Experimental Section

In a typical batch $Si(NH)_2$ (0.69 mmol), Ce (0.76 mmol), and SiO_2 (0.20 mmol) were thoroughly mixed in a glove box under a purified argon atmosphere. The reaction batch then was transferred into a tungsten crucible, and placed into the reactor of a radio frequency (rf) furnace which was inductively heated[25] under a purified N_2 atmosphere (1 bar). During the reaction the crucible was heated to 850 °C within 5 min. After 10 min at this temperature, it was heated to 1540 °C over 3 h and held at this temperature for 1 h. Afterwards the crucible was allowed to cool down to 1200 °C over 53 h and to 900 °C over 15 h. Finally the reaction product was quenched to room temperature. In accordance with the X-ray structure determination, the analytical composition of $Ce_{16}Si_{15}O_6N_{32}$ was confirmed by energy-dispersive X-ray microanalysis (Ce, Si). The absence of hydrogen (N–H) was checked by IR spectroscopy.

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A Paramagnetic Copper(III) Complex Containing an Octahedral $Cu^{III}S_6$ Coordination Polyhedron[**]

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Thomas Weyhermüller, Wolfram Meyer-Klaucke,
and Karl Wieghardt[*]

Most inorganic chemistry textbooks[1] comment on the coordination chemistry of copper in the "unusual", that is rare, oxidation state +III with d^8 electron configuration that there is only one *paramagnetic* ($S = 1$) species containing an octahedral coordination polyhedron known, namely $K_3[Cu^{III}F_6]$.[2] On the other hand, a number of diamagnetic, square-planar Cu^{III} complexes have been described and have even been structurally characterized. We report here the synthesis, as well as the molecular and electronic structure of a new paramagnetic Cu^{III} species containing an octahedral $Cu^{III}S_6$ coordination polyhedron.

It is well established that thiolato ligands can lower the Cu^{III}/Cu^{II} redox potential.[3] In principle, they can stabilize high formal oxidation states of a given transition metal ion.

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On the other hand, the conceivable generation of thiyl radical complexes during synthesis cannot be a priori rejected. Thus the electronic structures of a thiyl radical – $\mathrm{Cu^{II}}$ complex and that of a genuine thiolato – $\mathrm{Cu^{III}}$ species must be carefully—if possible experimentally—distinguished.

The reaction of mononuclear $[\mathrm{Co^{III}L}]$,[4] in which $\mathrm{L^{3-}}$ is the hexadentate macrocyclic trianion 1,4,7-tris(4-*tert*-butyl-2-sulfidobenzyl)-1,4,7-triazacyclononane, with $\mathrm{Cu^{II}(OAc)_2 \cdot H_2O}$ (2:1) in methanol affords upon addition of $\mathrm{NaPF_6}$ red crystals of the heterotrinuclear complex **1**-$(\mathrm{PF_6})_2$. One-electron oxidation of **1** in acetone using one equivalent of $[\mathrm{Ni^{III}(tacn)_2}](\mathrm{ClO_4})_3$[5] (tacn = 1,4,7-triazacyclononane) and addition of $\mathrm{NaClO_4}$ yields blue-black microcrystals of **2**-$(\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$. Complex **2** is stable in the solid state for weeks but decomposes rapidly within minutes in solution (reduction).

$[\mathrm{LCo^{III}Cu^{II}Co^{III}L}](\mathrm{PF_6})_2$ **1**-$(\mathrm{PF_6})_2$

$[\mathrm{LCo^{III}Cu^{III}Co^{III}L}](\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$ **2**-$(\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$

Single crystals of **1**-$(\mathrm{BPh_4})_2 \cdot 6\,\mathrm{CH_3CN}$ were found to be suitable for X-ray crystallography,[6] and Figure ¼1 shows the structure of the trinuclear dication. Both diamagnetic $\mathrm{Co^{III}}$ ions are in the terminal positions in an octahedral *cis*-$\mathrm{N_3S_3}$ donor atom environment, whereas the central $\mathrm{Cu^{II}}$ ion is in a severely Jahn – Teller distorted, octahedral $\mathrm{Cu^{II}S_6}$ polyhedron. The cation has crystallographically imposed C_i symmetry; the three independent $\mathrm{Cu^{II}}$ – S bond lengths differ significantly, whereas the $\mathrm{Co^{III}}$ – N and $\mathrm{Co^{III}}$ – S bond lengths are identical within experimental error, respectively. They are the same as observed in diamagnetic, mononuclear $[\mathrm{Co^{III}L}]$.[4]

