

Bis(thioacethydrazidato)nickel(II)**The Preparation from Thioacetamide, Hydrazine and Nickel(II) Ions
and Its Structural Confirmation from an X-Ray
Diffraction Investigation**

ERIK LARSEN and P. TRINDERUP

*Chemical Laboratory I, H. C. Ørsted Institute, The University of Copenhagen,
DK-2100 Copenhagen Ø, Denmark*

BENTE OLSEN and K. J. WATSON

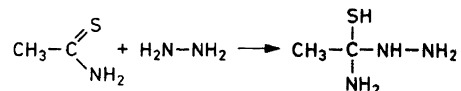
*Chemical Laboratory IV, H. C. Ørsted Institute, The University of Copenhagen,
DK-2100 Copenhagen Ø, Denmark*

Direct substitution of the amide group with a hydrazide group occurs in thioacetamide in the presence of nickel(II) ions and hydrazine, and *trans*-bis(thioacethydrazidato)nickel(II) is formed. This structure has been confirmed by the results of a partial analysis of two-dimensional photographic X-ray diffraction data from a single crystal of the complex. The crystal packing of the molecules is very similar to that found for bis(thiosemicarbazidato)nickel(II).

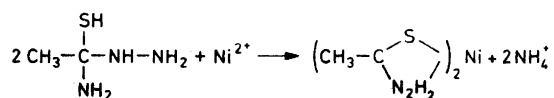
Recently, the use of hydrazine as a catalyst for the hydrolysis of thioacetamide in weakly acid solution has been proposed by King and Anson.¹ This procedure has been investigated here in connection with the intended hydrolytic formation of hydrogen sulfide, to be used for the precipitation of cobalt and nickel sulfides from acetate buffer. As observed previously the precipitate obtained with nickel ions was very coarse. However, its colour was suspiciously light brown for a nickel sulfide and so chemical analyses of it were made. These indicated that not nickel sulfide, but possibly a nickel salt of thioacethydrazide, had been formed. This conclusion was confirmed by the results of a partial single crystal structure analysis of the compound using X-ray diffraction data.

It seems that neither thioacethydrazide nor its nickel complex have been described in the literature.²

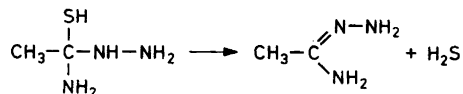
From mainly kinetic studies¹ of the reaction between thioacetamide and hydrazine in weakly acid solutions it was concluded that the first step in the reaction is:



That this compound is formed during the process is strongly supported by the formation of bis(thioacetylhydrazidato)nickel(II), with the liberation of ammonium ions, when the reaction is carried out in the presence of nickel(II) ions:



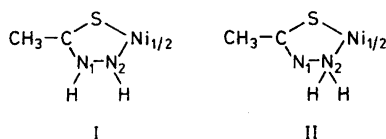
Also, in the absence of nickel(II) ions hydrogen sulfide is liberated, suggesting that acetylhydrazidine is probably produced from the intermediate derivative of *ortho*-acetic acid first formed:



Bis(thioacetylhydrazidato)nickel(II) forms brown, prismatic crystals (thick plates rather than elongated prisms) which are moderately soluble in dimethylsulfoxide, pyridine, diglyme, and *N,N'*-dimethylformamide but which are insoluble in most other usual solvents. In dimethylsulfoxide solution the visible spectrum changes rapidly with time.

The direct substitution of an amide group with hydrazine is so unusual that it seemed of interest to investigate whether the phenomenon is general or specific to only thioacetamide. Experiments towards this end have shown that α -phenylthioacetamide, but not benzthiamide, reacts similarly to thioacetamide. This is notable, since benzthiohydrazide³ and its nickel(II) complex⁴ are known. Phenylthioacetylhydrazide is unstable and decomposes on standing to hydrogen sulphide and 2,5-dibenzyl-1,3,4-thiadiazole.⁵ It seems from these results that aliphatic thiohydrazides with at least one α -hydrogen atom might be too unstable to be isolated.⁵

Whilst the results of the two-dimensional X-ray diffraction study described below leave little doubt about the geometric relations between the heavy (non-hydrogen) atoms of the complex, it has not been possible to determine which of the likely tautomeric forms I or II exists in the crystal structure.



In the analogous *cis*- and *trans*-bis(thioacetylhydroxymato)nickel(II)^{6,7} it is clear that the structures have the formula III.

