

Fig. 2. Crystal structure of the complex **1** (*tert*-butyl groups and H atoms omitted). Important distances [Å]: V(1)–O(1) 2.110(5), V(1)–O(6) 2.118(5), V(1)–O(7) 2.122(4), V(1)–O(7a) 2.149(5), V(1)–O(8) 2.158(5), V(1)–O(9) 2.142(5), V(2)–O(1a) 1.970(5), V(2)–O(3) 2.010(5), V(2)–O(4) 2.036(4), V(2)–O(5) 1.980(5), V(2)–O(6) 1.954(5), V(2)–O(7a) 2.060(5), V(1)···V(2) 3.059(2), V(1)···V(1a) 3.193(2), V(1)···V(2a) 3.241(2), Na–O(10) 2.285(7), Na–O(11) 2.292(6), Na–O(3) 2.246(6), Na–O(5) 2.296(6), Na···V(2) 3.250(4), O(2)···H···O(3a) 2.796(5), O(9)···H···O(2) 2.815(5), O(8)···H···O(4) 2.644(5). The index a indicates the centrosymmetrical coordinate transformation.

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 **1** is a characteristic feature of the V^{II} system with dbcat. In the V^{II} systems with another catechols,^[6] a mixed valence V^{II}/V^{III} complex is not formed, and all initial V^{II} is oxidized to the mononuclear V^{III} complex containing three ligands. An X-ray analysis of this type of complex, e.g. K₃[V^{III}(cat)₃], 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^{II} complex is not substantially different from that of the initial V^{II} complex that reduces molecular nitrogen.

Experimental Procedure

N₂ reduction and H₂ evolution kinetics have been performed as previously described [2d]. VCl₃ was synthesized by dissolving vanadium metal in hydrogen chloride under argon. The mixed valence V^{II}/V^{III} complex **1** was crystallized from the solution containing VCl₃ (3 × 10⁻⁴ mol), dbcat (1.5 × 10⁻³ mol), and NaOCH₃ (4 × 10⁻³ mol) in 10 mL of methanol. Thirty to forty hours are required for the formation of proper crystals from the initial reaction mixture (yield about 10–15% of total vanadium). The crystals dissolve easily in methanol. The concentration of V^{II} in the solution has been determined by titration with (NH₄)₂Fe(SO₄)₂ in sulfuric acid in the presence of safranin T. The total V concentration has been determined by atomic absorption analysis.

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[1] a) A. Butler, C. J. Carrano, *Coord. Chem. Rev.* **1991**, *109*, 61–105; b) L. V. Boas in *Comprehensive Coordination Chemistry*, Vol. 3 (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, pp. 462–473.

[2] a) A. E. Shilov, N. T. Denisov, O. N. Efimov, V. F. Shuvalov, N. I. Shuvalova, A. K. Shilova, *Nature (London)* **1971**, *231*, 460–462; b) L. A. Nikonova, S. A. Isaeva, N. I. Pershikova, A. E. Shilov, *J. Mol. Catal.* **1975/76**, *1*, 367–374; c) S. A. Isaeva, L. A. Nikonova, A. E. Shilov, *Nouv. J. Chim.* **1981**, *5*, 21–25; d) N. P. Luneva, A. P. Moravsky, A. E. Shilov, *ibid.* **1982**, *6*, 245–251; R. A. Henderson, G. J. Leigh, C. J. Pickett, *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197; e) J. Y. Becker, B. Rosin, *J. Electroanal. Chem.* **1988**, *250*, 385–397; e) C. Woitha, D. Rehder, *Angew. Chem.* **1990**, *102*, 1495–1497, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1438–1440; f) G. J.

Leigh, R. Prieto-Alcón, J. R. Sanders, *J. Chem. Soc. Chem. Commun.* **1991**, 921–922; g) C. Woitha, D. Rehder, W. Priebsch, H. Gailus, *ibid.* **1992**, 364–365.

[3] According to Equations (a) and (b) the hydrogen and ammonia yields are (2 a_{H₂}/a_V) × 100%, (3 a_{NH₃}/a_V) × 100%, where a_{H₂} is the amount of H₂ evolved, a_{NH₃} the amount of NH₃ formed, and a_V the amount of V^{II} consumed, all in moles.

