UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

FACULTAD DE QUÍMICA

MONOMERIC, OLIGOMERIC, AND POLYMERIC COPPER(II)
COMPLEXES OF CALIX[4]ARENE-DERIVED LIGANDS

ACTIVIDAD DE INVESTIGACIÓN

QUE PARA OBTENER EL TÍTULO DE

QUÍMICO DE ALIMENTOS

PRESENTA

JOSÉ LUIS MARTÍNEZ MARTÍNEZ

MÉXICO, D.F.   2010

JURADO ASIGNADO:

PRESIDENTE:	Profesor	José Manuel Méndez Stivalet
VOCAL:	Profesor	Ivan Castillo Pérez
SECRETARIO:	Profesor	Arturo Navarro Ocaña
1er SUPLENTE:	Profesor	Agustín Reyo Herrera
2° SUPLENTE:	Profesor	Francisco Ruiz Terán

SITIO DONDE SE DESARROLLÓ EL TEMA:

Laboratorio 4C, Instituto de Química, UNAM.

ASESOR DEL TEMA:
_____
Dr. Ivan Castillo Pérez

SUSTENTANTE:
_____
José Luis Martínez Martínez

AGRADECIMIENTOS

*Al **Dr. Ivan Castillo Pérez** por permitirme formar parte de su equipo de trabajo; por el apoyo y enseñanzas brindadas durante el desarrollo de este trabajo. Gracias por su amistad.*

*Al **Dr. Rubén A. Toscano** por el trabajo de cristalografía.*

*A la **M. en C. Virginia Gómez Vidales** por las mediciones de RPE.*

*A la **Universidad Nacional Autónoma de México** por brindarme un espacio en la máxima casa de estudios, y proporcionarme las herramientas necesarias para formarme profesionalmente.*

DEDICATORIAS

A mis padres

Por brindarme todo el apoyo y comprensión.

Por todas sus enseñanzas y sacrificios.

Por estar siempre a mi lado.

Por dejarme alcanzar mis metas y sueños.

Especialmente por confiar en mí.

Los amo.

Gracias.

A mi esposa e hija Lizzeth y Yaretzi

Por el apoyo incondicional.

Por estar presentes en mis pensamientos.

Por los grandiosos momentos.

Por tolerar mis ausencias.

Por creer en mí.

Las amo.

A mis hermanos Adriana, Alejandro y Roberto Carlos

Por estar a mi lado en todo momento, apoyándonos el uno al otro para salir adelante y saber que no hay trago amargo cuando estamos juntos, gracias, los amo

ÍNDICE   **PÁGINA**

1. INTRODUCCIÓN

Entre los campos emergentes de la química moderna se encuentra el estudio de los "ensambles moleculares y el enlace intermolecular" o química supramolecular, según la definición de Jean-Marie Lehn.[1,2] La importancia de ésta rama de la química, que va mas allá de las dimensiones de la molécula convencional, radica en que su campo de estudio se extiende hacia otras disciplinas tales como la biología molecular y la ciencia de materiales.[3,4] Un ejemplo de esto es el crecimiento acelerado de la química bioinorgánica, mismo que ha permitido esclarecer dudas relacionadas con el funcionamiento de las metaloproteínas; además, como resultado de tratar de crear sistemas modelo para el estudio de sistemas bioinorgánicos complejos, se han sintetizado catalizadores más eficientes. En el caso de la ciencia de materiales el crecimiento se ha dado en la química supramolecular, ya que el entendimiento de las fuerzas débiles permitirá diseñar materiales con propiedades específicas.

Un sistema modelo idóneo que permite crear tanto sistemas modelo para el estudio de metaloproteínas, así como bloques constructores para sistemas supramoleculares es el de los calixarenos. Los calix[4]arenos (C4) en particular son sistemas bien conocidos, tanto en su reactividad como en síntesis,[5] lo que los hace buenos candidatos para desarrollar ambos tipos de sistemas. A pesar de sus altos pesos moleculares, las rutas sintéticas de derivados de dichos macrociclos están muy bien definidas,[5] además de poderse encontrar comercialmente. Una de las cualidades que poseen este tipo de moléculas es la de contar con una cavidad hidrofóbica, la cual permite recrear el sitio activo de algunas enzimas, ya que se sabe que en ciertos casos el sitio activo es también hidrofóbico. Aunado a esto, la introducción de sustituyentes con grupos donadores similares a los encontrados en las esferas de coordinación de las metaloenzimas es relativamente fácil. En concreto, la simulación de la enzima metano monooxigenasa, misma que es responsable de la transformación de metano en metanol como fuente principal de energía en bacterias metanotróficas, requiere de los metales de transición Fe ó Cu.[6,7] En ambos tipos de enzimas los centros metálicos se encuentran unidos a átomos de nitrógeno provenientes de grupos imidazol de histidinas, así como a átomos de oxígeno de grupos carboxilatos (Figura 1). Es por esto

que al tratar de funcionalizar al C4 con sustituyentes con donadores nitrogenados con hibridación sp^2, así como con grupos carboxílicos, podría aportar ligantes con potencial de simular dicha enzima.
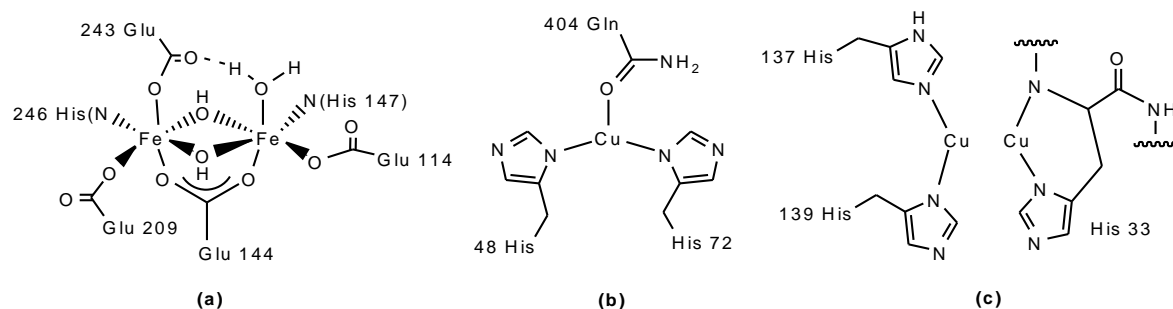

Figura 1. Sitios activos de las metano monooxigenasas dependientes de (a) Hierro en su forma oxidada, (b) Cobre – sitio mononuclear y (c) Cobre – sitio binuclear.

Adicionalmente, estos ligantes pueden ser empleados con bloques constructores en química supramolecular, ya que gracias al arreglo geométrico predefinido del C4 se podrá tener de uno a cuatro sitios de interacción (Figura 2). En el caso de un ligante monodentado, esté permitirá la interacción simple metal-ligante; en el caso de la disustitución permitirá crear arquitecturas unidimensionales lineales; en los casos de los C4 tri y tetrasistituidos, se favorecerá la obtención de redes tridimensionales.
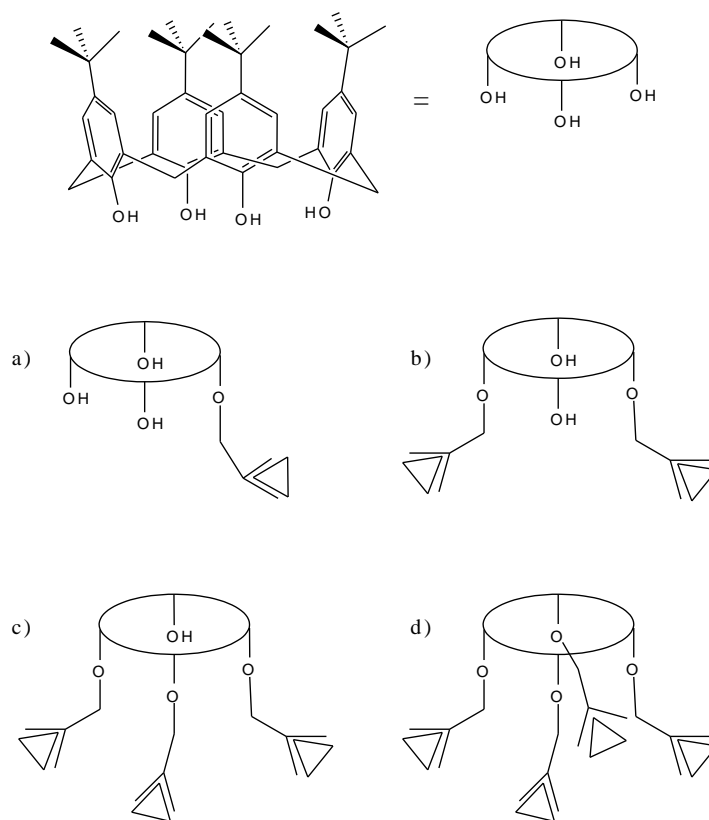
Figura 2. Bloques constructores derivados de calix[4]areno. a) unidimensional, b) lineal, c) y d) bloques con posibilidad de formar redes tridimensionales.

