Acta Chemica Scandinavica A 31 (1977) 657—665

Nickel(II) Complexes of Thiohydrazonates. I

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Dedicated to Professor K. A. Jensen on his 70th birthday

New condensation products of aliphatic thiohydrazides and mono- and diketones have been synthesized as ligands in nickel(II) inner complexes. These complexes have been characterized by means of ^{1}H NMR, UV-VIS spectroscopy and cyclic voltametry. The protonated complexes may exist at high acidities in solutions of low water activity but the free ligands are not stable. For comparison some nickel(II) complexes of thiosemicarbazonates were prepared as well.

Complexes of thiosemicarbazides and of thiosemicarbazones were first described by K. A. Jensen in 1934, and in 1952 he investigated nickel(II) complexes of the closely related thiobenzhydrazide.[1–4] Another homologous ligand, *e.g.* thioacethydrazide, could not be isolated and accordingly no complexes were made.[5] However, it was recently found that bis(thiohydrazidato) nickel(II) is formed from thioacetamide, hydrazinium ions and nickel(II) ions at pH ~ 4.[6]

While attempting to grow crystals of this complex for a single crystal X-ray diffraction investigation, it was found that this compound when dissolved in dimethyl sulfoxide, reacts at room temperature for months with acetone forming a red crystalline product very distinctly different from the starting material. Chemical analysis indicated that a template reaction analogous to that discovered by Curtis [7] could have taken place or that a complex of acetone thioacethydrazone (*cf.* Fig. 1) had been formed. The latter explanation turned out to be correct, and a series of compounds has been prepared by analogous condensations. However, it became evident that it is not necessary first to isolate bis(thioacethydrazidato)nickel(II) in order to obtain the condensation products. Aqueous mixtures of thioacetamide, hydrazine and a suitable ketone enters with nickel(II) ions into template reactions and the non-electrolyte products can readily be isolated. For acetone the reaction scheme is

$$Ni^{2+} + 2CH_3CSNH_2 + 2N_2H_5^+ + 2(CH_3)_2CO \xrightarrow{pH \sim 4} \text{complex (shown in Fig. 1)} + 2H^+ + 2NH_4^+ + 2H_2O$$

Complexes of thiosemicarbazones and their anions closely related to compounds investigated in this work have for some time been studied with the main emphasis on either the antitumor activity shown by some copper(II) derivatives [8] or on the fascinating ability for some of the reaction products to exist in many oxidation states. The field has recently been reviewed by Campbell.[9] The present preparative investigation has been undertaken to clarify the stereochemistry of thioacylhydrazonato nickel-(II) complexes by means of spectroscopy and

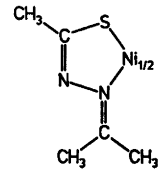

Fig. 1.

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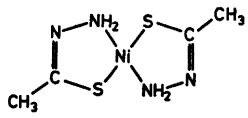

Fig. 2.

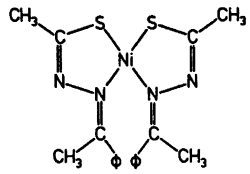

Fig. 3.

X-ray diffraction. So far, the crystal and molecular structure of bis(thioacethydrazidato)-nickel(II) [6] and bis(acetophenone thioacethydrazonato)nickel(II) [10] have been published (Figs. 2 and. 3).

EXPERIMENTAL

Starting materials. Bis(thioacethydrazidato-nickel(II) and bis(thiophenylacethydrazidato-nickel(II) were prepared as previously described,[6] while bis(thiosemicarbazidato)nickel(II) was prepared according to Jensen and Rancke-Madsen.[2] Phenylacetthiamide was prepared according to Berntsen [11] and Kindler.[12] Anal. C_8H_9NS: C, H, N, S. Reagents were commercial chemicals of analytical grade.

Physical measurements. Absorption spectra were measured with Cary 14 and Perkin Elmer IR 337 spectrophotometers, diffuse reflectance spectra with a Spectronic 505, and ^1H NMR spectra with Varian A-60, A-100 and Bruker X90 spectrographs using TMS as internal standard. Polarographic data were obtained using a three electrode polarograph constructed by Dr. E. Pedersen in this laboratory, with a Beckman 19001 Pt electrode as working electrode, a Pt wire as auxiliary electrode, and a Metrohm EA 429 Ag/AgCl reference electrode with a salt bridge consisting of a 0.2 M $(n\text{-}C_4H_9)_4NClO_4$ solution in dimethylformamide saturated with $(n\text{-}C_4H_9)_4NCl$. Reported $E_{\frac{1}{2}}$ values are in V relative to aqueous SCE.

Complexes. All complexes prepared were characterized by chemical analysis, ^1H NMR and absorption spectra and checked for small amounts of impurities by thin layer chromatography normally using chloroform as the solvent and silica gel as the stationary phase. Melting points given below are uncorrected.

The abbreviations used are: thioacethydrazide = tahH, phenylacetthiohydrazide = pathH, thiosemicarbazide = tscH, and 2,4-pentandione = acacH. A condensation product of a thiohydrazide and a ketone is denoted by means of parentheses including the abbreviation for the thiohydrazide and the name of the ketone.

