Interplay between Metal Aminoalkoxides and β-Diketonates: Volatile Mixed-Metal Pr−Cu and Y−Cu Species without Fluorinated Ligands − Molecular Structures of [PrCu(η^2-thd)$_3$(μ,η^2-$OC_2H_4NMe_2$)$_2$] and of [Y_2(η^2-thd)$_4${μ,η^2-$OCH(CH_2NMe_2)_2$}$_2$]

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The reactions between copper or lanthanide (Y, Pr) 2,2,6,6-tetramethylheptane-3,5-dionates and copper or barium aminoalkoxides were investigated in hexane. Aminoalkoxide ligands of different constraints and/or flexibility namely 2,4,6-tris(dimethylaminomethyl)phenoxide (Otamp), 2-dimethylaminoethoxide $OC_2H_4NMe_2$, 2-dimethylamino-2-propoxide $OCH(Me)CH_2NMe_2$, and 1,3-bis(dimethylamino)-2-propanol $OCH(CH_2NMe_2)_2$ were selected. Mixed-metal BaCu, PrCu, $PrCu_2$, and YCu species, as well as β-diketonatoalkoxides of barium and yttrium were isolated and characterised by analytical data, FT-IR, ^{1}H NMR, and ESR spectroscopy. Their thermal behaviour was investigated by TGA. The tridentate aminoalkoxide $OCH(CH_2NMe_2)_2$ was found to destabilise mixed-metal species with tetramethylheptanedionate as ancillary ligands. [BaCu(η^2-thd)$_2$(μ,η^3-Otamp)(μ,η^2-Otamp)(H_2O)], [PrCu(η^2-thd)$_3$(μ,η^2-$OC_2H_4NMe_2$)$_2$], and [Y_2(η^2-thd)$_4${μ,η^2-$OCH(CH_2NMe_2)_2$}$_2$] were also characterised by single crystal X-ray diffraction. The latter two were volatile, whereas the volatility of the former was reduced by intramolecular hydrogen bonding. The assembling aminoalkoxide ligands ensure high coordination numbers for the heavy metals, namely seven for barium and yttrium, eight for praseodymium. The formation of the mixed-metal species improves stability toward ambient atmosphere, especially for the systems involving copper aminoalkoxides. The [Ba(thd){$OCH(CH_2NMe_2)_2$}$_2${$OHCH(CH_2NMe_2)_2$}$_2$] species distils at 130 °C/10^{-3} Torr.

Introduction

The exploitation of the properties of anisotropic ceramics such as high T_c superconductors requires the elaboration of textured or epitaxial layers.[1] Although epitaxial layers might be obtained by sol-gel processing, this goal is more easily achieved by MOCVD techniques.[2] However, this requires appropriate precursors, namely volatile molecules which can be decomposed into the oxide within a comparable temperature range, and that are reasonably stable thermally in the container for reuse.[3] β-Diketonates are the most commonly used precursors, especially the tetramethylheptanedionate β-diketonates.[4] Besides the problems related to the use of solids as precursors, volatility and stability properties remain unsatisfactory in the case of barium, despite a large body of synthetic efforts.[5] Various liquid-source MOCVD delivery techniques that assist the transport of the precursor to the substrate and allow for maintaining the precursors at room temperature have been considered as ways to overcome the drawbacks.[6] Solubility of the precursors becomes a crucial issue for high growth rates since a solvent is an undesired ballast in a CVD process. The use of heterometallic species is an approach which reduces the number of precursors, and might improve solubility.[7] If these species are volatile, a reduction of the temperature of pyrolysis can sometimes be achieved. A large number of Ba−Cu,[8,9] Y(Ln)−Cu,[10] and a few Y−Ba[11] species of different stoichiometries have been reported. Only a few of them are volatile, they are supported by fluorinated ligands, mainly alkoxides, as assembling ligands. High Lewis acidity resulting in facile hydration or solvation and thus change in the physical properties, as well as fluoride residues in the deposits are the most common drawbacks. Aminoalkoxide ligands are often more favourable for increasing volatility than alkoxyalkoxides.[12] Schiff bases have been used recently as an alternate assembling ligand, and species such as [M(salen)Ln(hfac)$_3$] [M = Ni, Cu; Ln = Y, Gd; H_2salen = *N*,*N′*-ethylenebis(salicylideneimine)] have been reported.[13]

We report here our investigations of the interactions between metal aminoalkoxides and tetramethylheptanedionate derivatives related to the formulation of high T_c superconductors. These were aimed at the building of mixed-metal species as well as obtaining insight into the compositions of solutions using precursors of different types.[6] The OR-type ligands, namely 2,4,6-tris(dimethylaminomethyl)phenoxide (Otamp), 2-dimethylaminoethoxide OR^n = $OC_2H_4NMe_2$, 2-dimethylamino-2-propoxide OR^N = $OCH(Me)CH_2NMe_2$, and 1,3-bis(dimethylamino)-2-propoxide OR'^N = $OCH(CH_2NMe_2)_2$, were selected in order to cover different constraints and/or flexibility. Mixed-metal species namely [BaCu(thd)$_2$(Otamp)$_2$(H_2O)], [MCu(thd)$_3$(OR)$_2$]

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(M = Y, Pr, R = R^n, R'^N) and $[MCu_2(thd)_3(OR^n)_4]$ could be stabilised. By contrast, the trifunctional aminoalkoxide ligand $OCH(CH_2NMe_2)_2$ favoured the formation of volatile homometallic Y and Ba β-diketonatoalkoxides. The various species were characterised by elemental analyses, FT-IR, NMR, ESR, and TGA, and in the case of $[BaCu(\eta^{2-}thd)_2(\mu\text{-}Otamp)_2(H_2O)]$, $[PrCu(\eta^2\text{-}thd)_3(\mu,\eta^2\text{-}OR^n)_2]$, and $[Y(\mu,\eta^2\text{-}OR'^N)(\eta^2\text{-}thd)_2]_2$, by single crystal X-ray diffraction.

