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Structural Investigations of Nickel(II) Complexes. Part I. Crystal Structure of Bisaquotetrakisquinolinedithiocyanatenickel(II) Complex

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The green crystals of $Ni(NCS)_2(qn)_4(H_2O)_2$ are of triclinic symmetry with the space group $P\bar{1}$ and the dimensions of the unit cell: $a = 12.502(8)$, $b = 8.966(8)$, $c = 7.558(4)$ Å, $\alpha = 95.69(6)$, $\beta = 92.58(5)$, $\gamma = 92.18(7)^\circ$ *and* $V = 841(1)$ Å^3, *the number of formula units being Z = 1. The structure was refined by the method of full matrix least squares, the final value of R was 0.073. The nickel atoms lie in the centre of the symmetry and are pseudooctahedrally coordinated by four N atoms (two of the NCS groups, Ni–N = 2.04 Å, and two from the quinoline molecules, Ni–N = 2.18 Å) and two O atoms (from the water molecules, Ni–O = 2.13 Å). The bond angles in the coordination polyhedra are near to 90°. Two other quinoline molecules form hydrogen bridges with the coordinated water molecules. The thiocyanate group is a monodentate ligand and is nearly linear with the interatomic distances of N–C = 1.16 and C–S = 1.62 Å. The quinoline molecules are planar and exhibit the interatomic distances of C–N of 1.32 to 1.37 Å and C–C of 1.32 to 1.47 Å.*

Introduction

Isothiocyanate complex compounds with heterocyclic nitrogen ligands in the solid state may by prepared with the composition $Ni(NCS)_2L_x \cdot nH_2O$, where L = pyridine (py), quinoline (qn), isoquinoline (iqn), occasionally their methyl derivatives, x = 2 or 4 and n = 0 or 2 [1–9]. While it was found that in $Ni(NCS)_2py_4$ all four pyridine molecules are coordinated to Ni(II) [1], the spectral data of the compound $Ni(NCS)_2(qn)_4(H_2O)_2$ indicate that only two of four quinoline molecules are coordinated to the central atom [2]. The decomposition of this compound under different conditions yields two isomers of the composition $Ni(NCS)_2(qn)_2$ [9]. So far both isomers could be prepared in the solid state in powder form only. Based on the results obtained by indirect structural methods it has been found that they are two configurational isomers with octahedral and square coordination, respectively, of the central atom.

The aim of the investigation of the crystal structure of $Ni(NCS)_2(qn)_4(H_2O)_2$ was to elucidate by its solution the mechanism of the formation of isomers in the decomposition process, to determine the composition of the coordination sphere, and also the nature of the differently bonded quinoline (kind of bonding, orientation *etc.*). In wider connections the obtained structural results will serve as a contribution to the study of the mutual influence of ligands, the consequence of which for Ni(II) complex compounds with a suitable combination of its ligands is the formation of configurational isomers.

Experimental

Preparation

The compound has been prepared by E. Jóna [2] as light green crystals.

Collection of X-ray data

The compound $Ni(NCS)_2(C_9H_7N)_4(H_2O)_2$, $M_r = 727.56$, forms prismatic crystals. The unit cell dimensions and intensity data were measured on a Syntex P 2_1 computer-controlled four-circle diffractometer equipped with a graphite crystal monochromator, using MoK_α radiation. A least squares fit of the four position angles for thirteen reflections produced the orientation matrix required to control data collection and afforded the following unit cell dimensions: $a = 12.502(8)$, $b = 8.966(8)$, $c = 7.558(4)$ Å, $\alpha = 95.69(6)$, $\beta = 92.58(5)$, $\gamma = 92.18(7)^\circ$, $V = 841(1)$ Å^3. The measured density $D_{Meas} = 1.426$ g cm^{-3}; assuming Z = 1 the density 1.436 g cm^{-3} was calculated. The crystal belongs to the triclinic system with the space group $P\bar{1}$ [10].

