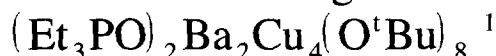


A heterometallic alkoxide combining hard and soft Lewis acids



Björn Borup, John C. Huffman, Kenneth G. Caulton *

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405-4001, USA

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Abstract

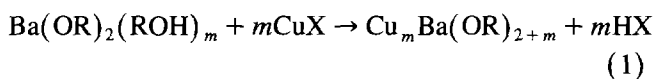
Reaction of copper(I) mesityl with $[\text{Ba}(\text{O}^t\text{Bu})_2(^t\text{BuOH})_2]_4$ occurs with 'replacement' of all protons by copper to give an insoluble solid of empirical formula $\text{BaCu}_2(\text{O}^t\text{Bu})_4$. This reacts with Et_3PO to give a soluble product characterized by spectroscopic, combustion analytical, and X-ray diffraction as $(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$, an elongated octahedron (*trans* Ba_2) with O^tBu groups doubly bridging eight edges. The phosphine oxide has broken up an apparent polymer by coordination of one Et_3PO to each barium. © 1997 Elsevier Science S.A.

Keywords: Barium; X-ray diffraction; Copper; Alkoxide

1. Introduction

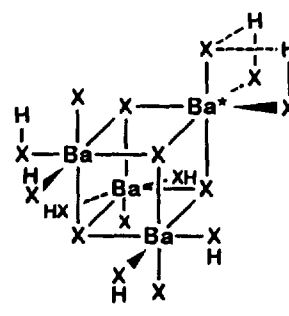
The molecular precursor approach to the production of complex oxide materials like $\text{YBa}_2\text{Cu}_3\text{O}_7$ from a single alkoxide precursor (e.g. $\text{YBa}_2\text{Cu}_3(\text{OR})_{14}$) requires sophisticated synthetic control to produce the required ternary metal alkoxides. Relying on inherent Lewis acidity of $\text{Y}(\text{OR})_3$, $\text{Ba}(\text{OR})_2$ and $\text{Cu}(\text{OR})_n$ to assemble the necessary 1:2:3 stoichiometry into a single aggregate is a daunting task, in part because many of the binary alkoxides $\text{M}(\text{OR})_p$ are insoluble polymers for large metals, and even for copper(II).

A second synthetic method involves reaction of a soluble alcohol adduct of $\text{Y}(\text{OR})_3$ or $\text{Ba}(\text{OR})_2$ with a copper compound carrying an acid-sensitive anionic ligand X (Eq. (1)). The proton transfer provides the favorable thermodynamics, and the m stoichiometry 'guides' the reaction selectively to a single product.



We have earlier reported the synthesis and characterization of $\text{Ba}(\text{O}^t\text{Bu})_2(^t\text{BuOH})_2$ [1] as a cubane tetramer

with four μ_3 - O^tBu groups, and four terminal O^tBu groups, each involved in hydrogen bonding to two hydroxyl protons of alcohol molecules, bound to the same Ba as the terminal O^tBu group (I, where the hydrogen bonding is drawn only at Ba^* , for simplicity, and $\text{X} = \text{O}^t\text{Bu}$). We describe here the results of trying to 'replace' these hydroxylic protons by Cu(I).



2. Experimental

All manipulations were carried out under inert atmosphere (argon, nitrogen) or in vacuo using standard Schlenk techniques. All solvents were purchased from

* Corresponding author.

¹ Especially in recent years, Yuri Struchkov developed an interest in and influence on metal alkoxide chemistry. This paper is dedicated to the memory of this extraordinary scientist.

Fischer Scientific and dried over alkali metal/benzophenone. They were distilled and stored under nitrogen/argon. In reactions involving copper(I), the solvents were degassed in three consecutive freeze-pump-thaw cycles. Barium metal was purchased from Alfa/Aesar chemicals and stored in a glove-box under argon. Hexamethyldisilazane was purchased from Janssen Chimica and Aldrich, PEt_3 was purchased from Strem, and all other reagents from Aldrich. The starting materials $\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ [2] and copper mesityl (CuMes) [3,4] were synthesized according to literature methods. Elemental analyses were performed by Desert Analytics or in-house using a Perkin–Elmer PE2400 CHN/S Elemental Analyzer. Copper analyses were done by iodometry. A *tert*-butanol/heptane azeotrope was prepared by refluxing the mixture over calcium hydride and distilling under 1 atm nitrogen, resulting in a concentration of 5.4 M determined by ^1H NMR.

