probably stabilized by the intramolecular hydrogen bonds, whose geometrical parameters correspond to hydrogen bonds of the medium strength. The OH groups of the coordinated methanol molecules and "free" OH groups of dbcat ligands are the proton donors in these hydrogen bonds. The formation of relatively stable I is a characteristic feature of the V(VI) system with dbcat. In the V(VI) systems with another catechols,[6] a mixed valence V(VI)/V(IV) complex is not formed, and all initial V(VI) is oxidized to the mononuclear V(IV) complex containing three ligands. An X-ray analysis of this type of complex, e.g. K[dbcat][cat], showed that six O atoms of three catechol (cat) molecules are arranged octahedrally around the metal center.[7] In the case of dbcat, the coordination of the third ligand is hindered sterically, and it is possible that structure of the isolated V(IV) complex is not substantially different from that of the initial V(VI) complex that reduces molecular nitrogen.

Experimental Procedure

N4 reduction and H2 evolution kinetics have been performed as previously described.[2] VCl5 was synthesized by dissolving vanadium metal in hydrogen from the solution containing VCl5, (3 mol). The doubly bidentate bridging ligand L' is formally obtained by the template coupling of two dimethyl malonate monoanions with oxalyl chloride to form tetramethyl 2,3-dihydroxy-1,3-butanediol-1,4,4-tetraacarbonylate followed by subsequent spontaneous double deprotonation. The doubly bidentate bridging ligand L1 is formally obtained by the template coupling of two dimethyl malonate monooanions with oxalyl chloride to form tetratethyl 2,3-dihydroxy-1,3-butanediol-1,4,4-tetraacarbonylate followed by subsequent spontaneous double deprotonation.

The First Neutral Adamanantoid Iron(III)--chelate Complex: Spontaneous Formation, Structure, and Electrochemistry**

By Rolf W. Saaflfrank,* Bernd Hörner, Dietmar Stalke, and Josef Salbeck

One of the most interesting new aspects of synthetic chemistry is endohedral chemistry, that is, the chemistry inside cages.[2] Consequently it is necessary to be able easily to build up intramolecular cavities with variable diameters.

On treatment of dimethyl malonate with methylmagnesium iodide or methylmagnesium iodide and oxalyl chloride followed by subsequent spontaneous double deprotonation.

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3) According to Equations (a) and (b) the hydrogen and ammonia yields are (2nh3/nh4%) = 100%. The amount of H2 evolved, pNH3, and the amount of NH3 formed, aNH3, are the amounts of H2 evolved, aNH3, and the amount of NH3 formed, aNH3, are the amounts of H2 evolved.
We were convinced that the size of the cavity of the tetrametallate(4-) ions 1a could be tailored with suitable spacers. In place of the anions 1a, it should also be possible to obtain neutral tetranuclear metal–chelate complexes by using M^{3+}, instead of M^{2+}, ions.

\[ \text{[NH}_4^+\text{]}_4 \text{Fe}^{3+} \]

\[ \text{Fe}^{2+} \]

\[ \text{L}^2 \]

Consequently we doubly deprotonated tetramethyl 2,2'-terephthaloyldimalonate with sodium hydride at 20 °C. We then treated the resulting dianion L^2 with an iron(III) chloride solution and obtained ruby-red crystals upon workup. According to elemental analysis and FAB-MS data (FAB = Fast Atom Bombardment) the compound, of composition Fe_4L^2, is the tetranuclear iron(III) chelate complex 1c (for details see [8]).

The \(^1\)H and \(^{13}\)C NMR spectra of Fe_4L^2 (1c) do not unambiguously establish the structure of this compound. Thus an X-ray crystallographic structure analysis of this complex was carried out. According to this analysis, 1c crystallizes as a neutral, adamantanoid, tetranuclear iron(III) chelate complex (Fig. 1)—the first of its kind. The nucleus of the complex forms an almost ideal tetrahedron, with an Fe(III) ion in each of the corners. The six edges of the tetrahedron are each formed by the doubly bidentate, doubly negatively charged, bridging ligands L^2 (distances between facing phenyl centers approximately 10 Å). Six oxygen atoms surround each of the four Fe^{III} ions in an octahedral arrangement (Fig. 2).

Two enantiomeric pairs [(A), (A)-fac, and (A), (A)-mer] are principally possible for octahedral complexes of the type MA_2B_2 [with bidentate ligands M(AB)]. The Fe_4L^2 complex has an exact \( S_8 \) symmetry in the crystal and is thus achiral (meso form). This means that the ligands L^2 around the four iron centers in 1c are arranged facially and that two of the four iron centers have the same configuration [(A, A)-fac or (A, A, A, A)-fac].

The cyclic voltammogram under aprotic conditions shows the reduction of the Fe_4L^2 complex 1c as a quasi-reversible signal pair centered at -550 mV (Fig. 3, left). The peak potential difference \( \Delta E_p \) at a scan rate of 250 mV s\(^{-1}\) is 170 mV; the reduction peak is slightly broadened (\( E_p = E_{p/2} = 135 \) mV), but shows no further splitting. In thin-layer voltammetry, at a layer thickness of 15 μm and a scan rate of 10 mVs\(^{-1}\), the reduction is also seen as a quasi-reversible signal pair with a peak potential difference of 60 mV. The half-peak widths are also broader (\( \Delta E_{p/2} = 220 \) mV for the reduction, 170 mV for the reoxidation), but the signals show no further structure. Thin-layer coulometry shows that four electrons are transferred under every signal, whereas a multi-
sweep experiment shows the complete chemical reversibility of the redox process. This reversibility is confirmed by spectro-electrochemical as well as voltamperometric measurements. Following the reduction spectroelectrochemically gives continuously changing absorption signals, but no recognizable intermediates for a partially reduced complex are observed. It is conspicuous that the lowest wave absorption signal of 1c at 450 nm does not completely disappear, but only reduces in intensity to a quarter of its extinction. Also, no further absorptions at long wavelengths for mixed-valent species occur (Fig. 3, right). In the UV region the spectral changes are analogous. Thus no, or only very weak, electronic interactions ("metalloautism") exist between the iron centers in 1c. The redox process is therefore formally a one-electron-transfer.