Data were collected in the range of $0^\circ < 2\theta < 100^\circ$. The θ –2 θ scan technique with a variable scan rate from 4.0 to 24.0 deg min^{-1} was used. The scan range was from $2\,\theta MoK_{\alpha 1} - 1^\circ$ to $2\theta MoK_{\alpha 2} + 1^\circ$. The background counts were taken at each end of the range for a time equal to one half of the scan time. The intensity I was equal to scan rate [total scan counts – (sum of background counts)/back-

TABLE I. Fractional Atomic Coordinates (× 10^5) and Temperature Factors (× 10^2) for the Asymmetric Unit of $Ni(NCS)_2(H_2O)_2(C_9H_7N)_4$ (with standard deviations in parentheses).

Name	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0 (0)	0 (0)	0 (0)	259 (16)	161 (14)	168 (15)	−23 (11)	−21 (12)	34 (11)
S	82263 (32)	17412 (44)	50861 (53)	621 (26)	529 (23)	329 (23)	283 (21)	−30 (21)	43 (20)
N1	06686 (87)	01879(113)	24650(146)	530 (74)	258 (59)	281 (65)	−18 (49)	−28 (57)	43 (49)
N2	06531 (79)	23075(105)	01783(147)	278 (60)	236 (55)	345 (67)	34 (45)	68 (52)	19 (51)
N3	65797(104)	06378(204)	88938(177)	432 (87)	813(107)	444 (75)	−133 (84)	148 (65)	12 (83)
O1	85374 (59)	08668 (80)	08929(109)	319 (47)	293 (45)	393 (49)	96 (37)	99 (39)	48 (38)
C1	88627(106)	08047(146)	64922(166)	381 (83)	291 (74)	152 (69)	−86 (59)	30 (59)	−148 (37)
C2	04900(103)	30689(151)	17315(176)	426 (85)	344 (77)	233 (71)	55 (62)	140 (64)	55 (62)
C3	08526(105)	45970(145)	21546(184)	370 (83)	256 (76)	395 (82)	77 (65)	−74 (67)	−99 (65)
C4	13863(107)	53313(155)	10232(187)	390 (85)	525 (85)	288 (76)	−44 (68)	72 (66)	101 (78)
C5	15773(106)	45289(143)	92832(195)	413 (86)	136 (68)	431 (88)	−19 (57)	−45 (70)	11 (61)
C6	11947 (99)	30163(155)	89379(189)	236 (75)	339 (82)	332 (79)	75 (61)	−28 (62)	68 (65)
C7	13788(101)	22376(136)	72835(194)	353 (80)	259 (69)	355 (80)	−21 (58)	75 (66)	100 (66)
C8	19486(115)	29289(156)	60714(186)	485 (92)	315 (78)	347 (83)	62 (67)	78 (72)	54 (67)
C9	23176(119)	44147(189)	63955(217)	477 (99)	493(102)	490 (98)	−55 (80)	88 (80)	196 (83)
C10	21264(121)	51956(154)	79313(224)	551(102)	289 (80)	504(101)	−63 (68)	140 (85)	81 (77)
C11	60295(165)	18450(202)	86840(228)	748(131)	553(117)	543(111)	−123 (95)	668(101)	−11 (91)
C12	50240(155)	18554(210)	78057(235)	578(114)	712(118)	539(108)	206 (93)	76 (91)	362 (92)
C13	44960(133)	05674(203)	71397(218)	687(123)	501(101)	535(103)	−123 (96)	214 (87)	285 (86)
C14	54145(127)	21957(249)	32230(235)	272 (96)	762(130)	654(110)	17 (95)	−67 (81)	−29(105)
C15	49561(120)	07848(233)	26243(205)	170 (85)	874(132)	385 (89)	99 (84)	87 (70)	130 (90)
C16	39049(138)	06774(227)	17754(211)	398(111)	658(121)	350 (89)	−3 (95)	33 (78)	135 (86)
C17	33955(132)	19932(270)	15341(252)	352(103)	900(149)	696(123)	106(105)	−139 (86)	99(120)
C18	38775(176)	32973(237)	21124(292)	671(138)	833(148)	848(152)	379(113)	128(118)	140(119)
C19	49017(160)	34346(206)	29977(252)	599(118)	636(119)	770(130)	15 (94)	−23(104)	−86(100)
H1	35030 (0)	43982 (0)	19327 (0)	300 (0)					
H2	52736 (0)	45750 (0)	35478 (0)	300 (0)					
H3	62381 (0)	23148 (0)	38800 (0)	300 (0)					
H4	40603 (0)	−02898 (0)	78065 (0)	300 (0)					
H5	46413 (0)	29692 (0)	76848 (0)	300 (0)					
H6	63884 (0)	29804 (0)	29835 (0)	300 (0)					
H8	25730 (0)	20183 (0)	09079 (0)	300 (0)					
H9	27948 (0)	49684 (0)	53914 (0)	300 (0)					
H10	23903 (0)	63982 (0)	81703 (0)	300 (0)					
H11	16042 (0)	57099 (0)	−02304 (0)	300 (0)					
H12	06529 (0)	51928 (0)	34533 (0)	300 (0)					
H13	00632 (0)	25052 (0)	27402 (0)	300 (0)					
H15	10936 (0)	10635 (0)	69582 (0)	300 (0)					
H16	21052 (0)	23078 (0)	47688 (0)	300 (0)					

