

- State University and Institute for Atomic Research, Ames, Iowa, 1971.
- (22) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
- (23) D. H. Templeton in "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215-216.
- (24) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error, Program", U.S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
- (25) J. E. Fergusson in "Preparative Inorganic Reactions", Vol. 7, W. L. Jolly, Ed., Wiley-Interscience, New York, N.Y., 1971, pp 93-163.
- (26) E. T. Maas, Jr., and R. E. McCarley, *Inorg. Chem.*, **12**, 1096 (1973).
- (27) R. J. Ziegler and W. M. Risen, *Inorg. Chem.*, **11**, 2796 (1972).
- (28) H. Jahn and E. Teller, *Phys. Rev.*, **49**, 874 (1937).

Contribution from the Department of Chemistry,  
Emory University, Atlanta, Georgia 30322

## Synthesis and Crystal Structure of (Dimethylthiocarboxamido)(dimethylamino[dimethyldithiocarbamato]carbene)nickel(II)

### Tetraphenylborate, $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{BPh}_4$ , a Stable Nickel Carbene Complex

WALTER K. DEAN,\* ROBERT S. CHARLES, and DONALD G. VANDERVEER

Received May 16, 1977

AC170349K

The title compound  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{BPh}_4$  has been prepared by the direct reaction of dimethylthiocarbamoyl chloride with nickel carbonyl or with bis(cyclopentadienyl)nickel, followed by metathesis with  $\text{NaBPh}_4$ . The compound crystallizes in the monoclinic space group  $P2_1/n$  with four formula units in a unit cell with dimensions  $a = 9.208$  (2) Å,  $b = 22.837$  (8) Å,  $c = 15.823$  (5) Å, and  $\beta = 99.01$  (2)°. Full-matrix least-squares refinement of 2496 independent counter data yielded a final unweighted  $R$  factor of 0.074. The planar cation contains a chelating thiocarboximido group and a (dimethylamino)dimethyldithiocarbamatocarbene ligand in which the dithiocarbamato group is coordinated to the nickel by one sulfur atom, forming a unique chelating carbene ligand. The structural features of this complex are discussed and compared with those of related compounds. The two nickel-carbon distances are 1.854 (11) Å (to the thiocarboxamido group) and 1.909 (10) Å (to the carbene ligand); there appears to be no indication of substantial  $\pi$  interaction between the nickel atom and the carbenoid carbon atoms in this compound.

### Introduction

In previous papers we have reported reactions of dimethylthiocarbamoyl chloride with metal carbonyl anions,<sup>1</sup> and recently we have extended these investigations to include reactions of this versatile reagent with neutral metal carbonyls as well.<sup>2</sup> These reactions yield a variety of metal complexes containing dithiocarbamate ligands, chelating and bridging thiocarboxamido groups, and various exotic carbene ligands.

In this paper we report the reaction of dimethylthiocarbamoyl chloride with nickel tetracarbonyl or nickelocene to give complexes initially formulated as  $[\text{Ni}(\text{CSNMe}_2)_3]\text{X}$  ( $\text{X}^- = \text{Cl}^-, \text{PF}_6^-, \text{BPh}_4^-$ ). These products are isolated as orange, diamagnetic solids which are stable indefinitely in air. Their NMR spectra show all methyl groups to be nonequivalent, and no clues to their structure were provided by other spectroscopic methods. Accordingly a crystal structure study was undertaken of the tetraphenylborate salt with a view to its structural characterization. The results of this study, along with an account of the syntheses of the complexes, are reported here.

### Experimental Section

**Synthesis of the Complexes.** All reagents were obtained from commercial sources. Dimethylthiocarbamoyl chloride ( $\text{ClCSNMe}_2$ ) was recrystallized from diethyl ether before use. Tetrahydrofuran was distilled from calcium hydride. All operations were performed under a nitrogen atmosphere.

Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer. Proton NMR measurements were made with a Jeol JNM-MH-100 instrument. Analyses were performed by the Atlantic Microanalytical Laboratories, Atlanta, Ga.

**Reaction of Nickel Carbonyl with  $\text{ClCSN}(\text{CH}_3)_2$ .**  $\text{Ni}(\text{CO})_4$  (1.00 g, 5.85 mmol) and  $\text{ClCSNMe}_2$  (2.17 g, 17.6 mmol) were stirred in 50 mL of tetrahydrofuran. Evolution of CO was observed and the product separated as an orange precipitate. After 18 h the reaction was complete; the mixture was diluted with 100 mL of diethyl ether, stirred for 1 h, and filtered, yielding 1.23 g (3.42 mmol, 58.4%) of



The same compound was obtained in 48.5% yield by the reaction of bis(cyclopentadienyl)nickel with  $\text{ClCSNMe}_2$  under the same conditions.

Because the chloride was rather hygroscopic, it was converted quantitatively into the hexafluorophosphate or tetraphenylborate (by treatment with aqueous  $\text{NH}_4\text{PF}_6$  or  $\text{NaBPh}_4$ ) before analysis.

Analytical, NMR, and infrared data on these compounds are given in Table I.

**Collection of X-Ray Diffraction Data.** Suitable crystals of  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{BPh}_4$  were obtained by slow cooling of an acetone solution of the salt. Crystals were mounted on glass fibers with epoxy cement. Examination of preliminary Weissenberg and precession photographs showed systematic absences ( $0k0$ ,  $k = 2n + 1$ ;  $h0l$ ,  $h + l = 2n + 1$ ) indicating space group  $P2_1/n$ , a nonstandard setting of space group  $P2_1/c$  which was maintained throughout the structure solution and refinement because of the near orthogonality of the axes.

