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Carbamates of Polyamines – Versatile Building Blocks for the Construction of Polynuclear Metal Complexes[‡]

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A new concept for the design of polynuclear metal complexes is described: Partial aeration of a polyamine solution with CO_2 generates a system where both, a chelating agent (the unreacted polyamine) and a bridging agent (the polycarbamate) are present. Together with a metal cation, these components constitute an ideal set of building blocks for the construction of extended molecular architectures. These considerations are exemplified in the reaction of the well-known triamine 6-methyl-1,4-diazepan-6-amine (L) with Fe^{II} under aerobic conditions. After partial conversion of L into its dicarbamate derivative $H_{-2}L(CO_2)_2^{2-}$, the components spontaneously assemble to the tetranuclear complex $[(\mu\text{-O})_2(Fe^{III}L)_4\{\mu\text{-}H_{-2}L(CO_2)_2\}_2]^{4+}$ ($\mathbf{1}^{4+}$). $\mathbf{1}(ClO_4)_4$ was characterized by single-crystal X-ray analysis, Mössbauer spectroscopy, and magnetic susceptibility measurements.

Introduction

Polyamines such as 1,2-diaminoethane (en), 1,4,7-triazaheptane (den), 1,4,7,10-tetraazadecane (trien) or corresponding cyclic derivatives constitute one of the best studied class of ligands for di- or trivalent transition metal cations.[1,2] These amines are classical chelating agents, forming usually mononuclear species with the nitrogen donors incorporated in five- or six-membered chelate rings. It is well known that solutions of free amines readily absorb CO_2 to yield the corresponding carbamates,[3] and a variety of metal complexes with carbamates of monoamines have been described in the literature.[3–5] However, the synthetic procedures used, such as CO_2 insertion into the metal–nitrogen bond of the corresponding metal amide, was often rather demanding.[4] The motivation of this research was primarily to study one-carbon sources[5] in synthetic applications and modeling of CO_2 fixation[6] in biological systems. However, the possibility to use carbamates of the above-mentioned polyamines[6c,6e,7,8] as particularly suitable building blocks for the construction of polynuclear structures has, to the best of our knowledge, not widely been considered. This is surprising since coordination of a monocarbamate derivative with its *O*–C–N–C–C–*N* substructure and in particular the dicarbamate derivative with its *O*–C–N–C–C–N–C–*O* substructure in a mononuclear complex would enforce the formation of unfavorable seven- or even nine-membered chelate rings. Consequently, a bridging coordination mode would be expected to be more suitable. In this communication, we will demonstrate that polycarbamates are indeed promising synthons for the construction of extended metal-organic architectures.

Results and Discussion

Under aerobic conditions, the addition of iron(II) perchlorate and 6-methyl-1,4-diazepan-6-amine (= L) to a solution of L, which has been aerated previously with CO_2, resulted in the spontaneous formation of the tetranuclear complex $[(\mu\text{-O})_2(FeL)_4\{\mu\text{-}H_{-2}L(CO_2)_2\}_2]^{4+}$ ($\mathbf{1}^{4+}$). It could be crystallized as a perchlorate salt of composition $\mathbf{1}(ClO_4)_4\cdot 6MeOH\cdot H_2O$, and the structure could be elucidated by X-ray diffraction analysis (Figure 1). The complex contains four $Fe^{III}L$ units, with the triamine L adopting a facial orientation in the distorted FeN_3O_3 octahedron. In $\mathbf{1}^{4+}$, each two $Fe^{III}L$ units are connected through a μ-oxido bridge to two $LFe^{III}\text{–O–}Fe^{III}L$ fragments which in turn are further fused by two bis(carbamate) derivatives $H_{-2}L(CO_2)_2^{2-}$ to the tetranuclear cation. Only CO_2 addition at the two secondary amino groups is observed; the primary amino groups are not affected. The entire complex closely adopts C_{2v} symmetry; however, in the crystal structure, the two mirror planes are destroyed by an asymmetric conformation of the two central seven-membered diazepane rings. The true crystallographic symmetry is therefore C_2. The Vis spectrum of this complex is in agreement with the charac-

