Preparation and Characterization of Tris(thioacethydrazide)-nickel(II) and Cobalt(III) Complexes

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Tris(thioacethydrazide)nickel(II) salts have been prepared by disproportionation of acidified bis-(thioacethydrazidato)nickel(II). This reaction proves that thioacethydrazide has more stability than formerly believed. Tris(thioacethydrazide)nickel(II) reacts in acidified ethanol with *trans*-dichloridotetra-pyridinecobalt(III) ions to produce *fac*-tris(thio-acethydrazide)cobalt(III) ions. This complex has been resolved into its catoptric forms and characterized by various spectroscopic means (visible and UV absorption, circular dichroism and ^{1}H NMR). The absolute configuration has been established by considering the exciton coupling of the ligand $\pi \rightarrow \pi^*$ transition. The acidity strengths of *fac*-tris(thioacethydrazide)cobalt(III) and *fac*-tris(thio-semicarbazide)cobalt(III) have been determined and the pronounced difference rationalized.

While thiosemicarbazide has been known since 1895[1] the closely analogous thioacethydrazide is until now only known as a ligand in bis(thio-acethydrazidato)nickel(II). This complex precipitates when nickel(II) ions, thioacetamide and hydrazine are all present in an aqueous solution at pH near 4.[2] The ligand has been identified by an X-ray investigation and also complexes of a number of ketone thioacylhydrazones have been characterized structurally.[3–6] It has been inferred that a thiohydrazide derived from an acid having one or more α-hydrogen atoms should be unstable because of a tendency for ring closure reactions.[7,8] In accordance with this, thioacethydrazide has not yet been isolated. However, the molecule must at least be robust enough to survive the transfer from one metal ion to another as this paper will demonstrate, and it can therefore be anticipated that thio-acethydrazide, Htah, can be isolated.

EXPERIMENTAL

Tris(thioacethydrazide)nickel(II) chloride. 100 g (0.4 mol) of [Ni(tah)$_2$][2] was stirred vigorously in 300 ml 6 M hydrochloric acid for 12 h at ambient temperature. After cooling to 5 °C for 1 h the blue precipitate was filtered and washed with 100 ml of a cold 1:1 mixture of 4 M hydrochloric acid and ethanol and then with 3 × 50 ml of ethanol. Yield 104 g (0.25 mol) [Ni(Htah)$_3$]Cl$_2$.H$_2$O. The product was purified by dissolving 5 g in 100 ml of hot water. A small amount of unreacted [Ni(tah)$_2$] was removed by filtration. The volume of the solution was reduced to 20 ml on a rotatory evaporator. 4 g of [Ni(Htah)$_3$]Cl$_2$.H$_2$O was isolated after the addition of 10 ml 12 M hydrochloric acid. Analysis C, H, N, S, Cl, Ni.

The nitrate, sulfate and perchlorate were isolated by analogous procedures.

Tris(thioacethydrazide)cobalt(III) chloride. 4.2 g (10 mmol) of [Ni(Htah)$_3$]Cl$_2$.H$_2$O was dissolved in 50 ml of water. To the solution was added 5 ml 12 M hydrochloric acid and 25 ml of ethanol. This mixture was poured into a solution of 8.9 g (15 mmol) of *trans*-dichloridotetrapyridinecobalt(III) chloride hexahydrate in 200 ml of ethanol. The solution was evaporated to dryness on a rotatory evaporator. From the green crude material the red cobalt complex was obtained either by repeated washing with 50 ml portions of ethanol (up to 1 l) or by ion exchange. For the isolation by ion exchange the crude product was dissolved in 200 ml

of water. After filtration the solution was placed on a 2.5 × 12 cm^2 column of Dowex 50 W X-2 (200 – 400 mesh) in hydrogen ion form. The complex was eluted with 10 M hydrochloric acid. 3 g (6.7 mmol) [Co(Htah)$_3$]Cl$_3$.H$_2$O precipitated from the eluate on standing at 5 °C for 2 h. Analysis C, H, N, S, Cl, Co.

Resolution of [Co(Htah)$_3$]$^{3+}$. Initial experiments involving cation exchange chromatography of 20 mg portions on SP Sephadex C 25 (2 × 50 cm^2) eluted with 0.02 M sodium antimony(III) (+)$_D$-tartrate showed that the complex could be separated into two bands each containing one catoptric form. On a larger scale the method invariably failed because a precipitate formed on the column and functioned as a cement resulting in a very slow flow. Instead of using chromatography for larger scale resolution the diastereoisomeric salt (−)$_D$-*fac*-tris-(thioacethydrazide)cobalt(III) bromocamphor-π-sulfonate dichloride hydrate was precipitated from an aqueous solution made up at 60 °C from 8 g of *fac*-[Co(Htah)$_3$]Cl$_3$.H$_2$O and 8 g of (+)$_D$-ammonium bromocamphor-π-sulfonate (from natural (+)$_D$-camphor). Analysis C, H, N, S.

