A New Class of Easily Obtained Carbonate-Related μ_3-Ligands and a Protein-Sized Doughnut-Shaped Coordination Oligomer[**]

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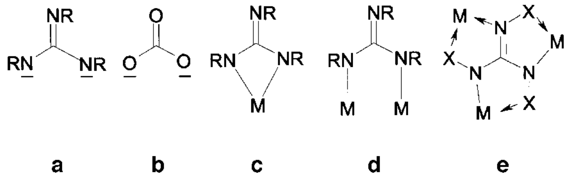
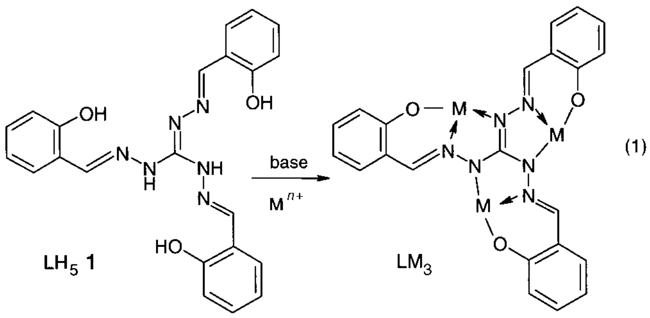
A possible way to achieve more robust coordination polymer frameworks is to put the powerfully stabilizing chelate effect to use in the bridging ligands.[1] Presented herein is a strategy for the synthesis of a new class of easily accessible and widely variable ligands based on a central dianionic, carbonate-like CN_3 core that can bind three metal centers at chelating sites. Dianionic guanidinates **a** (R = H, *i*Pr, *t*Bu, cyclohexyl, and phenyl) which are isoelectronic with carbonate ions **b**, have been shown to form 4-membered chelate rings (**c**)[2] or to bridge two metal ions (**d**).[3] What we are proposing is that if appropriate donor centers are introduced into the three substituents on the CN_3 core, then it may be possible to chelate three metal centers strongly and symmetrically (**e**). With regard to optimizing metal–metal communication it is difficult to imagine any other system capable of simultaneously chelating three metal centers in a roughly planar fashion to provide a closer metal–metal contact than this.



Herein we report on the metal-binding properties of tris(2-hydroxybenzylidene)triaminoguanidine LH_5 (**1**), which is very easily made from triaminoguanidine and salicylaldehyde. The structure of **1** was determined by X-ray crystallography.[4] Before exploring the coordination polymers afforded by this ligand, it appeared desirable and worthwhile to attempt to synthesize discrete molecular trimetallic derivatives to determine how easily, if at all, the intended central dianionic carbonate-like unit could be generated and whether or not three metal centers could be bound, as we hoped, in the manner LM_3 [Eq (1)].



Reaction of LH_6Cl with $(Et_4N)_2[PdCl_4]$ in acetonitrile in the presence of Et_4NOH yielded dark red crystals of $(Et_4N)_2[LPd_3Cl_3]\cdot CH_3CN$ (**2**). The chiral propeller-like structure of the $[LPd_3Cl_3]^{2-}$ ion, determined by X-ray crystallography,[5] is shown in Figure 1a. Diffusion of ammonia into an aqueous ethanolic solution containing LH_6Cl and $ZnCl_2$ gave yellow crystals of $[LZn_3(NH_3)_3(H_2O)_3]Cl\cdot 3H_2O$ (**3**)[6] the cationic component of which was found to have the structure shown in Figure 1b. Like the Pd derivative, it also adopts a propeller-like conformation. The three NH_3 ligands are found on one face of the ion and the three H_2O ligands on the other; these ligands participate in an extensive hydrogen bonded network involving the lattice H_2O molecules and Cl^- counterions.

