

Nickel(II) Complexes of Thiohydrazonates. II. The Crystal and Molecular Structure of [Butanedione di(phenylacetthiohydrazone)]nickel(II)

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Dedicated to Professor K. A. Jensen on his 70th birthday

The crystal structure of the title compound has been determined by X-ray diffraction methods using diffractometer data. The crystals are monoclinic, space group $P2_1/a$, $Z=4$, with unit cell dimensions $a=14.202 \text{ \AA}$, $b=9.754 \text{ \AA}$, $c=13.620 \text{ \AA}$, $\beta=93^\circ 35'$. The final least squares refinement based on the 4080 observed reflections gave a unit weighted residual of 0.044.

The structure shows that the nickel atom has a planar coordination. The phenyl groups stick out on each side of the coordination plane. Apart from the phenyl groups the molecule possesses a pseudo twofold axis of symmetry. Strain within the tetradentate ligand causes the coordination angles and distances to be somewhat different from those found in other *cis* Ni—S complexes.

The ligand contains a series of alternating single and double bonds but the conjugation has only a slight effect on the observed bond lengths.

The synthesis and spectroscopic characterization of a series of nickel complexes with mono- or diketone thioacetylhydrazones have been described in a preceding paper.¹ The organic ligands have previously been unknown and it seems that the apparently unstable molecules are stabilized as nickel(II) complexes.

One of these compounds has already been studied structurally, namely bis(acetophenone thioacetylhydrazonato)nickel(II).² This complex has a tetrahedrally distorted *cis* planar configuration and the phenyl groups are in a *syn* arrangement.

The equivalent complexes made from diketones are bound to have a *cis* configuration and one could anticipate that the backbone of the ligand would be considerably more planar than

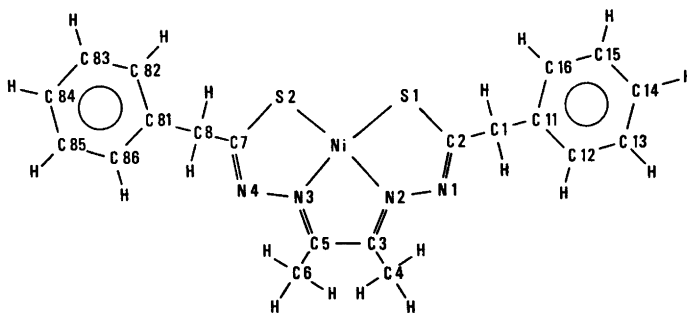


Fig. 1. A schematic drawing of [butanedione di(phenylacetthiohydrazone)]nickel(II), $[\text{Ni}(\text{path})_2\text{-diac}]$, illustrating the atomic labelling.

the equivalent monoketone complex. To obtain structural information about these complexes the crystal structure analysis was undertaken of [butanedione di(phenylacetthiohydrazonato)nickel(II), [Ni(path)₂diac]. From the schematic drawing of this compound shown in Fig. 1, the ligand can be seen to contain alternating double and single bonds and it could be expected that conjugation within the ligand would affect its bond lengths. The crystals of the equivalent acetic acid derivatives are twinned and to avoid this complication the structure analysis was performed for the equivalent phenylacetic acid derivative.

EXPERIMENTAL

A sample of [butanedione di(phenylacetthiohydrazonato)nickel(II)] was supplied by Erik Larsen. This compound crystallizes as intensely coloured rhombic prisms. In polarized light they are red when the electric vector is parallel to the rhombic face. X-Ray diffraction photographs showed that the crystals are monoclinic. The space group is uniquely determined to be $P2_1/a$ from the systematically absent reflections. The density of the crystals was measured by flotation in bromobenzene.

A single crystal 0.11 mm thick and 0.43 by 0.36 mm along the rhombic diagonals was used for the data collection and for the accurate determination of unit cell parameters, using $MoK\alpha$ radiation and a graphite monochromator. The setting angles for 14 relatively high angle reflections were optimized automatically on a Picker FACS-1 diffractometer and these angles were used in a least squares refinement of the unit cell parameters and the orientation matrix. The intensity data were collected by operating the diffractometer in a $\theta - 2\theta$ scan mode at a scan rate of 1° min in 2θ . The scan range was symmetrical and increased with 2θ following the expression $\Delta 2\theta_{sc} = 3.8^\circ + 0.629 \tan \theta$.

