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Trapping Intermediates

An Unstable Paramagnetic Isopolyoxomolybdate Intermediate Non-Homogeneously Reduced at Different Sites and Trapped in a Host Based on Chemical Adaptability**

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Dedicated to Professor Pierre Gouzerh on the occasion of his 70th birthday

Under special conditions, solutions of polyoxometalates can "behave" as unique constitutional dynamic libraries (CDLs) containing building blocks that may reversibly associate, thereby allowing a continuous change in constitution through reorganization, while external stimulants can influence the scenario.[1] This is especially valid in case of polyoxomolybdate chemistry; for related basic aspects of CDLs see Refs. [2,3]. In this context, a variety of nanosized clusters with fascinating structures and properties[4–6] could be even deliberately obtained.[1a,c] The mentioned solution properties[1a,c] can be related to the chemical adaptability of related clusters based on the flexibility of their building blocks, for example, in case of the giant molecular wheels of the type $\{Mo_{154}\}$ and $\{Mo_{176}\}$[1b] with the formulas $[\{Mo_1\}\{Mo_2\}\{Mo_8\}]_n^{m-}$ ($n = 14$, 16; $m = 28$, 32).[5] Here we report on a reduction pathway of an aqueous solution of the diamagnetic $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$[7a,b] (structure in Figure S1, Supporting Information), which leads to an unprecedentedly reduced polyoxomolybdate, that is, a paramagnetic unstable derivative of the $\{Mo_{36}\}$-type cluster trapped in an appropriately enlarged $\{Mo_{154}\}$-type wheel/host formed on the release of special building blocks. Results from X-ray crystallography, EPR spectra, and DFT calculations prove that the paramagnetic $\{Mo_{36}\}$ cluster shows an unprecedented type of electronic and magnetic structure with different uncoupled Mo^V centers—an interesting result, as all known reduced polyoxomolybdates with an even number of 4d electrons are according to a literature search diamagnetic.[7c] This offers the option to study not only new types of exchange interactions, but also interesting reactivities of the Mo^V centers. The whole system and especially the trapped cores are stabilized by an unprecedented dense hydrogen-bonding system in between the two mentioned highly reduced components. Altogether we can refer here to an extremely complex system in which several parts are intrinsically related, that is, structurally, electronically, and magnetically.

Wheel-shaped $\{Mo_{154}\}$- and $\{Mo_{176}\}$-type clusters and their derivatives are usually obtained without encapsulated guests upon reduction of acidic aqueous solutions of molybdates.[1c,5a] However, based on an appropriate (deficit) amount of reducing agent, it was now possible to obtain compound **1**, in which the paramagnetic eight-electron reduced $\{Mo_{36}\}$ clusters/intermediates are trapped in defective/enlarged $\{Mo_{154}\}$-type wheel segments (Figure 1), which are linked to chains (Figure S2, Supporting Information).

$$Na_{25.6}\{[Mo^{VI}{}_{28}Mo^{V}{}_{8}(OH)_2O_{110}(H_2O)_{16}]_{0.4} \subset$$
$$[H_{14}Mo^{VI}{}_{120}Mo^{V}{}_{28}O_{447}(H_2O)_{59}]\} \cdot 250\,H_2O \equiv$$
$$Na_{25.6}\mathbf{1a} \cdot \text{ca.}\,250\,H_2O \equiv \mathbf{1}$$

Compound **1** (see Experimental Section) was characterized by elemental analysis, cerimetric titration for the determination of the number of Mo^V centers (a formal description because of delocalized 4d electrons), spectroscopic methods (IR, Vis-NIR and especially EPR), DFT calculations, and X-ray crystallography (for crystal data see Experimental Section).

The formula of the discrete $\{Mo_{154}\}$ cluster without defects, the materials properties of which were studied by several groups (see the reviews in Refs. [1c] and [6c]) can be simply written based on building blocks as $[\{Mo_1\}_{14}\{Mo_2\}_{14}\{Mo_8\}_{14}]^{28-}$.[5a] However, in case of compound **1** we have to consider its more complicated chain construction (Figure S2) as well as the presence of three $\{Mo_2\}$-type defects (see formula and Figure 1), two of which are necessary for the

