Synthesis, X-Ray Crystal Structure and Magnetic Characterization of the First "$Ni_3S_4N_3$" Nickel Thiolate Cluster

Albrecht Berkessel*[a], Jan W. Bats[b], Martina Hüber[c], Wolfgang Haase[c], Thomas Neumann[d], and Lutz Seidel[a]

Organisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-69120 Heidelberg

Institut für Organische Chemie der Universität Frankfurt/Main[b],
Marie-Curie-Straße 11, D-60439 Frankfurt/Main

Institut für Physikalische Chemie der Technischen Hochschule Darmstadt[c],
Petersenstraße 20, D-64287 Darmstadt

Institut für Organische Chemie der Universität Göttingen[d],
Tammannstraße 2, D-37077 Göttingen

Received June 6, 1994

Key Words: Nickel cluster / Nickel thiolate / Hydrogenase

The tridentate N,O,S-ligand (*RS*)-2-[(2-mercapto-1-methylamino)ethyl]phenol (*rac*-**1**) was prepared from *ortho*-hydroxychloroacetophenone in three steps. When this ligand was treated with nickel(II) acetate, the novel "$Ni_3S_4N_3$" cluster *rac*-**3** was obtained. The X-ray crystal structure of *rac*-**3** unambiguously revealed the *pseudo*-C_3 symmetric structure of this novel nickel cluster, which is made up by three nickel ions, one sulfide sulfur atom, and three *homochiral* ligand molecules, each contributing one thiolate sulfur atom and one amine nitrogen atom to the ligation of the metal ions. According to NMR-spectroscopic results, this highly symmetric structure is maintained in solution. The magnetic studies revealed diamagnetic behavior in the solid state, although antiferromagnetic interaction of the metal centers cannot absolutely be excluded.

Transition metal complexes of oligodentate ligands with N, O and S heteroatoms play an important role as models for the active sites of metallo-enzymes such as methyl-coenzyme-M-reductase[1], nitrogenase[2], and in particular hydrogenases[2a,3]. The latter enzymes catalyze the reaction shown in eq. (1). This simple process is of vital importance for all hydrogen-metabolizing and -producing microorganisms. Thus, hydrogenases have been developed to highly efficient catalysts, operating at H_2 partial pressures as low as 10^{-4} – 10^{-5} atm. In the case of the so-called [Ni, Fe]-hydrogenases, the coordination sphere around the catalytically active nickel ion is most likely made up by N, O and S atoms[4], but the exact number and position of the ligating heteroatoms are not known. We reasoned that simple N,O,S ligands such as *rac*-**1** might afford tetrahedral 1:1 nickel complexes *rac*-**2** of the "tripod" type[5]. These complexes should have a labile fourth coordination site and could serve as hydrogenase models, i.e. for the binding and activation of molecular hydrogen. In this paper we describe the synthesis of the ligand *rac*-**1** and its complexation with nickel(II) ions, affording the novel nickel thiolate cluster *rac*-**3** and *not* the 1:1 complexes of the type *rac*-**2** (eq. 2). Whereas nickel complexes of the "Ni_3S_7" type, i.e. with only sulfur atoms ligating the metal ions, are known[6-9], *rac*-**3** is the first example of a "$Ni_3S_4N_3$" nickel cluster combining coordination of three nickel ions by one μ_3-sulfide sulfur atom, three μ_2-thiolate groups and three secondary amine nitrogen atoms.