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

teristics reported previously for the bis(μ-carboxylato)(μ-oxido)diiron(III) unit (Supporting Information).[9] The compound is paramagnetic, and the dependence of χ on T in the range of 2–290 K can simply be interpreted by adopting two independent, antiferromagnetically coupled Fe^{III}–O–Fe^{III} dimers with high-spin configuration for the ferric ions ($S_1 = S_2 = 5/2$, Figure S1 in the Supporting Information). The resulting exchange coupling constant J of $-108.4\ cm^{-1}$ ($H = -2JS_1 \cdot S_2$) lies at the low end of the range known for $(\mu\text{-}RCO_2)_2(\mu\text{-}O)(Fe^{III})_2$ systems.[9–11] Additional interactions between the two diiron centers within the tetranuclear unit are obviously not significant. The zero-field Mössbauer spectrum (Figure S2 in the Supporting Information) is also in agreement with literature values.[9,11] The data measured at 80 K could be fitted by two symmetric quadrupole doublets, each having a relative intensity of 50 %. The observation of two slightly different quadrupole doublets with isomer shifts of 0.47 und 0.48 mm/s and quadrupole splittings of 1.50 und 1.72 mm/s is obviously due to the different configuration of the two Fe^{III} centers in the diiron unit: with regard to the free amino groups of the two $H_{-2}L(CO_2)_2^{2-}$ bridges, one of the Fe centers adopts a *cisoid*, the other a *transoid* arrangement.

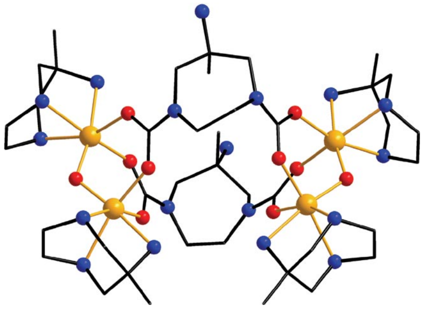

Figure 1. Ball-and-stick representation of the tetranuclear cation **1**$^{4+}$ (yellow: Fe, red: O, blue: N); the C backbone is shown as a stick model in black; H atoms were omitted for clarity.

The bis(μ-carboxylato)(μ-oxido)diiron(III) unit has been observed in a variety of biological compounds. A particularly prominent example is hemerythrin.[11] Several model complexes have been prepared,[9–11] and a few specific bridging agents have been designed and prepared to fuse two such diiron units to a tetranuclear system.[10] However, the synthesis of such bridging agents often enforces extensive synthetic procedures. The L/CO_2 concept presented here obviously offers ideal prerequisites for the spontaneous formation and isolation of such polynuclear species. The particular advantage of our approach is the possibility to use the triamine unit at the same time not only as a chelating agent, stabilizing the cation and preventing further hydrolysis, but also as the bridging agent in its dicarbamate form.

Conclusions and Outlook

In this communication, we present a promising and easily applicable concept for the construction of polynuclear metal complexes by using simple solutions of a metal salt and a polyamine ligand which was partially converted into a polycarbamate derivative.

(i) We have demonstrated that the dicarbamate unit with its *O*–C–N–C–C–N–C–*O* substructure has a low tendency to bind both donor atoms to the same metal cation. This generates an easy route to obtain a bridging agent $H_{-2}L(CO_2)_2^{2-}$ from the chelating agent L. The ability of the $H_{-2}L(CO_2)_2^{2-}$ anion for bridging interactions gains further support by the well-known tendency of the carbamate group for M–O–C(NRR′)–O–M interactions.[5]

(ii) Controlled dosage of CO_2 to the amine allows a specific fine tuning of the amount of free amino groups and carbamate groups, i.e. a fine tuning of the chelating vs. bridging properties of this system. It is hoped that such considerations will allow a specific control of the amount of aggregation in framework architectures.

