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The Crystal and Molecular Structure of Bis(quinoxaline-2,3-dithiolato)nickel(II)–Bis(*N*,*N*-dimethylformamide), $[(C_6H_4NHNC_2S_2)_2Ni^{II}].2(CH_3)_2NC(O)H$

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The crystal structure of bis(quinoxaline-2,3-dithiolato)nickel(II)–bis(*N*,*N*-dimethylformamide), $[(C_6H_4NHNC_2S_2)_2Ni^{II}].2(CH_3)_2NC(O)H$ [hereinafter $(HQS_2)_2Ni.2DMF$] was determined by direct methods and three-dimensional Fourier syntheses, and was refined by least-squares methods (1940 reflexions collected with a four-circle diffractometer), including anisotropic temperature factors for non-hydrogen atoms and isotropic for H, to a final $R = 0.034$. The crystals are monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14), $a = 7.356$ (2), $b = 15.528$ (4), $c = 11.707$ (2) Å, $\beta = 105.68$ (2)°, $Z = 2$. The structure consists of alternating layers of $(HQS_2)_2Ni$ and DMF molecules parallel to the *ac* plane. Each $(HQS_2)_2Ni$ molecule is centrosymmetrically linked to two DMF molecules by two NH···O hydrogen bonds (H···O 1.80 Å). Both the $(HQS_2)_2Ni$ and DMF molecules are planar within r.m.s. atom deviations of 0.036 and 0.012 Å, respectively, from their non-hydrogen atoms least-squares planes. Principal bond lengths are: Ni–S 2.165, 2.168; S–C 1.703, 1.732; C–N 1.333, 1.313; N–C 1.378, 1.380; O–C 1.233; and C–N(0) 1.306 Å.

Introduction

In previous work we have carried out spectrochemical studies of quinoxaline-2,3-dithiol (H_2QS_2) and related compounds (Peyronel, Pignedoli & Malavasi, 1976) and of the cationic, neutral and anionic Ni^{II} complexes of this chelating ligand (Pignedoli, Peyronel & Malavasi, 1976). The crystal and molecular structure of tetraethylammonium bis(quinoxaline-2,3-dithiolato)-nickelate(II) dihydrate $[(Et_4N)_2(QS_2)_2Ni.2H_2O]$ (Pignedoli, Peyronel & Antolini, 1974) has been determined by X-ray three-dimensional analysis. In order to compare the molecular structures of the neutral and anionic Ni^{II} complexes of quinoxaline-2,3-dithiol we have determined the crystal structure of $(HQS_2)_2Ni.2DMF$.

Experimental

Crystals of the complex $(HQS_2)_2Ni.2DMF$ were prepared, as previously described (Pignedoli, Peyronel & Malavasi, 1976), by prolonged heating of the green cationic complex $(H_2QS_2)_3NiCl_2.2H_2O$ in its mother DMF + HCl solution on a water bath. The neutral complex grows in this solution to large crystals, black in mass and dark bronze under reflected light. The crystals used were eight-faced prismatic in shape, elongated along **c**, with angles between the normals to the faces in the *hk*0 zone of about 66° 30′ and 23° 30′, measured with an optical goniometer. The crystal used for collecting the intensities was 0.2 × 0.4 × 0.7 mm.

The cell parameters were determined and the intensities of the reflexions were recorded within $\sin\theta/\lambda = 0.62$ with monochromated Mo $K\alpha$ radiation (0.71069 Å) on a Philips PW 1100 automatic four-circle diffractometer, connected on-line to a computer. The systematic absences of reflexions were observed on Weissenberg and precession photographs and with the diffractometer. The observed reflexions obey the conditions: $0k0$ ($k = 2n$), $h0l$ ($h + 1 = 2n$), hkl (no condition).