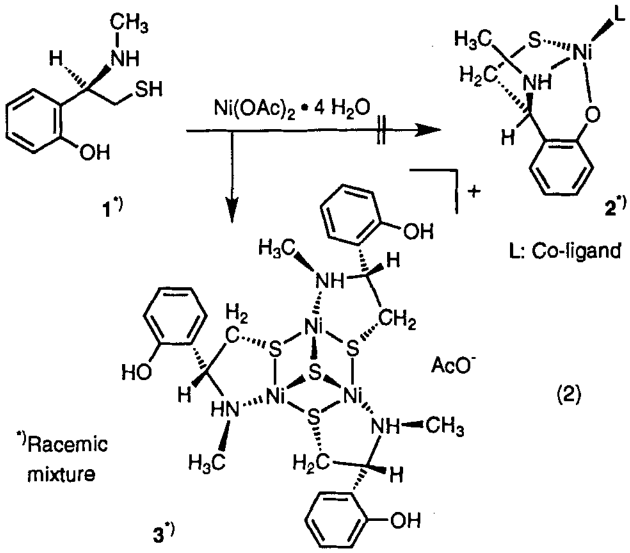
$$H_2 \overset{\boxed{\text{Hydrogenase}}}{\rightleftharpoons} 2\,H^+ + 2\,e^- \qquad (1)$$

Results

*Synthesis of the Ligand rac-***1**: The synthetic sequence employed for the preparation of the ligand *rac*-**1** is summarized in Scheme 1. First, *ortho*-hydroxychloroacetophenone[10] (**4**) has been treated with sodium phenylmethanethiolate, to afford the benzyl thioether **5**. Reductive alkylation with methylamine and sodium borohydride gives the amine *rac*-**6**, which can be reductively deprotected to give the thiol *rac*-**1** by treatment with sodium in liquid ammonia/THF.

*Reaction of the Ligand rac-***1** *with Nickel(II) Salts*: Treatment of nickel(II) salts such as anhydrous nickel(II) bromide or chloride in various solvents results in the formation of amorphous black powders of varying elemental composition. However, when nickel(II) acetate tetrahydrate is allowed to react with *rac*-**1** in ethanol, a black crystalline material (*rac*-**3**) is reproducibly obtained in 30–40% yield. Its

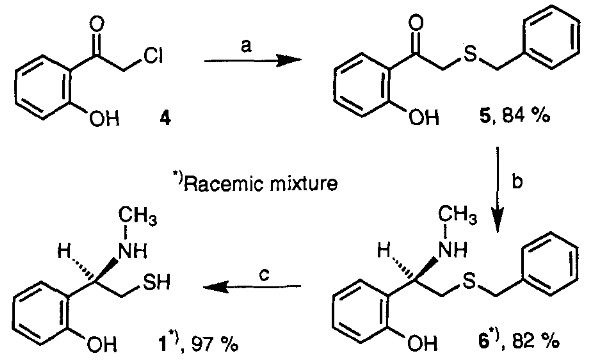
0009–2940/95/0202–0125 $ 10.00+.25/0



(2)

elemental composition is not compatible with a 1:1 complex but corresponds with the formula $[Ni_3(L\text{-}H^+)_3S]^+$ OAc^- · 1/2 H_2O (L: ligand **1** or *ent*-**1**). Luckily, the material is diamagnetic in solution and thus susceptible to NMR analysis. Its ^{13}C-NMR spectrum in $CDCl_3$ shows just the same number and multiplicity of resonances as the free ligand *rac*-**1**, although with moderate shifts of the δ-values (for NMR data see Experimental). Thus, the ligand structure is basically unchanged, and – at least in solution – the complex must be of high symmetry. The ^{1}H-NMR spectrum of the material reveals that the deprotonation of the ligand (cf. molecular formula, vide supra) has taken place at the thiol group, and that the acidic phenolic hydroxyl is still present ($CDCl_3$, broad singlet at δ = 11.81). Besides, the pattern of signals observed further supports the assumption of a structurally unaltered ligand. The molecular structure of the complex in the crystalline state has been finally elucidated by X-ray crystallography.

