Preparation and X-ray Crystal Structure of the First Trimeric Nickel Thiosemicarbazone Complex: The First Example of Oligomerization by both Ni–O–Ni and Ni–S–Ni Bridging

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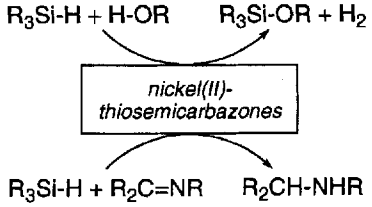
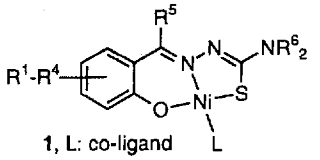
Monomeric nickel(II) thiosemicarbazone complexes are an attractive new class of homogeneous catalysts for the activation of silanes. However, their activity is limited by the formation of inactive oligo- and polymers. The pathway by which aggregation takes place was elucidated by the preparation and X-ray structural analysis of the first trimeric nickel(II) thiosemicarbazone complex. Aggregation was shown to proceed via Ni–O–Ni and Ni–S–Ni bridging, giving rise to both fourfold planar and pseudooctahedral coordination of the nickel ions.

Nickel^{II} complexes derived from the thiosemicarbazones of aromatic *ortho*-hydroxy aldehydes, in particular salicylaldehyde, have recently attracted considerable attention as homogeneous catalysts. As shown by Crabtree et al.[1] and us[2,3], they are able to activate the Si–H bond in silanes. As a result, alcoholysis affording silyl ethers[1,2] (eq. 1) or the reduction of imines to primary or secondary amines[3] (eq. 2) can be catalyzed by these nickel chelates.

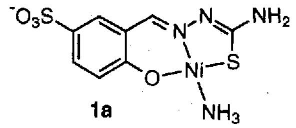


(1,2)

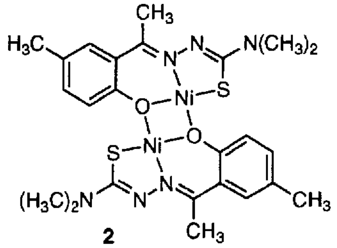
A crucial feature of nickel thiosemicarbazone complexes of the general structure **1** is their ability to aggregate to di- and oligomers or even polymers. Aggregation is induced by the tendency of the Lewis basic heteroatoms of the ligand of one chelate molecule to bind to the Lewis acidic nickel ion of another molecule etc. The X-ray crystal structures of a variety of monomeric nickel thiosemicarbazone complexes carrying inert coligands, like e.g. ammonia, at the fourth coordination site of the nickel ion are known[4,6]. These materials are all planar, tetracoordinated nickel complexes and catalytically inactive. As an example from our own laboratory, the crystal structure of the sulfonated[5] complex **1a** is shown in Figure 1. Clearly, only those monomeric complexes carrying a fourth, *kinetically labile* coligand, such as DMSO, are catalytically active. As a consequence, reactions catalyzed by nickel thiosemicarbazones are usually carried out in DMSO. This solvent is able to (partly) monomerize the polymeric catalyst preparations *and* it is a kinetically labile ligand[1–3], allowing the silane molecule to reach the fourth coordination site at the nickel ion.



1, L: co-ligand



1a



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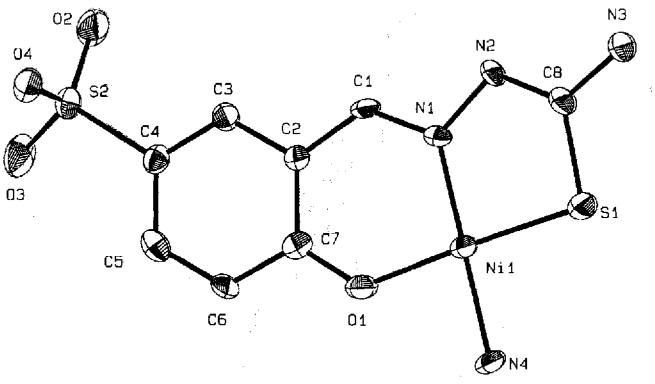
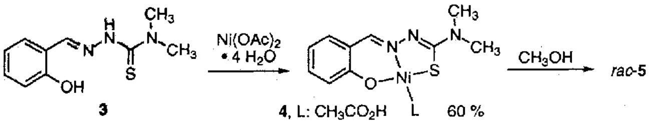
Thus, in the context of using such nickel complexes as catalysts, it is of importance to study and understand their aggregation behavior. Along the way from the monomeric thiosemicarbazones to the hardly soluble polymeric materials formed in the absence of coligands, only one dimeric structure has been characterized so far: this is the O–Ni–O bridged dimer **2** reported by Crabtree et al.[7]. The Ni–O–Ni bridging pattern is in sharp contrast to the usually observed pronounced tendency of nickel thiolate complexes to form higher aggregates by Ni–S–Ni bonding[8]. In this paper we report on the first example of a crystallographically characterized *trimeric* nickel thiosemicarbazone complex. As it turned out, this complex *rac*-**5** combines Ni–O–Ni with Ni–S–Ni bridging.

