

Preparation and Properties of Dithio- and Diselenocarbazic Acids

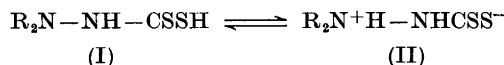
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Five representative dithiocarbazic acids and their nickel(II) salts have been prepared and the infrared spectra recorded. Evidence is presented for the argument that the acids have a zwitterionic structure. The novel compounds $R_2N^+H-NH-CSeSe^-$ have been prepared by the same methods. A comparison of their infrared spectra with the sulfur analogues have permitted the assignments of the symmetrical CSS^- and $CSeSe^-$ vibrations to $680-691\text{ cm}^{-1}$ and $581-623\text{ cm}^{-1}$, respectively. The infrared data of bis-(dimethyldiselenocarbazato)-nickel(II) are best explained by assigning the structure $(Me_2N-N=C(SeH)Se)_2Ni$ to this compound.

The literature on the free dithiocarbazic acids is sparse. Renouf¹ reported the preparation of dimethyldithiocarbazic acid; however, all details of experimentation and characterization were omitted. Phenyl- and diphenyldithiocarbazic acid have also been briefly reported in earlier papers.²⁻⁴ Recently,⁵ *N,N*-pentamethylenedithiocarbazic acid has been shortly mentioned.

A priori considerations pointed to the existence of these compounds in dipolar forms, *viz.*:



To test the compatibility of this concept we re-examined the dithiocarbazic acids described previously. In addition, the hitherto unknown nickel(II) salts, as well as some selenium analogues, were prepared. All products were found to be rather stable, well-defined substances with substantial thermal stability, even in the case of the selenium compounds. The high stability of these compounds supports the contention that they exist mainly as hydrazinio-dithiocarbazates, *i.e.* with the structure (II). Addition of hydrochloric acid to the dithiocarbazic acids resulted in a complete breakdown to carbon disulfide and the hydrazinium salt. This may be interpreted as support for the above hypothesis, as protonisation is followed by the formation of the unstable

—NHCSSH grouping. It should be mentioned that dithiocarbamic acid, which obviously has only little tendency to form dipolar structures, has been reported recently⁶ to decompose within a short time.

Conclusive proof for this was forthcoming from the infrared spectra of these compounds. Table 1 summarises the absorptions observed for the dimethyl derivatives. The principal absorptions for the other compounds are given in the experimental part.

The N—H stretching bands occurring in the 2000—3500 cm^{-1} region are of two types, those belonging to the NH^+ -grouping and those belonging to the NH-grouping. The latter give rise to absorptions in the 3000—3100 cm^{-1} region in the free dithio- and diselenocarbazic acids. This frequency range is below that normally found for the N—H stretching vibrations, but the reason for this must be found in the inductive effect of the positive charge on the neighbouring nitrogen atom.⁷ In line with this, a displacement towards higher frequencies is observed in the infrared spectra of the nickel(II) salts, in which the neighbouring nitrogen atom is uncharged. The N—H stretching vibrations due to the NH^+ -grouping are only observed in the free dithiocarbazic acids, which reinforces the conclusions concerning their dipolar structure stated above. The identity of the absorptions in question were confirmed by deuteration.

The characteristic N—H stretching band in the 3100—3200 cm^{-1} region is apparently missing in the spectra of bis-(dimethyldiselenocarbazato)-nickel(II). However, a strong absorption occurs at 2100 cm^{-1} which shows a shift to the 1500 cm^{-1} region on deuteration. According to Sharghi *et al.*,⁸ the Se—H stretching frequencies are found at 2280—2300 cm^{-1} in five investigated selenols and we therefore propose bis-(dimethyldiselenocarbazato)-nickel(II) to have the structure $(\text{Me}_2\text{N}-\text{N}=\text{C}(\text{SeH})\text{Se})_2\text{Ni}$ instead of the expected $(\text{Me}_2\text{N}-\text{NH}-\text{C}(=\text{Se})\text{Se})_2\text{Ni}$.