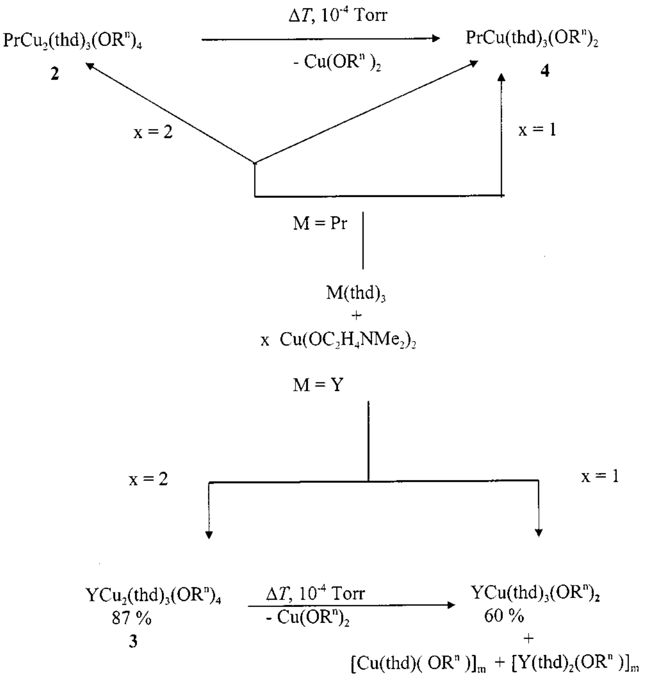
Results and Discussion

Synthesis and Characterization

Direct liquid injection MOCVD techniques are attractive for overcoming the drawbacks of the limited stability and/or volatility of solid oxide precursors such as barium derivatives.[2,6] Whereas β-diketonates are generally attractive precursors due to their commercial accessibility and easy handling, the limited solubility of the copper derivatives − as compared to the Ba and Y analogues − determines the concentration.[2c] Besides high solubility, the compounds used as sources of the metal oxide should be inert toward evolution into insoluble species during storage of the solution. This requirement is especially important for multimetallic oxides, since a unique container is generally used for convenience, and a constant stoichiometry between the different elements in solution is crucial for the composition of the multimetallic material. Previous studies have revealed the limitation encountered by mixing β-diketonates and β-oxo esters due to rapid ligand scrambling.[6−14] Copper alkoxides based on aminoalkoxide ligands are highly soluble and volatile, but quite hydrolysable.[15] The mixing of metal alkoxides and β-diketonates, namely 2,2,6,6-tetramethylheptane-3,5-dionates was expected to be more favourable despite the fact that higher susceptibility to moisture could result. The Cu−M systems (M = Y, Pr, or Ba) were investigated. Indeed, whereas yttrium is involved in the formula of superconducting YBCO materials, the praseodymium analogue is an insulator, and is thus of interest for building up heterostructures.[1]

Aryloxide-type ligands allow a great deal of control of steric hindrance, and thus solubility, volatility, and robustness toward atmosphere via the substituents in 2- and 6- positions.[12] An aryloxide with potentially chelating dimethylaminomethyl arms (Otamp) could also act as an efficient "pincer" ligand. A Ba−Cu species, $[BaCu(thd)_2(Otamp)_2(H_2O)]$ (**1**) was obtained in high yield by reaction of either Cu(thd)2 and $Ba_4O(Otamp)_6$ or $Cu(O\text{-}tamp)_2$ and $[Ba(thd)_2]_4$.

The reactions between the 2,2,6,6,-tetramethylheptane-3,5-dionates $M(thd)_3$ (M = Y or Pr) and copper 2-dimethylamino-2-propoxide $Cu(OR^N)_2$ in hexane afforded mixed-metal species $[MCu(thd)_3(OR^N)_2]$ in nearly quantitative yields by self-assembly. The same compounds were obtained using $M(thd)_2(OR^N)$, but in lower yields (ca. 60%). More complex reactions were observed with copper 2-dimethylaminoethoxide $Cu(OC_2H_4NMe_2)$. Indeed, mixed-metal β-diketonatoalkoxides of two stoichiometries, MCu and MCu_2, could be stabilised. Whereas the reaction between $Y(thd)_3$ and $Cu(OR^n)_2$ (1:2 stoichiometry) afforded only $[YCu_2(thd)_3(OR^n)_4]$ (**3**) (87% yield), for praseodymium the complexes $[PrCu_2(thd)_3(OR^n)_4]$ (**2**) and $[PrCu(thd)_3(OR^n)_2]$ (**4**) crystallised under similar conditions (35 and 45% yields, respectively). On the other hand, the yield of $[YCu(thd)_3(OR^n)_2]$, obtained by reaction of $Y(thd)_3$ and $Cu(OR^n)_2$ (1:1 stoichiometry), is reduced to ca. 60% by the formation of the homometallic species $[Cu(thd)(OR^n)]_m$ and $[Y(thd)_2(OR^n)]_m$ as by-products (established by comparison with authentic samples). The $[MCu_2(thd)_3(OR^n)_4]$ (M = Y, Pr) species are both volatile, but their sublimation (140 °C, 10^{-4} Torr) proceeds with decomposition to $[MCu(thd)_3(OR^n)_2]$ and copper aminoalkoxide. The lower stability of the MCu_2 species with respect to the MCu ones is also reflected in their sensitivity to hydrolysis and partial dissociation in solvents such as toluene. The absence of isolation of MCu_2 species in the case of the bis(2-dimethylamino-2-propoxide) ligand is probably related to its greater bulkiness. The lower stability of $[YCu(thd)_3(OR^n)_2]$ with respect to the praseodymium analogue might be due to the lower tendency of yttrium to attain octa-coordination as observed for the solid-state structure of **4** (see below) The various synthetic pathways for the aminoethoxide derivatives are summarised in Scheme 1.



Scheme 1. Synthetic routes to M−Cu (M = Y, Pr) β-diketonatoaminoethoxides ($OR'^n = OC_2H_4NMe_2$) (all reactions in hexane at room temperature)

Reactions with derivatives of the trifunctional aminoalkoxide $OR'^N = OCH(CH_2NMe_2)_2$ were also investigated. By contrast with reactions between a copper aminoalkoxide generated in situ and acetates or trifluoroacetates of alkaline-earth metals,[16] the reaction between $Y(thd)_3$ and $Ba(OR'^N)_2$, obtained in situ by alcoholysis of barium bis-

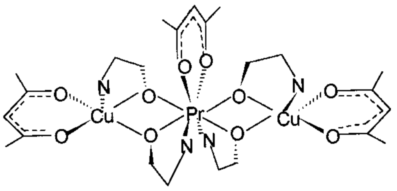
Table 1. FT-IR data (cm^{-1}) of the various compounds

Compound	υOH	δOH	υC=O, νC=C	υMO, νMN
$BaCu(thd)_2(Otamp)_2(H_2O)$	3162 m	[a]	1590 vs, 1572 vs, 1547 w, 1531 sh, 1525 vs, 1513 sh, 1511 vs, 1480 vs	598 w, 578 m, 569 m, 559 m, 525 w, 514 w, 477 m, 470 m, 456 w, 429 sh,408 m, 393 m
$PrCu_2(thd)_3(OR^n)_4$	–	–	1589 vs, 1575 vs, 1546 m 1531 s, 1502s, 1486	564 m, 502 sh, 482 m457 w, 422 w, 405 w
$PrCu(thd)_3(OR^n)_2$	–	–	1590 vs, 1554 vs, 1537 vs1515 vs, 1496 vs, 1480 m	596 m, 586 w, 510 sh, 489 sh, 473 m, 438 w, 426 w, 397 w
$YCu_2(thd)_3(OR^n)_4$	–	–	1600 sh, 1592 vs, 1577 vs, 1551 m, 1535 vs, 1530 sh, 1501 vs, 1484 vs	574 w, 507 m, 474 vs, 449 w, 430 m, 401 w
$YCu(thd)_3(OR^N)_2$	–	–	1592 vs, 1581 vs, 1572 vs, 1554 m, 1536 vs, 1505 vs, 1496 sh	570 w, 514 sh, 508 w490 m, 476 m, 442 w406 w
$PrCu(thd)_3(OR^N)_2$	–	–	1590 vs, 1578 vs, 1552 m, 1536 vs, 1504 w, 1495 vs	598 m, 509 w, 488 m,473 m, 435 w403 w
$Ba(thd)(OR'^N)(HOR'^N)$	3442 m, 3178 w	1653 w	1597 vs, 1591 vs, 1574 vs, 1531 vs, 1503 vs	588 w, 528 m, 516 w,469 m, 447 w, 400 w,387 w, 375 w
$[Y(thd)_2(OR'^N)]_2$	–	–	1594 vs, 1581 vs, 1573 vs, 1551 vs, 1538 vs, 1506 vs, 1494 vs	572 w, 527 w, 514 w, 474 m, 442 w,429 w, 408 w, 396 w

[a] Masked by the C=C and C=O absorption bands.