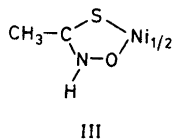


Table 1. Comparison of the reported inter-atomic distances and angles for a number of compounds related to bis(thioacetylhydrazidato)nickel(II). A: bis(thioacetylhydrazidato)nickel(II), predicted from the present study (the distances marked * were assumed — see text); B: bis(thiosemicarbazidato)nickel(II);⁸ C(1): dithiosemicarbazidenickel(II) sulphate trihydrate (“ α -form”);⁹ C(2): dithiosemicarbazidenickel(II) sulphate (“ β -form”);¹⁰ D: *cis*-bis(thioacetylhydroxymato)nickel(II);⁶ E: *trans*-bis(thioacetylhydroxymato)nickel(II).⁷

Distance (Å)	A	B	C(1)	C(2)		D	E
				<i>trans</i> -	<i>cis</i> -		
Ni—S	2.16 *	2.16	2.16	2.17	2.15	2.15	2.18
S—C	1.73 *	1.75	1.75	1.72	1.73	1.73	1.71
C—CH ₃ (or C—NH ₂)	1.45	(1.44)	(1.29)	(1.32)	(1.33)	1.49	1.51
C—N	1.43	1.25	1.33	1.33	1.34	1.29	1.30
N—N (or N—O)	1.48	1.54	1.44	1.43	1.43	(1.35)	(1.37)
N—Ni (or O—Ni)	1.92 *	1.91	1.90	1.93	1.93	(1.87)	(1.86)
Angles (degrees)							
N—Ni—S (or O—Ni—S)	88.7	81.7	90.0	90.0	89.1	(89.0)	(89.4)
Ni—S—C	100.9	102.9	97.2	96.7	97.8	96.5	95.1
S—C—N	117.0	120.9	118.1	120.2	119.3	117.0	118.7
S—C—CH ₃ (or S—C—NH ₂)	125.2	(122.3)	(121.2)	(120.5)	(121.5)	123.5	122.5
N—C—CH ₃ (or N—C—NH ₂)	117.7	(116.4)	(120.6)	(119.3)	(119.2)	119.5	118.8
C—N—N (or C—N—O)	115.3	109.8	119.4	119.2	118.3	(122.5)	(121.6)
N—N—Ni (or N—O—Ni)	117.0	123.8	114.9	113.8	115.2	(115.5)	(115.0)

The molecular geometries found for these and some other, related molecules are very similar to that predicted in this work for bis(thioacetylhydrazidato)nickel(II) (Table 1). Also it is likely that the positively-charged nickel ion would enhance the acidity of the hydrogen atom on N₂ more than on N₁ so that tautomer I is favoured on these grounds. However, from a rather inaccurate crystal structure analysis in which the hydrogen atoms were not directly located, Cavalca *et al.*⁸ conclude, on the basis of a short C—N distance and a proposed intermolecular hydrogen bonding scheme, that both hydrazine hydrogens are bonded to the same nitrogen atom (equivalent to N₂) in struc-

turally similar bis(thiosemicarbazidato)nickel(II). But the inter-atomic angles do not seem to be consistent with this deduction; the same nitrogen, for example, would appear from the Ni—N₂—N₁ angle to have *sp*² hybridized bonds. Some doubt therefore remains about the positions of these hydrogens in crystals of both this molecule and bis(thioacetylhydrazidato)nickel(II). This should be resolved for the latter compound by the results of the detailed X-ray diffraction structure determination which is in progress.

A later communication will describe the formation of condensation products of bis(thioacetylhydrazidato)nickel(II) with certain oxo compounds, which suggests that tautomer II may exist in solution.

EXPERIMENTAL

Bis(thioacetylhydrazidato)nickel(II). To a cold, filtered solution of 25 g (0.1 mole) of nickel acetate tetrahydrate in 400 ml of water and 75 ml of glacial acetic acid was added a solution of 15 g (0.2 mole) of thioacetamide in 200 ml of water. To this a further solution, of 10 ml (0.2 mole) of hydrazine hydrate in 100 ml of water, was added. After standing for two days at room temperature 19 g (0.08 mole) of the desired product had precipitated from the reaction mixture. Recrystallization from dimethylsulfoxide is possible but was not necessary to obtain a pure product. Larger crystals for the X-ray investigation were made by placing a layer of a liquid in which the complex is insoluble (water, dioxane for example) over a diluted solution of the compound in dimethylsulfoxide. After slow diffusion of the two layers into each other crystals appeared in the mixing zone at the glass walls of the container. (Found: C 19.95; H 4.21; N 23.24; S 26.57; Ni 24.75. Calc. for NiC₄H₁₀N₄S₂: C 20.22; H 4.22; N 23.62; S 27.00; Ni 24.81).