Crystal data

Bis(quinoxaline - 2,3 - dithiolato)nickel(II) – bis(*N*,*N*-dimethylformamide), $[(C_6H_4NHNC_2S_2)_2Ni^{II}].2(CH_3)_2NC(O)H$, $(HQS_2)_2Ni.2DMF$; monoclinic prismatic, space group $P2_1/n$ (C_{2h}^5, No. 14) from systematic absences; $a = 7.356$ (2), $b = 15.528$ (4), $c = 11.707$ (2) Å, $\beta = 105.68$ (2)° at 24°C, $V = 1287.5$ Å^3, FW 591.45, $Z = 2$; $F(000) = 612$, $D_o = 1.52$, $D_c = 1.53$ g cm^{-3}.

The intensities were corrected only for Lorentz and polarization factors; 1940 reflexions were used for the calculations. The crystal structure was solved by direct methods with the *LSAM* program (Germain, Main & Woolfson, 1971) which allowed the allocation of signs to 204 reflexions, enabling the Ni, 2 S, 2 N and 7 C atoms of the complex and the O atom of dimethylformamide to be located. The other non-hydrogen atoms were identified by three-dimensional Fourier syntheses with the *FOUR3D* program of Immirzi (1967*a*), which gives the coordinates of the maxima and their distances immediately.

The structure was then refined by the block-diagonal least-squares method with the *MIQUAD* program of Immirzi (1967*b*) on a CDC 7600 computer. The

Table 1. *Fractional coordinates and thermal parameters*

Coordinates are $\times 10^5$ for non-hydrogen and $\times 10^4$ for hydrogen atoms. Thermal parameters for non-hydrogen atoms are defined by: $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl) \times 10^{-3}]$. Thermal parameters, B(Å^2), for hydrogen atoms are defined by $\exp[-B(\sin\theta/\lambda)^2]$. Standard deviations are in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	2895 (24)	2581 (23)	1520 (22)	80 (22)	345 (18)	−439 (21)
S(1)	140 (15)	6063 (6)	16673 (8)	4705 (47)	3144 (39)	1626 (34)	1129 (35)	324 (32)	−402 (30)
S(2)	16928 (14)	−10700 (6)	8939 (8)	4302 (44)	3106 (38)	1872 (35)	885 (34)	326 (31)	−643 (30)
N(1)	16551 (39)	1121 (18)	38716 (23)	3419 (122)	2794 (120)	1883 (111)	138 (103)	597 (95)	−235 (96)
N(2)	31156 (42)	−13908 (18)	31805 (25)	3790 (136)	2812 (121)	2267 (125)	267 (105)	433 (104)	−40 (99)
C(1)	13128 (44)	−699 (22)	27205 (28)	2954 (133)	2583 (132)	1880 (129)	−133 (121)	591 (106)	−192 (116)
C(2)	21000 (46)	−8560 (21)	23936 (29)	2839 (148)	2782 (140)	2016 (139)	−183 (114)	473 (115)	−310 (113)
C(3)	27418 (48)	−4244 (22)	47276 (29)	3074 (147)	3006 (143)	1892 (137)	−485 (120)	559 (115)	117 (116)
C(4)	34578 (49)	−11743 (22)	43610 (30)	3333 (153)	2766 (144)	2098 (144)	−430 (120)	546 (118)	126 (114)
C(5)	31398 (54)	−2068 (24)	59340 (31)	4050 (168)	3855 (179)	2050 (147)	−442 (137)	810 (128)	−82 (126)
C(6)	46006 (56)	−17147 (25)	52310 (34)	4391 (192)	3219 (162)	3103 (180)	269 (140)	649 (142)	630 (137)
C(7)	42446 (59)	−7498 (27)	67548 (32)	4813 (198)	4745 (197)	1688 (146)	−901 (162)	246 (137)	291 (138)
C(8)	49788 (59)	−14976 (27)	64001 (34)	4529 (193)	4432 (197)	2537 (168)	−383 (159)	20 (145)	1172 (147)
O	6253 (40)	16071 (18)	46720 (24)	5261 (142)	3672 (121)	3517 (129)	661 (108)	885 (107)	−483 (101)
N(0)	−8773 (44)	28786 (20)	41759 (27)	3899 (143)	3439 (139)	2947 (141)	−4 (114)	1064 (115)	−592 (113)
C(0)	−2023 (56)	21428 (26)	39369 (34)	4171 (187)	4150 (182)	2926 (173)	−307 (150)	1182 (144)	−1152 (148)
C(01)	−6154 (75)	31529 (30)	53879 (41)	7591 (288)	4731 (224)	4186 (224)	−48 (208)	2746 (209)	−1431 (180)
C(02)	−18485 (69)	34669 (32)	32445 (45)	5568 (246)	5286 (246)	5560 (266)	1109 (201)	1562 (206)	1103 (208)