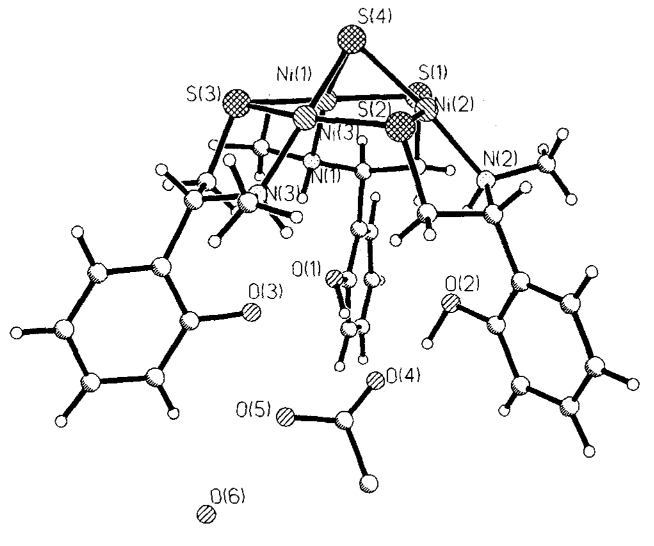
Scheme 1:



a: Bn-S$^-$ Na$^+$.- b: $NaBH_4$, $H_2N\text{-}CH_3$.- c: $Na/NH_{3\,liquid}$.-

*X-Ray Crystal Structure of the Cluster rac-*3: The crystal structure of the "$Ni_3S_4N_3$" cluster *rac*-**3** is shown in Figure 1. Three homochiral ligand molecules of **1** or *ent*-**1**, respectively, together with the three nickel ions Ni1–Ni3 form a cone-shaped cluster which is topped by the μ_3-sulfide ion S4. Each of the nickel ions is coordinated by two thiolate sulfur atoms (S1–S3) and the apical sulfide ion S4, in addition to one amine nitrogen atom (N1–N3). The atoms Ni1–Ni3 and S1–S3 lie approximately in a plane, the sulfide sulfur atom lies 1.47 Å above this plane. The Ni1–S1, Ni2–S2, and Ni3–S3 bonds all have an average length of 2.17 Å. Also, the three Ni–S bonds involving the apical sulfur atom S4 have lengths of 2.17 Å. The remaining three Ni–S bonds are slightly longer, with an average length of 2.22 Å. Clearly, the Ni–N distances are shorter, namely 1.95 Å. The nickel ions are coordinated in an almost perfectly planar fashion, their deviation from the best plane formed by the ligating S and N atoms is less than 0.16 Å. Each of the three Ni–S–C–C–N rings approximately has an envelope conformation in which the CH_2 unit lies outside the approximate plane defined by the four other ring atoms (C, N, Ni and S). The molecule is stabilized by intramolecular hydrogen bonds between the N-H groups and the hydroxyl O atoms. The N1–H···O1 and N2–H···O2 hydrogen bonds are of intermediate strength with NH···O distances of about 2.0 Å. The N3–H···O3 hydrogen bond is comparatively weak with a NH···O distance of 2.3 Å. Consequently, the latter phenol unit shows larger displacement parameters than the other two phenol units. No intermolecular contacts – such as further axial coordination of the nickel ions by neighboring cluster molecules – could be detected.

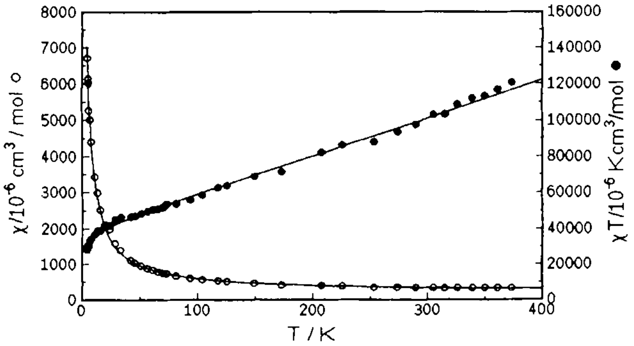
Figure 1. X-Ray crystal structure of the nickel cluster *rac*-**3** {only one of the two enantiomorphic cluster units (**3**) shown, including the acetate counterion and the water molecule [O(6)]}. Selected bond lengths [Å]: Ni1–N1 1.95(1), Ni1–S1 2.171(4), Ni1–S3 2.219(4), Ni1–S4 2.168(4), Ni2–N2 1.956(7), Ni2–S1 2.232(4), Ni2–S2 2.170(4), Ni2–S4 2.167(3), Ni3–N3 1.94(1), Ni3–S2 2.209(4), Ni3–S3 2.168(4), Ni3–S4 2.173(4).