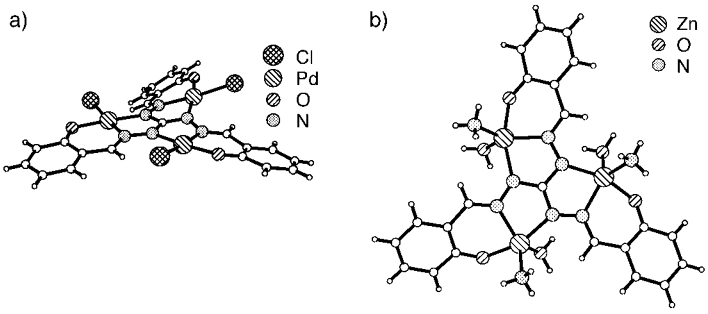


Figure 1. a) The structure of the $[LPd_3Cl_3]^{2-}$ ion in **2**. b) The structure of the $[LZn_3(NH_3)_3(H_2O)_3]^+$ ion in **3**.

The wide scope offered by these types of LM_3 species as 3-connecting building blocks in the construction of networks is immediately apparent.[7] One possibility would be to substitute the ligands external to the LM_3 core (such as the Cl ligands in the LPd_3 system or the NH_3 and H_2O ligands in the LZn_3 system) by appropriate bridging ligands linking one LM_3 unit to another. Another possibility would be to link two L^{5-} units directly to a single shared metal center. With regard to future attempts to obtain coordination networks it is reassuring to know that (as was revealed in the preparation of the zinc complex **3** above) a base as weak as ammonia is all that is required to generate the central carbonate-like dianionic CN_3 core.

Although the L^{5-} unit remains intact during the formation of the trimetallic complexes **2** and **3**, it does undergo secondary reactions under certain circumstances. Thus, upon heating with base, the azine of salicylaldehyde ($(HOC_6H_4CH{=}N{-})_2$) is formed, which indicates fission of a C–N bond within the central guanidine CN_3 unit. In the presence of Cd^{II} and triethylamine cycloisomerization of the ligand occurs to produce a new triazole-containing ligand $L'H_5$. This ligand appears, in deprotonated form, as one

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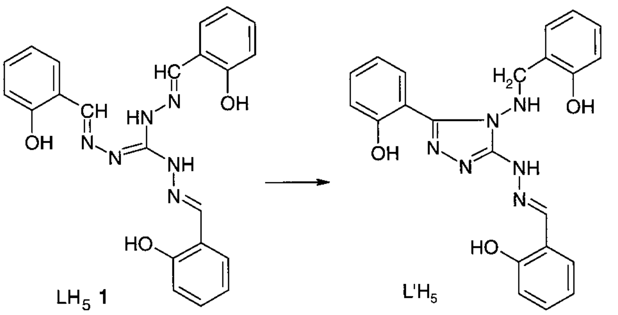

component of a remarkable and very large coordinative oligomer (**4**), which resembles a doughnut in shape. The isomerization of LH_5 to $L'H_5$ involves oxidative cyclization to form a triazole ring accompanied by the reduction of one CH=N link to CH_2–NH. A related cyclization has been reported.[8] The oligomer **4** contains 24 Cd centers, 12 LH_2^{3-}, and 6 $L'H_2^{3-}$ ligands and has the composition $[\{[Cd_4(LH_2)_2(L'H_2)(H_2O)(DMF)](Et_3NH)\}_6]$.[9] The asymmetric unit containing four different cadmium centers, two different LH_2^{3-} ligands and one $L'H_2^{3-}$ ligand is shown in Figure 2, together with a schematic representation to aid identification of the various components. The complete assemblage consists of six such asymmetric units arranged around a $\bar{3}$ axis (Figure 3); the resemblance to a doughnut is clear. The six Et_3NH^+ ions are buried inside the doughnut in crevices within the anionic oligomer, hydrogen bonded to an oxygen atom of the LH_2^{3-} ligand (N···O, 2.73(1) Å). The large size of the oligomer ($M_W > 11\,000\ g\,mol^{-1}$, diameter > 30 Å), external shape and internal folding of the assemblage are reminiscent of a protein; the system also has features in common with the large annular metal–oxo species reported recently by Müller et al.[10] and with the coordinate "molecular loop" reported recently by Beer et al.[11]

