THE CRYSTAL STRUCTURE OF NITRO-BIS(ETHYLENEDIAMINE)NICKEL CHLORIDE \([\mathrm{Nien}_2\mathrm{NO}_

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THE CRYSTAL STRUCTURE OF NITRO-BIS(ETHYLENEDIAMINE)NICKEL CHLORIDE $[Nien_2NO_2]Cl$

Crystals of $Nien_2NO_2Cl$ were synthesized at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences in the form of violet octahedra elongated along the (short) y axis. There, in the crystal-chemical laboratory, all the experimental X-ray material was obtained from a single crystal ground into a sphere of $\emptyset 0.15$–0.20 mm (Mo-K_α radiation, KFOR X-ray goniometer). The orthorhombic cell ($a = 18.321 \pm 0.003$, $b = 8.777 \pm 0.001$, $c = 13.025 \pm 0.003$ Å) contains $Z = 8$ units of the indicated composition. The acentric (diamond) Fedorov group is $Fdd2 = C_{2v}^{19}$. On an MF-2 microphotometer, the blackenings of the film were estimated from the difference between the instrument readings when set on a reflection and on the background near it, at a constant slit width somewhat larger than the size of the reflections. The transition to intensities was made according to a calibrated blackening scale. The array used in the structural analysis consisted of 212 structure factors differing from zero and derived from the intensities with allowance only for the angular factor Lp ($\sin\vartheta/\lambda < 0.65$). The structure determination was carried out entirely at the Computing Center of Moscow University by the material-point method recently developed there ([1]).

The group $Fdd2$ fixes the atoms Ni, Cl, and N (from NO_2) on twofold axes and permits the position of one of these atoms (Ni) to be taken as the origin of coordinates. Patterson synthesis on the same twofold axis also brings out the atom Cl($00z$).

The limited experience of previous structure determinations made probable for Ni an octahedral coordination of Cl and five N ([2]), with four N from two ethylenediamine ligands having to form a rectangle with semidiagonals Ni—N = 2.1 Å at an angle of $\sim 86^\circ$. This pseudosquare must lie in the xOy plane, i.e., be perpendicular to the z axis. The distances from Ni to the fifth N (on a twofold axis) are ~ 2.0 Å, and to the Cl atom (on the same axis) ~ 2.5 Å. To be determined were the azimuth of one of the four N and the azimuth of the NO_2 triangle (N—O ~ 1.3 Å), which remains in the plane passing through the twofold axis, and, in addition, the 6 coordinates of two independent C atoms (Fig. 1).

Fig. 1. A priori model of the complex [Nien$_2$NO$_2$Cl]. en = NH$_2$—CH$_2$—CH$_2$—NH$_2$; $Z = 8$; $a = 18.321 \pm 0.003$ Å, $b = 8.877 \pm 0.001$ Å, $c = 13.025 \pm 0.005$ Å; $Fdd2$

Figure 1: Fig. 1. A priori model of the complex [Nien$_2$NO$_2$Cl]. en = NH$_2$—CH$_2$—CH$_2$—NH$_2$; $Z = 8$; $a = 18.321 \pm 0.003$ Å, $b = 8.877 \pm 0.001$ Å, $c = 13.025 \pm 0.005$ Å; $Fdd2$

Fig. 2. Real bidentate structure of the complex chloride [Nien$_2$NO$_2$]$^+$Cl$^-$

Figure 2: Fig. 2. Real bidentate structure of the complex chloride [Nien$_2$NO$_2$]$^+$Cl$^-$

Accordingly—in the rigid conditions indicated—the first stage of the solution did not give an acceptable result, and the discrepancy factor varied only within small limits around 60%.

At the second stage the atoms on the twofold axes (Cl and N(O$_2$)) were loosened, and the restrictions on the O atoms were also removed; however, the pseudosquare of four N atoms remained rigidly fixed in the xOy plane. Under the relaxed conditions the material-point method immediately destroyed the proposed coordination scheme. The Ni—Cl distance increased to 4.5 Å, and Ni—N(O$_2$) to 2.45 Å, i.e., the halogen atom left the first coordination sphere entirely, while the NO$_2$ group, with respect to the central Ni, "turned over" and became attached to this Ni by both of its O atoms; the R factor fell sharply to 24% at $B_0 = -2$, but further refinement did not reduce it.

The electron-density synthesis constructed at the conclusion of this stage did not reveal one pair of ethylenediamine N atoms, which now appears to be a natural consequence of placing the Ni octahedron "on an edge" O—O, to which there must correspond (along the z axis) a parallel upper edge of the ···

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two N(en), sharply emerging from the xOy plane. Thus, an important consequence of the halogen leaving the coordination octahedron was the change from the trans configuration of the two en groups to the cis configuration.