TABLE II. Interatomic Distances and Bond Angles for Crystals of $Ni(NCS)_2(H_2O)_2(C_9H_7N)_4$ (with e.s.d. in parentheses).

Distance	Å	Angle	(°)
Ni–N1	2.038(11)	N1–Ni–N2	89.03(40)
Ni–N2	2.183(10)	O1–Ni–N1	95.81(36)
Ni–O1	2.128(7)	O1–Ni–N2	88.01(34)
Nl–C1	1.159(17)	Ni–Nl–C1	153.74(1.03)
Cl–S	1.620(14)	Nl–Cl–S	177.31(1.23)
N2–C2	1.329(17)	Ni–O1–N3	125.06(44)
N2–C6	1.376(17)	C6–N2–C2	118.78(1.09)
C2–C5	1.427(19)	N2–C2–C3	122.40(1.19)
C3–C4	1.320(19)	C2–C3–C4	121.53(1.26)
C4–C5	1.472(20)	C3–C4–C5	117.68(1.25)
C5–C6	1.416(19)	C4–C5–C10	123.43(1.26)
C6–C7	1.406(20)	C4–C5–C6	118.18(1.21)
C7–C8	1.368(20)	C6–C5–C10	118.39(1.26)
C8–C9	1.387(22)	C5–C6–N2	121.41(1.20)
C9–C10	1.384(23)	C5–C6–C7	118.61(1.22)
C10–C5	1.425(21)	C7–C6–N2	119.98(1.19)
N3–C11	1.323(25)	C6–C7–C8	119.93(1.24)
N3–C16	1.347(26)	C7–C8–C9	121.70(1.35)
C11–C12	1.399(28)	C8–C9–C10	119.67(1.47)
C12–C13	1.340(26)	C9–C10–C5	121.62(1.42)
C13–C15	1.437(26)	C16–N3–C11	115.49(1.56)
C15–C16	1.434(23)	N3–C11–C12	125.60(1.73)
C16–C17	1.386(30)	C11–C12–C13	121.23(1.72)
C17–C18	1.320(31)	C12–C13–C15	115.53(1.59)
C18–C19	1.415(30)	C14–C15–C16	119.20(1.61)
C19–C14	1.325(28)	C13–C15–C16	119.15(1.55)
C14–C15	1.393(29)	C13–C15–C14	121.64(1.60)
O1–H···N3	2.812(15)	C15–C16–N3	122.90(1.61)
		C15–C16–C17	118.37(1.66)
		C17–C16–N3	118.60(1.67)
		C16–C17–C18	119.55(1.91)
		C17–C18–C19	123.26(1.99)
		C18–C19–C14	118.49(1.83)
		C19–C14–C15	121.10(1.77)

ground to scan ratio] with a $\sigma(I)$ equal to the scan rate [total scan counts + (sum of background count/background to scan ratio)^2]$^{1/2}$. In order to check the stability of the measurement four reflections were selected as standards and their intensities were recorded periodically through data collection every 640 reflections. Their intensities showed no significant change with time. 7863 reflections were collected and the 1632 reflections with $I > 1.96\sigma(I)$ were used in the analysis. The intensities and their standard deviations were corrected for Lorentz polarization factor and the polarization of the monochromator. Absorption of crystal with $\mu R = 0.146$ for MoK_α has been neglected.

