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# Molecular-Programmed Self-Assembly of Homo- and Heterometallic Penta- and Hexanuclear Coordination Compounds: Synthesis, Crystal Structures, and Magnetic Properties of Ladder-Type $Cu^{II}_2M^{II}_x$ (M = Cu, Ni; $x$ = 3, 4) Oxamato Complexes with $Cu^{II}_2$ Metallacyclophane Cores

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New homo- and heterometallic, hexa- and pentanuclear complexes of formula $\{[Cu_2(mpba)_2(H_2O)F][Cu(Me_5dien)]_4\}(PF_6)_3\cdot 5H_2O$ (**1**), $\{[Cu_2(Me_3mpba)_2(H_2O)_2][Cu(Me_5dien)]_4\}(ClO_4)_4\cdot 12H_2O$ (**2**), $\{[Cu_2(ppba)_2][Cu(Me_5dien)]_4\}(ClO_4)_4$ (**3**), and $[Ni(cyclam)]\{[Cu_2(mpba)_2][Ni(cyclam)]_3\}(ClO_4)_4\cdot 6H_2O$ (**4**) [mpba = 1,3-phenylenebis(oxamate), $Me_3mpba$ = 2,4,6-trimethyl-1,3-phenylenebis(oxamate), ppba = 1,4-phenylenebis(oxamate), $Me_5dien$ = *N,N,N′N′′,N′′*-pentamethyldiethylenetriamine, and cyclam = 1,4,8,11-tetraazacyclotetradecane] have been synthesized through the use of the "complex-as-ligand/complex-as-metal" strategy. The structures of **1**–**3** consist of cationic $Cu^{II}_6$ entities with an overall [2 × 2] ladder-type architecture which is made up of two oxamato-bridged $Cu^{II}_3$ linear units connected through two *m*- or *p*-phenylenediamidate bridges between the two central copper atoms to give a binuclear metallacyclic core of the cyclophane-type. Complex **4** consists of cationic $Cu^{II}_2Ni^{II}_3$ entities with an incomplete [2 × 2] ladder-type architecture which is made up of oxamato-bridged $Cu^{II}Ni^{II}$ and $Cu^{II}Ni^{II}_2$ linear units connected through two *m*-phenylenediamidate bridges between the two copper atoms to give a binuclear metallacyclophane core. The magnetic properties of **1**–**3** and **4** have been interpreted according to their distinct "dimer-of-trimers" and "dimer-plus-trimer" structures, respectively, ($\mathbf{H} = -J(\mathbf{S}_{1A}\cdot\mathbf{S}_{3A} + \mathbf{S}_{1A}\cdot\mathbf{S}_{4A} + \mathbf{S}_{2B}\cdot\mathbf{S}_{5B} + \mathbf{S}_{2B}\cdot\mathbf{S}_{6B}) - J'\mathbf{S}_{1A}\cdot\mathbf{S}_{2B}$). Complexes **1**–**4** exhibit moderate to strong antiferromagnetic coupling through the oxamate bridges ($-J_{Cu-Cu} = 81.3$–$105.9\ cm^{-1}$; $-J_{Cu-Ni} = 111.6\ cm^{-1}$) in the trinuclear and/or binuclear units. Within the binuclear metallacyclophane core, a weak to moderate ferromagnetic coupling ($J'_{Cu-Cu} = 1.7$–$9.0\ cm^{-1}$) operates through the double *m*-phenylenediamidate bridge, while a strong antiferromagnetic coupling ($J'_{Cu-Cu} = -120.6\ cm^{-1}$) is mediated by the double *p*-phenylenediamidate bridge.

## Introduction

Polynuclear complexes with first-row transition metal ions have been actively investigated in the field of molecular magnetism, notably for the design and synthesis of high-spin molecules as potential candidates for single-molecule magnets (SMMs).[1−5] This new class of magnetic molecules combines a high-spin ground state ($S$) with a large and negative axial magnetic anisotropy ($D$) which results in an

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(1) Winpenny, R. E. P. *Adv. Inorg. Chem.* **2001**, *52*, 1.

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energy barrier ($U = -DS^2$) for the magnetization reversal between the two lowest $m_S = \pm S$ states that are responsible for the slow magnetic relaxation behavior. The strategies used so far to obtain polynuclear 3d metal complexes are essentially based on self-assembling methods.[6] In general, the nature of the final product resulting from the self-assembly of ligands and metal ions cannot be determined a priori and it depends critically on the reaction conditions used. However, discrete polynuclear complexes can be readily obtained in a controlled fashion when using mononuclear complexes that contain potential donor groups for another metal ion with partially blocked coordination sites.[7] This molecular-programmed self-assembly, so-called "complex-as-ligand/complex-as-metal" approach, provides thus an alternative route to serendipitous self-assembly. In this case, the nuclearity and the topology of the final product can be mastered by the synthetic chemist and, furthermore, the preparation of heterometallic species containing metal centers of different nature can be envisaged. Moreover, the judicious choice of the metal complexes acting as a ligand or a metal allows one to gain control of the ground spin state ($S$) as well as of the magnetic anisotropy ($D$) of the polymetallic species. Although the use of binuclear complexes as ligands has received limited attention compared to the more common mononuclear complexes, it constitutes a step further for the obtainment of high-nuclearity coordination compounds.[8]

Oxamato copper(II) complexes, either mono- or binuclear, have been used for the rational design of homo- and heteropolynuclear, high-spin molecules following the "complex-as-ligand/complex-as-metal" approach.[9,10] Along this line, we have recently described two new binuclear copper(II) complexes of the metallacyclophane-type which are built upon the binucleating ligands 1,3-phenylenebis(oxamate) (mpba) and 1,4-phenylenebis(oxamate) (ppba) (Chart 1).[11] The two $Cu^{II}$ ions are moderately ferromagnetically coupled in $[Cu_2(mpba)_2]^{4-}$ ($J = +16.8$ cm$^{-1}$)[11a] and strongly antiferromagnetically coupled in $[Cu_2(ppba)_2]^{4-}$ ($J = -81.0$ cm$^{-1}$),[11b] leading thus to triplet ($S = 1$) and singlet ($S = 0$) ground states, respectively. Both effects result from the spin density alternation in the $\pi$-conjugated bond system of the phenylenediamidate bridges with meta- and para-substitution pattern (spin polarization mechanism). Complexes $[Cu_2L_2]^{4-}$ (L = mpba or ppba) constitute thus a rare example of the spin control in metal complexes by the topology of the bridging ligand.[12] Interestingly, $[Cu_2(mpba)_2]^{4-}$

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(2) (a) McCusker, J. K.; Schmitt, E. A.; Hendrickson, D. N. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; Vol. 198, pp 297−319. (b) Aromi, G.; Aubin, S. M. J.; Bolcar, M. A.; Christou, G.; Eppley, H. J.; Folting, K.; Hendrickson, D. N.; Huffman, J. C.; Squire, R. C.; Tsai, H. L.; Wang, S.; Wemple, M. W. *Polyhedron* **1998**, *17*, 3005.

(3) (a) Gatteschi, D.; Caneschi, A.; Sessoli, R.; Cornia, A. *Chem. Soc. Rev.* **1996**, *25*, 101. (b) Gatteschi, D.; Sessoli, R.; Cornia, A. *Chem. Commun.* **2000**, *725*.

(4) (a) Brechin, E. K. *Chem. Commun.* **2005**, 5141. (b) Jones, L. F.; Low, D. M.; Helliwell, M.; Raftery, J.; Collison, D.; Aromi, G.; Cano, J.; Mallah, T.; Wernsdorfer, W.; Brechin, E. K.; Mcinnes, E. J. L. *Polyhedron* **2006**, *25*, 325.

(5) (a) Marvaud, V.; Herrera, J. M.; Barilero, T.; Tuyèras, F.; Garde, R.; Scuiller, A.; Decroix, C.; Cantuel, M.; Desplanches, C. *Monatsh. Chem.* **2003**, *134*, 149. (b) Beltran, L. M. C.; Long, J. R. *Acc. Chem. Res.* **2005**, *38*, 325.

(6) (a) Real, J. A.; De Munno, G.; Chiappetta, R.; Lloret, F.; Journaux, Y.; Colin, J. C.; Blondin, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1184. (b) Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491. (c) Brechin, E. K.; Harris, S. G.; Harrison, A.; Parsons, S.; Whittaker, A. G.; Winpenny, R. E. P. *Chem. Commun.* **1997**, 653. (d) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774. (e) Heinrich, J. L.; Berseth, P. A.; Long, J. R. *Chem. Commun.* **1998**, 1231. (f) Brechin, E. K.; Cador, O.; Caneschi, A.; Cadiou, C.; Harris, S. G.; Parsons, S.; Vonci, M.; Winpenny, R. E. P. *Chem. Commun.* **2002**, 1860. (g) Andres, H.; Basler, R.; Blake, A. J.; Cadiou, C.; Chaboussant, G.; Grant, C. M.; Gudel, H.; Murrie, M.; Parsons, S.; Paulsen, C.; Semadini, F.; Villar, V.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem.—Eur. J.* **2002**, *8*, 4867. (h) Dendrinou-Samara, C.; Alexiou, M.; Zaleski, C. M.; Kampf, J. W.; Kirk, M. L.; Kessissoglou, D. P.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3763. (i) Hegetschweiler, K.; Morgenstern, B.; Zubieta, J.; Hagrman, P. J.; Lima, N.; Sessoli, R.; Totti, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3763. (j) Christian, P.; Rajamaran, G.; Harrison, A.; McDouall, J. J. W.; Raftery, J. T.; Winpenny, R. E. P. *Chem. Commun.* **2004**, 1511. (k) Scott, R. T. W.; Parsons, S.; Murugesu, M.; Wernsdorfer, W.; Christou, G.; Brechin, E. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6540. (l) Ako, A. M.; Hewitt, I. J.; Mereacre, V.; Clérac, R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4926.