[4] **1**: C₉₄H₁₆₀O₂₂V₂Na₂, M = 1892.1, monoclinic, space group P2₁/n, a = 16.748(3), b = 16.459(3), c = 21.764(3) Å, β = 109.53(2)°, V = 5654.2(3.5) Å³, ρ_{calc} = 1.12 g cm⁻³, Z = 2, T = 140 K. Siemens P3/PC diffractometer, MoK_α radiation, graphite monochromator, θ/2θ-scan. 2θ ≤ 46° were used. At T = 140 K 6740 independent reflections were measured; 3111 observed reflections with I ≥ 2σ(I) were used in the calculations: direct methods; Na, V, O anisotropic; C and H atoms of the OH groups isotropic; least-squares refinement (H atoms of the Me groups and phenyl rings included in the calculated positions as fixed contributors with constant temperature factors U_{iso} = 0.08 Å²); 369 refined parameters, R = 0.064, R_w = 0.053, GOF = 1.92. All calculations were performed by the PC/AT computer using SHELXTL PLUS programs. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

[5] M. Yu. Antipin, L. P. Didenko, L. M. Kachapina, A. K. Shilova, A. E. Shilov, Yu. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1989**, 1467–1468.

[6] S. A. Isaeva, L. A. Nikonova, *Izv. Akad. Nauk SSSR Ser. Khim.* **1977**, 1968–1971.

[7] S. R. Cooper, Yu. B. Koh, K. N. Raymond, *J. Am. Chem. Soc.* **1982**, *104*, 5092–5102.

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

By Rolf W. Saalfrank,* 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 methyllithium/metal(II) chloride and oxalyl chloride at –78 °C in tetrahydrofuran and subsequent workup with aqueous ammonium chloride, we obtained, by spontaneous self-assembly,^[1, 3, 4] the tetranuclear chelate complexes **1a** (M²⁺ = Mg, Mn, Co, Ni, Zn).^[1, 5]

The doubly bidentate bridging ligand L¹ is formally obtained by the template coupling of two dimethyl malonate monoanions with oxalyl chloride to form tetramethyl 2,3-di-hydroxy-1,3-butadiene-1,1,4,4-tetracarboxylate followed by subsequent spontaneous double deprotonation.

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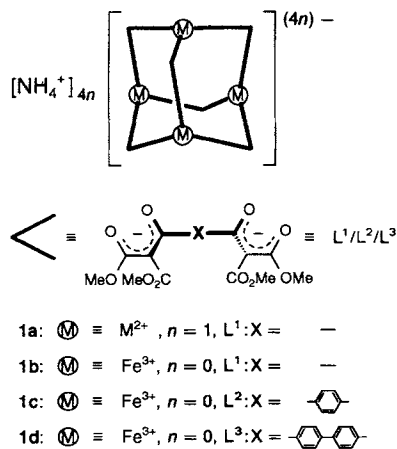
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We were convinced that the size of the cavity of the tetrametallate(4-) ions **1a** could be tailored with suitable spacers. In place of the anions **1a**, it should also be possible to obtain *neutral* tetranuclear metal-chelate complexes by using M^{3+} , instead of M^{2+} , ions.



Consequently we doubly deprotonated tetramethyl 2,2'-terephthaloyldimalonate^[6] 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 $Fe_4L_6^2$, is the tetranuclear iron(III) chelate complex **1c** (for details see [8]).

The 1H and ^{13}C NMR spectra of $Fe_4L_6^2$ (**1c**) do not unambiguously establish the structure of this compound. Thus an X-ray crystallographic structure analysis of this complex was carried out.^[9] According to this analysis, **1c** crystallizes as a neutral, adamantanoid, tetranuclear iron(III) chelate complex (Fig. 1)—the first of its kind.^[12] 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).^[13]

Two enantiomeric pairs [(*A*)-, (*A*)-*fac*, and (*A*)-, (*A*)-*mer*] are principally possible for octahedral complexes of the type MA_3B_3 [with bidentate ligands $M(AB)_3$].^[14] The $Fe_4L_6^2$ complex has an exact S_4 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*)-/(*A*, *A*)-*fac*]. This is in contrast to the chiral, racemic, *T*-symmetrical complexes **1a**, in which all four metal centers ($M^{2+} = Mg, Mn, Co, Ni, Zn$) are identically coordinated [(*A*, *A*, *A*, *A*)-*fac* or (*A*, *A*, *A*)-*fac*].^[1, 5]