Figure 1. X-ray crystal structure of the nickel(II) thiosemicarbazone complex **1a**; selected interatomic distances [Å]: Ni1−S1 2.150(3), Ni1−O1 1.845(5), Ni1−N1 1.854(6), Ni1−N4 1.941(7), S1−C8 1.744(8), N2−C8, 1.29(1)



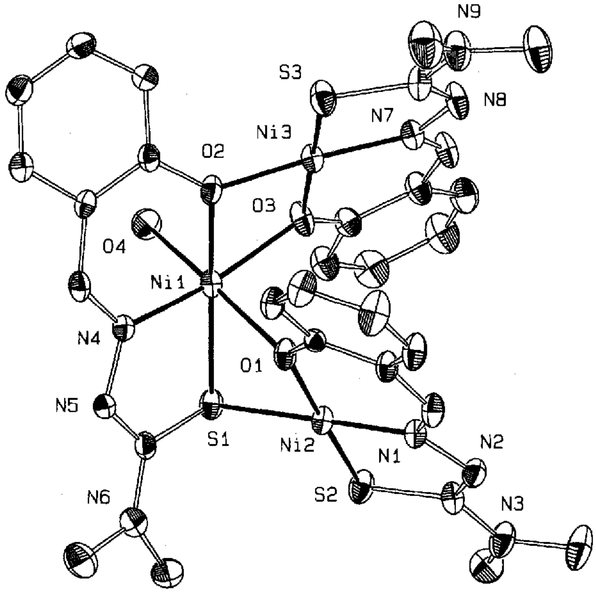
Scheme 1



Starting from the ligand **3**, we were able to isolate and characterize (^{1}H-NMR, IR, elemental analysis, UV/Vis) the 1:1 complex **4** formed by reaction with nickel(II) acetate. The analytical data indicate that the complex **4** contains one equivalent of acetic acid, most likely as a coligand at the fourth coordination site of the nickel ion (Scheme 1). Careful crystallization of **4** from methanol afforded black cubes of the complex *rac*-**5** (Scheme 1) that proved suitable for X-ray structural analysis. The result is shown in Figure 2. As in the dimer **2**, each of the nickel ions is coordinated by one ligand molecule in a tridentate fashion. The ligands are doubly deprotonated, thus acting as dianionic phenolate-azaenethiolates. In the absence of coligands, the fourth coordination sites of the nickel ions are filled by heteroatoms belonging to the ligands of other monomers. Again, as in the dimer **2**, two monomers combine to a butterfly-shaped dimer by mutual Ni−O−Ni bonding (Ni1, O2, Ni3, O3). However, in our example, a third monomer binds to the dimer via Ni−S−Ni bridging. A second four-membered ring is established involving the atoms Ni1, O1, Ni2, and S1. Thus, one nickel ion of the "Ni−O−Ni-dimeric substructure" becomes pentacoordinated (Ni1). Its sixth coordination site is finally filled by a water molecule (O4), rendering Ni1 of the trimer pseudooctahedrally coordinated. Ni2 and Ni3 of the trimeric complex remain planar, tetracoordinated. The high-spin nature of Ni1 is nicely reflected by its comparatively long bonding distances to O1−O4, Ni4 and S1. For example, the "intramolecular" distance N1−S1 [2.389(3) Å] even exceeds the "intermolecular" distance Ni2-S1 [2.245(2) Å]. In contrast, the "intramolecular" Ni−S bond lengths of the two other subunits (Ni2, Ni3 as central ions) are virtually the same as in complex **1a**, i.e. ca. 2.15 Å. The different spin states of the nickel ions also account for the inequality of bond lengths in the four-membered ring Ni1−O2−Ni3−O3: In the low-spin dimer **2**, the corresponding Ni−O bond lengths are approximately equal [1.850(3)−1.912(4) Å][7]. Inspection of Figure 2 reveals that the two four-membered rings are not planar, but significantly puckered: The planes defined by the atoms Ni1−O2−Ni3 and Ni1−O3−Ni3 intersect at an angle of 149.2(3)°, and those defined by Ni1−S1−Ni2 and Ni1−O1−Ni2 at 138.5(2)°. This structural feature can be interpreted by steric effects (interference between the two phenyl rings of the two monomeric subunits bound to Ni1) and by the sp^3-like character of O2/O3 and O1/S1.