Intensity data were collected on a Syntex  $P2_1$  automated four-circle diffractometer equipped with a graphite monochromator. The data were corrected for Lorentz and polarization effects, using the form of the  $Lp$  factor given in eq 1. (This equation assumes that the

$$Lp = \frac{0.5}{\sin 2\theta} \left[ \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{1 + \cos^2 2\theta_m} + \left( \frac{1 + |\cos 2\theta_m| \cos^2 2\theta}{1 + |\cos 2\theta_m|} \right) \right] \quad (1)$$

graphite monochromator crystal is 50% perfect and 50% mosaic; the monochromator angle  $2\theta_m$  is 12.2° for Mo  $K\alpha$  radiation.)

Standard deviations  $\sigma(I)$  were estimated by the procedure of Doedens and Ibers,<sup>3</sup> using an "ignorance factor" of 0.05. No corrections were made for absorption.

Because the first crystal diffracted weakly, giving an abnormally high percentage of unobserved reflections, a second data set was collected using a different crystal. The two sets were of comparable quality and were correlated before the final refinement. A total of

Table I. Analytical and Spectroscopic Data

	[Me <sub>2</sub> NCSNiC(NMe <sub>2</sub> )SC(NMe <sub>2</sub> )S]PF <sub>6</sub>	[Me <sub>2</sub> NCSNiC(NMe <sub>2</sub> )SC(NMe <sub>2</sub> )S]BPh <sub>4</sub>
	Orange powder, mp 197–198 °C	Orange crystals, mp 122–123 °C
Analysis, % calcd (found)	C, 23.1 (23.0); H, 3.9 (3.9); N, 9.0 (8.9); S, 20.5 (20.4)	C, 61.7 (61.5); H, 5.9 (6.2); N, 6.6 (6.6); S, 15.0 (14.9)
NMR spectrum (acetone- <i>d</i> <sub>6</sub> )	CH <sub>3</sub> : singlets, τ 5.90 (3), 6.19 (6), 6.23 (3), 6.42 (3), 6.64 (3)	CH <sub>3</sub> : singlets, τ 5.96 (3), 6.28 (3) 6.32 (3), 6.36 (3), 6.45 (3), 6.60 (3) C <sub>6</sub> H <sub>5</sub> : multiplet, τ 2.4–3.4 (20)
Prominent IR peaks (C=N stretch, KBr disk, cm <sup>-1</sup> )	1600 s, 1535 vs, 1400 s	1590 vs, 1576 s, sh, 1525 vs, 1395 s

Table II. Crystal Data and Details of Intensity Data Collection

(A) Crystal Data	
Formula (mol wt)	C <sub>33</sub> H <sub>38</sub> BN <sub>3</sub> S <sub>3</sub> Ni (642.40)
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å (25 °C)	9.208 (2) <sup>a</sup>
<i>b</i> , Å	22.837 (8)
<i>c</i> , Å	15.823 (5)
β, deg	99.01 (2)
<i>V</i> , Å <sup>3</sup>	3286.3 (17)
<i>Z</i>	4
<i>d</i> exptl (calcd), g cm <sup>-3</sup>	1.291 <sup>b</sup> (1.298)
<i>F</i> (000), electrons	1352
Crystal dimensions, mm	0.18 × 0.18 × 0.50 (1st data set) 0.20 × 0.10 × 0.50 (2nd data set)
μ, cm <sup>-1</sup>	7.81
Est'd range of transmission coeff	0.84–0.92
(B) Collection of Intensity Data	
Radiation	Mo Kα (λ = 0.710 730 Å)
Monochromator angle, deg	12.2
Takeoff angle, deg	6.9
Reflections meas'd	± <i>h</i> , + <i>k</i> , + <i>l</i>
2θ range, deg	5–50
Scan type	θ(crystal)–2θ(counter)
Scan speed, deg/min	4.9
Scan range	[2θ(Kα <sub>1</sub> ) – 1.4°] → [2θ(Kα <sub>2</sub> ) + 1.4°]
Background measurements	At beginning and end of each scan, each for half the total scan time
Standards	3 every 100 reflections

<sup>a</sup> Based on a least-squares fit to the setting angles of the unresolved Mo Kα peaks of 15 reflections with 2θ = 9–18°.

<sup>b</sup> Measured by neutral buoyancy in aqueous NaI.

6200 independent reflections were measured, of which 2496 were considered observed [*I* ≥ 3σ(*I*)]. Only the observed reflections were used in the refinement of the structure.

Further unit cell, crystal, and intensity collection data are given in Table II.

**Determination of the Structure.** The structure was solved by heavy-atom methods. A three-dimensional Patterson map yielded coordinates for the nickel atom, and a Fourier map phased on this position revealed the three sulfurs. These four positions were least-squares refined, and a second Fourier map showed all remaining nonhydrogen atoms.

The refinement of the structure proceeded smoothly; details are given in Table III.

The final model included anisotropic thermal parameters for the atoms of the cation; the atoms of the tetraphenylborate anion were refined isotropically, with the inclusion of phenyl hydrogen atoms in calculated idealized positions.

All least-squares cycles were based on the minimization of  $\sum w||F_o| - |F_c||^2$ , where  $w = \sigma(F_o)^{-2}$ . The atomic scattering factors of Cromer and Mann<sup>4a</sup> for neutral atoms were used, with corrections for both the real and imaginary components of anomalous dispersion for the nickel and sulfur atoms.<sup>4b</sup> Discrepancy indices used are defined in eq 2 and 3. The goodness of fit (GOF) is defined in eq 4, where *n*

$$R = (\sum ||F_o| - |F_c||) / \sum |F_o| \quad (2)$$

$$R_w = [(\sum w ||F_o| - |F_c||^2) / \sum w |F_o|^2]^{1/2} \quad (3)$$

$$\text{GOF} = (\sum w (|F_o| - |F_c|)^2) / (n - \nu) \quad (4)$$

Table III. Refinement of the Structure Model

All atoms isotropic	<i>R</i> = 0.099, <i>R<sub>w</sub></i> = 0.134
Cation atoms anisotropic; anion atoms isotropic; calculated phenyl hydrogen positions	<i>R</i> = 0.074, <i>R<sub>w</sub></i> = 0.081
No. of variables	245
Final data:parameter ratio	10.2:1
Max electron density on final difference Fourier map, e Å <sup>-3</sup>	0.36
GOF	2.45

is the number of observations and *ν* is the number of variables.