The cyclic voltammogram under aprotic conditions^[15] shows the reduction of the $Fe_4L_6^2$ complex **1c** as a quasi-reversible signal pair centered at -550 mV (Fig. 3, left). The peak potential difference ΔE_p at a scan rate of 250 mVs⁻¹ is 170 mV; the reduction peak is slightly broadened ($E_p - E_{p/2} = 135$ mV), but shows no further splitting.^[16] 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

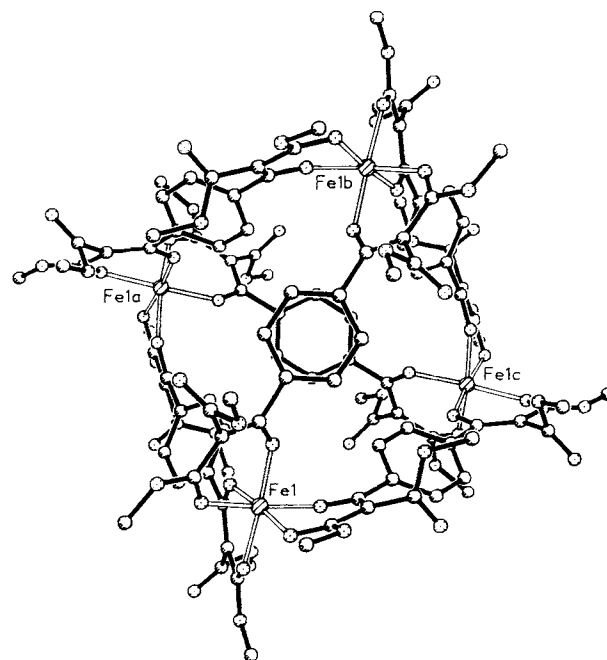


Fig. 1. Top: Crystal structure of **1c** (view along the crystallographic S_4 axis; H atoms omitted; C atoms white; O atoms dotted). Bottom: Stereoview of the crystal packing of **1c** (view along the crystallographic S_4 axis; for reasons of clarity the methoxy and methoxycarbonyl groups as well as the solvents of crystallization $C_4H_{10}O$, C_3H_6O , and H_2O have been omitted).

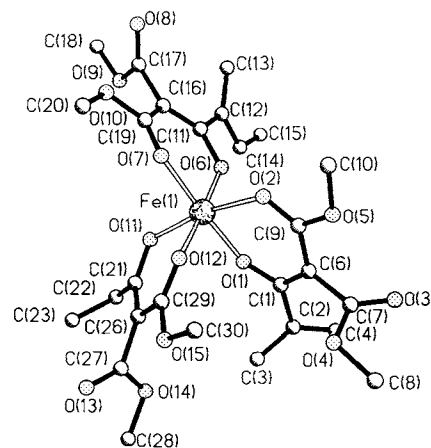


Fig. 2. Coordination sphere of a Fe^{3+} ion in **1c**. Selected distances [Å] and angles [°]: Fe(1)-O(1) 1.946(4), Fe(1)-O(2) 2.039(4), Fe(1)-O(6) 1.926(4), Fe(1)-O(7) 2.016(4), Fe(1)-O(11) 1.950(4), Fe(1)-O(12) 2.043(4), Fe(1)···Fe(1a) 10.028, Fe(1)···Fe(1b) 10.375, O(1)-Fe(1)-O(2) 85.66(15), O(6)-Fe(1)-O(7) 85.7(2), O(11)-Fe(1)-O(12) 85.0(2).

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 spectroelectrochemical as well as voltabsorptometric measurements. Following the reduction spectroelectrochemically gives continually changing absorption signals, but no recognizable intermediates for a partially reduced complex are observed. It is conspicuous that the longest 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-potential four-electron transfer.^[17, 20]

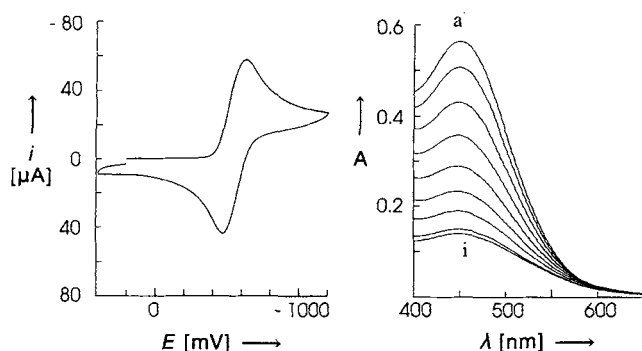


Fig. 3. Left: Cyclic voltammogram of **1c** in a 0.1 M solution of tetraethylammonium tetrafluoroborate in acetonitrile, $c = 10^{-3}$ M, scan speed 250 mV s^{-1} . Potentials vs. ferrocene/ferrocenium (Fc/Fc^+). Right: Spectroelectrochromogram of **1c** in solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Potentials (a–i): –300, –400, –500, –550, –600, –700, –750, –800 (vs. Fc/Fc^+).