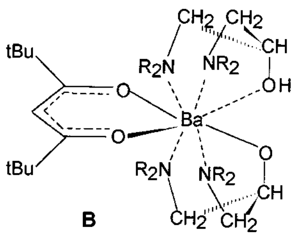
(trimethylsilylamide), gave no evidence of stable mixed-metal species, and $[Y(thd)_2(OR'^N)]_2$ (**8**) was isolated in nearly quantitative yields. The barium by-product, assumed to be a barium β-diketonatoalkoxide, could not be crystallised under such conditions. An adduct $[Ba(thd)(OR'^N)(R'^NOH)]$ (**7**) was however isolated by ligand exchange reactions applied to the insoluble homometallic alkoxide $Ba(OR^N)_2$. Similar observations, namely redistribution reactions, were made for the $Cu(thd)_2$–$Ba(OR'^N)_2$ system. Adduct **7** was quite air-sensitive, and attempts to make the species more robust toward ambient atmosphere by ligand exchange reactions, between the coordinated alcohol and diglyme for instance were not successful.

The various species were characterised by elemental analysis, FT-IR, ^1H-NMR, or ESR spectroscopy (Table 1). Their FT-IR spectra display strong absorption bands between 1600–1480 cm^{-1} characteristic of νC=O and νC=C vibrations of the β-diketonate ligands, other absorption bands correspond to νC–N and C–O vibrations between 1230 and 1000 cm^{-1}, and to νM–OR vibrations below 500 cm^{-1}. Compound **7** also displays absorption bands at 3178 and 3442 cm^{-1}, confirming the presence of an alcohol molecule in the metal coordination sphere. The similarity of the FT-IR spectra of the $PrCu_2$ and PrCu species suggests limited structural differences between their solid-state structures. Their FT-IR data indicate the absence of bridging thd ligands. The solid-state structure of **2** could not be solved due to disorder problems, but the cell parameters are definitely different from those of **4**. A plausible structure corresponds to **A**, in which the metal atoms are assembled by bridging alkoxide ligands where each metal centre bears a terminal η^2-thd ligand. Such a framework allows the metal atoms to reach common coordination numbers, namely eight for praseodymium and five for both copper centres. The transformation of **2** to **4** implies redistribution of one thd and OR^n ligand.



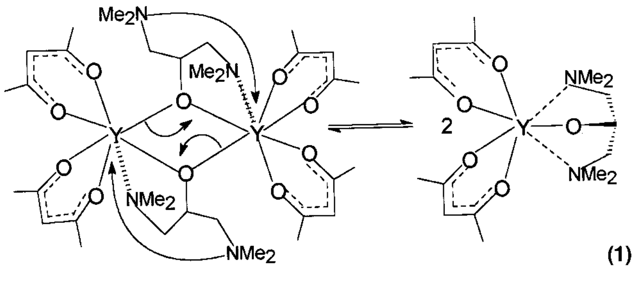
The paramagnetic praseodymium–copper and yttrium–copper species **2**, **4**, **5**, and **6** were characterised by ESR spectroscopy. The isotropic spectra at room temperature display a four line pattern centred around $<g> = 2.10$, characteristic of the coupling of the unpaired electron with copper [coupling constants A ranging from 78.6 to 92.4 G (^{63}Cu: $N = 69\%$, $I = 3/2$; ^{65}Cu: $N = 31\%$, $I = 3/2$).

The solubility of the diamagnetic species, namely the homometallic (β-diketonato)yttrium and -barium alkoxides **7** and **8** allowed us to gain structural information by ^1H NMR. The poor stability of **7** under the X-ray beam at room temperature, and a destructive phase transition at lower temperature, precluded structural information in the solid state. Its molecular complexity was established by the Signer method. The value obtained in benzene accounts for a monomer. Its volatility (distillation at 130 °C/10^{-3} Torr) is in agreement with a low molecular weight, and thus a monomeric character. Its ^1H-NMR spectra in $CDCl_3$ are a function of the dilution, and suggest the presence of several molecular species as indicated by three resonances for the CH group of the thd ligand. The CH resonance of the aminoalkoxide at $\delta = 3.91$ is broad, suggesting fast-exchange on the NMR time scale between the aminoalkoxide and the coordinated amino alcohol molecule – each of them having the potential for different coordination modes. The signals of the CH_2NMe_2 moieties appear as a complex pattern around $\delta = 2.25$. The signal due to the OH group was found as a very broad resonance at $\delta = 5.0$. In view of the complexity of the spectra (the carbon atom in α-position becomes asymmetric for a bidentate coordination mode) the behaviour in solution was not further investigated. Compound **7** distils as the adduct. The coordinated alcohol could not be exchanged by diglyme, dissociation of the adduct in solution is thus not very likely. Octa-coordination can be achieved for **7** when all NMe_2 donor sites are involved in interactions with the metal centre, resulting in, for instance, structure **B**. Other isomers are, however, possible, since 1,3-bis(dimethylamino)-2-propoxide can display bidentate and tridentate coordination modes and barium can quite easily adopt coordination numbers from six to eight.[4,5]



B

The ^1H-NMR spectra of **8** are also very complicated, and are a function of the dilution. The presence of a species in which the 1,3-bis(dimethylamino)propoxide ligand is bidentate is illustrated by the unequivalence of the protons of the CH_2 groups in α-position to the asymmetric carbon atom. The signal at $\delta = 4.21$ was attributed to an aminoalkoxide ligand displaying a symmetrical, tridentate coordination behaviour. The overall behaviour of **8** in solution can be rationalised on the basis of an equilibrium between a dimeric species **8a** (see below), having the structure found in the solid state, and a monomeric one $[Y(\eta^2\text{-thd})_2(\eta^3\text{-OR}'^N)]$ (**8b**) according to Equation (1). The signals due to the thd ligands were observed at $\delta = 5.59$ and 1.05, and at $\delta = 5.67$ and 1.09 for **8a** and **8b**, respectively.



(1)

8a 8b

Compound **8** sublimes, although the sublimate displays small modifications in the FT-IR spectrum (with respect to **8**). Analytical and NMR data of the sublimate were identical to those of the species before sublimation. The behaviour observed in solution suggests that sublimation of **8** proceeds with partial dissociation into monomer **8b**, which might be responsible of the additional bands observed in the FT-IR at 1001, 917, 653, and 540 cm^{-1}. Yttrium is hepta-coordinated in both species **8a** and **8b**, but the Y−N coordination bonds are probably less labile in **8a** than **8b**, and this might explain the higher hydrolytic susceptibility of the compound in solution.