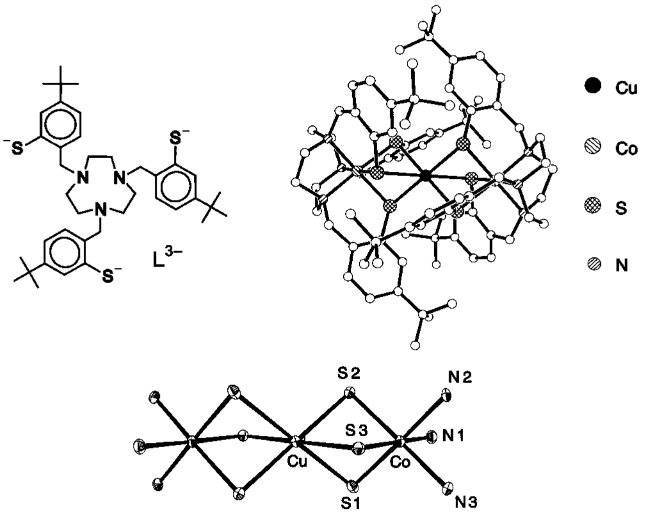

Figure 1. View of the 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane ligand (top left), structure of the dication in **1**-$(\mathrm{BPh_4})_2 \cdot 6\,\mathrm{CH_3CN}$ (top right), and section of its structure (bottom). Selected bond lengths [Å] and angles [°]: Cu–S1 2.516(2), Cu–S2 2.388(1), Cu–S3 2.477(1), average Co–S 2.244(2), average Co–N 2.026(2), Cu⋯Co 3.153(1); Co-S1-Cu 82.64(4), Co-S2-Cu 85.79(4), Co-S3-Cu 83.61(5).

The cyclic voltammogram of **1** recorded in $\mathrm{CH_3CN}$ (0.10 M $(n\mathrm{Bu_4N})\mathrm{PF_6}$) displays a reversible one-electron oxidation at $E_{1/2} = +0.35$ V versus ferrocenium/ferrocene ($\mathrm{Fc^+/Fc}$), which is assigned to the $\mathrm{Cu^{III}/Cu^{II}}$ redox couple. In addition, a second quasi-reversible one-electron oxidation step at $+0.90$ V versus $\mathrm{Fc^+/Fc}$ has been observed which might correspond to the $\mathrm{Cu^{IV}/Cu^{III}}$ couple. At $E_p^{red} = -1.96$ V versus $\mathrm{Fc^+/Fc}$ complex **1** is irreversibly reduced ($\mathrm{Cu^{II} \rightarrow Cu^{I}}$). Note the analogous cadmium species $[\mathrm{LCo^{III}Cd^{II}Co^{III}L}](\mathrm{PF_6})_2$ does not display any redox activity in the potential range $+0.7$ to -1.1 V versus $\mathrm{Fc^+/Fc}$.

Temperature-dependent magnetic susceptibility measurements (SQUID, 2 – 300 K; 1.0 T) on powdered samples revealed a temperature-independent magnetic moment of $1.74\,\mu_B$ (10 – 300 K) for **1**-$(\mathrm{PF_6})_2$ and slightly temperature-dependent moments between 2.4 and $2.6\,\mu_B$ (20 – 300 K) for **2**-$(\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$ in reasonable agreement with the expected spin-only values for $\mathrm{Cu^{II}}$ ($S = ½$) and high-spin $\mathrm{Cu^{III}}$ ions ($S = 1$).