Preparations. In general, two methods of preparation are possible. In the first method solutions in suitable solvents of nickel acetate, hydrazine hydrate, the thiamide, and the ketone are mixed and refluxed, whereupon the complex precipitates. In the second method, the ketone is condensed with the nickel thiohydrazide complex either in a homogeneous reaction using dimethyl sulfoxide (DMSO) as the solvent, or in a heterogeneous reaction usually with ethanol as the solvent. It may be necessary to catalyze the reaction by adding a drop of 12 M hydrochloric acid. For most of the complexes with thiosemicarbazones as ligands a third method of preparation is available. This involves the preparation of the ligand by a standard procedure, followed by reaction with nickel(II) by adding an ethanol solution of the ligand to an ammoniacal solution of an equivalent amount of nickel. The methods of preparation mentioned below are those found to yield the purest product.

$[Ni(tah\ acetone)_2]$. In the first method 9.0 g (0.035 mol) of nickel acetate tetrahydrate, 5.0 g (0.067 mol) of thioacetamide, 3.5 ml (0.07 mol) of hydrazine hydrate, and 25 ml (0.34 mol) of acetone were dissolved in a mixture of 25 ml of glacial acetic acid and 125 ml of water. The mixture was refluxed for 24 h. After cooling, the solid was filtered off, washed with water and ethanol, and dried in air. Yield: 9.0 g (82 %). The crude product was dissolved in 1 l of chloroform, and the solution was filtered and evaporated to 1/10 of the original volume. The recrystallization was repeated once or twice.

According to the second method the complex was prepared in a homogeneous reaction by dissolving 2.0 g (0.0084 mol) of $[Ni(tah)_2]$ in 100 ml of DMSO and adding 100 ml (0.84 mol) of acetone. After refluxing for 24 h the mixture was cooled to room temperature, the solid filtered off, and washed with ethanol. Yield: 1.75 g. By adding 100 ml of water to the mother liquor, further 0.5 g was isolated (total yield: 85 %).

The product was a violet microcrystalline powder m.p. 290 – 291 °C with decomposition. (Found: C 37.80; H 5.74; N 17.92; S 20.04. Calc. for $C_{10}H_{18}N_4NiS_2$: C 37.89; H 5.68;, N 17.68; S 20.21).

$[Ni(path\ acetone)_2]$. This complex is prepared in the same way as the corresponding tah-derivative. The small plates obtained exhibited pleochroism with colour changes from red to green, and melted unsharply at 190 – 196 °C. Anal. $C_{22}H_{26}N_4NiS_2$: C, H, N, S, Ni.

$[Ni(tsc\ acetone)_2]$. The compound was best prepared from $[Ni(tsc)_2]$ according to the second method in a homogeneous reaction with DMSO as the solvent. The light brown, crystalline

powder was recrystallized from 2-ethoxyethanol. M.p. 236–237 °C with decomposition. Anal. $C_8H_{14}N_6NiS_2$: C, H, N, S.

[Ni(tah butanone)$_2$]. A solution of 2.4 g (0.010 mol) of [Ni(tah)$_2$] and 5 ml (0.055 mol) of 2-butanone in 50 ml of DMSO was heated at 100 °C for 1.5 h, whereupon 10 ml of water was added. After cooling to room temperature, the mixture was filtered and the precipitate washed with small portions of ethanol. After drying at 50 °C the yield was 1.0 g (29 %) of small, violet plates melting at 178–180 °C. TLC revealed that three isomers had formed. By column chromatography on silica gel with 5 % ethyl acetate in benzene as eluent one isomer could be obtained rather pure. (Found: C 41.00; H 6.56; N 15.78; S 18.59. Calc. for $C_{12}H_{22}N_4NiS_2$: C 41.77; H 6.38; N 16.26; S 18.57).

[Ni(path butanone)$_2$]. The preparation is analogous to that of the corresponding tah derivative. The small, violet crystals melted unsharply at 91–94 °C. Anal. $C_{24}H_{30}N_4NiS_2$ C, H, N, Ni, S.

[Ni(tsc butanone)$_2$]. To a solution of 5 g (.017 mol) of nickel nitrate hexahydrate in 200 ml of water a slight excess of *conc.* ammonia was added, and the resulting solution was mixed with a solution of 5 g (0.034 mol) of butanone thiosemicarbazone in 750 ml of hot methanol. After standing overnight, the precipitate was filtered off, washed with water and ethanol, and dried. Yield 4.8 g (41 %) dark brown thin plates m.p. 218.5–220 °C. Soxhlet extraction with CH_3CN did not improve the purity of the product, but produced small red-brown crystals. (Found: 33.95; H 3.94; N 24.35; Ni 16.81; S 17.90 Calc. for $C_{10}H_{20}N_6NiS_2$: C 34.59; H 5.82; N 24.21; Ni 16.91; S 18.47).

[Ni(tah acetophenone)$_2$]. Both methods mentioned first were used successfully to prepare this complex. The crystals obtained are irregularly shaped polyhedra, exhibiting pleochroism with colour changes from red to green. Unsharp m.p. at 258–262 °C. TLC on silica gel and aluminium oxide with a variety of eluents failed to prove the existence of more than one isomer. Anal. $C_{20}H_{22}N_4NiS_2$: C, H, N, S.