Bis(α-phenylthioacetylhydrazidato)nickel(II) monohydrate. The preparation is analogous to that given above except that the thiamide was dissolved in ethanol to provide a homogeneous starting solution. (Found: C 47.58; H 4.92; N 13.75; S 15.49. Calc. for NiC₁₆H₁₈N₄S₂·H₂O: C 47.21; H 4.91; N 13.77; S 15.74).

A thick, rectangular prismatic plate 0.23 × 0.20 × 0.08 mm³ was used for the structure analysis of bis(thioacetylhydrazidato)nickel(II). When viewed perpendicular to the plate faces in polarized light, the crystal was brown and yellow-brown when the electric vector was parallel to the respective pairs of plate edges. Under crossed Nicol prisms there was sharp, parallel extinction in these faces. When the light was propagated parallel to the plate faces and in the former yellow-brown direction, the crystal appeared red-brown and dark brown when the electric vector was perpendicular and parallel, respectively, to the plate faces. There was oblique extinction under crossed Nicols.

Preliminary oscillation and Weissenberg photographs showed that the crystal is monoclinic, the space group being uniquely determined from systematically absent reflections. The unit cell dimensions (see Crystal data) were measured from zero layer Weissenberg photographs taken about the *b* and *c* axes, respectively. The crystal density was measured by flotation in a mixture of tetrabromoethane and bromobenzene.

Multiple-film equi-inclination Weissenberg photographic X-ray diffraction data were collected for the zero layer with rotation axis *b* using CuKα radiation. Their intensities were measured visually by comparison with a standard scale. Lorentz and polarization corrections, but no absorption corrections, were made, after which inter-film scale factors were computed using the least squares method of Hamilton, Rollett and Sparks,¹² and applied to produce a set of 115 independent, non-zero structure amplitudes.

All the computations described were performed on an IBM 7094 computer using modifications of programmes written by Hamilton, Rollett and Sparks¹² (data reduction and scaling), Sly, Shoemaker and van den Hende¹³ (difference electron density map), and Busing, Martin and Levy^{14,15} (full matrix least squares refinement and molecular geometry). The following X-ray atomic scattering factors were used to calculate structure factors: Watson and Freeman¹⁶ for Ni⁺, Dawson¹⁷ for S, Hoerni and Ibers¹⁸ for N and C. The Ni⁺ scattering factor was corrected for the real part of the anomalous dispersion effect.¹⁹

CRYSTAL DATA

Bis(thioacethydrizidato)nickel(II), $\text{Ni}(\text{C}_2\text{H}_5\text{N}_2\text{S})_2$; $M=236.99$. Monoclinic, $a=12.15 \pm 0.02 \text{ \AA}$, $b=4.32 \pm 0.02 \text{ \AA}$, $c=8.74 \pm 0.02 \text{ \AA}$, $\beta=94.1 \pm 0.1^\circ$, $U=460 \pm 3 \text{ \AA}^3$, $D_m=1.71 \pm 0.02 \text{ g/cm}^3$, $Z=2$, $D_c=1.71 \pm 0.02 \text{ g/cm}^3$. Linear absorption coefficient for X-rays ($\lambda_{\text{CuK}\alpha}=1.5418 \text{ \AA}$), $\mu=65 \text{ cm}^{-1}$. Number of electrons per unit cell, $F(000)=244$. Systematically absent reflections: $h0l$ when h is odd, $0k0$ when k is odd; space group $P2_1/a$. Crystals grow as prisms or thick plates which are sometimes elongated and often have inclined faces terminating the elongated growth direction. The plate faces are $\{100\}$ and the other more-developed faces are $\{100\}$ and $\{010\}$; the elongation direction is parallel to b , and is the optically "brown" direction.

STRUCTURE DETERMINATION

The (010) projection of the crystal structure was determined by a symbolic addition procedure²⁰⁻²² using the computer programme written for centrosymmetric distributions by Dewar and Stone, University of Chicago, U.S.A. After computation of a Wilson plot the programme prepared a set of normalized structure amplitudes, $|E_h|$, from which the fifty largest were selected to be used in the sign determination, which was based exclusively upon the satisfaction of the \sum_2 relationship,²¹

$$s E_h \approx s \sum_k E_h \cdot E_{h-k}$$

where s and \approx have their usual meanings of "the sign of" and "probably equals", respectively.