	x	y	z	B		x	y	z	B
H(1)	1217 (47)	591 (22)	4124 (30)	0·66 (0·72)	H(11)	−437 (73)	2687 (35)	5821 (46)	5·75 (1·44)
H(5)	2547 (44)	246 (20)	6145 (28)	0·17 (0·68)	H(12)	−1820 (66)	3326 (31)	5567 (42)	4·15 (1·18)
H(6)	5162 (53)	−2169 (23)	4974 (34)	1·36 (0·77)	H(13)	171 (80)	3550 (37)	5442 (49)	6·79 (1·62)
H(7)	4443 (46)	−602 (22)	7550 (30)	0·52 (0·71)	H(21)	−1660 (66)	3229 (32)	2507 (44)	4·48 (1·25)
H(8)	5767 (46)	−1843 (22)	6922 (30)	0·58 (0·71)	H(22)	−1179 (68)	3933 (33)	3236 (44)	4·84 (1·31)
H(0)	−316 (52)	2062 (24)	3148 (33)	1·68 (0·85)	H(23)	−3169 (65)	3551 (31)	3321 (42)	4·18 (1·21)

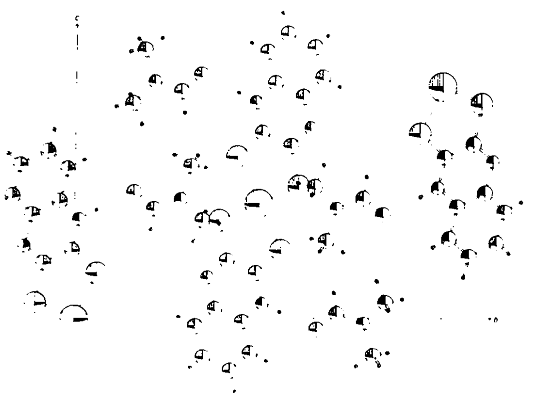


Fig. 1. Orthographic projection on the bc plane of the asymmetric units x,y,z; $1-x, 1-y, 1-z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

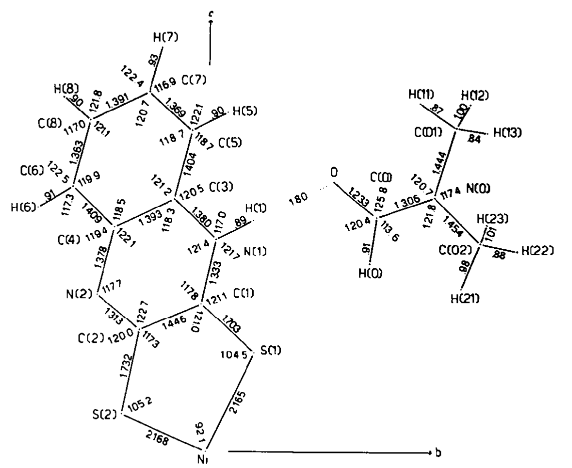


Fig. 2. Interatomic distances (Å) and angles (°) for the asymmetric unit.

atomic scattering factors (Hanson, Herman, Lea & Skillman, 1964) of the Ni and S atoms were corrected for the real part of the anomalous dispersion (*International Tables for X-ray Crystallography*, 1962).