The three phenolic hydroxyl groups form the rim of a cage which contains the acetate counterion. The oxygen atom O4 of the acetate ion is hydrogen-bonded to the phenolic hydroxyl groups H···O1 and H···O2, whereas O5 of the anion forms a single hydrogen bond to H···O3. Finally, the water molecule (O6) forms two hydrogen bonds of equal length (2.81 Å) to the oxygen atoms O5 and O5′ of two acetate ions of two enantiomorphic cluster units. The water molecule thus lies on a twofold axis of symmetry, and each of the cluster cones is of approximate C_3 symmetry.

Magnetic Data of the Nickel Cluster rac-**3**: Plots of the experimentally determined data of the molar susceptibility χ_M and $\chi_M \cdot T$ as a function of the temperature and a fit to the Curie-Weiss expression are displayed in Figure 2. The magnetic moment increases continuously from 0.47 μ_B at 4.2 K to 0.98 μ_B at 373 K. Assuming a diamagnetic behavior of the Ni^{II} centers in a square-planar coordination sphere, we can explain the resulting magnetism by the presence of small amounts of paramagnetic impurities. The values satisfactorily fit the Curie-Weiss expression with a Landé factor $g = 2.2$, a Curie-Weiss constant $\Theta = -1.69$ K, a contribution of paramagnetic impurities ($S = 1$) $x_{para} = 3.2\,\%$, as well as with a term referring to the temperature-independent paramagnetism (TIP) = $208.8 \cdot 10^{-6}$ cm³mol⁻¹. Here, Θ mainly characterizes the zero-field splitting of the spin state $S = 1$, a typical feature of Ni^{II} compounds.

Figure 2. Plot of the experimental data of the molar susceptibility χ_M) open circles) and $\chi_M \cdot T$ (full circles) vs. temperature and fit (–) to the Curie-Weiss expression.



Although a square-planar coordination geometry of the Ni^{II} centers in *rac*-**3** is well established by X-ray crystallography and hence a diamagnetic behavior is predicted, it should be mentioned that the experimental data could also be fitted assuming three equal Ni^{II} centers ($S_1 = S_2 = S_3 = 1$), interacting by extraordinary and unusually high antiferromagnetic spin coupling ($-2J > 600$ cm⁻¹).

Discussion

The reaction of the ligand *rac*-**1** with nickel(II) acetate tetrahydrate affords the monocationic cluster *rac*-**3**, the first example of a nickel cluster with a "$Ni_3S_4N_3$" core. The exact mechanism by which the μ_3-sulfide ion is eliminated from the starting ligand *rac*-**1** is as yet unclear. However, the phenomenon itself is not unprecedented: Even methanethiolate was reported by Henkel et al.[7] to eliminate a sulfide anion when treated with nickel(II) salts. In that case, a C_3-symmetric dianionic "Ni_3S_7" cluster, structurally related to our system, resulted.

As indicated by ¹H- and ¹³C-NMR spectroscopy, the highly symmetric structure of the cluster *rac*-**3** in the crystalline state is also maintained in solution. Its diamagnetism in solution is in accord with the planar fourfold coordination of the nickel(II) ions. In contrast to many known linear trimeric Ni^{II} complexes[6,11], only few Ni^{II} complexes with a triangular arrangement of the metal ions are described in the literature[6–9,12,13]. These triangular Ni^{II} compounds all have in common that they are coordinated by 4 S atoms in a square planar geometry. All these complexes are accordingly said to be diamagnetic, although no detailed magnetic studies have been performed so far. Only one paramagnetic Ni^{II}_3 complex is described in the literature which consists of a polyoxotungstate framework[14].

