DALTON
FULL PAPER

Preparation of the first sulfur-containing cobalt and nickel complexes stabilised by the macrocyclic cyclam ligand; observation of S–H bond activation

Rainer J. Pleus, Harald Waden, Wolfgang Saak, Detlev Haase and (the late) Siegfried Pohl

Fachbereich Chemie, Carl-von-Ossietzky Universität, Postfach 2503, D-26111 Oldenburg, Germany

Received 15th March 1999, Accepted 17th June 1999

Cobalt and nickel complexes bearing the ligand 1,4,8,11-tetraazacyclotetradecane (cyclam/[14]aneN_4) besides S_2^{2-}, SH^- and S^{2-} anions were prepared for the first time by treatment of the corresponding metal perchlorates with sodium and potassium hydrogensulfide or disulfide in the presence of the macrocycle. The reaction of $Co(ClO_4)_2\cdot 6MeCN$ with cyclam and SH^- led to the formation of the almost identical polymeric complexes $[Co(SH)(cyclam)][ClO_4]\cdot\frac{1}{2}DMF$ **1** and $[Co(SH)(cyclam)][ClO_4]\cdot MeOH$ **2**, in which the Co atoms are bridged by SH groups to give unusual linear co-ordination polymers. These structures seem to be determined essentially by packing effects, which was verified by the synthesis and characterisation of $[CoCl(cyclam)][ClO_4]\cdot\frac{1}{2}DMF$ **3**. Despite the replacement of the bridging SH^- groups by Cl^- anions, **3** has bond lengths and angles similiar to those of **1** and **2**. In contrast, the reaction of the corresponding nickel salt under the same conditions afforded the trinickel compound $[\{Ni(\mu\text{-}SH)(cyclam)\}_2][Ni(SH)_2(cyclam)][ClO_4]_2$ **4**, which contains a mononuclear neutral $Ni(SH)_2$ and a binuclear cationic $Ni_2(\mu\text{-}SH)_2$ fragment probably connected by hydrogen bridges. The thiol-bridged binuclear complex $[\{Co(\mu\text{-}SH)(cyclam)\}_2]^{2+}$ **5** and the isostructural cation $[\{Ni(\mu\text{-}SH)(cyclam)\}_2]^{2+}$ **6**, both with SH^- counter ions, were prepared by addition of two molar equivalents of SH^- to cobalt perchlorate or by heating of **4**, respectively. The reaction of $[Ni(cyclam)][ClO_4]_2$ with S_2^{2-} instead of SH^- yielded the disulfido complex $[Ni_2(\mu\text{-}S_2)(cyclam)_2][ClO_4]_2$ **7**, while with Co^{II} the binuclear sulfido-bridged complex $[\{Co(\mu\text{-}S)(cyclam)\}_2][ClO_4]_2$ **8** was obtained. This was formed by cleavage of the S–S bond of the S_2^{2-} anion, and the enhancement of the oxidation state of cobalt from +2 to +3. Furthermore, it was also generated by reaction of complex **2** with azobenzene. Thus, the S–H bonds seem to be activated by the cyclam-stabilised cobalt(II) ion, and transfer of the hydrogen atoms to the unsaturated N=N bond of azobenzene led to the formation of diphenylhydrazine.

Introduction

Co-ordination compounds of the transition metals bearing the ligands SH^-, S^{2-}, S_2^{2-}, and H_2S found increasing interest during the last decades because they potentially could serve as models for biological systems. Besides cubane-like complexes, which have been studied extensively, binuclear species with bridging sulfur atoms play an important role in active sites of metalloenzymes such as nitrogenase, hydrogenase or CO-dehydrogenase.[1]

At present we are interested in synthesizing sulfur containing transition metal co-ordination compounds, which have structures similar to the active sites in proteins and may have similar or new interesting properties. Many multinuclear and binuclear complexes of sulfur have been described, in which the metal atoms are bridged by unsubstituted sulfur atoms.[2] The problem of the synthesis of such soluble metal complexes containing SH^-, S^{2-}, S_2^{2-} and H_2S ligands is, however, the tendency to form binary sulfides, which are quite stable and precipitate due to their generally low solubility. Therefore, the stability of binuclear or mononuclear sulfur-containing metal complexes strongly depends on the co-ordination and steric shielding by suitable ligands and the nature of their donor atoms. Different types of ligands have proved to be suitable for the stabilisation of such complexes: phosphine, cyclopentadienyl and thiolate groups with a broad variation of their substitution pattern as well as CO. Most previously published transition metal sulfur complexes, which are listed in ref. 2, have been prepared with one of these types of ligands.

Only recently, the first transition metal sulfur complex was isolated and completely characterised, which was not stabilised by π-acceptor ligands, but by a triaza macrocycle. In this compound three disulfido groups bridge two iron atoms, which further are terminally co-ordinated by the nitrogen atoms of 1,4,7-triazacyclononane.[3] Besides their function as model complexes for the active sites in particular enzymes, such compounds are of great interest in view of catalytic processes like the metal-catalysed hydrodesulfurisation (HDS)[4] or S–H bond activation including hydrogenation processes.[5] They may further serve as a source of organosulfur compounds.[6] Despite the large number of complexes cited in ref. 2, only a few binuclear species with 3d transition metals are known. Examples include dimeric Fe/S species with terminal halide ligands, which have been used as starting compounds for substitution reactions in order to prepare model complexes of the Rieske protein.[7] Furthermore, some transition-metal complexes containing unsubstituted sulfur atoms were synthesized by the reaction of nickel, iron and cobalt salts with hydrogensulfide in the presence of tripod-like tertiary phosphine ligands.[8]

In this paper we report on the reactions of cobalt(II) and nickel(II) perchlorate with SH^- and S_2^{2-} salts in the presence of the chelating nitrogen ligand 1,4,8,11-tetraazacyclotetradecane (cyclam/[14]aneN_4). Moreover, we present the successful hydrogenation of azobenzene with sodium hydrogensulfide (NaSH) in presence of $[Co(cyclam)]^{2+}$.

Results and discussion

Reaction of cobalt perchlorate with one equivalent of SH^-

The addition of sodium hydrogensulfide to a solution of $Co(ClO_4)_2\cdot 6MeCN$ and cyclam in molar ratio 1 : 1 : 1 in a mix-

Table 1 Selected bond lengths [pm] and angles [°] of complexes **1**, **2**, **3**, **5** and **8**

(a) $[Co(SH)(cyclam)][ClO_4]\cdot\frac{1}{2}DMF$ **1**					
Co(1)–N(1)	199.1(5)	N(1)–Co(1)–N(2)	93.9(2)	N(2)–Co(1)–S(1)	94.4(2)
Co(1)–N(2)	198.8(5)	N(1)–Co(1)–N(3)	179.5(2)	N(3)–Co(1)–S(1)	86.9(2)
Co(1)–N(3)	198.5(5)	N(1)–Co(1)–N(4)	85.4(2)	N(4)–Co(1)–S(1)	85.2(2)
Co(1)–N(4)	199.2(5)	N(2)–Co(1)–N(3)	86.0(2)	S(2)–Co(1)–S(1)	177.96(7)
Co(1)–S(1)	272.0(2)	N(3)–Co(1)–N(4)	94.7(3)	Co(1)–S(2)–Co(2)	172.74(8)
Co(1)–S(2)	268.1(2)	N(2)–Co(1)–N(4)	179.2(3)	Co(3)–S(1)–Co(1)	175.05(8)
		N(1)–Co(1)–S(1)	92.7(2)	H(2S)–S(2)–Co(2)	87(5)
				H(1S)–S(1)–Co(1)	92(6)
(b) $[Co(SH)(cyclam)][ClO_4]\cdot MeOH$ **2**					
Co(1)–N(1)	198.1(4)	N(1)–Co(1)–N(2)	85.6(2)	N(2a)–Co(1)–S(1)	87.5(2)
Co(1)–N(2)	198.9(4)	N(1)–Co(1)–N(2a)	94.4(2)	Co(1a)–S(1)–Co(1)	177.55(11)
Co(1)–S(1)	274.94(3)	N(1)–Co(1)–S(1)	87.0(2)	H(1S)–S(1)–Co(1)	90.9(2)
		N(1)–Co(1)–S(1a)	93.0(2)		
(c) $[CoCl(cyclam)][ClO_4]\cdot\frac{1}{2}DMF$ **3**					
Co(1)–N(1)	198.3(6)	N(1)–Co(1)–N(2)	93.4(3)	N(1)–Co(1)–Cl(1)	93.9(2)
Co(1)–N(2)	198.0(7)	N(1)–Co(1)–N(3)	179.2(3)	N(2)–Co(1)–Cl(1)	94.6(2)
Co(1)–N(3)	196.9(7)	N(1)–Co(1)–N(4)	85.5(3)	N(3)–Co(1)–Cl(1)	85.6(2)
Co(1)–N(4)	199.8(7)	N(2)–Co(1)–N(3)	86.1(3)	N(4)–Co(1)–Cl(1)	84.4(2)
Co(1)–Cl(1)	266.4(2)	N(3)–Co(1)–N(4)	95.0(3)	Cl(2)–Co(1)–Cl(1)	177.64(8)
Co(1)–Cl(2)	262.9(2)	N(2)–Co(1)–N(4)	178.5(3)	Co(1)–Cl(2)–Co(2)	174.66(9)
				Co(3)–Cl(1)–Co(1)	176.91(9)
(d) $[\{Co(\mu\text{-}SH)(cyclam)\}_2][SH]_2$ **5**					
Co–N(1)	203.5(5)	N(1)–Co–N(2)	83.6(2)	N(1)–Co–S(1)	95.46(14)
Co–N(2)	208.1(5)	N(1)–Co–N(3)	169.2(2)	N(2)–Co–S(1)	171.54(13)
Co–N(3)	203.4(4)	N(1)–Co–N(4)	88.9(2)	N(3)–Co–S(1)	92.77(14)
Co–N(4)	207.0(4)	N(2)–Co–N(3)	89.3(2)	N(4)–Co–S(1)	93.00(14)
Co–S(1)	230.3(2)	N(3)–Co–N(4)	83.7(2)	S(2)–Co–S(1)	78.01(6)
Co–S(2)	229.2(2)	N(4)–Co–N(2)	95.4(2)	Co–S(2)–Co(a)	101.99(6)
(e) $[\{Co(\mu\text{-}S)(cyclam)\}_2][ClO_4]_2$ **8**					
Co(1)–N(1)	205.5(8)	N(1)–Co(1)–N(2)	89.1(9)	N(1a)–Co(1)–S(1)	169.4(3)
Co(1)–N(2)	197.3(9)	N(1)–Co(1)–N(1a)	96.3(5)	N(2a)–Co(1)–S(1)	93.2(5)
Co(1)–S(1)	226.6(2)	N(1)–Co(1)–S(1)	94.2(3)	Co(1a)–S(1)–Co(1)	104.69(14)
		N(2)–Co(1)–S(1)	93.2(7)	S(1a)–Co(1)–S(1)	75.31(14)