Metal K-edge X-ray absorption spectra (XAS)[7] measured at the Co *and* Cu K-edges of **1**-$(\mathrm{PF_6})_2$ and **2**-$(\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$ show unambiguously that oxidation of **1** to **2** affects only the central Cu ion. As displayed in Figure 2 the Co K-edge energies of **1** and **2** are identical, whereas the spectra measured at the Cu K-edge are significantly different. The Cu K-edge energy in **2** is about 0.7 eV higher than that in **1** in accord with a metal-centered one-electron oxidation of **1** to **2**.[8] Furthermore, the analysis of the Co and Cu K-edge EXAFS spectra (*e*xtended *X*-ray *a*bsorption *f*ine *s*tructure) of **1** and **2** shows that oxidation of **1** to **2** does not affect the Co – N and Co – S bond lengths (2.02(1) and 2.239(6) Å, respectively); they are in excellent agreement with the crystallographically determined values for **1**-$(\mathrm{BPh_4})_2 \cdot 6\,\mathrm{CH_3CN}$. Even the Cu – S distances in **1** and **2** appear to be identical (but see

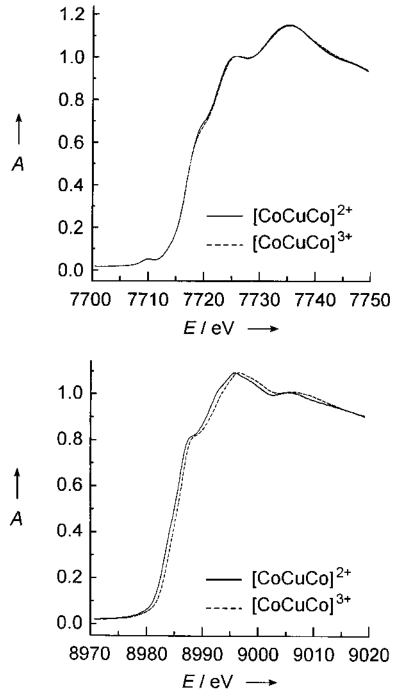

Figure 2. Metal K-edge X-ray absorption spectra (XAS spectra) of **1**-$(\mathrm{PF_6})_2$ and **2**-$(\mathrm{ClO_4})_3 \cdot 2\,\mathrm{Me_2CO}$. Top: Co K-edge, bottom: Cu K-edge. A = normalized absorption.

the comment in ref. [9]). Clearly, the cations in **1** and **2** are isostructural and the Cu K-edge XAS and EXAFS spectra conclusively rule out a Cu^{II} – thiyl formulation for **2**. Therefore, **2** is considered to be a genuine Cu^{III} species which is isoelectronic with the structurally characterized species $[LCo^{III}Ni^{II}Co^{III}L]^{2+}$. We have shown previously[10] that this compound can be oxidized by two successive one-electron steps to give a paramagnetic Ni^{III} and a diamagnetic Ni^{IV} complex.

Figure 3 shows the EPR spectra of **1** and **2** in CH_3CN solution and their simulations.[11] The rhombic signal displaying Cu hyperfine splitting for **1** is characteristic for a Cu^{II} ion with $S = ½$ ground state. In contrast, the spectrum of **2** is typical for a triplet ground state ($S = 1$) with small zero-field splitting. In summary, we have shown that six bridging thiolato ligands are capable of stabilizing a high-spin d^8 electron configuration of a Cu^{III} ion.

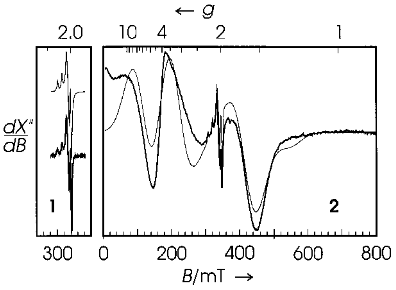

Figure 3. X-Band EPR spectra of **1**-$(PF_6)_2$ (left) at 10 K and of **2**-$(ClO_4)_3 \cdot 2Me_2CO$ (right) at 4 K in acetone and simulations (thin lines).[11] Experimental conditions for **1**-$(PF_6)_2$ (in parentheses for **2**-$(ClO_4)_3 \cdot 2Me_2CO$): frequency 9.46 GHz (9.65 GHz); energy 0.1 mW (1.0 mW), modulation amplitude 1.9 mT (1.3 mT); modulation frequency 100 kHz (100 kHz).