At the third stage of the determination, by the same method of the material point, all forced parametrization was discarded (apart from that dictated by the group $Fdd2$ and by the number $Z = 8$ of units in the cell), and only the initial coordinates—for continuous variation—were taken from the second stage. The factor R fell to 13.5% at $B_0 = -2.5$. In the electron-density synthesis at the variable specified position, one of the C atoms did not appear, but a new position for it was indicated sufficiently clearly, to which it was transferred.

Table 1

Coordinates of the atoms of the $Nien_2NO_2Cl$ **structure and "errors" in the determination of the coordinates**

Atoms	Coordinates	Isotropic structural factors B	"Errors"	Atoms	Coordinates	Isotropic structural factors B	"Errors"
Ni	000	2.49	0.02	N_2(en)	x − 0.05332 y 0.21321 z 0.00450	2.50	0.00098 0.00021 0.00074 0.20
Cl	x 0 y 0 z 0.3479[illegible]	[illegible].74	0.00094 0.13	O	x 0.05177 y 0.0[illegible] z 0.1[illegible]	[illegible]	[illegible] 0.00011 0.00100 0.60
$N(O_2)$	x 0 y 0 z − 0.19424	2.52	0.00105 0.12	C_1(en)	x − 0.03182 y 0.28178 z 0.10256	3.68	0.00273 0.00065 0.00254 0.40
N_1(en)	x 0.06909 y 0.1[illegible] z [illegible]	[illegible]	[illegible]	C_2(en)	x [illegible]350 y 0.2[illegible]0 z [illegible]	[illegible]	[illegible] 0.00718 0.00858 0.40

As a result of introducing isotropic individual temperature factors, the final value of R was obtained in the range 8.2–8.6%. Its change by 0.2–0.4% within the indicated interval was regarded as a random effect, especially since the use of correcting weight functions (1) led to results that fluctuated only slightly around the mean values. Therefore the solution giving the best N–C and C–C distances in the ethylenediamine group was accepted as final (Tables 1 and 2).

Table 2

Interatomic distances and valence angles in the complex $[Nien_2NO_2]^+ + Cl^-$

Distance	Value	Distance	Value	Angle	Value	Angle	Value
Ni–Cl	4.532 Å	Ni–N_1(en)	2.142 Å	$ON(O_2)O$	106°44′	NiN_1C_2	110°39′
Ni–$N(O_2)$	2.530	Ni–N_2(en)	2.131	ONiO	61°36′	NiN_2C_1	105°36′
$N(O_2)$–O	1.303	N_2–C_1	1.469	N_1NiN_1	96°22′	$N_1C_2C_1$	104°54′
O–O	2.091	N_1–C_2	1.452	N_2NiN_2	176°50′	$N_2C_1C_2$	108°34′
Ni–O	2.041	C_1–C_2	1.573	N_1NiN_2	81°18′		

The scatter in the coordinates over 7 variants with correcting functions may be taken as an objective estimate of the "errors" of the solution.

Figure 2 shows the complex $[Nien_2NO_2]^+(Cl^-)$ in the form of an octahedron placed on the shortest edge, O–O = 2.09 Å; the upper edge is N(en)—N(en) =

3.24 Å, to which correspond the angles ONiO = 61°36′ and N(en)NiN(en) = 96°22′. Accordingly, two other N(en) emerge from the xOy plane ("rise") up to the angle N'(en)NiN'(en) = 176°50′.

The angle (valence angle) in the ONO group is 106°44′ for bond lengths N—O = 1.30 Å. The distances are Ni—O = 2.04 Å, Ni—N(en) = 2.14 and 2.13 Å, and Ni—$N(O_2)$ = 2.53 Å, N—C = 1.47 and N—C_2 = 1.45 Å for C_1—C_2 = 1.57 Å. All interatomic distances and angles within the complex are collected in Table 2.

The four atoms of the ethylenediamine group deviate from the plane of the best least-squares fit by ±0.2—0.3 Å. The C atoms deviate from the plane Ni—two N(en) by 0.5 and 0.3 Å. The angle of inclination of the C_1—C_2 direction to the z axis is 84°. The distances between Cl and the atoms O, N, C, as well as between atoms of neighboring enantiomorphic complexes, are close to the corresponding sums of intermolecular radii.

One may emphasize the parallelism of the established orientation of the octahedral complex—namely, along the N(en)—N(en) axis in the xOy plane—to the corresponding morphological feature of the octahedral crystals [Nien$_2$NO$_2$]Cl, which was noted at the beginning of the article.

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1. B. M. Shchedrin, N. V. Belov, N. P. Zhidkov, *DAN*, **170**, No. 5 (1966).

2. A. E. Shvelashvili, *X-ray structural study of several diacidodiethylenediamine nickel compounds of the type* Nien$_2XY$, Dissertation, Moscow, 1965.

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