ture of dimethylformamide and methanol, eqn. (1), yielded a

$$Co(ClO_4)_2\cdot 6MeCN + [14]aneN_4 + NaSH \xrightarrow{-MeCN} \underset{\mathbf{1,2}}{\{[Co(SH)([14]aneN_4)]ClO_4\}_x} + NaClO_4 \quad (1)$$

reddish solution from which after slow diffusion of ether yellowish-brown rhombic crystals of $[Co(SH)(cyclam)][ClO_4]\cdot\frac{1}{2}DMF$ **1** were isolated. Surprisingly, the same reaction in a solvent mixture of acetonitrile and methanol afforded long yellow needles of the same complex $[Co(SH)(cyclam)][ClO_4]\cdot MeOH$ **2**, in which, however, the solvent molecule of DMF was replaced by methanol. The precipitation of black cobalt sulfide was not observed in either case. Thus, in contrast to open chain ligands with exclusively nitrogen as donor atoms, the "macrocyclic effect" of the tetradentate cyclam seems to be strong enough to protect the cationic cobalt complex from decomposition into the binary sulfide. The crystals of both compounds were suitable for crystal structure analyses. Complex **1** crystallises in the monoclinic space group *P*2$P2_1/n$. The asymmetric unit contains one complete Co(SH)(cyclam) group beside two molecular halves, and two Co atoms (Co2 and Co3) are located on crystallographic inversion centres (Fig. 1). Apart from the different solvent, compound **2** is quite similar, but the space group changed to $P2_1/m$ with two molecules in the unit cell. The Co atom and the SH group reside on a crystallographic mirror plane, which intersects the bonds C(5)–N(1a) and C(5a)–N(1) of the macrocycle. Owing to the similarity of **1** and **2**, only the ORTEP[9] plot of **1** is shown. Selected bond lengths and angles of both compounds are summarised in Table 1.

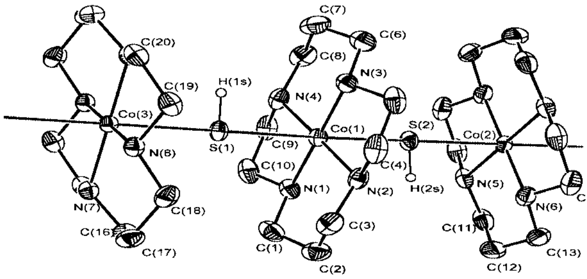


Fig. 1 Part of the crystal structure of the polymeric complex $[Co(SH)(cyclam)]^+$ **1** (only SH protons are included).

The cobalt ions in complexes **1** and **2** have an almost ideal square-planar co-ordination by four nitrogen donor atoms of the macrocycle. The Co–N distances are in the range 198 to 200 pm, and the N–Co–N angles are 85.4 to 94.7° between *cis* and about 180° on average between *trans* arranged nitrogen atoms. The $[Co(cyclam)]^{2+}$ units form one-dimensional co-ordination polymers by the axial co-ordination to two bridging SH^- anions, and the co-ordination by both sulfur atoms results in a tetragonally elongated distorted octahedral surrounding of each cobalt atom. The distances between cobalt and the sulfur atoms in **1** (Co–S 271 pm on average) are much longer than M–S bonds to bridging SH^- groups reported before, which lie in the range 234.3 to 238.3 pm in the cluster $[Co_3(\mu_3\text{-}S)(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6][ClO_4]_2$[10] and 233.4 to 236.2 pm in the comparable cationic iron complex $[Fe_2(\mu\text{-}SH)_3(triphos)_2]$ [triphos = bis(2-diphenylphosphinoethyl)phenylphosphine].[11] The Co-S-Co groups [Co(1)–S(2)–Co(2) 172.74(8) and Co(3)–S(1)–Co(2) 175.05(8)°] are almost linear, which has never been observed before in similar co-ordination compounds. In the isostructural complex **2** the Co–S–Co angle is *ca.* 180° due to the crystallographic symmetry, and the Co–S distance [274.94(3) pm] is lengthened by about 4 pm compared with that in **1**.

The SH protons could be unambiguously located in a Fourier-difference map and refined isotropically. The SH bonds stand almost perpendicular to the linear Co–S–Co groups [H(2S)–S(2)–Co(2) 87(5), H(1S)–S(1)–Co(1) 92(6)° for **1** and 90.9(2)° for **2**]. They alternately occupy positions above and below the chain of the Co–S polymer. The macrocycles adopt an almost ideal staggered conformation.

Owing to the very long Co–S distances in **1** and **2**, the compounds may best be described as ion pairs with cationic $[Co(cyclam)]^{2+}$ complexes and SH^- anions. The formation of chains could be the consequence of the most favoured parallel packing of the cyclam units. In order to get more insight to this unusual kind of polymerisation and co-ordination, we synthesized a similar compound, which has the SH^- groups replaced by chloride ions, by the addition of potassium chloride instead of sodium hydrogensulfide to a solution of $Co(ClO_4)_2\cdot 6MeCN$ in the presence of cyclam. The reaction was carried out in a solvent mixture of dimethylformamide and methanol. In contrast to KSH, KCl is only slightly soluble in that solvent mixture, but much better than in acetonitrile–methanol. Owing to the low solubility a longer reaction time was required compared with the formation of the hydrogensulfide complexes. Yellowish brown crystals, suitable for crystal structure determination, were obtained by diffusion of ether into the reaction mixture.

The product $[CoCl(cyclam)]ClO_4\cdot\frac{1}{2}DMF$ **3** is isotypic to **1** with one Co atom (Co1) in a general position and two on crystallographic centres of symmetry. As in **1** and **2**, the cationic complexes $[Co(Cl)(cyclam)]^+$ form one-dimensional co-ordination polymers with the chlorine atoms in the bridging positions. Two slightly different Co–Cl–Co angles [174.66(9) and 176.91(9)°] are observed, which correspond well to the Co–S–Co angles of **1** and **2**. The Co–Cl distances [Co(1)–Cl(1) 266.4(2), Co(1)–Cl(2) 262.9(2) pm)] are about 10 pm shorter than the Co–S distances in the Co–SH structures, but still in a similar range. They are long compared with bond lengths observed in cobalt(II) complexes, which have a distorted octahedral co-ordination sphere of four nitrogen and two chlorine atoms. Usually these compounds form monomers in the solid state and show Co–Cl bond lengths below 250 pm.[12] Remarkably, a longer Co–Cl distance of 274.7 pm was observed in a co-ordination compound of $CoCl_2$ with a macrocyclic tetraaza ligand similar to cyclam; this compound is, however, also a monomer in the solid state.[13] Only $[CoCl_2(py)_2]$ forms a chain polymer, in which the cobalt(II) atoms are co-ordinated by four chlorine and two nitrogen atoms in a distorted octahedral surrounding.[14] Two Co atoms are bridged by two chlorine atoms similar to those in **3**, but the Co–Cl distances (249 pm) are shorter. The results obtained with compound **3** confirm that the crystal structures of **1** and **2** with the unusual long bond lengths and the almost linear Co-S chains may mainly be determined by packing effects in the solid state.

Reaction of nickel perchlorate with one equivalent of SH^-

Analogous to the preparation of the cobalt complexes **1** and **2**, we tried to prepare the corresponding nickel co-ordination compounds. The treatment of $[Ni(cyclam)][ClO_4]_2$ with one equivalent of potassium hydrogensulfide in a mixture of THF and MeOH (10:1) yielded, however, pale purple $[\{Ni(\mu\text{-}SH)(cyclam)\}_2][Ni(SH)_2(cyclam)][ClO_4]_2$ **4**, which contains the neutral mononuclear $[Ni(SH)_2(cyclam)]$ complex and the binuclear cation $[\{Ni(\mu\text{-}SH)(cyclam)\}_2]^{2+}$ with two nickel atoms bridged by two SH groups, eqn. (2).