The magnetic measurements described in this paper do not unambiguously clarify whether the nickel cluster *rac*-**3** exists as a low-spin system or as an antiferromagnetically coupled Ni^{II} high-spin system. Although diamagnetism – as is usually observed with square-planar Ni^{II} low-spin complexes – is the most plausible interpretation of our results, the existence of a paramagnetic Ni^{II}_3 complex cannot totally be excluded.

Finally, it should be pointed out again that the enantiomorphic cones of the cluster *rac*-**3** are made up by three homochiral ligand moieties **1** and *ent*-**1**, respectively. Consequently, the enantiomerically pure cluster **3** or *ent*-**3** should be available from the enantiomerically pure ligand **1** or *ent*-**1**, respectively. The use of chiral, enantiomerically pure clusters of this type may be envisaged as hosts for enantioselective binding of – or reactions on bound – anionic substrates similar to the acetate ion bound to the "bottom" of the cluster (Figure 1). Furthermore, due to the hydrophobic interior of the cone, structures of this type may have potentials as hosts for binding apolar guests.

This work was supported by the *Bundesministerium für Forschung und Technologie* (grant no. 9342 A/H2-04-17-92), by the *Deutsche Forschungsgemeinschaft* (grant nos. Be 998/2, Ha 782/22-5) and by the *Fonds der Chemischen Industrie*.

Experimental

General Remarks: Melting points are uncorrected. – IR: Perkin-Elmer 1600. – ¹H-NMR: 270 MHz, Bruker WH 270 or 250 MHz, Bruker AM 250. – ¹³C-NMR: 75.5 MHz, Bruker AM 300; the DEPT technique was used for the assignment of multiplicities; δ (TMS) = 0. – UV/VIS: Cary 15. – Variable temperature magnetic susceptibility measurements in the range 4.2 – 290 K were performed at an applied field of 1.56 T by using a Faraday-type magnetic balance, equipped with a Cahn D-200 microbalance and a Bruker B-MN 200/60 electromagnet[15]. In the temperature range 280–380 K, magnetic susceptibility measurements were performed with a Faraday magnetometer equipped with an electromagnetic microbalance Cahn RG and a Bruker BE 20aV electromagnet, the applied field was 1.2 T. The sample consisted of microcrystals contained in a quartz bucket which was calibrated independently by using $HgCo(SCN)_4$ as calibrant. Pascal's constants were used to calculate the diamagnetic corrections of the molar magnetic susceptibility[16]. *ortho-Hydroxychloroacetophenone* (**4**) was prepared according to a literature procedure[10].

2-Benzylthio-1-(2-hydroxyphenyl)ethanone (**5**): A 250-ml three-necked flask, equipped with an addition funnel and a magnetic stirring bar, was charged under nitrogen with a solution of 17.1 g (100 mmol) of *ortho*-hydroxychloroacetophenone (**4**) in 35 ml of abs. 1,4-dioxane. The addition funnel was charged with a solution of sodium ethoxide in ethanol and 12.0 ml (12.6 g, 101 mmol) of phenylmethanethiol. The ethoxide solution was prepared from 2.30 g (100 mmol) of sodium and 58 ml of abs. ethanol. The ethanolic solution of sodium phenylmethanethiolate was added dropwise at ca. 20°C with vigorous stirring within 45 min. A cream-colored precipitation occurred and stirring at ca. 20°C was continued for another 30 min. The reaction mixture was then poured into ca. 700 ml of ice water with stirring. The solid was filtered off and washed first with water and then with *n*-hexane until a color- and odorless material was obtained. After drying over phosphorus pentoxide in vacuo and recrystallization from little methanol, 21.7 g (84 %) of colorless crystals was obtained, m.p. 64°C. – IR (KBr): $\tilde{\nu}$ = 1626 cm^{-1} (CO). – ^1H-NMR ($CDCl_3$) ; δ = 3.66 (s, 2 H, CH_2-Ph or 2-H), 3.80 (s, 2H, CH_2-Ph or 2-H), 6.85–7.66 (m, 9H, aromatic H), 12.05 (s, 1H, OH). – $C_{15}H_{14}O_2S$ (258.3): calcd. C 69.75, H 5.46; found C 69.80, H 5.63.