Por las razones anteriormente expuestas, los derivados del C4 permitirán el estudio de diversas áreas de la química, tales como la supramolecular,[8,9] la bioinorgánica,[10] y la catálisis.[10] En síntesis, este trabajo plantea la preparación de diversos ligantes derivados del *p*-terbutilcalix[4]areno; dichos derivados permitirán sintetizar compuestos de coordinación de cobre(II). Estos compuestos serán potencialmente activos en catálisis, ya que se ha observado que los complejos de cobre y C4 presentan actividad catalítica en la transferencia de electrones.[11,12] Dadas las características estructurales de dichos compuestos, estos permitirán asimismo el estudio de nuevos sistemas supramoleculares mediante la inclusión de diversos sustratos en la cavidad de los derivados del C4.

2. OBJETIVOS

- Sintetizar y caracterizar los derivados de calix[4]areno con grupos picolilo.
- Sintetizar y caracterizar compuestos de coordinación de cobre(II) con dichos ligantes.
- Analizar el potencial de dichos ligantes como tectónes moleculares, así como analizar las arquitecturas obtenidas en los compuestos de coordinación en los casos que sea posible obtener estructuras cristalinas.

3. MATERIALES

Los reactivos y solventes fueron obtenidos de los proveedores comerciales y se utilizaron como se han recibido. THF, MeOH, EtOH, se secaron mediante destilación sobre Na. Los espectros de Resonancia Magnética nuclear de protón (RMN^{1}H) y carbono 13 (^{13}C) se obtuvieron con un espectrómetro JEOL Eclipse 300. Los espectros de infrarrojo se obtuvieron con un espectrómetro Perkin-Elmer 203-B en la región espectral comprendida entre 4000 y 400 cm^{-1} en pastillas de KBr. Los análisis elementales se realizaron en el laboratorio de microanálisis del Instituto de Química.

4. METODOLOGÍA

En nuestro grupo de investigación, inicialmente llevamos a cabo la síntesis de nuevos derivados de los C4, ampliando así la gama de tectónes disponibles con grupos funcionales variados y con cavidades de diferentes dimensiones. Las rutas sintéticas para obtener los derivados disustituidos en las posiciones fenólicas alternadas son conocidas desde hace varios años. El método general de síntesis es una variante de la síntesis de éteres de Williamson, en el cual el halogenuro de arilo deseado es introducido en la mezcla de reacción con *p*-terbutilcalix[4]areno y un exceso de carbonato de potasio como base. De esta manera se prepararan compuestos que han sido reportados previamente y algunos de nueva síntesis.
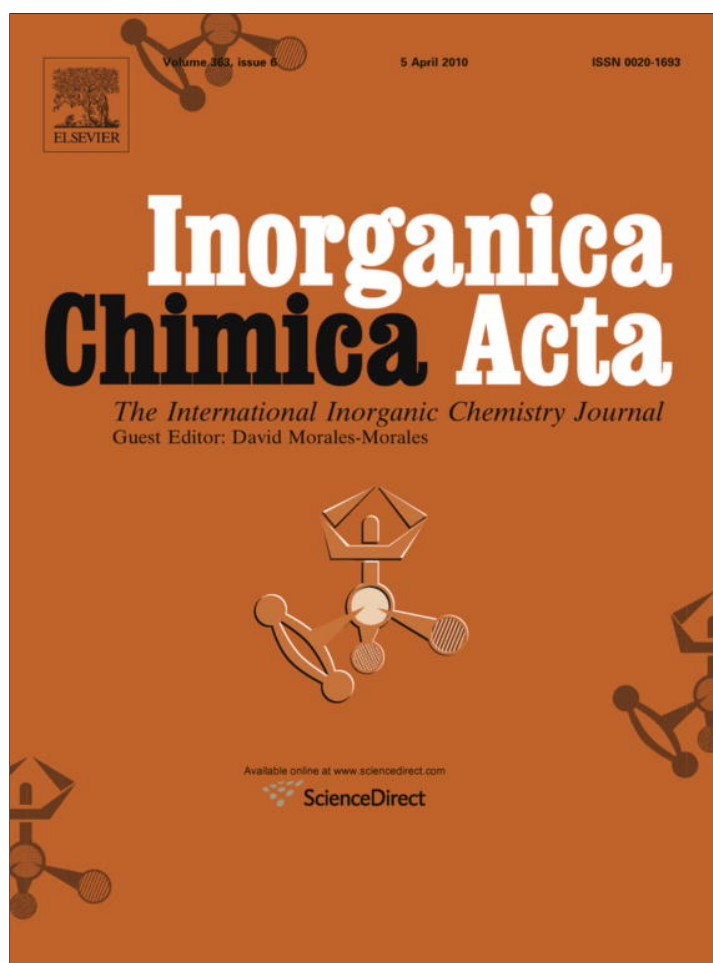
Por ejemplo, el uso de clorometilpiridina en diferentes proporciones estequiométricas permite la obtención de derivados con donadores nitrogenados, entre

ellos el bispicolil-calix[4]areno. Este permitirá la introducción de metales de interés como el Cu^{2+}, lo cual se realizará con diferentes sales de cobre, por ejemplo cloruro de cobre, perclorato de cobre, entre otras. Estos compuestos serán caracterizados por espectroscopia de infrarrojo, UV-visible, espectrometría de masas, resonancia paramagnética electrónica (RPE) y en los casos en los que sea posible por difracción de rayos-X.

5. BIBLIOGRAFÍA

[1] (a) Comprehensive Supramolecular Chemistry, Vols. 1-11; Lehn, J.M., Atwood, J.L., Davis, J.E.D., MacNicol, D.D., Vögtle, F., Eds. Pergamon: Oxford, 1990-1996. (b) Supramolecular Chemistry: Concepts and Perspectives; Lehn J.M., VCH: Weinheim, 1995. (c) Supramolecular Chemistry; Steed, J. W., Atwood, J.L. John Wiley: New York, 2000.

[2] (a) Crystal Enginneering: From Molecule and Crystal to Materials, A NATO Advanced Study Institute and a Euroconference, Vol. 538; Braga, B., Grepioni, F., Orpen, A. G., Eds Kluwer: Dordrecht, 1999. (b) Moulton, B., Zaworotko, M. J. Chem. Rev.**2001**, (101), 1629. (c) Desiraju, G.R. Acc. Chem. Res. **2002**, (35), 565.

[3] (a) Whitesides, G. M., Mathias J. P., Seto, C. T. Science **1991**,(254), 1312. (b) Manners, I. J. Polym. Sci. A. **2002**,(40), 179.

[4] Molecular Biology of the Cell; Alberts, B., et al. Garland: New York, 2002**.**

[5] (a) Gutsche, C. D. Calixarenes: Royal Society of Chemistry: London 1989. (b) Gutsche, C. D. Calixarenes Revisited, Royal Society of Chemistry: Cambridge; 1998.

[6] Lieberman R. L., Rosenzweig A. C., Nature **2005**, (434), 177.

[7] Merkx M., Koop D. A., Sazinsky M. H., Blazyk J. L., Lippard S. J., Angew. Chem. Int Ed., **2001**, (40), 2782.

[8] Hosseini M. W., Acc. Chem. Res., **2005**, (38), 313.

[9] Hosseini M. W., De Cian A., Chem Commun., **2005**, 5603.

[10] Jeunesse C., Armspach D., J. Org. Chem., **1998**, (27), 89.

[11] Gutche D.C., Xie D., J. Org. Chem., **1998**, (63) 9270.

[12] (a) Molenveld P., Engbersen J.F.J., Kooijman H., Spek A.L. Reinhoudt D.N., J. Am. Chem. Soc., **1998**, (120), 6726. (b) Molenveld P., Engbersen J.F.J., Reinhoudt D.N., J. Org. Chem., **1999**, (64), 6337.

Volume 363, issue 6   5 April 2010   ISSN 0020-1693

ELSEVIER

Inorganica Chimica Acta

The International Inorganic Chemistry Journal
Guest Editor: David Morales-Morales

Available online at www.sciencedirect.com
ScienceDirect

Monomeric, oligomeric, and polymeric copper(II) complexes of calix[4]arene-derived ligands

Adrián Castillo, José L. Martínez, Paulina R. Martínez-Alanis, Ivan Castillo *

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México, D.F. 04510, Mexico

ARTICLE INFO

ABSTRACT

Deprotonation of the *p-tert*-butylcalix[4]arene disubstituted at alternate phenolic positions with picolyl groups **2** was achieved with alkali metal hydrides LiH, NaH, and KH. The dianionic calixarene derivatives were subjected to complete substitution at the phenolic rim with allyl bromide, providing the tetraalkylated derivatives in cone **3a** and partial-cone conformations **3b**; both compounds were crystallographically characterized. Compound **2**, as well as **3a** and **3b** were tested as ligands towards CuCl$_2$, affording Cu^{2+} complexes in the first two cases. Polymeric [**2**·CuCl$_2$] was obtained from **2** and CuCl$_2$ in MeOH/ CH$_2$Cl$_2$ solutions, and consists of chains of the ditopic calixarene acting as an N-donor towards Cu^{2+} ions outside the macrocyclic cavity. Employment of EtOH/CH$_2$Cl$_2$ mixtures results in the tricopper complex [(**2**)$_2$Cu$_3$Cl$_6$(EtOH)$_2$]. In contrast, reactions of ligand **3a** with CuCl$_2$ afforded monomeric [**3a**·CuCl$_2$], while no Cu^{2+} complexes could be obtained when **3b** was employed. The presence of intramolecular hydrogen bonds in **2** appears to control the formation of oligomeric or polymeric copper complexes, while the lack of such hydrogen bonds allows the proper alignment of N-donors to coordinate Cu^{2+} directly above the macrocyclic cavity.