Refinement of X-ray data

The structure has been solved by the heavy atom method. The nickel and sulphur atoms were located in a three-dimensional Patterson map. The solution and the refinement of the structure was carried out by the Fourier syntheses and full-matrix least-squares refinement. The positions and temperature factors of all atoms were in the first steps refined isotropically using a block-diagonal matrix, at the final stage the full-matrix anisotropic refinement was applied. The final discrepancy indices of R_1 defined as $\Sigma\,(|F_o| - |F_c|)/\Sigma|F_o|$ had value of 0.133 and R_2 defined as $[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$ reached the value of 0.073, where $w = 1/\sigma_F^2$ and $\sigma_F = (F_o - \sigma_I/Lp)^{1/2} - F_o$. Parameter changes in the final cycle were all less than 0.25 times the esd of the parameter. The refined atomic coordinates and anisotropic temperature coefficients are listed in Table I. The most important interatomic distances and bond angles are shown in Table II.

All calculations were carried out on a CDC 3300 computer using the programs written by P. Gantzel, R. Sparks and K. Trueblood, DRF and DISTAN by A. Zalkin. All mentioned programs were modified by

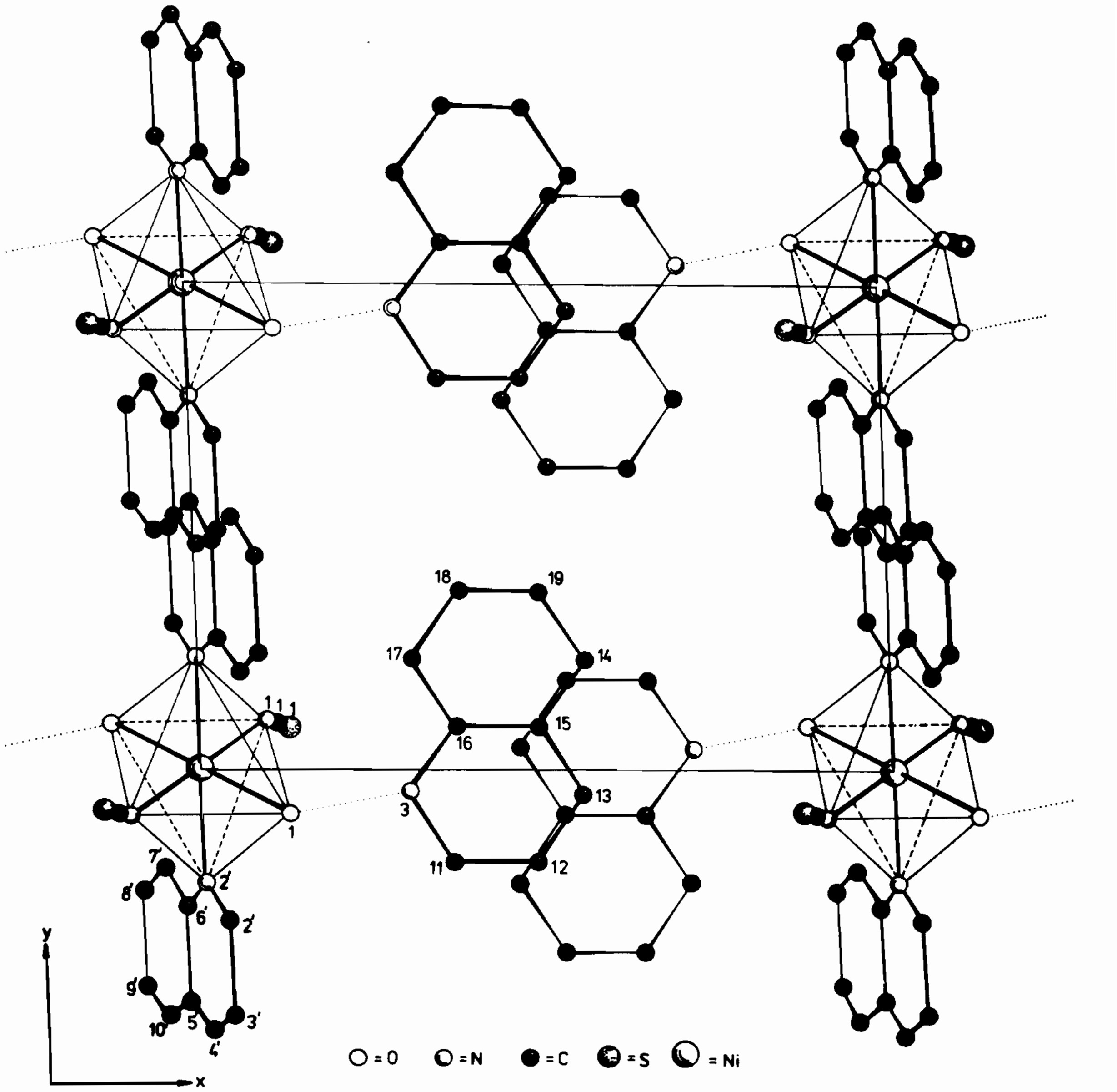

Figure 1. The scheme of the crystal structure of $[Ni(NCS)_2(qn)_2(H_2O)_2] \cdot 2qn$.

O. Lindgreen. The atomic scattering factors were from Cromer and Waber [11] for all atoms.