Background counts were made for 20 s at each end of the scan range. The intensities of three standard reflections measured after every 40 reflections indicated that no deterioration or misalignment of the crystal had occurred during the data collection. The relative intensities were measured for all the independent reflections where $2.4^\circ \leq 2\theta \leq 60^\circ$. Of the 5733 reflections obtained 4080 had $I/\sigma(I) \geq 2.5$, where $\sigma(I)$ is the standard derivation of the intensity calculated from counting statistics. The data was corrected for Lorentz and polarization effects, but not for absorption.

For the crystallographic calculations use was made of the following computer programs: The Vanderbilt System³ for all diffractometer operations, a local modification of the program

NRC-2Å⁴ for data reduction, ORTEP II⁵ for the illustrations, and the X-Ray System⁶ for the crystal structure analysis.

The atomic scattering factors used in the calculations were those given by Cromer and Mann⁷ using the values for the uncharged atoms, except for hydrogen where the scattering factor calculated by Stewart *et al.*⁸ was employed. The anomalous dispersion corrections added to the scattering factors for nickel and sulfur were those given by Cromer and Liebermann.⁹

CRYSTAL DATA

[Butanedione di(phenylacetthiohydrazonato)nickel(II); C₂₀H₂₀N₄S₂Ni; M = 439.3. Monoclinic, $a = 14.802(9)$ Å, $b = 9.754(6)$ Å, $c = 13.620(8)$ Å, $\beta = 93^\circ 35'(2)$; $V = 1962.6$ Å³; $d_{obs} = 1.49$ g/cm³; $Z = 4$; $d_{calc} = 1.486$ g/cm³. $\mu(MoK\alpha) = 12.08$ cm⁻¹, $F(000) = 912$. Systematically absent reflections: $h0l$ when h odd, $0k0$ when k odd; spacegroup $P2_1/a$ (C_{2h}^5 , No. 14). Developed faces are $\{110\}$ and $\{001\}$.

Table 1. Final coordinates for the non-hydrogen atoms. The estimated standard deviations are given in parenthesis. The labelling corresponds to Fig. 1.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ni ¹	0.12215(2)	0.09917(3)	0.53572(2)
S1 ¹	0.14942(5)	0.30505(7)	0.48941(5)
S2 ¹	0.08576(6)	0.12828(7)	0.68479(5)
N1 ¹	0.1756(2)	0.1339(2)	0.3384(2)
N2 ¹	0.1512(2)	0.0429(2)	0.4117(2)
N3 ¹	0.1039(1)	-0.0867(2)	0.5551(2)
N4 ¹	0.0760(2)	-0.1420(2)	0.6419(2)
C1 ¹	0.1958(2)	0.3708(3)	0.2994(2)
C2 ¹	0.1737(2)	0.2581(3)	0.3705(2)
C3 ¹	0.1490(2)	-0.0882(3)	0.3954(2)
C4 ¹	0.1724(3)	-0.1565(4)	0.3028(2)
C5 ¹	0.1203(2)	-0.1669(2)	0.4816(2)
C6 ¹	0.1102(3)	-0.3179(3)	0.4818(3)
C7 ¹	0.0654(2)	-0.0456(3)	0.7061(2)
C8 ¹	0.0309(2)	-0.0876(4)	0.8035(2)
C11 ¹	0.1135(2)	0.4372(3)	0.2470(2)
C12 ¹	0.1256(3)	0.5110(4)	0.1614(2)
C13 ¹	0.0522(4)	0.5732(4)	0.1114(3)
C14 ¹	-0.0325(4)	0.5635(4)	0.1461(3)
C15 ¹	-0.0446(3)	0.4933(4)	0.2303(3)
C16 ¹	0.0280(2)	0.4303(3)	0.2807(3)
C81 ¹	0.0895(2)	-0.0456(3)	0.8928(2)
C82 ¹	0.1496(3)	-0.1374(4)	0.9385(2)
C83 ¹	0.2012(3)	-0.1000(5)	1.0227(3)
C84 ¹	0.1928(3)	0.0292(6)	1.0618(3)
C85 ¹	0.1330(4)	0.1205(5)	1.0170(3)
C86 ¹	0.0816(3)	0.0823(4)	0.9340(3)

Table 2. Final thermal parameters, u_{ij} , in units of $\text{\AA}^2 \times 10^4$ for the heavier atoms. The expression for the temperature factor is $\exp\{-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}k lb^*c^*)\}$. The estimated standard deviations are given in parenthesis.