For the Ni−O−Ni-bridged dimer **2** it was argued[7] that the normal tendency of nickel thiolate monomers to aggregate by Ni−S bridging is weakened when a deprotonated thioamide (i.e. an azaenethiolate, see formulae **1**, **1a** and **2**) is the S donor instead of an alkane- or arenethiolate. Indeed, the deprotonated thioamide group resembles the carboxylate anion. For the latter it is known that the so-called "*syn*"-lone pair is more nucleophilic than the "*anti*"-lone pair[10]. Our trimeric complex *rac*-**5** proves, however, that one of the other lone pairs at the sulfur atom ("non-*syn*" to the imino moiety) may well bind an additional nickel ion. Most likely, the structures found in the crystal are a delicate balance between crystal packing effects and the solvent used for crystallization (our crystals of *rac*-**5** contain two molecules of methanol bound via hydrogen bonds to the water molecule O4). In solution, both **2** and *rac*-**5** (and other nickel thiosemicarbazone complexes) behave similarly: They show no significant paramagnetism (as evidenced by the Evans method[11], but their NMR spectra exhibit unusually broad lines[1,2]. This puzzling observation made by us[2] and others[1] can now be explained: In the absence of kinetically inert coligands, the monomeric units assemble reversibly to dimers, trimers and higher aggregates. Each subunit becomes pseudooctahedral and thus paramagnetic from time to time, although the overall susceptibility of the bulk solution remains negligible. Thus, rapid nuclear relaxation and broad NMR lines result.

Figure 2. X-ray crystal structure of the trimeric nickel(II) thiosemicarbazone complex *rac*-**5** (only one enantiomer shown); selected interatomic distances [Å] and angles [°]: Ni1−S1 2.389(3), Ni1−O1 2.187(5), Ni2−S1 2.245(2), Ni2−O1 1.886(5), Ni2−S2 2.137(3), Ni1−O2 2.028(5), Ni1−O3 2.057(5), Ni1−O4 2.073(6), Ni3−S3 2.155(3), Ni3−O3 1.887(6), Ni3−O2 1.898(5); Ni1−S1−Ni2 84.13(8), Ni1−O1−Ni2 99.1(2), S1−Ni1−O1 76.5(2), S1−Ni2−O1 86.3(2), Ni1−O2−Ni3 100.0(2), Ni1−O3−Ni3 99.3(2), O2−Ni1−O3 73.5(2), O2−Ni3−O3 80.4(2)



In summary, we have prepared and characterized the first trimeric nickel(II) thiosemicarbazone complex. The structure and bonding pattern of this trimer greatly improved our understanding of the reaction pathways leading from monomeric nickel(II) thiosemicarbazone complexes to their polymers. The structure found shows that aggregation can take place via Ni–O–Ni *and* Ni–S–Ni bridging. The combination of fourfold planar and sixfold pseudooctahedral coordination of the nickel ions offers an explanation for the puzzling observation that nickel(II) thiosemicarbazone complexes show broad NMR lines in solution without being significantly paramagnetic.

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Experimental

Nickel Complex **1a**: The complex **1a** was prepared in analytically pure form according to Gyepes et al.[6] Crystals suitable for X-ray structural analysis were obtained from solutions of **1a** in methanol/ethanol mixtures at 4°C. Crystal data for **1a**: Crystal dimensions: 0.2 · 0.3 · 0.3 mm; $C_8H_6N_3O_4S_2Ni \cdot NH_3 \cdot 0.5\,[Ni(H_2O)_6]$ (empirical formula of the complex without solvent molecules), M = 461.21, triclinic, space group $P1$ (Nr. 2); a = 13.789(6), b = 14.992(6), c = 17.242(6) Å, α = 95.31(3)°, β = 99.70(3)°, γ = 94.40(3)°, V = 3483(2) Å^3, Z = 8, $\rho_{calcd.}$ = 1.759 g · cm^{-3}; intensities were recorded at 200 K for 11460 reflections [2Θ range 2.7–48.1°, scan speed $4.5 \le \omega \le 29.3$ (° · min^{-1})] with a Siemens (Nicolet-Syntex)-R3m/V diffractometer by using Mo-K_α radiation, 10945 symmetry-independent reflections. 6927 Reflections had $I > 2\sigma(I)$; empirical absorption correction based on Ψ scans. All reflections were used for the structure solution and the refinement [SHELXTL PLUS (G. M. Sheldrick, Universität Göttingen, 1988), SHELXL-93 (G. Sheldrick, Universität Göttingen, 1993)]; R_1 = 0.059, R_w = 0.141 (F^2 refinement); data-to-parameter ratio = 9.9:1, maximum residual electron density 0.80 e · Å^{-3}. Further details of the crystal structure investigation of **1a** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-400584, the names of the authors, and the journal citation.