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 δ 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 μ_{eff} .^[24] This result agrees well with the calculated value of the magnetic moment ($\mu_{\text{calc}} = 11.83 \mu_B$) for four magnetically isolated high-spin iron(III) centers that show no interactive phenomena in the investigated temperature range.^[25]

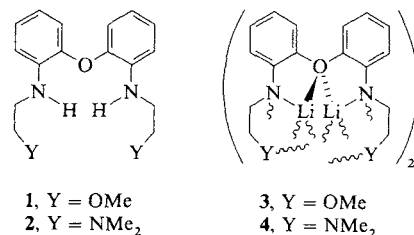
We shall report elsewhere on the simple iron(III) chelate complex **1b** and the iron(III) chelate complex **1d** with biphenyl as spacer.

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- [1] R. W. Saalfrank, A. Stark, M. Bremer, H.-U. Hummel, *Angew. Chem.* **1990**, *102*, 292–294; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 311–314.
[2] T. Weiske, T. Wong, W. Krättschmer, J. K. Terlouw, H. Schwarz, *Angew. Chem.* **1992**, *104*, 242–244; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 183–185; H. Hopf, *ibid.* **1991**, *103*, 1137–1139 and **1991**, *30*, 1117–1118; C. Seel, F. Vögtle, *ibid.* **1992**, *104*, 542–563 and **1992**, *31*, 528–549.
[3] P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92–95; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69–72; J.-M. Lehn in *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Merbach), VCH, Weinheim, **1992**, pp. 447–462.
[4] Reviews: J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91–116; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89–112, *ibid.* **1990**, *102*, 1347–1362 and **1990**, *29*, 1304–1319.
[5] R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem.* **1988**, *100*, 878–880; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851–853.