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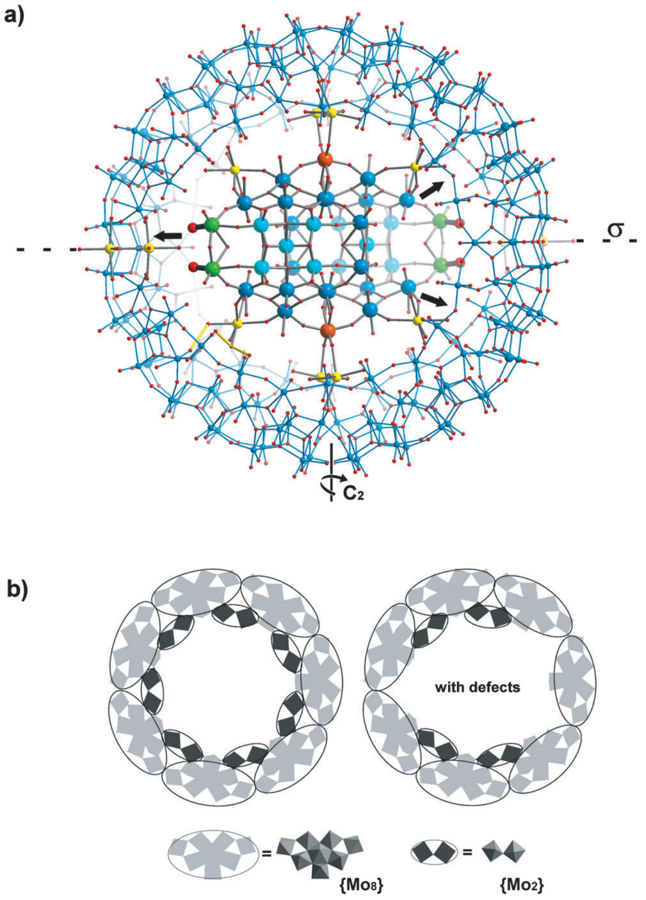

Figure 1. a) Ball-and-stick representation of a core–shell segment of a chain of compound **1** with the trapped reduced paramagnetic $\{Mo_{36}\}$ cluster and its C_2 axis and the mirror plane perpendicular to it (the nature of the reduced Mo centers is explained in Table 1), and in part the stabilizing hydrogen-bond network (shown in more detail in Figure 2). The three black arrows point in the direction of the $\{Mo_2\}$-type wheel defects: the two right ones (corresponding to four symmetry-related $\{Mo_2\}$ groups, each with an underoccupation of 30%) and the left one pointing in the direction of the influential $\{Mo_2\}$-type defect (corresponding to two symmetry-related $\{Mo_2\}$ groups with underoccupation of 90%; unit not shown, see text) that is necessary for the guest trapping. The release of altogether three $\{Mo_2\}$ groups is in agreement with the formula of **1** (color code: Mo blue (reduced ones in green, orange, and light blue), O red, Na yellow); b) Comparison of two wheel-type clusters with (right: symmetry-related not emphasized) and without defects (left) and formed with $\{Mo_2\}$ and $\{Mo_8\}$ units.[5a] The mentioned influential defect (pointed out by the left arrow in a) is emphasized, too. In agreement with all results, the presence of the two symmetry-equivalent $\{Mo_2\}$ groups should not allow encapsulation of a guest because its two terminal O atoms (shown as enlarged red spheres in a) would be too near to O atoms of the host-type $\{Mo_2\}$ units (not shown in a).

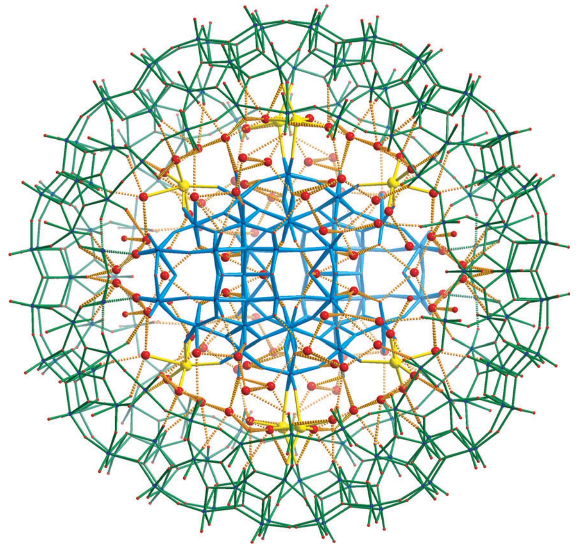

Figure 2. Shown is the integration/trapping of a reduced $\{Mo_{36}\}$ guest into one wheel segment of compound **1**—both constituents having complementary shapes (wireframe representation)—and the interesting hydrogen-bonding framework (dashed lines) in between: H_2O molecules (discrete and coordinated), bridging and terminal O^{2-} (of the two cluster surfaces), and the important Na^+ ions, which are especially necessary for the stabilization. The lines in yellow correspond to O···O distances between 2.6 and 3.2 Å while not all 100 H_2O and 8 Na^+ positions are fully occupied (color code as in Figure 1 a).