[Ni(path acetophenone)$_2$]. A mixture of 3 g (0.0074 mol) of [Ni(path)$_2$].H_2O and 5 ml (0.042 mol) of acetophenone in 100 ml of 96 % ethanol, to which 3 drops of 12 M HCl was added, was refluxed for 24 h. After cooling to −10 °C the reaction mixture was filtered, and the precipitate washed with small amounts of ethanol. After drying in vacuum over NaOH pellets, the yield was 2.9 g of a brown crystalline powder. The crude product was extracted with 250 ml of boiling 96 % ethanol and filtered. Next the filtrate was cooled to −10 °C, and the first formed crystals were filtered off and dried in air. Yield: 0.2 g (5 %) of brown crystals melting at 209–210 °C. (Found: C 64.55; H 4.98; N 9.22; Ni 9.73; S 10.80. Calc. for $C_{32}H_{30}N_4NiS_2$: C 64.76; H 5.11; N 9.44; Ni 9.89; S 10.80).

[Ni(tsc acetophenone)$_2$]. The complex was prepared by mixing an ammoniacal solution of nickel nitrate and a solution of acetophenone thiosemicarbazone in methanol. The product was purified by Soxhlet extraction with acetonitrile for 24 h. The small, black crystals melted at about 270 °C with decomposition. Anal. $C_{18}H_{20}N_6NiS_2$: C, H, N, Ni, S.

[Ni(tah$_2$ butanedione)]. A solution containing 9.0 g (0.035 mol) of nickel acetate, 5.0 g (0.067 mol) of thioacetamide, 3.5 ml (0.07 mol) of hydrazine hydrate in a mixture of 25 ml of glacial acetic acid and 125 ml of water was refluxed for 15 min. whereupon a solution of 3.5 ml (0.040 mol) of butanedione in 50 ml of ethanol was added slowly. It is of importance for the purity of the product not to introduce the solution too rapidly. The mixture was refluxed for 2 h, allowed to cool to room temperature, and filtered. The crude product was washed with ethanol and recrystallized from chloroform. Yield: 9.3 g (96 %) of small, dark, violet crystals, which decomposed above 250 °C without melting. (Found: C 33.04; H 4.16; N 19.38; S 22.29. Calc. for $C_8H_{12}N_4NiS_2$: C 33.48; H 4.19; N 19.53; S 22.32).

[Ni(path$_2$ butanedione)]. The preparation is the same as for the tah derivative. The intense red, almost black crystals melted at 253–254 °C with decomposition. (Found: C 54.75; H 4.63; N 12.85; Ni 13.13; S 14.39. Calc. for $C_{20}H_{20}N_4NiS_2$: C 54.67; H 4.59; N 12.76; Ni 13.37; S 14.60).

[Ni(tsc$_2$ butanedione)]. The second method was followed using 10.0 g (0.031 mol) of [Ni(tsc)$_2$] amd 5.0 ml (0.057 mol) of butanedione dissolved in 50 ml of DMSO. The mixture was kept at 100 °C for 6 h and then allowed to stand overnight at room temperature. The crude product was filtered off, washed with ethanol, and recrystallized from 100 ml of DMSO. The yield was 5.0 g (42 %) of small green crystals which did not melt below 330 °C. (Found: C 25.15; H 3.80; N 28.51; S 22.40. Calc. for $C_6H_{10}N_6NiS_2$: C 24.92; H 3.49; N 29.08; S 22.18).

[Ni(tah$_2$ benzil)]. A slurry of 9.0 g (0.035 mol) of nickel acetate, 5.0 g (0.067 mol) of thioacetamide, 3.5 ml (0.07 mol) of hydrazine hydrate, and 7.4 g (0.035 mol) of benzil in 275 ml of 96 % ethanol was refluxed for 24 h. After cooling and filtering, the solid was washed thoroughly with ethanol and acetone. The crude product (7.7 g) was recrystallized from chloroform, giving 3.1 g (22 %) of green needles. M.p; 272 °C with decomposition. (Found: C 52.19. H 3.94; N 13.88; Ni 14.28; S 15.16. Calc. for $C_{18}H_{16}N_4NiS_2$: C 53.58; H 3.92; N 13.63; Ni 14.28; S 15.60).

[Ni(path$_2$ benzil)]. A mixture of 3.7 g (0.0091 mol) of [Ni(path)$_2$].H_2O and 2.0 g (0.0095 mol) of benzil in 150 ml of 96 % ethanol containing 0.5 ml of 12 M HCl, was refluxed for 4 days. The hot mixture was filtered, and the solid washed with ethanol. After drying, 4.4 g of crude product was obtained. For purification 2.0 g of this was extracted with 150 ml of boiling tetra-

hydrofuran. The solution was filtered and the filtrate evaporated to 25 ml. After cooling to 0 °C, the solid was filtered off, and dried in air. Yield: 0.3 g of small, dark green crystals melting at 249 – 251 °C with decomposition. (Found: C 63.65; H 4.37; N 9.83; Ni 10.10; S 11.47. Calc. for $C_{30}H_{24}N_4NiS_2$: C 63.95; H 4.30; N 9.95; Ni 10.42; S 11.38).

[Ni(tsc_2 benzil)]. The complex was prepared in the same way as the corresponding path derivative using DMSO as the solvent. The crude product was Soxhlet extracted with acetone yielding dark, red crystals. (Found: C 47.40; H 3.87; N 18.97; S 14.24. Calc. for $C_{14}H_{41}N_6NiS_2$: C 46.51; H 3.42; N 20.34; S 14.21).