- [6] Synthesis based on ref. [7] starting with dimethyl malonate, triethylamine, anhydrous magnesium(II) chloride and terephthaloyl chloride in acetonitrile at -10°C (16 h) and workup with 15 percent hydrochloric acid.
[7] M. W. Rathke, M. A. Nowak, *Synth. Commun.* **1985**, *15*, 1039–1049; M. W. Rathke, M. A. Nowak, *J. Org. Chem.* **1985**, *50*, 2624–2626; M. W. Rathke, P. J. Cowan, *ibid.* **1985**, *50*, 2622–2624.
[8] **1c** (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 iron(III) chloride (0.3 g, 2 mmol) in THF (40 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%). Decomp. above 150°C . IR (KBr): $\tilde{\nu} = 1720 \text{ cm}^{-1}$ (C=O). FAB-MS (3-nitrobenzyl alcohol matrix): m/z : 2578 [$\text{Fe}_4\text{L}_6^+ + \text{H}^+$], 2185 [$\text{Fe}_4\text{L}_5^+ + \text{H}^+$], 1793 [$\text{Fe}_4\text{L}_4^+ + \text{H}^+$]. Correct C, H, N analyses.
[9] Crystal data for **1c**: $\text{C}_{108}\text{H}_{96}\text{O}_{60}\text{Fe}_4 \cdot \text{C}_4\text{H}_{10}\text{O} \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{H}_2\text{O}$, $M_r = 777.49$, tetrahedral, space group $P4n2$, $a = b = 21.631(1)$, $c = 17.371(3) \text{ \AA}$, $V = 8127.9(15) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calc}} = 1.271 \text{ Mg m}^{-3}$, $F(000) = 3240$, $\lambda = 0.71073 \text{ \AA}$, $T = 180 \text{ K}$, $\mu (\text{MoK}\alpha) = 0.439 \text{ mm}^{-1}$. The data were collected on a Stoe-Siemens AED diffractometer. Intensity determinations were performed on a shock-cooled crystal (dimensions $1.2 \times 1.0 \times 0.8 \text{ mm}$) in an oil drop according to the $2\theta/\omega$ method in the region $8^\circ < 2\theta < 45^\circ$. Of the 7537 collected reflections, 5328 were unique and were absorption-corrected according to a semiempirical method; highest minima and maxima: 1.0 and -0.46 e^{-3} , respectively; $R1 = 0.068$ and $wR2 = 0.179$ (all data), the absolute structure was refined by using the Flack parameters (H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876) to 0.01(3). The structure was solved by direct methods (SHELXS-90) [10] and refined according to the least-squares method (SHELXL 92) [11]. All hydrogen atom positions were located in a difference Fourier map and refined by using a riding model. The U values for chemically equivalent hydrogen atoms were refined together in groups. Further details concerning the X-ray structure analysis can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.
[10] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
[11] G. M. Sheldrick, *SHELXL-92*, University of Göttingen, **1992**.
[12] Tetranuclear iron(III) complexes: S. R. Boone, G. H. Purser, H.-R. Chang, M. D. Lowery, D. N. Hendrickson, C. G. Pierpont, *J. Am. Chem. Soc.* **1989**, *111*, 2292–2299; J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *ibid.* **1989**, *113*, 3012–3021; K. S. Hagen, A. D. Watson, R. H. Holm, *ibid.* **1983**, *105*, 3905–3913; M. A. Whitener, J. K. Bashkin, K. S. Hagen, J.-J. Girerd, E. Gamp, N. Edelstein, R. H. Holm, *ibid.* **1986**, *108*, 5607–5620; J. L. Sessler, J. D. Hugdahl, V. Lynch, B. Davis, *Inorg. Chem.* **1991**, *30*, 334–336; Q. Chen, J. B. Lynch, P. Gomez-Romero, A. Ben-Hussein, G. B. Jameson, C. J. O'Connor, L. Que, Jr., *ibid.* **1988**, *27*, 2673–2681.
[13] In regard to the topology of the four-centered chelate complex **1c** (bridge-heads: Fe^{3+} ions), compare also the conditions in spherical tricycles (bridge-heads: N atoms): Ref. [4]. F. P. Schmidtchen, *Angew. Chem.* **1977**, *89*, 751–752; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 720–721; J.-M. Lehn, *Pure Appl. Chem.* **1977**, *49*, 857–870; E. Graf, J.-M. Lehn, *J. Am. Chem. Soc.* **1975**, *97*, 5022–5024; E. Weber, F. Vögtle, *Kontakte (Darmstadt)* **1981**, (1), 24–36; E. Weber: *Phase Transfer Catalysts, Properties and Applications* (Merck-Schuchardt publication, **1987**, pp. 32–76; F. P. Schmidtchen, *Nachr. Chem. Tech. Lab.* **1988**, *36*, 8–1.
[14] M. Becke-Goehring, H. Hoffmann, *Komplexchemie*, Springer, Berlin **1970**, p. 26ff; see also *Nomenclature of Inorganic Chemistry* (Ed.: G. J. Leigh), Blackwell, Oxford, **1991**, p. 179ff. (in octahedral complexes of type $\text{MA}^1\text{B}^1\text{A}^2\text{B}^2\text{A}^3\text{B}^3$, five enantiomeric pairs occur: J. Leong, K. N. Raymond, *J. Am. Chem. Soc.* **1975**, *97*, 293–296). See also the descriptions OC-6-22 (for facial) and OC-6-21 (for meridional) recommended by IUPAC.
[15] Amel System 5000 with IR compensation. Undivided cell with Pt-disc electrodes. Potentials vs. Fc/Fc^+ . For experimental details on electrochemistry, spectroelectrochemistry and voltabsorptometry, see J. Salbeck, *J. Electroanal. Chem.* **1992**, *340*, 169–195.
[16] The peak potential difference ΔE_p of 170 mV, and also the peak width $E_p - E_{p/2}$ 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: $\Delta E_p = 300 \text{ mV}$, $E_p - E_{p/2} = 299 \text{ mV}$ at 250 mV s^{-1} .
[17] A random number of noninteracting identical redox centers in a molecule should show a current potential behavior with the same characteristics as a reversible one-electron transfer (e.g. $\Delta E_p = 58 \text{ mV}$). This is only valid, however, when the redox centers show Nernstian behavior [18]. 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].
- [18] J. B. Flanagan, S. Margel, A. J. Bard, F. C. Anson, *J. Am. Chem. Soc.* **1978**, *100*, 4248–4253.
- [19] K. Hinkelmann, J. Heinze, *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 243–249.
- [20] See refs. [21–23] for details concerning multielectron transfer processes.
- [21] D. E. Fenton, R. R. Schroeder, R. L. Lintvedt, *J. Am. Chem. Soc.* **1978**, *100*, 1931–1932; D. E. Fenton, R. L. Lintvedt, *ibid.* **1978**, *100*, 6367–6375; D. T. Pierce, W. E. Geiger, *ibid.* **1989**, *111*, 7636–7638; B. Tulyathan, W. E. Geiger, *ibid.* **1985**, *107*, 5960–5967; J. Salbeck, J. Schöberl, J. Daub, *Z. Phys. Chem.* **1991**, *171*, 191–212.
- [22] E. Kimura, S. Joko, T. Koike, M. Kodama, *J. Am. Chem. Soc.* **1987**, *109*, 5528–5529.
- [23] W. F. Sokol, D. H. Evans, K. Niki, T. Yagi, *J. Electroanal. Chem.* **1980**, *108*, 107–115; K. Fan, H. Akutsu, K. Niki, N. Higuchi, Y. Kyogoku, *ibid.* **1990**, *278*, 295–306.
- [24] The diamagnetic corrections were determined by using Pascal constants: E. A. Budreaux, L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, J. Wiley, New York, **1976**; A. Weiss, H. Witte, *Magnetochemie*, VCH, Weinheim, **1973**.
- [25] F. E. Mabbs, D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, **1973**; A. Bencini, D. Gatteschi, *EPR of Exchange Coupled Systems*, Springer, Berlin, **1990**.