(7) (a) Birkelbach, F.; Winter, M.; Florke, U.; Haupt, H. J.; Butzlaff, C.; Lengen, M.; Bill, E.; Trautwein, A.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1994**, *33*, 3990. (b) Tandon, S.; Thompson, L. K.; Bridson, J. N.; Benelli, C. *Inorg. Chem.* **1995**, *34*, 5507. (c) Mallah, T.; Auberger, C.; Verdaguer, M.; Veillet, P. *Chem. Commun.* **1995**, 61. (d) Scuiller, A.; Mallah, T.; Verdaguer, M.; Nivorozkhin, A.; Tholence, J. L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1. (e) Verani, C. N.; Weyhermüller, T.; Rentschler, E.; Bill, E.; Chaudhuri, P. *Chem. Commun.* **1998**, 2475. (f) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655. (g) Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdaguer, M. *Chem.—Eur. J.* **2003**, *9*, 1677. (h) Marvaud, V.; Decroix, C.; Scuiller, A.; Tuyèras, F.; Guyard-Duhayon, C.; Vaissermann, J.; Marrot, J.; Gonnet, F.; Verdaguer, M. *Chem.—Eur. J.* **2003**, *9*, 1692. (i) Yang, J. Y.; Shores, M. P.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2003**, *42*, 1403. (j) Berlinguete, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523. (k) Choi, H. J.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2004**, *43*, 1606. (l) Wang, S.; Zuo, J.; Zhou, H.; Choi, H. J.; Ke, Y.; Long, J. R.; You, X. *Angew. Chem., Int. Ed.* **2004**, *43*, 5940.

(8) (a) Krebs, C.; Winter, M.; Weyhermüller, T.; Bill, E.; Wieghardt, K.; Chaudhuri, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1913. (b) Nazari-Verani, C.; Weyhermüller, T.; Rentschler, E.; Bill, E.; Chaudhuri, P. *Chem. Commun.* **1998**, 2475. (c) Nazari-Verani, C.; Rentschler, E.; Weyhermüller, T.; Bill, E.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **2000**, 251. (d) Ikeda, K.; Ohba, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **2001**, 3119. (e) Khanra, S.; Weyhermüller, T.; Chaudhuri, P. *Inorg. Chem.* **2006**, *45*, 5911.

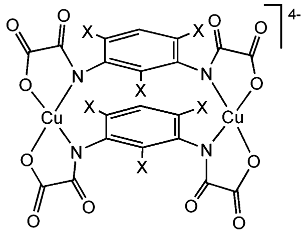
(9) (a) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1988**, *27*, 399. (b) Ribas, J.; Díaz, C.; Costa, R.; Journaux, Y.; Mathonière, C.; Kahn, O.; Gleizes, A. *Inorg. Chem.* **1990**, *29*, 2042. (c) Costa, R.; García, A.; Ribas, J.; Mallah, T.; Journaux, Y.; Sletten, J.; Solans, X. *Inorg. Chem.* **1993**, *32*, 3733.

(10) (a) Aukauloo, A.; Ottenwaelder, X.; Ruiz, R.; Journaux, Y.; Pei, Y.; Rivière, E.; Cervera, B.; Muñoz, M. C. *Eur. J. Inorg. Chem.* **1999**, 209. (b) Aukauloo, A.; Ottenwaelder, X.; Ruiz, R.; Journaux, Y.; Pei, Y.; Rivière, E.; Muñoz, M. C. *Eur. J. Inorg. Chem.* **2000**, 951.

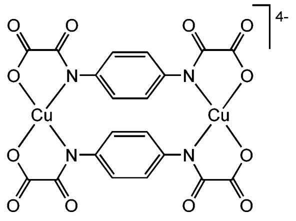
(11) (a) Fernández, I.; Ruiz, R.; Faus, J.; Julve, M.; Lloret, F.; Cano, J.; Ottenwaelder, X.; Journaux, Y.; Muñoz, M. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 3039. (b) Pardo, E.; Faus, J.; Julve, M.; Lloret, F.; Muñoz, M. C.; Cano, J.; Ottenwaelder, X.; Journaux, Y.; Carrasco, R.; Blay, G.; Fernández, I.; Ruiz-García, R. *J. Am. Chem. Soc.* **2003**, *125*, 10770.

(12) (a) Cargill-Thompson, A. M. W.; Gatteschi, D.; McCleverty, J. A.; Navas, J. A.; Rentschler, E.; Ward, M. D. *Inorg. Chem.* **1996**, *35*, 2701. (b) Ung, V. A.; Cargill-Thompson, A. M. W.; Bardwell, D. A.; Gatteschi, D.; Jeffery, J. C.; McCleverty, J. A.; Totti, F.; Ward, M. D. *Inorg. Chem.* **1997**, *36*, 3447. (c) Lloret, F.; De Munno, G.; Julve, M.; Cano, J.; Ruiz, R.; Caneschi, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 135. (d) Ung, V. A.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.; Totti, F.; Gatteschi, D. *Inorg. Chem.* **1999**, *38*, 365.

**Chart 1.** Binuclear Copper(II) Complexes



**$[Cu_2(mpba)_2]^{4-}$** (X = H)
**$[Cu_2(Me_3mpba)_2]^{4-}$** (X = Me)



**$[Cu_2(ppba)_2]^{4-}$**

and $[Cu_2(ppba)_2]^{4-}$ are potentially tetrakis-bidentate ligands that can coordinate up to four coordinatively unsaturated metal complexes through the two cis carbonyl-oxygen atoms of the four oxamate groups, as reported previously in a preliminary communication.[13] The corresponding hexanuclear copper(II) complexes possess a $S = 1$ or $S = 0$ ground state resulting from the ferro- or antiferromagnetic coupling between the two $Cu^{II}$ ions within the $[Cu_2(mpba)_2]^{4-}$ and $[Cu_2(ppba)_2]^{4-}$ metallacyclophane cores, respectively. This represents a successful extension to inorganic complexes of the concept of magnetic coupling units, which has been used earlier to control the spin in either purely organic (polyradicals) or mixed organic−inorganic molecules (metal−polyradical complexes).[14,15] In this work, we extend the use of the binuclear copper(II) complexes $[Cu_2L_2]^{4-}$ with the bridging ligands L = 1,4-phenylenebis(oxamate) (ppba) and 1,3-phenylenebis(oxamate) (mpba) and its derivative 2,4,6-trimethyl-1,3-phenylenebis(oxamate) ($Me_3$mpba) (Chart 1) as precursors for the preparation of both homo- and heterometallic complexes. Either hexa- or pentanuclear complexes may be obtained depending on the number of oxamate groups that coordinate to other coordinatively unsaturated mononuclear copper(II) or nickel(II) complexes, $[ML']^{2+}$ (M = Cu, Ni).

Here we report the synthesis and the structural and magnetic characterization of three hexanuclear copper(II) complexes, $\{[Cu_2(mpba)_2(H_2O)F][Cu(Me_5dien)]_4\}(PF_6)_3\cdot 5H_2O$ (**1**), $\{[Cu_2(Me_3mpba)_2(H_2O)_2][Cu(Me_5dien)]_4\}(ClO_4)_4\cdot 12H_2O$ (**2**), and $\{[Cu_2(ppba)_2][Cu(Me_5dien)]_4\}(ClO_4)_4$ (**3**), together with one pentanuclear copper(II)−nickel(II) complex, $[Ni(cyclam)]\{[Cu_2(mpba)_2][Ni(cyclam)]_3\}(ClO_4)_4\cdot 6H_2O$ (**4**), where *N,N,N′,N″,N″*-pentamethyldiethylenetriamine ($Me_5$dien) and 1,4,8,11-tetraazacyclotetradecane (cyclam) are open-chain tridentate and macrocyclic tetradentate blocking ligands, respectively. By replacement of $Cu^{II}$ with $Ni^{II}$ as the peripheral metal ions along this series, our goal is to obtain heterometallic copper(II)−nickel(II) complexes with higher ground spin states and larger magnetic anisotropies than their homometallic copper(II) analogues as potential SMMs exhibiting slow magnetic relaxation behavior.

## Experimental Section

**General.** All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received. The copper(II) complex $Na_4[Cu_2(Me_3mpba)_2]\cdot 9H_2O$ was synthesized by following standard procedures (Supporting Information), as previously reported for $Na_4[Cu_2(mpba)_2]\cdot 8H_2O$ and $Li_4[Cu_2(ppba)_2]\cdot 10H_2O$.[11] The nickel(II) complex $[Ni(cyclam)](ClO_4)_2$ was obtained by literature methods.[16] Elemental analyses (C, H, N, F) were performed at the Microanalytical Service of the Universitat de València (Spain) and at the Service Central d’Analyse du CNRS in Vernaison (France).

**Syntheses of the Complexes.** The cationic complexes of general formula $[(Cu_2L_2)(ML')_x]^{(2x-4)+}$ (M = Cu, L′ = $Me_5$dien, L = mpba (**1**), $Me_3$mpba (**2**), and ppba (**3**) with $x = 4$; M = Ni, L′ = cyclam, L = mpba (**4**) with $x = 3$) were synthesized in water by the stoichiometric reaction (1:4) of the previously isolated sodium or lithium salts of the anionic binuclear copper(II) precursors, $[Cu_2L_2]^{4-}$, with the perchlorate salts of the cationic mononuclear copper(II) or nickel(II) complexes, $[ML']^{2+}$. The former complexes were prepared in situ from a mixture of $Cu(ClO_4)_2$ and L′ (L′ = $Me_5$dien) in a 1:1 stoichiometry, whereas the last one was isolated previously (L′ = cyclam). Complex **1** was obtained as a mixed hexafluorophosphate/fluoride salt by addition of $KPF_6$, which would undergo metal-assisted partial hydrolysis to give $F^-$ anions under the reaction conditions.[17] Complexes **2**−**4** were isolated as the perchlorate salts, with a square-planar mononuclear nickel(II) complex $[NiL']^{2+}$ (L′ = cyclam) as an additional countercation in the latter case. Satisfactory elemental analyses were obtained for **1**−**4**.