2.1. Synthesis of OPEt_3

To 40 ml of acetone, 2.0 ml (21 mmol) of PEt_3 was added via syringe. To this solution, 4 ml of 30% H_2O_2 was added slowly. The solution was stirred for 5 h and then most of the acetone was removed in vacuo, leaving about 8 ml of solution. About 20 ml of water and 0.5 g of MnO_2 were added, and after 2 h the MnO_2 was removed via filtration and the solution was extracted three times with CHCl_3 . The combined organic fractions were dried with MgSO_4 and the solvent was removed in vacuo to yield a yellowish oil. This oil was distilled at 30°C (10^{-2} Torr) to yield 1.6 g of a colorless solid (86%), m.p. $50\text{--}52^\circ\text{C}$. ^{31}P NMR (CHCl_3): 55.8 ppm.

2.2. Synthesis of $[\text{BaCu}_2(\text{O}^t\text{Bu})_4]_x$

A Schlenk flask was charged with 5.0 g (8.3 mmol) of $\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ and 40 ml of pentane was added. To this suspension, 4.0 ml (22 mmol) of 5.4 M *tert*-butanol azeotrope was added via syringe. After 2 h of stirring, all volatiles were removed in vacuo. To the resulting white solid, 30 ml of pentane and 3.5 ml (19 mmol) of 5.4 M *tert*-butanol azeotrope were added. To the colorless solution, 3.1 g (17 mmol) of copper mesityl was added via solid addition tube. Within 20 min, the color of this slightly yellow suspension had turned orange. After 4 h, the orange color had disappeared and a white precipitate was left. The solvent was decanted and the solid was washed twice with diethyl ether yielding 4.6 g of white solid (99%, based on barium). Anal. Found: Cu, 22.3; C, 34.28; H, 6.55. $\text{BaCu}_2\text{O}_4\text{C}_{16}\text{H}_{36}$ Calc.: Cu, 22.8; C, 34.51; H, 6.52%.

2.3. Synthesis of $(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$

To a suspension of 800 mg (1.4 mmol) of $[\text{BaCu}_2(\text{O}^t\text{Bu})_4]_x$ in 30 ml of THF, 200 mg (1.5 mmol)

Table 1

Crystallographic data for $(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8 \cdot 0.5$ toluene \cdot 1.5 THF

formula $\text{C}_{55}\text{H}_{121}\text{O}_{10}\text{P}_2\text{Cu}_4\text{Ba}_2$	FW = 1533.37 g mol^{-1}
$a = 18.800(5) \text{ \AA}$	space group $P\bar{1}$
$b = 25.535(7) \text{ \AA}$	$T = -168^\circ\text{C}$
$c = 17.591(6) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}^a$
$\alpha = 107.71(1)^\circ$	$\rho_{\text{calc}} = 1.356 \text{ g cm}^{-3}$
$\beta = 94.01(1)^\circ$	$\mu = 22.3 \text{ cm}^{-1}$
$\gamma = 69.12(1)^\circ$	unique reflections 19592
$V = 7509.21 \text{ \AA}^3$	reflections with $F > 2.336(F)$ 11033
$Z = 4$	$R(F_o) = 0.0780^b$
	$R_w(F_o) = 0.0725^c$

^a Graphite monochromator.

^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

of OPEt_3 was added via solid addition tube. After 4 h of stirring, the solvent was removed in vacuo and the solid extracted with toluene. Crystallization from toluene resulted in 540 mg (55%) of beige crystals. ^{31}P NMR (C_6D_6): 55.3 ppm. ^1H NMR (C_6D_6): ^tBu , 1.80 (s, 72H), OPCH_2CH_3 (m, 18H) 0.67, OPCH_2CH_3 (m, 12H) 1.02 ppm. Anal. Found: C, 39.21; H, 7.42. $\text{Ba}_2\text{Cu}_4\text{P}_2\text{O}_{10}\text{H}_{102}$ Calc.: C, 38.24; H, 7.44%.