Discussion

The crystal structure of the compound under investigation is formed by the centrosymmetrical complex molecules $[Ni(NCS)_2(H_2O)_2(qn)_2] \cdot 2qn$. The scheme of the crystal structure is shown in Fig. 1.

The Ni atoms occupy a special position in the centre of symmetry with the coordinates (0, 0, 0). Their heterogeneous coordination sphere forms a distorted octahedral configuration, consisting of two N atoms from the NCS groups (Ni–N1 = 2.038 Å), two O atoms from the H_2O molecules (Ni–O1 = 2.128 Å) and two N atoms from the quinoline molecules (Ni–N2 = 2.183 Å), all being in *trans* position (Fig. 1, Table II). The interatomic distances in the primary coordination sphere indicate that the equatorial plane of the coordination pseudooctahedron is formed by two nitrogen atoms (NCS) and two oxygen atoms (H_2O). The N2 atoms from the quinoline molecules are in axial positions.

The thiocyanate group is nearly linear (the angle N1–C1–S1 being 177.31°) and is deviated from the equatorial plane of the coordination polyhedron Ni 2O 2N by 26.26°. The value of the interatomic

TABLE III. Deviations of Atom Centres from Mean Planes of Quinoline Molecules (in Å).

Atom	Å	Atom	Å
N2	0.0015	N3	–0.013
C2	–0.0064	C11	0.0306
C3	–0.0030	C12	0.0000
C4	–0.0105	C13	–0.0105
C5	0.0065	C14	0.0053
C6	0.0077	C15	–0.0057
C7	0.0160	C16	–0.0343
C8	–0.0221	C17	–0.0094
C9	–0.0117	C18	0.0167
C10	0.0220	C19	0.0086