Due to the slight solubility of the nickel salts it is impossible to decide whether they are monomeric or polymeric. By analogy with the metal dithiocarbamates the metal ion might be supposed to be chelated to the dithiocarboxylate or diselenocarboxylate grouping. However, as proposed for the red nickel dithiocarbazate,⁹ the nickel ion might also form a five membered chelate ring with the nitrogen atom number 1 and one of the sulfur (or selenium) atoms. The alleged presence of the SeH-grouping in the nickel salt of 1,1-dimethyldiselenocarbazic acid points to the existence of a ring of the latter type since a SeH-group would not be expected to coordinate to a metal ion.

All the nickel compounds are soluble in excess sodium hydroxide, undoubtedly with the formation of anions of the type $[(\text{R}_2\text{N}-\text{N}=\text{CS}_2)_2\text{Ni}]^{2-}$.

A very strong band found in both dimethyldithio- and dimethyldiselenocarbazic acids at 1282 cm^{-1} and 1291 cm^{-1} , respectively, was only little effected on deuteration, but showed an upwards shift to 1525 cm^{-1} and 1560 cm^{-1} , respectively, on formation of the nickel(II) salts. We believe this band to be analogous to the B band,¹⁰ *i.e.* being essentially a C—N vibration in the dithiocarbazic acids, but having an enhanced double-bond character in the nickel(II) salts. A doublet found in the range 1160—1190 cm^{-1} in the dithiocarbazic acids as well as in the nickel(II) salts is attributed to a C—N—C skeletal vibration. A corresponding strong absorption is found in 1,1-dimethylhydrazine¹¹ at 1140 cm^{-1} . Apart from the strong absorptions found around

850 cm^{-1} , which are considered due to a torsional CH_3 -vibration, only two strong absorptions in each compound remains to be explained. One of these is centered around 1035 cm^{-1} in the dithiocarbazic acids and in the nickel(II) salts, but is found at lower frequencies (*ca.* 930 cm^{-1}) in the diseleno analogues. The antisymmetrical CSS^- and CSeSe^- vibrations have been studied by Jensen *et al.*,¹²⁻¹⁴ and are concluded to appear at 1000–1100 cm^{-1} and at *ca.* 900 cm^{-1} , respectively. The assignments given in Table 1 are in complete accord with these data.

The absorptions found at *ca.* 685 cm^{-1} in the dithiocarbazic acids and in the nickel(II) salts are displaced to 581 cm^{-1} in the diselenocarbazic acids and to 623 cm^{-1} in the investigated nickel(II) salt. We believe these absorptions are due to the symmetrical CSS^- and CSeSe^- vibrations, which is in accordance with other unpublished data from this laboratory. On deuteration, the symmetrical as well as the antisymmetrical CSS^- absorptions were displaced 20–40 cm^{-1} towards lower frequencies both in the dithiocarbazic acids and in the nickel(II) salts, which reveals a minor amount of coupling with the neighbouring NH-group.

The conclusions concerning the dipolar structure of the dimethyl derivatives are strongly corroborated by considering the infrared spectra of the other carbazic acids and their nickel(II) salts listed in the experimental part. They all show the antisymmetrical CSS^- absorption in the range 1010–1060 cm^{-1} , and the symmetrical CSS^- absorption between 675 cm^{-1} and 695 cm^{-1} . Therefore in our opinion, infrared confirmation for the presence of the CSS^- grouping should be sought in both regions. The infrared evidence taken in connection with the physical data seems therefore to constitute a conclusive proof for the dipolar structure of the investigated dithio- and diselenocarbazic acids.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory. Melting points were taken in capillary tubes and are not corrected. The infrared spectra of the solid compounds in KBr were recorded on a Perkin-Elmer model 337 Grating Infrared Spectrophotometer. The deuterated materials used for infrared investigation were prepared in an identical manner as described for the normal compounds, except that deuterated solvents were used.