Molecular Structures of $[BaCu(thd)_2(Otamp)_2(H_2O)]$ and of $[PrCu(thd)_2(\mu,\eta^2\text{-OR}^n)_2]$

The structure of **1** corresponds to $[BaCu(\eta^2\text{-thd})_2(\mu,\eta^3\text{-Otamp})(\mu,\eta^2\text{-Otamp})(H_2O)]$ as depicted in Figure 1. Despite the limited number of reflections, the connectivity between the atoms could be established unambiguously. The most salient feature is the presence of a water molecule in the coordination sphere of barium. Barium and copper are clamped together by two aryloxide ligands. These display different coordination behaviours, one is bidentate (μ,η^2-), the other is tridentate (μ,η^3-). The Ba···Cu distance of 3.680(3) Å is comparable to the value reported for other Ba−Cu β-diketonatoalkoxides.[6] Barium surrounded by two NMe_2 groups (one of each Otamp ligand) and five oxygen atoms due to a chelating tetramethylheptanedionate. It is thus hepta-coordinated, with a distorted pentagonal-bipyramidal stereochemistry, the nitrogen atoms being in apical positions. Copper is five-coordinated with a tetragonal-pyramidal surrounding, and also bears a chelating tetramethylheptanedionate ligand. The Cu−O bond lengths vary from 1.89(1) to 2.11(2) Å. The longest one corresponds to Cu−O(5). The disymmetrical linkage of the thd ligand is most probably due to the elongation of the Cu−O(5) bond − with respect to the Cu−O(6) one − by Jahn−Teller effect, as commonly observed for copper.[9,17] The Ba−O distances are spread over the range 2.57(2) to 2.67(1) Å. The Ba−O(tamp) bond lengths are comparable to the values reported in the literature for aryloxides.[18] They are slightly shorter when the ligand is tridentate [Ba−O(1) 2.62(1) to compare to Ba−O(2) 2.67(1) Å and Cu−O(1) = 1.92(1) vs 1.99(1) Å for Cu−O(2)]. The Ba−N coordination bonds [2.97(2) Å av.] are longer than the Ba−O ones, but in agreement with the data reported in the literature for other barium derivatives such as $Ba_4O(Otamp)_6$ [19] or $[Ba_2Cu(thd)_4(OR^N)_2(i\text{PrOH})_2]$.[9] The Cu−N distance of 2.14(2) Å is comparable to the values observed for other Cu^{II} aminoalkoxides.[15] The short contacts between $O(7)(H_2O)$ and two dangling nitrogen atoms of the aryloxide ligand [O(7)···N(4) 2.72 Å and O(7)···N(1) 2.79 Å, respectively] indicate the presence of intra- and intermolecular hydrogen bonding.[20] These observations are supported by a broad absorption band at 3162 cm^{-1} in the infrared spectra, and account for the poor volatility. The presence of water is most probably due to the hygroscopic phenol, as previously observed for $Pr(Otamp)_3(H_2O)_2$.[21] It also indicates that **1** is relatively stable toward hydrolysis. A number of Ba−Cu species of various stoichiometries have been reported.[8,9] Those having a 1:1 stoichiometry are usually tetranuclear species such as $[Ba_2Cu_2(\beta\text{-diket})_4(OC_2H_4OMe)_4(OHC_2H_4OMe)_2]$ (β-diket = acac, thd), in which copper is planar whereas barium is 7-coordinate.[8] The presence of one Otamp ligand acting as a tetradentate ligand and water as additional ligand allows barium to reach hepta-coordination in a monomeric unit.

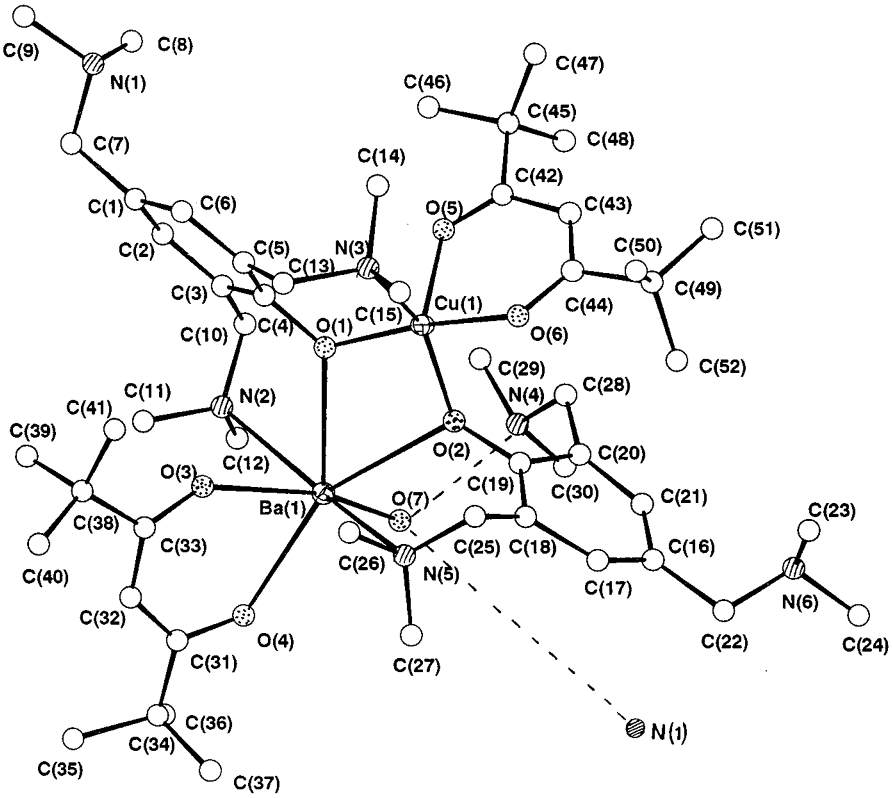


Figure 1. Molecular structure of [BaCu(η^2thd)$_2$(Otamp)$_2$(H$_2$O)] showing the atom numbering scheme (dotted lines indicate H bonding)

Compound **4** is obtained by the self-assembly between Cu(OR^n)$_2$ and Pr(thd)$_3$. Its molecular structure [PrCu(η^2-thd)$_3$(μ,η^2-OR^n)$_2$] is depicted in Figure 2. Selected bond lengths and angles are collected in Table 2. From a structural point of view it can be considered as the assembly between Pr(thd)$_2$(OR^n) and Cu(thd)(OR^n) moieties. These

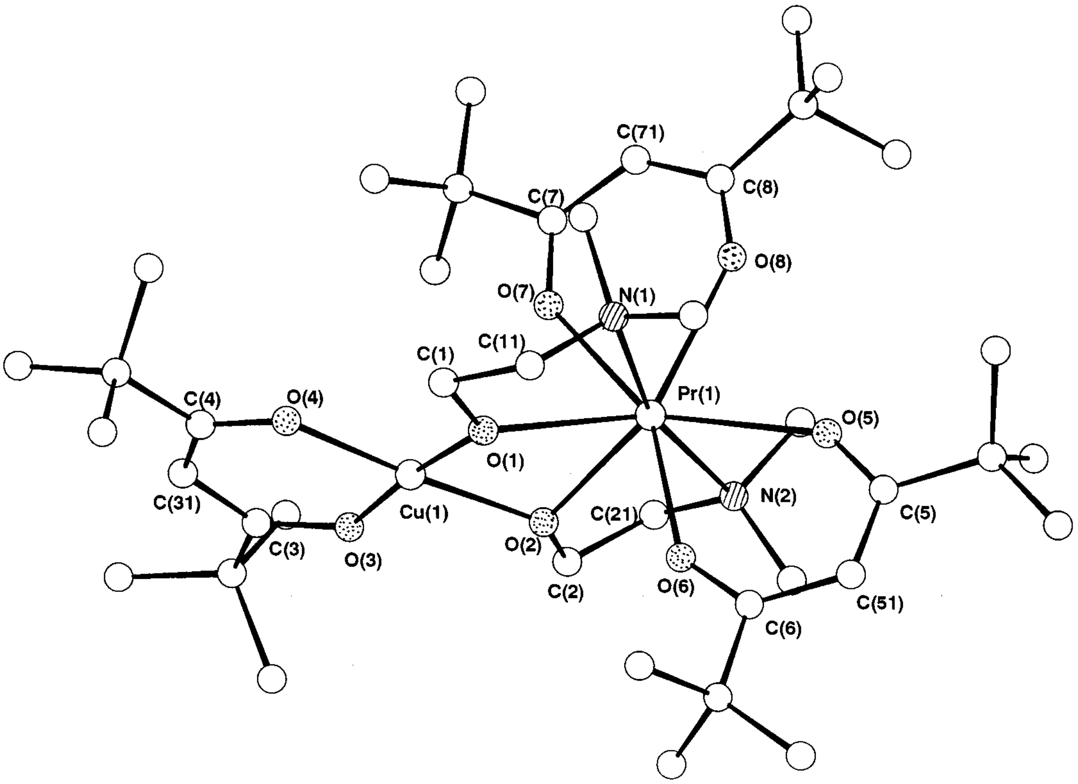


Figure 2. Crystal structure of [PrCu(η^2-thd)$_3$(μ,η^2-OC$_2$H$_4$NMe$_2$)$_2$]