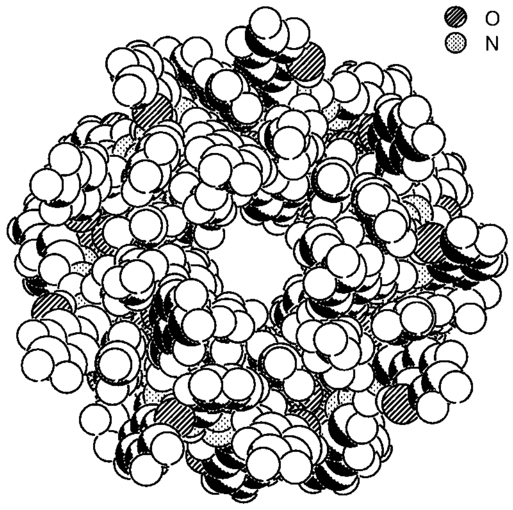

Figure 3. The structure of **4**.

In conclusion, it is clear that these very easily obtained guanidine-based bridging ligands promise a rich coordination chemistry and access to a wide range of oligomers and polymers.

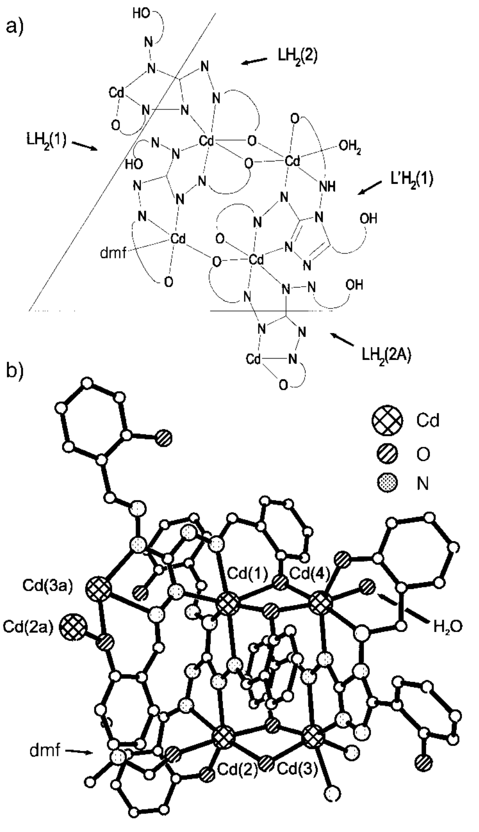

Figure 2. a) A schematic representation of the components present in the asymmetric unit of **4**. b) The structure of the asymmetric unit in **4**. The triethylammonium ion and the protons have been omitted for clarity.

Experimental Section

$[C_{22}H_{21}N_6O_3]Cl$ (**1**·HCl): Triaminoguanidinium chloride (4.215 g; 30 mmol), prepared as in ref[12] was dissolved in a hot mixture of H_2O (30 mL) and ethanol (60 mL). HCl was added until the pH = 3. The mixture was allowed to cool to room temperature and a solution of salicylaldehyde (11.1 mL, 0.10 mol) in ethanol (15 mL) was slowly added. The yellow mixture was warmed until the first precipitate formed. The mixture was stirred over night at room temperature and the crude product was recrystallized from methanol (180 mL) and water (70 mL). Yield: 10.406 g (23 mmol, 77%); elemental analysis found (%): C 58.05, H 4.63, N 18.74; calcd C 58.34, H 4.67, N 18.56; ^1H NMR (400 MHz, CD_3OD): $\delta = 8.884$, 8.015, 7.311, 6.934, 6.901, 3.339; ^{13}C NMR (100 MHz, CD_3OD): $\delta = 158.7$, 150.8, 150.3, 133.9, 129.2, 120.9, 120.6, 117.2. Crystals suitable for X-ray crystallography were grown by slow diffusion of HCl gas into a solution of **1** in aqueous $NaHCO_3$ (pH 8).

