# X-Ray Structural Data on the Composition and Structure of One of the Hydrazinecarbonic Compounds of Nickel

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## Abstract

## Full Text

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## CRYSTALLOGRAPHY

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# X-Ray Structural Data on the Composition and Structure of One of the Hydrazinecarbonic Compounds of Nickel

*(Presented by Academician I. I. Chernyaev, 5 XI 1965)*

In paper ([1]) a method was described for synthesizing a compound with hydrazinecarbonic acid of the proposed composition $[(N_2H_3COO)_2Ni(N_2H_5)_2]CO_3$. The composition was adopted on the basis of chemical-analysis data for Ni, N, and C, data on electrical conductivity (a bi-ionic electrolyte), and certain chemical properties. In order to check the correctness of the structural formula, and also because of the absence in the literature of structural data on hydrazinecarbonic salts, an X-ray structural investigation of the compound obtained was undertaken.

The investigation was carried out with Cu $K$ radiation from projections of the interatomic function and the three-dimensional distribution of electron density, followed by refinement of the atomic coordinates and the constants of isotropic thermal vibrations of the atoms by the least-squares method to a value $R = 0.15$. It is intended subsequently to carry out several further cycles of refinement.

**Table 1**

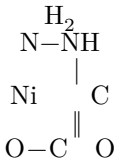
*Atomic coordinates obtained by refinement by the least-squares method*

| Atom | $x/a$ | $y/b$ | $z/c$ | Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|---|---|---|
| Ni | 0.499 | 0.573 | 0.249 | $O_7$ | 0.518 | 0.224 | 0.439 |
| $C_1$ | 0.295 | 0.425 | 0.210 | $N_1$ | 0.374 | 0.702 | 0.069 |
| $C_2$ | 0.736 | 0.442 | 0.440 | $N_2$ | 0.435 | 0.424 | 0.104 |
| $C_3$ | 0.484 | 0.818 | 0.340 | $N_3$ | 0.665 | 0.597 | 0.235 |
| $C_4$ | 0.617 | 0.457 | 0.418 | $N_4$ | 0.771 | 0.524 | 0.366 |
| $O_2$ | 0.550 | 0.726 | 0.389 | $N_5$ | 0.316 | 0.370 | 0.090 |
| $O_3$ | 0.353 | 0.520 | 0.285 | $N_6$ | 0.379 | 0.813 | 0.155 |
| $O_4$ | 0.201 | 0.367 | 0.219 | $N_7$ | 0.579 | 0.094 | 0.242 |
| $O_5$ | 0.818 | 0.382 | 0.537 | $N_8$ | 0.632 | 0.207 | 0.193 |

| Atom | $x/a$ | $y/b$ | $z/c$ | Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|---|---|---|
| $O_6$ | 0.509 | 0.923 | 0.395 | | | | |

Dark-violet monoclinic crystals belong to the space group $Cc$:
$a = 12.10$, $b = 10.75$, $c = 10.25$ Å; $\angle\beta = 120°$, and $z = 4$, with $\rho_{\text{peak}} = 1.911$ g/cm$^3$. The atomic coordinates obtained at this stage of refinement are given in Table 1.

In the course of refinement of the three-dimensional electron-density distribution, the positions were determined of the Ni atoms, of two $N_2H_3COO^-$ groups, which form with Ni five-membered metallocycles,



and the arrange-

arranged in cis positions relative to one another, as well as two additional atoms completing the coordination to octahedral. The absence, in the distribution, of flat triangular groupings of maxima corresponding to the group $CO_3^{2-}$, and the presence of two maxima closing a third ring around the Ni atom, forced us to revise the chemical formula and, with the same gross composition, to take as the basis the structure $[Ni(N_2H_3COO)_3]N_2H_5H_2O$. Further refinement of the electron density confirmed this structure of the complex and made it possible to find the positions of the hydrazonium ions and water molecules.

Two of the hydrazinecarboxylate metallocycles are, within the limits of error, planar, with Ni–N bonds of length 2.05-2.08 Å, Ni–O 2.03-2.04 Å, N–N′ 1.44-1.47 Å, N′–C 1.37-1.46 Å, and C–O 1.23-1.32 Å. The third ring is appreciably nonplanar: the N′ and C atoms are displaced from the NiNO plane to the same side by 0.2 Å. The angle between the NiNO and NN′CO planes is 170°, and the N′–C bond is substantially weakened (1.55 Å). The Ni–N bond is also weakened (2.16 Å).

This difference in the structure of the third ring evidently determines its increased reactivity and, in particular, the nature of the reactions that occur under the action of hydrochloric acid. Interaction with HCl, calculated as 1 or 2 moles of HCl per 1 mole of salt, leads to the cleavage of the third $N_2H_3COO^-$ residue, which, together with $N_2H_5^+$, passes into solution. From the solution a precipitate of composition $Ni(N_2H_3COO)_2 \cdot 2H_2O$ separates. If the mixture is then heated on a water bath, the precipitate dissolves, and after some time another compound of composition $Ni(N_2H_3COO)_2 \cdot N_2H_4 \cdot H_2O$ precipitates.

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*Note: Figure translations are in progress. See original paper for figures.*