1. Introduction

Calixarenes are an important class of macrocyclic molecules in supramolecular and coordination chemistry [1–12], mainly due to their preorganized structure, and to the ease of introduction of different types of donor groups. Synthetic procedures for the preparation of *p-tert*-butylcalix[4]arene derivatives are well established, and include the complete substitution at the phenolic rim by formation of ethereal C–O bonds. In coordination chemistry, this has resulted in the development of heteroatom-containing calix[4]arenes as ligands for main group and transition metal complexes. Among the functional groups that have been incorporated to calixarenes, nitrogen-containing heterocycles represent a vast group of compounds due to their versatility as ligands, with examples reported of picolyl [13,14], imidazolyl [15], bipyridyl [16], and phenanthrolyl functionalities [17]. In the specific case of *p-tert*-butylcalix[4]arene, the bispicolyl derivative substituted in alternate phenolic positions has allowed us to prepare copper–calix[4]arene complexes, as an organic–inorganic coordination polymer of dimeric Cu^{2+} paddle-wheel units with bridging acetate ligands [18].
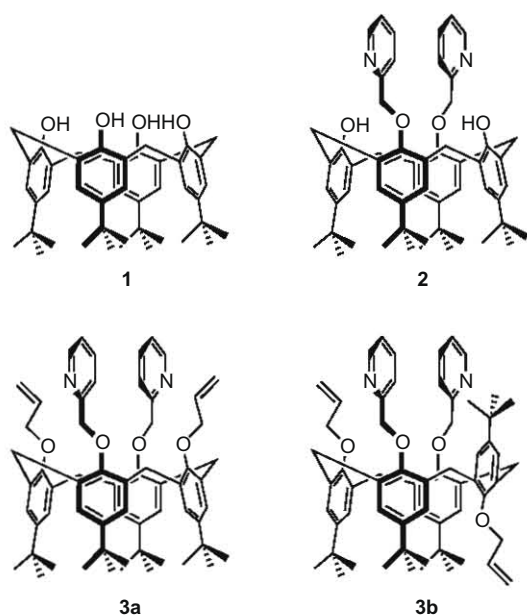
We have recently extended the use of calixarene derivatives to obtain cupric complexes, starting from cone conformers of picolyl-substituted derivatives of *p-tert*-butylcalix[4]arene (for example, **2** in Scheme 1), which have allowed us to study the ability of these calixarenes to form extended organic–inorganic networks, as well as discrete copper–calix[4]arene complexes with Cu$_2$(μ-OAc)$_4$ as an inorganic building block [19]. In these systems, the choice of anion appears to be crucial, since our efforts and those of other groups to obtain Cu^{2+}–calixarene complexes amenable for structural characterization with PF$_6^-$, ClO$_4^-$, and NO$_3^-$ as copper counterions have thus far been unsuccessful [13,14]. In the case of Cu$_2$(μ-OAc)$_4$, the polymeric structure of the picolyl–calix[4]arene complexes does not appear to be maintained in coordinating solvents due to solvation of copper acetate. These observations prompted us to search for combinations of calix[4]arenes/Cu^{2+} salts that might allow the preparation of more robust, and crystalline complexes.

To this end, we have prepared calix[4]arenes with mixed substituents in alternate positions of the phenolic rim, and in particular derivatives substituted with functional groups amenable to further functionalization by post-synthetic modification [20,21]. These modifications may allow the introduction of functionalities that are incompatible with complex formation, while enabling the development of organic–inorganic networks with enhanced stability via covalent bonding [22–24]. Unfortunately, the development of calix[4]arene derivatives with heterotopic groups in alternate phenolic positions, including nitrogen heterocycles, have so far focused on cone conformers of the macrocycle, thus limiting

* Corresponding author. Fax: +52 55 56162217.
E-mail address: joseivan@unam.mx (I. Castillo).

Scheme 1. *p-Tert*-butylcalix[4]arene and picolyl-containing ligands

the potential topologic diversity of calixarene complexes. In this context, we have devised a synthetic method which allows us to control the conformational outcome upon complete substitution of the phenolic positions of **2** by sequential etherification steps by deprotonation of phenolic O–H groups with different alkali metal hydrides MH (M = Li, Na, and K) [25]. By adapting this protocol, we have been able to selectively prepare the new ligands **3a** and **3b**, which correspond to the cone and partial-cone conformers of bispicolyl–bisallyl-substituted calix[4]arene (Scheme 1). The coordination properties of **2**, **3a**, and **3b** towards CuCl$_2$ were tested, in an extension of our previous reports on the discrete and polymeric complexes that have been prepared with picolyl-substituted calix[4]arene derivatives and copper(II) acetate.

2. Experimental

2.1. Reagents and techniques

Reagents and solvents were obtained from commercial suppliers and used as received unless otherwise stated. THF, MeOH, and EtOH were dried by standard procedures. Compound **2** was prepared as previously reported [12]. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Eclipse 300 spectrometer. Infrared spectra were obtained with a Perkin–Elmer 203-B spectrometer in the 4000–400 cm^{-1} spectral region as KBr disks. Combustion analyses were performed at the microanalytical laboratory of the Instituto de Química.

2.2. Synthetic procedures

2.2.1. 5,11,17,23-Tetra-tert-butyl-25,27-bisallyl-26,28-bis(2-pyridylmethoxy)calix[4]arene (3a)

To a stirred solution of **2** (250 mg, 0.30 mmol) in anhydrous THF (10 mL) was added solid LiH (5.20 mg, 0.65 mmol) under N$_2$. After 30 min of stirring, allyl bromide (56 µL, 0.65 mmol) was added via syinge, and the mixture was heated to reflux for 15 h. Upon cooling volatile materials were removed under reduced pressure, and the products were extracted with CH$_2$Cl$_2$ (2 × 20 mL), filtered, and concentrated to dryness. Crystallization from hexanes/CH$_2$Cl$_2$ afforded **3a** as a colorless solid (170 mg, 62.2%). X-ray quality crys-

tals were obtained by slow evaporation of a CH$_3$CN solution. *Anal.* Calc. for C$_{62}$H$_{74}$N$_2$O$_4$: C, 81.72; H, 8.19; N, 3.07. Found: C, 82.04; H, 8.65; N, 2.59%. M.p. 100–101 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): δ = 0.87 (s, 18 H, ^{t}Bu), 1.31 (s, 18 H, ^{t}Bu), 3.10 (d, 4 H, –CH$_2$–, $^{2}J_{H,H}$ = 12.6 Hz), 4.40 (d, 4 H, –CH$_2$–, $^{2}J_{H,H}$ = 12.6 Hz), 4.51 (d, 4 H, –OCH$_2$–, $^{3}J_{H,H}$ = 6.3 Hz), 4.82–4.94 (m, 4 H, –OCH$_2$–, allyl), 4.87 (s, 4 H, –OCH$_2$Py), 6.30 (m, 2 H, vinyl), 6.49 (s, 4 H, ArH), 7.05 (s, 4 H, ArH), 7.24 (m, 2 H, Py), 7.70 (m, 4 H, Py), 8.60 (d, 2 H, Py, $^{3}J_{H,H}$ = 5.22 Hz) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 30.15, 30.38, 30.66, 31.88, 33.03, 74.51, 77.57, 114.01, 121.56, 122.32, 123.65, 124.44, 131.02, 134.57, 135.24, 136.47, 143.50, 143.93, 148.08, 151.31, 152.77, 156.91 ppm. IR (KBr): ν = 3068, 2959, 2906, 2866, 1592, 1479, 1362, 1300, 1240, 1199, 1123, 1005, 918, 871, 774, 750, 640 cm^{-1}.

