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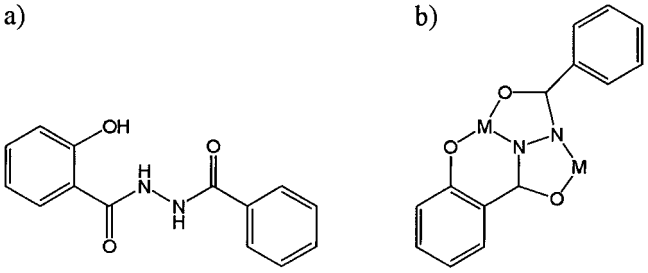
[16] The titrations were undertaken in 95% CD_2Cl_2/5% CD_3OD since the zinc(II) perchlorate salt is not soluble in neat CD_2Cl_2.
[17] The chemical shifts of the protons on trispyridyl ligands are quite different in $[ML]^{n+}$ and $[ML_2]^{n+}$ environments, with H6 being most affected; see, for example: R. T. Jonas, T. D. P. Stack, *Inorg. Chem.* **1998**, *37*, 6615–6629, and refs therein.

[30]Metallacrown-10 Compounds: $[Mn(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 5CH_2Cl_2\cdot 16CH_3OH\cdot H_2O$ and $[Fe(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 3CH_2Cl_2\cdot 12.5CH_3OH\cdot 5H_2O$**

Shi-Xiong Liu,* Shen Lin, Bi-Zhou Lin, Chi-Chang Lin, and Jian-Quan Huang

Metallacrowns are a new class of multinuclear clusters that are analogous to crown ethers in both structure and function.[1, 2] One may substitute heteroatoms such as transition metals and nitrogen atoms for the methylene carbon atoms of the parent crown ether complexes to form metallacrowns. Therefore, there has been considerable interest in metallacrown chemistry owing to its potential applications in chemically modified electrodes, anion-selective separation agents, liquid-crystal precursors, and magnetic materials.[3] Salicylhydroxamic acid (H_3shi) was used as the template ligand in the synthesis of the early metallacrowns. Many examples of this kind of metallacrown are known, for example, [9]metallacrowns-3,[3, 4] [12]metallacrowns-4,[1, 2, 5–8] and [15]metallacrowns-5,[9] which have a $[M\text{-}N\text{-}O]_n$ repeat unit that forms a cyclic structure. Several compounds with the metallacrown structure type have been developed.[10] Recently, an [18]metallacrown-6 using *N*-formylsalicylhydrazide (H_3fshz) as a ligand was reported.[11] This metallacrown is the second kind of metallacrown with a $[M\text{-}N\text{-}N]_n$ repeating unit in which nitrogen atoms replace all the oxygen atoms in the cyclic structure.

Although some [9]metallacrowns-3, [12]metallacrowns-4, [15]metallacrowns-5, and an [18]metallacrown-6 are known, there has yet been no report of any [30]metallacrown-10. Taking the limitations of metallacrowns based solely on shi^{3-} and $fshz^{3-}$ templates into account, we have greatly expanded the types of precursor ligands with the intention of modifying the ring size, as well as the electronic, magnetic, and other physical properties of the metallacrowns. We found that the choice of ligand plays an important role in preparing new metallacrowns with high nuclear number, such as the title [30]metallacrowns-10. Herein we provide a new potential pentadentate ligand *N*-phenylsalicylhydrazidate (**1**) (H_3bzshz, Scheme 1 a) and the first two [30]metallacrowns-10, **2** and **3**.



Scheme 1. Ligand H_3bzshz (a) and basic biding sites in compounds **2** and **3** (M = Mn, Fe) (b).

The two title [30]metallacrowns-10 are also the second kind of metallacrown with a $[M{-}N{-}N]_n$ repeating unit, which may be more appropriately called an azametallacrown.[12]

$[Mn(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 5CH_2Cl_2\cdot 16CH_3OH\cdot H_2O$ **2**

$[Fe(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 3CH_2Cl_2\cdot 12.5CH_3OH\cdot 5H_2O$ **3**