After several cycles of isotropic and anisotropic refinement for the non-hydrogen atoms, the H atoms could be located, by three-dimensional Fourier difference syntheses, very near to their calculated positions. They were then introduced into the calculations, and after several cycles of anisotropic refinement for non-hydrogen atoms and isotropic for H the reliability index ($R = \Sigma\,|F_o - F_c|/\Sigma\,|F_o|$) converged to the final value of 0·034. The positional and thermal parameters are reported in Table 1.

Interatomic distances and angles with their e.s.d.'s (Table 2 and Fig. 2) were calculated with the *MIQUAD* and *IMPACC* programs (Immirzi, 1967*b*). The more relevant least-squares planes and the atomic distances from them (Table 3) were calculated with *PIAMED* (Immirzi, 1967*b*). An orthographic projection of the unit cell (Fig. 1) and the thermal ellipsoids of the asymmetric unit (Fig. 3) were plotted with *ORTEP* (Johnson, 1965).*

Results and discussion

The *bc* orthographic projection of the unit cell (Fig. 1) shows that the crystal structure consists of alternating layers of $(HQS_2)_2Ni$ and DMF molecules almost parallel to the *ac* plane. The $(HQS_2)_2Ni$ and DMF molecules are planar (Table 3) within a r.m.s. atom deviation for non-hydrogen atoms of 0·036 Å for $(HQS_2)_2Ni$ and 0·012 Å for DMF. Their least-squares planes form acute angles of 34·5 and 29·6° respectively with the *bc* plane. The $(HQS_2)_2Ni$ and DMF molecules are almost coplanar, their least-squares planes making an acute angle of 9·2°.

The $(HQS_2)_2Ni$ molecule is centrosymmetrically linked to two DMF molecules by two NH · · · O hydro-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32261 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

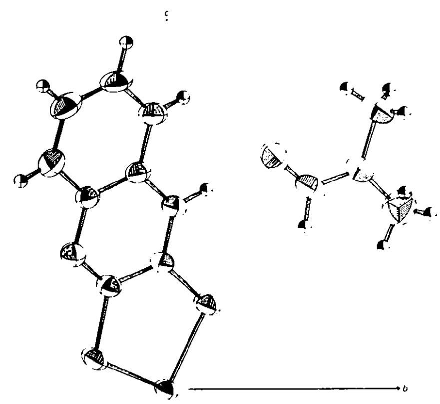


Fig. 3. *ORTEP* plot of thermal ellipsoids scaled to include 50% probability (asymmetric unit *x,y,z*).

Table 2. *Interatomic distances* (Å) *and angles* (°) *with their e.s.d.'s*

Bond distances

Ni–S(1)	2·165 (1)	C(1)–C(2)	1·446 (4)	C(3)–C(5)	1·404 (5)	N(0)–C(01)	1·444 (6)
Ni–S(2)	2·168 (1)	C(3)–C(4)	1·393 (5)	C(4)–C(6)	1·409 (6)	N(0)–C(02)	1·454 (7)
S(1)–C(1)	1·703 (4)	H(1)–N(1)	0·89 (3)	C(5)–C(7)	1·369 (6)	H(11)–C(01)	0·87 (6)
S(2)–C(2)	1·732 (4)	H(5)–C(5)	0·90 (3)	C(6)–C(8)	1·363 (6)	H(12)–C(01)	1·00 (5)
C(1)–N(1)	1·333 (4)	H(6)–C(6)	0·91 (3)	C(7)–C(8)	1·391 (6)	H(13)–C(01)	0·84 (6)
C(2)–N(2)	1·313 (5)	H(7)–C(7)	0·93 (4)			H(21)–C(02)	0·98 (5)
N(1)–C(3)	1·380 (5)	H(8)–C(8)	0·90 (4)	O–C(0)	1·233 (6)	H(22)–C(02)	0·88 (5)
N(2)–C(4)	1·378 (5)	H(0)–C(0)	0·91 (4)	C(0)–N(0)	1·306 (5)	H(23)–C(02)	1·01 (5)

Other distances

N(1) · · · O	2·69	H(1) · · · O	1·80 (3)