Nickel Complexes **4**, *rac*-**5**: The ligand **3** was prepared in 61% yield from salicyclic aldehyde and *N,N*-dimethylthiosemicarbazide[9]. Pale yellow crystals, m.p. 203–204°C (methanol). Satisfactory C, H, N analysis [Δ% (C,H,N) < 0.16], ^{1}H-NMR, and IR spectra. Under argon, a solution of 330 mg (1.34 mmol) of nickel(II) acetate tetrahydrate in 10 ml of ethanol was added to a solution of 300 mg (1.34 mmol) of the ligand **3** in 30 ml of ethanol. The mixture was refluxed for 1 h. After cooling to room temperature, the dark green-brown precipitate was filtered off, washed with ethanol and dried in vacuo. Under these conditions, the nickel(II) complex **4** was obtained as a brown microcrystalline solid [240 mg (60%)], m.p. (dec.) 257°C. On the basis of the analytical data **4** was identified as [Ni(3-2H$^+$) · CH_3COOH]. – $C_{12}H_{15}N_3O_3SNi$ (340.02): calcd. C 42.39, H 4.45, N 12.36; found C 42.64, H 4.62, N 12.54. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.89 (s; 3H, C*H*$_3$COOH), 2.93 [br. s; 6H, N(CH$_3$)$_2$], 6.51–6.56 (m; 1H, aryl-H), 6.74–6.77 (m; 1H, aryl-H), 7.11–7.13 (m; 1H, aryl-H), 7.27–7.29 (m; 1H, aryl-H), 7.86 (br. s; 1H, CH=N), 11.95 (br. s; 1H, CH$_3$COO*H*). – IR (KBr): $\tilde{\nu}$ = 2921, 1598, 1554, 1526, 1444, 1388, 1280, 1265, 1149, 914, 754 cm^{-1}. – UV (EtOH): λ_{max} (lg ε) = 417 nm (3.94), 368 (4.17), 302 (4.18), 246 (4.44), 213 (4.45). – Crystals of *rac*-**5** suitable for X-ray structural analysis were obtained by slow cooling of a solution of **4** in methanol. Under these conditions, the trimer *rac*-**5** was obtained as black cubes. – $C_{32}H_{43}N_9O_6S_3Ni_3$ (922.00): calcd. C 41.69, H 4.70, N 13.67; found C 41.80, H 4.86, N 13.47. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.94 [br. s; 6H, N(CH$_3$)$_2$], 3.28 (s; 2H, C*H*$_3$OH), 6.50–6.57 (m; 1H, aryl-H), 6.74–6.78 (m; 1H, aryl-H), 7.10–7.17 (m; 1H, aryl-H), 7.26–7.30 (m, 1H, aryl-H), 7.88 (br. s; 1H, CH=N). – ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 40.34 [q; N(*C*H$_3$)$_2$], 48.58 (q; CH$_3$OH), 114.95, 118.82 (2 d; aryl-CH), 119.19 (s; aryl-C), 131.42 (d; 2 aryl-CH), 150.32 (d; CH=N), 159.07 (s; aryl-C), 171.03 (s; CS). – IR (KBr): $\tilde{\nu}$ = 3422, 2920, 1597, 1552, 1522, 1475, 1443, 1424, 1386, 1347, 1283, 1258, 1138, 912, 749 cm^{-1}. – UV (EtOH): λ_{max} (lg ε) = 416 nm (4.03), 368 (4.24), 302 (4.25), 248 (4.52), 214 (4.51). – Crystal data of *rac*-**5**: Crystal dimensions: 0.3 · 0.3 · 0.2 mm; $(C_{10}H_{11}N_3NiOS)_3 \cdot 2\,CH_3OH \cdot H_2O$, M = 922.00, monoclinic, space group $P2_1/c$; a = 13.360(3), b = 18.770(4), c = 17.370(3) Å, β = 102.53(3)°, V = 4252(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.440 g · cm^{-3}; intensities were recorded at 298 K for 6973 reflections (2Θ range 3.1–48.0°, scan speed $5 \le \omega \le 29.3$ [° · min^{-1}]) with a Siemens (Nicolet-Syntex)-R3m/V diffractometer using Mo-K_α radiation, 6674 symmetry-independent reflections, empirical absorption correction based on Ψ scans; 4190 reflections had $I > 2\sigma(I)$. All reflections were used for the structure solution and the refinement [SHELXTL PLUS (G. M. Sheldrick, Universität Göttingen, 1988), SHELXL-93 (G. Sheldrick, Universität Göttingen, 1993)]; R_1 = 0.066, R_w = 0.1828 (F^2 refinement); maximum residual electron density 1.02 e · Å^{-3}. Further details of the crystal structure investigation of *rac*-**5** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-401641, the names of the authors, and the journal citation.

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