Symbols were assigned to five $|E_h|$'s chosen from as many groups as possible and favouring the larger $|E_h|$'s and those which had most \sum_2 interactions with other $|E_h|$'s of the group. The phases of a further 42 $|E_h|$'s were then determined in three cycles of the usual iterative symbolic addition procedure.²² No probability criteria were applied, all interactions that were satisfied being accepted as long as there were no inconsistencies when several indications for a given phase were produced. After one of the symbols had been given a plus sign to fix an origin it was found that four of the sign combinations possible for the other symbols were equally probable solutions. However, the all-plus combination seemed favoured because the nickel ions were known to be at the centres of symmetry of the structure, and indeed the E -map computed using this solution clearly showed all the (non-hydrogen) atoms in the projection.

The parameters postulated from the E -map were improved by nine cycles of least squares refinement, the first three with individual atomic isotropic temperature factors varied with the positional coordinates and a data scale factor, and the remaining six cycles with anisotropic thermal parameters replacing the isotropic values. Equal weights were given to all data. The final R factor²³ is 0.106. A difference map plotted from the final structure factors, although containing no large peaks or hollows, was not sufficiently clear to indicate the positions of the hydrogen atoms.

the Ni—S (2.163 Å), Ni—N (1.92 Å) and S—C (1.72 Å) inter-atomic distances)⁶⁻¹¹ were assumed as a basis for a prediction of the likely three-dimensional molecular geometry of bis(thioacethydrizidato)nickel(II) (Table 1).

Acknowledgements. All the computations were performed at the Northern European Universities Computing Centre, Lundtofte, Denmark. The valuable observations of J. F. Hansen and J. Gabel are gratefully acknowledged. Two of the authors (B.O. and K.J.W.) express their gratitude to Professor C. J. Ballhausen, in whose excellently appointed laboratory part of the work was undertaken.

REFERENCES

1. King, D. M. and Anson, F. C. *Anal Chem.* **33** (1961) 572.
2. Jensen, K. A. and Pedersen, C. *Acta Chem. Scand.* **15** (1961) 1097.
3. Holmberg, B. *Arkiv Kemi, Mineral. Geol.* **A 17** (1944) No. 23.
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) 1124.
6. Sato, T., Nagata, K., Shiro, M. and Koyama, H. *Chem. Commun.* **1966** 192.
7. Sato, T., Nagata, K., Tsukuda, Y., Shiro, M. and Koyama, H. *Chem. Commun.* **1967** 215.
8. Cavalca, L., Nardelli, M. and Fava, G. *Acta Cryst.* **15** (1962) 1139.
9. Grønbaek, R. and Rasmussen, S. E. *Acta Chem. Scand.* **16** (1962) 2325.
10. Grønbaek Hazell, R. *Acta Chem. Scand.* **22** (1968) 2171.
11. Taylor, M. R., Gabe, E. J., Glusker, J. P., Minkin, J. E. and Patterson, A. L. *J. Am. Chem. Soc.* **88** (1966) 1845.
12. Hamilton, W. C., Rollett, J. S. and Sparks, R. A. *Acta Cryst.* **18** (1965) 129.
13. Sly, W. G., Shoemaker, D. P. and van den Hende, J. H. *Two and Three Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer*, Esso Research and Engineering Company, publication CBRL-22M-62 (1962).
14. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS, A Fortran Crystallographic Least Squares Program*, Oak Ridge National Laboratory, publication ORNL-TM-305 (1962).
15. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFFE, A Fortran Crystallographic Function and Error Program*, Oak Ridge National Laboratory, publication ORNL-TM-306 (1964).
16. Watson, R. E. and Freeman, A. J. *Acta Cryst.* **14** (1961) 27.
17. Dawson, B. *Acta Cryst.* **13** (1960) 403.
18. Hoerni, J. A. and Ibers, J. A. *Acta Cryst.* **7** (1954) 744.
19. Dauben, C. H. and Templeton, D. H. *Acta Cryst.* **8** (1955) 841.
20. Zachariassen, W. H. *Acta Cryst.* **5** (1952) 68.
21. Hauptman, H. and Karle, J. *Solution of the Phase Problem. I. The Centrosymmetric Crystal*, A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service 1953.
22. Karle, J. and Karle, I. L. *Acta Cryst.* **21** (1966) 849.
23. Defined, as usual, as $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ where F_o and F_c are the observed and calculated structure factors. The summations were for non-zero observed data only.

Received July 1, 1969.