Table 2. Selected bond lengths [Å] and angles [°] for $PrCu(\eta^2\text{-}thd)_3(\mu,\eta^2\text{-}OR^n)_2$

Bond lengths	
Pr(1)···Cu(1) 3.345(1)	Pr(1)−N(1) 2.701(9)
Pr(1)−O(1) 2.368(7)	Pr(1)−N(2) 2.691(9)
Pr(1)−O(2) 2.367(7)	Cu(1)−O(1) 1.896(7)
Pr(1)−O(5) 2.460(7)	Cu(1)−O(2) 1.909(7)
Pr(1)−O(6) 2.394(7)	Cu(1)−O(3) 1.910(7)
Pr(1)−O(7) 2.457(7)	Cu(1)−O(4) 1.907(7)
Pr(1)−O(8) 2.426(7)	
Angles	
O(1)−Pr(1)−O(2) 63.6(3)	O(1)−Pr(1)−O(5) 143.1(2)
O(2)−Pr(1)−O(5) 131.4(3)	O(1)−Pr(1)−O(6) 83.1(2)
O(2)−Pr(1)−O(6) 85.9(3)	O(5)−Pr(1)−O(6) 67.2(2)
O(1)−Pr(1)−O(7) 74.9(3)	O(2)−Pr(1)−O(7) 73.7(3)
O(5)−Pr(1)−O(7) 137.7(2)	O(6)−Pr(1)−O(7) 154.9(2)
O(1)−Pr(1)−O(8) 124.9(3)	O(2)−Pr(1)−O(8) 133.9(3)
O(5)−Pr(1)−O(8) 72.5(2)	O(6)−Pr(1)−O(8) 137.0(2)
O(7)−Pr(1)−O(8) 67.5(2)	O(1)−Pr(1)−N(1) 65.7(3)
O(2)−Pr(1)−N(1) 129.2(3)	O(5)−Pr(1)−N(1) 89.2(3)
O(6)−Pr(1)−N(1) 84.6(3)	O(7)−Pr(1)−N(1) 96.9(3)
O(1)−Pr(1)−N(2) 128.8(3)	O(2)−Pr(1)−N(2) 65.3(3)
O(5)−Pr(1)−N(2) 77.6(3)	O(6)−Pr(1)−N(2) 95.8(3)
O(7)−Pr(1)−N(2) 88.9(3)	O(8)−Pr(1)−N(1) 80.4(3)
O(8)−Pr(1)−N(2) 89.6(3)	N(2)−Pr(1)−N(1) 165.4(3)
O(1)−Cu(1)−O(2) 82.0(3)	O(1)−Cu(1)−O(3) 174.8(3)
O(2)−Cu(1)−O(3) 93.1(3)	O(1)−Cu(1)−O(4) 93.1(3)
O(2)−Cu(1)−O(4) 175.0(3)	O(3)−Cu(1)−O(4) 91.8(3)
Pr(1)−O(1)−Cu(1) 102.8(3)	Pr(1)−O(2)−Cu(1) 102.4(3)

units are connected by the O centre of the aminoalkoxide ligand, the pendant amino functionalities being both linked to the praseodymium atom. Praseodymium is thus eight-coordinated with a bipyramidal hexagonal geometry, in which the nitrogen atoms occupy the axial positions. Copper has a square-planar distorted surrounding. The Pr···Cu distance has a value of 3.345(1) Å, comparable to those observed for $[PrCuL(hfac)_2(O_2CCF_3)(R'^NOH)_2]$[22] [L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato] and $[PrCu(OH)(hfac)_3(bdmmp)(bdmmpH)]$[16] [bdmmp = 2,6-bis(dimethylaminomethyl)-4-methylphenoxide]. The Pr−O bond lengths are spread over the range 2.367(1) to 2.460(7) Å, they vary according to the generalisation: Pr−μOR < Pr−O(thd), in agreement with the literature.[22−24] The Pr−N coordination bonds are considerably longer [2.695(9) Å] as reported previously.[16,21,22,25] The Cu−O bond lengths are similar for the tetramethylheptanedionate as well as the bridging alkoxide ligands [1.896(7)−1.9101(7) Å].[17] The bite angles of the thd and aminoalkoxide ligands are also similar with values of 67.3(2)° and 65.5(2)°, respectively.

Molecular Structure of $[Y_2(\eta^2\text{-thd})_4(\mu,\eta^2\text{-}OR'^N)_2]$

The structure of **8** is that of a centrosymmetric dimer $[Y_2(\eta^2\text{-thd})_4(\mu,\eta^2\text{-}OR'^N)_2]$ (Figure 3, Table 3). The yttrium atoms are hepta-coordinated, and are connected by two bridging-chelating aminoalkoxide ligands with one NMe_2 of each alkoxide ligand remaining pendant (Y···N distance of 5.22 Å). The Y···Y non-bond length has a value of 3.739(2) Å, comparable to that observed for other dinuclear yttrium species such as $[Y_2(O_2CCF_3)_6(OR'^N_2)]^{2-}$ [25], or polynuclear clusters.[12] The OR'^N ligand is generally tridentate − both NMe_2 sites interacting with the metallic centres. The only example of a μ,η^2-coordination mode is that of $Cu_2Cl_4(R'^NOH)_2$.[26] Although octa-coordination has been achieved for yttrium in β-diketonatoalkoxides such as $[Y_3(acac)_4(OC_2H_4OMe)_5]$,[27] the steric hindrance of the tetramethylheptanedionate ligands probably precludes coordination of the second N-donor site for **8**. The Y−O bond lengths are spread over the range 2.236(5) to 2.307(5) Å. These values are in agreement with the literature.[28] The Y−O−Y bridge is unsymmetrical, the intra-chelate Y−O(5′) distance being about 0.069 Å longer than Y−O(5). The Y(1)−N(1) coordination bond of 2.544(7) Å is in the range of the values observed.[25,29]The structure of **8** is related to that of $[Y(\mu,\eta^2\text{-}OAc)(acac)_2(H_2O)]_2$ [30] and of $[Pr(hfac)_2(\mu,\eta^3\text{-}OR'^N)(H_2O)(THF)]_2$.[22] However, the larger ionic radius of praseodymium (1.013 Å as compared to 0.880 Å for Y) allows the metal to attain nona-coordination via a tridentate assembling coordination mode of the aminoalkoxide ligand and two additional neutral ligands.