mentioned cluster trapping (see below). It should be noted that a type of chain compound exists also without trapped $\{Mo_{36}\}$ clusters.[8] But whereas in the latter compound, linking occurs through four Mo-O-Mo bonds,[8] the ring segments of **1** are linked by five groups (see also Ref. [9]).

The $\{Mo_{36}\}$ guests are "connected" to the wheel segments by a unique stabilizing hydrogen-bond network, which includes components of both cluster surfaces, discrete water molecules, and sodium cations (see Figure 2). The occupation of the wheel cavities by the $\{Mo_{36}\}$ clusters is only 40% (all Mo and O atoms have the corresponding occupation number 0.4 in agreement with the formula of **1**) and can occur only(!) in appropriately enlarged segments that exhibit two very specific symmetry-related $\{Mo_2\}$ defects, which increase the size and deform the wheel segments (see Figure 1). The related elliptical deformation leads to a shape complementarity between the host segments and the guests (Figures 1 and 2). In this context, we can refer to a nice example of chemical adaptability of the wheel segments, as these can easily release the $\{Mo_2\}$ units necessary for the encapsulation of the guests.

The electronic and magnetic structure of the trapped reduced $\{Mo_{36}\}$ cluster is unprecedented in polyoxomolybdate chemistry: EPR spectra and DFT as well as BVS calculations prove the presence of different types of reduced Mo^V centers, including paramagnetic ones in stoichiometrical amounts, which was never before reported in case of a reduced polyoxomolybdate containing an even number of 4d electrons (see Table 1, Figure 1 and below).[7c,d]

The EPR spectrum of compound **1** (Figure 3) under N_2 or Ar atmosphere recorded at 102 K proves unambiguously the presence of "isolated" Mo^V centers (the spectrum is similar to that measured at room temperature, which shows slightly increased peak broadenings; Figure S3a, Supporting Information). The intensity of the signal versus temperature follows approximately Curie's law, as the signal at 298 K is about three times less intense than that at 102 K.

The experimental EPR spectrum (Figure 3) is composed of an intense signal with axial symmetry with $g_{\perp} > g_{\parallel}$ (Mo isotopes with $I = 0$), and an additional less intense hyperfine structure composed of six lines, which results from the

Table 1: Characterization of the reduced Mo^V centers of the trapped $\{Mo_{36}\}$-type cluster as constituents of compound **1**.

Reduced atoms/groups	Positions of symmetry-related parts in Figure 1xfigr1 > (spheres in different colors)	Bond valence sum (BVS) per Mo atom[a]	Average Mulliken population[c]	Total number of 4d electrons
2 Mo^V	orange (top and bottom atoms far apart and linking two $\{Mo_{17}\}$ units)	BVS = 5.2	0.42	two: trapped/unpaired
2 $\{Mo_2\}$	green (groups far apart from each other)	BVS = 5.5[b]	0.15	two: one on each $\{Mo_2\}$ group[d]
2 $\{Mo_5O_6\}$	cyan (double-cubane-type compartments)	BVS = 5.6	0.38	four: two spin coupled

[a] See Figure S4 for details. [b] Because of the disorder problem and the low guest occupations, the BVS values are not accurate (see Figure S4a). [c] Atomic electron population computed at DFT level for a nonaplet state assuming eight unpaired electrons. [d] The relatively high electron density at the reduced Mo atoms and the corresponding rather long Mo=O bond lengths favor (disordered) protonations of the related four terminal O atoms (red, partly enlarged spheres in Figure 1; see also formula of **1**). The number 2 in the first column is due to symmetry. The two paramagnetic units/centers in the first two rows refer to the A and B centers in the EPR spectrum of Figure 3 and Table 2 without distinguishing between them.