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ni	325(1)	232(1)	317(1)	-1(1)	14(1)	-4(1)
S1	468(4)	258(3)	426(3)	-38(3)	9(3)	11(2)
S2	558(4)	338(3)	362(3)	-29(3)	89(3)	-48(3)
N1	422(13)	373(11)	341(11)	0(10)	32(9)	74(9)
N2	372(12)	280(9)	316(10)	-2(9)	10(9)	21(8)
N3	352(11)	250(9)	357(10)	-34(8)	22(8)	26(8)
N4	396(12)	323(10)	371(11)	-57(9)	48(9)	28(9)
C1	420(16)	403(15)	513(17)	-66(13)	48(13)	153(13)
C2	338(14)	340(12)	392(13)	-13(11)	-8(10)	63(10)
C3	364(13)	296(12)	343(12)	33(11)	-12(10)	-36(10)
C4	622(22)	431(16)	398(15)	99(16)	69(15)	-65(13)
C5	348(13)	239(11)	391(13)	-12(10)	0(10)	-30(9)
C6	525(19)	259(12)	598(19)	-38(13)	55(16)	-72(12)
C7	343(14)	412(13)	356(12)	-55(11)	29(10)	27(11)
C8	503(18)	574(20)	385(14)	-139(16)	96(12)	44(13)
C11	523(17)	252(11)	367(13)	-58(11)	-31(12)	25(9)
C12	732(25)	516(19)	445(16)	23(17)	74(16)	129(14)
C13	1075(38)	666(25)	540(21)	103(24)	-72(22)	265(18)
C14	817(31)	569(22)	806(28)	112(21)	-267(24)	184(20)
C15	507(22)	556(21)	875(28)	10(18)	-142(20)	145(19)
C16	471(18)	471(17)	590(19)	-64(14)	-44(14)	184(14)
C81	440(16)	426(14)	329(12)	-34(12)	123(11)	41(11)
C82	642(23)	569(20)	472(17)	68(17)	126(16)	65(15)
C83	627(24)	990(34)	516(20)	76(24)	-1(17)	209(22)
C83	849(31)	1046(36)	399(17)	-403(28)	4(19)	96(21)
C85	1129(37)	591(23)	470(19)	-279(24)	184(22)	-83(16)
C86	771(25)	431(17)	472(17)	-13(17)	117(16)	23(13)

Table 3. Positional parameters and isotropic temperature factors for the hydrogen atoms. The temperature factors are $\exp\{-8\pi^2 U \sin^2 \theta/\lambda^2\}$. Standard deviations are in parenthesis.

Atom	x	y	z	$U \times 10^3 \text{\AA}^2$
H1(C1)	0.233(2)	0.329(3)	0.251(2)	5(1)
H2(C1)	0.226(3)	0.442(4)	0.340(2)	6(1)
H1(C4)	0.122(3)	-0.203(4)	0.277(3)	8(1)
H2(C4)	0.189(4)	-0.087(6)	0.249(4)	12(2)
H3(C4)	0.221(3)	-0.209(5)	0.312(3)	7(1)
H1(C6)	0.065(4)	-0.342(5)	0.434(4)	10(2)
H2(C6)	0.153(3)	-0.360(5)	0.444(3)	9(1)
H3(C6)	0.107(4)	-0.353(6)	0.554(4)	12(2)
H1(C8)	0.025(3)	-0.187(4)	0.800(2)	7(1)
H2(C8)	-0.029(3)	-0.044(4)	0.805(3)	6(1)
H(C12)	0.187(3)	0.512(5)	0.139(3)	8(1)
H(C13)	0.441(3)	0.129(5)	0.953(3)	7(1)
H(C14)	0.079(3)	0.396(4)	0.889(3)	7(1)
H(C15)	-0.098(4)	0.486(6)	0.252(4)	11(2)
H(C16)	0.018(3)	0.378(4)	0.338(3)	7(1)
H(C82)	0.157(3)	-0.217(4)	-0.091(3)	6(1)
H(C83)	0.241(3)	-0.174(5)	0.055(3)	9(1)
H(C84)	0.231(4)	0.059(6)	0.118(4)	11(2)
H(C85)	0.122(3)	0.206(5)	0.045(3)	8(1)
H(C86)	0.035(3)	0.141(5)	0.908(3)	9(1)