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 (C₂H₅)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^[6] 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).^[7, 8]

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.^[1, 2] Until recently however, the structures of only simple monolithiated complexes of secondary amines were known. To our knowledge only two dilithiated amide complexes exist. Recently we published the results of dilithiating naphthylamine, providing the first example of a dilithiated primary amine; it is a Li₂₀ species held together by (NaphN)²⁻ anions (Naph = naphthyl) and ether ligands.^[3] We have also obtained the structure of a dilithiated diamine (PhLiNCH₂CH₂NLiPh) · 3 HMPA^[4] (HMPA = hexamethylphosphoric triamide), containing the commonly observed^[2] Li₂N₂ core. Such a core also featured in the first lithiated diazacrown.^[5] We now report on the dilithiation of two diamines, 2,2'-bis(2-methoxyethylamino)diphenyl ether (**1**) and 2,2'-bis(*N,N*-dimethylethylenediamino)diphenyl ether (**2**), which give the lithium amides **3** and **4**, respectively.

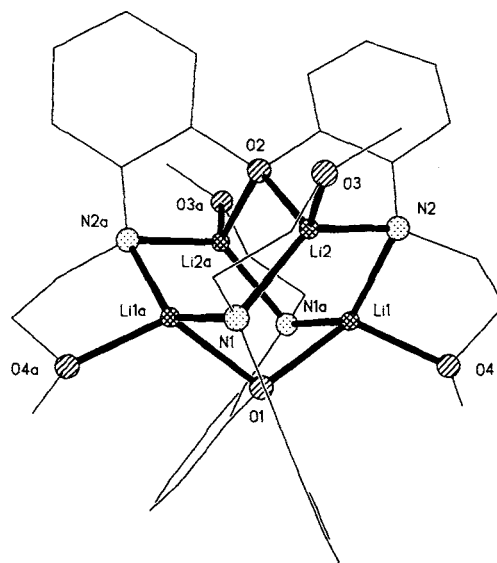


Fig. 1. Molecular structure of **3** (for clarity, the carbon framework is not shown in detail and hydrogen atoms have been omitted).

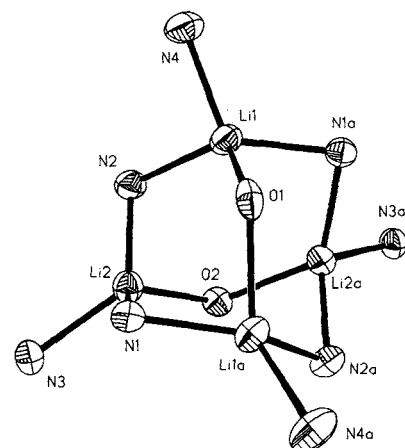


Fig. 2. Adamantanoid Li₄O₂N₄ central core of **4** (thermal ellipsoids at the 50% probability level).

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