2.2.2. 5,11,17,23-Tetra-tert-butyl-25,27-bisallyl-26,28-bis(2-pyridylmethoxy)calix[4]arene (3b)

Same procedure as for **3a** using 30% KH dispersion in mineral oil (90 mg, 0.65 mmol), and allyl bromide (56 µL, 0.65 mmol). Crystallization from hexanes/CH$_2$Cl$_2$ afforded **3b** as a colorless solid (158 g, 57.8%). X-ray quality crystals were obtained by slow evaporation of a CH$_3$CN solution. *Anal.* Calc. for C$_{62}$H$_{74}$N$_2$O$_4$: C, 81.72; H, 8.19; N, 3.07. Found: C, 81.65; H, 8.68; N, 2.87%. M.p. 157–160 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C): δ = 1.03 (s, 9 H, ^{t}Bu), 1.08 (s, 18 H, ^{t}Bu), 1.30 (s, 9 H, ^{t}Bu), 3.05 (d, 2 H, –CH$_2$–, $^{2}J_{H,H}$ = 12.6 Hz), 3.68 (d, 2 H, –CH$_2$–, $^{2}J_{H,H}$ = 14.5 Hz), 3.76 (d, 2 H, –CH$_2$–, $^{2}J_{H,H}$ = 14.5 Hz), 3.86 (br, 2 H, –CH$_2$O–), 4.02 (d, 2 H, –CH$_2$O–, $^{2}J_{H,H}$ = 6.3 Hz), 4.10 (d, 2 H, –CH$_2$–, $^{2}J_{H,H}$ = 12.6 Hz), 4.68–4.82 (m, 4 H, vinyl), 4.94 (d, 4 H, –OCH$_2$–, $^{3}J_{H,H}$ = 12.1 Hz), 5.72 (m, 2 H, vinyl), 6.69 (d, 2 H, ArH, $J_{H,H}$ = 2.4 Hz), 6.84 (d, 2 H, ArH, $J_{H,H}$ = 2.4 Hz), 7.05 (s, 4 H, ArH), 7.27 (m, 2 H, Py), 7.55 (d, 2 H, Py, $^{3}J_{H,H}$ = 7.6 Hz), 7.77 (d, 2 H, Py, $^{3}J_{H,H}$ = 7.6 Hz) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ = 31.48, 31.65, 31.83, 33.86, 33.93, 34.16, 72.62, 74.23, 115.21, 122.83, 123.82, 125.44, 125.68, 125.76, 126.41, 127.58, 131.99, 132.70, 133.46, 135.44, 136.90, 137.15, 143.67, 144.60, 145.15, 148.37, 148.71, 152.65, 153.30, 154.84, 157.57 ppm. IR (KBr): ν = 3069, 2959, 2906, 2866, 1592, 1479, 1363, 1300, 1240, 1199, 1122, 1006, 919, 871, 796, 773, 750, 640, 610 cm^{-1}.

2.2.3. [2·CuCl$_2$]$_n$

To a stirred solution of **2** (200 mg, 0.24 mmol) in CH$_2$Cl$_2$ (4 mL) was added a solution of CuCl$_2$·2H$_2$O (50 mg, 0.24 mmol) in MeOH (4 mL). After 30 min of stirring the solution was filtered, and concentrated by slow evaporation of solvents. The product was obtained as a blue solid (162 mg, 67.2%). *Anal.* Calc. for C$_{56}$H$_{66}$Cl$_2$CuN$_2$O$_4$: C, 69.66; H, 6.89; N, 2.90. Found: C, 69.84; H, 6.96; N, 3.11%. IR (KBr): ν = 3514, 3044, 2961, 2908, 2869, 1606, 1576, 1484, 1441, 1363, 1302, 1196, 1105, 1026, 979, 871, 758, 717, 640 cm^{-1}.

2.2.4. [(2)$_2$Cu$_3$Cl$_6$(EtOH)$_2$]

To a stirred solution of **2** (80 mg, 0.10 mmol) in CH$_2$Cl$_2$ (4 mL) was added a solution of CuCl$_2$·2H$_2$O (25 mg, 0.12 mmol) in ethanol (4 mL). After 30 min of stirring the solution was filtered, and concentrated by slow evaporation of solvents from a CH$_2$Cl$_2$/EtOH solution. The product was obtained as a green solid (50 mg, 48.1%). *Anal.* Calc. for C$_{116}$H$_{144}$Cl$_6$Cu$_3$N$_4$O$_{10}$: C, 64.57; H, 6.73; N, 2.60. Found: C, 64.57; H, 6.47; N, 2.69%. IR (KBr): ν = 3464, 3045, 2960, 2907, 2869, 1607, 1580, 1484, 1364, 1301, 1200, 1117, 1031, 981, 872, 765, 640 cm^{-1}.

2.2.5. [(3a·CuCl$_2$)$_2$(CH$_2$Cl$_2$)]

To a stirred solution of **3a** (58 mg, 0.06 mmol) in CH$_2$Cl$_2$ (4 mL) was added a solution of CuCl$_2$·2H$_2$O (13 mg, 0.06 mmol) in MeOH (4 mL). After 30 min of stirring the solution was filtered, and concentrated by slow evaporation of solvents. The product was ob-

tained as a turquoise solid (69 mg, 84.8%). *Anal.* Calc. for $C_{125}H_{150}Cl_6Cu_2N_4O_8$: C, 68.98; H, 6.95; N, 2.57. Found: C, 69.00; H, 6.94; N, 2.68%. IR (KBr): $\nu = 3066, 2960, 2907, 2867, 1605, 1577, 1479, 1362, 1299, 1238, 1196, 1123, 997, 928, 871, 771$ cm^{-1}.

2.3. X-ray crystallography

Colorless X-ray quality crystals were obtained by slow evaporation of solvents. Data were collected on a Bruker SMART X-ray diffractometer equipped with an Apex CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell constants were obtained from the least-squares refinements of the observed reflections using the ω scan mode. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically, including the carbon atoms of the disordered *tert*-butyl groups commonly observed in *p-tert*-butylcalix[4]arenes, which resulted in large thermal parameters. In the case of [(3a·CuCl$_2$)$_2$(CH$_2$Cl$_2$)], the carbon atoms of the disordered *tert*-butyl groups were modeled isotropically. Hydrogen atoms were placed in idealized positions, with C–H distances of 0.93 and 0.98 Å for sp^2 and sp^3 hybridized carbon atoms, respectively. The isotropic thermal parameters of the hydrogen atoms were assigned the values of $U_{iso} = 1.2$ times the displacement parameters of the atoms to which they are attached.

2.4. EPR spectroscopy

EPR measurements were made in quartz tubes at room temperature with a JEOL JES-TE300 spectrometer operating at X band frequency (near 9.4 GHz) at 100 KHz field modulation, with a cylindrical cavity (TE$_{011}$ mode). The external measurement of the static magnetic field was made with a precision JEOL ES-FC5 Gaussmeter. For low-temperature measurements, an ITC^{503} (Oxford) variable temperature controller unit was employed. Spectral acquisition and manipulations were performed using the program ESPRIT-382, v1.916. The parameters obtained for all complexes: [2·CuCl$_2$] $g_\perp = 2.06$ and $g_{II} = 2.23$, [(2)$_2$Cu$_3$Cl$_6$(EtOH)$_2$] $g_\perp = 2.06$ and $g_{II} = 2.21$, and [3a·CuCl$_2$] $g_\perp = 2.05$ and $g_{II} = 2.27$, correspond to Cu^{2+} centers in an axial coordination environment.

3. Results and discussion

3.1. Calixarene derivatives

Preparation of the tetrasubstituted derivatives **3a** and **3b** was accomplished by initial deprotonation of **2** with 2 equivalents of MH in anhydrous THF solution, to yield the dianionic species [2-2H]$^{-2}$2 M$^+$ (M = Li$^+$, Na$^+$, K$^+$). In the specific case of [2-2H]$^{2-}$2Li$^+$, subsequent treatment with a slight excess of allyl bromide resulted in the formation of a single product (as well as a small amount of unreacted **2**), as determined by thin layer chromatographic analysis of the reaction mixture. The new compound **3a** (Scheme 1) was isolated in 62% yield after workup, and was initially characterized by IR and NMR spectroscopic methods, as well as mass spectrometry. FAB$^+$ mass spectra feature a molecular ion at m/z 911, confirming the presence of two picolyl and two allyl groups attached to the calix[4]arene framework. ^{1}H NMR spectra of **3a** display two singlets corresponding to the *p-tert*-butyl groups, and two doublets arising from an AX coupled system due to the ArCH$_2$Ar protons of the macrocyclic framework (δ 3.10 and 4.40 ppm, $J = 12.6$ Hz). ^{13}C NMR spectra are also consistent with a C_{2v} symmetric calix[4]arene, featuring 7 aliphatic and 15 aromatic/vinylic

signals, that correspond to equivalent picolyl and allyl substituents of a cone conformer.