STRUCTURE DETERMINATION AND REFINEMENT

The position of the nickel atom was deduced from the three dimensional Patterson function and the positions for the other non-hydrogen atoms were located from two successive Fourier syntheses.

The structure has been refined by the method of least squares, minimizing $R = \sum w(|F_o| - K|F_c|)^2$ using the 4080 observed reflections. Initially a unit weighted full matrix refinement of the scalefactor, the atomic parameters and individually isotropic temperature factors, was performed. Later when anisotropic temperature factors were introduced a block diagonal refinement was used. After this refinement had converged, a calculated difference Fourier showed peaks in all the expected positions for the hydrogen atoms of the structure. Positional and isotropic temperature factors for the hydrogen atoms were included in the final cycles of the least squares refinement. The weights were $w = 1/(A\sigma(F)^2 + BF + CF^2 + D \sin \theta)$. The numerical values for the coefficients, A , B , C and D were derived by minimizing $S = \sum_{i=1}^{NREF} p_i \log p_i$, where $p_i = (w_i |\Delta F_i|^2) / \sum_{i=1}^{NREF} w_i |\Delta F_i|^2$

with respect to the parameters in the weighting function. NREF is the number of reflections. This method is described and programmed by Kurt Nielsen¹⁰ and it has resulted in the following values: $A = 3.84$, $B = 0.0649$, $C = 0.0004$, $D = -2.05$.

After convergence of this refinement, the maximum shift for the parameters was 0.025σ and the unit weighted and weighted residuals were 4.4 and 5.1 %, respectively.

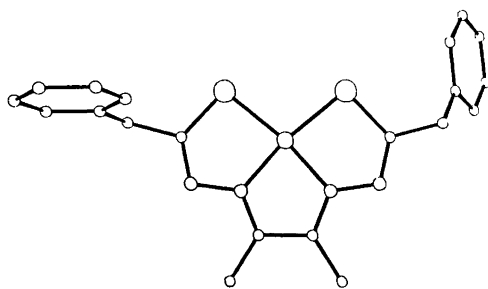


Fig. 2. ORTEP drawing of the molecule seen perpendicular to the coordination plane.

Table 4. Distances (Å) from the least squares plane. The atoms marked with an asterisk are those defining the least squares plane.

Atom	Plane I	Atom	Plane I
Ni	0.005*	C8	-0.10
S1	0.02*	C11	-1.49
S2	0.02*	C12	-1.71
N1	-0.01*	C13	-2.96
N2	0.00*	C14	-4.00
N3	-0.01*	C15	-3.80
N4	-0.02*	C16	-2.54
C1	-0.09	C81	1.00
C2	-0.03*	C82	2.09
C3	0.03*	C83	3.09
C4	0.07	C84	3.00
C5	0.02*	C85	1.92
C6	0.02	C86	0.93
C7	-0.02*		

Table 5. Bond lengths (Å) in [Ni(path)₂dia]. Standard deviations in parenthesis.