(−)$_D$-[Co(Htah)$_3$]Cl$_3$ was obtained from the diastereoisomer by dissolving 1 g in 25 ml H$_2$O and passing it first through a 0.5 × 2 cm^2 column of the weak anion exchanger Amberlite CG 4 B as chloride. (From this column the ammonium bromocamphorsulfonate was later isolated by eluting with aqueous ammonia). From the solution passing through the column (−)$_D$-[Co(Htah)$_3$]Cl$_3$ was isolated by ion exchange on Dowex 50 W. Specific rotations at 25 °C were [α]$_{589}$ −4410; [α]$_{578}$ −3950; [α]$_{546}$ −3320; [α]$_{436}$ 5920; [α]$_{364}$ 7800. The most soluble diastereoisomer was not isolated but (+)$_D$-*fac*-[Co(Htah)$_3$]Cl$_3$.H$_2$O was obtained by ion exchange.

Tris(thiosemicarbazide)cobalt(III) chloride trihydrate. The complex was prepared as described in the literature.[10] Analysis C, H, N, S.

Acid-base titrations. Co(Htah)$_3$Cl$_3$.H$_2$O and Co(Htsc)$_3$Cl$_3$.3H$_2$O were both titrated in a 1 M (Na)ClO$_4$ medium thermostated to 25.0 °C with 0.1 M NaOH (+0.9 M NaClO$_4$). pH was measured with Radiometer glass and calomel electrodes on a Radiometer PHM 64 pH-meter. A least squares minimization program written by O. Mønsted[9] was used to calculate pK_a values.

Apparatus. Absorption spectra were recorded on a Cary 118 spectrophotometer and circular dichroism spectra were obtained with an R-J Dichrograph IIIs interfaced with a Tektronix 4051 minicomputer. Optical rotations were measured with a Perkin Elmer 141 polarimeter.

RESULTS AND DISCUSSION

It has been demonstrated that bis(thioacethydrazidato)nickel(II) disproportionates on treatment with excess acid analogously to the behaviour of the bis(thiosemicarbazidato)nickel(II) complex. The preparative yield is close to 100 % based on [Ni(tah)$_2$] and this indicates that the reaction

$$3[Ni(tah)_2] + 6H^+ \rightarrow Ni^{2+} + 2[Ni(Htah)_3]^{2+}$$

is not seriously affected by side reactions leading to destruction of the ligand. Some destruction is, however, obvious from the smell of the reaction mixture. The chloride, sulfate, nitrate, and perchlorate salts have been made. These salts were found to have X-ray powder photographs different from their thiosemicarbazide analogs.

[Ni(Htah)$_3$]$^{2+}$ reacts with base to reform the inner complex quantitatively. Thereby free ligand is liberated and accordingly the mother liquor from the reaction precipitates further [Ni(tah)$_2$] when a solution of [Ni(NH$_3$)$_6$]$^{2+}$ is added. [Ni(Htah)$_3$]$^{2+}$ has the same colour as [Ni(Htsc)$_3$]$^{2+}$ and it is labile in solution. This latter point is demonstrated very dramatically in the preparation of [Co-(Htah)$_3$]$^{3+}$ according to the scheme:

$$[Ni(Htah)_3]^{2+} + trans[Co(pyridine)_4Cl_2]^+ \rightarrow$$
$$[Co(Htah)_3]^{3+} + NiCl_2 + 4 \text{ pyridine}$$

The red cobalt complex is shown to be the *facial* isomer by ^{1}H NMR of D$_2$O and DMSO-d_6 solutions. In both solvents there is observed only one signal due to the three methyl groups giving evidence for the presence of a threefold axis of symmetry. The complex has been resolved into its catoptric forms by precipitation of the salt (−)$_D$-tris(thioacethydrazide)cobalt(III) dichloride (+)$_D$-bromocamphor-π-sulfonate. From the diastereoisomeric salt the cation was isolated as the chloride by ion exchange chromatography. The absorption and circular dichroism spectra shown in Fig. 1 are similar (but CD mirror image) to those reported[10] for (+)$_D$-[Co(Htsc)$_3$]$^{3+}$. Empirical rules connecting the absolute configurations of cobalt(III) complexes with the circular dichroism components of the first spin-allowed absorption band was used to predict that (+)$_D$-*fac*-[Co(Htsc)$_3$]$^{3+}$ has the absolute configuration Λ.[10] However, it is possible to obtain a certain assignment of the absolute configuration based on the exciton coupling of the π-
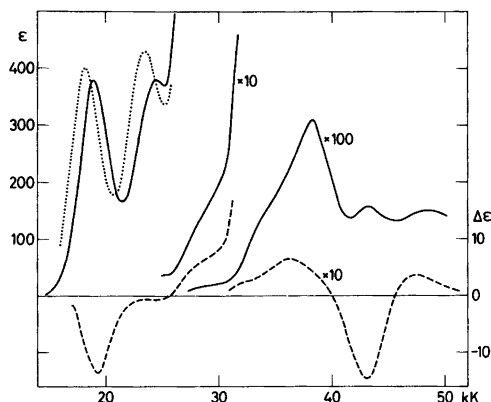
Fig. 1. The absorption (———) and circular dichroism (– – –) spectra for *fac*-[Co(Htah)₃]Cl₃.H₂O in 1 M aqueous perchloric acid (solid lines) and the *vis* absorption of *fac*-[Co(Htsc)₃]Cl₃.3H₂O (· · ·) also in 1 M HClO₄.
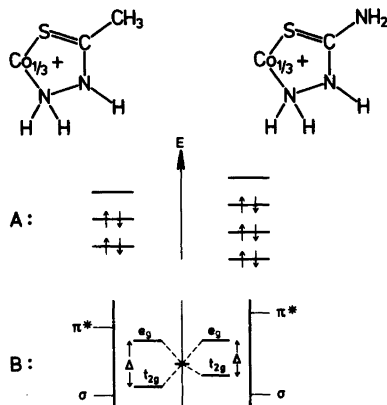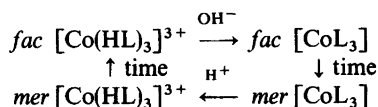