The values of |*F<sub>o</sub>*| and |*F<sub>c</sub>*| (in electrons × 10) for those reflections used in the refinement are given in Table IV (supplementary material). The positional and thermal parameters for all atoms are presented in Table V. Interatomic distances and angles are given in Table VI.

Computer programs used included locally written programs for data reduction and correlation, hydrogen atom location, and least-squares planes. Also used were modified versions of Zalkin's FORDAP (Patterson and Fourier maps; ORFLS (least-squares refinement) and ORFFE (function and error program), both by Busing, Martin, and Levy; and Johnson's ORTEP plotting program.

## Results

**General Description of the Structure.** The compound [Me<sub>2</sub>NCSNiC(NMe<sub>2</sub>)SC(NMe<sub>2</sub>)S]BPh<sub>4</sub> consists of discrete complex cations and tetraphenylborate anions. The cation, which is shown in Figure 1, contains Ni(II) coordinated by two chelating ligands. One of these is a thiocarboxamido group, such as has been found in other complexes.<sup>1,2</sup> The other ligand can best be described as a chelating (dimethylamino)dimethyldithiocarbamatocarbene ligand, formed by the joining of two thiocarboxamido groups through a carbon–sulfur bond; it is coordinated through the carbenoid carbon and the more remote sulfur atom.

The nickel atom is four-coordinate and the complex is nearly planar; the dihedral angle between the planes defined by the two ligands (see Table VI) is 169.3°. It is, however, highly distorted away from a square-planar geometry by the compactness of thiocarboxamido ligand, which results in a very acute S(1)–Ni–C(1) angle of 50.0°. The remaining angles about the nickel atom open up somewhat to compensate (S(3)–Ni–C(4), 95.7°; S(3)–Ni–C(1), 102.4°; S(1)–Ni–C(4), 113.6°). The thiocarboxamido ligand is quite planar, but the carbene ligand is less so; the atoms of the dimethylamino groups lie as much as 0.26 Å from the least-squares plane through this ligand.

The tetraphenylborate anion is distorted slightly from tetrahedral symmetry, with B–C distances of 1.64–1.66 Å and C–B–C angles of 104–114°. Within the phenyl rings, the C–C–C angles about the carbon bonded to boron are all well under 120° (ranging from 114.1 to 117.0°). Similar distortions have been observed in other EPh<sub>4</sub> species (E = B, C, Si, Ge, but not As); the range of angles seen here is comparable to that found in BPh<sub>4</sub><sup>-</sup> in other studies.<sup>5</sup>

Table V

Final Atomic Parameters								
Atom <sup>a</sup>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å <sup>2</sup>	Atom <sup>a</sup>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	0.1886 (1)	0.00748 (5)	0.08209 (8)		H(11) <sup>b</sup>	0.1925	-0.1635	0.3038
S(1)	0.3059 (4)	-0.0707 (1)	0.1344 (2)		H(12)	0.4302	-0.1240	0.3109
S(2)	0.0441 (3)	0.1289 (1)	0.1351 (2)		H(13)	0.5592	-0.0964	0.4408
S(3)	0.1322 (3)	0.0685 (1)	-0.0202 (2)		H(14)	0.4522	-0.1051	0.5650
N(1)	0.3546 (9)	-0.0666 (4)	-0.0317 (5)		H(15)	0.2151	-0.1459	0.5581
N(2)	0.0906 (9)	0.0395 (4)	0.2456 (5)		H(17)	-0.0403	-0.0777	0.4964
N(3)	0.0337 (8)	0.1777 (4)	-0.0120 (5)		H(18)	-0.1808	0.0045	0.4551
C(1)	0.2983 (10)	-0.0477 (4)	0.0337 (7)		H(19)	-0.3216	0.0090	0.3221
C(2)	0.4461 (13)	-0.1210 (5)	-0.0235 (7)		H(20)	-0.3230	-0.0677	0.2280
C(3)	0.3315 (13)	-0.0365 (5)	-0.1157 (6)		H(21)	-0.1766	-0.1499	0.2678
C(4)	0.1062 (10)	0.0518 (4)	0.1652 (7)		H(23)	-0.2497	-0.2325	0.3396
C(5)	0.0326 (14)	0.0814 (5)	0.3038 (6)		H(24)	-0.3016	-0.3133	0.2506
C(6)	0.1299 (15)	-0.0179 (5)	0.2825 (7)		H(25)	0.1174	-0.3698	0.2125
C(7)	0.0686 (10)	0.1280 (5)	0.0286 (6)		H(26)	0.1281	-0.3479	0.2658
C(8)	-0.0158 (14)	0.2302 (4)	0.0329 (7)		H(27)	0.1814	-0.2665	0.3545
C(9)	0.0444 (13)	0.1843 (5)	-0.1049 (6)		H(29)	0.1482	-0.2591	0.5406
C(10)	0.1766 (9)	-0.1593 (4)	0.4304 (5)	3.4 (2)	H(30)	0.0889	-0.2993	0.6698
C(11)	0.2446 (10)	-0.1520 (4)	0.3579 (5)	4.0 (2)	H(31)	-0.1213	-0.2723	0.7168
C(12)	0.3874 (10)	-0.1283 (4)	0.3617 (6)	4.6 (2)	H(32)	-0.2792	-0.2062	0.6456
C(13)	0.4623 (10)	-0.1119 (4)	0.4377 (6)	4.7 (2)	H(33)	-0.2285	-0.1658	0.5127
C(14)	0.3996 (11)	-0.1175 (4)	0.5115 (6)	5.4 (2)				
C(15)	0.2569 (10)	-0.1417 (4)	0.5070 (6)	4.2 (2)				
C(16)	-0.0951 (9)	-0.1255 (4)	0.3877 (5)	3.2 (2)				
C(17)	-0.0981 (10)	-0.0769 (4)	0.4410 (5)	4.3 (2)				
C(18)	-0.1815 (11)	-0.0275 (4)	0.4167 (6)	5.3 (2)				
C(19)	-0.2637 (12)	-0.0249 (5)	0.3384 (7)	6.2 (3)				
C(20)	-0.2647 (11)	-0.0696 (5)	0.2830 (6)	5.4 (2)				
C(21)	-0.1780 (10)	-0.1191 (4)	0.3080 (6)	4.5 (2)				
C(22)	-0.0252 (9)	-0.2397 (3)	0.3562 (5)	3.1 (2)				
C(23)	-0.1708 (10)	-0.2553 (4)	0.3247 (5)	4.1 (2)				
C(24)	-0.2017 (10)	-0.3038 (4)	0.2715 (6)	4.7 (2)				
C(25)	-0.0941 (11)	-0.3372 (4)	0.2494 (6)	5.1 (2)				
C(26)	0.0504 (11)	-0.3241 (5)	0.2803 (6)	5.2 (2)				
C(27)	0.0812 (10)	-0.2753 (4)	0.3333 (5)	4.0 (2)				
C(28)	-0.0340 (9)	-0.2071 (4)	0.5128 (5)	3.4 (2)				
C(29)	0.0596 (10)	-0.2476 (4)	0.5603 (6)	4.9 (2)				
C(30)	0.0245 (12)	-0.2719 (5)	0.6381 (7)	6.2 (3)				
C(31)	-0.0986 (12)	-0.2558 (5)	0.6652 (7)	6.0 (3)				
C(32)	-0.1926 (12)	-0.2172 (5)	0.6234 (6)	5.9 (2)				
C(33)	-0.1608 (10)	-0.1924 (4)	0.5437 (6)	4.4 (2)				
B	0.0059 (10)	-0.1828 (4)	0.4200 (6)	3.1 (2)				

