Synthesis and spectroscopic characterisation of a new class of heterobimetallic homoleptic diethanolaminate complexes of niobium(V) and tantalum(V)[†]

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Nine heterobimetallic homoleptic diethanolaminate complexes of the types: $[Nb(Rdea)_3\{Ta(Rdea)_2\}]$ (where Rdea $= RN(CH_2CH_2O^-)_2$ and R = H, **2**; Me, **3**; Bu^n, **4**; Ph, **5**), $[Nb(Rdea)_3\{Al(Rdea)\}]$ (R = H, **6**; Me, **7**; Bu^n, **8**; Ph, **9**), and $[Nb(Phdea)_3\{Sb(Phdea)\}]$ **10** have been prepared for the first time by the equimolar reactions of $[Nb(Rdea)_2(RdeaH)]$ with $[Ta(Rdea)_2(OPr^i)]$ or $[Al(Rdea)(OPr^i)]$ or $[Sb(Phdea)(OPr^i)]$ in benzene. The structural features of the new complexes have been elucidated by IR and NMR (^1H, ^{27}Al) spectroscopies.

Keywords: heterobimetallic complexes, homoleptic diethanolaminates, niobium(V) complexes, *N*-substituted diethanolaminates.

The homometallic diethanolaminate derivatives of niobium(V) and tantalum(V) were reported as early as 1967.[1,2] Surprisingly, heterobimetallic diethanolaminate complexes of niobium(V)/ tantalum(V) appear to have not been investigated so far.[3] The reactivity of metal alkoxides are in general modified[4,5] by chelating ligands,[5-8] so that the resulting complexes are more suited as precursors for the preparation of oxide ceramic materials via a sol-gel process.[9,10] Recently, we have developed a novel route for the synthesis of heterobimetallic alkoxide coordination complexes[11] utilising the higher reactivity of the hydroxy functionality in homometallic complexes derived from polyols such as glycols, di- and triethanolamines.[11] This strategy has been successful in the synthesis of novel heterobimetallic glycolate-,[12,16] diethanolaminate-[17-20] and triethanolaminate-[13,21,22] isopropoxide complexes. Due to the presence of isopropoxy groups, these types of complexes show a strong propensity for hydrolysis[3,11] even in the presence of only traces of moisture. In an attempt to prepare less moisture-sensitive heterobimetallic complexes of chelating ligands, we report in here for the first time the synthesis and characterisation of heterobimetallic homoleptic diethanolaminate complexes of niobium and tantalum.

Results and discussion

Homometallic precursor complexes of the type, $[Nb(Rdea)_2(RdeaH)]$ (R = H, **1a**; Me, **1b**; Bu^n, **1c**; Ph, **1d**) incorporating seven-coordinate niobium(V) have been prepared by the literature methods.[23]

Bis-(diethanolaminate)-isopropoxide complexes of tantalum(V), $[Ta(Rdea)_2(OPr^i)]$ (R = H, **1e**; Me, **1b**; Bu^n, **1g**; Ph, **1h**) have been synthesised by 1: 2 molar reactions of $[Ta(OPr^i)_5]$ with different diethanolamines, (Eqn (1)).
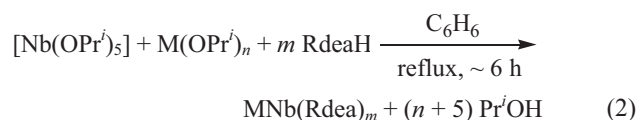
$$[Ta(OPr^i)_5] + 2\ RdeaH_2 \xrightarrow[\text{reflux}]{C_6H_6} \text{(I)} + 4\ Pr^iOH\uparrow \quad (1)$$

(I)
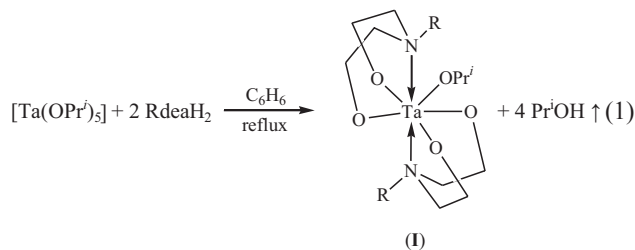
R = H, **1e**; Me, **1f**; Bu^n, **1g**; Ph, **1h**

Homometallic aluminium complexes, $[Al(Rdea)(OPr^i)]$ (R = H, **1i**; Me, **1j**; Bu^n, **1k**; Ph, **1l**) have been synthesised by the method reported in the literature.[24]