[Ni(tah_2 acacH)]. A slurry of 4 g (0.017 mol) of [Ni(tah)$_2$] and 15 ml (0.15 mol) of 2,4-pentanedione in 150 ml of 50 % ethanol was refluxed for 4 h and then cooled to 5 °C. The solid was filtered off, washed with water and dried in vacuum over *conc.* H_2SO_4. The yield was 4.7 g (80 %) of a fairly pure product corresponding to the composition [Ni(tah_2 acacH)].C_2H_5OH. The complex could be purified by Soxhlet extraction with ethanol, preferably under an atmosphere of nitrogen since the complex tended to oxidize somewhat when wet. (Found: C 37.95; H 5.81; N 16.42; S 18.52. Calc. for $C_{11}H_{20}N_4NiS_2$: C 38.05; H 5.82; N 16.14; S 18.47). The solvent of crystallization could easily be removed by heating at 100 °C for 3 h in a vacuum. The red-brown crystals thus obtained melted unsharply at about 300 °C with decomposition. (Found: C 36.00; H 4.72; N 18.72; S 21.23. Calc. for $C_9H_{14}N_4NiS_2$: C 35.90; H 4.70; N 18.61; S 21.30).

[Ni($path_2$ acacH)]. The compound was prepared analogously to [Ni(tah_2 acacH)], but the chocolate-brown crystals obtained did not contain solvent of crystallization. M.p. 203 – 205.5 °C. (Found: C 55.85; H 5.04; N 12.36; S 14.38. Calc. for $C_{21}H_{22}N_4NiS_2$: C 55.65; H 4.89; N 12.36; S 14.15).

[Ni(tsc_2 acacH)]. The preparation of this complex is the same as that given for the corresponding tah derivative. However, since the compound is easily oxidized by atmospheric oxygen all preparations were performed under an atmosphere of nitrogen. The product was light brown and fairly stable in air when perfectly dry. (Found: C 27.71; H 4.04; N 27.88; S 19.83. Calc. for $C_7H_{12}N_6NiS_2$. C 27.74; H 4.00; N 27.74; S 19.37).

(n-C_4H_9)$_4$N[Ni(tah_2 acac)]. 6.5 g (0.019 mol) of [Ni(tah_2 acacH)]. C_2H_5OH was dissolved in 70 ml of 0.6 M NaOH, and after filtration a solution of 6.5 g (0.019 mol) of tetrabutylammonium perchlorate in 600 ml of acetone was added. The mixture was evaporated to a volume of 150 ml and then cooled at – 10 °C for 2 h. The precipitate was filtered off and dried in vacuum over *conc.* H_2SO_4. Yield: 8.0 g (78 %) of orange-red plates melting at 143 – 144 °C. (Found: C 55.25; H 9.42; N 13.04; S 11.50. Calc. for $C_{25}H_{49}N_5NiS_2$: C 55.33; H 9.12; N 12.91; S 11.82).

(n-C_4H_9)$_4$N[Ni($path_2$ acac)]. To a filtered solution of 0.95 g (0.0021 mol) of [Ni($path_2$ acacH)] in a mixture of 3 ml 40 % aqueous tetrabutylammonium hydroxide (0.0046 mol) and 20 ml of ethanol was added another solution containing 1.0 g (0.0029 mol) of tetrabutylammonium perchlorate in 100 ml of acetone. The solution was evaporated until crystals began to separate and then kept at – 10 °C overnight. The product was filtered off, washed with water, and dried in vacuum over conc. H_2SO_4. Yield: 1.1 g (74 %) of a reddish-brown crystalline powder melting at 135.5 – 136.5 °C. (Found: C 63.80; H 7.23; N 10.12; S 9.54. Calc. for $C_{37}H_{57}N_5NiS_2$: C 63.95; H 8.29; N 10.08; S 9.23).

(n-C_4H_9)$_4$[Ni(tsc_2 acac)]. This complex is prepared analogously to the corresponding tah derivative using [Ni(tsc_2 acacH)] as the starting material, and all operations were carried out under an atmosphere of nitrogen. Even when dry this compound was oxidized rapidly in the air forming a dark, green product. (Found: C 48.34; H 8.08; N 17.91. Calc. for $C_{23}H_{47}N_7NiS_2$: C 50.72; H 8.72; N 18.01).

[Ni(tah_2 2,5-hexanedione)]. To a suspension of 10.0 g (0.042 mol) of [Ni(tah)$_2$] in 200 ml of 50 % ethanol was added 11.0 g (0.097 mol) of 2,5-hexanedione, and the mixture was refluxed for 12 h. After cooling to room temperature 200 ml of water was added, and the mixture was kept at 5 °C overnight. The precipitate was filtered off, washed with water, and dried in vacuum over conc. H_2SO_4. Yield: 9.5 g (72 %) of brown crystalline powder. The crude product was purified by Soxhlet extraction with ethanol under an atmosphere of nitrogen. M.p. 190.5 – 192.5 °C. (Found: C 37.95; H 5.16; N 17.68; Ni 19.16; S 20.20. Calc. for $C_{10}H_{16}N_4NiS_2$: C 38.11; H 5.12; N 17.78; Ni 18.63; S 20.35).

[Ni(path 2,5-hexanedione)]. The complex was prepared in the same way as the corresponding tah derivative. The brown-red crystal plates melted at 139 – 140 °C. Anal. $C_{22}H_{24}N_4NiS_2$: C, H, N, S.