Anisotropic Thermal Parameters<sup>a</sup>

Atom	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>	Atom	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Ni	5.32 (7)	4.32 (7)	4.67 (6)	0.48 (6)	1.63 (5)	0.35 (6)	C(2)	10.3 (8)	5.7 (6)	6.1 (6)	4.2 (6)	1.2 (6)	0.0 (5)
S(1)	8.6 (2)	6.2 (2)	5.5 (2)	2.9 (1)	1.6 (1)	1.5 (1)	C(3)	10.4 (8)	5.7 (6)	3.7 (5)	2.3 (6)	1.7 (5)	1.6 (5)
S(2)	7.2 (2)	4.7 (1)	5.6 (1)	0.9 (1)	2.1 (1)	0.3 (1)	C(4)	4.3 (5)	3.4 (5)	7.4 (7)	-0.4 (4)	1.2 (5)	0.4 (5)
S(3)	7.3 (2)	4.5 (1)	5.5 (1)	1.1 (1)	1.7 (1)	0.1 (1)	C(5)	11.5 (9)	5.9 (7)	4.5 (5)	0.4 (6)	3.8 (6)	-1.2 (5)
N(1)	5.7 (5)	5.2 (5)	5.3 (5)	0.6 (4)	1.2 (4)	-1.9 (4)	C(6)	12.5 (9)	4.7 (6)	7.7 (7)	1.4 (6)	4.5 (6)	3.6 (5)
N(2)	7.1 (5)	5.0 (5)	5.0 (5)	-1.4 (4)	2.9 (4)	0.5 (4)	C(7)	3.5 (5)	4.7 (6)	6.0 (6)	0.0 (4)	1.1 (4)	-1.6 (5)
N(3)	5.3 (5)	3.9 (4)	6.3 (5)	1.0 (4)	0.8 (4)	1.2 (4)	C(8)	10.7 (8)	3.3 (5)	7.2 (7)	2.5 (5)	1.9 (6)	-0.9 (5)
C(1)	4.8 (5)	3.7 (5)	6.0 (6)	0.4 (4)	0.3 (5)	1.1 (5)	C(9)	8.7 (7)	6.3 (7)	5.0 (6)	2.0 (6)	2.3 (5)	2.6 (5)

<sup>a</sup> The atoms of the cation are numbered as shown in Figure 1. The ring carbon atoms of the tetraphenylborate anion are numbered thus:

B-10-11-12-13-14-15; B-16-17-18-19-20-21; B-22-23-24-25-26-27; B-28-29-30-31-32-33. H(11) is bonded to C(11), etc. <sup>b</sup> The positions of the hydrogen atoms were calculated as follows. The hydrogen atom was placed 0.95 Å from the carbon atom to which it is bonded, along a line in the plane of and bisecting the angle between this carbon and its two neighboring carbon atoms. Each hydrogen was assigned an isotropic temperature factor equal to that of the carbon to which it is bonded. <sup>c</sup> Anisotropic temperature factors of the form  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$  were used for these atoms.

The crystal packing in this compound is determined primarily by electrostatic and van der Waals forces, as shown by the intermolecular distances, the shortest of which are given in Table VI.

**Bonding in the [Me<sub>2</sub>NCSNiC(NMe<sub>2</sub>)SC(NMe<sub>2</sub>)S]<sup>+</sup> Ion.** Carbene complexes of nickel are rather rare. In addition to a few very unstable nickel(0) complexes,<sup>6,7</sup> several carbene complexes of nickel(II) have been reported, including [C]Ni[CN(Me)CH<sub>2</sub>CH<sub>2</sub>N(Me)]<sub>3</sub>BF<sub>4</sub>,<sup>8</sup> [Cl][Ph<sub>3</sub>P]<sub>2</sub>Ni[CN-MeCH<sub>2</sub>CH<sub>2</sub>CHMeS]BF<sub>4</sub>,<sup>9</sup> and some CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>-

Ni(CNR)[C(NHR)NR'] complexes.<sup>10</sup> No crystal structures of nickel(II) complexes with carbene ligands have previously been reported, and no data concerning the relationship of structure and bonding in such complexes have been available.