**$\{[Cu_2(mpba)_2(H_2O)F][Cu(Me_5dien)]_4\}(PF_6)_3\cdot 5H_2O$ (1).** An aqueous solution (5 mL) of $Na_4[Cu_2(mpba)_2]\cdot 8H_2O$ (0.22 g, 0.25 mmol) was added dropwise to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.37 g, 1.0 mmol) and $Me_5$dien (0.21 mL, 1.0 mmol) in water (10 mL) while stirring. Solid $KPF_6$ (0.19 g, 1.0 mmol) was added at the end of the reaction. X-ray quality blue prisms of **1** were obtained by slow evaporation at room temperature of the deep blue filtered solution after 1 day. They were filtered off and air-dried. Yield: 0.31 g (63%). Anal. Calcd for $C_{56}H_{112}Cu_6F_{19}N_{16}O_{18}P_3$ ($M$ = 2133): C, 31.50; H, 5.25; N, 10.50; F, 16.92. Found: C, 32.23; H, 5.32; N, 10.64; F, 17.09. IR (KBr, $cm^{-1}$): 3433 (O−H), 1631 (C=O), 843 (P−F).

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[13] Pardo, E.; Bernot, K.; Julve, M.; Lloret, F.; Cano, J.; Ruiz-García, R.; Delgado, F. S.; Ruiz-Pérez, C.; Ottenwaelder, X.; Journaux, Y. *Inorg. Chem.* **2004**, *43*, 2768.

[14] (a) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744. (b) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872.

[15] (a) Caneschi, A.; Dei, A.; Lee, H.; Shultz, D. A.; Sorace, L. *Inorg. Chem.* **2001**, *40*, 408. (b) Caneschi, A.; Dei, A.; Mussari, C. P.; Shultz, D. A.; Sorace, L.; Vostrikova, K. E. *Inorg. Chem.* **2002**, *41*, 1086.

[16] Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.

[17] (a) Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 490. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319. (c) Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* **1978**, *31*, 267. (d) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369. (e) Bauer, H.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 219. (f) Fernández-Galán, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309.

**Table 1.** Summary of Crystallographic Data for **1**−**4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| formula | $C_{56}H_{112}Cu_6F_{19}N_{16}O_{18}P_3$ | $C_{62}H_{140}Cl_4Cu_6N_{16}O_{42}$ | $C_{56}H_{100}Cl_4Cu_6N_{16}O_{28}$ | $C_{60}H_{116}Cl_4Cu_2N_{20}Ni_4O_{34}$ |
| $M$ (g mol$^{-1}$) | 2132.77 | 2304.94 | 1968.56 | 2165.45 |
| crystal system | triclinic | monoclinic | triclinic | orthorhombic |
| space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_12_12_1$ |
| $a$ (Å) | 14.821(3) | 20.580(5) | 21.470(4) | 16.8431(17) |
| $b$ (Å) | 17.246(7) | 16.392(2) | 21.508(5) | 17.2353(19) |
| $c$ (Å) | 19.253(9) | 31.014(4) | 20.3051(17) | 31.392(4) |
| α (deg) | 88.69(4) | | 93.678(10) | |
| $\beta$ (deg) | 78.06(3) | 105.013(9) | 93.388(11) | |
| $\gamma$ (deg) | 77.72(2) | | 85.662(13) | |
| $V$ (Å$^3$) | 4703(3) | 10106(3) | 9316(3) | 9113.0(18) |
| $Z$ | 2 | 4 | 4 | 8 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.495 | 1.515 | 1.403 | 1.528 |
| $F$(000) | 2162 | 4808 | 4056 | 4232 |
| $\mu$ (mm$^{-1}$) | 1.483 | 1.436 | 1.534 | 1.473 |
| $T$ (K) | 298(2) | 298(2) | 298(2) | 298(2) |
| $R^a$ [$I > 2\sigma(I)$] | 0.0968 | 0.0864 | 0.0836 | 0.0752 |
| $R_w{}^b$ [$I > 2\sigma(I)$] | 0.1864 | 0.2287 | 0.1995 | 0.1413 |
| $S^c$ | 0.983 | 1.028 | 1.043 | 0.986 |

$^a$ $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b$ $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $^c$ $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

**{[$Cu_2(Me_3mpba)_2(H_2O)_2$][$Cu(Me_5dien)$]$_4$}($ClO_4$)$_4$·$12H_2O$ (2).** An aqueous solution (5 mL) of $Na_4[Cu_2(Me_3mpba)_2]·9H_2O$ (0.24 g, 0.25 mmol) was added dropwise to a solution of $Cu(ClO_4)_2·6H_2O$ (0.37 g, 1.0 mmol) and Me$_5$dien (0.21 mL, 1.0 mmol) in water (10 mL) while stirring. X-ray quality blue prisms of **2** were obtained by slow evaporation at room temperature of the deep blue filtered solution after 1 week. They were filtered off and air-dried. Yield: 0.51 g (87%). Anal. Calcd for $C_{62}H_{140}Cl_4Cu_6N_{16}O_{42}$ ($M$ = 2305): C, 32.28; H, 6.07; N, 9.72. Found: C, 31.84; H, 5.81; N, 9.56. IR (KBr, cm$^{-1}$): 3440 (O−H), 1638, 1593 (C═O), 1091 (Cl−O).

**{[$Cu_2(ppba)_2$][$Cu(Me_5dien)$]$_4$}($ClO_4$)$_4$ (3).** An aqueous solution (5 mL) of $Li_4[Cu_2(ppba)_2]·10H_2O$ (0.20 g, 0.25 mmol) was added dropwise to a solution of $Cu(ClO_4)_2·6H_2O$ (0.37 g, 1.0 mmol) and Me$_5$dien (0.21 mL, 1.0 mmol) in water (10 mL) while stirring. X-ray quality green prisms of **3** were obtained by slow evaporation at room temperature of the deep green filtered solution after 1 week. They were filtered off and air-dried. Yield: 0.36 g (76%). Anal. Calcd for $C_{56}H_{100}Cl_4Cu_6N_{16}O_{28}$ ($M$ = 1969): C, 34.13; H, 5.08; N, 11.38. Found: C, 34.25; H, 5.12; N, 11.41. IR (KBr, cm$^{-1}$): 3441 (O−H), 1612 (C═O), 1119, 1113, 1091 (Cl−O).

**[Ni(cyclam)]{[$Cu_2(mpba)_2$][Ni(cyclam)]$_3$}($ClO_4$)$_4$·$6H_2O$ (4).** An aqueous solution (5 mL) of $Na_4[Cu_2(mpba)_2]·8H_2O$ (0.215 g, 0.25 mmol) was added dropwise to a solution of [Ni(cyclam)]($ClO_4$)$_2$ (0.345 g, 0.76 mmol) in water (10 mL) while stirring. X-ray quality green prisms of **4** were obtained by slow evaporation at room temperature of the orange-greenish filtered solution after a few days. They were filtered off and air-dried. Yield: 0.23 g (53%). Anal. Calcd for $C_{60}H_{116}Cl_4Cu_2N_{20}Ni_4O_{34}$ ($M$ = 2165): C, 33.26; H, 5.36; N, 12.93. Found: C, 33.12; H, 5.28; N, 13.01. IR (KBr, cm$^{-1}$): 3431 (O−H), 3273 (N−H), 1618 (C═O), 1116, 1111, 1087 (Cl−O).

**Physical Techniques.** IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. Variable-temperature (2−300 K) magnetic susceptibility measurements were carried out on powdered samples of complexes **1**−**4** under an applied field of 1 T ($T \geq 25$ K) and 250 G ($T < 25$ K) with a Quantum Design SQUID magnetometer. The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

**Crystal Structure Data Collection and Refinement.** The structures of complexes **1**−**4** were solved by direct methods and refined with the full-matrix least-squares technique on $F^2$ using the SHELXS-97 and SHELXL-97 programs.[18a] Data collection and data reduction were done with the COLLECT[18b] and EVALCCD[18c] programs. Empirical absorption corrections were carried out using SADABS[18d] for all compounds. All calculations for data reduction, structure solution, and refinement were done by standard procedures (WINGX).[18e] The final geometrical calculations and the graphical manipulations were carried out with PARST97[18f] and CRYSTAL MAKER[18g] programs, respectively. The hydrogen atoms from the organic ligands were calculated and refined with isotropic thermal parameters, while those from the water molecules were neither found nor calculated. A summary of the crystallographic data for **1**−**4** is listed in Table 1. Selected bond lengths and angles for **1**−**4** are summarized in Tables S1−S4 (Supporting Information).