[Ni(tsc 2,5-hexanedione)]. The ligand was prepared separately and added to an ammoniacal solution of nickel. After stirring overnight the solid was filtered off, washed with water and dried. Yield: 15 g (94 %). The product was purified by Soxhlet extraction with ethanol. The red-violet crystals melted at 297 – 298 °C with decomposition. (Found: C 30.37; H 4.72; N 26.30; S 20.23. Calc. for $C_6H_{14}N_6NiS_2$: C 30.30; H 4.46; N 26.51; S 20.22).

[Ni(tah_2 acacO)] = (5,7-dimethyl-6-oxo-3,4,8,9-tetraazaundeca-2,4,7,9-tetraene-2,10-dithiolato-N^4,N^8,S,S')nickel(II). A suspension of 4.0 g (0.0012 mol) of [Ni(tah_2 acacH)].C_2H_5OH and 8.0 g (0.08 mol) of powdered calcium carbonate in 400 ml of water was stirred and refluxed under an atmosphere of nitrogen for 24 h. The mixture was filtered and a brisk current of air was drawn through the red filtrate for 4 days at room temperature. An olive-green precipitate

formed, and it was extracted with four 250 ml portions of toluene. After drying with 50 g of anhydrous magnesium sulfate and filtering, the toluene phase was evaporated to dryness, and the solid extracted with 200 ml of boiling acetone. After filtering the green solution was kept at −10 °C overnight. The product was filtered off and dried in vacuum over conc. H_2SO_4. Yield: 0.5 g (14 %) of dark green needles. M.p. 263 – 265 °C with decomposition. (Found: C 34.30; H 3.96; N 17.82; S 20.07. Calc for $C_9H_{12}N_4NiOS_2$: C 34.31; H 3.85; N 17.76; S 20.35).

Attempts to prepare the corresponding path and tsc compounds were unsuccessful.

[Ni(tah$_2$ 3-methyl-2,4-pentanedione)]. 3-Methyl-2,4-pentanedione was prepared by adding first 37 g (0.37 mol) of 2,4 pentanedione and then 52 g (0.37 mol) of methyl iodide to a chilled solution of 8.5 g (0.37 mol) of sodium metal in 85 g of ethanol, refluxing the mixture for 36 h, cooling to −10 °C, and adding 250 ml of ether to precipitate the sodium iodide formed. The ether was distilled off, and one third of the resulting solution (70 ml, containing 0.125 mol of 3-methyl-2,4-pentanedione) was refluxed with 24.0 g (0.10 mol) of [Ni(tah)$_2$] for 2 days. After cooling to −10 °C the solid was filtered off, washed with ethanol, and dried in air. Yield: 23.5 g of red-brown powder. This was purified by double extraction with ethanol, the second time under an atmosphere of nitrogen. Red-brown crystals were obtained melting at 238 – 240 °C with decomposition. The product was not quite pure but attempts to purify it were unsuccessful. (Found: C 36.81; H 5.25; N 17.73; Ni 17.60; S 19.75. Calc. for $C_{19}H_{16}N_4NiS_2$: C 38.11; H 5.13; N 17.78; Ni 18.63; S 20.35).

During a search for another preparative route to the above complex a compound of composition [Ni(tah$_2$ acacH)].CH_3I was isolated: A mixture of 5 g (0.0092 mol) of (n-C_4H_9)$_4$N[Ni(tah$_2$ acac)] and 6 g (0.042 mol) of methyliodide in 75 ml of ethanol was refluxed for 3 days. After cooling to −10 °C the solid was filtered off, washed with a small portion of ethanol, and dried in air. Yield: 3.5 g (86 %) of a brown-red powder which did not melt below 330 °C. Recrystallization from a variety of solvents invariably led to loss of iodine. (Found: C 26.94; H 3.85; I 28.42; N 13.33; S 14.6. Calc. for $C_{10}H_{17}IN_4NiS_2$: C 27.11; H 3.88; I 28.64; N 12.65; S 14.47).

[Ni(tsc $CH_3COC_6H_4$-4-$SO_3Na)_2$].$4H_2O$. 31.0 g (0.105 mol) of the sodium salt of 4-sulfoacetophenone thiosemicarbazone and 12.5 g (0.053 mol) of nickel chloride hexahydrate were dissolved in 250 ml of water, and a solution of 25 g (0.62 mol) of sodium hydroxide in 25 ml of water was added with stirring. After stirring overnight the mixture was centrifuged, and the solid was washed with water until the colour of the washings changed from yellow to red. The precipitate was extracted with 1 l of hot water, and the red solution was filtered and evaporated to a volume of 500 ml. The precipitate was removed by centrifugation, washed with acetone, and dried at 75 °C. Yield: 15.4 g (46 %) of a dull-green powder. (Found: C 29.81; H 3.66; N 11.85; Na 6.40; Ni 8.6; S 17.63. Calc. for $C_{18}H_{18}N_6Na_2NiO_6S_4 \cdot 4H_2O$: C 30.05; H 3.65; N 11.68; Na 6.39; Ni 8.16; S 17.83).

RESULTS

UV and VIS spectra of a representative series of compounds in aprotic and acid (F_3CCOOH) media are collected in Table 1. Generally one or two weak absorption components in the visible region were found which can be ascribed to $d-d$ transitions. The remainder of the spectrum consists of broad uncharacteristic bands reaching $\varepsilon = (5-30) \times 10^3$. The ^1H NMR spectra are relatively simple because couplings are absent in nearly all the cases studied.