Bond angles

S(1)–Ni–S(2)	92·06 (2)	C(1)–N(1)–C(3)	121·4 (2)	O–C(0)–N(0)	125·8 (2)
Ni–S(1)–C(1)	104·5 (1)	C(2)–N(2)–C(4)	117·7 (2)	C(0)–N(0)–C(01)	120·7 (2)
Ni–S(2)–C(2)	105·2 (1)	C(3)–C(4)–C(6)	118·5 (2)	C(0)–N(0)–C(02)	121·8 (2)
S(1)–C(1)–N(1)	121·1 (2)	C(3)–C(5)–C(7)	118·7 (2)	C(01)–N(0)–C(02)	117·4 (2)
S(2)–C(2)–N(2)	120·0 (2)	C(4)–C(3)–C(5)	121·2 (2)	H(11)–C(01)–H(12)	95·9 (1·9)
S(1)–C(1)–C(2)	121·0 (2)	C(4)–C(6)–C(8)	119·9 (2)	H(11)–C(01)–H(13)	125·1 (4·2)
S(2)–C(2)–C(1)	117·3 (2)	C(5)–C(7)–C(8)	120·7 (2)	H(11)–C(01)–N(0)	106·6 (0·8)
N(1)–C(1)–C(2)	117·8 (1)	C(6)–C(8)–C(7)	121·1 (2)	H(12)–C(01)–H(13)	114·8 (3·7)
N(2)–C(2)–C(1)	122·7 (2)	H(6)–C(6)–C(4)	117·3 (5)	H(12)–C(01)–N(0)	113·2 (0·8)
N(1)–C(3)–C(4)	118·3 (2)	H(6)–C(6)–C(8)	122·5 (6)	H(13)–C(01)–N(0)	101·4 (0·8)
N(2)–C(4)–C(3)	122·1 (2)	H(7)–C(7)–C(5)	116·9 (5)	H(21)–C(02)–H(22)	95·0 (2·5)
N(1)–C(3)–C(5)	120·5 (2)	H(7)–C(7)–C(8)	122·4 (5)	H(21)–C(02)–H(23)	119·7 (2·4)
N(2)–C(4)–C(6)	119·4 (2)	H(8)–C(8)–C(6)	117·0 (5)	H(21)–C(02)–N(0)	105·4 (0·7)
H(1)–N(1)–C(1)	121·7 (5)	H(8)–C(8)–C(7)	121·8 (5)	H(22)–C(02)–H(23)	116·9 (2·3)
H(1)–N(1)–C(3)	117·0 (5)	H(0)–C(0)–O	120·4 (5)	H(22)–C(02)–N(0)	111·3 (0·8)
H(5)–C(5)–C(3)	118·7 (5)	H(0)–C(0)–N(0)	113·6 (7)	H(23)–C(02)–N(0)	107·7 (0·7)
H(5)–C(5)–C(7)	122·1 (5)				

Other angles

N(1)–H(1) · · · O	173·0 (6)	H(1) · · · O–C(0)	117·6 (6)

gen bonds (N···O 2·69, H···O 1·80 Å; N—H···O 173°) nearly parallel to the least-squares planes of both molecules (Table 2, Fig. 1). All the other intermolecular contacts are of the van der Waals type. The H···O=C(0) angle of 117·6° indicates that the proton points to an electron lone pair of the O atom lying in the OC(0)H(0)N(0) plane at about 120° from the O=C bond. The NH···O hydrogen bond is so strong that the crystals may be exposed to the air for several months without losing dimethylformamide.

The Ni atom, lying on a centre of symmetry, forms an intrachelate S–Ni–S angle of 92·06° and has almost identical Ni–S bond distances (2·165, 2·168 Å), very close to the values observed for the $(QS_2)_2Ni^{2-}$ anionic complex (Pignedoli, Peyronel & Antolini, 1974).