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Novel heterobimetallic coordination compounds incorporating Nb/Ta (**2–5**), Nb/Al (**6–9**), and Nb/Sb (**10**) derived from bifunctional tridentate (ONO) aminoalkoxide ligands, $RN(CH_2CH_2O)_2$ (where R = H, Me, Bu^n, and Ph) have been conveniently prepared in quantitative yields by the reactions illustrated in Scheme 1. The structures (**II**), (**III**), and (**IV**) shown in Scheme 1 are each a suggested one out of the many other possible structures for seven-coordinated complexes. The IR data on these compounds are not sufficient to pin-point the precise stereochemistry. It is worthwhile to mention that three important geometries are possible for seven-coordinate complexes: (a) pentagonal bipyramidal (D_{5h}), (b) capped octahedron (C_{3v}), and (c) capped trigonal prism (C_{2v}). These three structures are of similar stability and interconversions are not likely to seriously hindered, so that these complexes should be prone to fluxionality. In each of these geometries for complexes of the type NbN_2O_5, different arrangements for the ligation of two nitrogen atoms, particularly in the both halves of (**II**) and one half of (**III**) and (**IV**) are possible making selection of a precise structure on the basis of the limited IR data more difficult. However, this could be solved in the solid state by X-ray crystallographic data, but unfortunately our attempts in this direction have not been successful so far. Therefore, the structures (**II**), (**III**), and (**IV**) shown in Scheme 1 are the one chosen out of many other possibilities. Even for a pentagonal bipyramid structure the two nitrogen atoms may occupy: (i) the two axial sites (as shown in Scheme 1); (ii) one axial and one equatorial position; and (iii) the two equatorial sites.

The complexes (**5**), (**7**), and (**10**) have also been prepared by the *in situ* reactions of component metal isopropoxides and *N*-substituted diethanolamines in desired molar ratios (Eqn (2)):

$$[Nb(OPr^i)_5] + M(OPr^i)_n + m\ RdeaH \xrightarrow[\text{reflux, ~ 6 h}]{C_6H_6}$$

$$MNb(Rdea)_m + (n + 5)\ Pr^iOH \quad (2)$$

M = Ta (R = Ph, n = 5, m = 5) **5**,

Al (R = Me, n = 3, m = 4) **7**,

Sb (R = Ph, n = 3, m = 4) **10**

These heterobimetallic complexes (**2–10**) are yellow or white solids (Table 1), soluble in typical organic solvents, (*e.g.*, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran), and are monomeric in benzene solution. Molecular weights of (**2**) and (**6**) by the cryoscopic method could not be determined as these are only soluble in dichloromethane and chloroform.
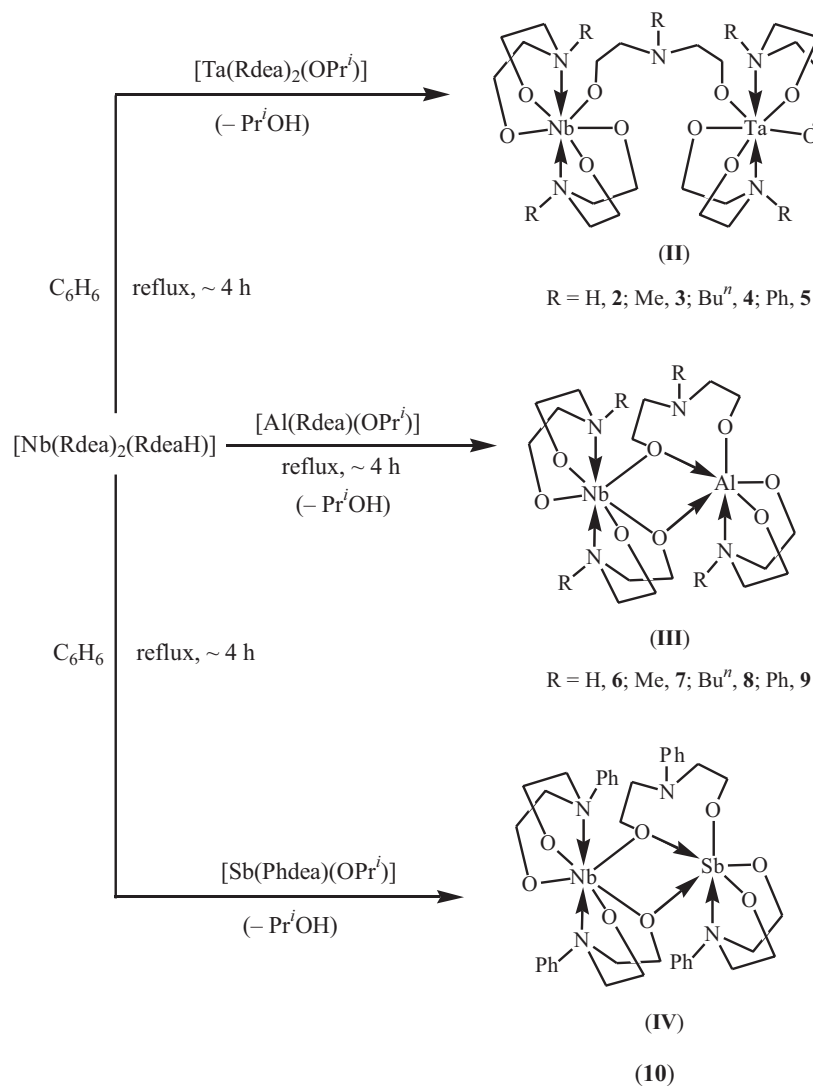
Scheme 1