$[(C_2H_5)_4N]_2[(PdCl)_3(C_{22}H_{15}N_6O_3)]\cdot CH_3CN$ (**2**): $PdCl_2$ (266.7 mg, 1.50 mmol) and Et_4NCl (527.3 mg, 3.19 mmol) were dissolved in acetonitrile (36 mL). A solution of **1**·HCl (226.3 mg, 0.50 mmol) in acetonitrile (30 mL) and Et_4NOH (1.7 mL, 25% in water) was slowly added dropwise yielding a deep red solution. Na_2SO_4 (2 g) was added and the mixture stirred for 5 min to remove most of the water. The Na_2SO_4 was removed by filtration and the filtrate left to stand open to the air for two days resulting in the formation of dark red crystals of **2**. Yield: 384.1 mg (0.35 mmol, 70%); elemental analysis found (%): C 42.26, H 5.25, N 10.89; calcd: C 42.20, H 5.13, N 11.07.

$[\{Zn(OH_2)(NH_3)\}_3(C_{22}H_{15}N_6O_3)]Cl\cdot 3H_2O$ (**3**): $ZnCl_2\cdot H_2O$ (61.2 mg, ~0.35 mmol) and **1**·HCl (48.8 mg, 0.11 mmol) were dissolved in water (4 mL) and ethanol (8 mL). After filtration ethanol (2 mL) was added. Slow diffusion of NH_3 into the reaction mixture resulted in the formation of yellow crystals of **3** within 3 days. Yield: 45.8 mg (0.057 mmol, 52%); elemental analysis found (%): C 32.89, H 4.70, N 15.71; calcd: C 32.94, H 4.52, N 15.72.

$[C_{450}H_{456}Cd_{24}N_{120}O_{66}]\cdot x\,H_2O\cdot y\,DMF$ (**4**): $Cd(NO_3)_2\cdot 4\,H_2O$ (48.3 mg, 0.16 mmol) and **1**$\cdot$HCl (46.0 mg, 0.10 mmol) were dissolved in DMF (10 mL). Water (10 mL) followed by triethylamine (2 mL) in methanol (8 mL) were carefully layered on top. Over a period of two months orange crystals of **4** grew. Yield: 6.2 mg (0.55×10^{-3} mmol, 8.2 %); elemental analysis found (%): C 45.51, H 3.85, N 14.46; calcd (for $x=30$, $y=10$): C 45.82, H 4.66, N 14.48.

Crystallography: Intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing the ω-2θ scan method, the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for **2** and **4**.[13] All structures were solved using direct methods (SHELXS-97)[14] and refined using a full-matrix least-squares refinement procedure (SHELXL-97).[15] The data of **4** were corrected using the "SQUEEZE" routine in PLATON.[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146818–146821 for **1**, **2**, **3**, and **4**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[4] $0.10\times0.10\times0.10$ mm^3, triclinic, $P\bar{1}$, $a=8.905(2)$, $b=9.807(2)$, $c=13.086(3)$ Å, $\alpha=88.10(3)$, $\beta=78.50(3)$, $\gamma=83.89(3)^\circ$, $V=1113.5(4)$ Å^3, $\rho_{calcd}=1.378$ g cm^{-3}, $2\theta_{max}=120^\circ$, $\lambda=1.54178$ Å, $T=293$ K, 3774 measured reflections, 3278 independent reflections ($R_{int}=0.0359$), $\mu=1.856$ mm^{-1}, 340 parameters, $R_1=0.0678$, $wR2=0.1880$, max. residual electron density 0.354 e Å^{-3}.