2.4. X-ray structure determination

The sample tended to decompose rapidly when warmed to room temperature, and was therefore stored and handled at low temperature. At no time during the handling of the crystals was the temperature allowed to go above 0°C . After transferring to the goniostat, a systematic search of a limited hemisphere of reciprocal space was used to determine that no symmetry or systematic absences were present. Based on the size of the resulting triclinic cell (Table 1), $Z = 4$ was assumed for the suggested structure. Subsequent solution and refinement confirmed the triclinic cell and Z value. The

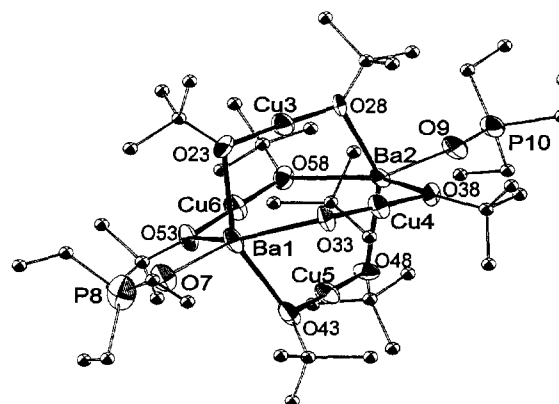


Fig. 1. ORTEP view of the non-hydrogen atoms of one molecule of $(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$ showing selected atom labeling. Unlabeled atoms are carbons.

data were collected ($6^\circ < 2\theta < 45^\circ$) using a standard moving-crystal/moving-detector technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged. Initial attempts to solve the structure showed two independent octahedral fragments which correspond to Ba_2Cu_4 clusters. Subsequent

least-squares and Fourier maps revealed the remainder of the two independent molecules, as well as three THF and one toluene molecules incorporated in the lattice. All non-solvent hydrogen atoms were placed in fixed idealized positions for the final cycles of refinement. A final difference Fourier was featureless, the largest peaks (ca. $2.0 \text{ e } \text{\AA}^{-3}$) lying at the barium positions. The results

Table 2
Selected bond distances (\AA) and degrees ($^\circ$) for $(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$