Single-crystal X-ray analysis of compound **2** (Figure 1) showed that there is a planar decanuclear 30-membered ring in the manganese metallacrown core. The 30-membered core ring exhibits crystallographic centrosymmetry and is a $[Mn\text{-}N\text{-}N]_{10}$ ring with neighboring Mn···Mn interatomic distances of 4.906(1)–4.986(2) Å. The size of the cavity in the 30-membered ring, measured between the opposite carbon atoms (less 1.57 Å for the van der Waals radii of carbon) is 6.80, 7.61, 6.39, 7.48, and 7.23 for C(13)–C(13a), C(26)–

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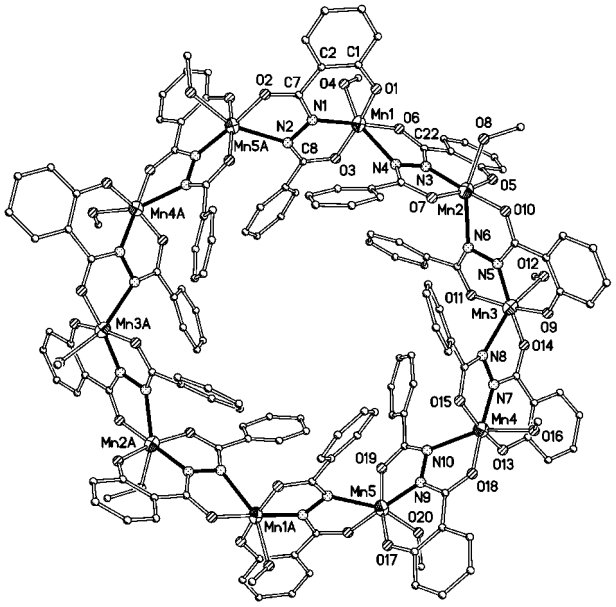

Figure 1. Perspective view of **2** (solvent molecules and all hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Mn1-O1 1.878(5), Mn1-O3 1.888(5), Mn1-O6 1.969(5), Mn1-N1 1.959(6), Mn1-O4 2.267(6), Mn1-N4 2.350(6); O1-Mn1-O3 170.1(2), O3-Mn1-N1 79.7(2), O3-Mn1-O6 92.0(2), O1-Mn1-O4 90.7(2), N1-Mn1-O4 89.1(2), O1-Mn1-N4 88.7(2), N1-Mn1-N4 115.1(2), O4-Mn1-N4 155.9(2), O1-Mn1-N1 90.9(2), O1-Mn1-O6 97.7(2), N1-Mn1-O6 168.8(2), O3-Mn1-O4 92.2(2), O6-Mn1-O4 83.7(2), O3-Mn1-N4 92.5(2), O6-Mn1-N4 72.5(2); average neighbor Mn···Mn distance 4.953(2), average near-neighbor Mn···Mn distance 9.274(2); Mn···Mn···Mn 137.52–139.50.