Table 1 Preparative and analytical data for heterobimetallic complexes (**2–10**)

Reactants (g, mmol)		Complex Colour and state	Yield g (%)	Liberated Pr^{i}OH (g) Found (Calcd.)	Analysis (%) Found (Calcd.)					M.wt. Found (Calcd.)
					Nb	M	C	H	N	
(**1a**) (2.01, 4.98)	(**1e**) (2.22, 4.97)	Nb(Hdea)$_3${Ta(Hdea$_2$}(**2**) Colourless solid	2.76 (70)	0.27 (0.30)	34.50 (34.69)		30.12 (30.42)	5.61 (5.74)	8.70 (8.87)	– (789)
(**1b**) (1.64, 3.68)	(**1f**) (1.75, 3.69)	Nb(Medea)$_3${Ta(Medea)$_2$}(**3**) Colourless solid	2.62 (83)	0.21 (0.22)	31.72 (31.86)		34.85 (34.93)	6.49 (6.45)	8.01 (8.14)	861 (859)
(**1c**) (0.97, 1.69)	(**1g**) (0.95, 1.70)	Nb(Budea)$_3${Ta(Budea)$_2$} (**4**) Colourless stictysolid	1.69 (93)	0.09 (0.10)	25.30 (25.59)		44.79 (44.90)	7.87 (8.01)	6.31 (6.54)	1025 (1070)
(**1d**) (1.40, 2.22)	(**1h**) (1.33, 2.22)	Nb(Phdea)$_3${Ta(Phdea)$_2$} (**5**) Yellow solid	2.01 (77)	0.13 (0.13)	23.29 (23.40)		51.25 (51.32)	5.61 (5.60)	5.87 (5.98)	1182 (1170)
(**1a**) (1.86, 4.61)	(**1i**) (0.87, 4.60)	Nb(Hdea)$_3${Al(Hdea)} (**6**) White semisolid	1.69 (69)	0.27 (0.28)	17.32 (17.45)	4.91 (5.07)	36.89 (36.09)	6.77 (6.82)	10.39 (10.52)	– (532)
(**1b**) (1.72, 3.86)	(**1j**) (0.78, 3.84)	Nb(Medea)$_3${Al(Medea)} (**7**) White semisolid	1.76 (77)	0.21 (0.23)	15.62 (15.79)	4.50 (4.59)	40.82 (40.81)	7.49 (7.54)	9.40 (9.51)	605 (588)
(**1c**) (1.31, 2.29)	(**1e**) (0.56, 2.29)	Nb(Budea)$_3${Al(Budea)} (**8**) Colourless stickysolid	1.44 (83)	0.12 (0.14)	12.09 (12.28)	3.42 (3.57)	50.69 (50.78)	9.00 (9.06)	7.21 (7.40)	743 (756)
(**1d**) (1.64, 2.60)	(**1l**) (0.69, 2.60)	Nb(Phdea)$_3${Al(Phdea)} (**9**) Yellow solid	1.79 (82)	0.15 (0.16)	11.01 (11.10)	3.14 (3.23)	57.23 (57.41)	6.31 (6.26)	6.52 (6.69)	851 (836)
(**1d**) (1.72, 2.72)	(**1m**) (0.98, 2.72)	Nb(Phdea)$_3${Sb(Phdea)} (**10**) Yellow solid	1.78 (70)	1.14 (1.15)	9.80 (9.98)	12.79 (13.07)	51.42 (51.57)	5.68 (5.63)	5.92 (6.01)	904 (931)

IR spectral studies

Homometallic precursor complexes (**1a**–**1d**) exhibit IR absorption bands[23] characteristic of metal-attached diethanolaminate moieties in which at least one amino-nitrogen of the diethanolaminate moieties remains uncoordinated.