Ni-S1	2.150(1)	Ni-S2	2.152(1)
Ni-N2	1.852(2)	Ni-N3	1.854(2)
S1-C2	1.743(3)	S2-C7	1.750(3)
C2-N1	1.289(4)	C7-N4	1.301(4)
N1-N2	1.400(3)	N3-N4	1.386(3)
C2-C1	1.514(4)	C7-C8	1.507(4)
N2-C3	1.298(3)	N3-C5	1.305(3)
C3-C4	1.486(4)	C5-C6	1.481(4)
C1-C11	1.517(4)	C8-C81	1.507(4)
C11-C12	1.391(4)	C81-C82	1.382(5)
C12-C13	1.385(7)	C82-C83	1.387(6)
C13-C14	1.370(8)	C83-C84	1.377(8)
C14-C15	1.356(7)	C84-C85	1.372(7)
C15-C16	1.383(6)	C85-C86	1.374(6)
C16-C11	1.376(5)	C86-C81	1.375(5)
C3-C5	1.486(4)		
C1-H1(C1)	0.97(3)	C8-H1(C8)	0.97(4)
C1-H2(C1)	0.99(4)	C8-H2(C8)	0.98(4)
C12-H(C12)	0.98(5)	C82-H(C82)	0.89(4)
C13-H(C13)	1.04(4)	C83-H(C83)	1.02(5)
C14-H(C14)	0.90(4)	C84-H(C84)	0.96(5)
C15-H(C15)	0.87(6)	C85-H(C85)	0.93(5)
C16-H(C16)	0.95(4)	C86-H(C86)	0.95(5)
C4-H1(C4)	0.92(4)	C6-H1(C6)	0.94(5)
C4-H2(C4)	1.04(6)	C6-H2(C6)	0.94(5)
C4-H3(C4)	0.88(4)	C6-H3(C6)	1.04(6)

The final atomic parameters are listed in Tables 1-3. A list of observed and calculated structure amplitudes may be obtained from the authors upon request.

Table 6. Selected bond angles ($^{\circ}$) in $[\text{Ni}(\text{path})_2\text{diac}]$.

S2-Ni-S1	102.49(3)	N3-Ni-N2	83.33(10)
S1-Ni-N2	87.18(7)	S2-Ni-N3	87.00(7)
Ni-S1-C2	94.6(1)	Ni-S2-C7	94.8(1)
S1-C2-C1	117.9(2)	S2-C7-C8	118.7(2)
S1-C2-N1	124.9(2)	S2-C7-N4	124.1(2)
C1-C2-N1	117.1(2)	C8-C7-N4	117.2(3)
C2-N1-N2	110.0(2)	C7-N4-N3	110.3(2)
N1-N2-Ni	123.2(2)	N4-N3-Ni	123.7(2)
N1-N2-C3	120.5(2)	N4-N3-C5	120.1(2)
Ni-N2-C3	116.3(2)	Ni-N3-C5	116.2(2)
N2-C3-C5	112.3(2)	N3-C5-C3	111.9(2)
N2-C3-C4	125.6(3)	N3-C5-C6	124.8(3)
C4-C3-C5	122.2(2)	C6-C5-C3	123.3(2)
C2-C1-C11	114.4(3)	C7-C8-C81	115.3(3)
C1-C11-C12	118.3(3)	C8-C81-C82	120.6(3)
C1-C11-C16	123.4(3)	C8-C81-C86	121.1(3)
C16-C11-C12	118.3(3)	C86-C81-C82	118.2(3)
C11-C12-C13	120.0(4)	C81-C82-C83	120.5(4)
C12-C13-C14	120.4(4)	C82-C83-C84	120.1(4)
C13-C14-C15	119.9(4)	C83-C84-C85	119.6(3)
C14-C15-C16	120.3(4)	C84-C85-C86	119.9(4)
C15-C16-C11	121.0(3)	C85-C86-C81	121.6(4)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The overall molecular structure is illustrated by the ORTEP drawing shown in Fig. 2. Except for the phenyl groups the molecule is planar. The calculation of a least squares plane confirms this, see Table 4. The phenyl groups lie on either side of the plane of the ligand. The planes of the phenyl groups, C11 to C16 and C81 to C86 form angles of 60° and 76° , respectively, with the coordination plane.

Bond angles and bond lengths are shown in Tables 5 and 6. A comparison of the values for

the two equivalent halves of the molecules shows that there are no significant differences. Thus, apart from the phenyl groups the molecule has a pseudo twofold axis of symmetry in agreement with ^1H NMR spectra of the complex in solution.¹

The related complex derived from acetophenone has a tetrahedrally distorted planar configuration, the angle between the two ligand planes being 19° , and it crystallizes with the nickel atom on a crystallographic twofold axis.²

There are interesting similarities and differences between the two structures. The angles,