## Results and Discussion

**Description of the Structures. {[$Cu_2(mpba)_2(H_2O)F$][$Cu(Me_5dien)$]$_4$}($PF_6$)$_3$·$5H_2O$ (1).** The structure of complex **1** consists of hexanuclear copper(II) cations, {[$Cu_2(mpba)_2(H_2O)F$][$Cu(Me_5dien)$]$_4$}$^{3+}$ (Figure 1), coordinated and uncoordinated hexafluororophosphate anions, and crystallization water. The $Cu^{II}_6$ entity exhibits a “dimer-of-trimers” structure with a ladderlike architecture of the [2 × 2]L type. The two *m*-phenylene spacers act as “rungs” between the two oxamate-bridged $Cu^{II}_3$ linear units which then serve as “rails”. This leads to a metallamacrocyclic binuclear copper(II) core of the [3,3]metacyclophane-type with a $\pi$-stacked arrangement of the aromatic rings connected by the two N−Cu−N linkages. The values of the intratrimer distance between the central and peripheral copper atoms through the oxamate bridge average 5.308(2) Å, a value which is comparable to those reported for related oxamate-bridged linear trinuclear copper(II) complexes (5.12−5.30 Å).[9c] The value of the

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(18) (a) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis*, release 97-2; Institüt für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1998. (b) Hooft, R. W. W. *COLLECT*; Nonius BV: Delft, The Netherlands, 1999. (c) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220 (EVALCCD). (d) *SADABS*, version 2.03; Bruker AXS Inc.: Madison, WI, 2000. (e) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837 (WINGX). (f) Nardelli, M. *J. Appl. Crystallogr.* **1995**, *28*, 659. (g) Palmer, D. *CRYSTAL MAKER*; Cambridge University Technical Services: Cambridge, U.K., 1996.

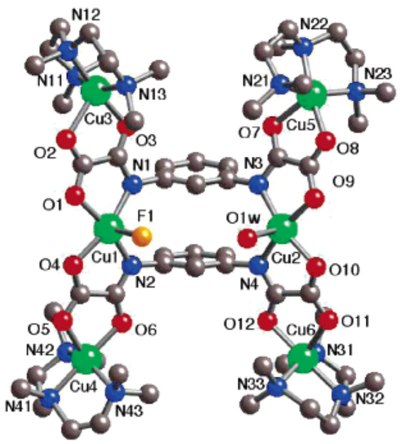

**Figure 1.** Perspective view of the noncentrosymmetric cationic hexanuclear unit of **1** with the numbering scheme for the metal coordination environments.

intertrimer distance between the two central copper atoms through the double *m*-phenylenediamidate bridge is 6.636(2) Å, a value which is similar to that found in the binuclear copper(II) complex $Na_4[Cu_2(mpba)_2]{\cdot}8H_2O$ (6.822(2) Å).[11a]

The two central copper atoms, Cu(1) and Cu(2), have five-coordinated square pyramidal, $CuN_2O_2F$, and six-coordinated tetragonally elongated octahedral, $CuN_2O_3F$, surroundings, respectively. Two amidate-nitrogen atoms (Cu−N = 1.950(8)−1.990(9) Å) and two carboxylate-oxygen atoms (Cu−O = 1.973(7)−1.999(8) Å) from the oxamate groups of the mpba ligands build the basal plane, whereas the apical positions are occupied by one fluoride anion (Cu−F = 2.264(7) Å) for Cu(1) and by a water molecule (Cu−O = 2.397(14) Å) and a weakly coordinated hexafluorophosphate anion (Cu−F = 2.938(12) Å) for Cu(2) (Table S1, Supporting Information). Both copper atoms are slightly displaced out of their basal planes toward the apical position occupied by the fluoride anion and the water molecule (average deviations of 0.221(2) and 0.158(2) Å, respectively). The coordination environment of the four peripheral copper atoms, Cu(3) through Cu(6), is best described as five-coordinated square pyramidal rather than trigonal bipyramidal. The average value of the geometric $\tau$ parameter is 0.35 ($\tau = 0$ and 1 for ideal square planar and trigonal bipyramidal geometries, respectively).[9c] Three amine-nitrogen atoms from the $Me_5$dien ligand (Cu−N = 1.963(13)−2.049(13) Å) and one carbonyl-oxygen atom from the oxamate group of the mpba ligand (Cu−O = 1.956(9)−1.986(6) Å) build the basal plane of the square pyramid, $CuN_3O_2$, whereas the apical position is occupied by the other carbonyl-oxygen atom (Cu−O = 2.159(8)−2.206(8) Å) (Table S1, Supporting Information). Importantly, the basal planes of the central and the two peripheral copper atoms of each $Cu^{II}_3$ linear unit are almost perpendicular to each other (dihedral angles in the range 84.0(3)−89.0(5)°). Within the $Cu^{II}_2$ metacyclophane core, there exists an almost perfect face-to-face alignment of the two benzene rings. Hence, the basal planes of the two central copper atoms are disposed perpendicularly to the phenylene planes (dihedral angles in the range 83.3(4)−89.8(3)°) which are in turn almost parallel to each other (dihedral angle of 8.1(4)°), as previously observed in $Na_4[Cu_2(mpba)_2]{\cdot}8H_2O$ (dihedral angles between the copper and phenylene planes are in the range 72.1(3)−82.0(3)°).[11a]

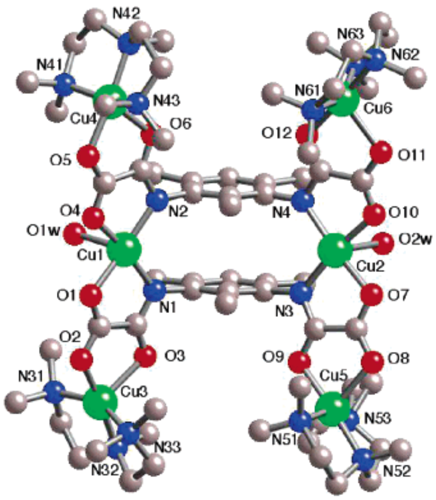

**Figure 2.** Perspective view of the noncentrosymmetric cationic hexanuclear unit of **2** with the numbering scheme for the metal coordination environments.

In the crystal lattice, the $Cu^{II}_6$ entities are connected through hydrogen bonds involving the axially coordinated fluoride anion and a coordinated carbonyl-oxygen atom from the oxamate groups through a crystallization water molecule, forming thus centrosymmetric dimers (F(1)···O(3w) = 2.772(12) Å; O(3w)···O($2^{I}$) = 2.831(10) Å) (Figure S1a, Supporting Information). The values of the intermolecular Cu(1)−Cu($1^{I}$) and Cu(1)−Cu($3^{I}$) distances between neighboring $Cu^{II}_6$ entities are 6.147(3) and 8.013(3) Å, respectively. These centrosymmetric dimers are well separated from each other by uncoordinated hexafluorophosphate anions (Figure S1b, Supporting Information).

**$\{[Cu_2(Me_3mpba)_2(H_2O)_2][Cu(Me_5dien)]_4\}(ClO_4)_4{\cdot}12H_2O$ (2).** The structure of complex **2** consists of hexanuclear copper(II) cations, $\{[Cu_2(Me_3mpba)_2(H_2O)_2][Cu(Me_5dien)]_4\}^{4+}$ (Figure 2), coordinated and uncoordinated perchlorate anions, and crystallization water molecules. As for complex **1**, the $Cu^{II}_6$ entity exhibits a "dimer-of-trimers" structure with a [2 × 2] ladderlike architecture which is made up of two oxamate-bridged $Cu^{II}_3$ linear units connected through two trimethyl-substituted *m*-phenylene spacers between the two central copper atoms to give a binuclear metallacyclic core of the [3,3]metacyclophane-type. The average value of the intratrimer distance between the central and peripheral copper atoms through the oxamate bridge is 5.330(15) Å, a value which is almost identical to that reported for **1** (5.308(2) Å). The value of the intertrimer distance between the two central copper atoms through the trimethyl-substituted *m*-phenylenediamidate bridges is 7.087(19) Å, a value which is slightly longer than that through the *m*-phenylenediamidate bridges in **1** (6.636(2) Å).

The two central copper atoms, Cu(1) and Cu(2), have five-coordinated square pyramidal, $CuN_2O_3$, and six-coordinated tetragonally elongated octahedral, $CuN_2O_4$, surroundings, respectively. Two amidate-nitrogen atoms (Cu−N = 1.987(5)−1.992(5) Å) and two carboxylate-oxygen atoms (Cu−O = 1.968(5)−2.000(4) Å) from the oxamate groups of the

$Me_3$mpba ligands build the basal plane, whereas the apical positions are occupied by a water molecule (Cu−O = 2.303(9) Å) for Cu(1) and one water molecule (Cu−O = 2.457(10) Å) and a weakly coordinated perchlorate anion (Cu−O = 2.668(8) Å) for Cu(2) (Table S2, Supporting Information). Both copper atoms are slightly displaced out of their basal planes toward the apical position occupied by the water molecules (average deviations of 0.1538(26) and 0.0734(26) Å, respectively). The coordination environment of the four peripheral copper atoms, Cu(3) through Cu(6), is best described as five-coordinated square pyramidal rather than trigonal bipyramidal (average $\tau$ value of 0.39). Three amine-nitrogen atoms from the $Me_5$dien ligand (Cu−N = 2.011(5)−2.068(7) Å) and one carbonyl-oxygen atom from the oxamate group of the $Me_3$mpba ligand (Cu−O = 1.984(4)−1.993(4) Å) build the basal plane of the square pyramid, $CuN_3O_2$, whereas the apical position is occupied by the other carbonyl-oxygen atom (Cu−O = 2.185(4)−2.204(5) Å) (Table S2, Supporting Information). As for complex **1**, the basal planes of the central and the two peripheral copper atoms of each $Cu^{II}_3$ linear unit are almost perpendicular to each other (dihedral angles in the range 78.54(16)−89.44(14)°). Within the $Cu^{II}_2$ metacyclophane core, there exists a slight twisting of the two benzene rings from the perfect face-to-face alignment due to the steric hindrance between the equivalent methyl groups of each ring (C−C = 3.317(14)−3.721(16) Å). However, the basal planes of the two central copper atoms are perpendicular to the phenylene planes (dihedral angles in the range 82.75(16)−88.32(17)°) which are in turn almost parallel to each other (dihedral angle of 4.81(15)°), as observed for **1** (dihedral angles in the range 83.3(4)−89.8(3)° and 8.1(4)°, respectively).