The electrochemical behaviour in dimethylformamide (0.2 M in (n-C_4H_9)$_4$$NClO_4$) of all the compounds have been investigated by cyclic voltametry. It was essential to add activated Al_2O_3 (Woelm neutral alumina) to the solutions in the cell to eliminate protic impurities. Table 2 summarizes the obtained results.

DISCUSSION

The compounds described in the experimental section are all made very easily using template reactions. The thioacylhydrazides are unknown except for those having tertiary α-carbon atoms, and likewise the ketone thioacylhydrazones are unknown. It is therefore interesting that it is possible to trap these hydrazones as their nickel(II) inner complexes. When the complexes precipitate from aqueous solution their stability might be due to their insolubility in water. However, the complexes may be prepared in a homogeneous solution in dimethylsulfoxide and they are generally soluble in polar organic solvents. We thus conclude that the chelation stabilizes the ligand system. In conc. sulfuric acid and in trifluoroacetic acid the complexes are soluble as protonated species. These solutions gave intensely coloured precipitates with conc. perchloric acid, and solutions of zirconium(IV) chloride and antimony(V) chloride in 12 M hydrochloric acid. These precipitates, however, could not be washed or dried without yielding the neutral (and usually differently coloured) complexes. Thus, although the protonated

Table 1. Electronic spectra of nickel complexes given at maximum (or as shoulders) in 10^3 cm^{-1} with molar absorptivity in parenthesis.

Complex	Solvent [a]	
[Ni(tah)$_2$] [b]	DMF	16.4(45), 22.7(135)sh, 23.4(139), 26.2(99)sh, 27.3(130)sh
[Ni(tah)$_2$] [c]	DMF	15.7(386), 21.7(195)sh, 24.7(246)
[Ni(tah)$_2$] [d]		14.5, 17.8, 23.2
[Ni(tah acetone)$_2$]	$CHCl_3$	16.7(120)sh,19.4(250), 28.0(5000)sh, 35.5(19700)sh, 37.0(20800)
[Ni(tah acetophenone)$_2$]	MeCN	18.7(250), 26.2(6000), 41.0(33800)
[Ni(tah$_2$ butanedione)]	$CHCl_3$	15.9(250)sh, 16.8(335), 25.0(2200)sh, 27.4(4500), 35.4(10900)
[Ni(tsc$_2$ butanedione)]	DMSO	15.1(495), 16.7(430)sh, 25.1(11500), 31.5(7500)sh,
[Ni(tah$_2$ acacH)]	MeCN	19.5(230), 24.0(10600), 32.3(7700), 36.4(15100), 40.8(28400)
Bu_4N[Ni(tah$_4$ acac)]	MeCN	19.5(235), 25.0(11300), 34.3(7500)sh, 40.0(27000)sh, 44.9(31200)
[Ni(tah$_2$ acacO)]	MeCN	16.0(340), 19.2(220)sh, 28.8(10050), 32.8(8500), 41.0(20600), 45.6(24000)
[Ni(tah$_2$ 2,5-hexane-dione)]	MeCN	16.4(57)sh, 21.1(253), 36.4(2380)sh, 37.5(13300), 41.7(11920)
[Ni(tah acetophenone)$_2$]	TFAA	17.6(42), 24.1(440)sh, 33.5(8050)
[Ni(tsc acetophenone)$_2$]	TFAA	17.2(97), 20.8(41)sh, 29.4(3800)sh, 40.0(72900)
[Ni(tah$_2$ butanedione)]	TFAA	17.6(300), 25.5(1030)sh, 28.5(2500)sh, 31.0(4700)
[Ni(tah$_2$ acacH)]	TFAA	19.5(99), 24.1(6100), 25.4(3900)sh, 27.2(3100), 31.4(5700)
[Ni(tah$_2$ acacO)]	TFAA	18.2(650), 19.3(660), 30.9(10150), 33.5(9600)

[a] The solvents used are DMF dimethylformamide, MeCN acetonitrile, DMSO dimethyl sulfoxide, TFAA trifluroacetic acid and chloroform. [b] Extrapolated back to time of dissolution. [c] 30 min after dissolution. [d] Diffuse reflectance spectrum.

Table 2. Half wave potentials from cyclic voltametry in dimethylformamide at 10 °C.

Complex	$E°_{\frac{1}{2}}$ V	Peak separation mV	Sweep rate mV/s
Ni(tah acetone)$_2$]	−1.21	90	20
[Ni(path acetone)$_2$]	−1.16	190	100
Ni(tsc acetone)$_2$]	−1.31	310	100
[Ni(tah acetophenone)$_2$]	−1.17	108	25
[Ni(path acetophenone)$_2$]	−1.12	160	5
[Ni(tsc acetophenone)$_2$]	−1.26	105	5
[Ni(tah$_2$ butanedione)]	−0.66	80	10
	−1.58	80	10
[Ni(path$_2$ butanedione)]	−0.65	130	100
	−1.53	185	200
[Ni(tsc$_2$ butanedione)]	−1.28	80	40
	−1.85	95	40
[Ni(bth$_2$ butanedione)] [a]	−0.53		
	−1.24		
[Ni(tah$_2$ benzil)]	−0.42	80	20
	−1.34	90	20
[Ni(tsc$_2$ benzil)]	−1.05	105	15
	−1.64	112	15
[Ni(tah$_2$ acacH)]	no reduction waves observed		
[Ni(tah$_2$ acacO)]	−0.35	171	80
	−1.15	irr.	
[Ni(tah$_2$ 2,5-hexanedione)]	−1.34	80	4
[Ni(tsc 2,5-hexanedione)]	−1.41	145	100
[Ni(tsc 3-hexene-2,5-dione)] [b]	−1.22		