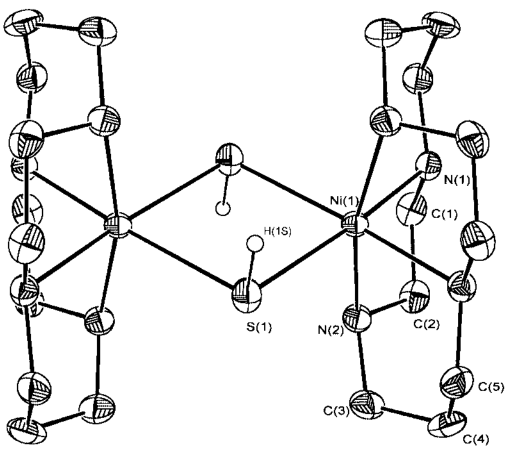


Fig. 2 Structure of the cation $[\{Ni(\mu\text{-}SH)(cyclam)\}_2]^{2+}$ of complex **4** (only SH and NH protons are included).

$$3[Ni([14]aneN_4)][ClO_4]_2 + 4\,KSH \longrightarrow \underset{\mathbf{4}}{[Ni_2(\mu\text{-}SH)_2([14]aneN_4)_2][Ni(SH)_2([14]aneN_4)][ClO_4]_2} + 4\,KClO_4 \quad (2)$$

Fig. 2 shows the cationic part of the crystal structure of complex **4**. The SH groups are located on a crystallographic mirror plane, and the Ni atoms occupy positions on a crystallographic twofold rotational axis. Both nickel atoms are co-ordinated by all four nitrogen atoms of the macrocyclic ligand and two SH groups in a *cis* position, so that a distorted octahedral co-ordination of Ni results. The distortion can be verified by the deviation of the angles N–Ni–N, S–Ni–S, and N–Ni–S (Table 2) from the ideal values of 90 or 180°; the strongest deviation is observed for N(2)–Ni(1)–N(2a) [165.9(2)°]. The conformation of the macrocycle changes from a square-planar arrangement of the four nitrogen atoms in **1** and **2** to a more bisphenoidal arrangement in **4**. The SH groups bridge both $[Ni(cyclam)]^{2+}$ units to form a four-membered Ni_2S_2 heterocycle, which has a long Ni–S distance of 249.0(2) pm and inner ring angles Ni–S–Ni and S–Ni–S of 98.56 and 81.44°, respectively. Owing to the crystallographic symmetry, the heterocycle is exactly planar. Four nickel complexes bearing SH groups are known: *e.g.* $[Ni(SH)(pp_3)]^+$ [15] and $[Ni(SH)(n_2p_2H)]^{2+}$ [pp_3 = tris(2-diphenylphosphinoethyl)phosphine, n_2p_2H = protonated *N*,*N*′-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine];[16] both these compounds have terminal co-ordinated sulfur atoms and exhibit significant shorter Ni–S bond lengths than those found in **4** [225.6(4) and 214.4(3) pm].

Two positions were found for each of the hydrogen atoms bound to sulfur in the Fourier-difference map, and both models could be refined satisfactorily. One is shown in Fig. 2 with the expected trigonal-pyramidal co-ordination of sulfur by Ni(1), Ni(1a), and H(1S). The second position is located slightly above the centre of the Ni_2S_2 plane with the hydrogen atom near both sulfur atoms. This observation may be interpreted in terms of a sulfur–hydrogen–sulfur bridge with one hydrogen atom of both S–H groups terminally attached to only one sulfur atom, and the other one in the bridging position. Both hydrogen atoms may alternately occupy both possible positions (terminal or bridging). Owing to the restrictions of structure analyses concerning the determination of the positions of hydrogen atoms, it is, however, an open question whether this observation is the consequence of a statistical disorder, a dynamic process, or an artefact.

Besides this cationic binuclear fragment, **4** contains a neutral mononuclear nickel complex with crystallographic symmetry 2/*m*, in which nickel is co-ordinated by the four nitrogen atoms of the cyclam ring in a square planar fashion and has further two SH^- groups bound in axial positions. Both Ni–S distances

Table 2 Selected bond lengths [pm] and angles [°] of complexes **4**, **6** and **7**

(a) [{Ni(μ-SH)(cyclam)}$_2$][Ni(SH)$_2$(cyclam)][ClO$_4$]$_2$ **4**					
Ni(1)–N(1)	214.3(4)	N(1)–Ni(1)–N(2)	82.34(14)	N(1)–Ni(1)–S(1a)	92.21(10)
Ni(1)–N(2)	211.9(3)	N(1)–Ni(1)–N(1a)	94.2(2)	N(1)–Ni(1)–S(1)	173.22(11)
Ni(1)–S(1)	249.0(2)	N(2)–Ni(1)–N(2a)	165.9(2)	N(2a)–Ni(1)–S(1)	94.94(11)
		N(3)–Ni(2)–S(2)	91.56(11)	S(1a)–Ni(1)–S(1)	81.44(8)
		N(2)–Ni(1)–S(1)	95.77(11)	Ni(1)–S(2)–Ni(1a)	98.56(8)
		N(1a)–Ni(1)–S(1)	92.21(10)	H(1S)–S(1)–N(1)	49.7(6)
Ni(2)–N(3)	206.4(4)			S(2a)–Ni(2)–S(2)	180.0
Ni(2)–S(2)	260.3(2)				
(b) [{Ni(μ-SH)(cyclam)}$_2$][SH]$_2$ **6**					
Ni(1)–N(1)	213.0(4)	N(1)–Ni(1)–N(2)	82.3(2)	N(1)–Ni(1)–S(1)	95.61(11)
Ni(1)–N(2)	214.8(3)	N(1)–Ni(1)–N(3)	165.7(2)	N(2)–Ni(1)–S(1)	173.91(11)
Ni(1)–N(3)	213.1(4)	N(1)–Ni(1)–N(4)	87.9(2)	N(3)–Ni(1)–S(1)	95.03(11)
Ni(1)–N(4)	212.4(3)	N(2)–Ni(1)–N(3)	88.0(2)	N(4)–Ni(1)–S(1)	91.37(12)
Ni(1)–S(1)	250.69(13)	N(4)–Ni(1)–N(2)	94.3(2)	S(1)–Ni(1)–S(1a)	82.61(5)
Ni(1)–S(1a)	247.00(12)	N(3)–Ni(1)–N(4)	82.36(14)	Ni(1)–S(2)–Ni(1a)	97.39(5)
(c) [Ni$_2$(μ-S$_2$)(cyclam)$_2$][ClO$_4$]$_2$ **7**					
Ni(1)–N(1)	208.7(5)	N(1)–Ni(1)–N(2)	83.4(2)	N(2)–Ni(1)–S(1)	94.8(2)
Ni(1)–N(2)	212.6(6)	N(1)–Ni(1)–N(3)	102.0(2)	N(3)–Ni(1)–S(1)	100.3(2)
Ni(1)–N(3)	209.3(6)	N(1)–Ni(1)–N(4)	91.0(2)	N(4)–Ni(1)–S(1)	93.3(2)
Ni(1)–N(4)	209.9(6)	N(2)–Ni(1)–N(3)	90.8(2)	S(1)–Ni(1)–S(1a)	58.36(9)
Ni(1)–S(1)	235.3(2)	N(4)–Ni(1)–N(2)	170.3(7)	Ni(1)–S(2)–Ni(1a)	121.64(9)
Ni(1)–S(1a)	235.9(2)	N(3)–Ni(1)–N(4)	82.6(2)		
S(1)–S(1a)	229.7(4)	N(1)–Ni(1)–S(1)	157.6(2)		

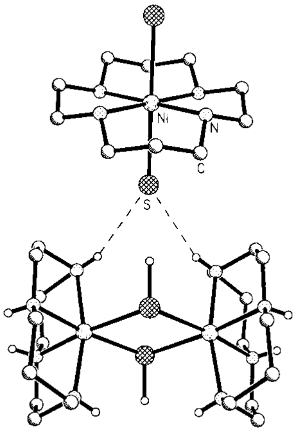


Fig. 3 Crystal structure of [{Ni(μ-SH)(cyclam)}$_2$][Ni(SH)$_2$(cyclam)]$^{2+}$ in **4** (part of the chain).

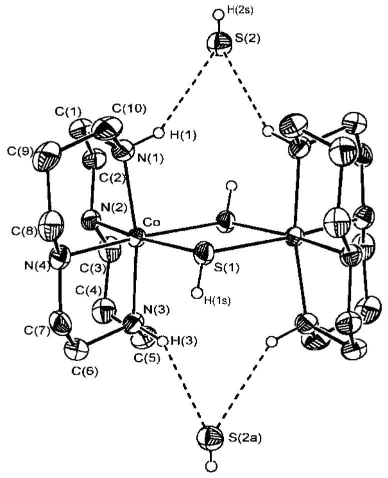


Fig. 4 Crystal structure of [{Co(μ-SH)(cyclam)}$_2$][SH]$_2$ **5** (only SH protons and the NH protons of the hydrogen bonds are included).

are very long [260.3(2) pm] compared with those observed for the bridging SH$^-$ groups in the cationic part of the molecule. These lengths are only about 10 pm shorter than the long Co–S distances in **1**. Similar long distances have been detected in the structurally related complexes [Ni(SPh)$_2$(cyclam)] [259.5(1) pm] and [Ni(tipt)$_2$(cyclam)] [266.2 pm] (tipt = 2,4,6-triisopropylbenzenethiolate), which have aromatic thiolate groups instead of the hydrogen sulfide ligand.[17]

In the crystal structure chains are formed with an alternating arrangement of the cationic and the neutral complexes. A part of a chain is shown in Fig. 3. Both components probably interact by hydrogen bridges between NH protons of the macrocycle and the sulfur atoms of the mononuclear complex, which may be indicated by the remarkably small distances between the nitrogen and the sulfur atoms of 348.8 pm. Up to now, all attempts to prepare the dimeric Ni$_2$(SH)$_2$ unit without the neutral nickel complex were unsuccessful. Thus, the Ni(SH)$_2$ bridges seem to be essential for stabilisation of the binuclear complex.