In the crystal lattice, the $Cu^{II}_6$ entities are connected through hydrogen bonds between axially coordinated water molecules and perchlorate anions, forming thus chains along the *b*-axis (Ow···O = 2.884(14) Å) (Figure S2a, Supporting Information). The value of the intermolecular Cu(1)−Cu($2^I$) distance between neighboring $Cu^{II}_6$ entities is 9.412(5) Å. The chains are arranged side-by-side leading to layers which are well separated from each other by uncoordinated perchlorate anions (Figure S2b, Supporting Information).

**$\{[Cu_2(ppba)_2][Cu(Me_5dien)]_4\}(ClO_4)_4$ (3).** The structure of complex **3** consists of hexanuclear copper(II) cations, $\{[Cu_2(ppba)_2][Cu(Me_5dien)]_4\}^{4+}$ (Figure 3), and coordinated perchlorate anions. The $Cu^{II}_6$ entity exhibits a "dimer-of-trimers" structure with a [2 × 2] ladderlike architecture which is made up of two oxamate-bridged $Cu^{II}_3$ linear units connected through two *p*-phenylene spacers between the two central copper atoms to give a binuclear metallacyclic core of the [3,3]paracyclophane-type. The average value of the intratrimer distance between the central and the peripheral copper atoms through the oxamate bridge is 5.340(5) Å, a value which is almost identical to that observed in **1** and **2** (5.308(2) and 5.330(15) Å, respectively). The average value of the intertrimer distance between the two central copper atoms through the double *p*-phenylenediamidate bridge is 8.059(2) Å, a value which is similar to that found in the binuclear copper(II) complex $Na_4[Cu_2(ppba)_2]\cdot 11H_2O$ (7.910(2) Å)[11b] and longer than that through the double *m*-phenylenediamidate-type bridges in **1** and **2** (6.636(2) and 7.087(19) Å, respectively).

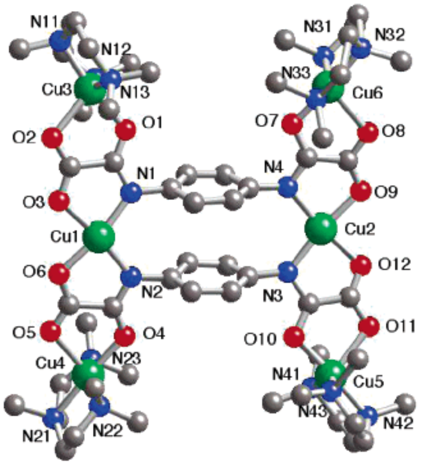

**Figure 3.** Perspective view of the noncentrosymmetric cationic hexanuclear unit of **3** with the numbering scheme for the metal coordination environments.

The two central copper atoms, Cu(1) and Cu(2), have six-coordinated tetragonally elongated octahedral, $CuN_2O_4$, surroundings. Two amidate-nitrogen atoms (Cu−N = 1.942(17)−2.016(16) Å) and two carboxylate-oxygen atoms (Cu−O = 1.926(14)−2.021(13) Å) from the oxamate groups of the ppba ligands build the basal plane, whereas the apical positions are occupied by two oxygen atoms from weakly coordinated perchlorate anions (Cu−O = 2.596(5)−3.254(5) Å) (Table S3, Supporting Information). Both copper atoms are slightly displaced out of their basal planes toward one of the apical positions occupied by the perchlorate anions (average deviation of 0.114(3) Å). The coordination environment of the four peripheral copper atoms, Cu(3) through Cu(6), is intermediate between five-coordinated square pyramidal and trigonal bipyramidal. The average $\tau$ value of 0.42 is somewhat greater than that observed in **1** and **2** ($\tau = 0.35$ and 0.39, respectively). Three amine-nitrogen atoms from the $Me_5$dien ligand (Cu−N = 1.87(4)−2.141(18) Å) and one carbonyl-oxygen atom from the oxamate group of the ppba ligand (Cu−O = 1.923(15)−1.988(14) Å) build the basal plane of the square pyramid, $CuN_3O_2$, whereas the apical position is occupied by the other carbonyl-oxygen atom (Cu−O = 2.151(19)−2.254(14) Å) (Table S3, Supporting Information). As for complexes **1** and **2**, the basal planes of the central and the two peripheral copper atoms of each $Cu^{II}_3$ linear unit are almost perpendicular to each other (dihedral angles in the range 77.2(6)−88.7(6)°). However, the $Cu^{II}_3$ linear units show a more folded conformation as compared to those in **1** and **2**. Within the $Cu^{II}_2$ paracyclophane core, the two benzene rings are not eclipsed but slightly glided perpendicularly to the Cu−Cu vector. The deviations from the face-to-face alignment are, however, smaller than in $Na_4[Cu_2(ppba)_2]\cdot 11H_2O$.[11b] Hence, the basal planes of the two central copper atoms are almost perpendicular to the phenylene planes (dihedral angles in the range 75.4(6)−77.8(6)°) which are in turn parallel to each other (dihedral angles in the range 1.2(7)−5.4(6)°), whereas a rather large deviation

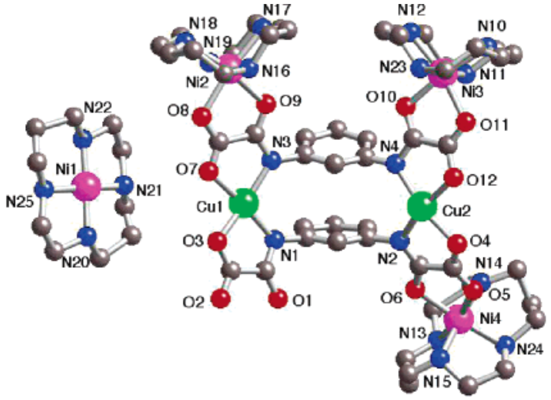

**Figure 4.** Perspective view of the cationic mononuclear and pentanuclear units of **4** with the numbering scheme for the metal coordination environments.

from this situation is observed in $Na_4[Cu_2(ppba)_2]\cdot 11H_2O$ (dihedral angles between the copper and phenylene planes in the range 57.4(2)−62.9(2)°).[11b]

In the crystal lattice, there are three crystallographically independent hexanuclear copper(II) cations, two centrosymmetric and one noncentrosymmetric, which are however structurally and stereochemically equivalent (Figure S3a, Supporting Information). The $Cu^{II}_6$ entities are perfectly isolated from each other by the weakly coordinated perchlorate anions (Figure S3b, Supporting Information).

**$[Ni(cyclam)]\{[Cu_2(mpba)_2][Ni(cyclam)]_3\}(ClO_4)_4\cdot 6H_2O$ (4).** The structure of complex **4** consists of both mononuclear nickel(II) and pentanuclear copper(II)−nickel(II) cations, $[Ni(cyclam)]^{2+}$ and $\{[Cu_2(mpba)_2][Ni(cyclam)]_3\}^{2+}$ (Figure 4), respectively, coordinated and uncoordinated perchlorate anions, and crystallization water molecules. The $Cu^{II}_2Ni^{II}_3$ entity exhibits a "dimer-plus-trimer" structure with an incomplete [2 × 2] ladderlike architecture which is made up of oxamate-bridged $Cu^{II}Ni^{II}$ and $Cu^{II}Ni^{II}_2$ linear units connected through two *m*-phenylene spacers between the two copper atoms to give a binuclear metallacyclic core of the [3,3]metacyclophane-type. The value of the intramolecular distance between the two copper atoms through the double *m*-phenylenediamidate bridge is 6.937(7) Å, while those between the copper and the nickel atoms through the oxamate bridge average 5.319(4) Å, a value which is comparable to those reported for a related oxamate-bridged linear trinuclear copper(II)−nickel(II) complex (5.305(2)−5.326(2) Å).[9b]

The nickel atom of the mononuclear entity, Ni(1), has a four-coordinated square-planar, $NiN_4$, surrounding which is formed by four amine-nitrogen atoms from the cyclam ligand in a planar conformation (Ni−N = 1.809(17)−1.948(14) Å) (Table S4, Supporting Information). The three nickel atoms of the pentanuclear entity, Ni(2) through Ni(4), have six-coordinated distorted octahedral, $NiN_4O_2$, surroundings which are formed by four amine-nitrogen atoms from the cyclam ligand in a cis-$\beta$ conformation (Ni−N = 2.065(16)−2.137(11) Å) and two carbonyl-oxygen atoms from the oxamate group of the mpba ligand in cis positions (Ni−O = 2.062(7)−2.164(7) Å) (Table S4, Supporting Information). The average value of the Ni−N distance in the pentanuclear unit is 2.097(11) Å, which is typical of high-spin $Ni^{II}$ ions ($S = 1$), whereas the average value of the Ni−N distance in the mononuclear entity is 1.890(4) Å, much shorter and characteristic of low-spin $Ni^{II}$ ions ($S = 0$). The two copper atoms of the pentanuclear entity, Cu(1) and Cu(2), have five-coordinated square pyramidal, $CuN_2O_3$, surroundings. Two amidate-nitrogen atoms (Cu−N = 1.950(8)−1.991(8) Å) and two carboxylate-oxygen atoms (Cu−O = 1.930(7)−2.001(7) Å) from the oxamate groups of the mpba ligands build the basal plane, whereas the apical position is occupied by an oxygen atom from a weakly coordinated perchlorate anion (Cu−O = 2.578(2)−2.642(2) Å) (Table S4, Supporting Information). The copper and nickel basal planes are almost coplanar in the $Cu^{II}Ni^{II}$ unit (dihedral angle of 9.4(3)°), but they deviate slightly from coplanarity in the $Cu^{II}Ni^{II}_2$ linear unit (dihedral angles in the range 20.5(3)−30.1(4)°), leading thus to a folded conformation. Within the $Cu^{II}_2$ metacyclophane core, there is a rather large distortion from the face-to-face alignment of the two benzene rings as compared to the situation observed in **1** and **2**, reflecting thus the nonequivalence of the copper atoms as a consequence of the absence of a nickel coordination site. Hence, the copper basal planes are not exactly perpendicular to the phenylene planes (dihedral angles in the range 67.7(2)−85.2(2)°) and, moreover, the phenylene planes are not exactly parallel to each other (dihedral angle of 15.2(4)°).