The nickel-carbon bond distances in the [Me<sub>2</sub>NCSNiC(NMe<sub>2</sub>)SC(NMe<sub>2</sub>)S]<sup>+</sup> ion are 1.854 Å (to the carbon of the thiocarboxamido group, C(1)) and 1.909 Å (to the carbon of the chelating carbene ligand, C(4)). These distances are almost exactly equal to the sum of the covalent radii of the atoms: C(sp<sup>2</sup>), 0.72 Å; Ni, 1.15 Å<sup>11</sup> or 1.18 Å.<sup>12</sup> They are

Table VI. Interatomic Distances, Angles, and Least-Squares Planes

A. Interatomic Distances (Å)				C. Bond Angles (deg)			
Cation				Cation (Continued)			
Ni-S(1)	2.181 (3)	N(1)-C(2)	1.495 (13)	C(4)-S(2)-C(7)	102.9 (5)	Ni-C(4)-S(2)	116.9 (6)
Ni-S(3)	2.138 (3)	N(1)-C(3)	1.481 (12)	Ni-S(3)-C(7)	103.6 (4)	Ni-C(4)-N(2)	131.2 (7)
Ni-C(1)	1.854 (11)	N(2)-C(4)	1.332 (11)	C(1)-N(1)-C(2)	119.6 (9)	S(2)-C(4)-N(2)	111.9 (7)
Ni-C(4)	1.909 (10)	N(2)-C(5)	1.485 (12)	C(1)-N(1)-C(3)	122.7 (9)	S(2)-C(7)-S(3)	120.1 (6)
S(1)-C(1)	1.668 (10)	N(2)-C(6)	1.458 (12)	C(2)-N(1)-C(3)	117.6 (8)	S(2)-C(7)-N(3)	117.3 (7)
S(2)-C(4)	1.783 (10)	N(3)-C(7)	1.321 (11)	C(4)-N(2)-C(5)	124.0 (9)	S(3)-C(7)-N(3)	122.5 (8)
S(2)-C(7)	1.737 (11)	N(3)-C(8)	1.499 (12)	C(4)-N(2)-C(6)	121.1 (9)		
S(3)-C(7)	1.710 (10)	N(3)-C(9)	1.496 (11)				
N(1)-C(1)	1.302 (11)						
Anion				Anion			
B-C(10)	1.645 (12)	C(20)-C(21)	1.405 (12)	C(10)-B-C(16)	104.9 (7)	C(18)-C(19)-C(20)	120.7 (10)
B-C(16)	1.640 (12)	C(21)-C(16)	1.376 (11)	C(10)-C-C(22)	113.1 (7)	C(19)-C(20)-C(21)	118.8 (9)
B-C(22)	1.642 (12)	C(22)-C(23)	1.402 (11)	C(10)-C-C(28)	111.1 (7)	C(20)-C(21)-C(16)	123.6 (9)
B-C(28)	1.664 (12)	C(23)-C(24)	1.392 (11)	C(16)-B-C(22)	113.9 (7)	B-C(22)-C(23)	119.0 (7)
C(10)-C(11)	1.400 (10)	C(24)-C(25)	1.340 (12)	C(16)-B-C(28)	110.4 (7)	B-C(22)-C(27)	124.8 (7)
C(11)-C(12)	1.415 (12)	C(25)-C(26)	1.377 (12)	C(22)-B-C(28)	103.7 (7)	C(27)-C(22)-C(23)	116.1 (8)
C(12)-C(13)	1.343 (11)	C(26)-C(27)	1.398 (12)	B-C(10)-C(11)	119.9 (7)	C(22)-C(23)-C(24)	120.8 (8)
C(13)-C(14)	1.388 (12)	C(27)-C(22)	1.365 (11)	B-C(10)-C(15)	123.8 (7)	C(23)-C(24)-C(25)	121.4 (9)
C(14)-C(15)	1.417 (12)	C(28)-C(29)	1.400 (11)	C(11)-C(10)-C(15)	116.1 (8)	C(24)-C(25)-C(26)	119.9 (9)
C(15)-C(10)	1.377 (11)	C(29)-C(30)	1.431 (13)	C(10)-C(11)-C(12)	122.8 (8)	C(25)-C(26)-C(27)	118.7 (9)
C(16)-C(17)	1.397 (11)	C(30)-C(31)	1.326 (13)	C(11)-C(12)-C(13)	119.3 (9)	C(26)-C(27)-C(22)	123.2 (8)
C(17)-C(18)	1.385 (12)	C(31)-C(32)	1.334 (13)	C(12)-C(13)-C(14)	120.3 (9)	B-C(28)-C(29)	119.5 (9)
C(18)-C(19)	1.349 (12)	C(32)-C(33)	1.453 (12)	C(13)-C(14)-C(15)	119.9 (9)	B-C(28)-C(33)	123.3 (8)
C(19)-C(20)	1.344 (13)	C(33)-C(28)	1.377 (11)	C(14)-C(15)-C(10)	121.6 (8)	C(33)-C(28)-C(29)	117.0 (8)
B. Nonbonding Distances Less Than 3.5 Å				D. Least-Squares Planes			
C(2)···C(29)	3.381	C(5)···C(32)	3.547	1. Plane through Ni, S(1), C(1)			
Ni···S(3)	3.434	C(8)···C(32)	3.562	7.291x + 12.479y + 2.300z = -1.657			
C(24)···C(30)	3.483	C(3)···C(20)	3.570	Atomic Displacements from the Plane, Å			
C(8)···C(33)	3.512	C(5)···C(33)	3.571	Ni	0.000	N(1)	0.024
C(2)···C(30)	3.531			S(1)	0.000	C(2)	0.031
C. Bond Angles (deg)				C(1)	0.000	C(3)	0.038
Cation				2. Plane through Ni, S(2), S(3), C(4), C(7)			
S(1)-Ni-S(3)	150.2 (1)	C(5)-N(2)-C(6)	114.9 (8)	8.140x + 8.785y + 1.963z = -1.699			
S(1)-Ni-C(1)	50.0 (3)	C(7)-N(3)-C(8)	121.7 (8)	Atomic Displacements from the Plane, Å			
S(1)-Ni-C(4)	113.6 (3)	C(7)-N(3)-C(9)	121.1 (8)	Ni	0.063	N(2)	-0.133
S(3)-Ni-C(1)	102.4 (3)	C(8)-N(3)-C(9)	117.2 (8)	S(2)	0.014	N(3)	0.113
S(3)-Ni-C(4)	95.7 (3)	Ni-C(1)-S(1)	76.3 (5)	S(3)	-0.061	C(5)	-0.122
C(1)-Ni-C(4)	161.1 (4)	Ni-C(1)-N(1)	149.7 (8)	C(4)	-0.055	C(6)	-0.245
Ni-S(1)-C(1)	55.7 (4)	S(1)-C(1)-N(1)	133.9 (8)	C(7)	0.040	C(8)	0.259
						C(9)	0.075