When the reaction was carried out with NaH as a base, reaction of the initially formed [2-2H]$^{2-}$2Na$^+$ with allyl bromide resulted in a mixture of the aforementioned **3a**, as well as a new product **3b** in approximately 1:1 ratio, based on chromatographic analysis. The products were separated by column chromatography, and the latter compound was characterized by spectroscopic methods; its FAB$^+$ mass spectrum indicates that it also corresponds to a diallyl–dipicolyl-substituted calix[4]arene. ^{1}H NMR data indicate that in **3b** one of the allyl-containing phenol moieties is inverted with respect to the rest of the phenolic substituents, thus corresponding to the partial-cone conformer. This is reflected in the complex pattern around δ 4.68–4.82 ppm, as well as the overlapping signals at δ 5.72 ppm, all of which are assigned to inequivalent vinylic protons. The 3 singlets in the high field region of the spectrum in a 2:1:1 ratio are associated to the *p-tert*-butyl groups, while the four doublets of two AX coupled systems correspond to the bridging ArCH$_2$Ar protons (δ 3.05 and 4.10 ppm, $J = 12.6$ Hz; 3.68 and 3.76 ppm, $J = 14.5$ Hz). In addition, the ^{13}C NMR spectra contain 11 aliphatic and 23 aromatic/vinylic resonances, all of which are consistent with a C_s symmetric species. Compound **3b** can also be obtained as the sole product of the reaction of **2** with KH, followed by alkylation with a slight excess of allyl bromide. These results are in line with our previous observations on the dialkylation of **2** with *tert*-butylbromoacetate, which results in similar atropisomeric ratios depending on the metal hydride employed in the deprotonation [25]. Once the tetrasubstituted calix[4]arenes **3a** and **3b** are formed, thermal interconversion of the conformers is not accessible under the synthetic conditions employed (*i.e.* refluxing THF). This was evidenced by heating samples of both compounds in different solvents, and monitoring by ^{1}H NMR spectroscopy, which revealed no change in the composition of the solutions; extended heating at 150 °C in deuterated dmso resulted in decomposition of both compounds.

The conformation of compounds **3a**, and **3b** was unambiguously established in the solid state by X-ray crystallography. Single crystals of **3a** were obtained by slow evaporation of a concentrated acetonitrile solution. The solid-state structure (triclinic space group $P\bar{1}$, selected crystallographic data are presented in Table 1) confirmed that all phenolic substituents are on the same side of the macrocycle, with one of the picolyl nitrogen atoms pointing in, and the other one out of the calixarene cavity in order to avoid lone pair repulsion. In contrast with disubstituted calix[4]arenes, which usually display alternating short and long phenol O···O distances due to intramolecular hydrogen bonding (for example in **2**) [25], the lack of hydrogen bonds in tetrasubstituted **3a** results in comparable O···O distances for all adjacent phenolic moieties (Fig. 1). A molecule of acetonitrile is hosted within the calixarene cavity, although the intermolecular interactions are weak based on the acetonitrile C···aromatic ring centroid contacts between the two molecules, which are longer than 4 Å.

In the case of **3b**, crystals in the monoclinic space group $P2_1$ were also obtained by slow evaporation of an acetonitrile solution. The solid-state structure confirmed the inversion of one of the allyl-substituted phenol moieties with respect to the calix[4]arene framework, in agreement with the spectroscopic data. The inversion of the allyl group places the corresponding O atom further from the rest of the oxygen atoms of the macrocycle, thus resulting in a long O2···O4 distance of 5.244(5) Å between the two allyl-containing phenolic groups. A molecule of acetonitrile is also hosted within the macrocyclic cavity, with close C–H···π contacts of the acetonitrile –CH$_3$ group to all but the inverted aromatic ring centroids of the calixarene. The clathrate is characterized by C67(acetonitrile)···ring centroid distances of 3.544(5), 3.508(6), and 3.609(6) Å, and C–H···ring centroid angles of 157°, 161°, and

Table 1
Crystallographic data.

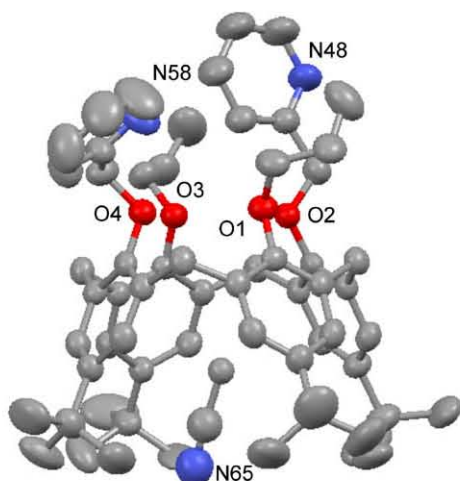| Compound	$C_{64}H_{77}N_3O_4$	$C_{64}H_{77}N_3O_4$	$C_{56}H_{66}Cl_2CuN_2O_4$	$C_{118}H_{156}Cl_{10}Cu_3N_4O_{14}$	$C_{63}H_{76}Cl_4CuN_2O_4$
Molecular mass	952.29	952.29	965.55	2399.59	1130.60
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.243(1)	13.142(3)	11.627(3)	12.562(1)	12.246(1)
b (Å)	13.408(1)	13.131(3)	12.076(4)	12.629(1)	21.361(3)
c (Å)	18.625(1)	15.885(4)	21.809(6)	21.164(2)	24.142(3)
α (°)	107.500(1)	90	105.123(6)	94.228(2)	105.302(2)
β (°)	99.534(1)	92.970(4)	90.520(7)	91.305(2)	91.510(2)
γ (°)	91.390(1)	90	116.085(6)	116.575(2)	95.111(2)
V (Å^3)	2866.7(4)	2737.6(1)	2627.9(1)	2988.7(6)	6058.6(1)
Z	2	2	2	1	4
D (calcd.) (g cm^{-3})	1.103	1.155	1.220	1.333	1.240
μ (Mo Kα) (mm^{-1})	0.068	0.071	0.562	0.813	0.583
$F(0\,0\,0)$	1028	1028	1022	1261	2388
Crystal size (mm)	$0.312 \times 0.232 \times 0.176$	$0.344 \times 0.224 \times 0.148$	$0.284 \times 0.168 \times 0.074$	$0.234 \times 0.142 \times 0.086$	$0.444 \times 0.384 \times 0.378$
Temperature (K)	298(2)	173(2)	100(2)	100(2)	173(2)
Radiation, λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$\theta_{min,max.}$ (°)	1.60, 25.40	1.96, 25.25	1.92, 25.39	1.81, 25.35	1.67, 25.40
Data set (h; k; l)	−14/14; −16/16; −22/22	−15/15; −15/15; −19/19	−14/13; −14/14; 0/26	−15/15; −15/15; −25/25	−14/14; −25/25; −29/29
Total, unique data, R_{int}	32 553, 10 530, 0.0616	19 962, 5207, 0.0720	8429, 8429, 0.0000	31 209, 10 876, 0.0519	66 149, 22 135, 0.0454
Observed data $I > 2.0\sigma(I)$	4630	3408	6762	8481	16 736
$N_{reflections}$, $N_{parameters}$	10 530, 833	5207, 838	8429, 599	10 876/707	22 135/1577
R_1, wR_2, S	0.0504, 0.1007, 0.802	0.0580, 0.1141, 1.025	0.0732, 0.1405, 1.073	0.0510, 0.1181, 1.023	0.0605, 0.1564, 1.028
Minimum, maximum residues (e Å^{-3})	−0.173, 0.241	−0.179, 0.190	−0.901, 0.577	−0.778, 0.717	−1.116, 1.088