In the crystal lattice, the $Cu^{II}_2Ni^{II}_3$ entities are connected through hydrogen bonds between the coordinated and uncoordinated carbonyl-oxygen atoms from the oxamate groups of the $Cu^{II}Ni^{II}$ units and the crystallization water molecules, forming thus zigzag chains along the *a*-axis (O···Ow = 2.786(3)−2.966(4) Å and Ow···Ow = 2.595(3)−2.850(4) Å) (Figure S4a, Supporting Information). The value of the intermolecular Cu($1^I$)−Ni(2) distance between neighboring $Cu^{II}_2Ni^{II}_3$ entities through the linear three-water hydrogen-bonded motif is 12.967(4) Å. Interestingly, this zigzag arrangement leads to small cylindrical-shaped channels which are filled by mononuclear $Ni^{II}$ cations stacked almost perpendicularly to each other (Figure S4b, Supporting Information). The value of the intermolecular Ni(1)−Ni($1^I$) distance between neighboring mononuclear $Ni^{II}$ cations within the stack is 9.164(4) Å.

**Magnetic Properties.** The magnetic properties of the hexanuclear copper(II) complexes **1**−**3** in the form of $\chi_MT$ versus $T$ plots, $\chi_M$ being the molar magnetic susceptibility per $Cu^{II}_6$ unit and $T$ the temperature, are shown in Figure 5. At room temperature, the values of $\chi_MT$ for **1**−**3** are in the range 2.07−2.11 cm$^3$ K mol$^{-1}$, values which are smaller than that expected for six magnetically isolated $Cu^{II}$ ions ($S_{Cu} = {}^1/_2$) ($\chi_MT$ = 2.48 cm$^3$ K mol$^{-1}$ with $g = 2.1$). $\chi_MT$ first decreases upon cooling for **1** and **2** to reach a plateau at approximately 30 K with $\chi_MT$ values of 0.83 and 0.84 cm$^3$ K mol$^{-1}$, respectively. These values are close to that expected for two doublet ($S = {}^1/_2$) states from each $Cu^{II}_3$ linear unit ($\chi_MT$ = 0.83 cm$^3$ K mol$^{-1}$ with $g = 2.1$). When the compounds were cooled further, $\chi_MT$ slightly increases for **1** and **2** to reach $\chi_MT$ values at 2.0 K of 0.85 and 0.94 cm$^3$ K mol$^{-1}$, respectively (inset of Figure 5). These values are somewhat lower than that expected for a triplet ($S = 1$)

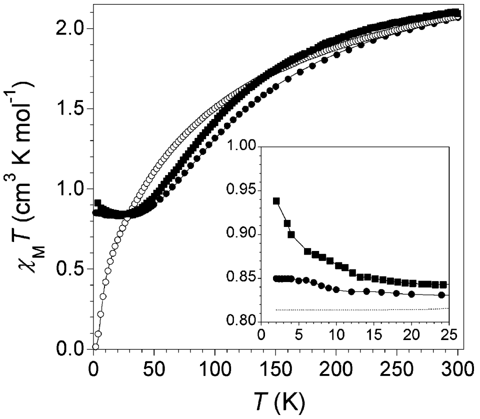

**Figure 5.** Temperature dependence of $\chi_M T$ of **1** (●), **2** (■), and **3** (○). The inset shows the temperature dependence of $\chi_M T$ for **1** and **2** in the low-temperature region. Solid and dotted lines correspond to the best fits (see text).

ground state ($\chi_M T = 1.10$ cm$^3$ K mol$^{-1}$ with $g = 2.1$). In contrast, $\chi_M T$ for **3** continuously decreases upon cooling and it vanishes at 2.0 K, which indicates a singlet ($S = 0$) ground state.

The magnetic behavior of **1**−**3** is qualitatively consistent with their "dimer-of-trimers" structure (Scheme 1). In the high-temperature region, the observed trends are reminiscent of that of two $Cu^{II}_3$ linear units with a moderate to strong antiferromagnetic intratrimer coupling between central and peripheral $Cu^{II}$ ions ($J = J_{13} = J_{14} = J_{25} = J_{26}$). The linear topology results in a regular spin state structure for each trinuclear copper(II) unit,[9c] with an $S = {}^1/_2$ ground state separated by $-J$ and $-3J/2$ from the $S = {}^1/_2$ and $S = {}^3/_2$ excited states, respectively (Scheme 1a). In this case, $\chi_M T$ would decrease to attain a plateau at low temperatures where only the $S = {}^1/_2$ ground states of the two magnetically isolated linear trinuclear units are thermally populated. Thus, the deviations observed in the low-temperature region for **1** and **2** are the signature of a moderate to weak ferromagnetic intertrimer coupling ($j_{\mathrm{eff}} > 0$) between the $S = {}^1/_2$ $Cu^{II}_3$ units, yielding an $S = 1$ ground state and an $S = 0$ excited-state separated by $j_{\mathrm{eff}}$ for the $Cu^{II}_6$ molecule (Scheme 1b). In contrast, a strong antiferromagnetic intertrimer coupling ($j_{\mathrm{eff}} < 0$) between the $S = {}^1/_2$ $Cu^{II}_3$ units operates in **3** leading to a singlet ground state for the entire hexanuclear molecule (Scheme 1c). This effective ferro- or antiferromagnetic coupling ($j_{\mathrm{eff}}$) between the $Cu^{II}_3$ linear units occurs between the central $Cu^{II}$ ions of each trinuclear unit within the $Cu^{II}_2$ metallacyclophane core ($J' = J_{12}$), while the next-nearest neighbor (crossed) interactions between central and peripheral $Cu^{II}$ ions of the two different trinuclear units ($J'' = J_{15} = J_{16} = J_{23} = J_{24}$) are negligible.

The temperature dependence of the magnetic susceptibility data of **1** and **2** was then fitted through an effective spin Hamiltonian for a "dimer-of-trimers" model that takes into account the intertrimer coupling between the $S = {}^1/_2$ ground states of each $Cu^{II}_3$ linear unit,

$$\mathbf{H} = -J(\mathbf{S}_{1A}\cdot\mathbf{S}_{3A} + \mathbf{S}_{1A}\cdot\mathbf{S}_{4A} + \mathbf{S}_{2B}\cdot\mathbf{S}_{5B} + \mathbf{S}_{2B}\cdot\mathbf{S}_{6B}) - j_{\mathrm{eff}}\mathbf{S}_{A}\cdot\mathbf{S}_{B} + g\beta(\mathbf{S}_{1A} + \mathbf{S}_{3A} + \mathbf{S}_{4A} + \mathbf{S}_{2B} + \mathbf{S}_{5B} + \mathbf{S}_{6B})B \quad (1)$$

**Scheme 1**. (a) Spin State Structure for a Trinuclear $Cu^{II}_3$ Linear Complex and (b, c) Energy Levels of the Low-Lying Spin States for a "Dimer-of-Trimers" $[Cu^{II}_3]_2$ Complex with an Intertrimer Ferro- and Antiferromagnetic Coupling, Respectively

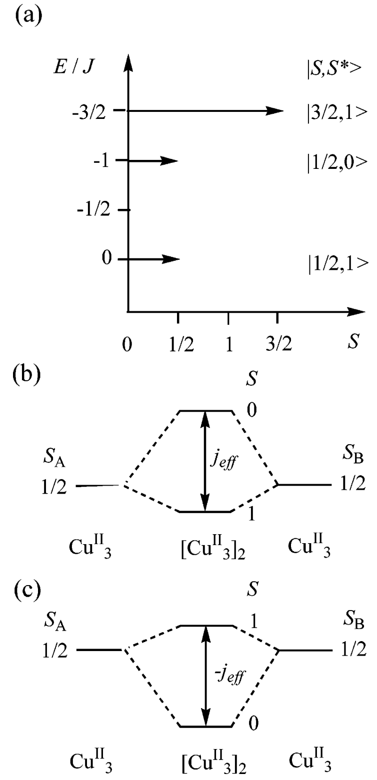

**Table 2.** Selected Magnetic Data for **1**−**4**

| complex | $J$ (cm$^{-1}$)[a] | $j_{\mathrm{eff}}$ (cm$^{-1}$)[a] | $J'$ (cm$^{-1}$)[a] | $g$[b] | $R$[c] |
|---|---|---|---|---|---|
| **1** | −105.9 ± 0.2 | +0.19 ± 0.01 | +1.7 ± 0.1 | 2.11 ± 0.01 | $1.4 \times 10^{-5}$ |
| **2** | −92.6 ± 0.1 | +1.00 ± 0.04 | +9.0 ± 0.3 | 2.11 ± 0.01 | $0.8 \times 10^{-5}$ |
| **3** | −81.3 ± 0.1 |  | −120.6 ± 0.2 | 2.09 ± 0.01 | $1.0 \times 10^{-5}$ |
| **4** | −111.6 ± 0.2 | +0.28 ± 0.01 | +4.2 ± 0.2 | 2.22 ± 0.01 | $1.1 \times 10^{-4}$ |

[a] $J$, $J'$, and $j_{\mathrm{eff}}$ are the exchange coupling parameters as defined in eqs 1−3 (see text). [b] The Zeeman factor is $g$. [c] $R$ is the agreement factor defined as $R = \Sigma[(\chi_M T)_{\mathrm{exp}} - (\chi_M T)_{\mathrm{calcd}}]^2/\Sigma[(\chi_M T)_{\mathrm{exp}}]^2$.