also comparable with Ni-C(sp<sup>2</sup>) distances in complexes containing C<sub>6</sub>H<sub>5</sub> (1.87 Å<sup>13</sup>), C<sub>6</sub>F<sub>5</sub> (1.914,<sup>14</sup> 1.978,<sup>15</sup> 1.880 Å<sup>16</sup>), C<sub>6</sub>Cl<sub>5</sub> (1.905 Å<sup>15</sup>), C<sub>2</sub>(CN)<sub>4</sub> (1.951-1.956 Å<sup>17</sup>), C(NR)C(CN)<sub>2</sub> (1.855 Å<sup>18</sup>), and COCH<sub>3</sub> (2.02 Å<sup>19</sup>) ligands and only slightly shorter than observed Ni-C(sp<sup>3</sup>) distances of 1.89-2.03 Å.<sup>19-23</sup>

Thus there seems to be no evidence of significant nickel-carbon π interaction reflected in either of the Ni-C bond distances in this complex. This is in contrast to the usual observation of short metal-carbon bonds in carbene complexes. Although the bond to the thiocarboxamido carbon is shortened very slightly, it is only a bit shorter than the Mn-C distance in Ph<sub>3</sub>Mn(CO)<sub>3</sub>CSNMe<sub>2</sub> (1.924 Å) in which the bond distance is less than that expected for a Mn-C(sp<sup>2</sup>) bond by some 0.24 Å.<sup>24</sup>

The remaining bond distances in the complex cation are of about the expected lengths. The two Ni-S distances are within the range (2.10-2.20 Å) observed in other compounds. The C-S and C-N distances within the thiocarboxamido group are essentially the same as those found in Ph<sub>3</sub>PMn(CO)<sub>3</sub>CSNMe<sub>2</sub>.<sup>24</sup> The three C-S distances within the chelating carbene ligand are all appreciably longer than the C-S distance in the thiocarboxamido group; C(7)-S(3) (1.710 Å) is of the expected length for a dithiocarbamate group, while C(7)-S(2) (1.737 Å) and C(4)-S(2) (1.783 Å) are longer, the

latter approaching a C-S single bond distance. This last is a rather surprising observation; in the absence of significant Ni-C(4) π interaction, a greater degree of π bonding between the carbenoid carbon and the adjacent sulfur atom would probably be expected. However, the observed bond lengths indicate appreciable π bonding only between C(4) and N(2); in fact all the C-N bond lengths (1.30-1.33 Å) are much shorter than single-bond distances and are comparable with C-N distances in dithiocarbamate complexes.

There is also no evidence of any bonding interaction between complex cations. Although these lie in the unit cell in more or less parallel, centrosymmetrically related pairs, the closest approach between atoms of these pairs is Ni···S(3), 3.434 Å.

## Discussion

The most interesting structural feature of the [Me<sub>2</sub>NCSNiC(NMe<sub>2</sub>)SC(NMe<sub>2</sub>)S]<sup>+</sup> ion is the chelating carbene ligand, and the question of how it is formed is an interesting one. Unfortunately, detailed mechanistic information on the formation of the complex is not available; however, it is tempting to speculate that this reaction takes place via three successive oxidative additions of the C-Cl bond

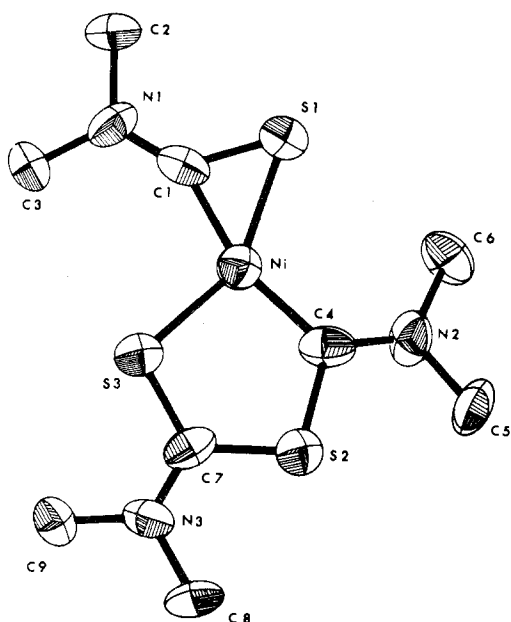
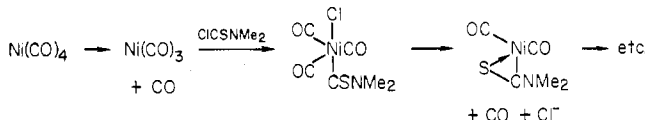
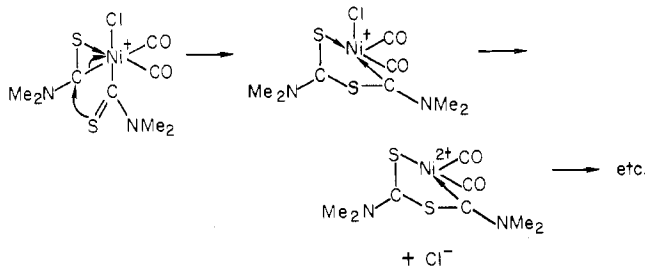