(RS)-2-[(2-Benzylthio-1-methylamino)ethyl]phenol (*rac*-**6**): A 250-ml flask was charged with a solution of 20.0 g (77.4 mmol) of the ketone **5** in 150 ml of abs. methanol, and 13.4 ml (155 mmol, 2.00 equiv.) of a 40 % aqueous solution of methylamine was added. The yellow solution was stirred at ca. 20°C for 30 min, and 1.46 g (38.7 mmol, 0.50 equiv.) of sodium borohydride was added carefully in portions. Stirring was continued for another 60 min. The reaction mixture was then cooled with ice and acidified with concd. hydrochloric acid to pH = 2. The solvents were removed in a rotary evaporator, the oily residue was taken up in water (300 ml), and the solution extracted with ether. The ether phase was discarded. The aqueous phase was adjusted to alkaline pH by addition of solid potassium hydroxide. It was then extracted with methylene chloride, and the organic phase was dried with anhydrous potassium carbonate. After evaporation of the solvent in a rotary evaporator and drying of the residue in vacuo, a colorless solid was obtained. Recrystallization from abs. methanol and washing with *n*-pentane afforded 17.3 g (82 %) of colorless crystals, m.p. 60°C. – IR (KBr): $\tilde{\nu}$ = 3308 cm^{-1} (NH, OH). – ^1H-NMR ($CDCl_3$): δ = 2.30 (s, 3H, CH_3), 2.68–2.84 (m, 2H, $CHC\mathit{H}_2$), 3.42 (dd, J = 9.8 Hz, J = 5.1 Hz, 1H, CH), 3.71, 3.74 (AB system, J = 13.7 Hz, 2H, $C\mathit{H}_2Ph$), 6.71–7.38 (m, 9H, aromatic H), OH, NH extremely broad and varying with concentration. – $C_{16}H_{19}NOS$ (273.4): calcd. C 70.29, H 7.01, N 5.12; found C 70.13, H 6.92, N 5.25.

(RS)-2-[(2-Mercapto-1-methylamino)ethyl]phenol (*rac*-**1**): A flame-dried 500 ml three-necked flask, equipped with an efficient magnetic stirring bar, was charged under nitrogen with a solution of 4.00 g (14.6 mmol) of the benzyl thioether *rac*-**6** in 40 ml of abs. THF. After cooling to –70°C, ca. 200 ml of dry ammonia was condensed into the flask. The solution was vigorously stirred and 674 mg (29.3 mmol, 2.00 equiv.) of sodium was added in small portions. At the end of the addition, the blue color persisted and 2.00 g (37.4 mmol, 2.00 equiv.) of ammonium chloride was carefully added. The cooling bath was removed and the flask was allowed to warm to ca. 20°C. After evaporation of the ammonia and evaporation of the residual solvents in a rotary evaporator, a colorless, semisolid material remained which was extracted with methylene chloride (200 ml). After evaporation of the solvent in a rotary evaporator and drying of the residue in vacuo, a colorless oil was obtained. Flash chromatography on deoxygenated silica gel (adsorbent/substrate, 40:1; eluant ethyl acetate/*n*-hexane, 1:2) afforded 2.60 g (97 %) of a colorless oil. – IR (film): $\tilde{\nu}$ = 2557 cm^{-1} (SH). – UV ($CHCl_3$) : λ_{max} (lg ε) = 277 nm (3.418). – ^1H-NMR ($CDCl_3$): δ = 1.39 (br s, 1H, SH), 2.45 (s, 3H, CH_3), 2.74 (dd, J = 14.0 Hz, J = 10.5 Hz, 1H, CH_2), 2.96 (dd, J = 14.0 Hz, J = 4.0 Hz, 1H, CH_2), 3.55 (dd, J = 10.5 Hz, J = 4.0 Hz, 1H, CH), 6.76–7.26 (m, 4H, aromatic H), OH, NH extremely broad and varying with concentration. – ^{13}C-NMR ($CDCl_3$): δ = 30.18 (CH_2), 34.14 (CH_3), 67.94 (CH), 116.91 (aromatic CH), 119.18 (aromatic CH), 123.38 (aromatic C), 128.95 (aromatic CH), 129.03 (aromatic CH), 157.38 (aromatic C). – $C_9H_{13}NOS$ (183.3): calcd. C 58.79, H 7.15, N 7.64; found C 59.02, H 7.17, N 7.83.