Complexes (**1e**–**1h**) show absorptions (Experimental Section) at: (i) 1217 ± 7 cm^{-1} for aliphatic[25] ν(C–N), with a lowering of ~25 cm^{-1} wavenumber in comparison to those found in the parent ligands, which suggests the formation of N→Ta dative bonds, (ii) 1335 cm^{-1} for aromatic[26] ν(C–N) in complex (**1h**), which is also shifted to lower wavenumber (~50 cm^{-1}) due to the same reason, (iii) 1175 ± 5 and 1146 ± 7 cm^{-1} due to metal-attached isopropoxy groups, and (iv) absorptions at 518 ± 4 and 462 ± 7 cm^{-1} due to ν(Ta–O) and ν(Ta←N), respectively.

As expected the heterobimetallic complexes (**2**–**10**) exhibit IR absorption bands (Table 2) characteristic of organic groups attached to the metal atoms. The ν(C–N) stretching vibrations of aliphatic amino group in complexes (**2**–**10**) appear as the two sets of bands in the 1242–1257 and 1192–1210 cm^{-1} regions and follow in general the pattern exhibited by the homometal complexes (**1a**–**1d**). Complexes (**5**), (**9**) and (**10**) also exhibit aromatic[25] ν(C–N) at 1390 ± 2 and 1358 ± 2 cm^{-1}. The above IR spectral data are indicative of the involvement of both the tri-and bi-dentate ligating modes of diethanolaminate moieties (Structures **II**, **III**, and **IV**) in these complexes. Absorptions due to ν(C–O), ν(Nb–O), ν(Nb←N), ν(Ta–O), and ν(Ta←N) appear almost at the same positions as found in the corresponding homometal precursor complexes. Derivatives (**6**–**9**) exhibit bands of variable intensity assignable to ν(Al–O)[17] and ν(Al←N)[17] at 656 ± 5 and 525 ± 10 cm^{-1}, respectively.

NMR spectral studies

The observed ^{1}H NMR spectral data[23] for the precursor complexes [Nb(Rdea)$_2$(RdeaH)] (**1a**–**1d**) suggest that at least one out of three available amino nitrogen atoms of a diethanolaminate group remains uncoordinated. The appearance of only one signal due to N–**R** protons in (**1e**–**1h**), exhibiting a downfield shifting of ~ δ 0.40 ppm with respect to their positions in the parent ligands, supports tridentate ligation of both the diethanolaminate moieties (Structure **I**).

Heterobimetallic complexes (**2**–**10**) show ^{1}H NMR signals (Table 2) characteristic of diethanolaminate moieties bonded to the metal centres. Some useful structural informations obtained by the ^{1}H NMR studies are (i) the appearance of two singlets due to N–**Me** protons at δ 2.34 and 2.68 ppm (1: 4 integrated intensity ratio) in the spectrum of (**3**) indicating that at least one amino group remains uncoordinated (Structure **II**), (ii) complex (**7**) exhibits two singlets for N–**Me** protons at δ 2.36 and 2.66 ppm (1: 3 integrated intensity ratio) arising from bi-and tri-dentate bonding modes of diethanolaminate moieties (Structure **III**), and (iii) the signals due to O**H** and OPr^i group protons are absent in these complexes.

The complexes (**6**–**9**) show ^{27}Al NMR signals (Table 2) in the δ 5.55–8.95 ppm region consistent with the six-coordinate[27] aluminium (Structure **III**).