Fig. 2. A: Qualitative MO energies for the π systems of the above given formulas.

B: Schematical demonstration of the interactions between the Co(III) 3d orbitals and the antibonding ligand π orbital of thioacethydrazide and thiosemicarbazide.

chromophores. The $\pi \rightarrow \pi^*$ transition in H_2tsc^+ is found at 41 600 cm^{-1} and it is expected to be at nearly the same energy in H_2tah^+. Near these frequencies the two *fac* complexes $(+)_D$-$[Co(Htsc)_3]^{3+}$ [10] and $(+)_D$-$[Co(Htah)_3]^{3+}$ have strong absorption bands and circular dichroism components of the typical shape [11] for exciton coupled transitions of the absolute configuration Λ.

The absorption maximum at lowest energy is found at 19 100 cm^{-1} for *fac*-$[Co(Htah)_3]^{3+}$ and at 18 200 cm^{-1} for *fac*-$[Co(Htsc)_3]^{3+}$. Considering the similarity between the two ligands this difference in excitation energy may seem large. The difference can be rationalized by simple π-MO theory assuming that the σ conditions are identical for the two complexes. The observed excitation is due to the one electron transition $t_{2g} \rightarrow e_g$ (for simplicity expressed as if the symmetry was O_h). Of these two sets of orbitals the filled d_π orbitals, t_{2g}, interact with the empty antibonding ligand π orbital spanned by $S=C-N$ in Htah and by $S=C(NH_2)-N$ in Htsc. The latter ligand π^*-orbital must have higher energy than that of Htah and therefore the stabilizing effect on the t_{2g} orbitals is largest in $[Co(Htah)_3]^{3+}$ producing the largest difference in $E(e_g) - E(t_{2g})$ which equals Δ in the schematical illustration of these aspects in Fig. 2.

$[Co(Htah)_3]^{3+}$ is an acid and spectroscopic properties will depend on the pH conditions used. The above spectra were obtained from 1 M perchloric

acid solutions. From titration curves of solutions at 25 °C containing 1 M NaClO₄ the pK_a values 1.4, 3.17, and 4.63 have been found. The corresponding pK_a values for the analogous tris(thiosemicarbazide)cobalt(III) complex have been determined under the same conditions to 4.77, 6.16, and 7.53. The difference between the two sets of constants demonstrates very clearly the donation of π-electron density from the amide groups of thiosemicarbazide to the chelate rings.

In spite of the above demonstrated differences between *fac*-$[Co(Htah)_3]^{3+}$ and *fac*-$[Co(Htsc)_3]^{3+}$ the two complex ions resemble each other. On base addition both yield first the *fac* isomer of the neutral complex. This isomer is unstable relative to the *mer* isomer which on acid addition will give first the *meridional* 3+ charged complexes: [10]

$$fac\ [Co(HL)_3]^{3+} \xrightarrow{\ OH^-\ } fac\ [CoL_3]$$
$$\uparrow time \quad _{H^+} \qquad \downarrow time$$
$$mer\ [Co(HL)_3]^{3+} \xleftarrow{\quad} mer\ [CoL_3]$$

The relative instability of thioacethydrazide compared to thiosemicarbazide may be the reason why the above scheme is to some extent disturbed by decompositions and only the *fac* trication form has been characterized as a pure substance. The very fact that the stabilities vary as shown above is in

accordance with the intuitive description behind the formulas I and II.
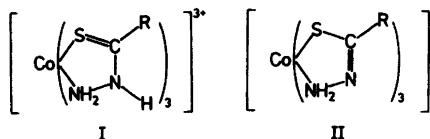
For $[Co(HL)_3]^{3+}$ the *fac* form is most stable mainly because the *mer* isomer has some repulsion between sulfur and the hydrogen on nitrogen. However, in the neutral complexes the sulfur atoms are formally negatively charged and the coulombic repulsion in the *fac* isomer is larger than the S---H repulsion in the *mer* form.

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