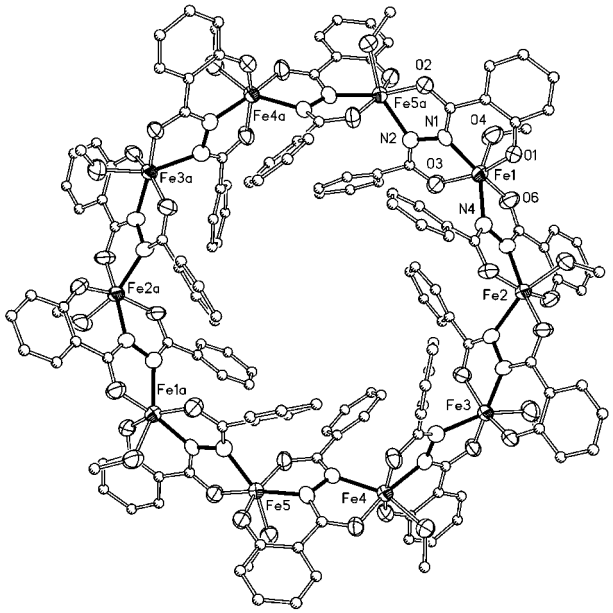

Figure 2. Perspective view of **3** (solvent molecules and all hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe1-O1 1.936(8), Fe1-O3 2.012(8), Fe1-O6 1.984(8), Fe1-N1 2.073(9), Fe1-O4 2.142(9), Fe1-N4 2.183(9); O1-Fe1-O3 161.6(3), O3-Fe1-N1 75.6(3), O3-Fe1-O6 96.2(3), O1-Fe1-O4 91.1(4), N1-Fe1-O4 86.2(3), O1-Fe1-N4 90.4 (3), N1-Fe1-N4 118.4(4), O4-Fe1-N4 155.3(4), O1-Fe1-N1 86.3(3), O1-Fe1-O6 102.2(4), N1-Fe1-O6 163.5(3), O3-Fe1-O4 91.1(4), O6-Fe1-O4 79.6(3), O3-Fe1-N4 95.2(3), O6-Fe1-N4 76.0(3); average neighbor Fe···Fe distance 4.946(2), average near-neighbor Fe···Fe distance 9.315(2); Fe···Fe···Fe 138.92–141.84.

C(26a), C(41)–C(41a), C(55)–C(55a), and C(71)–C(71a), respectively. The approximate dimensions of the oval-shaped cavity are approximately 6.39 Å in diameter at the entrance, approximately 13.19 Å (less 1.37 Å for the van der Waals radii of the manganese atom) at its largest diameter at the center of the cavity, and approximately 3.79 Å in depth.

All manganese atoms in compound **2** (Figure 1) are in a distorted octahedral MnN_2O_4 environment. The deprotonated ligand bzshz^{3-} acts as a multidentate ligand: one phenolate oxygen atom, one carbonyl oxygen atom, and one hydrazide nitrogen atom in the ligand are bound to each manganese atom, whereas the other carbonyl oxygen atom and the other hydrazide nitrogen atom in the ligand are chelated to an adjacent manganese atom. Therefore, the ligand induces the stereochemistry of the manganese(III) ions into a propeller configuration owing to the meridianal coordination of the O1, N1, and O3 atoms of the ligand to the metal ion. The average axial manganese–oxygen/nitrogen distance of 2.310 Å in compound **2** is approximately 0.386 Å longer than the average base Mn–O/N distance of 1.924 Å. This typical Jahn–Teller elongation along the *z* axis of the manganese(III) ion was also observed in some manganese(III) compounds.[10] All the manganese ions in the ring of the title compound **2** adopt a propeller configuration, despite the Jahn–Teller distortion of high-spin d^4 manganese(III) ions.

The crystal structure of compound **3** (Figure 2) is similar to that of compound **2** (Figure 1). The neighboring Fe···Fe interatomic distances in the 30-membered ring with an $[Fe\text{-}N\text{-}N]_{10}$ repeat unit are 4.923(2)–4.966(2) Å. The approximate dimensions of the oval-shaped cavity are approximately 5.70 Å in diameter at the entrance, approximately 13.67 Å (less 1.24 Å for the van der Waals radii of the iron atom) at its largest diameter at the center of the cavity, and approximately 4.16 Å in depth.

All the iron atoms of the ring adopt a distorted octahedron coordination geometry of the FeN_2O_4 type. Compared with the MnN_2O_4 octahedron, there is no Jahn–Teller distortion in the FeN_2O_4 octahedron of compound **3**, owing to the d^5 high-spin electronic configuration of the iron(III) ion.

Several [9]metallacrown-3 compounds[3, 4] and a [15]metallacrown-5[9b] have the metal centers of the ring in a propeller configuration and with the same chiralities. The manganese and iron atoms in the [30]azametallacrown-10 compounds **2** and **3** exhibit a propeller configuration; however, the chiralities of the ten mamganese/iron atoms in the two compounds alternate between the *Λ* and *Δ* forms.[13] In each azametallacrown, five methanol groups coordinated to the metal centers with *Λ* configuration are found on one face of the azametallacrown, and the remaining five methanol groups coordinated to the other metal centers with *Δ* configuration are found on the other face of the azametallacrown. The two faces of each azametallacrown have opposite chiralities.

The planar decanuclear structures in the [30]azametallacrowns-10 **2** and **3** are quite different from the planar hexanuclear structures in several [18]metallacrowns-6.[14] The average M···M···M interatomic angles in the 30-membered core ring of **2** and **3** are 138.87° and 140.67°, respectively. These values are close to the interior angle of 144° in an *n*-decagon. However, the average M···M···M

angles in the [18]metallacrowns-6 are 116.89(2)° for $[Mn_6(C_8H_6N_3O_2S)_6(CH_3OH)_6]\cdot 11.5\,CH_3OH$, and 118.16(4)° for $[Fe_6(C_8H_6N_3O_2S)_6(CH_3OH)_6]\cdot 12\,CH_3OH\cdot 2\,H_2O$,[14] which are close to the ideal internal angle of 120° in an *n*-hexagon. The change in the ring size between the [30]metallacrowns-10 and the [18]metallacrowns-6 is probably caused by the steric interactions between the bridging multidentate ligands in the different metallacrowns.