Cyclo-1,1:2;2,2:3;3,1:3-tris-{μ-[2-((1RS)-2-mercapto-1-(SR)-methylaminoethyl)phenolato](1–)-N,S:S}-μ

tion are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58254, the names of the authors, and the journal citation.

---

[1] [1a] A. Berkessel, *Bioorg. Chem.* **1991**, *19*, 101–115. – [1b] A. Berkessel, M. Bolte, C. Griesinger, G. Huttner, T. Neumann, B. Schiemenz, H. Schwalbe, T. Schwenkreis, *Angew. Chem.* **1993**, *105*, 1776–1780; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1777–1780.

[2] [2a] W. Kaim, B. Schwederski, *Bioanorganische Chemie*, Teubner, Stuttgart, **1991**. – [2b] D. Sellmann, W. Soglowek, F. Knoch, M. Moll, *Angew. Chem.* **1989**, *101*, 1244–1245; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1271. – [2c] D. Sellmann, E. Böhlen, M. Waeber, G. Huttner, L. Zsolnai, *Angew. Chem.* **1985**, *97*, 984–985; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 981.

[3] [3a] H.-J. Krüger, R. H. Holm, *J. Am. Chem. Soc.* **1990**, *112*, 2955–2963. – [3b] S. Fox, Y. Wang, A. Silver, M. Millar, *J, Am. Chem. Soc.* **1990**, *112*, 3218–3220.– [3c] D. Sellmann, J. Käppler, M. Moll, *J. Am. Chem. Soc.* **1993**, *115*, 1830–1835.

[4] [4a] J. P. Whitehead, R. J. Gurbiel, C. Bagyinka, B. M. Hoffmann, M. J. Maroney, *J. Am. Chem. Soc.* **1993**, *115*,5629–5635. – [4b] C. Bagyinka, J. P. Whitehead, M. J. Maroney, *J. Am. Chem. Soc.* **1993**, *115*, 3576–3585.

[5] L. Sacconi, F. Mani in *Transition Metal Chemistry*, Vol. 8 (Eds.: G. A. Melson, B. N. Figgis), Marcel Dekker, New York, **1982**.

[6] B. Krebs, G. Henkel, *Angew. Chem.* **1991**, *103*, 785–804; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 769–788.

[7] G. Henkel, M. Kriege, K. Matsumoto, *J. Chem. Soc., Dalton Trans.* **1988**, 657–659.

[8] W. Tremel, B. Krebs, G. Henkel, *Inorg. Chim. Acta* **1983**, *80*, L31–L32.

[9] K. Matsumoto, H. Nakano, S. Ooi, *Chem. Lett.* **1988**, 823–826.

[10] K. Fries, W. Pfaffendorf, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 212–219.

[11] W. Tremel, M. Kriege, B. Krebs, G. Henkel, *Inorg. Chem.* **1988**, *27*, 3886–3895.

[12] J. Weiss, *Angew. Chem.* **1982**, *94*, 719–720; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 705.

[13] K. S. Ratliff, G. K. Broeker, P. E. Fanwick, C. P. Kubiak, *Angew. Chem.* **1990**, *102*, 405–407; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 395.

[14] C. J. Gómez-García, E. Coronado, L. Ouahab, *Angew. Chem.* **1992**, *104*, 660–662; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 649.

[15] S. Gehring, P. Fleischhauer, H. Paulus, W. Haase, *Inorg. Chem.* **1993**, *32*, 54–60.

[16] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim, **1973**.

[217/94]