Fig. 1. ORTEP diagram of **3a** at the 50% probability level; hydrogen atoms, and minor-occupancy disordered atoms are omitted for clarity (color code: carbon atoms, gray; nitrogen, blue; oxygen, red). Selected interatomic distances (Å): O1···O2 3.058(2), O1···O3 4.496(2), O1···O4 3.138(2), O2···O3 2.978(2), O2···O4 4.207(2), O3···O4 3.145(2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
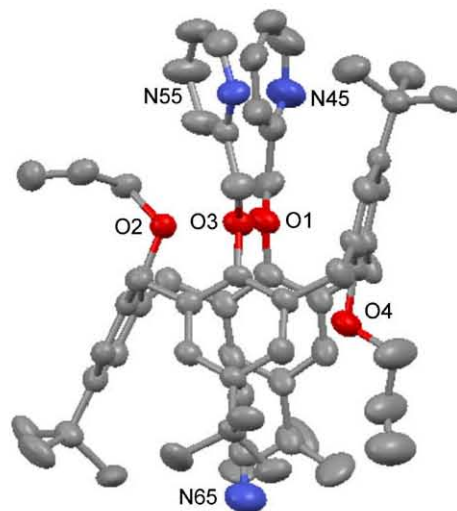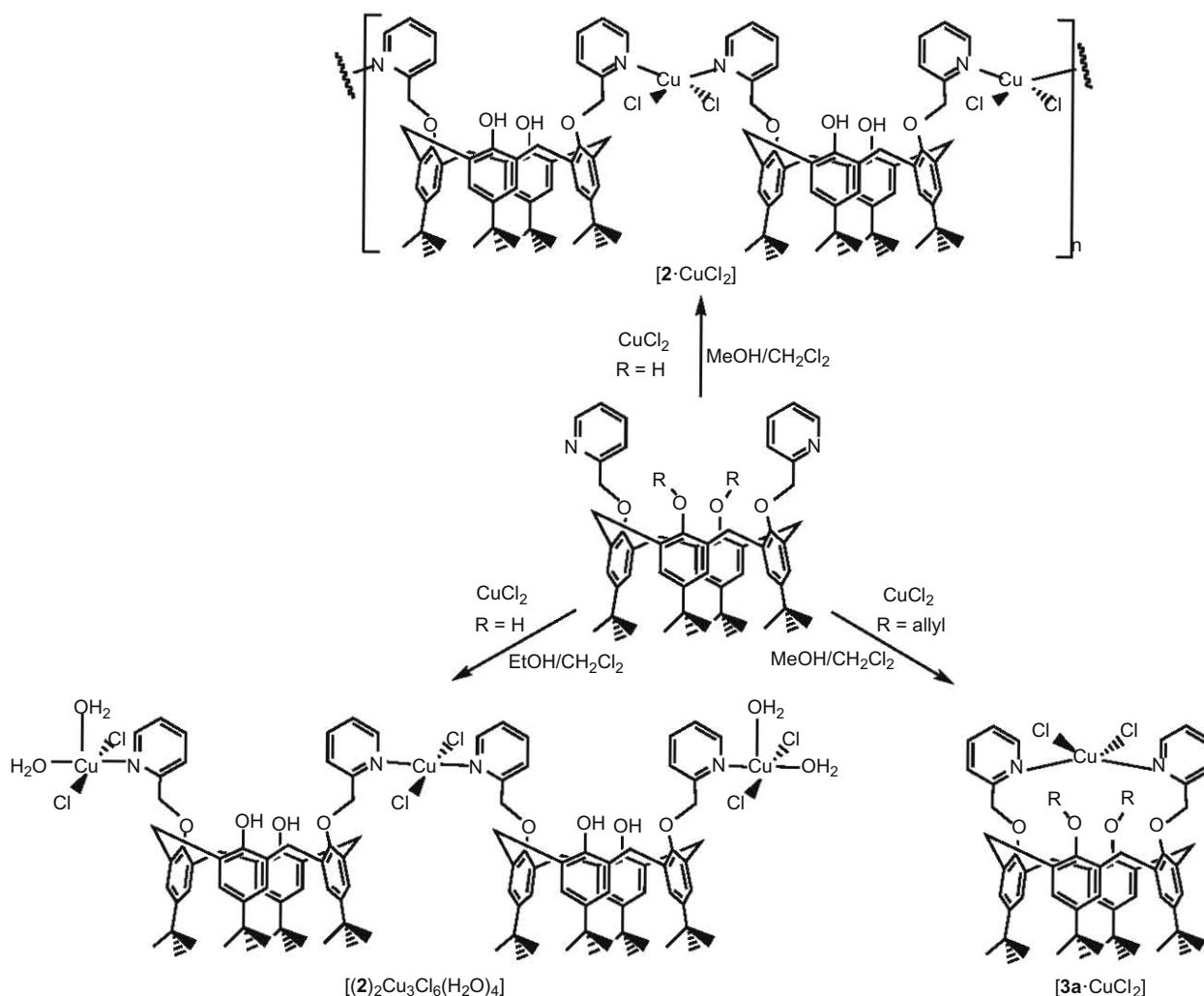

Fig. 2. ORTEP diagram of **3b** at the 50% probability level; hydrogen atoms, and minor-occupancy disordered atoms are omitted for clarity. Selected interatomic distances (Å): O1···O2 3.201(4), O1···O3 4.608(4), O1···O4 4.279(6), O2···O3 3.213(4), O2···O4 5.244(5), O3···O4 4.117(4).

144°, respectively. An ORTEP diagram of **3b** with the hosted molecule of acetonitrile is shown in Fig. 2.

3.2. Cu^{2+}–calixarene complexes

In previous work, we obtained coordination polymers from **2** and related picolyl-substituted calix[4]arenes as polytopic organic connectors, and Cu$_2$(μ-OAc)$_4$ acting as an inorganic linear spacer [18,19]. As an extension to this work we attempted to prepare analogous coordination polymers with compounds **3a** and **3b**, which contain additional allyl groups. All attempts to prepare hybrid materials with Cu$_2$(μ-OAc)$_4$ failed, as did the efforts to obtain crystalline materials with Cu(ClO$_4$)$_2$·6H$_2$O and Cu(NO$_3$)$_2$·2.5H$_2$O. In the latter two cases, decomposition of the calixarene

ligands was observed. Thus, we turned our attention to CuCl$_2$ as a potential monocopper linker. We initially tested the reaction between CH$_2$Cl$_2$ solutions of **2** and alcoholic solutions of CuCl$_2$·2H$_2$O, which resulted in blue (MeOH) or green (EtOH) microcrystalline solids (Scheme 2). Both products were characterized as calixarene-containing copper complexes based on IR and EPR spectroscopy, which confirmed the presence of picolyl-substituted calix[4]arenes and Cu^{2+} ions, respectively. In the IR spectra, strong absorptions due to the ν(OH) of the intramolecularly hydrogen-bonded phenol O–H groups were observed around 3500 cm^{-1}, while the absorption bands between 1610–760 cm^{-1} are characteristic of the picolyl-substituted macrocycle. EPR spectra acquired on solid samples at X band frequency correspond to isolated Cu^{2+} centers in an axial environment, from ambient temperature to

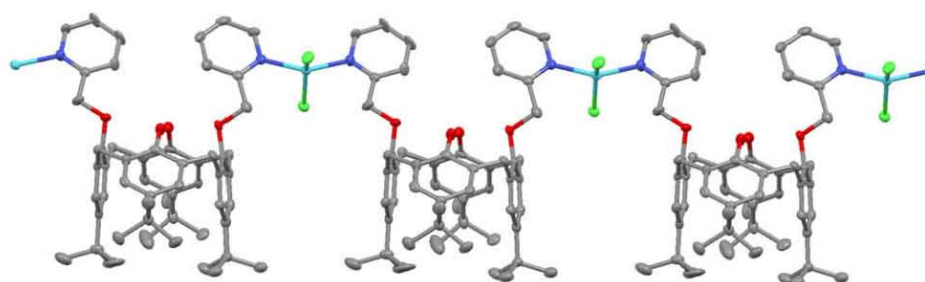**Scheme 2.** Synthesis of Cu^{2+} complexes of calix[4]arene-derived ligands

Fig. 3. ORTEP diagram of a chain of [2·CuCl$_2$] at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Cu1–Cl1 2.240(2), Cu1–Cl2 2.229(3), Cu1–N45 2.004(4), Cu1–N52 1.997(6). (Color code: chlorine atoms, green; copper, turquoise). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

77 K, with virtually identical values of $g_\perp$ = 2.06 and $g_\parallel$ = 2.22 for both blue and green complexes.

Combustion analyses of the complexes are consistent with the empirical formulae [2·CuCl$_2$] and [(2)$_2$Cu$_3$Cl$_6$(EtOH)$_2$]. In both cases X-ray quality crystals were obtained by slow evaporation from either MeOH/CH$_2$Cl$_2$, or EtOH/CH$_2$Cl$_2$ solvent mixtures. The former blue complex consists of a linear coordination polymer [2·CuCl$_2$]$_n$ similar to the one reported with 2 and Cu$_2$(μ-OAc)$_4$ [18,19], with alternating molecules of 2 as organic building blocks, and CuCl$_2$ as inorganic connectors (Fig. 3). The Cu^{2+} ions are in a distorted square planar coordination environment, as evidenced in the bond angles between pseudo-*trans* ligands of Cl1–Cu1–Cl2 150.03 and N45–Cu1–N52 151.04°, as well as the angles between *cisoid* ligands of Cl1–Cu2–N45 94.89, Cl1–Cu2–N52 93.87, Cl2–Cu1–N45 92.04, and Cl2–Cu1–N52 94.01°. A quantitative measurement of the deviation from the ideal square planar (or tetrahedral) geometry would require analysis by the continuous symmetry measure method for tetracoordinate transition-metals [26,27].

The green crystals obtained from the two-component reaction between CH$_2$Cl$_2$ solutions of 2 and ethanolic solutions of
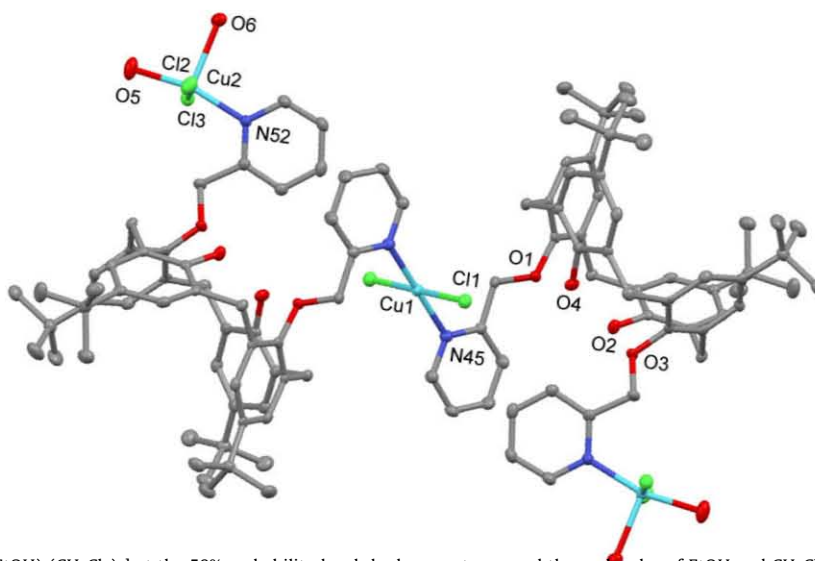
Fig. 4. ᴏʀᴛᴇᴘ diagram of [(**2**)$_2$Cu$_3$Cl$_6$(H$_2$O)$_4$(EtOH)$_2$(CH$_2$Cl$_2$)$_2$] at the 50% probability level; hydrogen atoms, and the molecules of EtOH and CH$_2$Cl$_2$ are omitted for clarity.