distance N1–C1, 1.159 Å, is between the sum of the covalent radii of N and C bonded by a double bond (1.29 Å) and a triple one (1.15 Å), and the distance C1–S1 of 1.62 Å is between the sum of the covalent radii of C and S, bonded by a single (1.81 Å) and a double bond (1.61 Å) [12]. The quinoline molecules which are not coordinated to the Ni atom form hydrogen bonds to the molecules of H_2O, the distance N3•••H–O1 being 2.81 Å (Table II, Fig. 1). Both the coordinated and the noncoordinated quinoline molecules were found to be planar. The deviation in the coordinated quinoline molecule does not exceed 0.022 Å and 0.034 Å, respectively, in the noncoordinated one (Table III). The coordination does not essentially influence the shape of the quinoline molecules, as is shown by the comparison of interatomic distances and angles for both types of quinoline molecules (Table II). The distances C–N have the values of 1.32 to 1.37 Å, those of C–C being in the range of 1.32 to 1.47 Å. The plane of the coordinated quinoline molecule, the equatorial plane of the coordination pseudo-octahedron built up by the atoms Ni 2O 2N (from the NCS groups), and the plane of noncoordinated quinoline molecule include together angles of 90°, while the plane of the coordinated quinoline molecule and that built up by the atoms Ni and 4N (two atoms N are from the quinoline molecules and two from the NCS groups) confine the angle of 47°. For complexes with bulky ligands, such as quinoline, such an orientation is influenced by the tendency of the best suitable spatial arrangement.

In the crystal structure of this compound the complex molecules $[Ni(NCS)_2(qn)_2(H_2O)_2]$ form "layers" approximately normal to the direction [100], between which there are "layers" of the noncoordinated quinoline molecules, in the projection partially overlapping in the direction of [001]. The noncoordinated quinoline molecules in these layers are alternatively bonded on both sides by means of hydrogen bonds with the complexes $[Ni(NCS)_2(qn)_2(H_2O)_2]$ (Fig. 1).

It follows from the crystal structure that in the thermal decomposition of the compound the two noncoordinated quinoline molecules are easily released. By the escape of water molecules changes take place in the coordination polyhedra, resulting in one of two isomers of different colour (depending on the conditions of decomposition) [3]. The red isomer is diamagnetic with a square coordination of Ni 4N and thus it exhibits a molecular structure. The green form is paramagnetic with a pseudooctahedral coordination of Ni 4N 2S. In the solid state this compound contains terminal bonding as well as tridentate bridging NCS groups (–NCS<) [3], the consequence of which is the polymeric structure of the green crystals $Ni(NCS)_2(qn)_2$. This way of NCS bonding has been found *e.g.* in $Cu(NCS)_2(NH_3)_2$ by X-ray analysis [13].

It may be suggested that in the formation of the red isomer no essential changes of the coordination of the NCS groups and quinoline molecules occur. On the other hand the formation of the green isomer requires in addition to the release of the quinoline and the water molecules also a rearrangement of the coordination sphere of the complex and a change in the crystal lattice. The result is the netting of the coordination polyhedra by means of the NCS groups.

References

1 M. A. Poraj-Košic and A. S. Ancyškina, *Kristallografija, 3,* 686 (1958).

2 T. Šramko, E. Jóna, and A. Sirota, *Proc. of the 2nd Conf. Coord. Chem.,* Smolenice, Bratislava (1969) p. 239.

3 E. Jóna, T. Šramko, J. Kohout, A Sirota and J. Gažo, *Chem. Zvesti, 25,* 241 (1971).

4 H. C. A. King, E. Körös and S. M. Nelson, *J. Chem. Soc.,* 5449 (1963).

5 S. Buffagni, L. M. Vallarino and J. V. Quagliano, *Inorg. Chem., 3,* 480 (1964).

6 E. Jóna, T. Šramko and J. Gažo, *J. Thermal Anal., 4,* 61 (1972).

7 S. M. Nelson and T. M. Shepherd, *Inorg. Chem., 4,* 813 (1965).

8 M. Goodgame and J. M. Weeks, *J. Chem. Soc. A,* 1156 (1966).

9 E. Jóna, M. Jamnický, T. Šramko and J. Gažo, *Coll.* Czech. Chem. Commun., 37, 3676 (1972).

10 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England (1965).

11 D. T. Cromer and J. T. Waber, *Acta Crystallogr., 18,* 104 (1965).

12 L. Pauling, "The Chemical Bond", Cornell, New York (1967).

13 M. Kabešová, J. Garaj and J. Gažo, *Coll. Czech. Chem. Commun., 37,* 942 (1972).