Reaction of cobalt perchlorate with two equivalents of SH$^-$

When cyclam was added to Co(ClO$_4$)$_2$·6MeCN dissolved in a mixture of acetonitrile and methanol and subsequently treated with two equivalents of sodium hydrogensulfide, dark red, almost black rhombic crystals were obtained after slow diffusion of ether into the reaction mixture, eqn. (3). As confirmed

$$2\,\mathrm{Co(ClO_4)_2{\cdot}6MeCN} + 4\,\mathrm{NaSH} + 2[14]\mathrm{aneN_4} \xrightarrow[-\mathrm{MeCN}]{} \underset{\mathbf{5}}{[\mathrm{Co_2(\mu\text{-}SH)_2([14]aneN_4)_2][SH]_2}} + 4\,\mathrm{NaClO_4} \quad (3)$$

by elemental analysis, the perchlorate anions are completely replaced by SH$^-$, and furthermore the characteristic bands for ν(ClO$_4$) at ≈1090 and ≈625 cm^{-1} were not detected in the infrared spectrum. The composition corresponds to the formula [{Co(μ-SH)(cyclam)}$_2$][SH]$_2$ **5**. The molecular structure is shown in Fig. 4 (selected bond lengths and angles in Table 1).

The structure comprises a binuclear cobalt(II) complex, in which both cobalt ions are co-ordinated by a cyclam ligand and bridged by two SH$^-$ groups. It is very similar to the cationic part of the nickel species **4**. The SH$^-$ counter ions are located above and below the planar Co$_2$S$_2$ ring and seem to have the function of the mononuclear complex [Ni(SH)$_2$(cyclam)] in **4**. The existence of hydrogen bonds between the NH groups of the macrocycle and the hydrogen sulfide anions may be deduced from small N···S distances of 341.6 pm on average. Possibly they support the folding of the macrocycle from the planar geometry, which is lower in energy, to a bisphenoidal surrounding around the cobalt atom. Each cobalt is co-ordinated in a distorted octahedral geometry by four nitrogen atoms and two SH^- ions. The Co–S–Co angle (102°) is comparable with the Ni–S–Ni angle of **4** [98.56(8)°]. The Co–S bond lengths are quite similar [229.2(2) and 230.3(2) pm] and about 20 pm shorter than the Ni–S distances in the $Ni_2(SH)_2$ part of **4**. They are much shortened in comparison with the Co–SH distances in the polymeric compounds **1** and **2**, but correspond well to M–S bond lengths of 233 to 238 pm, reported in the cobalt cluster and comparable binuclear iron species mentioned above.[10,11]

The complex $[\{Ni(\mu\text{-}SH)(cyclam)\}_2][SH]_2$ **6**, isostructural and isotypic to **5**, was obtained by heating **4** in methanol *via* a redistribution reaction. The bond lengths and angles do not show any significant difference to the values observed for the $Ni_2(SH)_2$ complex in **4** (Table 2). In contrast to **4** the Ni–S distances within the planar Ni_2S_2 ring show a slight difference similar to complex **5** [Ni(1)–S(1a) 247.0 and Ni(1)–S(1) 250.7 pm]. The transannular distance between the sulfur atoms S(1) · · · S(1a) is 328.4 pm and similar to **4** [324.9; **5**, 289.2 pm].

IR spectroscopy

The S–H absorptions could be observed in the IR spectra of all compounds. Those of polymeric **1** and **2** with long Co–S distances (2557 cm^{-1} on average) are quite similar to those of potassium hydrogensulfide (2556 cm^{-1}) or the H_2S molecule (2550 cm^{-1}). Possibly, these observations confirm the hypothesis that both compounds are essentially ionic and their one dimensionally polymeric structure is due to a packing effect. Only one absorption (2527 cm^{-1}) is observed for the nickel compound **4** despite the presence of two chemical different SH groups. Similar vibrations are detected for **5** and **6** (2531 and 2529 cm^{-1}, respectively). They may be caused by the SH groups of the four-membered $M_2(SH)_2$ heterocycle (M = Ni or Co) present in the molecular centre of all three compounds. Besides these absorptions at about 2530 cm^{-1} the derivatives **5** and **6** show each an additional SH stretching vibration at 2577 and 2579 cm^{-1}, respectively, which are shifted about 20 cm^{-1} to higher wavenumbers in comparison with KSH. They may be attributed to the terminal SH groups, which probably interact by hydrogen bonds with the NH protons of the cyclam macrocycle. The origin of the SH vibration in compound **4** could be verified by the FT-IR spectrum of the deuteriated complex $[\{Ni(\mu\text{-}SD)(D_4\text{-}cyclam)\}_2][Ni(SD)_2(D_4\text{-}cyclam)][ClO_4]_2$, which was synthesized by a similar method as for **4**, but in the solvent deutieromethanol (MeOD) instead of MeOH. The S–D band lies at ν(S–D) 1836 cm^{-1}, which corresponds exactly to the value calculated by simply using the higher reduced mass of the fragment S–D compared with S–H.[18]

Reaction of cobalt and nickel perchlorate with S_2^{2-}

We were further interested in the treatment of the cobalt and nickel perchlorate salts with disulfide (S_2^{2-}) in the presence of cyclam, because disulfide complexes of Ni or Co are to be expected as oxidation products of the SH derivatives in the course of chemical reactions. In accordance with our expectation, $[Ni(cyclam)][ClO_4]_2$ reacts with K_2S_2 in a mixture of acetonitrile and methanol to yield the binuclear complex $[Ni_2(\mu\text{-}S_2)(cyclam)_2]^{2+}$ **7** with two perchlorate counter ions, eqn. (4). Its molecular structure in the solid state is shown in Fig. 5. Selected bond lengths and angles are given in Table 2.

$$2\,[Ni([14]aneN_4)][ClO_4]_2 + K_2S_2 \longrightarrow \underset{\mathbf{7}}{[Ni_2(\mu\text{-}S_2)([14]aneN_4)_2][ClO_4]_2} + 2\,KClO_4 \quad (4)$$

Each Ni_2S_2 group of complex **7** is located on a crystallographic inversion centre and each Ni atom is side-on co-ordinated to the disulfido bridge. The macrocyclic ligand adopts a folded conformation as in the complexes **4**, **5**, and **6**. Thus, each nickel atom is co-ordinated to the four nitrogen atoms of the macrocycle and both sulfur atoms of the disulfide anion S_2^{2-} in a distorted octahedral geometry. The Ni–S distances in **7** are quite similar [Ni(1)–S(1) 235.3(2) and Ni(1)–S(1a) 235.9(2) pm] and longer than found in the comparable complex $[Ni_2(\mu\text{-}S_2)(triphos)_2][ClO_4]$ [Ni–$S_{(av)}$ 222.5(8) pm, Ni–S–Ni 120.5(2)°, S–S 220.8(4) pm].[19] Thus, the planar Ni_2S_2 framework in **7** is enlarged compared with the nickel phosphine complex, and the Ni–S bonds as well as the S–S bond [229.7 pm] are significantly lengthened. The long S–S distance indicates only a weak bond, but it still is much shorter than in the dimers with SH^- bridges [**4**, 324.9; **5**, 289.2; **6**, 328.4 pm]. Usually, smaller S–S distances of 198 to 213 pm are observed for disulfide ligands co-ordinated to transition metal ions.[20]

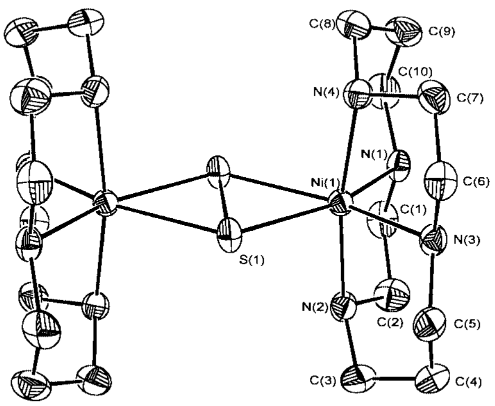


Fig. 5 Crystal structure of $[Ni_2(\mu\text{-}S_2)(cyclam)_2]^{2+}$ **7** (hydrogen atoms are omitted for clarity).