CuCl$_2$·4H$_2$O crystallize in the monoclinic space group $P\bar{1}$. The trimetallic complex [(**2**)$_2$Cu$_3$Cl$_6$(H$_2$O)$_4$(EtOH)$_2$(CH$_2$Cl$_2$)$_2$] consists of a central copper ion located at the crystallographic inversion center, coordinated by Cl1 and N45 (and the symmetry-related Cl1* and N45* atoms), with bond lengths of Cu1–N45 1.997(3) and Cu1–Cl1 2.250(1) Å, defining a square planar coordination environment (Fig. 4). Two calixarene derivatives coordinate through one picolyl group to the central Cu1 ion, while the second picolyl group on each calixarene acts as a nitrogen donor toward an independent Cu2 ion, characterized by a Cu2–N52 bond length of 1.993(2) Å. The coordination environment around Cu2 is complemented by two chloride ligands [Cu2–Cl2 and Cu2–Cl3 at 2.274(1), and 2.280(1) Å], and two water molecules, defining a square pyramidal geometry. The bond angles between the *trans*-basal ligands are N52–Cu2–O5 165.03, and Cl2–Cu2–Cl3 171.12°, while the corresponding angles between *cis*-ligands are N52–Cu2–Cl2 88.59, N52–Cu2–Cl3 91.74, O5–Cu2–Cl2 90.61, and O5–Cu2–Cl3 86.76°. As expected for a Jahn–Teller system, the Cu2–O6 distance (2.260(3) Å) to the apical water molecule is considerably longer than the basal Cu2–O5 bond length of 1.972(3) Å; the corresponding O6–Cu2-*L* angles to the basal ligands *L* range from 94.01° to 100.16°.

In addition to the intramolecular hydrogen bonds that are commonly observed between phenolic OH groups and ethereal O atoms of substituted calixarenes, several intermolecular interactions are present in the structure of [(**2**)$_2$Cu$_3$Cl$_6$(H$_2$O)$_4$(EtOH)$_2$(CH$_2$Cl$_2$)$_2$]. The chloride ligand coordinated to Cu1 participates in a Cl1···H–O6 hydrogen bond to the apical water ligand on an adjacent molecule of the complex, and is characterized by a Cl1···O6 distance of 3.116 Å. O6 further acts as a hydrogen donor toward Cl2 on another molecule of [(**2**)$_2$Cu$_3$Cl$_6$(H$_2$O)$_4$(EtOH)$_2$(CH$_2$Cl$_2$)$_2$], and as an acceptor toward a molecule of ethanol that contains O7; the latter bridges O6 and O5 from a basal water ligand (*cis* relative to Cl2, Fig. 5), thus generating an extended one-dimensional hydrogen-bonded network. The corresponding distances are Cl2···O6 3.088, O5···O7 2.707, and O6···O7 2.768 Å.

The crystallographic data clearly indicates that the blue and green crystalline products, [**2**·CuCl$_2$] and [(**2**)$_2$Cu$_3$Cl$_6$(EtOH)$_2$], have copper centers in different coordination environments. Therefore, the apparently identical EPR spectra obtained in the range observed from ambient temperature to 77 K probably correspond to unresolved signals in the powder samples. This is particularly evident in the case of [(**2**)$_2$Cu$_3$Cl$_6$(EtOH)$_2$], for which the spectra must correspond to unresolved signals arising from the two Cu^{2+} centers in an axial coordination environment.
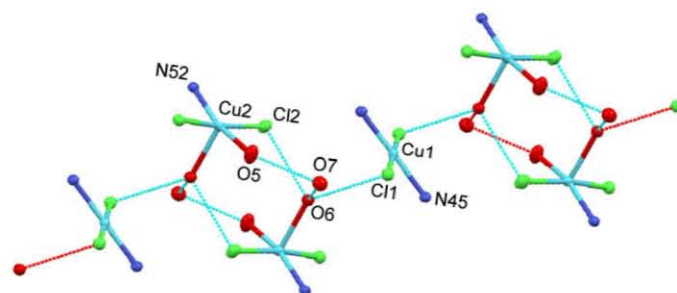

Fig. 5. Hydrogen bond network of [(**2**)$_2$Cu$_3$Cl$_6$(H$_2$O)$_4$(EtOH)$_2$(CH$_2$Cl$_2$)$_2$]; carbon atoms of the molecule of EtOH (O7) are omitted for clarity.

In the case of the completely substituted calixarene **3a**, the reactions of its CH$_2$Cl$_2$ solutions with either methanolic or ethanolic solutions of CuCl$_2$·4H$_2$O resulted in green microcrystals upon evaporation of solvents; combustion analysis of the solid obtained is consistent with the empirical formula [(**3a**·CuCl$_2$)$_2$(CH$_2$Cl$_2$)] (Scheme 2). As in the case of the corresponding complexes of **2** and CuCl$_2$, IR and EPR spectroscopy confirmed the presence of substituted calix[4]arenes and Cu^{2+} ions, respectively. As expected for a tetrasubstituted calixarene, the IR spectra lack the absorption band around 3500 cm^{-1}, which is commonly observed when phenolic O–H groups are present. X band frequency EPR spectra of solid samples also correspond to Cu^{2+} centers in an axial coordination environment, $g_\perp$ = 2.05 and g_{II} = 2.27.

Triclinic ($P\bar{1}$) X-ray quality crystals of [**3a**·CuCl$_2$(CH$_2$Cl$_2$)] were obtained by slow evaporation of MeOH/CH$_2$Cl$_2$ solutions. In contrast to the oligomeric and polymeric species obtained from the reaction of **2** and CuCl$_2$·4H$_2$O, the structure of [**3a**·CuCl$_2$(CH$_2$Cl$_2$)] consists of monomeric complexes with the copper ion located above the calixarene cavity. The two crystallographically independent Cu^{2+} ions have very similar coordination environments, which can be best described as distorted square planar (or distorted tetrahedral, Fig. 6). Thus, each copper center is coordinated by two chloride and two picolyl ligands, with average Cu–Cl and Cu–N bond lengths of 2.241 and 1.995 Å, respectively (see Table 2). The bond angles around the copper centers are similar to those in [**2**·CuCl$_2$], with pseudo-*trans* angles ranging from 143.28° to 153.64°, while the corresponding angles between *cisoid* ligands
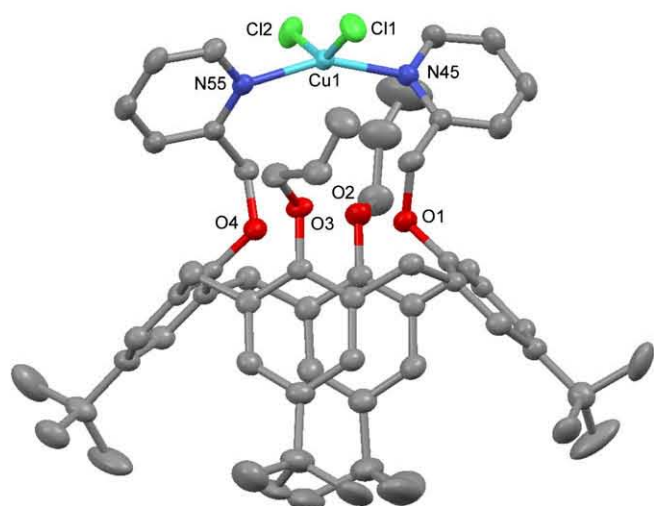
Fig. 6. ORTEP diagram of one of the crystallographically independent [**3a**·CuCl₂] complexes at the 50% probability level; hydrogen atoms, a molecule of CH₂Cl₂, and minor-occupancy disordered atoms are omitted for clarity.

Table 2
Selected structural parameters for the complexes [**2**·CuCl₂], [(**2**)₂Cu₃Cl₆(H₂O)₄(EtOH)₂(CH₂Cl₂)₂], and [**3a**·CuCl₂(CH₂Cl₂)].