The nonequivalence of the N and N(H) atoms may explain some differences in symmetrical bond lengths on the two sides of the molecule:

	N side	N(H) side
S–C	1·732	1·703
C–N	1·313	1·333
	3·045	3·036

Their sum is, however, almost equal. These differences may be a result of a mesomeric shift of electron density towards the C(2)–N(2) bond greater than that towards the C(1)–N(1)(H) bond, as a consequence of the removal of a proton from the N(2) atom.

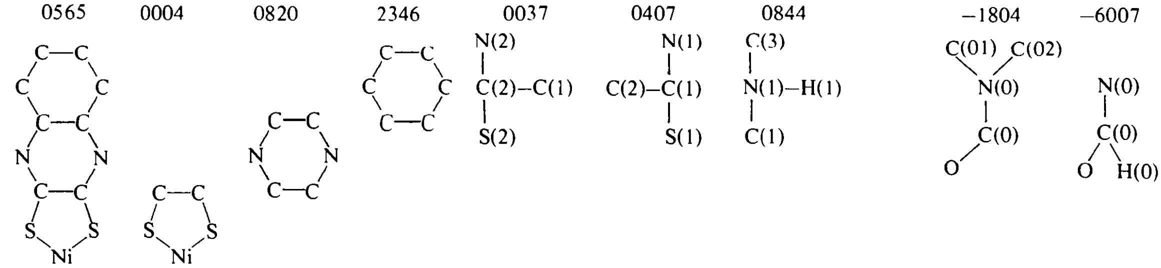
The N–C bonds (1·378 and 1·380 Å) are equal within their standard deviations and significantly greater

Table 3. *Least-squares planes and acute angles between planes*

The equation in the form $Ax + By + Cz - D = 0$ is referred to the crystallographic axes a, b and c; the plane coefficients A,B,C,D are $\times 10^4$. Deviations of the atoms from the planes and their r.m.s. deviations are in Å ($\times 10^3$); the deviations of the atoms not included in the mean plane are indicated by asterisks.

Ni	−56	0	−82*	−235*			
S(1)	−4	2	−26*	−136*		−1	
S(2)	−25	−2	−58*	−165*	−2		
C(1)	25	−4	−2	−67*	−2	4	−2
C(2)	26	4	−5	−69*	7	−1	
N(1)	32	−33*	6	−26*		−2	6
N(2)	42	−7*	7	−23*	−3		
C(3)	25	−68*	−4	0			−2
C(4)	31	−54*	−2	2			
C(5)	−13	−144*	−42*	−3			
C(6)	−3	−118*	−41*	0			
C(7)	−38	−196*	−69*	4			
C(8)	−41	−191*	−77*	−3			
H(1)			−2*				−3
H(5)				94*			
H(6)				−92*			
H(7)				40*			
H(8)				−52*			
R.m.s.	36	5	7	4	8	5	7
A	−8667	−8684	−8684	−8627	−8681	−8710	−8677
B	−4974	−4958	−4943	−5014	−4963	−4906	−4956
C	2713	2451	2717	2970	2468	2614	2721
D	0565	0004	0820	2346	0037	0407	0844

O	5	−6
C(0)	−11	18
N(0)	11	−5
C(01)	−5	−128*
C(02)	−1	37*
H(0)	104*	−7
R.m.s.	12	21
A	−9022	−8906
B	−4313	−4486
C	2406	1687
D	−1804	−6007



NiS(1)S(2)C(1)C(2) ∧ C(1)C(2)N(1)N(2)C(3)C(4) = 1·6°
C(1)C(2)N(1)N(2)C(3)C(4) ∧ C(3)C(4)C(5)C(6)C(7)C(8) = 1·7°
OC(0)N(0) ∧ N(0)C(01)C(02) = 2·7°
NiS(1)S(2)C(1)C(2)N(1)N(2)C(3)C(4)C(5)C(6)C(7)C(8) ∧ OC(0)N(0)C(01)C(02) = 9·2°
NiS(1)S(2)C(1)C(2)N(1)N(2)C(3)C(4)C(5)C(6)C(7)C(8) ∧ *bc* plane = 34·5°
OC(0)N(0)C(01)C(02) ∧ *bc* plane = 29·6°