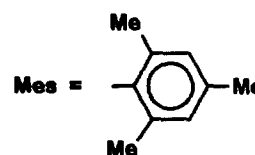
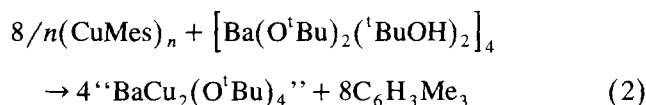
Cu(3)	O(23)	1.832(12)	P(72)	O(71)	1.484(11)		
Cu(3)	O(28)	1.798(12)	Ba(1)	O(7)	2.635(13)		
Cu(4)	O(33)	1.802(11)	Ba(1)	O(23)	2.604(11)		
Cu(4)	O(38)	1.796(11)	Ba(1)	O(33)	2.589(7)		
Cu(5)	O(43)	1.832(11)	Ba(1)	O(43)	2.563(8)		
Cu(5)	O(48)	1.819(10)	Ba(1)	O(53)	2.601(3)		
Cu(6)	O(53)	1.830(12)	Ba(2)	O(9)	2.613(11)		
Cu(6)	O(58)	1.813(13)	Ba(2)	O(28)	2.603(7)		
Cu(65)	O(85)	1.814(9)	Ba(2)	O(38)	2.622(5)		
Cu(65)	O(90)	1.812(9)	Ba(2)	O(48)	2.622(11)		
Cu(66)	O(95)	1.794(8)	Ba(2)	O(58)	2.601(7)		
Cu(66)	O(100)	1.805(8)	Ba(63)	O(69)	2.651(10)		
Cu(67)	O(105)	1.824(10)	Ba(63)	O(85)	2.608(14)		
Cu(67)	O(110)	1.838(9)	Ba(63)	O(95)	2.589(6)		
Cu(68)	O(115)	1.830(11)	Ba(63)	O(105)	2.622(15)		
Cu(68)	O(120)	1.838(9)	Ba(63)	O(115)	2.625(5)		
P(8)	O(7)	1.485(13)	Ba(64)	O(71)	2.630(10)		
P(10)	O(9)	1.505(12)	Ba(64)	O(90)	2.623(10)		
P(70)	O(69)	1.477(11)	Ba(64)	O(100)	2.610(7)		
Ba(64)	O(110)	2.613(14)	Ba(63)	Cu(68)	3.5792(20)		
Ba(64)	O(120)	2.581(8)	Ba(64)	Cu(65)	3.5871(20)		
Ba(1)	Cu(3)	3.599(3)	Ba(64)	Cu(66)	3.6594(19)		
Ba(1)	Cu(4)	3.6355(24)	Ba(64)	Cu(67)	3.615(3)		
Ba(1)	Cu(5)	3.5536(18)	Ba(64)	Cu(68)	3.6128(21)		
Ba(1)	Cu(6)	3.6439(20)	Cu(3)	Cu(4)	3.4336(27)		
Ba(2)	Cu(3)	3.6544(18)	Cu(3)	Cu(6)	3.4921(19)		
Ba(2)	Cu(4)	3.5911(19)	Cu(4)	Cu(5)	3.5514(20)		
Ba(2)	Cu(5)	3.648(3)	Cu(66)	Cu(67)	3.6157(21)		
Ba(2)	Cu(6)	3.5884(24)	Cu(67)	Cu(68)	3.500(4)		
Ba(63)	Cu(65)	3.616(3)	Cu(5)	Cu(6)	3.4603(27)		
Ba(63)	Cu(66)	3.5570(21)	Cu(65)	Cu(66)	3.429(4)		
Ba(63)	Cu(67)	3.6046(23)	Cu(65)	Cu(68)	3.4692(20)		
O(23)	Cu(3)	O(28)	177.08(28)	Cu(3)	O(23)	C(24)	120.4(13)
O(33)	Cu(4)	O(38)	178.78(17)	Cu(3)	O(28)	C(29)	119.3(6)
O(43)	Cu(5)	O(48)	177.8(3)	Cu(4)	O(33)	C(34)	121.0(10)
O(53)	Cu(6)	O(58)	178.6(3)	Cu(4)	O(38)	C(39)	121.4(9)
O(85)	Cu(65)	O(90)	178.58(24)	Cu(5)	O(43)	C(44)	118.3(8)
O(95)	Cu(66)	O(100)	176.14(22)	Cu(5)	O(48)	C(49)	120.9(11)
O(105)	Cu(67)	O(110)	178.19(26)	Cu(6)	O(53)	C(54)	120.7(6)
O(115)	Cu(68)	O(120)	178.6(6)	Cu(6)	O(58)	C(59)	119.1(9)
Cu(65)	O(85)	C(86)	121.9(12)	O(9)	Ba(2)	O(28)	110.7(4)
Cu(65)	O(90)	C(91)	122.6(6)	O(9)	Ba(2)	O(38)	107.49(27)
Cu(6)	O(95)	C(96)	120.1(8)	O(9)	Ba(2)	O(48)	110.16(28)
Cu(66)	O(100)	C(101)	120.7(8)	O(9)	Ba(2)	O(58)	109.31(27)
Cu(67)	O(105)	C(106)	121.3(10)	O(69)	Ba(63)	O(85)	110.5(4)
Cu(67)	O(110)	C(111)	121.1(12)	O(69)	Ba(63)	O(95)	105.64(22)
Cu(68)	O(115)	C(116)	119.7(6)	O(69)	Ba(63)	O(105)	106.8(5)
Cu(68)	O(120)	C(121)	118.7(8)	O(69)	Ba(63)	O(115)	109.64(26)
O(7)	Ba(1)	O(23)	111.9(3)	O(71)	Ba(64)	O(90)	109.3(4)
O(7)	Ba(1)	O(33)	109.34(25)	O(71)	Ba(64)	O(100)	110.10(28)
O(7)	Ba(1)	O(43)	103.9(4)	O(71)	Ba(64)	O(110)	106.7(4)
O(7)	Ba(1)	O(53)	110.49(28)	O(71)	Ba(64)	O(120)	109.43(27)
Ba(1)	O(7)	P(8)	173.1(7)	Ba(63)	O(69)	P(70)	170.3(10)
Ba(2)	O(9)	P(10)	173.9(5)	Ba(64)	O(71)	P(72)	175.1(6)

of the structure determination are shown in Table 2 and Fig. 1. Atom coordinates, thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