[a] Recorded in dimethyl sulfoxide. bth=$C_6H_5C(S)=N-N=$. See Ref. 22. [b] Ref. 20.

species are analogous to the acid nickel(II) complexes of thiosemicarbazones, they are much weaker bases. The latter kind of complexes have been investigated by X-ray diffraction [13] and spectroscopy.[14,15] It seems established that the complexes are five coordinated in the solid but six coordinated in methanol solutions. From the near-IR bands (Table 1) it seems reasonable to conclude that the thioacylhydrazone nickel complexes behave similarly to the thiosemicarbazone nickel complexes. Bähr [16,17] has earlier prepared nickel(II) complexes of thiosemicarbazonates, and the preparations given here are in some cases easier. For derivatives of diketones like acetylacetone where the thiosemicarbazone is unknown the reported methods of preparation seem to be of general utility.

The planar inner complexes of monoketone derivatives can give rise to *cis-trans* isomerism. Bis(thioacethydrazidato)-nickel(II) [6] (*cf.* Fig. 2) is known to assume the *trans*-form like bis-(thiosemicarbazidato)nickel(II),[18] but bis(acetophenone thioacethydrazonato)nickel(II) was found to have a structure which may be described as a tetrahedrally distorted *cis* planar complex having the phenyl groups in a *syn* configuration (Fig. 3). The electronic spectra reported in Table 1 seem to indicate that also the inner complexes of acetone thioacylhydrazides are *cis* complexes. The diffuse reflectance spectrum of *trans* [Ni(tah)$_2$] shows maxima at 14.5, 17.8 and 23.2 kK. The compound is soluble in dimethyl sulfoxide and dimethylformamide, however, in these solvents the absorption spectrum varies with time presumably because of *trans-cis* rearrangement or extension of the coordination number. Extrapolations to time of dissolution in DMF indicate absorption maxima at 13.4, 15.4 and 23.5 kK. These values are significantly different from the absorption shown by [Ni(tah acetone)$_2$] (16.7 (Sh) and 19.4 kK) in a variety of solvents and on this basis the latter complex is believed to be *cis*. The same conclusion is reached for the butanone derivative. The rather large variation in the position of the maxima for these *cis* complexes and for [Ni(tah acetophenone)$_2$] may reflect the variation of the deviation from co-planarity of the two ligands or the difference in conjugation of the acetophenone derivative compared to the aliphatic derivatives.

Thin layer and column chromatography and the ^{1}H NMR spectra show that [Ni(tah acetophenone)$_2$] exists as only one isomer whereas the product derived from butanone consists of three isomers. Thus it is also demonstrated that the inner complexes are robust in organic solvents as chloroform and benzene used in these experiments. The number of isomers formed by the butanone derivatives can be explained as the *syn*, *anti* and amphi forms of either the *cis* or the *trans* complex. If the assignment of the *cis* planar configuration based on the electronic spectra is correct, it seems that the determining factor in the *cis-trans* isomerism must be the bulkiness of the sulfur atoms and the substantial van der Waal interactions possible in the *cis* complex. This phenomenon was observed [10] for [Ni(tah acetophenone)$_2$].

The ^{1}H NMR spectra of the compounds with the structures shown in Figs. 3, 4, and 6 show a number of peaks corresponding to the presence of a twofold axis of symmetry in each molecule. For [Ni(tah$_2$ acacH)] the low solubility in $CDCl_3$ is a problem, and this complex because of its acid character could in principle have a nitrogen bound proton judged from the acid character of the compound. The complex derived from 3-methyl-2,4-pentanedione was therefore prepared for ^{1}H NMR spectroscopy. The spectrum shows a signal for a methyl group split into a doublet ($J = 7.5$ Hz) and this proves that the methyl group and the acid proton are bound to the same carbon atom.

The colour variation within the series [Ni(tah acetone)$_2$] (reddish-violet), [Ni(tah$_2$ butanedione)] (green), [Ni(tah$_2$ acacH)] (yellow) and [Ni(tah$_2$ acacO)] (green), Figs. 4–6 indicate that the degree of conjugation plays a large role for the spectral properties. The bands in the visible region attributable to the $d-d$ transitions are rather similar for [Ni(tah acetone)$_2$] and [Ni(tah$_2$ acacH)] in accordance with the proposed *cis* structure for the former complex. The smaller $d-d$ transition energies for

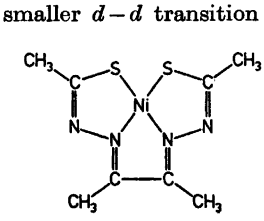

Fig. 4.

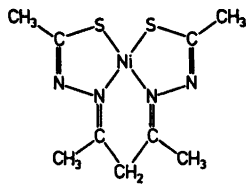

Fig. 5.