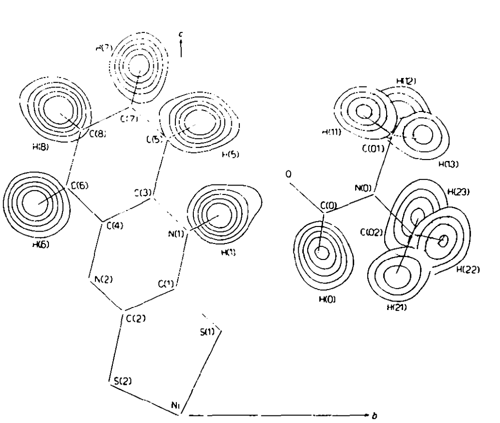


Fig. 4. Sections of the difference electron-density map, projected on the *bc* plane, corresponding to the refined *x* positions for H atoms, calculated with the reflexions having sin $\theta/\lambda < 0{\cdot}5$. Contours are at 0·1 e Å^{-3} intervals, beginning with the 0·6 e Å^{-3} contour.

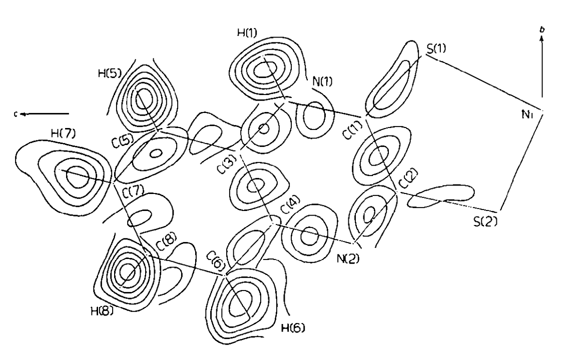


Fig. 5. Sections of the residual difference electron-density map, projected on the *bc* plane, corresponding to the mid-point of the interatomic bond distances (calculated with all the reflexions). Contours are at 0·05 e Å^{-3} intervals, beginning with the 0·5 e Å^{-3} contour.

than the C—N bonds. This difference, observed also in the anionic $(QS_2)_2Ni^{2-}$ complex, may be due to the electron-withdrawing effect of the benzene ring adjacent to these N—C bonds.

The S—C bonds seem to be the more sensitive to the cationic, neutral and anionic nature of the thioamidic complexes because of the 'soft' character of the S atom and independent of the type of ligand and the number of atoms in the chelated ring (Pignedoli, Peyronel & Antolini, 1974).

Each of the three rings of the complex is planar within a r.m.s. atom deviation of 0·004–0·007 Å from its least-squares plane. Acute angles between the adjacent planes are 1–2°. The atoms C(1), C(2) and N(1)(H) of the $(HQS_2)_2Ni$ molecule have an almost planar sp^2 hybridization, like the C(0) and N(0) atoms of the DMF molecule (Tables 2 and 3, Fig. 2).

Most of the bond lengths and angles reported here agree well with those published by Ito, Kashino & Haisa (1976) in a summary of DMF parameters from several crystal-structure analyses.

All the H atoms are very well represented in their *yz* difference Fourier sections (Fig. 4) obtained from the reflexions with sin $\theta/\lambda < 0{\cdot}50$. Above this value the contribution of the scattering factor of the H atom is very small and the contour lines are much more disturbed by other effects.

The *yz* difference Fourier sections (Fig. 5) of the residual electron density were also calculated through the mid-point of the interatomic bonds, all the reflexions being used and the H contributions included in F_c. These sections show that for the complex molecule there is appreciable electron density on the C—S, C—C and C—N bonds which is attributable to their double-bond character. There is also a very high electron density on C—H and N—H bonds located at about $\frac{1}{3}$ the bond distance from the H atom. The residual electron density for the DMF molecule appears to be high and well localized for the formyl H—C bond but lower and much more disturbed for the methyl H—C and the O=C and C—N bonds.

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