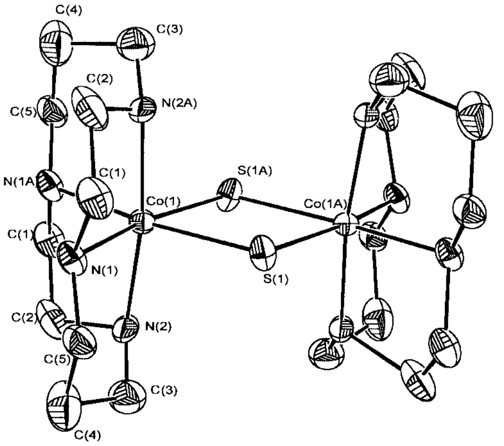


Fig. 6 Crystal structure of $[\{Co(\mu\text{-}S)(cyclam)\}_2]^{2+}$ **8** (hydrogen atoms are omitted for clarity).

In contrast, the reaction (5) of cobalt perchlorate with Na_2S_2

$$2\,Co(ClO_4)_2{\cdot}6MeCN + Na_2S_2 + 2\,[14]aneN_4 \longrightarrow \underset{\mathbf{8}}{[Co_2(\mu\text{-}S)_2([14]aneN_4)_2][ClO_4]_2} + 2\,NaClO_4 \quad (5)$$

under the same conditions did not yield the expected disulfido bridged binuclear cobalt complex isostructural to the nickel derivative **7**. Instead, it afforded the binuclear sulfido-bridged compound $[Co_2(\mu\text{-}S)_2(cyclam)_2][ClO_4]_2$ **8**, for which an ORTEP plot is shown in Fig. 6.

Obviously, the S–S bond of the starting anion S_2^{2-} was cleaved. The long distance between the sulfur atoms (S · · · S 276.8 pm) indicates no significant bonding interaction. Nevertheless, the dimeric complex possesses the overall charge of +2 with one non-co-ordinating perchlorate anion per cobalt atom.

Table 3 Comparison of important bond lengths, angles and interatomic distances of some first row transition metal complexes containing SH^-, S^{2-} and S_2^{2-} ligands

Complex	M–S/pm	M–S–M/°	M···M/pm	S···S/pm	Ref.
1 $[Co(SH)(cyclam)]^+$	268.1/272.0	172.74/175.05	—	—	This work
2 $[Co(SH)(cyclam)]^+$	274.94	177.55	—	—	This work
$[Co_3(\mu_3\text{-}S)_2(\mu\text{-}SH)_2(\mu\text{-}PEt_2)(PHEt_2)_6]^+$	234.3–238.3	78.1	297.8–314.4	—	10
5 $[\{Co(\mu\text{-}SH)(cyclam)\}_2][SH]_2$	229.2/230.3	101.99	357.0	289.2	This work
8 $[\{Co(\mu\text{-}S)(cyclam)\}_2]^{2+}$	226.6	104.69	358.7	276.8	This work
$[\{Co(\mu\text{-}S)(triphos)\}_2]^+$	214.2–216.6	105.7–106.3	343.4	258.4	21
7 $[Ni_2(\mu\text{-}S_2)(cyclam)_2]^{2+}$	235.3/235.9	121.64	411.4	229.7	This work
$[Ni_2(\mu\text{-}S_2)(triphos)_2]^+$	$222.5_{(av)}$	120.5	386.5	220.8	19
4a $[\{Ni(\mu\text{-}SH)(cyclam)\}_2]^{2+}$	249.0	98.56	377.6	324.9	This work
4b $[Ni(SH_2)(cyclam)]$	260.3	—	—	—	This work
$[Fe_2(\mu\text{-}SH)_3(triphos)_2]^+$	233.4	84.5	—	—	11
6 $[\{Ni(\mu\text{-}SH)(cyclam)\}_2][SH]_2$	250.7/247.0	97.39	373.7	328.4	This work
$[Ni(SH)(pp_3)]^+$	225.6	—	—	—	15
$[Ni(SH)(n_2p_2H)]^{2+}$	214.4	—	—	—	16

This observation indicates an electron transfer from the cobalt ions to the sulfur atoms with oxidation of the cobalt ions from +2 to +3 and reduction of the sulfur atoms to an oxidation state of −2 accompanied by simultaneous opening of the S–S bond.

The macrocycle shows the same bisphenoidal geometry as in the preceding binuclear complexes. Each cobalt atom is octahedrally co-ordinated by the four nitrogen atoms of the macrocycle and two sulfur atoms in a *cis* position. The Co–N distances (201.4 pm on average) are smaller than in the cobalt(II) compound **5** (205.5 pm on average) in which the macrocycle also adopts the bisphenoidal structure. Owing to the crystallographic symmetry both Co–S distances [226.6(2) pm] are identical and about 10 pm shorter than the Ni–S separation in the disulfido bridged nickel complex **7**. As expected, the Co–S bond length is much shorter than that of the polymeric SH^- bridged compounds **1** and **2**, while only a small shortening is observed compared with the dimeric SH^- bridged compound **5**. The cleavage of the S–S bond and as the consequence the larger separation of the sulfur atoms result in a small Co–S–Co angle of 104.69° compared with the Ni–S–Ni angle of 121.64° in **7**.

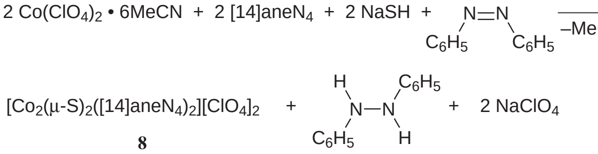
The similar cationic complex $[Co_2(\mu\text{-}S)_2(triphos)_2]^+$,[21] prepared by reaction of H_2S with the dimeric hydroxo compound $[Co_2(\mu\text{-}OH)_2(triphos)_2][BPh_4]_2$, shows Co–S bond lengths of 214.2 to 216.6 pm. They are, thus, 10 pm shorter than in complex **8**, while the Co–S–Co angles (105.7–106.3°) are similar to those found in **8**. For a better comparison some characteristic bond lengths and angles of the new complexes described here and of similar known co-ordination compounds are summarised in Table 3.

Reaction of complexes 2 and 4 with azobenzene

The oxidation of $[Co(H_2O)_6]^{2+}$ to Co^{III} in an aqueous solution is not favoured and cobalt(II) cations are stable in simple salts. The stability of Co^{III} is, however, dramatically enhanced in the presence of nitrogen ligands, for example NH_3 or 1,2-diaminoethane.[22] Owing to the stability of the kinetically inert cobalt(III) complexes, we hoped to realise a reaction in which **1** and **2** with bivalent cobalt cations and SH groups could be transformed to **8** with trivalent cobalt cations and two sulfido bridges. This reaction would formally be accompanied by the release of elemental hydrogen, which may be trapped by a suitable unsaturated molecule. Such reactions are of particular interest because they are potentionally useful in catalytic processes.

It is well known that thiols or thiolates are able to reduce many different compounds, for instance phenylimines to anilines[23] or nitroalkanes to the corresponding alkanes.[24] Interestingly, the synthesis of diphenylhydrazine was first realised by Hoffmann who reduced azobenzene with H_2S in an alcoholic solution of ammonia in 1863.[25] Tschunker and Eichler improved this reaction when they introduced gaseous H_2S into a solution containing azobenzene and sodium hydrogensulfide.[26]

The hydrogenation of unsaturated organic compounds by sulfur-bridged dimeric complexes has been achieved before by the reaction of $[\{(\eta^5\text{-}C_5H_4Me)Mo\}_2(\mu\text{-}SH)(\mu\text{-}SCH_3)(S_2CH_2)]$ with azobenzene, and Rakowski Dubois and co-workers[27] succeeded in reducing azobenzene to diphenylhydrazine in THF. The yields were ≈ 0.4–0.5 mol of hydrazine per mol of the molybdenum dimer. To the best of our knowledge this kind of hydrogen transfer has never been observed with complexes of first row transition metals bearing hydrogensulfido ligands. Thus, we carried out a similar experiment with the *in situ* generated compound **2** as shown in eqn. (6).



8

(6)

In order clearly to exclude the hydrogenation by hydrogensulfide alone without any influence of transition metal salts, we first of all treated azobenzene with sodium hydrogensulfide in 1 : 2 molar ratio in a solvent mixture of methanol and acetonitrile. The solution was stirred for 16 h at room temperature and, after evaporation, the residue suspended in ether to dissolve either azobenzene or diphenylhydrazine and to separate the ionic compounds of the reaction mixture. After filtration and removal of the solvent *in vacuo* an orange residue remained, in which only azobenzene and no trace of the hydrogenated product diphenylhydrazine could be detected by NMR and FT-IR spectroscopy. However, a second ether soluble compound was formed in trace amounts, which showed a weak absorption at 1728 cm^{-1} in the IR spectrum characteristic for carbonyl or C=N groups. The by-product may be formed by a reaction between acetonitrile and methanol in the presence of the base SH^-. Pure azobenzene was isolated from the mixture by recrystallisation from methanol, which gave 95% of the originally applied compound.

To conduct the hydrogenation experiment, eqn. (6), we dissolved cobalt perchlorate, cyclam and azobenzene in a 2 : 2 : 1 molar ratio in a mixture of acetonitrile and methanol and added two equivalents of sodium hydrogensulfide. The orange solution turned darker within a few minutes as was characteristic for the formation of complex **8**. After stirring for 16 h the solvents were distilled off under reduced pressure, and the residue was treated with ether and filtered. After removal of the ether *in vacuo*, the ^1H NMR spectrum of the residue showed that azobenzene was quantitatively hydrogenated to the corresponding hydrazine derivative. Recrystallisation of the product from hexane afforded light yellow crystals, which were identified by NMR and IR spectroscopy as pure diphenylhydrazine. The yield of the isolated product was 89%. This is the first time that the hydrogenation of a π bond has been achieved by a CoSH co-ordination compound, and the very selective reaction gave the hydrogenation product in a high yield. As expected, the disulfido bridged compound **8** was formed in the course of this reaction and identified by NMR and IR spectra. It precipitated and was isolated by filtration in a yield of 37%.