Experimental Section

1-$(PF_6)_2$: To a suspension of $[LCo^{III}]$[4] (0.35 g) in methanol (120 mL) was added $Cu(OAc)_2 \cdot H_2O$ (0.05 g). After heating the mixture to reflux for 30 min, $NaPF_6$ (1.60 g) dissolved in methanol (20 mL) was added. Filtration and cooling to 4 °C initiated the precipitation of red crystals of **1**-$(PF_6)_2$ in 91 % yield (0.39 g). Single crystals of **1**-$(BPh_4)_2 \cdot 6CH_3CN$ were obtained by allowing an acetonitrile solution containing $Na(BPh_4)$ to slowly diffuse into an acetonitrile solution of **1**-$(PF_6)_2$. ESI-MS (CH_3CN): 1641 [**1**-$(PF_6)_2 - PF_6]^+$, 751 [**1**-$(PF_6)_2 - 2PF_6]^{2+}$; UV/Vis/NIR (CH_3CN): λ_{max} (ε) = 273 (52100), 455 (2870), 532 (3090), 797 nm (6380); elemental analysis calcd for $C_{78}H_{108}N_6S_6Co_2CuP_2F_{12}$ (%): C 52.2, H 6.1, N 4.7, S 10.7, Co 6.6, Cu 3.5; found: C 51.9, H 6.1, N 4.5, S 10.9, Co 6.5, Cu 3.5.

2-$(ClO_4)_3 \cdot 2Me_2CO$**:** The synthesis was carried out under an argon blanketing atmosphere. To a solution of **1** (130 mg) in dry acetone (20 mL) was added $[Ni^{III}(tacn)_2](ClO_4)_3$ (53 mg).[5] After stirring the mixture for 10 min at 40 °C, $NaClO_4$ (2.00 g) dissolved in acetone (20 mL) was added and the reaction volume was reduced by one half by rotary evaporation of the solvent. Storage of the resulting solution at −80 °C produced within 30 min blue-black crystals of **2** in 60 % yield (0.08 g). ESI-MS (CH_3CN) 1602 [**2**-$(ClO_4)_3 \cdot 2Me_2CO - (2Me_2CO, ClO_4)]^+$, 751 [**2**-$(ClO_4)_3 \cdot 2Me_2CO - (2Me_2CO, 3ClO_4)]^+$; UV/Vis/NIR ($CH_3CN$): λ_{max} (ε) = 275 (63000), 560 (7000), 700 (5100), 1019 nm (1340); elemental analysis calcd for $C_{84}H_{120}N_6S_6O_{14}Co_2CuCl_3$ (%): C 52.6, H 6.3, N 4.4, S 10.0, Co 6.2, Cu 3.3, Cl 5.5; found: C 52.4, H 6.2, N 4.4, S 9.9, Co 6.2, Cu 3.3, Cl 5.5.

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[7] XAS and EXAFS spectra measured at the Co and Cu K-edge of **1**-$(PF_6)_2$ and **2**-$(ClO_4)_3 \cdot 2Me_2CO$ were recorded at Messplatz D2 (EMBL-EXAFS) DORIS (DESY, Hamburg). Reduction of the data and normalization of the K-edge energies were performed with EXPROG, analysis of the fine structure with FEFF6 and FEFFIT: For more details see T. Glaser, T. Beissel, E. Bill, T. Weyhermüller, V. Schünemann, W. Meyer-Klaucke, A. X. Trautwein, K. Wieghardt, *J. Am. Chem. Soc.*, submitted.

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[11] The simulation of the spectrum of **1** for an $S = ½$ system was achieved with a rhombic g tensor $g = (2.022, 2.053, 2.118)$ and anisotropic Lorentzian line shapes $W = (5.2, 7.9, 4.4)$ mT. The first-order hyperfine splitting was only included for g_z with $A_z = 126 \times 10^{-4}$ cm^{-1} ($I = 3/2$). The spectrum of **2** was simulated by using a spin Hamiltonian operator for $S = 1$:[12] $|D| = 0.20$ cm^{-1}; $E/D = 0$ (fixed), $g = 2.051$ with Gaussian line width $W = 88$ mT. (The weak signal at $g = 2$ is due to Cu^{II} impurity of **1** (< 1 %)). Cu hyperfine structure is not resolved. A similar zero-field parameter $D = -0.188$ cm^{-1} has been reported for Cu^{III} ions in an Al_2O_3 matrix.[13] Within the ligand field model for **2** the observed values for D and g are consistent with an octahedrally coordinated Cu^{III} ion (high-spin d^8) with large splitting of the $^2A_{2g}$ ground and a ^2T excited state ($10Dq > 20000$ cm^{-1}).

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