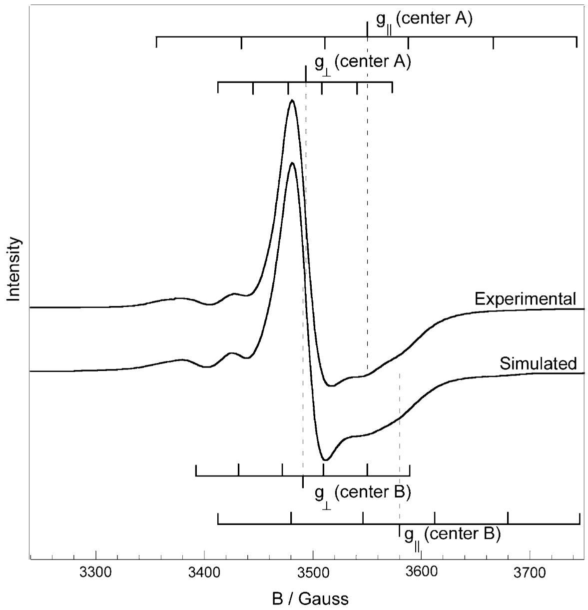

Figure 3. Experimental and simulated EPR spectra of compound **1** recorded at 102 K. The dotted lines are shown for an easier visualization of the $g_{\parallel}$ and $g_{\perp}$ central positions of each of the reduced Mo centers A and B (see Table 1 and Table 2).

interaction of the unpaired 4d electrons with the $^{95,97}Mo$ isotopes (I = 5/2). The relative intensity of the main signal with respect to that of the hyperfine structure is in complete agreement with the natural abundances of Mo isotopes. The double integration of the overall EPR signal at 298 K has been compared to that of a pure anhydrous $CuSO_4$ reference sample, which is consistent with (about) four EPR-active Mo^V centers per $\{Mo_{36}\}$ unit and thus in complete agreement with the formula of compound **1**.

In order to get the best simulation, two different Mo^V-type centers (**A** and **B** in Figure 3) with equal proportions had to be considered. The obtained g values (Table 2) are similar to those of oxomolybdenum(V) species with related distorted O_h environments,[10] while the hyperfine A values are close to those observed for several polyoxomolybdates containing one Mo^V center, for example, $[PMoW_{11}O_{40}]^{4-}$ and $[Mo_6O_{19}]^{3-}$[7a] (see also Ref. [11]).

Table 2: Simulated EPR g-tensors (uncertainty in the last decimals) and A-tensors of compound **1** measured at 102 K referring to the two different corresponding metal centers (see Table 1 and Figure 1).

Sample	Center	$g_{\parallel}$/Width [Gauss]	$g_{\perp}$/Width [Gauss]	$A_{\parallel}$ [Gauss]	$A_{\perp}$ [Gauss]	Proportion [%]
1	A	1.899/30	1.935/23	76	30	50
	B	1.882/30	1.932/23	66	41	50

DFT calculations were extensively used in the study of the electronic properties of polyoxometalates.[12] In order to get more evidence about the electronic state of the guest of compound **1**, (approximate) DFT calculations of the $\{Na_8[Mo_{36}O_{112}(H_2O)_{16}]\}^{8-}$ system—not considering spin couplings of the 4d electrons—were performed (for the results see Figure 4), confirming that the eight extra 4d electrons located on the $\{Mo_{36}\}$ cluster are not equally distributed. An assumed nonaplet state was computed to analyze the spin density distribution of the eight 4d-metal electrons (for the average atomic spin density populations see Table 1). The involved singly occupied molecular orbitals (SOMOs; Figure 4) are symmetry-adapted combinations of molybdenum d and oxygen p orbitals; they are found in a rather small energy range (−3.5 to −3.0 eV) and accommodate, with increasing energy, two electrons in each of the two double-cubane moieties (cyan), one electron at each of the two discrete Mo^V sites (orange), and one at each of the $\{Mo_2\}$ units (green), but showing further electron delocalization (for details including colors see Figure 1 and Table 1). The SOMOs and the Mulliken population analysis show that the two single Mo sites (orange, Figure 1) concentrate more electron density. The reduction of the mentioned sites requires the incorporation of the Na^+ cations according to the present model.

The results and their explanations can be outlined as follows:

1. The chain formation (Figure S2) reduces the solubility of compound **1** and therefore favors its removal (from the solution), which is, besides the presence of a special section/interface between the guests and shell segments, important for preventing easy decomposition of the unstable reduced $\{Mo_{36}\}$ guests/intermediates because of their trapping.