The starting materials. The hydrazines used in this work were commercial products, which were purified by distillation before use. Diethylhydrazine (b.p. 96–99°C¹⁵) was obtained following the directions given for dimethylhydrazine in the literature.¹⁶ Carbon diselenide was available from the stock of chemicals of this laboratory.¹³

Dimethylhydrazinium dimethyldithiocarbazate. This compound was conveniently prepared by adding a solution of carbon disulfide (0.05 mole) in absolute ethanol (10 ml) dropwise to a cooled solution of dimethylhydrazine (0.1 mole) in dry ether (50 ml). Efficient stirring and cooling proved necessary to ensure that the temperature was held at 0–5°C. A fine crystalline, nearly colourless, precipitate of the hydrazinium salt began to settle within a few minutes. After 10 min the solution was filtered and the collected solid was washed with ether and vacuum dried. Yield 85%.

The same procedure was used for the preparation of the other dithiocarbazates but the higher members of this series generally gave a less satisfactory yield. They were used without further purification for the next step.

Dimethyldithiocarbazic acid. The crude dithiocarbazate was dissolved in as little water as possible. The solution was filtered and added dropwise to the equivalent amount of *ca.* 6 N hydrochloric acid cooled below –5°C in an efficient cooling mixture. Dimethyldithiocarbazic acid instantly separated as gleaming white crystals, which rapidly

Table 1. Infrared spectra of dimethyldithio- and dimethyldiselenocarbazic acid and their nickel(II) salts. (cm⁻¹).

	Me ₂ N ⁺ H-NHCSS ⁻	Me ₂ N ⁺ H-NHCS ₂ Se ⁻	(Me ₂ N-NHCSS) ₂ Ni	(Me ₂ N-NHCS ₂ Se) ₂ Ni
NH	3080 s	3030 s	3200 w	(see text)
NH ⁺	2880 vs 2700 m	2870 vs 2640 m	—	—
CH ₃	1450 m	1450 m	1440 m 1360 m	1465 m 1455 m
CN	1282 vs	1291 vs	1525 vs	1560 s
	1183 s 1165 vs	1178 vs 1166 vs	1189 w 1163 w	1168 w 1154 w
CSS ⁻	1035 s	—	1039 vs	—
CSeSe ⁻	—	927 s	—	930 m
CH ₃	840 s	826 s	859 s	859 s
CSS ⁻	680 s	—	687 s	—
CSeSe ⁻	—	581 s	—	623 m

developed an yellowish tinge. The crude product was separated by filtration in the cold and dried *in vacuo*. Yield 55 %. M.p. 122–123°C with decomposition. (Found: C 26.53; H 5.85; N 20.33. Calc. for C₃H₆N₂S₂: C 26.47; H 5.92; N 20.58). The melting point obtained is somewhat higher than that reported (112°C) in the literature.¹

The other dithiocarbazic acids were prepared in the same way. They all separated as pale yellow crystals, scratching in some instances being necessary to induce precipitation. The products could not be recrystallized owing to partial liberation of the parent hydrazine. However, elemental analyses proved the dithiocarbazic acids to be essentially pure. All the dithiocarbazic acids proved rather stable on storing for several months at -40°C.

Diethyldithiocarbazic acid. The yield was 40 %. M.p. 102–103°C (decomp.). (Found: C 36.59; H 7.52; N 17.25. Calc. for C₆H₁₂N₂S₂: C 36.58; H 7.37; N 17.07).

IR-spectrum: 3090 s, 2930 vs, 2770 w, 1635 w, 1450 s, 1390 m, 1350 m, 1250 vs, 1169 vs, 1047 vs, 968 s, 839 m, 799 vs, 678 s, 453 s.

Pentamethylenedithiocarbazic acid. The yield was 60 %. M.p. 67–68°C (decomp.). (Found: C 40.60; H 6.85; N 15.65. Calc. for C₆H₁₂N₂S₂: C 40.90; H 6.87; N 15.90). These results confirm those obtained by Podgornaya *et al.*⁵

IR-spectrum: 3120 s, 2970 s, 2860 w, 2835 w, 1520 vs, 1320 m, 1267 w, 1231 w, 1153 m, 1100 m, 1048 vs, 998 s, 871 s, 789 s, 684 m, 628 w, 584 w.

Phenyldithiocarbazic acid. The yield was 90 %. M.p. 106–107°C (decomp.). (Found: C 45.54; H 4.55; N 15.31. Calc. for C₇H₈N₂S₂: C 45.65; H 4.38; N 15.21).