Furthermore Mössbauer and magnetic measurements are in agreement with the results of the electrochemical studies on 1c. The Mössbauer spectrum shows a signal broadened by relaxation with an isomeric shift $\delta$ at 293 K of 0.6 mm s$^{-1}$. Magnetic measurements (SQUID-susceptometer, temperature range 10–300 K) give a temperature-independent value of 11.55 $\mu_B$ for the effective magnetic moment $\mu_{eff}$. This result agrees well with the calculated value of 11.83 $\mu_B$ for four magnetically isolated high-spin iron(III) centers that show no interactive phenomena in the investigated temperature range.

We shall report elsewhere on the simple iron(III) chelate complex 1b and the iron(III) chelate complex 1d with biphosphoryl as spacer.

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[5] Synthesis based on ref. [7] starting with dimethyl malonate, triethylamine, anhydrous magnesium(n) chloride and terephthaloyl chloride in acetonitrile at –10 °C (16 h) and workup with 15 percent hydrochloric acid.


[7] 1e (preparation): To sodium hydride (0.2 g, 8 mmol) in THF (10 ml) was added tetramethyl 2,2'-terephthaloyl dimalonate (6) in dry THF (40 ml) (under nitrogen) at 20°C, and the mixture stirred for 1 h. Then a solution of terephthaloyl chloride (10 mmol) in THF (10 ml) was added dropwise over 15 min, and the mixture was stirred for 16 h, filtered in air through a fluted filter, and concentrated to 15 ml. Acetone (50 ml) was added. After 3 d ruby-red microcrystals could be isolated from the solution. Yield: 0.73 g (57%). Decom. above 150°C. $K_{bc}= 1.72 cm$–1 (F18 O). $\Phi_{max}$ (absorpt.) in alcohol): $\lambda_{max}$ (mg/ml): $\Phi$(000): 1825 ($0.7; 0.6; 0.5$).


[12] The peak potential difference $\Delta E_p$ of 170 mV, and also the peak width $\Delta E_w$ of 135 mV, stay essentially constant with variation of the scan speed in the region 50–250 mV$^{-1}$. In the region 50–250 mV the ratio of peak current $i_p$ and the square root of the scan rate are constant. The use of tetrabutylammonium hexafluorophosphate as conducting salt leads to considerably larger values: $\Delta E_p = 300$ mV, $\Delta E_w = 220$ mV at 250 mV$^{-1}$.

[13] A random number of noninteracting identical redox centers in a molecule should show a current potential behavior with the same characteristics as a corresponding one-electron oxidant (e.g. $E_{1/2} = 58$ mV). This is only valid, however, when the redox centers show no interaction behavior. In the case of a partial diffusion control, signal broadening occurs. Signal forms comparable to ours result from the simulation of cyclic voltammograms for a
formal two-electron transfer under similar conditions for the rate constants of the charge transfers [19].


Dilithiation of Two Diphenyl Ethers Each Containing Two NHCH₂CH₂Y (Y = OMe, NMe₂) Side Arms in ortho Positions: Assembly of "Adamantanoid" Li₄O₂N₄ Cores**

By Ian Cragg-Hine, Matthew G. Davidson,* Oldrich Kocian, Francis S. Mair, Ehmke Pohl, Paul R. Raithby, Ronald Snaith, Neil Spencer, and J. Fraser Stoddart*

Lithium amides are important synthetic organic reagents, and consequently much work has been done in order to elucidate their structures both in solution and in the solid state. Until recently however, the structures of only simple monolithiated complexes of secondary amines were known. To our knowledge only two dilithiated amide complexes exist; it is a Li₁₀ species held together by (PhLiNCH₂CH₂NLiPh)₃ (1). We have also obtained the structure of a dilithiated diamine (PhLiNCH₂CH₂NLiPh) · 3 HMPA (HMPA = hexamethyldiphosphoric triamide), containing the commonly observed Li₂N₂ core. Such a core also featured in the first lithiated diaza crown. We now report on the dilithiation of two diamines, 2,2'-bis(2-methoxyethylamino)diphenyl ether (1) and 2,2'-bis(N,N-dimethylamidolino)diphenyl ether (2), which give the lithium amides 3 and 4, respectively.

The possibility of intramolecular coordination, coupled with the increased flexibility of 1 and 2 over the cyclic crown ethers suggested that the use of an additional Lewis base donor such as (C₆H₅)₂O or HMPA would be unnecessary. Indeed, dilithiation of the diamines 1 and 2 and the subsequent crystallization of products 3 and 4 from toluene solution was achieved in the absence of a Lewis base donor.

The X-ray crystal structure analyses of diamines 3 and 4 exhibit an adamantanoid metal-containing core, a structural motif that is unprecedented in the chemistry of Group I metal complexes (Fig. 1 and 2).17, 81

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The molecular structure of 3 (Fig. 1) shows a [Li₄O₂N₄] core (thermal ellipsoids at the 50% probability level).