and a Mattson 5000 series spectrophotometer. Powder X-ray diffraction patterns were collected at room temperature using a PAN analytical, X'Pert PRO diffractometer with Cu-K α radiation for complex (1) and a Bruker D8 Advance diffractometer with Cu-K α radiation for complex (2) in reflective mode and open sample cups. The data were analyzed and fitted to the database patterns using the EVA Application 7.001 software of SOCABIM (1996-2001), distributed by Bruker AXS, Madison, WI.

Syntheses:

[TlNi(acac)₂dmae]₂

A suspended solution on mixing of Ni(acac)₂ (0.257g, 1.0mmol) and Tl(acac) (0.303g, 1.0mmol) in dry warm toluene (20ml) was obtained at 60°C. N,N-dimethylaminoethanol (0.089g, 1.0mmol) was injected drop-wise by syringe to the stirring suspension through a rubber septum. Reactants were stirred at 60°C for two hours. The light bluish green solution was filtered and concentrated in vacuum to give blue colored crystals after fifteen days. m.p.: 138°C. Analysis: Calc. for C₂₈H₄₈N₂Ni₂O₁₀Tl₂; Mw, 1098.84; C, 30.6; H, 4.4; N, 2.5; Found C, 30.6; H, 4.9; N, 2.6%. FT-IR/cm⁻¹ 2959(m), 2922(s), 2854(m), 1948(w), 1592(s), 1515(s), 1395(br), 1257(s), 1154(m), 1093(s), 1038(s), 916(m), 902(s), 889(w), 781(w), 761(s), 657(m), 571(s), 410(s), 382(m), 290(w), 258(w). TGA: 100-94°C (9%), 197-243°C (21%), 243-298°C (18%); residue of 53.49%.

[Ba(acac)(OH)₂Ni₂(acac)₄Tl(dmae)₂]

A suspended solution on mixing of Ni(acac)₂ (0.514g, 2.0 mmol), Tl(acac) (0.303g, 1.0 mmol) and pieces of Ba metal (0.137g, 1.0 mmol) was obtained in dry toluene (20ml). DmaeH (0.178g, 2.0 mmol) was added to the above stirred suspension through an injection needle. After stirring for seven hours at 60°C, light green colored solution was filtered via cannula to remove traces of undissolved solid and the resulting solution was concentrated to 10 ml. After one month, green colored crystals suitable for X-ray analysis were obtained. yield (75%) based on Tl(acac). m.p; 124°C. Analysis: Calc. for C₃₃H₅₇N₂Ba₁Ni₂O₁₃Tl₁; Mw 1148.94; C, 34.4; H, 4.9; N, 2.4; Found: C, 33.7; H, 4.3; N, 2.3; FT-IR/cm⁻¹, 3478(m), 3070(m), 2970(m), 2914(m), 2858(m),

2831(s), 2689(w), 2450(w), 2132(w), 1950(w), 1587(br, s),
1518(br, s), 1387(br, s), 1257(s), 1194(m), 1073(s), 1018(s),
954(m), 922(s), 884(w), 787(w), 763(s), 655(m), 564(s),
414(s), 362(m), 299(w), 268(w). TGA: 102 - 167°C (4.7%).
167- 301°C (50.0%); residual mass of 45.3%.

Supporting Information (see footnote on the first page of
this article): [CIFs for complex (1) and (2)], CCDC number
for complex (1) is 296013 and for complex (2) is CCDC
296010.

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