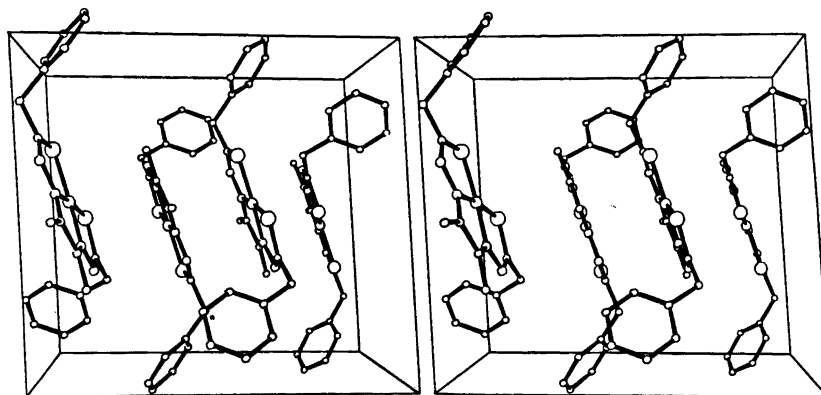


Fig. 3. Stereo pair showing the packing viewed along the b axis.

S-Ni-S and N-Ni-N, in the present structure are grossly different from the angles found in the equivalent acetophenone complex and other *cis*-nickel sulfur complexes.^{2,13} The S-Ni-S angle is 10° larger (102.5° compared to 92°) and similarly the N-Ni-N angle is 10° smaller. This significant change in the coordination angles is due to a considerable steric strain within the tetradentate ligand. Model building indicates that this strain may also cause the observed shortening of the Ni-N distances in this complex derived from diacetyl. The average Ni-N distance is 1.851 Å compared to 1.935 Å found in the equivalent acetophenone complex. The Ni-S distances, however, are virtually identical in the two structures (2.15 Å).

There are no significant differences between corresponding bonds within the ligands of the two structures. The C-N bond lengths in [Ni(path)₂diac] have values ranging from 1.289 to 1.305 Å as compared with the value 1.28 Å for the length of a C-N double bond.¹⁴ The N-N bonds average to 1.393 Å in the present structure and to 1.423 Å in the acetophenone complex.²

In the crystal structures of nickel thiosemicarbazide complexes¹²⁻¹⁴ and of [sulfato bis-(thiocarbonohydrazide-*N,S*)]copper(II) tetrahydrate,¹⁵ which contains coordinated hydrazine groups, the values for the N-N bond lengths vary from 1.406 to 1.436 Å. From the above it may be concluded that the system of conjugated double bonds in the ligand only causes small deviations from the accepted values for single and double bonds.

The molecular packing in the crystal is determined by van der Waals interactions as illustrated in Fig. 3. The molecules are arranged with the coordination planes nearly parallel to the *b*-axis.

REFERENCES

- Gabel, J., Larsen, E. and Trinderup, P. *Acta Chem. Scand. A* 31 (1977) 657.
- Larsen, S. *Acta Chem. Scand. A* 28 (1974) 779.
- Lehnert, P. G. *J. Appl. Crystallogr.* 8 (1975) 568.
- Ahmed, F. R. *N.R.C. Crystallographic Program System*, National Research Council, Ottawa 1968.

- Johnson, C. K. ORTEP: *A Fortran Ellipsoid Plot Program for Crystal Structure Illustrations*, Report ORNL-3794, Second Rev., Oak Ridge National Laboratory, Oak Ridge 1970.
- Stewart, J. M., Ed., *The X-Ray System 1972*, Technical Report Tr-192, Computer Science Center, University of Maryland, College Park.
- Cromer, D. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
- Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
- Cromer, D. and Liebermann, D. J. *J. Chem. Phys.* 53 (1970) 1891.
- Nielsen, K. *Acta Crystallogr. A* 33 (1977). *In press.*
- Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, N.Y. 1960.
- Hazell, R. G. *Acta Chem. Scand.* 22 (1968) 2809.
- Hazell, R. G. *Acta Chem. Scand.* 22 (1968) 2171.
- Hazell, R. G. *Acta Chem. Scand.* 26 (1972) 1365.
- Bigoli, F., Pellinghelli, M. A., Tiripicchio A. and Camellini, M. T. *Acta Crystallogr. B* 31 (1975) 55.

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