The magnetic behavior of **2** is illustrated in Figure 3. The molar effective magnetic moment (μ_{eff}) decreases slightly with decreasing temperature from 14.73 μ_B at 275 K to 13.32 μ_B at 60 K. Below 60 K, μ_{eff} decreases rapidly and reaches 4.38 μ_B at 4 K. Even at 275 K, the μ_{eff} value is smaller than the value of the sum expected for ten discrete paramagnetic systems with $S=2$ ($\mu_{eff}=15.18\,\mu_B$). This is characteristic of antiferromagnetic coupling, which is further suggested by a negative Weiss constant ($\theta=-16.0(1)$ K) using the data within $T>63$ K. Based on irreducible tensor operators[15] with the Hamiltonian operator given as $H=-\Sigma J_{ij}S_iS_j$, one can get the energy of 856945 spin states arising from the coupling of the 10 $S=2$ centers. Nevertheless, because of the different S values ranging from 0 to 20, the dimensions of the Hamiltonian matrices are too big for a true fitting procedure, even when taking the inverse center symmetry into account. Therefore, a simplified set of parameters for magnetic interactions were tested to analyze the magnetic properties quantitatively. Exchanges propagated between the neighboring centers (J_1), and between the near-neighboring centers (J_2) were considered. The distances between the paramagnetic centers in other positions are greater than 12.749(2) Å. Consequently, their interactions are weak and negligible. A least-squares fit for all the data gives rise to the parameters $J_1/k=-1.275(2)$ K, $J_2/k=-0.73(3)$ K, and the agreement factor $F=\Sigma[(\chi_{obs}-\chi_{cald})^2/\chi_{obs}]=7.893\times10^{-3}$. The negative values of J denote antiferromagnetic coupling between the manganese(III) centers. As expected, the interactions between neighboring centers dominate the others that are derived from the absolute values of J_1 and J_2. The antiferromagnetic nature of the interactions can be understood in terms of an overlap, through the bridging group, between the singly occupied metal d orbitals. Furthermore, Mn^{3+} in an elongated octahedral geometry exhibits magnetic anisotropy due to the zero-field splitting (ZFS), but the system is too complex to include the ZFS in magnetic analysis.

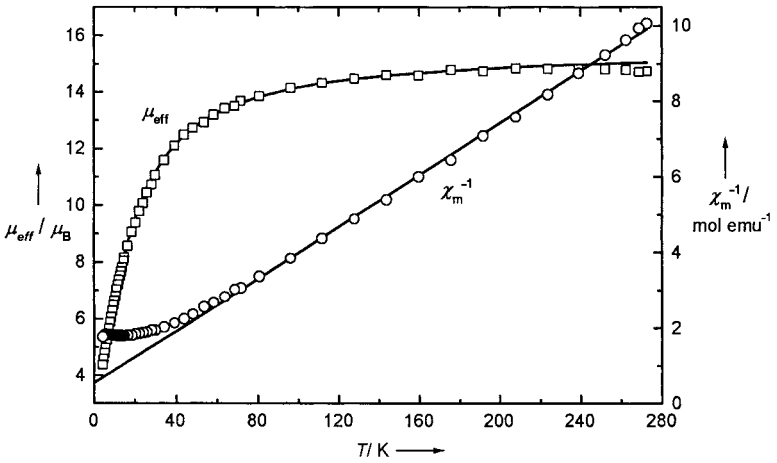

Figure 3. The effective magnetic moment (μ_{eff}) and the inverse susceptibility χ_m^{-1} data as a function of temperature for **2**. Open points represent observed results, and solid lines for χ_m^{-1} and μ_{eff} represent the fitting curves based on the Curie – Weiss law and on a simplified exchange fit as described in the text, respectively.