We also investigated the hydrogenation properties of the *in situ* synthesized NiSH complex **4** in a similar experiment and dissolved $Ni(ClO_4)_2·6MeCN$, cyclam and azobenzene in a 2 : 2 : 1 molar ratio in a mixture of methanol and acetonitrile. To this solution, we added two molar equivalents of sodium hydrogensulfide. In contrast to the cobalt compound, no reaction occurred between the nickel complex **4** and azobenzene after 16 h at room temperature, and no trace of diphenylhydrazine was detected by NMR spectroscopy.

The singular reactivity of the cobalt SH complex with respect to the hydrogenation of azobenzene may be due to an easy change of the oxidation state of the cobalt atoms from +2 to +3, which is favoured by the low spin configuration of almost all cobalt(III) complexes and the high CFSE associated with the t_{2g}^6 electronic configuration. Nickel, on the other hand, is not able to change the oxidation state as easily as cobalt, and +2 is the most stable state, which is largely inert to redox reactions. At present we are interested in synthesizing further SH^- complexes, which are able to hydrogenate unsaturated compounds, and to develop a catalytic system which allows hydrogenation in the presence of only traces of the co-ordination compounds.

Experimental

Reagents and materials

All operations were carried out under an atmosphere of pure nitrogen by using glove-boxes. The solvents were dried by using standard methods (dimethylformamide over CaH_2 by distillation under reduced pressure, acetonitrile over (i) P_4O_{10} and (ii) over FeI_2,[28] methanol over magnesium, ether over sodium–potassium alloy). The compounds $Co(ClO_4)_2·6MeCN$ and $Ni(ClO_4)_2·6MeCN$ were obtained by treating commercially available $Co(ClO_4)_2·6H_2O$ and $Ni(ClO_4)_2·6H_2O$, respectively, three times with molecular sieves (3 Å) in acetonitrile. 1,4,8,11-Tetraazacyclotetradecane,[29] potassium hydrogensulfide and sodium hydrogensulfide[30] as well as potassium disulfide[31] and sodium disulfide[32] were prepared according to literature procedures.

Preparations

[Co(SH)(cyclam)][ClO$_4$]·½DMF 1. The compound $Co(ClO_4)_2·6MeCN$ (200 mg, 0.397 mmol) was dissolved in DMF (15 cm^3) and methanol (7 cm^3); cyclam (80 mg, 0.397 mmol) was added to the stirred solution. The mixture changed from pink to orange. It was heated to 50 °C for 5 min, cooled to room temperature and treated with NaSH (22 mg, 0.397 mmol). After complete dissolution of NaSH, ether was allowed to diffuse into the solution, and within 36 h at room temperature dark, almost black rhombic crystals of compound **1** were obtained (suitable for X-ray crystallography). The crystals were isolated by filtration and washed with ether (0.72 g, 85%) (Found: C, 32.3; H, 6.6; N, 14.7; S, 7.4. $C_{11.5}H_{28.5}ClCoN_{4.5}O_{4.5}S$ requires C, 32.25; H, 6.7; N, 14.7; S, 7.5%).$\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3235, 3212 [ν(N–H)], 2947, 2866s [$\nu(CH_2)$], 2558 (SH), 1661 [ν(C=O), DMF], 1468, 1431, 1387, 1317, 1294, 1260, 1240, 1123, 1105, 1090, 1060 (ClO_4), 1022, 991, 887, 658, 623 (ClO_4), 469. λ_{max}/nm (DMF) 270 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 12900), 338 (9800) and 377(sh) (5800).

[Co(SH)(cyclam)][ClO$_4$]·MeOH 2. The compound $Co(ClO_4)_2·6MeCN$ (200 mg, 0.397 mmol) was dissolved in a mixture of methanol (20 cm^3) and acetonitrile (20 cm^3), cyclam (80 mg, 0.397 mmol) was added, heated to 50 °C for 5 min and treated with NaSH (22 mg, 0.397 mmol). The solution changed from orange to orange-red. Ether was allowed to diffuse into the solution at room temperature. Long yellow needles separated within 12 h, were filtered off and washed with ether (0.126 g, 75%). Addition of hexane to the filtrate afforded an additional microcrystalline fraction of the product (0.013 g, 8%) (Found: C, 31.1; H, 6.8; N, 13.4; S, 7.7. $C_{11}H_{29}ClCoN_4O_5S$ requires C, 31.2; H, 6.7; N, 13.2; S, 7.6%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3227, 3167 [ν(N–H)], 2949, 2872 [$\nu(CH_2)$], 2554 (SH), 1433, 1319, 1294, 1258, 1242, 1125 and 1099 (ClO_4), 1067, 1022, 991, 887, 623 (ClO_4), 478. λ_{max}/nm (MeOH–MeCN) 214 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 11500), 256 (2800) and 336(sh) (2900).

[CoCl(cyclam)][ClO$_4$]·½DMF 3. The compound cyclam (80 mg, 0.397 mmol) was added to a stirred solution of $Co(ClO_4)_2·6MeCN$ (0.2 g, 0.397 mmol) in DMF (15 cm^3) and methanol (4 cm^3). The resultant orange solution was heated to 50 °C for 5 min. After cooling to room temperature, KCl (29 mg, 0.397 mmol) was added and stirring was continued for 30 min. Ether was allowed to diffuse into the solution and yellow-brown crystals of complex **3** precipitated within 2 d. The crystals were isolated by filtration and washed with ether (0.149 g, 87%) (Found: C, 32.15; H, 6.4; Cl, 16.5; N, 14.7. $C_{11.5}H_{27.5}Cl_2CoN_{4.5}O_{4.5}$ requires C, 32.1; H, 6.4; Cl, 16.5; N, 14.6%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3231 [ν(N–H)], 2953, 2872 [$\nu(CH_2)$], 1663 [ν(C=O), DMF], 1472, 1458, 1433, 1391, 1296, 1260, 1125 and 1086 and 1067 (ClO_4), 1032, 993, 891, 623 (ClO_4). λ_{max}/nm(DMF) 258 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 1150).

[{Ni(μ-SH)(cyclam)}$_2$][Ni(SH)$_2$(cyclam)][ClO$_4$]$_2$ 4. The complex $[Ni(cyclam)](ClO_4)_2$ (229 mg, 0.5 mmol) was dissolved in a mixture (50 cm^3) of THF and MeOH in the ratio 10 : 1. The stirred solution was heated to 50 °C for 5 min, and anhydrous KSH (36 mg, 0.5 mmol) added. Within 1 h a clear solution had formed. After cooling to room temperature $KClO_4$ precipitated, which was filtered off after 12 h. The filtrate was concentrated under reduced pressure to about 30 cm^3, and pale purple crystals of **4** were obtained within 2 d (84 mg, 46%) (Found: C, 32.4; H, 7.1; N, 15.1. $C_{30}H_{76}Cl_2N_{12}Ni_3O_8S_4$ requires C, 32.5; H, 6.9; N, 15.2%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3271 [ν(N–H)], 3158 [ν(N–H)], 2953 [$\nu(CH_2)$], 2918 [$\nu(CH_2)$], 2849 [$\nu(CH_2)$], 2527 (SH), 1456, 1429, 1383, 1279, 1238, 1200, 1182, 1119 (ClO_4), 1042, 986, 974, 953, 899, 878, 849, 793, 623 (ClO_4), 415, 366 and 328.

[{Co(μ-SH)(cyclam)}$_2$][SH]$_2$ 5. The compound cyclam (80 mg, 0.397 mmol) was added to a stirred solution of $Co(ClO_4)_2·6MeCN$ (200 mg, 0.397 mmol) in acetonitrile (20 cm^3) and methanol (20 cm^3) at room temperature. The solution was heated to 50 °C for 5 min, and NaSH (45 mg, 0.794 mmol) added. The resultant, approximately black solution was heated under reflux for 2 h. A black solid precipitated, which was filtered off. After cooling to room temperature ether was allowed to diffuse into the solution. Within 5 d at room temperature deep red crystals of compound **5** were obtained (0.050 g, 39%) (Found: C, 36.7; H, 7.9; N, 16.95; S, 19.5. $C_{10}H_{26}CoN_4S_2$ requires C, 36.9; H, 8.05; N, 17.2; S, 19.7%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 3109 [ν(N–H)], 2940, 2899, 2853, 2834 [$\nu(CH_2)$], 2577 and 2531 (SH), 1466, 1451, 1383, 1346, 1290, 1279, 1238, 1202, 1186, 1121, 1096, 1061, 1028, 993, 922, 890, 856, 847, 805, 791 and 388. λ_{max}/nm (MeOH) 226 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 11600); 246(sh) (9200), 306 (3500), 334 (3900), 374 (3100) and 450 (700).