Experimental

All experiments and manipulations were conducted under moisture-free conditions using oven-dried (150°C) glassware fitted with interchangeable quickfit joints. Analytical (Merck, India) grade solvents were made anhydrous and purified by the literature methods.[28] Diethanolamines (RdeaH$_2$, where R = H, Me, Bu^n, Ph) were dried by refluxing over Al(OPr^i)$_3$ followed by distillation prior to use: HdeaH$_2$(Merck, 130°C/0.4 mm); MeN(CH$_2$CH$_2$OH)$_2$, MedeaH$_2$(Aldrich, 148°C/0.3 mm); BuN(CH$_2$CH$_2$OH)$_2$, BudeaH$_2$(Merck, 120°C/0.2 mm); PhN(CH$_2$CH$_2$OH)$_2$, PhdeaH$_2$ (Aldrich, 158°C/0.2 mm).

[Nb(OPr^i)$_5$],[29] [Ta(OPr^i)$_5$],[30] [Al(OPr^i)$_3$],[31] and [Sb(OPr^i)$_3$][32] were prepared by the literature methods. Homometallic aluminium derivatives [Al(Rdea)(OPr^i)] (R = H, (**1i**); Me, (**1j**); Bu^n, (**1k**); Ph, (**1l**)) were synthesised by the literature method.[24]

Niobium and tantalum were determined gravimetrically[33] as oxides and aluminium as oxinate. Antimony was determined iodometrically.[33] Nitrogen was determined by Kjeldahl's method.[33] Isopropyl alcohol liberated as an azeotrope with benzene was determined by an oxidimetric method.[34]

IR spectra (4000–400 cm^{-1}) were recorded as KBr pellets or Nujol mulls on a Nicolet Magna 550 spectrophotometer. NMR spectra for ^{1}H (300.40 MHz, TMS) and ^{27}Al (78.18 MHz, aqueous solution

Table 2 IR (cm^{-1}) and NMR (δ, ppm) spectral data for heterobimetallic complexes (**2**–**10**)

Complex	IR	^{1}H NMR	^{27}Al NMR
(**2**)	3204 ν(N–H); 1257, 1210 ν(C–N); 1080, 1054 ν(C–O); 562 ν(Nb–O); 531 ν(Ta–O); 470, 452 ν(M↔N) M = Nb/Ta	2.87(m, 4H, NCH$_2$); 3.40(br, 16H, NCH$_2$); 3.76(br, 5H, NH); 4.55(m, 20H, CH$_2$O)	–
(**3**)	1242, 1210, 1195 ν(C–N); 1078, 1031 ν(C–O); 578 ν(Nb–O); 531 ν(Ta–O); 460, 445 ν(M↔N) (M = Nb/Ta)	2.34(s, 3H, NMe); 2.68, 2.70(s, 12H, NMe); 3.11(m, 20H, NCH$_2$); 4.43(m, 20H, CH$_2$O)	–
(**4**)	1249, 1202, 1192 ν(C–N); 1093, 1034, 1020 ν(C–O); 570 ν(Nb–O); 538 ν(Ta–O); 470, 462 (M↔N) (M = Nb/Ta)	0.89(t, 3H, N(CH$_2$)$_3$Me); 0.95(t, J = 6.96 Hz, 12H, N(CH$_2$)$_3$Me); 1.30-1.44(m, 20H, NCH$_2$(CH$_2$)$_2$Me); 2.52(t, 2H, NCH$_2$(CH$_2$)$_2$Me); 2.66(m, 8H, NCH$_2$(CH$_2$)$_2$Me); 3.02-3.60(m, 20H, NCH$_2$); 4.49(m, 20H, CH$_2$O)	–
(**5**)	1390, 1359, 1249, 1202 ν(C–N); 1093, 1031 ν(C–O); 570 ν(Nb–O); 523 ν(Ta–O); 461, 445 (M↔N) (M = Nb/Ta)	3.65(br, 20H, NCH$_2$); 4.25(br, 20H, CH$_2$O); 6.47-7.40(m, 25H, aromatic-H)	–
(**6**)	1240, 1205, 1197 ν(C–N); 1079, 1030, 1021 ν(C–O); 660 ν(Al–O); 570(Nb–O); 520 ν(Al↔N); 456 ν(Nb↔N)	2.76(br, 4H, NCH$_2$); 3.14(br, 12H, NCH$_2$); 3.72(br, 4H, NH); 4.52(m, 16H, CH$_2$O)	8.16
(**7**)	1237, 1214, 1200 ν(C–N); 1080, 1037, 1020 ν(C–O); 660 ν(Al–O); 578 ν(Nb–O); 525 ν(Al↔N); 456 ν(Nb↔N)	2.36(s, 3H, NMe); 2.61, 2.66(s, 9H, NMe), 3.65(m, 16H, NCH$_2$); 4.37(m, 16H, CH$_2$O)	5.55
(**8**)	1241, 1214, 1200 ν(C–N); 1080, 1037, 1020 ν(C–O); 660 ν(Al–O); 578 (Nb–O); 525 ν(Al↔N); 456 ν(Nb↔N)	0.97(m, 9H, N(CH$_2$)$_3$Me); 1.31-1.42(m, 16H, NCH$_2$(CH$_2$)$_2$Me); 2.64(m, 2H, NCH$_2$(CH$_2$)$_2$Me); 2.81(m, 6H, NCH$_2$(CH$_2$)$_2$Me); 3.02(m, 4H, NCH$_2$); 3.65(m, 12H, NCH$_2$); 4.49(m, 16H, CH$_2$O)	6.16
(**9**)	1388, 1359, 1210, 1200 ν(C–N); 1078, 1040 1031 ν(C–O); 651 ν(Al–O); 570 ν(Nb–O); 535 ν(Al–N); 460 ν(Nb↔N)	3.68(m, 16H, NCH$_2$); 4.36(m, 16H, CH$_2$O); 6.46-7.42(m, 20H, aromatic-H)	8.95
(**10**)	1390, 1360, 1351, 1215, 1205 ν(C–N); 1081, 1042, 1020 ν(C–O); 572 ν(Nb–O); 500 ν(Sb–O); 461, 450, ν(M↔N) (M = Nb/Sb)	3.59(m, 16H, NCH$_2$); 4.36(m, 16H, CH$_2$O); 6.73-7.40(m, 20H, aromatic-H)	–