In summary, the manganese(III) and iron(III) [30]azametallacrown-10 compounds **2** and **3** expand the ring size of known metallacrown clusters from [9]metallacrown-3 to a 30-membered ring system. All the metal atoms in the rings of **2** and **3** adopt a propeller configuration, and have alternating Λ/Δ stereochemistries. The manganese azametallacrown molecules show large magnetic moments and have a remarkable toroid-like shape with a relatively large internal cavity. Hence it is possible that such molecules may act as a scaffold for the formation of supermolecules by guest binding within the cavity. It may also suggest a new approach for developing magnetic materials.

Experimental Section

1: Benzoyl chloride (5.55 g, 39.5 mmol) was added to a solution of sodium benzoate (5.688 g, 39.5 mmol) in chloroform (60 mL) at 5 °C. The reaction mixture was slowly warmed to 22 °C, stirred for 2 h, and then filtered. Salicylhydrazide (5.00 g, 32.9 mmol) was added to the filtrate to give a white suspension, which was collected and rinsed with chloroform and diethyl ether. Yield: 8.200 g, 95.0%, m.p. 255 °C.

2: A mixture of [Mn(acetylacetonate)$_2$] (35 mg, 0.1 mmol) in methanol (15mL) and *N*-phenylsalicylhydrazidate (25 mg, 0.1 mmol) in chloroform (15 mL) was stirred for 15 min. The resulting dark brown solution was filtered. After standing for six days, dark brown rectangular crystals were obtained from the filtrate. Compound **2** is air-sensitive. Elemental analysis: $C_{171}H_{206}Cl_{10}Mn_{10}N_{20}O_{57}$ (%): calcd: C 47.1, H 4.8, N 6.4, O 20.9; found: C 46.6, H 4.4, N 6.8, O 21.3.

3: A mixture of $Fe(OAc)_3$ (46.6 mg, 0.2 mmol) in methanol (15 mL) and *N*-phenylsalicylhydrazidate (51.4 mg, 0.2 mmol) in chloroform (15 mL) was stirred for 15 min. The resulting dark violet-red solution was filtered. After standing for seven days, black-brown rhombohedral crystals were separated from the filtrate. Compound **3** is air-sensitive. Elemental analysis: $C_{165.5}H_{196}Cl_6Fe_{10}N_{20}O_{57.5}$ (%): calcd: C 47.8, H 4.8, N 6.7, O 22.1; found: C 47.2, H 4.4, N 7.1, O 22.5.

Crystals of compounds **2** and **3** were mounted in a glass capillary with the mother liquor to prevent the loss of the structural solvents during X-ray diffraction data collection. The data were recorded on a Siemens Smart CCD area detector diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), the scan mode being ω. Programs used: Data correction: SMART (Siemens, 1996), cell refinement: SAINT (Siemens, 1996), and data reduction: SAINT (Siemens, 1996). The structures were solved by direct methods using SHELXS-86 and refined by full-matrix least-squares calculations with SHELXL-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the benzene ring in **2** and **3** were located at calculated positions (C–H = 0.93 Å) with isotropic displacement parameters set to 1.2 U_{eq}(C). Some of the other hydrogen atoms in **2** were located at calculated positions and/or at the positions found from a difference Fourier map. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148152 (**2**) and CCDC-148153 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Crystal data for **2** ($C_{171}H_{206}Cl_{10}Mn_{10}N_{20}O_{57}$): $M_r = 4357.46$, dark brown crystal ($0.35 \times 0.40 \times 0.55$ mm), triclinic, space group $P\bar{1}$, $a = 14.5331(2)$, $b = 18.1704(1)$, $c = 21.3923(2)$ Å, $\alpha = 76.545(1)$, $\beta = 74.220(1)$, $\gamma = 86.025(1)$, $V = 5287.03(9)$ Å^3, $Z = 1$, $T = 293(2)$ K, $\rho_{calcd} = 1.369$ g cm^{-3}, $F(000) = 2248$, $\mu = 0.782$ mm^{-1}. Of the 28654 reflections ($(2\theta)_{max} = 50.14°$), 18480 unique reflections were collected. From these, 9215 reflections with $I > 2\sigma(I)$ were used to solve the structure and were refined on F^2 by full-matrix least-squares techniques (SHELXL-97). At convergence, $R_1 = 0.0834$ and the goodness-of-fit on F^2 is 1.121. The maximum and minimum residual peaks on the final difference Fourier map were 0.934 and -0.879 e Å^{-3}, respectively.