[5] $0.33\times0.14\times0.03$ mm^3, triclinic, $P\bar{1}$, $a=12.848(1)$, $b=13.0504(6)$, $c=15.158(2)$ Å, $\alpha=92.667(7)$, $\beta=102.81(1)$, $\gamma=110.512(6)^\circ$, $V=2299.6(5)$ Å^3, $\rho_{calcd}=1.644$ g cm^{-3}, $2\theta_{max}=120^\circ$, $\lambda=1.54178$ Å, $T=293$ K, 7858 measured reflections, 6818 independent reflections ($R_{int}=0.0568$), $\mu=11.343$ mm^{-1}, min./max. transmission factors 0.141/0.698, 591 parameters, $R_1=0.0669$, $wR2=0.1424$, max. residual electron density 1.219 e Å^{-3}.

[6] $0.54\times0.46\times0.34$ mm^3, trigonal (hexagonal settings), $R\bar{3}$, $a=16.310(2)$, $c=21.552(3)$ Å, $V=4965(1)$ Å^3, $\rho_{calcd}=1.610$ g cm^{-3}, $2\theta_{max}=54.9^\circ$, $\lambda=0.71073$ Å, $T=140$ K, 3173 measured reflections, 2537 independent reflections ($R_{int}=0.0273$), numerical absorption correction, $\mu=2.296$ mm^{-1}, min./max. transmission factors 0.314/0.490, 181 parameters, $R_1=0.0391$, $wR2=0.1204$, max. residual electron density 1.141 e Å^{-3}.

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[9] $0.46\times0.43\times0.34$ mm^3, trigonal (hexagonal settings), $R\bar{3}$, $a=33.838(7)$, $c=46.23(1)$ Å, $V=45845(18)$ Å^3, $\rho_{calcd}=1.227$ g cm^{-3}, $2\theta_{max}=100^\circ$, $\lambda=1.54178$ Å, $T=130$ K, 11987 measured reflections, 10394 independent reflections ($R_{int}=0.1104$), $\mu=7.051$ mm^{-1}, min./max. transmission factors 0.120/0.264, 473 parameters, $R_1=0.1064$, $wR2=0.3105$, max. residual electron density 0.385 e Å^{-3}.

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Catalytic Enantioselective Fluorination of *β*-Ketoesters**

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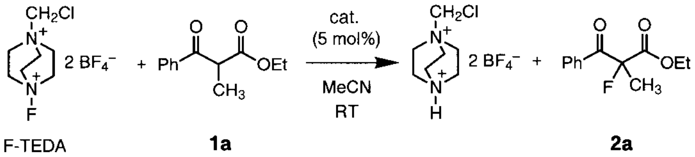
Although in nature organofluorine metabolites are extremely rare, bioactive fluoroorganic compounds are eminently important in medicinal chemistry.[1] Therefore, it is not surprising that research in the field of synthetic organofluorine chemistry is flourishing more than ever.[2, 3] Protocols for the introduction of the fluorine atom into organic molecules rely upon the use of dozens of different reagents,[4] the most successful of which contain the N–F fragment.[5, 6] Methods for the enantioselective fluorination (C–F bond-forming reactions) of organic molecules are quite rare, and catalytic methods are not known. An important breakthrough occurred when Differding and Lang reported the first example of enantioselective electrophilic fluorination of a *β*-ketoester enolate in up to 70 % *ee* by using an *N*-fluorosultam derived from camphor.[7] This strategy, requiring the intermediate generation of the enolate from an activated methylene compound, has been further developed more recently.[8–13] Another impetus in this field came also from the discovery and commerical availability of new N–F reagents, such as 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis{tetrafluoroborate} (F-TEDA; also called Selectfluor, see Scheme 1; TEDA = triethylenediamine).[14, 15] However, the total absence of an efficient catalytic reaction for stereoselective fluorination prompted us to embark in a study aimed at developing such a reaction. Recent reports had indicated



Scheme 1. The catalytic fluorination of **1a** with F-TEDA.

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