with $S_{1A} = S_{3A} = S_{4A} = S_{2B} = S_{5B} = S_{6B} = S_{\mathrm{Cu}} = {}^1/_2$ and $S_A = S_B = {}^1/_2$ (Appendix A, Supporting Information).[10b] Least-squares fit gave $J = -105.9$ cm$^{-1}$, $j_{\mathrm{eff}} = +0.19$ cm$^{-1}$, and $g = 2.11$ for **1** and $J = -92.6$ cm$^{-1}$, $j_{\mathrm{eff}} = +1.00$ cm$^{-1}$, and $g = 2.11$ for **2** (Table 2). The theoretical curves for **1** and **2** closely follow the experimental data over the whole temperature range when compared to that corresponding to two magnetically isolated trinuclear complexes ($j_{\mathrm{eff}} = 0$) (solid and dotted lines, respectively, in Figure 5). The small absolute values of the $j_{\mathrm{eff}}/J$ ratio of 0.002 and 0.011 for **1** and **2**, respectively, confirm the validity of the perturbational treatment. In this model, the value of $j_{\mathrm{eff}}$ is related to that of $J'$ by

$$j_{\mathrm{eff}} = J'(\mathbf{S}_{1A}\cdot\mathbf{S}_{A}/|\mathbf{S}_{A}|^2)(\mathbf{S}_{2B}\cdot\mathbf{S}_{B}/|\mathbf{S}_{B}|^2) \quad (2)$$

with $S_{1A} = S_{2B} = S_{\mathrm{Cu}} = {}^1/_2$ and $S_A = S_B = {}^1/_2$, which gives $j_{\mathrm{eff}} = ({}^1/_9)J'$ (Appendix A, Supporting Information).[10b] Accordingly, the calculated values of $J'$ are +1.7 and +9.0 cm$^{-1}$ for **1** and **2**, respectively (Table 2). However, this perturbational treatment cannot be used for **3** because of the antiferromagnetic intra- and intertrimer couplings are of the same order of magnitude. In this case, the temperature dependence of the magnetic susceptibility data was fitted by full-matrix diagonalization of the appropriate spin Hamiltonian for a hexanuclear $Cu^{II}_6$ molecule,

$$\mathbf{H} = -J(\mathbf{S}_{1A}\cdot\mathbf{S}_{3A} + \mathbf{S}_{1A}\cdot\mathbf{S}_{4A} + \mathbf{S}_{2B}\cdot\mathbf{S}_{5B} + \mathbf{S}_{2B}\cdot\mathbf{S}_{6B}) - J'\mathbf{S}_{1A}\cdot\mathbf{S}_{2B} + g\beta(\mathbf{S}_{1A} + \mathbf{S}_{3A} + \mathbf{S}_{4A} + \mathbf{S}_{2B} + \mathbf{S}_{5B} + \mathbf{S}_{6B})B \quad (3)$$

with $S_{1A} = S_{3A} = S_{4A} = S_{2B} = S_{5B} = S_{6B} = S_{Cu} = {}^1/_2$.[19] Least-squares fit gave $J = -81.3$ cm$^{-1}$, $J' = -120.6$ cm$^{-1}$, and $g = 2.08$ for **3** (Table 2). The theoretical curve for **3** closely follows the experimental data over the whole temperature range (solid line in Figure 5). Indeed, the least-squares fit of the magnetic susceptibility data of **1** and **2** by full-matrix diagonalization of the appropriate spin Hamiltonian for a hexamer model gave values for $J$, $J'$, and $g$ which are in excellent agreement with those obtained through the "dimer-of-trimers" model.

The values of the intratrimer coupling parameter for **1**−**3** are among the smallest ones reported for related oxamate-bridged linear trinuclear copper(II) complexes which show a moderate to strong antiferromagnetic coupling ($-J = 80-360$ cm$^{-1}$).[9c] This situation stems from the well-known orbital reversal phenomenon caused by the tridentate $Me_5$dien as the terminal ligand.[20] In this case, the attenuation of the antiferromagnetic coupling through the oxamate bridge is explained by the less efficient $\sigma$-overlap between the noncoplanar $d_{xy}$-type magnetic orbitals of central and peripheral $Cu^{II}$ ions. On the other hand, the values of the intertrimer coupling parameter for **1**−**3** agree both in sign and in magnitude with those found in the corresponding binuclear copper(II) complexes $Na_4[Cu_2(mpba)_2]\cdot 8H_2O$ ($J' = +16.8$ cm$^{-1}$),[11a] $Na_4[Cu_2(Me_3mpba)_2]\cdot 9H_2O$ ($J' = +11.0$ cm$^{-1}$),[21] and $Na_4[Cu_2(ppba)_2]\cdot 11H_2O$ ($J' = -81.0$ cm$^{-1}$)[11b] Thus, the weak to moderate ferromagnetic coupling through the *m*-phenylenediamidate-type bridges for **1** and **2** and the strong antiferromagnetic coupling through the *p*-phenylenediamidate bridges for **3** indicate that the spin polarization mechanism also applies for the propagation of the exchange interaction in the hexanuclear copper(II) complexes.

The magnetic properties of the pentanuclear copper(II)−nickel(II) complex **4** in the form of $\chi_M T$ versus $T$ plots, $\chi_M$ being the molar magnetic susceptibility per $Cu^{II}_2Ni^{II}_3$ unit, are shown in Figure 6. At room temperature, $\chi_M T$ is 3.71 cm$^3$ K mol$^{-1}$, a value which is lower than that expected for two $Cu^{II}$ ($S_{Cu} = {}^1/_2$) and three high-spin $Ni^{II}$ ($S_{Ni} = 1$) ions magnetically isolated ($\chi_M T = 4.54$ cm$^3$ K mol$^{-1}$ with $g = 2.2$). $\chi_M T$ first decreases upon cooling to reach a minimum at 60 K with a $\chi_M T$ value of 2.63 cm$^3$ K mol$^{-1}$, and then it increases to attain a sort of plateau at 15 K with a $\chi_M T$ value of 2.80 cm$^3$ K mol$^{-1}$. This $\chi_M T$ value is rather close to that expected for one quartet ($S = {}^3/_2$) and one doublet ($S = {}^1/_2$) state from a $Cu^{II}Ni^{II}_2$ and a $Cu^{II}Ni^{II}$ unit, respectively ($\chi_M T = 2.72$ cm$^3$ K mol$^{-1}$ with $g = 2.2$). When the complex was cooled further, $\chi_M T$ increases to reach a maximum at 2.5 K with a $\chi_M T$ value of 2.95 cm$^3$ K mol$^{-1}$, a value which is somewhat below that expected for a quintet ($S = 2$) ground state ($\chi_M T = 3.63$ cm$^3$ K mol$^{-1}$ with $g = 2.2$). The small decrease of $\chi_M T$ below 2.5 K is most likely due to the zero-field splitting (ZFS) of the $S = 2$ ground state of the $Cu^{II}_2$-$Ni^{II}_3$ molecule (inset of Figure 6).

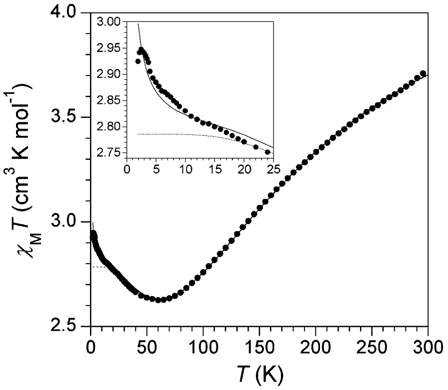

**Figure 6.** Temperature dependence of $\chi_M T$ of **4** (●). The inset shows the temperature dependence of $\chi_M T$ for **4** in the low-temperature region. Solid and dotted lines correspond to the best fits (see text).

The magnetic behavior of **4** is qualitatively consistent with its "dimer-plus-trimer" structure (Scheme 2). In the high-temperature region, the observed trend is reminiscent of that of one $Cu^{II}Ni^{II}_2$ linear unit and one $Cu^{II}Ni^{II}$ unit with an antiferromagnetic coupling between $Cu^{II}$ and high-spin $Ni^{II}$ ions within the trimer and the dimer units ($J = J_{13} = J_{14} = J_{25} = J_{26}$). In fact, the linear topology results in an irregular spin state structure for the trinuclear copper(II)−nickel(II) unit,[9b] with a $S = {}^3/_2$ ground state separated by $-J$, $-3J/2$, $-2J$, and $-5J/2$ from the $S = {}^1/_2$, $S = {}^1/_2$, $S = {}^3/_2$, and $S = {}^5/_2$ excited states, respectively (Scheme 2a). In this case, $\chi_M T$ would exhibit a minimum to further attain a plateau at low temperatures where only the $S = {}^3/_2$ and $S = {}^1/_2$ ground states of the magnetically isolated linear trinuclear and dinuclear units are thermally populated. Thus, the deviations observed in the low-temperature region are indicative of a ferromagnetic coupling ($j_{eff} > 0$) between the $S = {}^3/_2$ $Cu^{II}Ni^{II}_2$ and $S = {}^1/_2$ $Cu^{II}Ni^{II}$ units, yielding a $S = 2$ ground state and a $S = 1$ excited state separated by $2j_{eff}$ for the entire $Cu^{II}_2Ni^{II}_3$ molecule (Scheme 2b). This effective ferromagnetic coupling ($j_{eff}$) occurs between the $Cu^{II}$ ions within the $Cu^{II}_2$ metallacyclophane core ($J' = J_{12}$), while the next-nearest neighbors' (crossed) interactions between the $Cu^{II}$ and the high-spin $Ni^{II}$ ions from the trinuclear and the dinuclear units ($J'' = J_{15} = J_{16} = J_{23} = J_{24}$) are negligible.