Physical Properties: Solubility and Volatility Data

A general observation for these mixed-metal species is, as anticipated, an increase in solubility as well as a better stability toward ambient atmosphere. For instance, whereas soluble copper alkoxides are highly moisture-sensitive and the praseodymium tetramethylheptanedionate hygroscopic, **4** is air-stable. Stability to ambient atmosphere was also achieved for **1**, **5**, and **6**.

The Ba−Cu species **1** is soluble in polar, as well as nonpolar media. It is stable in solvents such as diglyme (UV evidence). It is non-volatile. The TGA analysis shows a first weight loss in the 95−125 °C temperature range, due to the elimination of the water ligand. An aminophenoxide ligand is eliminated at 170−280 °C. Two identical weight losses are observed between 280−550 °C. They correspond to the elimination of the two tetramethylheptanedionate ligands. The last Otamp ligand is only partially decomposed between 550 and 970 °C. Thus, despite a quite low onset of decomposition for an aryloxide, the amount of a residue (ca. 38%) is quite higher than that expected for $BaCuO_2$ (20.9%).

The heterometallic species MCu_2 and MCu were soluble in aliphatic or aromatic hydrocarbons, or ethers such as THF or diethyl ether, but only slightly in diglyme. The M−Cu species **4**, **5**, and **6** sublime at 155 °C/10^{-4}, 130 °C/10^{-4}, and 150 °C/10^{-4} Torr, respectively. They are the first volatile Ln−Cu or Y−Cu species not supported by fluorinated ligands. It is noticeable that none of the Pr−Cu and Pr species with related aminoalkoxide ligands such as $[PrCu(OH)(hfac)_3(bdmmp)(bdmmpH)]$ and $[Pr(hfac)(OR'^N)(H_2O)(THF)_2]$ were volatile, despite the presence of the fluorinated diketonate in the coordination sphere.[25,26] The thermal behaviour of the novel M−Cu species was analysed by TGA under nitrogen (1 atm). The amount of

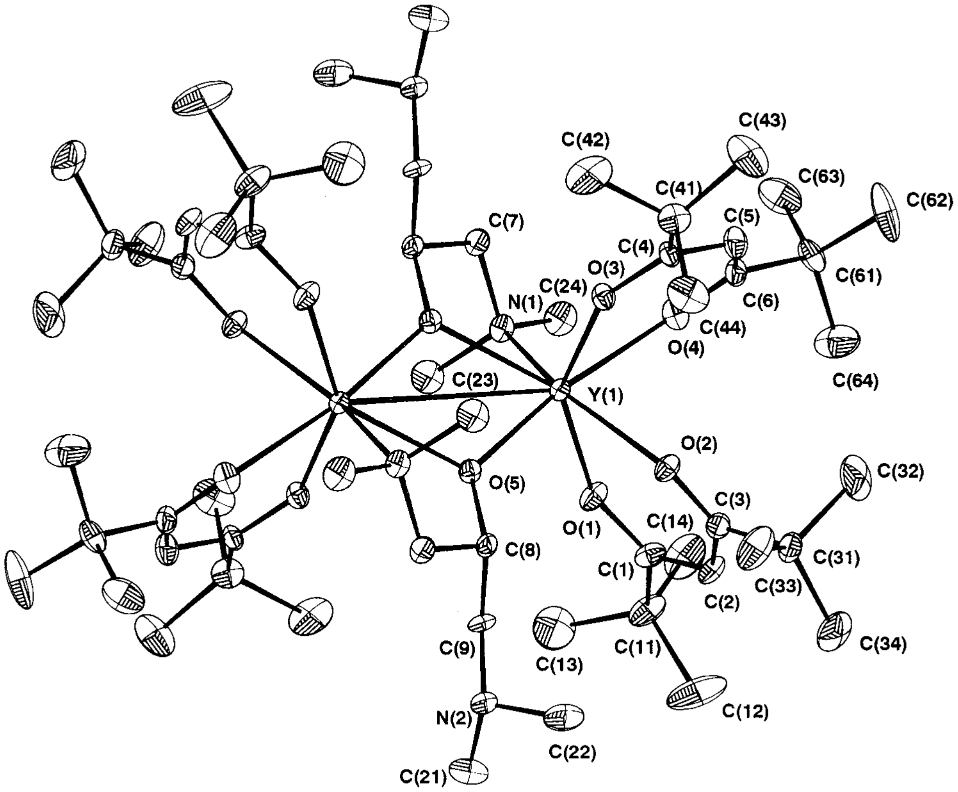


Figure 3. Molecular structure of [Y(η^2-thd)$_2$(μ,η^2-OR'^{N})$_2$]$_2$ (thermal ellipsoids at 30% probability)

Table 3. Selected bond lengths [Å] and angles [°] for [Y(thd)$_2$(OR'^{N})]$_2$

Bond lengths[a]			
Y(1)−Y(1')	3.739(2)	Y(1)−O(1)	2.273(6)
Y(1)−O(2)	2.294(6)	Y(1)−O(3)	2.280(6)
Y(1)−O(4)	2.303(6)	Y(1)−O(5)	2.236(5)
Y(1)−O(5')	2.307(5)	Y(1)−N(1)	2.544(7)
Bond angles			
O(1)−Y(1)−O(2)	74.9(2)	O(1)−Y(1)−O(3)	149.3(2)
O(2)−Y(1)−O(3)	78.8(2)	O(1)−Y(1)−O(4)	88.1(2)
O(2)−Y(1)−O(4)	83.0(2)	O(3)−Y(1)−O(4)	73.1(2)
O(1)−Y(1)−O(5)	93.3(2)	O(2)−Y(1)−O(5)	85.5(2)
O(3)−Y(1)−O(5)	100.2(2)	O(4)−Y(1)−O(5)	167.6(2)
O(1)−Y(1)−O(5')	127.3(2)	O(2)−Y(1)−O(5')	145.9(2)
O(3)−Y(1)−O(5')	83.3(2)	O(4)−Y(1)−O(5')	119.2(2)
O(1)−Y(1)−N(1)	78.5(2)	O(2)−Y(1)−N(1)	146.9(2)
O(3)−Y(1)−N(1)	118.7(2)	O(4)−Y(1)−N(1)	76.8(2)
O(5')−Y(1)−O(5)	69.2(2)	O(5)−Y(1)−N(1)	115.6(2)
O(5')−Y(1)−N(1)	67.2(2)	Y(1)−O(5)−Y(1')	110.9(3)

[a] Atoms labelled with ' are connected by an inversion centre.

residues obtained for the Y−Cu species **3** and **6** are lower than the values expected for $Y_2Cu_4O_7$ (24.3%) and $Y_2Cu_2O_5$ (21.5%), respectively. Partial sublimation has thus occurred during the TGA experiments. A similar thermal behaviour was observed for the praseodymium−copper species **2**, **4**, and **5**. The properties of the bimetallic Pr−Cu and Y−Cu species are compatible with their use in conventional as well as liquid delivery MOCVD techniques.