of aluminium nitrate) were recorded in CDCl$_3$ on a JEOL AL300 FTNMR spectrometer. Microelemental (C, H, and N) analyses were performed on Perkin Elmer 2400 CHNS/O analyser. Molecular weights were determined by the freezing point depression method in benzene.

Synthesis of homometallic precussor complexes

For the sake of brevity synthetic details only of a typical complex is given below.

Synthesis of [Ta(Hdea)$_2$(OPr^i)] (1e): The colourless benzene solution (~ 40 ml) obtained after addition of diethanolamine, HdeaH$_2$ (0.94 g, 8.95 mmol) to [Ta(OPr^i)$_5$] (2.14 g, 4.49 mmol) was refluxed with continuous removal of the liberated isopropyl alcohol over a period of ~4 h, during which the required amount (1.08 g) of isopropyl alcohol was distilled out. When the distillate showed negligible presence of an oxidisable species, refluxing was stopped and reaction mixture was allowed to cool to room temperature. Volatile components from the solution were removed under reduced pressure to obtain the colourless viscous compound (1e) (1.98 g, 99%). Recrystallisation from a 1: 3 mixture of dichloromethane and *n*-hexane at –20°C afforded a colourless sticky solid compound (1e). Yield: 1.70 g (85%). Anal. Calcd. For C$_{11}$H$_{25}$N$_2$O$_5$Ta(446): C, 29.6; H, 5.6; N, 6.3; Ta, 40.5%. Found: C, 29.3; H, 5.7; N, 6.2; Ta, 40.3%. M.Wt., 471. IR: 3290 ν(N–H); 1210 ν(C–N); 1178, 1139 ν(OPr^i); 1082, 1047 ν(C–O); 520 ν(Ta–O); 461 ν(Ta←N). ^{1}H NMR: 1.20 (d, J = 6.04 Hz, 6H, OCH**Me**$_2$); 2.73 (m, 8H, NCH$_2$); 3.82 (br, 2H, N**H**); 4.50 (m, 9H, CH$_2$O + OCH**Me**$_2$).

Adopting a procedure similar to that employed for (1e), complexes (1f–1h) were prepared using 1: 2 molar amounts of [Ta(OPr^i)$_5$] and appropriate *N*-substituted diethanolamines. Analytical and spectroscopic details are summarised below:

[Ta(Medea)$_2$(OPr^i)] (1f): Yellowish viscous liquid. Anal. Calcd. For C$_{13}$H$_{29}$N$_2$O$_5$Ta(474): C, 32.9; H, 6.2; N, 5.9; Ta, 38.1%. Found: C, 32.7; H, 6.2; N, 5.8; Ta, 38.0%. M.Wt., 494. IR: 1224 ν(C–N); 1171, 1142 ν(OPr^i); 1078, 1031 ν(C–O); 515 ν(Ta–O); 471 ν(Ta←N). ^{1}H NMR: 1.19(d, J = 6.05 Hz, 6H, OCH**Me**$_2$); 2.61(t, J = 5.50 Hz, 8H, NCH$_2$); 2.66(s, 6H, N**Me**); 3.67(m, 8H, CH$_2$O); 4.03(m, J = 6.05 Hz, 1H, OCH**Me**$_2$).