[{Ni(μ-SH)(cyclam)}$_2$][SH]$_2$ 6. A solution of complex **4** (60 mg, 0.054 mmol) in MeOH (30 cm^3) was heated under reflux for 6 h. After cooling to room temperature the product precipitated

Table 4 Crystal data, data collection parameters[a] and structure refinement of the cobalt and nickel compounds **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{23}H_{57}Cl_2Co_2N_9O_9S_2$	$C_{11}H_{29}ClCoN_4O_5S$	$C_{23}H_{55}Cl_4Co_2N_9O_9$	$C_{30}H_{76}Cl_2N_{12}Ni_3O_8S_4$	$C_{20}H_{52}Co_2N_8S_4$	$C_{20}H_{52}N_8Ni_2S_4$	$C_{24}H_{54}Cl_2N_{10}Ni_2O_8S_2$	$C_{24}H_{54}Cl_2Co_2N_{10}O_8S_2$
M	428.33	423.82	861.42	1108.3	650.80	650.36	863.22	863.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/m$	$P2_1/n$	$C2/m$	*Pbca*	*Pbca*	$P2_1/n$	*F*222
a/pm	1541.0(2)	949.65(11)	1503.1(2)	1394.1(2)	1248.2(6)	1262.50(10)	859.30(10)	1289.9(3)
b/pm	1514.80(10)	1099.50(10)	1492.40(10)	2021.2(2)	1469.9(7)	1489.10(10)	1270.5(2)	1387.9(3)
c/pm	1732.40(10)	997.85(15)	1768.3(2)	926.30(10)	1604.5(6)	1620.20(10)	1812.2(2)	2120.1(4)
β/°	110.720(10)	111.222(17)	109.740(10)	109.87(1)			99.26(1)	
V/nm^3	3.7824(6)	0.97124(15)	3.7336(7)	2.4547(5)	2.944(2)	3.0460(4)	1.9527(4)	3.7955(14)
Z	4	2	4	2	4	4	2	4
D_c/g cm^{-3}	1.504	1.449	1.532	1.499	1.468	1.418	1.468	1.511
μ/mm^{-1}	1.185	1.154	1.232	1.473	1.436	1.535	1.262	1.181
T/K	293	293	293	296	293	296	296	293
Dimensions/mm	0.57 × 0.42 × 0.21	1.55[b] × 0.19 × 0.04	0.68 × 0.49 × 0.30	0.38 × 0.25 × 0.11	0.42 × 0.42 × 0.17	0.36 × 0.36 × 0.08	0.68 × 0.23 × 0.11	0.44 × 0.34 × 0.15
Independent reflections	5925	1611	5837	2232	2304	2671	2385	844
Observed data [$I > 2\sigma(I)$]	3978	1121	4188	1559	1740	1683	1610	663
Parameters	427	120	416	161	170	184	230	108
$R1[I > 2\sigma(I)]$	0.0635	0.0564	0.0784	0.0473	0.0553	0.0461	0.0511	0.0563
$wR2[I > 2\sigma(I)]$	0.1296	0.1239	0.1880	0.0958	0.1114	0.0753	0.1078	0.1331

[a] Data collection on a Siemens-Stoe AED 2 four circle diffractometer; graphite-monochromated Mo-Kα radiation (λ = 71.073 pm). [b] Large needle correction.

within 1 week as pale purple crystals (15 mg, 42%). $\tilde{\nu}_{max}$/cm^{-1}(KBr) 3109 [ν(N–H)], 2945 [ν(CH$_2$)], 2901 [ν(CH$_2$)], 2855 [ν(CH$_2$)], 2837 [ν(CH$_2$)], 2579 and 2529 (SH), 1464, 1454, 1384, 1365, 1336, 1290, 1279, 1238, 1203, 1187, 1122, 1093, 1064, 1051, 1031, 995, 924, 893, 862, 850, 795, 389 and 339.

[Ni$_2$(μ-S$_2$)(cyclam)$_2$][ClO$_4$]$_2$·2MeCN 7. The compound K$_2$S$_2$ (36 mg, 0.25 mmol) was suspended in a solution of [Ni(cyclam)][ClO$_4$]$_2$ (228 mg, 0.5 mmol) in acetonitrile (50 cm^3) and heated under reflux for 30 min. During that time it changed to red. The hot solution was filtered, and within 12 h at room temperature crystals of complex **7** were obtained, washed with ether and dried *in vacuo*. Concentration of the mother-liquor gave a second fraction, which included an impurity of KClO$_4$ (first fraction: 121 mg, 56%) (Found: C, 30.6; H, 6.1; N, 14.0; S, 8.7. C$_{20}$H$_{48}$Cl$_2$N$_8$Ni$_2$O$_8$S$_2$ requires C, 30.8; H, 6.2; N, 14.35; S, 8.2%). $\tilde{\nu}_{max}$/cm^{-1}(KBr) 3269 [ν(N–H)], 3212 [ν(N–H)], 3146 [ν(N–H)], 2907 [ν(CH$_2$)], 2858 [ν(CH$_2$)], 1463, 1276, 1238, 1142, 1121 (ClO$_4$), 1090, 1029, 977, 852, 796, 623 (ClO$_4$) and 407. λ_{max}/nm (DMF) 851 (ε/dm^3 mol^{-1} cm^{-1} 1.4), 516 (1.93), 452 (1.94), 399 (2.57), 355 (3.61), 315 (3.2), 284 (3.41) and 229 (3.47).

[{Co(μ-S)(cyclam)}$_2$][ClO$_4$]$_2$ 8. The compound Co(ClO$_4$)$_2$·6MeCN (200 mg, 0.397 mmol) was dissolved in a mixture of acetonitrile (15 cm^3) and methanol (15 cm^3), cyclam (80 mg, 0.397 mmol) added under stirring, and the solution heated to 50 °C for 5 min. After cooling to room temperature the solution was treated with Na$_2$S$_2$ (22 mg, 0.199 mmol) and changed to deep red. Ether was allowed to diffuse into the solution. Within 24 h at room temperature deep red crystals of compound **8** were obtained, which were filtered off and washed with ether (0.135 g, 79%) (Found: C, 33.5; H, 6.4; N, 16.0; S, 7.5. C$_{24}$H$_{54}$Cl$_2$Co$_2$N$_{10}$O$_8$S$_2$ requires C, 33.4; H, 6.3; N, 16.25; S, 7.4%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3260, 3237 [ν(N–H)], 2972, 2940, 2917, 2861 [ν(CH$_2$)], 2284, 2247 [ν(C≡N), MeCN], 1456, 1427, 1389, 1386, 1300, 1273, 1242, 1196, 1177, 1109, 1082 (ClO$_4$), 1034, 986, 932, 864, 853, 812, 799, 623s (ClO$_4$) and 432. λ_{max}/nm (MeCN–MeOH 3 : 1) 214 (ε/dm^3 mol^{-1} cm^{-1} 8300), 250 (8200), 298(sh) (2200) and 382 (3000).

Reaction of azobenzene with NaSH (an attempt to reduce azobenzene). Azobenzene (0.3 g, 1.65 mmol) was dissolved in a solvent mixture of methanol (20 cm^3) and MeCN (20 cm^3) and NaSH (0.185 g, 3.3 mmol) added. After 16 h at room temperature the solvents were distilled of under reduced pressure, the residue was treated with ether (20 cm^3) and filtered. After removal of the solvent *in vacuo* an orange residue remained, which showed no bands of diphenylhydrazine in the IR spectrum. A weak absorption at 1728 cm^{-1} indicated the formation of an additional compound; NMR spectra gave no indication of reduced azobenzene. The residue was recrystallised from methanol, and orange crystals of pure azobenzene could be isolated (0.284 g, 95%).

Reaction of *in situ* generated compound 2 with azobenzene. The compounds Co(ClO$_4$)$_2$·6MeCN (0.2 g, 0.397 mmol) and cyclam (80 mg, 0.397 mmol) were dissolved in a mixture of methanol (15 cm^3) and acetonitrile (25 cm^3). Azobenzene (36 mg, 0.199 mmol) was added and the orange solution subsequently treated with NaSH (22 g, 0.397 mmol). After few minutes the solution turned darker. It was stirred at room temperature for 16 h. A reddish brown precipitate of complex **8** was formed, which was removed by filtration, washed with ether (0.063 g, 37%) and identified by FT-IR and NMR spectra. The filtrate was evaporated, the residue was treated with ether (20 cm^3) and filtered to yield a light yellow solution. After removal of the ether *in vacuo* a light yellow residue was obtained, which was recrystallised from hexane (20 h/−4 °C) to give pure diphenylhydrazine (0.033 g, 89%) as a microcrystalline solid.

Reaction of *in situ* generated compound 4 with azobenzene. The compounds Ni(ClO$_4$)$_2$·6MeCN (0.2 g, 0.397 mmol) and cyclam (80 mg, 0.397 mmol) were dissolved in a mixture of methanol (20 cm^3) and acetonitrile (20 cm^3). Azobenzene (36 mg, 0.199 mmol) was added followed by NaSH (22 mg, 0.397 mmol). The reaction mixture was stirred at room temperature for 16 h. The solvents were removed *in vacuo*. The residue was treated with ether (20 cm^3) and filtered. After removal of the ether under reduced pressure, an orange residue was left, which was identified as pure azobenzene (quantitatively) by FT-IR, ^{1}H and ^{13}C NMR spectroscopy.