The homometallic species based on the OR'^{N} ligand display quite limited solubility, even in polar solvents (THF, diglyme). Both **8** and **7** are volatile. The yttrium species sublimes at 215−220 °C/10^{-3} Torr. This temperature is quite high, but in agreement with the dimeric character and thus a relatively high molecular weight.[6] The TGA profile accounts for sublimation up to 350 °C. By contrast with the barium derivative, it is air-stable in the solid state (FT-IR evidence). [Ba(OR'^{N})(thd)(HOR'^{N})] distils as the adduct at 130 °C/10^{-3} Torr, it is thus one of the most volatile barium species reported to date.[4] The TGA analysis indicates a first weight loss from 120 to 245 °C, corresponding to the elimination of the coordinated alcohol. The second weight loss between 245 and 375 °C is due to the elimination of the aminoalkoxide ligand, the thd ligand is decomposed partially, leading to a $BaCO_3$ residue. Although no carbonate was observed under reduced pressure, the high moisture sensitivity of the compound is a hurdle. [Ba(tdfnd)$_2$(H_2O)]$_m$ and [Ba(tdfnd)$_2$(diglyme)] [tdfndH = $C_3F_7C(O)CH_2C(O)C_3F_7$ = tetradecafluorononane-4,6-dione], which are liquid at the temperature of use and could be repeatedly transported in the vapour without decomposition, remain the most attractive Ba species for Ba oxide, along with BaF_2.[31]

Experimental Section

All reactions were performed under an inert atmosphere using Schlenk tube techniques. Solvents were dried and purified by distillation. M(thd)$_3$ (M = Y, Pr),[32] Ba_4O(Otamp)$_6$,[19] Ba[N(SiMe$_3$)$_2$]$_2$ [33] and Cu aminoalkoxides[15]were obtained according to literature methods. Ba(OR'N)$_2$ was prepared by alcoholysis of the silylamide. Pr(thd)$_2$(OR^n) was obtained by alcoholysis of Pr silylamide followed by reaction with thdH. ^{1}H- and ^{13}C-NMR, and FT-IR spectra were run with Bruker AC-200 and IR-FTS 45 spectrometers, respectively. IR spectra were obtained as Nujol mulls. ESR spectra were done with a Bruker spectrometer. Analyses were obtained from the Centre de Microanalyses du CNRS. TGA analyses were done under nitrogen with a Setaram system using a temperature ramp of 5 °C/min. FT-IR data are collected in Table 1.

$BaCu(thd)_2(Otamp)_2(H_2O)$ (1): A solution of $[Ba(thd)_2]_4$ (2.80 g, 1.39 mmol) in 20 mL of hexane was added to $Cu(Otamp)_2$ (5.50 mmol) in 20 mL of hexane. The solution turned rapidly from blue to green and was concentrated to dryness after 17 h. The crude solid was recrystallized in diethyl ether at −25 °C (4.90 g, 80%). Compound **1** was very soluble in polar and nonpolar solvents. − $C_{52}H_{92}BaCuN_6O_7$: calcd. C 56.05, H 8.32, Ba 12.33, Cu 5.70; C 56.32, H 8.42, Ba 12.35, Cu 5.70. − ESR (solid, 20 °C): $<g> = 2.14$; $<A> = 106$ G. − TGA (N_2, 1 atm): 95−125 °C (− H_2O), 170−280 °C (− tampOH), 280−400 °C (− thdH), 400−500 °C (− thd), 550−970 − OH, residue 38%. A similar procedure applied to $Cu(thd)_2$ (0.37 g, 0.85 mmol) and $Ba_4O(Otamp)_6$ (0.46 g, 0.2 mmol) gave **1** (0.57 g, 60%).

$MCu_2(thd)_3(OR^n)_4$ [M = Pr (2), Y(3)]: $Pr(thd)_2(OR^n)$ (1.11 g, 1.96 mmol) in 20 mL of hexane was added to $Cu(OR^n)_2$ (0.93 g, 3.88 mmol) in 10 mL of hexane. $Cu(OR^n)_2$ dissolved. Compound **2** was isolated as needles by crystallisation (1.36 g, 63%). − $C_{49}H_{97}Cu_2N_4O_{10}Pr$: calcd. C 50.28, H 8.28, Cu 10.86, N 4.78, Pr 12.04; found C 49.80, H 8.12, Cu 10.92, N 4.84, Pr 12.35. − ESR (hexane, 20 °C): $<g> = 2.12$; $<A> = 79.3$ G. − Crystal data (−100 °C): $a = 9.806(3)$, $b = 19.792(6)$, $c = 31.535(7)$ Å, $\alpha = \beta = \gamma = 90°$. − Same procedure applied to $Y(thd)_3$ (1.06 mmol, 25 mL of hexane) and $Cu(OR^n)_2$ (2.12 mmol, 10 mL of hexane) gave **3** (1.02 g, 87%). − $C_{49}H_{97}Cu_2N_4O_{10}Y$ (***mol. mass?***): calcd. C 52.63, H 8.74, Cu 11.36, N 5.01, Y 7.95; found C 52.66, H 8.7, Cu 10.50, N 4.74, Y 7.50. − ESR (hexane, 20 °C): $<g> = 2.10$; $<A> = 92.4$ G. − TGA (N_2, 1 atm, °C): 155−230 (− 3 × R^NOH), 230−315 (− R^NOH − 2 × thd), 315−470 (− thd), residue 19.5%.

$PrCu(thd)_3(OR)_2$ [R = R^n (4), R^N (5)] and $YCu(thd)_3(OR^N)_2$ (6): Same procedure as for **2** applied to 0.10 g of $Cu(OR^n)_2$ (0.41 mmol) in 5 mL of hexane and $[Pr(thd)_3]_2$ (0.29 g, 0.21 mmol) in 12 mL of hexane gave **4** as needles (0.37 g, 94%). − $C_{41}H_{77}CuN_2O_8Pr$: calcd. C 52.91, H 8.27, Cu 6.80, N 3.00, Pr 15.10; found C 53.88, H 8.31, Cu 6.9, N 3.13, Pr 14.600. − ESR (hexane, 20 °C): $<g> = 2.10$; $<A> = 78.6$ G. − TGA (N_2, 1 atm, °C): 190−235 (− 2 × R^NOH), 235−365 (− 2.5 × thd), 365−550 (− 0.5 × thd), residue 21.8%. − $[Pr(thd)_3]_2$ (0.30 g, 0.21 mmol) in 20 mL of hexane added to $Cu(OR^N)_2$ (0.12 g, 0.43 mmol) in 10 mL of hexane gave **5** (0.38 g, 92%). This could also be obtained from $Pr(thd)_2(OR^N)$ and $Cu(OR^N)_2$ (1:1 stoichiometry), but in lower yield (61%). − $C_{43}H_{81}CuN_2O_8Pr$: calcd. C 53.87, H 8.45, Cu 6.62, N 2.92, Pr 14.69; found C 53.52, H 8.42, Cu 6.95, N 2.72, Pr 15.30. − ESR (hexane, 20 °C): $<g> = 2.18$; $<A> = 86.2$ G. − TGA (N_2, 1 atm): 125−220 °C (− 2 × R^NOH), 220−360 (− 2 × thd), 360−600 (− thd), residue 23%. − $Y(thd)_3$ (0.69 g, 1.08 mmol) in 20 mL of hexane added to $Cu(OR^N)_2$ (0.29 g, 1.08 mmol) in 10 mL of hexane gave **6** (0.87 g, 90%). Compound **6** was also obtained by reacting $Y(thd)_2(OR^N)$ and $Cu(OR^N)_2$ (1:1) in hexane (50%). − $C_{43}H_{81}CuN_2O_8Y$: calcd. C 56.97, H 9.01, Cu 7.01, N 3.09, Y 9.81; found C