Compound[a]	[**2**·CuCl₂]	[(**2**)₂Cu₃Cl₆(H₂O)₄]	[**3a**·CuCl₂]
Distances (Å)			
Cu1–Cl1	2.240(2)	2.250(1)	2.232(1)
Cu1–Cl2	2.229(3)		2.239(1)
Cu2–Cl3		2.274(1)	2.240(1)
Cu2–Cl4		2.280(1)	2.254(1)
Cu1–NA[b]	2.004(4)	1.977(3)	1.997(3)
Cu1–NB	1.997(6)		2.006(3)
Cu2–NC		1.993(2)	1.983(3)
Cu2–ND			1.994(3)
O1…O2	2.880(6)	2.903(3)	3.205(3)
O1…O3	4.931(5)	4.512(3)	3.452(4)
O1…O4	2.967(7)	2.761(3)	3.199(3)
O2…O3	3.158(7)	2.757(3)	3.257(3)
O2…O4	3.414(9)	3.289(4)	3.079(3)
O3…O4	3.047(6)	2.864(3)	5.316(3)

[a] Simplified formula.
[b] NA–ND denotes the numbered N atoms in ascending order.

are in the range from 91.93° to 96.80°. Related complexes of four-member calixarene derivatives incorporating nitrogen donors have been described in the literature as *endo*-copper species, with the metal ion located directly above the macrocyclic cavity [14,16,28–30]. Among the complexes featuring this geometric arrangement, the number that have been structurally authenticated remains scarce [15,31–33].

With respect to the copper counterions, the structures with the *endo*-configuration reported thus far feature either the non-coordinating PF₆⁻ anion [15,31,32], or require no counterion due to the anionic nature of the calixarene ligand [33]. In the case of [**3a**·CuCl₂], the chloride anion remains coordinated to the Cu²⁺ center, while allowing the metal ion to remain in close proximity to the calixarene cavity. In contrast, the use of other copper salts with coordinating anions, such as Cu(OAc)₂ results in complexes with the copper ion placed away from the cavity, and the acetate anion coordinated to the metal center [18,19,34,35]. The bulk associated to the acetate anions probably precludes the *endo*-type coordination of the picolyl–calix[4]arene ligand to Cu²⁺ observed in [**3a**·CuCl₂]. In the case of [**2**·CuCl₂] and [(**2**)₂Cu₃Cl₆(EtOH)₂], the *exo*-location of the Cu²⁺ ion can be rationalized in terms of the

intramolecular hydrogen bonds present in **2**. The hydrogen bonds force an alternate disposition of long and short phenolic O···O distances, which may preclude the alignment required of the two picolyl moieties in order to coordinate CuCl₂ in a quasi-linear fashion, as observed in [**3a**·CuCl₂]. This hypothesis needs further evaluation with different tetrasubstituted calix[4]arene derivatives, since all attempts to obtain crystalline compounds from the reactions of **3b** and CuCl₂ were unsuccessful, and will be studied in detail in forthcoming work.

4. Conclusions

We have established the conditions for the selective preparation of cone and partial-cone atropisomers of tetrasubstituted calix[4]arene derivatives, with heterotopic groups in alternate phenolic positions. The di- and tetrasubstituted derivatives **2**, and **3a**, both of which contain picolyl donors, provide access to monomeric, oligomeric, and polymeric CuCl₂ complexes. The results indicate that the presence of intramolecular hydrogen bonds at the phenolic rim may prevent the coordination of Cu²⁺ directly above the calixarene cavity by twisting the picolyl donors on alternate phenolic positions. The effect of intramolecular H-bonds on the coordination mode appears to operate only with nitrogen-based ligands, since related phosphine-substituted calix[4]arenes do not present this behavior [11]. The lack of hydrogen bonds in tetrasubstituted calixarenes may allow the alignment of the picolyl donors, thus resulting in the *endo*-type coordination of Cu²⁺ in the complex [**3a**·CuCl₂]. This latter hypothesis needs further confirmation with other tetrasubstituted calix[4]arene derivatives and their corresponding metal complexes. Nonetheless, the allyl groups offer the potential for functionalization of the calixarene–copper complex [**3a**·CuCl₂]. Additionally, the nuclearity of the Cu²⁺ complexes of **2** is also determined by the crystallization solvent; the effect of the solvents is yet to be determined, since in principle both MeOH and EtOH could stabilize structures with intra- and intermolecular hydrogen bonds, but in our studies only the latter is present in the solid-state structure of [(**2**)₂Cu₃Cl₆(H₂O)₄(EtOH)₂(CH₂Cl₂)₂].

Supplementary material

CCDC 739052, 739053, 739054, 739055 and 739056 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

References

[1] C.D. Gutsche, Calixarenes, Royal Society of Chemistry, London, 1989.
[2] V. Böhmer, Angew. Chem., Int. Ed. 34 (1995) 713.
[3] C.D. Gutsche, in: J.F. Stoddart (Ed.), Calixarenes Revisited, Royal Society of Chemistry, Cambridge, 1998.
[4] Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens (Eds.), Calixarenes 2001, Kluwer, Dordrecht, 2001.
[5] A. Ikeda, S. Shinkai, Chem. Rev. 97 (1997) 1713.
[6] A.F. Danil de Namor, R.M. Cleverley, M.L. Zapata-Ormachea, Chem. Rev. 98 (1998) 2495.
[7] M.W. Hosseini, Acc. Chem. Res. 38 (2005) 313.
[8] V.G. Organo, A.V. Leontiev, V. Sgarlata, H.V.R. Dias, D.M. Rudkevich, Angew. Chem., Int. Ed. 44 (2005) 3043.
[9] C. Wieser, C.B. Dieleman, D. Matt, Coord. Chem. Rev. 165 (1997) 93.
[10] W. Sliwa, J. Inclusion Phenom. Macrocyclic Chem. 52 (2005) 13.
[11] C. Jeunesse, D. Armspach, D. Matt, Chem. Commun. (2005) 5603.

[12] D.M. Homden, C. Redshaw, Chem. Rev. 108 (2008) 5086.
[13] S. Blanchard, L. Le Clainche, M.-N. Rager, B. Chansou, J.-P. Tuchagues, A.F. Duprat, Y. Le Mest, O. Reinaud, Angew. Chem., Int. Ed. 37 (1998) 2732.
[14] B.S. Creaven, T.L. Gernon, T. McCormac, J. McGinley, A.-M. Moore, H. Toftlund, Inorg. Chim. Acta 358 (2005) 2661.
[15] L. Le Clainche, M. Giorgi, O. Reinaud, Eur. J. Inorg. Chem. (2000) 1931.
[16] P.D. Beer, J.P. Martin, M.G.B. Drew, Tetrahedron 48 (1992) 9917.
[17] J.P.W. Eggert, J.M. Harrowfield, U. Lüning, B.W. Skelton, A.H. White, Polyhedron 25 (2006) 910.
[18] J. Olguín, V. Gómez-Vidales, E. Muñoz, R.A. Toscano, I. Castillo, Inorg. Chem. Commun. 9 (2006) 1096.
[19] J. Olguín, V. Gómez-Vidales, S. Hernández-Ortega, R.A. Toscano, E. Muñoz, I. Castillo, Supramol. Chem. 21 (2009) 502.
[20] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982.
[21] Z. Wang, S.M. Cohen, J. Am. Chem. Soc. 129 (2007) 12368.
[22] J.D. Hartgerink, Curr. Opin. Chem. Biol. 8 (2004) 604.
[23] W. Niu, C. O'Sullivan, B.M. Rambo, M.D. Smith, J.J. Lavigne, Chem. Commun. (2005) 4342.
[24] H.M. El-Kaderi, J.R. Hunt, J.L. Mendoza-Cortés, A.P. Côté, R.E. Taylor, M. O'Keeffe, O.M. Yaghi, Science 316 (2007) 268.
[25] J. Olguín, H. Vázquez Lima, A. Rubio, S. Hernández-Ortega, P. Guadarrama, I. Castillo, Supramol. Chem. 19 (2007) 587.
[26] M. Pinsky, D. Avnir, Inorg. Chem. 35 (1998) 5575.
[27] J. Cirera, P. Alemany, S. Alvarez, Chem. Eur. J. 10 (2004) 190.
[28] G. Arena, A. Contino, E. Longo, D. Sciotto, C. Sgarlatt, G. Spoto, Tetrahedron Lett. 44 (2003) 5415.
[29] A. Ali, S. Salunke-Gawali, C.P. Rao, J. Linares, Inorg. Chem. Commun. 7 (2004) 1298.
[30] I. Oueslati, P. Thuéry, O. Shkurenko, K. Suwinska, J.M. Harrowfield, R. Abidi, J. Vicens, Tetrahedron 63 (2007) 62.
[31] J.-B. Regnouf de Vains, R. Lamartine, B. Fenet, C. Bavoux, A. Thozet, M. Perrin, Helv. Chim. Acta 78 (1995) 1607.
[32] Y.-D. Cao, Q.-Y. Zheng, C.-F. Chen, H.-M. Hu, Z.-T. Huang, Inorg. Chim. Acta 357 (2004) 316.
[33] M. Dey, C.P. Rao, P. Guionneau, Inorg. Chem. Commun. 8 (2005) 998.
[34] M.J. McIldowie, M. Mocerino, M.I. Ogden, B.W. Skelton, Tetrahedron 63 (2007) 10817.
[35] A.D. Bond, B.S. Creaven, D.F. Donlon, T.L. Gernon, J. McGinley, H. Toftlund, Eur. J. Inorg. Chem. (2007) 749.