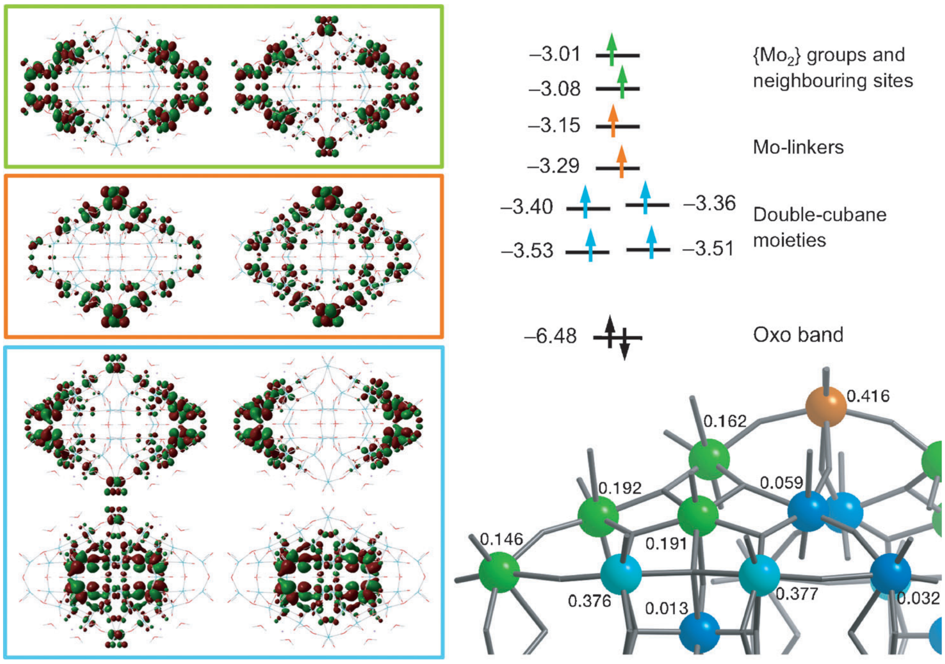

Figure 4. Representations and energies (in eV) of the eight singly occupied molecular orbitals in the formally (see text) nonaplet spin state ($S=4$) of the {$Na_8[Mo_{36}O_{112}(H_2O)_{16}]$}$^{8-}$ system, together with a simplified ball-and-stick view (only Mo atoms displayed) of the computed atomic spin populations (for related details and definitions see Figure 1 and Table 1). The rest of the structure (not shown) is obtained by symmetry operations. The color identifies the different regions occupied by electrons (see Table 1). As expected, the spin-coupled electrons within the {Mo_5O_6} compartments have the lowest energy above the oxo band level.

2. The interface (a type of solid electrolyte system) between the wheel segments and the {Mo_{36}} guests is unusual: it involves hydrogen bonding based on ingredients of the two cluster surfaces (terminal and bridging O^{2-} and H_2O ligands), discrete H_2O molecules as well as Na^+ ions (Figure 2).
3. The trapped polyoxomolybdate cluster is unprecedentedly reduced (Tables 1 and 2 as well as Figures 1 and 3, and Figure S4a), as all known pure isopolyoxomolybdates and heteropolyoxomolybdates (e.g. Keggin-type anions)[7a] that exhibit an even number of 4d electrons show (according to a general acceptance) spin coupling in context with electron delocalization combined with electronic repulsion.[7c,d] Apart from the presence of two different types of paramagnetic Mo^V groups/centers, there is another interesting result, namely that each of the two {Mo_5O_6} compartments (Figure 1 and Figure S1) acts as electronic sink for two spin-coupled 4d electrons, comparable to the scenario of the 14 corresponding compartments in the discrete diamagnetic {Mo_{154}}-type wheel.[4,5a,b] (Note: the environments of the compartments are different in both cases causing small changes in the electronic structure.) The Mo^V centers have been unambiguously identified on the basis of bond valence sum calculations, DFT calculations, and EPR spectra (see Tables 1 and 2, Figures 1 and 3, and Figure S4).
4. Interestingly, the isolation of compound **1** with the trapped guests is not (very) sensitive to a limited exposure to air (see Supporting Information, Part I, regarding reactions under changed conditions, i.e. different abundance of O_2). This is especially interesting as single paramagnetic Mo^V centers are considered to be rather sensitive to oxidation in the presence of oxygen[11] (see also point 1). The stabilization of the two Mo^V centers (Table 1) should be partly due to the presence of the linkages O(host) … Na^+ … OMo^V (guest); see Figure 1.
5. Chemical adaptability dominates in the reaction system, as the reduced {Mo_{36}} clusters are only trapped in appropriately enlarged and deformed chain-type wheel segments, generated by the release of two special symmetry-related {Mo_2}-type groups, thus leading to complementary shapes between the guests and the host segments (Figure 1). This is of course not visible in the nice space-filling presentation for the host–guest system shown in Figure S5, Supporting Information. The only partial occupancy of the wheel segments by the guests in compound **1** is due to the fact that not all of them contain the two mentioned {Mo_2} defects (see Figure 1); if all segments contain this defect, complete filling is possible.[9a,b] Normally synthesized wheel-type clusters of the {Mo_{154}} type without defects can therefore not contain the {Mo_{36}} guests.[4,5]