Table 4. Crystal data for **1**, **4** and **8**

	1	**4**	**8**
Empirical formula	$C_{52}H_{92}BaCuO_7N_6$	$C_{41}H_{77}CuN_2O_8Pr$	$C_{58}H_{110}O_{10}N_4Y_2$
Molecular mass	1114.2	929.7	1201.3
a [Å]	11.813(5)	16.973(5)	10.606(8)
b [Å]	20.419(7)	19.143(6)	20.511(5)
c [Å]	49.667(15)	30.225(5)	15.522(3)
α [°]	90	90	90
β [°]	90	90	98.27(4)
γ [°]	90	90	90
V [Å^3]	11980(7)	9821(5)	3341(21)
Z	8	8	2
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/n$
Linear absorption coefficient μ [cm^{-1}]	10.5	14.5	17.9
Density ρ [g·cm^{-3}]	1.23	1.26	1.19
Diffractometer	CAD4 − Enraf−Nonius	CAD4 − Enraf−Nonius	CAD4 − Enraf−Nonius
Radiation	Mo-K_α (λ= 0.71069 Å)	Mo-K_α (λ = 0.71069 Å)	Mo-K_α (λ = 0.71069 Å)
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan range [°]	1.0 + 0.345 tgθ	0.80 + 0.345 tgθ	0.80 + 0.345 tgθ
θ limits [°]	2−16	1−23	1−25
Temperature of measurement [°C]	163 K	room temperature	room temperature
Octants collected	h: 0−9; k: 0−15; l: 0−38	h: 0−18; k: 0−21; l: 0−33	h: 0−12; k: 0−24; l: −18−18
Number of data collected	3346	7499	6415
Number of unique data collected	2906	6811	5877
Number of unique data used for refinement	1923 $(F_o)^2 > 3\,\sigma(F_o)^2$	3311 $(F_o)^2 > 3\,\sigma(F_o)^2$	1999 $(F_o)^2 > 2\,\sigma(F_o)^2$
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.060	0.0407	0.0493
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.072, w = 1.0	0.0448, w = 1.0	0.0484, w =1.0
Absorption correction	DIFABS (min = 0.91, max = 1.16)	DIFABS (min = 0.87, max = 1.12)	DIFABS (min = 0.80, max = 1)
Goodness of fit s	3.5	1.8	0.94
Number of variables	280	480	335
$\Delta\rho_{min}$ [e·Å^{-3}]	−0.70	−0.33	−0.36
$\Delta\rho_{max}$ [e·Å^{-3}]	0.64	0.58	0.38

56.76, H 9.06, Cu 7.18, N 3.07, Y 9.97. − ESR (hexane, 20 °C): $<g> = 2.08$; $<A> = 92.4$ G. − Compounds **4**, **5**, and **6** are soluble in hexane, toluene, diethyl ether, and THF, and slightly soluble in diglyme.

Ba(thd)(OR′^{N})(HOR′^{N}) (7): A solution of thdH (0.43 g, 2.34 mmol) in 5 mL of THF was added to a suspension of Ba(OR′^{N})$_2$ (1.07 g, 2.34 mmol) in 35 mL of THF. Rapid dissolution was observed. The solid obtained by concentrating to dryness was recrystallised in hexane to yield compound **7** (1.36 g, 95%). Dist. 120−130 °C/10^{-3} Torr. − Soluble in usual solvents (hexane, toluene, diethyl ether, THF). − $C_{25}H_{54}BaN_4O_4$: calcd. C 49.05, H 8.82, N 9.15; found C 49.03, H 8.85, N 9.10. − ^{1}H NMR (CDCl$_3$, 20 °C): δ = 5.52, 5.47, 5.44 [s, 1 H, CH(thd)], 5.0 (br, 1 H, OH), 3.91 [s, br, 2 H, CH(OR′^{N})], 2.25 (m, 32 H, CH$_2$NMe$_2$), 1.08, 1.06 and 1.02 (s, 18 H, *t*Bu). − ^{13}C{^{1}H} NMR (C$_7$D$_8$, 28 mg/mL, 20 °C): δ = 197.3 (C=O), 88.5 [CH(thd)], 67.1 [CH(OR′^{N})], 66.2 (CH$_2$), 45.9 (NMe$_2$), 41.3 [C(*t*Bu)], 29.5 [Me(*t*Bu)]. − TGA (N$_2$, 1 atm): 120−245 °C (− R′^{N}OH), 245−375 (− R′^{N}OH), 375−970 (decomposition of thd), residue 34%. − Crystal data (20 °C): a = 10.652(2), b = 16.006(2), c = 19.486(3) Å, α = β = 97.03(1)°, γ = 90°.

[Y(thd)$_2$(OR′^{N})]$_2$ (8): Y(thd)$_3$ (1.24 g 1.94 mmol) in 35 mL of hexane was added to a suspension of Ba(OR′^{N})$_2$ (1.94 mmol, 0.83 g) in 25 mL of hexane. Ba(OR′^{N})$_2$ dissolved after 15 min. Compound **8** was isolated by crystallisation (1.11 g, 96%). It sublimes at 215−220 °C/10^{-3} Torr and is only slightly soluble even in polar solvents (acetonitrile, acetone, THF). − Compound **8** could also be obtained from Ba(thd)(OR′^{N})(HOR′^{N}) (0.15 mmol) and Y(thd)$_3$ (0.15 mmol) in 15 mL of hexane (80 mg, 90%). − $C_{58}H_{110}N_4O_{10}Y_2$: calcd. C 57.99, H 9.23, N 4.66; found C 57.22, H 9.01, N 4.50. − ^{1}H NMR (CDCl$_3$, 20 °C): δ = 5.67, 5.59 [s, 4 H, CH(thd)], 4.48 (m, J = 10.9 Hz), 4.21 (quint, J = 5.6 Hz), 3.67 [sept, J = 4.1 Hz, 2 H, CH (OR′^{N}, R′^{N}OH)], 3.67 [s, br, OH (R′^{N}OH)], 2.9, 1.9 (32 H, CH$_2$NMe$_2$), 1.09, 1.05 (s, 72 H, *t*Bu). − TGA (1 atm): sublimation between 225−400 °C.

X-ray Structure Determination for 1, 4, and 8: Suitable crystals were obtained from the reaction medium for **1** and **8**, and by recrystallisation in Et$_2$O for **4**, and were mounted onto an Enraf−Nonius CAD-4 automatic diffractometer. The unit cell parameters and basic information about data collection and structure refinement are given in Table 4. Accurate lattice parameters and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-centred reflections. The intensities of two standard reflections monitored every hour showed no decay. Corrections for Lorentz and polarization effects were applied. Computations were performed using the PC version of CRYSTALS.[34] Scattering factors and corrections for anomalous dispersion were taken from ref.[35] Structures were solved using direct methods (SHELXS)[36] and standard Fourier techniques. All non-hydrogen atoms were refined anisotropically for **4** and **8**, and only Ba and Cu were anisotropically refined for **1**, in view of the limited number of data. In addition, only a partial structure report will be given. Hydrogen atoms were calculated and included as fixed contributors in the last refinement. Models converged for the R and R_w values in Table 4. Tables of atomic coordinates, of thermal parameters, of non-essential bond lengths and angles for the structures reported have been deposited at Cambridge Crystallographic Data Centre. CCDC reference numbers for **1**, **4**, and **8**: 137676, 137675, and 101724. Copies of the data are available free of charge on application to CCDC 12 Union Road Cambridge CB2 IEZ, UK [Fax: (internat.) + 44-1223/336-033].

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