[Ta(Budea)$_2$(OPr^i)] (1g): Colourless sticky solid. Anal. Calcd. For C$_{19}$H$_{41}$N$_2$O$_5$Ta(558): C, 40.8; H, 7.4; N, 5.0; Ta, 32.4%. Found: C, 40.8; H, 7.3; N, 4.9; Ta, 32.2%. M.Wt., 569. IR: 1212 ν(C–N); 1180, 1153 ν(OPr^i); 1090, 1041 ν(C–O); 522 ν(Ta–O); 457 ν(Ta←N). ^{1}H NMR: 0.95 (t, 6H, N(CH$_2$)$_3$**Me**); 1.21 (d, J = 6.23 Hz, 6H, OCH**Me**$_2$); 1.24 - 1.48 (m, 8H, NCH$_2$(CH$_2$)$_2$Me); 2.66 (m, 4H, NCH$_2$(CH$_2$)$_2$Me); 3.11 (m, 8H, NCH$_2$); 4.45 (m, 9H, CH$_2$O + OCH**Me**$_2$).

[Ta(Phdea)$_2$(OPr^i)] (1h): White solid, m.p. 152–156°C. Anal. Calcd. For C$_{23}$H$_{33}$N$_2$O$_5$Ta(598): C, 46.2; H, 5.6; N, 4.7; Ta, 30.2%. Found: C, 46.1; H, 5.6; N, 4.5; Ta, 30.15%. M.Wt., 604. IR: 1335, 1210 ν(C–N); 1179, 1148 ν(OPr^i); 1101, 1039 ν(C–O); 515 ν(Ta–O); 461 ν(Ta←N). ^{1}H NMR: 1.20 (d, J = 6.06 Hz, 6H, OCH**Me**$_2$); 3.63 (br, 8H, NCH$_2$); 4.16 (m, J = 6.06 Hz, 1H, OCH**Me**$_2$); 4.50 (br, 8H, CH$_2$O); 6.43–7.47 (m, 10H, aromatic-**H**).

The derivatives [Al(Hdea)(OPr^i)] (1i), [Al(Medea)(OPr^i)] (1j), [Al(Budea)(OPr^i)] (1k), [Al(Phdea)(OPr^i)] (1*l*), and [Sb(Phdea)(OPr^i)] (1m) were prepared by the literature method.[24]

Synthesis of heterobimetallic complexes (2–10)

[{Nb(Hdea)$_2$}(μ-Hdea){Ta(Hdea)$_2$}] (2): A suspension of [Nb(Hdea)$_2$(HdeaH)] (1a) (2.01 g, 4.98 mmol) and [Ta(Hdea)$_2$(OPr^i)] (1e) (2.22 g, 4.97 mmol) in benzene (~ 40 ml) was refluxed with continuous azeotropic removal of the liberated isopropyl alcohol. After completion of the reaction, as was evident by the required amount (0.27 g) of the isopropyl alcohol collected in the azeotrope, refluxing was stopped. The insoluble product was separated from the mother liquor by decantation and dried under reduced pressure to obtain a yellowish-white solid (2) in 3.87 g (98%) yield. Recrystallisation from a 1: 1 mixture of dichloromethane and *n*-hexane at –20°C gave a colourless solid compound (2). Yield: 2.76 g (70%).

A similar procedure was used for the synthesis of (6). Analytical details are given in Table 1.

[Nb(Medea)$_3${Ta(Medea)$_2$}] (3): A colourless benzene solution (~ 40 ml) of [Nb(Medea)$_2$(MedeaH)] (1b) (1.64 g, 3.68 mmol) and [Ta(Medea)$_2$(OPr^i)] (1f) (1.75 g, 3.69 mmol) was refluxed with continuous removal of the liberated isopropyl alcohol, which was estimated periodically. After ~ 4 h, when the liberation of isopropyl alcohol ceased, refluxing was stopped and reaction mixture was allowed to cool to room temperature. Volatiles were removed under reduced pressure to obtain a colourless viscous compound (3), 3.10 g (98%). Recrystallisation from a 1: 1 mixture of dichloromethane

and *n*-hexane at –20°C afforded analytically pure complex (3) as a colourless sticky solid in 2.62 g (83%) yield. Analytical details are given in Table 1.