The most important discoveries have been presented in form of the five points listed above, especially mentioning that compound **1** can be considered a unique core–shell or host–guest system regarding the kind of trapping of an unstable reaction intermediate and its dependence on the chemical adaptability of the host system. Further investigations based on different reducing conditions would of course shed more light on the discovered reduction pathway, especially regarding the nature/properties of the reactive Mo^V centers. The present results could also initiate further investigations to understand properties of molybdate systems that form constitutional dynamic libraries, especially in context with compounds that show chemical adaptabilities based on the flexibility of the relevant building blocks. A further challenge will be to investigate the reactivities of the Mo^V centers—including their possible role in catalysis[11] and electrocatalysis—but also to explore options to trap reduced and unstable metal oxides in suitable small spaces, especially if they are reaction intermediates as in the present case.

Experimental Section

Synthesis of **1** (under exclusion of air, including degassed water): A solution of $Na_2MoO_4{\cdot}2H_2O$ (7.26 g, 29.76 mmol) in water (60 mL) was acidified with hydrochloric acid (7.3 mL, ROTIPURAN $\geq 25\,\%$, Carl Roth GmbH) and then reduced with powdered hydrazinium dichloride (0.14 g, 1.34 mmol, Acros Organics). After closing the flask with a stopper, it was shaken until the reducing agent was completely dissolved (ca. 2–3 min). The color of the solution finally became deep-blue, while rod-shaped crystals of **1** began to form after 2–3 days. The precipitate was filtered after 4 days and washed with a small amount of cold water. Yield: 2.6 g (47 % based on Mo). Elemental analysis calc. (%) for $H_{645.6}Mo_{162.4}Na_{25.6}O_{807.2}$: Na 1.97, Mo 52.39; found: Na 1.7, Mo 52.5 (for the infrared and electronic absorption spectrum see Supporting Information, Section III). Subtraction of the estimated volume of the structurally localized atoms (using increments) from the total volume of the unit cell shows that a maximum of ca. 250 crystal water molecules can in principle be present per formula unit. The calculated values refer to the compound with that crystal water content.

Crystal data for **1**: $M = 29\,735.16\ \text{g mol}^{-1}$, $H_{645.6}Mo_{162.4}Na_{25.6}O_{807.2}$, monoclinic, $C2/m$, $a = 29.5457(6)$, $b = 51.4968(10)$, $c = 30.5302(6)$ Å, $\beta = 115.2120(10)$, $V = 42\,026.9(14)\ \text{Å}^3$, $Z = 2$, $\rho = 2.350\ \text{g cm}^{-3}$, $\mu = 20.321\ \text{mm}^{-1}$, $F\ (000) = 28\,411$, crystal size $= 0.14 \times 0.08 \times 0.05\ \text{mm}^3$. A total of 217 314 reflections ($1.86 < \Theta < 66.81°$) were collected of which 37 595 reflections were unique ($R(\text{int}) = 0.0489$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0476$ for 29 872 reflections with $I > 2\sigma(I)$, $R = 0.0646$ for all reflections; max/min residual electron density 2.175 and $-1.819\ \text{e Å}^{-3}$. Crystals of **1** were removed from the mother liquor and immediately cooled to 100(2) K on a Bruker AXS APEX2 diffractometer (three circle diffractometer, Cu-Kα radiation, QuazarTM Montel Multilayer optics monochromator; hemisphere data collection in ω and ϕ at 0.3° scan width in three runs with 606, 435 and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5 cm) (SHELXS/L, SADABS from G.M. Sheldrick, University of Göttingen 1997/2003; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001).

Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-425782.

Methods used for the measurements of the EPR spectra and DFT calculations are found in the Supporting Information, Section VI.

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