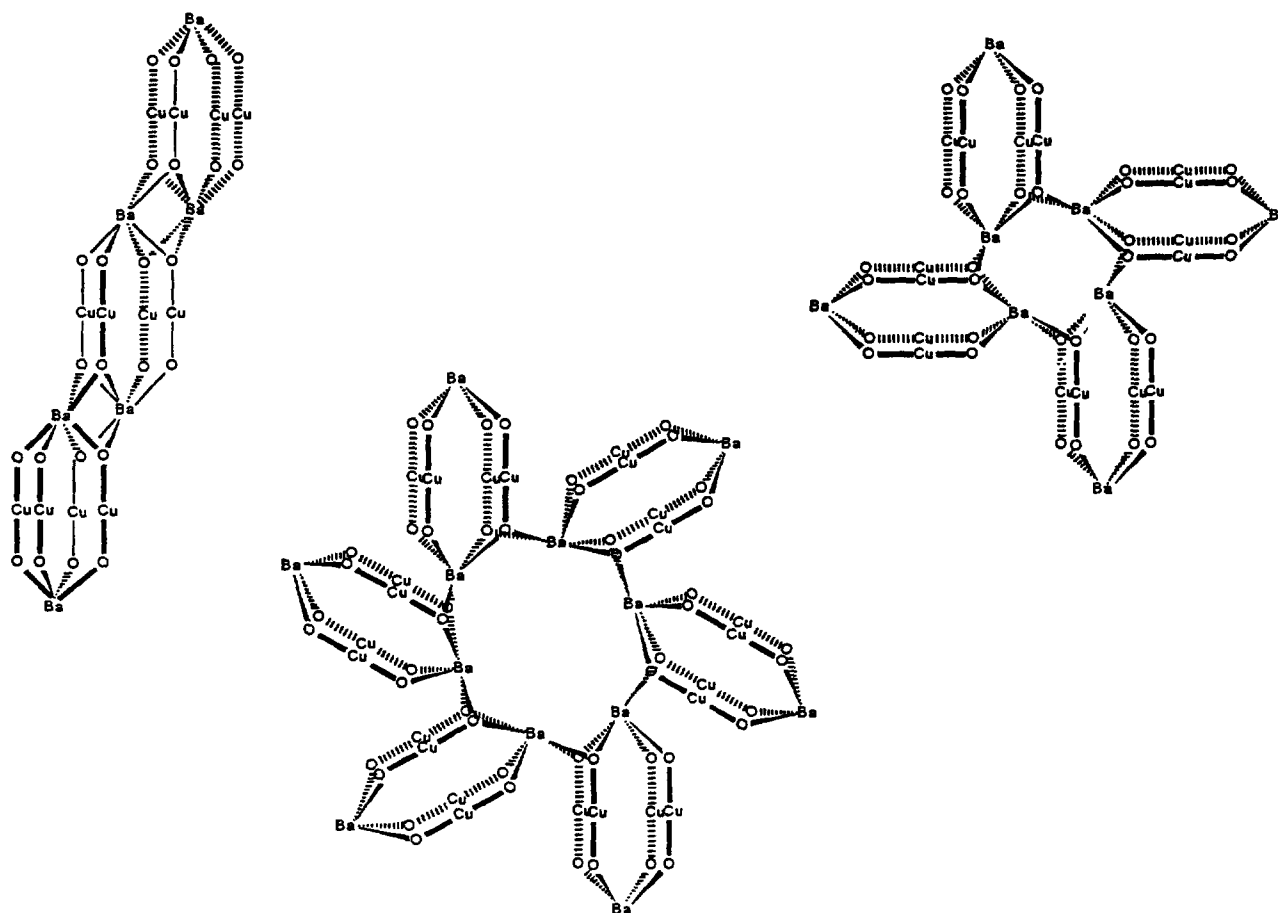
3. Results

Copper(I) mesityl was chosen as a very acid-sensitive (but also very O₂-sensitive) source of copper for use in Eq. (1). It is hydrocarbon-soluble. While the degree of aggregation of copper mesityl is not known with certainty (¹H NMR signals in toluene-*d*₈ or cyclohexane-*d*₁₂ have been assigned to dimer and pentamer) [4], this is of no consequence to the synthesis in Eq. (2), since all Cu–C bonds present are very proton-sensitive. The synthetic reaction in Eq. (2) is complete in 4 h at 25 °C, and the product precipitates. The product is insoluble in all hydrocarbons, as well as in Et₂O, THF, and 1,2-dimethoxyethane. We suspected a polymeric structure and attempted to cleave some of the alkoxide bridges with Lewis bases, but the solid is not dissolved by pyridine. Also, the addition of even excess OPPh₃, HO^tBu (which dissolves Ba(O^tBu)₂), TMEDA, THF,