[Ni(tah$_2$ butanedione)] (16–17 kK) than for [Ni(tah$_2$ acacH)] (19 kK) reflects the smaller difference between the σ^* and π^* d-orbitals in the complex of the most conjugated ligand.

In view of the common *cis* configuration, the largest structural difference arises in the different planarity of the ligand systems. Only the conjugated ligands can be expected to form planar complexes in which the ligand π orbitals have maximum overlap with the $d\pi$ orbitals. In [Ni(tah acetophenone)$_2$] the two planes defined by S–C=N–N form an angle of 19°. Some deviation from planarity is expected for [Ni(tah acetone)$_2$] for steric reasons but since [Ni(tah$_2$ acacH)] has a very similar spectral behaviour in the visible region one may conclude that the $d\pi$-ligandπ overlaps are roughly equal. The latter compound is soluble in base, and salts containing the anion have been isolated. In not too basic solvents [Ni(tah$_2$ acacH)] or its anion is oxidized by air forming a green complex of the structure shown in Fig. 6. The presence of a ketone group has been established by IR absorption. The compound exhibits a C=O band at 1655 cm^{-1} which compares favourably with the 1663 cm^{-1} band found [19] for $\Delta^{1,4}$-androstadienedione-3,17. The corresponding [Ni(tsc$_2$ acacH)] is much more easily oxidized but the solubility properties of the oxidized compound has so far hindered its isolation.

Electrochemistry. McCleverty *et al.* have reported on the electrochemical properties of

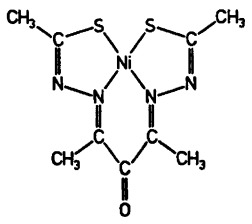

Fig. 6.

eleven nickel complexes of diketone bisthiosemicarbazones.[20] These authors found generally two one-electron reduction steps at *ca.* −1 and −2 V. The rather small variation in $E_{\frac{1}{2}}$ values (~0.2 V) was explained by various substitutional effects and the degree of conjugation in the chelate system. In Table 2 are shown the reduction potentials for a series of thiohydrazonato complexes in *N,N*,-dimethylformamide measured by cyclic voltametry. We have found the procedure of Hammerich and Parker [21] for removal of impurities with alumina very useful since with this technique it was easier to obtain reversible voltamograms for the second reduction.

From Table 2 it is evident that the acyl derivatives are more easily reduced than the corresponding thiosemicarbazones. The monoketone derivatives have reduction potentials more or less uninfluenced by substituents on the carbonyl carbon and the α-carbon of the acyl radical. For the complexes derived from the diketones butanedione and benzil there is a dramatic difference in the $E_{\frac{1}{2}}$ values while again the tah and path derivatives have nearly the same reduction potentials.

The acetylacetone derivatives [Ni(tah$_2$ acacH)] and [Ni(path$_2$ acacH)] give irreversible waves probably because of reactions involving a proton from the methylene group. The anions obtained as the tetrabutylammonium salts gave better voltamograms but they were still not quite reversible.

REFERENCES

1. Jensen, K. A. *Z. Anorg. Allg. Chem. 221* (1934) 11.
2. Jensen, K. A. and Rancke-Madsen, E. *Z. Anorg. Allg. Chem. 219* (1934) 243.
3. Jensen, K. A. *Z. Anorg. Allg. Chem. 229* (1936) 265.
4. Jensen, K. A. and Miquel, J. F. *Acta Chem. Scand. 6* (1952) 189.
5. Jensen, K. A. and Pedersen, C. *Acta Chem. Scand. 15* (1961) 1097.
6. Larsen, E., Trinderup, P., Olsen, B. and Watson, K. J. *Acta Chem. Scand. 24* (1970) 261.
7. Curtis, N. F. *J. Chem. Soc.* (1960) 4409.
8. Liebermeister, K. *Z. Naturforsch. Teil B 5* (1950) 79.
9. Campbell, M. J. M. *Coord. Chem. Rev. 15* (1975) 279.
10. Larsen, S. *Acta Chem. Scand. A 28* (1974) 779.

11. Berntsen, A. *Justus Liebigs Ann. Chem. 184* (1877) 293.
12. Kindler, K. *Justus Liebigs Ann. Chem. 431* (1923) 203.
13. Mathew, M., Palenik, G. J. and Clark, G. R. *Inorg. Chem. 12* (1973) 446.
14. Malik, M. A. and Philips, D. J. *Aust. J. Chem. 28* (1975) 305.
15. Beechroft, B., Campbell, M. J. M. and Grzeskowiak, R. *J. Inorg. Nucl. Chem. 36* (1974) 55.
16. Bähr, G. *Z. Anorg. Allg. Chem. 278* (1955) 136.
17. Bähr, G. *Z. Anorg. Allg. Chem. 280* (1955) 161.
18. Cavalca, L., Nardelli, M. and Fava, G. *Acta Crystallogr. 15* (1962) 1139.
19. Jones, R. N., Humphries, P. and Dobriner, K. *J. Am. Chem. Soc. 72* (1950) 956.
20. Bailey, N. A., Hule, S. E., Jones, C. J. and McCleverty, J. A. *Chem. Commun.* (1970) 124.
21. Hammerich, O. and Parker, V. C. *Electrochim. Acta 18* (1973) 537.
22. Holm, R. H., Balch, A. L., Davidson, A., Maki, A. H. and Berry, T. E. *J. Am. Chem. Soc. 89* (1967) 2866.

Received April 20, 1977.