IR-spectrum: 3245 m, 2930 w, 1605 s, 1520 vs, 1231 s, 1072 vs, 910 w, 859 w, 756 s, 691 s, 626 m, 488 m.

Dimethyldiselenocarbazic acid. This compound was synthesized in the same way as described for the thio analogue. The dimethylhydrazinium dimethyldiselenocarbazate is a red-yellow highly crystalline product, which was used without further purification for the next step in the synthesis. The overall yield of dimethyldiselenocarbazic acid was

70 %. The orange-red microcrystalline compound melted at 87–88°C with deflagration. (Found: C 15.80; H 3.62; N 12.20. Calc. for $C_3H_8N_2Se_2$: C 15.65; H 3.48; N 12.17).

Phenyldiselenocarbazic acid. This was prepared in the same manner as the phenyldithiocarbazic acid. Yield 75 % of yellow crystals melting at 76–78°C with decomposition. (Found: C 30.40; H 2.78; N 10.18. Calc. for $C_7H_8N_2Se_2$: C 30.21; H 2.87; N 10.04).

IR-spectrum: 3215 s, 3025 s, 2860 m, 1605 s, 1535 s, 1500 s, 1485 s, 1385 s, 1240 w, 1228 s, 1176 m, 1090 m, 1026 m, 954 s, 982 s, 858 s, 804 s, 768 vs, 691 s, 602 s, 520 m, 466 s.

The nickel compounds. An aqueous solution of the appropriate hydrazinium dithiocarbazate (2 mole) was mixed with an aqueous solution of nickel(II) chloride (1 mole). The olive to beige nickel(II) salt separated immediately in nearly quantitative yield. With the exception of the salt prepared from phenyldithiocarbazic acid, which was purified by dissolving in chloroform and precipitating with ether, the analyses given below refer to the crude products.

Bis-(dimethyldithiocarbazato)-nickel(II). M.p. 187°C (decomp.). (Found: C 21.95; H 4.15; N 17.02. Calc. for $C_6H_{12}N_4S_4Ni$: C 22.02; H 4.26; N 17.04).

Bis-(diethyldithiocarbazato)-nickel(II). M.p. 201°C (decomp.). (Found: C 31.24; H 5.99; N 14.56. Calc. for $C_{10}H_{22}N_4S_4Ni$: C 31.20; H 5.72; N 14.30).

IR-spectrum: 3120 m, 2980 s, 2940 w, 1630 m, 1525 m, 1455 m, 1375 m, 1306 m, 1175 w, 1142 m, 1058 s, 1032 vs, 853 m, 814 m, 683 s.

Bis-(pentamethylenedithiocarbazato)-nickel(II). M.p. 185°C (decomp.). (Found: C 35.46; H 5.66; N 13.94. Calc. for $C_{12}H_{26}N_4S_4Ni$: C 35.26; H 5.38; N 13.70).

IR-spectrum: 3160 m, 2950 s, 2860 w, 1635 m, 1515 s, 1450 m, 1480 m, 1262 w, 1153 m, 1105 w, 1061 m, 1036 m, 1011 s, 986 m, 868 m, 786 m, 682 m.

Bis-(phenyldithiocarbazato)-nickel(II). M.p. 155°C (decomp.). (Found: C 39.95; H 3.60; N 13.02. Calc. for $C_{14}H_{14}N_4S_4Ni$: C 39.56; H 3.30; N 13.19).

IR-spectrum: 3250 s, 3055 w, 1610 s, 1500 s, 1485 s, 1375 s, 1243 s, 1178 w, 1008 s, 754 s, 691 s.

Bis-(dimethyldiselenocarbazato)-nickel(II). This was prepared in an identical manner as the thio analogue. The crude yellow-brown microcrystalline product was analytically pure and melted at 122°C with decomposition. It is slightly soluble in chloroform but nearly insoluble in ether, ethanol, and acetone. (Found: C 14.02; H 2.93; N 10.80. Calc. for $C_3H_{12}N_4Se_2Ni$: C 13.92; H 2.72; N 10.82).

Bis-(phenyldiselenocarbazato)-nickel(II). The preparation of this compound was attempted. Analyses, however, showed the purity of the product, even after recrystallisation, to be unsatisfactory.

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