PEt₃, PPh₃, pyridine N-oxide, 18-crown-6, and ethylene carbonate to a THF suspension did not dissolve the polymer. We focused on furnishing a still harder Lewis base which would coordinate to barium, and found that Et₃PO dissolves the solid in THF. The resulting compound, “(Et₃PO)BaCu₂(O^tBu)₄”, is soluble in toluene. ¹H NMR spectroscopic studies in C₆D₆ showed a ratio of 6:8 for Et to ^tBu groups. ³¹P NMR showed a singlet at 55.3 ppm.



Crystals grown from toluene/THF by cooling were shown by X-ray diffraction to be composed of



Scheme 1.

$(\text{Et}_3\text{PO})_2\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$ molecules with a Fabergé egg shape. The unit cell contains two crystallographically-independent hexametal molecules. The central $(\text{O})_2\text{Ba}_2\text{Cu}_4(\text{O})_8$ unit has idealized C_4 symmetry, with all alkoxides doubly bridging (between Cu and Ba) and the phosphine oxide terminal on Ba. This gives a square-pyramidal five-coordinate geometry to Ba and a linear two-coordinate geometry to copper. This latter is very commonly found for Cu(I) in the presence of bulky ligands. For instance, $(\text{Cu}^t\text{O}^t\text{Bu})_4$ shows linear coordination of the copper center [5].

Another way to view this structure is as a *trans* disubstituted M_6 octahedron, with eight of the 12 edges carrying μ_2 - O^tBu ligands. The two barium apices are the only ones carrying terminal ligands. In this way, there is some vague similarity to the many M_6 octahedra. $\text{K}_4\text{Zr}_2(\mu_6\text{-O})(\text{O}^i\text{Pr})_{10}$ is a heterometallic example with *trans* Zr. In the (nearly perfect) Ba_2Cu_4 octahedron, Ba/Cu separations range from 3.55 to 3.66 Å and Cu/Cu separations range from 3.43 to 3.55 Å.

The geometry around each Cu(I) is within 3° of linear, so that this molecule can be viewed as two $\text{Et}_3\text{POBa}^{2+}$ electrophiles connected by four rod-shaped $\text{Cu}(\text{O}^t\text{Bu})_2^-$ ions. The μ_2 -alkoxides are consistently slightly non-planar at oxygen: the sum of angles around oxygen ranges from 354.0 to 358.2°. Overall the molecule is not only non-polar, but covered entirely by alkyl groups. The (square-pyramidal) (P)O–Ba–O(^tBu) angles range from 103.9(3) to 111.9(3)° and the P–O–Ba angles range from 170.3(10) to 175.1(6)°. The near-linearity at the Et_3PO oxygen suggests a significant electrostatic, not dative, character to the interaction with barium.

4. Discussion

The protonolysis synthetic procedure was successful in controlling the product metal stoichiometry according

to the available protons: the 2:1 $\text{H}^+:\text{Ba}$ stoichiometry in the reagent gives a 2:1 Cu:Ba product stoichiometry. With an empirical formula $\text{BaCu}_2(\text{O}^t\text{Bu})_4$ (i.e. with only four anions for three cations) it is clear that aggregation is required to give each metal an 'acceptable' coordination number. While Cu(I) can tolerate coordination number 2 (consider the isoelectronic monomeric Zn(II) alkyl ZnEt_2), the very large barium is more greedy. This is presumably why $\text{BaCu}_2(\text{O}^t\text{Bu})_4$ is wholly insoluble in all common solvents: a polymeric network is formed to increase the coordination number of barium.

While many Lewis bases fail to react with and solubilize $\text{BaCu}_2(\text{O}^t\text{Bu})_4$, the oxygen-basic Et_3PO is successful, and only one such ligand per Ba suffices. Given the structure of the product reported here, it is attractive to imagine that the polymer is made up of $\text{Ba}_2\text{Cu}_4(\text{O}^t\text{Bu})_8$ repeat units. A variety of ways of linking these repeat units can be envisioned (Scheme 1).

Acknowledgements

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