Figure 1. Structure of the  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]^+$  ion.

in  $\text{ClCSNMe}_2$  to the nickel, followed by loss of  $\text{CO}$  and  $\text{Cl}^-$  ligands:



Within this framework, the formation of the chelating carbene ligand can be explained by postulating attack by a sulfur atom on a ligand carbon atom:



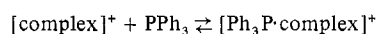
This step (which might occur following the addition of either the second or the third thiocarbonyl group) formally results in a two-electron reduction of the nickel atom. It seems necessary to postulate an additional two-electron reduction to account for the formation of a formal nickel(II) complex from  $\text{Ni}(\text{CO})_4$  via three oxidative additions of  $\text{ClCSNMe}_2$ . There is presently no indication of the source of these two electrons; the yield of the reaction was not improved when carried out in the presence of 1 equiv of hydroquinone or in the presence of excess dimethylthiocarbonyl chloride. The situation is even less clear for the reaction with nickelocene, in which the formal oxidation state of nickel does not change. We hope to present further data on the mechanisms of these reactions in the future.

One of the most striking features of the  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]^+$  ion is its stability—samples of its salts have been exposed to air for periods of several months without any apparent decomposition. This is a very surprising property for a compound containing two nickel-carbon bonds, especially

in view of the extreme instability of at least some nickel carbene complexes.<sup>6</sup> It is all the more surprising in a planar complex with two sides and an edge sterically open to attack (although it can be seen in Figure 1 that attack on the "open" edge of the complex is to some extent blocked by the rigid  $\text{N}(2)-\text{C}(5)-\text{C}(6)$  dimethylamino group).

It is clear from the observed bond distances that the source of this stability does not lie in any extraordinary degree of metal-carbon bonding; there is little or no evidence for  $\text{Ni}-\text{C}$   $\pi$  interaction. The chelating thiocarbonyl group seems from its appearance and behavior in other complexes to be a stable unit, and possibly the stability of the complex can be attributed at least in part to the fact that the carbene ligand is chelating also. We are currently engaged in preparing other complexes containing similar ligands in order to determine to what extent this may be the case.

In spite of its stability, the complex is susceptible to attack by other ligands. With triphenylphosphine, reversible complex formation takes place in acetone solution:



with an equilibrium constant of  $277 \pm 3$  (determined spectrophotometrically). However, the complex salt is recovered unchanged on precipitation by the addition of ether. With other, less bulky ligands ( $\text{P}(n\text{-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{NEt}_3\text{H}$ ,  $\text{CN}^-$ ,  $\text{S}_2\text{CNMe}_2^-$ ) similar complexes are rapidly formed, but this is followed by a slower, irreversible reaction, the products of which have not yet been fully characterized. A more complete account of this behavior will be presented in a later paper.

**Acknowledgment.** This work was supported by grants to W.K.D. from the Research Corp. and from the Emory University Research Committee and by assistance of the Emory University Computing Center. The authors also thank Dr. J. A. Bertrand and the Chemistry Department of the Georgia Institute of Technology for generously providing access to their facilities.

**Registry No.**  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{Cl}$ , 64315-03-3;  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{PF}_6$ , 64315-02-2;  $[\text{Me}_2\text{NCSNiC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)\text{S}]\text{BPh}_4$ , 64315-01-1;  $\text{Ni}(\text{CO})_4$ , 13463-39-3;  $\text{ClCSNMe}_2$ , 16420-13-6; nickelocene, 1271-28-9.

**Supplementary Material Available:** Table IV, listing structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

## References and Notes

- W. K. Dean and P. M. Treichel, *J. Organomet. Chem.*, **66**, 87 (1974).
- W. K. Dean, *J. Organomet. Chem.*, **135**, 195 (1977).
- R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
- "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 72-98; (b) pp 149-150.
- F. A. Cotton and C. A. Murillo, *Inorg. Chem.*, **14**, 2467 (1975), and references quoted therein.
- E. O. Fischer, *Pure Appl. Chem.*, **30**, 353 (1972).
- W. Petz, *J. Organomet. Chem.*, **55**, C42 (1973).
- B. Cetinkaya, P. Dixneuf, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 206 (1973).
- P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 102 (1974).
- C. H. Davies, C. H. Game, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 357 (1974).
- L. Pauling and M. L. Huggins, *Z. Kristallogr., Kristallgeom., Kristallphys. Kristallchem.*, **87**, 205 (1934).
- M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).
- P. Dapporto and L. Sacconi, *Inorg. Chim. Acta*, **9**, L2 (1974).
- M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).
- M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 3463 (1971).
- M. R. Churchill, K. C. Kalra, and M. V. Veidis, *Inorg. Chem.*, **12**, 1656 (1973).
- J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, **92**, 5333 (1970).