Adopting a method similar to that was used for (3), complexes (4), (5), and (7–10) were prepared by the reactions of [Nb(Rdea)$_2$(RdeaH)] with appropriate homometal mixed-ligand complexes in equimolar ratio. Preparative and analytical details are summarised in Table 1.

Single-pot synthesis of [NbTa(Phdea)$_5$] (5): A yellow solution of Nb(OPr^i)$_5$ (0.50 g, 1.29 mmol), Ta(OPr^i)$_5$ (0.62 g, 1.30 mmol) and PhdeaH$_2$(1.17 g, 6.46 mmol) in benzene (~ 40 ml) was refluxed with continuous azeotropic removal of the liberated isopropyl alcohol, which was collected and estimated. When the distillate showed negligible presence of an oxidisable species, refluxing was stopped and reaction mixture was allowed to cool to room temperature. Volatiles from the solution were removed under reduced pressure to obtain quantitatively (1.50 g, 99%) yellow solid compound (5). Recrystallisation from toluene at –20°C afforded analytically pure compound (5) as a yellow solid in 1.12 g (74%) yield, m.p. 149–151°C. Anal. Calcd. For C$_{50}$H$_{65}$N$_5$NbO$_{10}$Ta(1170): C, 51.3; H, 5.6; N, 6.0; Nb + Ta, 23.4%. Found: C, 51.2; H, 5.4; N, 5.8; Nb + Ta, 23.2%. M.Wt., 1159. IR (cm^{-1}): 1392, 1360, 1250, 1200 ν(C–N); 1087, 1042 ν(C–O); 570 ν(Nb–O); 520 ν(Ta–O); 469, 457 (M←N)(M = Nb/Ta). ^{1}H NMR (δ, ppm): 3.66 (br, 20H, NCH$_2$); 4.19 (br, 20H, CH$_2$O); 6.49–7.41 (m, 25H, aromatic-**H**).

A procedure similar to that used for (5) was used for the preparation of (7) and (10). Preparative and analytical details along with spectroscopic data are summarised below:

[NbAl(Medea)$_4$] (7): [Prepared from [Nb(OPr^i)$_5$] (0.86 g, 2.21 mmol), [Al(OPr^i)$_3$] (0.45 g, 2.20 mmol), and MedeaH$_2$(1.06 g, 8.89 mmol)]: White semisolid. Anal. Calcd. For C$_{20}$H$_{44}$N$_4$AlNbO$_8$(588): C, 40.8; H, 7.5; N, 9.5; Al, 4.6; Nb, 15.8%. Found: C, 40.7; H, 7.4; N, 9.2; Al, 4.4; Nb, 15.7%. M.Wt., 607. IR: 1240, 1200, 1190 ν(C–N); 1082, 1049, 1025 ν(C–O); 665 ν(Al–O); 578 ν(Nb–O); 512 ν(Al←N); 470 ν(Nb←N). ^{1}H NMR: 2.35(s, 3H, N**Me**); 2.61, 2.66(s, 9H, N**Me**); 3.67(m, 16H, NCH$_2$); 4.37(m, 16H, CH$_2$O). ^{27}Al NMR: δ 5.69 ppm.

[NbSb(Phdea)$_4$] (10): [Prepared from [Nb(OPr^i)$_5$] (0.93 g, 2.39 mmol), [Sb(OPr^i)$_3$] (0.72 g, 2.40 mmol), and PhdeaH$_2$ (1.74 g, 9.60 mmol)]: Yellow solid, m.p. 168–171°C. Anal. Calcd. For C$_{40}$H$_{52}$N$_4$NbO$_8$Sb(931): C, 51.6; H, 5.6; N, 6.0; Nb, 10.0; Sb, 13.1%. Found: C, 51.3; H, 5.5; N, 5.9; Nb, 9.8; Sb, 12.9%. M.Wt., 923. IR: 1390, 1360, 1351, 1245, 1205 ν(C–N); 1081, 1049, 1026 ν(C–O); 570 ν(Nb–O); 510 ν(Sb–O); 464, 449 ν(M←N)(M = Nb/Sb). ^{1}H NMR: 3.62(br, 16H, NCH$_2$); 4.38(br, 16H, CH$_2$O); 6.75–7.40(m, 20H, aromatic-**H**).

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