Crystal structure determination

Crystal, data collection and structure refinement parameters are summarised in Table 4. Single crystals of compounds **1**–**8** suitable for X-ray diffraction were grown by diffusion of ether into the solutions as described in the Experimental section. All structures were solved by direct methods and refined based on F^2 using the programs SHELXTL PLUS,[33] SHELXS 86,[34] and SHELXL 93.[35] Plots of the compounds **1**, **4**, **5**, **7** and **8** were drawn by using ORTEP 3 for Windows.[9]

The perchlorate anions in compounds **1**, **3**, **4**, **7** and **8** were statistically disordered over two positions. Their oxygen atoms were refined isotropically. Also, the atoms of the acetonitrile molecule of **8** were refined isotropically with occupancy factors of 0.5.

CCDC reference number 186/1524.

See http://www.rsc.org/suppdata/dt/1999/2601/ for crystallographic files in .cif format.

Physical measurements

The NMR spectra were recorded with a Bruker AM 300 spectrometer and referenced to solvent signals or TMS as internal standards, IR and UV/VIS spectra with a Bio-Rad FTS-7 and a Shimadzu UV-260 spectrometer, respectively. Elemental analyses were carried out by Beller Mikroanalytisches Labor (Göttingen). Samples were obtained as described and not further purified.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for generous financial support.

References

1 W. Kaim and B. Schwederski, *Bioanorganische Chemie*, 2. Auflage, Teubner, Stuttgart, 1995.

2 For example, H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 322 and refs. therein; C. Mealli, S. Midollini and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1975, 765; M. Herberhold and G. Süss, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 366; C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, 1976, **98**, 689; C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 632; M. Schmidt, G. G. Hoffmann and R. Höller, *Inorg. Chim. Acta*, 1979, **32**, L19; J. A. Ibers and R. H. Holm, *Science*, 1980, **209**, 223; G. Urban, K. Sünkel and W. Beck, *J. Organomet. Chem.*, 1985, **290**, 329; M. Di Vaira, P. Stoppioni and M. Peruzzini, *J. Organomet. Chem.*, 1987, **333**, C53; J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1987, **26**, 3328; M. J. Calhorda, R. Hoffmann and C. M. Friend, *J. Am. Chem. Soc.*, 1990, **112**, 50; J. Birnbaum, G. Godziela, M. Maciejewski, T. L. Tonker, R. C. Haltiwanger and M. Rakowski DuBois, *Organometallics*, 1990, **9**, 394; D. Sellman, P. Lechner, F. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 552; Y. Ozawa, A. Vázquez de Miguel and K. Isobe, *J. Organomet. Chem.*, 1992, **433**, 183; K.-Y. Shih, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 1992, **31**, 3663; P. G. Jessop, C.-L. Lee, G. Rastar, B. R. James, C. J. L. Lock and R. Faggiani, *Inorg. Chem.*, 1992, **31**, 4061; W. A. Howard and G. Parkin, *Organometallics*, 1993, **12**, 2363; J. Allshouse, B. B. Kaul and M. Rakowski DuBois, *Organometallics*, 1994, **13**, 28; G. Belchem, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton. Trans.*, 1994, 1949; Z. Tang,

Y. Nomura, Y. Ishii, Y. Mizobe and M. Hidai, *Organometallics*, 1997, **16**, 151 and refs. therein.

3 A. C. Moreland and T.B. Rauchfuss, *J. Am. Chem. Soc.*, 1998, **120**, 9376.

4 J. M. McCall and A. Shaver, *J. Organomet. Chem.*, 1980, **193**, C37; T. B. Rauchfuss and C. J. Ruffing, *Organometallics*, 1982, **1**, 400; M. Rakowski DuBois and C. J. Casewit, *J. Am. Chem. Soc.*, 1986, **108**, 5482; R. H. Holm, S. Ciurli and J. A. Weigel, *Prog. Inorg. Chem.*, 1990, **38**, 1; B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 769; T. Shibahara, *Coord. Chem. Rev.*, 1993, **123**, 73; I. Dance and K. Fisher, *Prog. Inorg. Chem.*, 1994, **41**, 637.

5 See, for example, M. Rakowski DuBois, M. C. VanDerveer, D. L. Dubois, R. C. Haltiwanger and W. K. Miller, *J. Am. Chem. Soc.*, 1980, **102**, 7456; A. M. Mueting, P. Boyle and L. H. Pignolet, *Inorg. Chem.*, 1984, **23**, 44; C.-L. Lee, G. Besenyei, B. R. James, D. A. Nelson and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1985, 1175; C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Inorg. Chem.*, 1986, **25**, 4617; G. Besenyei, C.-L. Lee, J. Gulinski, S. J. Rettig, B. R. James, D. A. Nelson and M. A. Lilga, *Inorg. Chem.*, 1987, **26**, 3622; A. F. Barnabas, D. Sallin and B. R. James, *Can. J. Chem.*, 1989, **67**, 2009; M. Rakowski DuBois, *Chem. Rev.*, 1989, **89**, 1; R. McDonald and M. Cowie, *Organometallics*, 1990, **9**, 2468; D. M. Antonelli and M. Cowie, *Inorg. Chem.*, 1990, **29**, 3339; D. P. Klein, G. M. Kloster and R. G. Bergman, *J. Am. Chem. Soc.*, 1990, **112**, 2022; D. Rabinovich and G. J. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 5904; R. McDonald and M. Cowie, *Inorg. Chem.*, 1993, **32**, 1671; L.-S. Wang, R. McDonald and M. Cowie, *Inorg. Chem.*, 1994, **33**, 3735.

6 A. M. Mueting, P. D. Boyle, R. Wagner and L. H. Pignolet, *Inorg. Chem.*, 1988, **27**, 271 and refs. therein.

7 C. Tonon, H. Ierno, J. Laugier, J.-M. Grenèche and J. Jordanov, *Chem. Ber.*, 1997, **130**, 235 and refs. therein.

8 F. Cecconi, C. A. Ghilardi and S. Midollini, *Inorg. Chem.*, 1983, **22**, 3802 and refs. therein.

9 ORTEP 3 for Windows, L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, 565.

10 C. A. Ghilardi, S. Midollini, A. Orlandini and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, 1992, 2909.

11 M. di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1979, **18**, 3466.

12 G. J. Lony and P. J. Clarke, *Inorg. Chem.*, 1978, **17**, 1394; J. Kansikas, M. Leskela, G. Kenessy, P. E. Wernerf and G. Liptay, *Acta Chem. Scand.*, 1994, **48**, 951; D. M. L. Goodgame, S. Menzer, A. T. Ross and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 2605, B. Umadevi, P. T. Muthiah, Xiugi Shui and D. S. Eggleston, *Inorg. Chim. Acta*, 1995, **234**, 149.

13 D. J. Szalda, E. Fujiti and C. Creutz, *Inorg. Chem.*, 1989, **28**, 1446.

14 J. D. Dunitz, *Acta Crystallogr.*, 1957, **10**, 307.

15 M. di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1977, **16**, 1518.

16 M. di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 816; C. Bianchini, D. Masi, C. Mealli and A. Meli, *Cryst. Struct. Commun.*, 1982, **11**, 145; C. A. Ghilardi, S. Midollini, A. Orlandini, C. Battistoni and G. Mattogni, *J. Chem. Soc., Dalton Trans.*, 1984, 939.

17 H. Waden, Dissertation, Universität Oldenburg, 1998.

18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley Interscience, New York, 1986.

19 C. Mealli and S. Midollini, *Inorg. Chem.*, 1983, **22**, 2785.

20 A. Müller, W. Jaegermann and J. H. Enemark, *Coord. Chem. Rev.*, 1982, **46**, 245.

21 C. A. Ghilardi, C. Mealli, S. Midollini, V. I. Nefedov, A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1980, **19**, 2454.

22 N. N. Greenwood and A. Earnshaw, *Chemie der Elemente*, VCH, Weinheim, Basel, Cambridge, New York, 1. korrigierter Nachdruck d. 1. Aufl., 1990, Kap. 26.3, S. 1430.

23 H. Gilman and J. B. Dickey, *Am. Chem. Soc.*, 1930, **52**, 4573.

24 N. Kornblum and R. G. Smith, *J. Am. Chem. Soc.*, 1979, **101**, 647.

25 Houben-Weyl, *Methoden der Organischen Chemie*, eds. E. Müller and R. Stoh, Georg Thieme Verlag, Stuttgart, 4. Aufl., 1967, Bd.10/2, S. 713.

26 Houben-Weyl, *Methoden der Organischen Chemie*, eds. E. Müller and R. Stoh, Georg Thieme Verlag, Stuttgart, 4. Aufl., 1967, Bd.10/2, S. 714.

27 C. J. Casewit, D. E. Coons, L. L. Wright, W. K. Miller and M. Rakowski DuBois, *Organometallics*, 1986, **5**, 951.

28 S. Pohl and W. Saak, *Z. Naturforsch., Teil B*, 1984, **39**, 1236.

29 N. F. Curtis, *Coord. Chem. Rev.*, 1986, **3**, 1.

30 G. Brauer, *Handbuch der präparativen Anorganischen Chemie*, S. Hirzel Verlag, Stuttgart, 3. Aufl., Bd. 1, 1975, p. 371.

31 G. Brauer, *Handbuch der präparativen Anorganischen Chemie*, S. Hirzel Verlag, Stuttgart, 3. Aufl., Bd. 1, 1975, p. 375.

32 G. Brauer, *Handbuch der präparativen Anorganischen Chemie*, S. Hirzel Verlag, Stuttgart, 3. Aufl., Bd. 1, 1975, p. 374.

33 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.

34 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.

35 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Structures, University of Göttingen, 1993.

Paper 9/02015B