- (18) D. J. Yarrow, J. A. Ibers, Y. Tatsuno, and S. Otsuka, *J. Am. Chem. Soc.*, **95**, 8590 (1973).  
 (19) L. Sacconi, P. Dapporto, and P. Stopponi, *J. Organomet. Chem.*, **116**, C33 (1976).  
 (20) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970).  
 (21) R. Countryman and B. R. Penfold, *J. Chem. Soc. D*, 1598 (1971).  
 (22) D. J. Brauer, C. Kruger, P. J. Roberts, and Y.-H. Tsay, *Chem. Ber.*, **107**, 3706 (1974).  
 (23) F. A. Cotton, B. A. Frenz, and D. C. Hunter, *J. Am. Chem. Soc.*, **96**, 4820 (1974).  
 (24) W. K. Dean, J. B. Wetherington, and J. W. Moncrief, *Inorg. Chem.*, **15**, 1566 (1976).

Contribution from the Metcalf Chemical Laboratories of Brown University, Providence, Rhode Island 02912

## Kinetics and Mechanism of the Oxidation of Thiourea and *N,N'*-Dialkylthioureas by Hydrogen Peroxide

MICHAEL HOFFMANN and JOHN O. EDWARDS\*

Received July 6, 1977

AIC704835

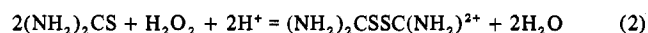
The oxidation of thiourea and two dialkylthioureas to their respective formamidine disulfide cations by hydrogen peroxide in acid solution has been studied kinetically. The rate law and other data indicate that the reactions proceed via a nucleophilic displacement by sulfur on oxygen. The scope of this mechanism for reaction of nucleophiles with peroxides is discussed.

### Introduction

Qualitatively, the oxidation of thiourea and its alkyl derivatives with hydrogen peroxide has been thoroughly studied. In acidic solution, the reaction of thiourea with an excess of hydrogen peroxide yields a mixture of ammonia, sulfur, sulfuric acid, and carbon dioxide,<sup>1,2</sup> whereas in neutral solution thiourea dioxide and water are formed.<sup>3</sup>



Marshall<sup>2</sup> was the first to report the isolation of the dibasic salt formamidine disulfide bis(hydrogen chloride) from a mixture of acid, thiourea, and hydrogen peroxide.



Formation of a disulfide salt is consistent with the fact that thiols are readily oxidized to disulfides.<sup>4</sup> In a neutral or weakly acidic medium, the disulfide ion spontaneously decomposes with the precipitation of sulfur.<sup>5</sup> Reactions of the type represented by eq 2 have been used to convert a number of *N*-alkylthioureas to *N,N'*-dialkylated dithioformamides.<sup>6,7</sup> The crystal structure of the formamidine disulfide ion verifies the existence of a discreet S-S single bond with a bond length of 2.04 Å. In addition, the dimensions and planarity of the thiourea groups are virtually unaltered in the disulfide product except for a slight lengthening of the C-S bond.<sup>8</sup>

Product formation is thermodynamically favorable as illustrated by the redox couples listed in Table I. The reduction potentials for the thiourea-formamidine disulfide systems range from -0.42 V to -0.46 V. Combination of these values with the peroxide-water reduction couple of +1.76 V indicates that there are powerful thermodynamic driving forces in these reactions.

Thiourea<sup>9</sup> and its analogue dithiobiuret<sup>10</sup> have been reported to react rapidly with hydrogen peroxide. These reactions were considered "too fast" to be measured; consequently, the rate law and mechanism were unknown. Edwards<sup>11</sup> has estimated

Table I. Electrode Potentials for the Thioureas and Hydrogen Peroxide

Couple	$E^0$
$(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2^{2+} + 2e^- \rightleftharpoons 2(\text{H}_2\text{N})_2\text{CS}$	-0.418 <sup>a</sup>
$(\text{CH}_3\text{NH})_2\text{CSSC}(\text{NHCH}_3)_2^{2+} + 2e^- \rightleftharpoons 2(\text{CH}_3\text{NH})_2\text{CS}$	-0.460 <sup>b</sup>
$(\text{C}_2\text{H}_5\text{NH})_2\text{CSSC}(\text{NHC}_2\text{H}_5)_2^{2+} + 2e^- \rightleftharpoons (\text{C}_2\text{H}_5\text{NH})_2\text{CS}$	-0.450 <sup>b</sup>
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.76 <sup>c</sup>

<sup>a</sup> P. W. Priesler and L. Berger, *J. Am. Chem. Soc.*, **69**, 322 (1947). <sup>b</sup> P. W. Priesler, *ibid.*, **71**, 2849 (1949). <sup>c</sup> W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1961.

that the nucleophilic reactivity of thiourea would place it between  $\text{I}^-$  and  $\text{S}_2\text{O}_3^{2-}$  on a scale of relative rates toward hydrogen peroxide.

In the present study we examine the kinetics of the thiourea and *N,N'*-alkylthiourea oxidations by hydrogen peroxide and propose a suitable mechanism.

### Experimental Section

**Reagents.** Reagent grade thiourea (tu) (Aldrich) was recrystallized twice from hot water. *N,N'*-Dimethylthiourea (dmtu) and *N,N'*-diethylthiourea (detu) (Chemical Samples Co.) were technical grade. The yellowish dmtu was recrystallized repeatedly from freshly distilled dioxane until clear white crystals were obtained. The resulting crystals, which were vacuum dried, were exceedingly deliquescent and melted in the range of 60–62 °C. Final IR and NMR spectra matched those listed in the Aldrich Spectral Handbook.

Technical grade detu was recrystallized four times from 20% methanol-water. The resulting crystals, which had been vacuum dried, were clear colorless plates. The melting range of 78–80 °C and the IR and the NMR spectra agreed with those reported in the literature. Hydrogen peroxide (90%, FMC) without added stabilizers and reagent grade perchloric acid (70%, B&A) were used as received.

**Product Identification.** The dihydrochloride salt of formamidine disulfide (dimer) was prepared using the technique of Preisler and Berger.<sup>9</sup> Recrystallized thiourea (4.8 g) was reacted with 5 mL of 30% hydrogen peroxide in 50 mL of 3 M HCl. After the addition of 200 mL of ethanol and 60 mL of concentrated HCl, white crystals