Crystal data for **3** ($C_{165.5}H_{196}Cl_6Fe_{10}N_{20}O_{57.5}$): $M_r = 4156.62$, black-brown crystal ($0.34 \times 0.35 \times 0.72$ mm), triclinic, space group $P\bar{1}$, $a = 14.7040(4)$, $b = 18.9081(5)$, $c = 21.0783(5)$ Å, $\alpha = 71.201(1)$, $\beta = 77.076(1)$, $\gamma = 84.757(1)$, $V = 5406.0(2)$ Å^3, $Z = 1$, $T = 293(2)$ K, $\rho_{calcd} = 1.277$ g cm^{-3}, $F(000) = 2151$, $\mu = 0.800$ mm^{-1}. Of the 23991 reflections ($(2\theta)_{max} = 47.10°$), 14784 unique reflections were collected. From these, 7372 reflections with $I > 2\sigma(I)$ were used to solve the structure and were refined on F^2 by full-matrix least-squares techniques (SHELXL-97). At convergence, $R_1 = 0.0945$ and the goodness-of-fit on F^2 is 1.017. The maximum and minimum residual peaks on the final difference Fourier map were 0.893 and -0.455 e Å^{-3}, respectively.

The magnetic susceptibility data were obtained by using a Quantum Design PPMS 6000 magnetometer in the temperature range from 4 to 275 K at an applied magnetic field of 10 KG; whereby the diamagnetic contributions were estimated from Pascal's constants.

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[14] $[Mn_6(C_8H_6N_3O_2S)_6(CH_3OH)_6] \cdot 11.5\,CH_3OH$ and $[Fe_6(C_8H_6N_3O_2S)_6 \cdot (CH_3OH)_6] \cdot 12\,CH_3OH \cdot 2\,H_2O$ were obtained by us, and their crystal structures are different from the structures of **2** and **3**. Details will be reported elsewhere.
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Coordination Chemistry in the Solid: Study of the Incorporation of Cu^{II} into Cyclam-Containing Hybrid Materials

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Nanostructured organic – inorganic hybrid materials have known a considerable expansion in the past decade,[1–5] because they may provide unique combinations of properties which cannot be obtained by other ways. Among the possibilities offered by this class of solids, the preparation of materials able to strongly chelate metal cations which could remain chemically accessible seemed to us to be of great interest. Indeed, such materials could be interesting to study the coordination chemistry within the solid state as well as for their potential applications in catalysis,[6] separations,[7] optical devices,[8] or magnetic properties for example. Such applications require the incorporation within the materials of a good chelating ligand. Saturated polyazamacrocycles and especially 1,4,8,11-tetraazacyclotetradecane[9–11] (cyclam) having attracted much attention because of their remarkable binding ability towards transition and heavy metal cations, we set out to prepare hybrid materials incorporating cyclam moieties by using the sol – gel process.

We have shown that nanostructured materials are kinetically controlled.[3, 4, 12] The texture of the solids is highly dependent on all the parameters able to modify the kinetics of polycondensation (catalyst,[13] concentration of the reagent,[13] solvent,[13] temperature,[13a] and the organic spacer[13]). Furthermore, the importance of the organic moiety in the arrangement of solids obtained by the sol – gel process was displayed, giving rise to a possible short-range organization.[3, 4, 14, 15] In this context, it seemed interesting to investigate the incorporation of metal salts into cyclam-containing hybrid materials by two routes: the hydrolysis and polycondensation of metal salt/silylated cyclam derivatives complexes (Scheme 1, route A) or by hydrolysis and polycondensation of silylated cyclam derivatives followed by the direct incorporation of metal salts into the xerogels (Scheme 1, route B).

We have shown that the hydrolysis and polycondensation of silylated cyclam Cu^{II} and Co^{II} complexes (route A, Scheme 1) gives rise quantitatively to hybrid materials incorporating the Cu^{II} and Co^{II} salts,[16] thus the complexation of metal cations survives the sol – gel process. Herein we describe the direct incorporation of $CuCl_2$ into hybrid materials (route B). By using X-ray fluorescence and ESR spectroscopy, we show that the two routes of incorporation of the salts are not equivalent

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