The temperature dependence of the magnetic susceptibility data of **4** was then fitted through an effective spin Hamiltonian that takes into account the coupling between the $S = {}^1/_2$ ground state of the $Cu^{II}Ni^{II}$ unit and the $S = {}^3/_2$ ground state of the $Cu^{II}Ni^{II}_2$ linear unit (eq 1, with $S_{1A} = S_{2B} = S_{Cu} = {}^1/_2$, $S_{3A} = 0$, $S_{4A} = S_{5B} = S_{6B} = S_{Ni} = 1$, $S_A = {}^1/_2$, and $S_B$

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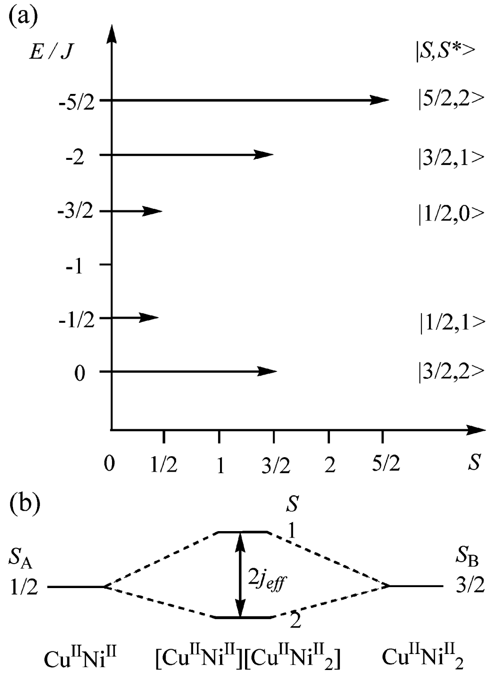
[19] Cano, J. *VPMAG*; University of Valencia: Valencia, Spain, 2001.

[20] (a) Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1984**, *23*, 3808. (b) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063.

[21] Complex $Na_4[Cu_2(Me_3mpba)_2]\cdot 9H_2O$ exhibits a magnetic behavior characteristic of a ferromagnetically coupled $Cu^{II}_2$ pair (Figure S5, Supporting Information). Least-squares fit of the magnetic susceptibility data to the appropriate analytical expression derived from the spin Hamiltonian $\mathbf{H} = -J\mathbf{S}_1\cdot\mathbf{S}_2 + g\beta(\mathbf{S}_1 + \mathbf{S}_2)B$ (with $S_1 = S_2 = {}^1/_2$) gave $J = +11.0$ cm$^{-1}$ and $g = 2.08$ (data reported elsewhere).

**Scheme 2.** (a) Spin State Structure for a Trinuclear Cu$^{II}$Ni$^{II}_2$ Linear Complex and (b) Energy Levels of the Low-Lying Spin States for a “Dimer-Plus-Trimer” [Ni$^{II}$Cu$^{II}$][Cu$^{II}$Ni$^{II}_2$] Complex with a Ferromagnetic Coupling between Dimer and Trimer



$= {}^3/_2$) (Appendix B, Supporting Information).[10b] Least-squares fit gave $J = -111.6$ cm$^{-1}$, $j_{\mathrm{eff}} = +0.28$ cm$^{-1}$, and $g = 2.22$ for **4** (Table 2). The theoretical curve for **4** closely reproduces the experimental data over the whole temperature range when compared to that corresponding to two magnetically isolated dinuclear and trinuclear complexes ($j_{\mathrm{eff}} = 0$) (solid and dotted lines, respectively, in Figure 6). The small absolute value of the $j_{\mathrm{eff}}/J$ ratio of 0.003 for **4** confirms the validity of the perturbational treatment used. In this model, the value of $j_{\mathrm{eff}}$ is related to that of $J'$ by $j_{\mathrm{eff}} = ({}^1/_{15})J'$ (eq 2, with $S_{1A} = S_{2B} = S_{\mathrm{Cu}} = {}^1/_2$, $S_A = {}^1/_2$, and $S_B = {}^3/_2$) (Appendix B, Supporting Information),[10b] which gives $J' = +4.2$ cm$^{-1}$ for **4** (Table 2). The magnetic susceptibility data of **4** were alternatively fitted by full-matrix diagonalization of the appropriate spin Hamiltonian for a pentanuclear Cu$^{II}_2$Ni$^{II}_3$ molecule (eq 3, with $S_{1A} = S_{2B} = S_{\mathrm{Cu}} = {}^1/_2$, $S_{3A} = 0$, $S_{4A} = S_{5B} = S_{6B} = S_{\mathrm{Ni}} = 1$).[19] Least-squares fit through the pentamer model gave values for $J$, $J'$, and $g$ which are in excellent agreement with those obtained through the “dimer-plus-trimer” model. The moderate to strong antiferromagnetic coupling through the oxamate bridges in **4** is consistent with those reported for related binuclear and trinuclear copper(II)−nickel(II) complexes ($-J = 90.3$−$94.6$ cm$^{-1}$).[9b] On the other hand, the weak to moderate ferromagnetic coupling through the *m*-phenylenediamidate bridges in **4** is intermediate between those found in the homometallic copper(II) complexes **1** and **2** ($J' = +1.7$ and $+9.0$ cm$^{-1}$, respectively), showing thus that the spin polarization mechanism is also operative for the propagation of the exchange interaction in heterometallic copper(II)−nickel(II) analogues.

## Conclusion

In this work, homo- and heteropolynuclear Cu$^{II}_6$ and Cu$^{II}_2$Ni$^{II}_3$ oxamato complexes have been rationally prepared by following the well-known “complex-as-ligand/complex-as-metal” approach. The binuclear copper(II) complexes with two aromatic-substituted dioxamates as bridging ligands, [Cu$^{II}_2$L$_2$]$^{4-}$ (L = mpba, Me$_3$mpba, and ppba), act as tetrakis- or tris-bidentate precursors toward coordinatively unsaturated mononuclear copper(II) or nickel(II) complexes with tri- and tetradentate polyamines as blocking ligands, [M$^{II}$L′]$^{2+}$ (L′ = Me$_5$dien and cyclam), respectively. The resulting hexanuclear copper(II) and pentanuclear copper(II)−nickel(II) complexes have “dimer-of-trimers” (T + T) and “dimer-plus-trimer” (D + T) structures, respectively, with an overall [2 × 2] ladder-type architecture. The two oxamate-bridged Cu$^{II}$M$^{II}$ and/or Cu$^{II}$M$^{II}_2$ linear units are connected through two meta- or para-substituted phenylenediamidate bridges in the corresponding [Cu$^{II}$M$^{II}_2$]$_2$ and [Cu$^{II}$M$^{II}$][Cu$^{II}$M$^{II}_2$] molecules, giving a Cu$^{II}_2$ metallacyclic core of the cyclophane type.

The nature of the ground spin state in this family of homo- and heterometallic, penta- and hexanuclear oxamato complexes can be rationally interpreted based on the concept of antiferro- and ferromagnetic coupling units. The binuclear copper(II) metallacyclophane with the ppba bridging ligand, [Cu$^{II}_2$(ppba)$_2$]$^{4-}$, acts as a “robust” antiferromagnetic coupling (AC) unit between the two Cu$^{II}_3$ linear fragments ($S_T = 2S_{\mathrm{Cu}} - S_{\mathrm{Cu}} = {}^1/_2$), leading to a singlet ground spin state for the Cu$^{II}_6$ complex ($S = S_T - S_T = 0$). On the contrary, the binuclear copper(II) metallacyclophanes with the mpba and Me$_3$mpba bridging ligands, [Cu$^{II}_2$(mpba)$_2$]$^{4-}$ and [Cu$^{II}_2$(Me$_3$mpba)$_2$]$^{4-}$, respectively, act as a more or less “robust” ferromagnetic coupling (FC) unit between the two Cu$^{II}_3$ linear fragments ($S_T = 2S_{\mathrm{Cu}} - S_{\mathrm{Cu}} = {}^1/_2$), leading to a triplet ground spin state for the Cu$^{II}_6$ complex ($S = S_T + S_T = 1$). Similarly, a high-spin quintet ground state is obtained for the Cu$^{II}_2$Ni$^{II}_3$ ($S = S_D + S_T = 2$) complex as a result of the ferromagnetic coupling between the Cu$^{II}$Ni$^{II}$ ($S_D = S_{\mathrm{Ni}} - S_{\mathrm{Cu}} = {}^1/_2$) and Cu$^{II}$Ni$^{II}_2$ ($S_T = 2S_{\mathrm{Ni}} - S_{\mathrm{Cu}} = {}^3/_2$) linear fragments. Current efforts are devoted to prepare new oxamate-based binuclear precursors with metal ions other than Cu$^{II}$ and connectivities greater than three or four in order to obtain high-nuclearity coordination compounds with larger spin and magnetic anisotropy values which are potential candidates for SMMs.

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**Supporting Information Available:** Preparation, physical characterization, and magnetic susceptibility data of Na$_4$[Cu$_2$(Me$_3$mpba)$_2$]·9H$_2$O (Figure S5), details of the theoretical model used to fit the magnetic data of **1**−**4** (Appendixes A and B and Tables S5 and S6), selected bond lengths and angles for **1**−**4** (Tables S1−S4), and crystal packing views of **1**−**4** (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the

Cambridge Crystallographic Data Centre as supplementary publica--tion numbers CCDC-637333 for **1**, CCDC-623027 for **2**, CCDC-637334 for **3**, and CCDC-637335 for **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, U.K. (fax, (+44) 1223 336 033; e-mail, deposit@ccdc.cam.ac.uk).

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