Experimental Section

Synthesis: 6-Methyl-1,4-diazepan-6-amine[12] (50 mg, 0.39 mmol) was dissolved in MeOH (3 mL) and aerated with CO_2 for a period of 30 min. To this solution was added $Fe(ClO_4)_2$ (99 mg, 0.39 mmol) dissolved in acetonitrile (2.5 mL). An additional portion of free 6-methyl-1,4-diazepan-6-amin (50 mg, 0.39 mmol) was directly added to the reaction mixture. The resulting clear, yellow-brownish solution was placed in an open beaker and was allowed to stand in a desiccator which contained an additional beaker with ethyl acetate. Within a period of 24 h, yellow-brownish crystals deposited. They were separated by filtration and dried at reduced pressure (yield: 120 mg, 0.07 mmol, 70 % in reference to Fe). C,H,N analysis (see Supporting Information) is in agreement with the composition $[(\mu\text{-}O)_2(FeL)_4\{\mu\text{-}H_{-2}L(CO_2)_2\}_2](ClO_4)_4\cdot 3MeOH\cdot 3H_2O$; the crystals of composition $[(\mu\text{-}O)_2(FeL)_4\{\mu\text{-}H_{-2}L(CO_2)_2\}_2](ClO_4)_4\cdot 6MeOH\cdot H_2O$ disintegrate rapidly; they were therefore directly moved from the mother liquor to the goniometer head without further characterization.

Instrumentation: A description of the equipment used for spectroscopy (UV/Vis and Mössbauer) and the magnetic susceptibility measurements is provided in the Supporting Information. The isomer shift in the Mössbauer spectra refers to α-iron at room temperature. The molar magnetic susceptibility ($\chi \times T$) was simulated by using a spin Hamiltonian for a symmetric dimer with two coupled spins of 5/2 (see the Supporting Information).

Crystal-Structure Analysis: Bruker-Nonius Kappa-CCD diffractometer, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å), crystal size: 0.05 × 0.10 × 0.26 mm, monoclinic, space group $C2/c$, a = 17.4978(5), b = 27.9355(7), c = 19.1930(6) Å, β = 108.277(3)°, V = 8908.4(5) Å^3, Z = 4 for $C_{46}H_{112}Cl_4Fe_4N_{18}O_{33}$ (M_r = 1810.74 $g\,mol^{-1}$), $\rho_{calcd.}$ = 1.350 $g\,cm^{-3}$, μ = 0.839 mm^{-1}, $2.96° < \theta < 26.00°$, T = 100(2) K. Intensities: 81435 measured, 8748 unique, 6928 observed [$I > 2\sigma(I)$], empirical absorption correction (T_{min}/T_{max} = 0.8345/0.9492). The structure was solved by direct methods (SHELXS-97), and refined on F^2 (512 parameters) using full-matrix least-squares calculations (SHELXL-97). The position of the water oxygen atom O100 was refined isotropically with an occupancy of 0.5; all other non-hydrogen atom positions were refined by using anisotropic displacement parameters. Treatment of hydrogen atom positions: H45A and H45B (free primary amino group) were located in a difference Fourier map and refined isotropically, all other hydrogen atoms of $\mathbf{1}^{4+}$ were calculated (riding model); hydrogen atoms of the solvent molecules were not considered. The two ClO_4^- ions were found to be disordered (superposition of each two ClO_4 entities). $R = 0.0727$ [$I > 2\sigma(I)$], $wR_2 = 0.2308$ (all data), $GOF = 1.028$. Residual electron density: +1.05, –0.69 $e\,Å^{-3}$. The high R values are not only due to the disorder of the counterions; they are also caused by some problems in the description of the solvent molecules. After subtraction of the corresponding electron density by the SQUEEZE program of the PLATON[13] package, the refinement of the remaining $\mathbf{1}(ClO_4)_4$ unit reached $R = 0.056$ and $wR_2 = 0.168$. CCDC-665611 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): C,H,N analysis for $\mathbf{1}(ClO_4)_4\cdot 3MeOH\cdot 3H_2O$; additional information for the instrumentation and evaluation of the physical measurements; calculated and measured magnetic susceptibility of $\mathbf{1}(ClO_4)_4$; calculated and measured Mössbauer spectrum of $\mathbf{1}(ClO_4)_4$.

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