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The Crystal Structure of Bis(methyl 3-benzylidenedithiocarbazato)nickel(II)

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The title compound crystallizes in the monoclinic space group P2_1/a with two molecules in a unit cell of dimensions; a=21.479(5), b=4.2092(6), c=14.257(3) Å, and β=129.53(2)°. The structure was refined by block-diagonal least-squares procedures to give a final R value of 0.032 for 1693 reflections with $I>3\sigma(I)$ collected on a four-circle X-ray diffractometer. The complex consists of two methyl 3-benzylidenethiocarbazate groups, each bound to the central Ni atom through the thiol S atom and the hydrazine N atom, to yield a five-membered chelate ring. The NiN_2S_2 moiety is *trans* square-planar, with Ni–S and Ni–N bond distances of 2.1767(9) and 1.927(3) Å respectively. An examination of the bond distances and the planarity of the molecule revealed a delocalization of the π electrons over the chelate ring. The intra-molecular contact of S···H is 2.35(4) Å, which indicates a definite C–H···S interaction or hydrogen bonding.

In the course of our ESR study of ^{63}Cu(II) doped in the title compound (abbreviated as Ni(bdc)$_2$), an extra hyperfine structure (hfs) due to azomethine protons was observed.[1,2] The proton hfs was large, though the proton is attached to a carbon atom which is not included in the chelate ring. This proton hfs can be expected to be enhanced through the π electron in a C=N bond, and so the A^H value is sensitive to the geometry around the C=N bond. Therefore, it is interesting to investigate the structure around the C=N bond. The coordination geometry around the nickel atom in Ni(bdc)$_2$ is *trans*, while those in related 1-(2-naphthyl)ethylidene-, 1-(*p*-tolyl)ethylidene-, 1-phenylethylidene-, 1-(*m*-nitrophenyl)ethylidene-, and 1-(*p*-nitrophenyl)ethylidene-dithiocarbazatonickel(II) complexes were found from ESR measurements to be *cis*.[1] This paper will describe the crystal structure of Ni(bdc)$_2$ determined by the single-crystal X-ray-diffraction method.

Experimental

Preparation of Methyl 3-Benzylidenedithiocarbazate. A methanol solution of *S*-methyl dithiocarbazate (10 g), prepared as previously described,[3] was added to a methanol solution of benzaldehyde (11 g). The mixture was heated on a steam bath for 10 min. The deposited crystals were filtered off, washed with methanol, and recrystallized from methanol to give pale yellow crystals of the Schiff base.

Preparation of Ni(bdc)$_2$. A hot methanol solution of the nickel acetate (0.001 mol) was added to a hot methanol solution of the Schiff base (0.002 mol), the solution was heated on the steam bath for 10 min; on cooling, crystals of the Ni(dbc)$_2$ were deposited. Single crystals were obtained by the slow evaporation of the chloroform–methanol solution. Found: C, 44.99, H, 3.71, N, 11.68%. Calcd for Ni(dbc)$_2$: C, 45.29, H, 3.80, N, 11.74%.

X-Ray Diffraction. Preliminary X-ray photographs showed the space group to be P2_1/a. The unit cell parameters and intensity data were measured on a Syntex P$\bar{1}$ automated four-circle X-ray diffractometer with monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The unit-cell parameters were determined by a least-squares procedure, using 30 reflections within the range of $30<2\theta<43°$. The crystal used for X-ray work was ground to a sphere 0.32 mm in diameter. The density was measured by flotation in an aqueous KI solution. The crystal data are given in Table 1.

Table 1. Crystal data[a)]

Molecular formula	$NiS_4N_4C_{18}H_{18}$
Molecular weight	477.31
Space group	P2_1/a
a=21.479(5) Å	Z=2
b=4.2092(6) Å	D_m=1.593 g cm^{-2}
c=14.257(3) Å	D_x=1.594 g cm^{-2}
β=129.53(2)°	μ=1.39 mm^{-1}
V=994.17(45) Å^3	(for Mo $K\alpha$ radiation)

a) Numbers in parentheses here and elsewhere in this paper are the e.s.d.'s in the last significant digits.

The intensity data of 2202 independent reflections within a range of $2\theta<56°$ were collected by the θ-2θ scan technique, with a variable scan rate from 4.0 to 24.0° min^{-1}. Of these, the intensities of 505 reflections were less than $3\sigma(I)$; these reflections were not used in the least-squares refinement. The intensity data were corrected for Lorentz and polarization effects, but not for absorption and extinction.

Structure Determination and Refinement

The Ni atoms must lie on a set of twofold special positions, since there are only two molecules in a unit cell; therefore, the molecule is required to have a center of symmetry. The positions of all the non-hydrogen atoms were deduced from a Patterson synthesis and a subsequent Fourier synthesis. Refinement was carried out by the block-diagonal least-squares method. The function minimized was $\sum\omega(|F_o|-|F_c|)^2$, in which ω was chosen according to Cruickshank's weighting schemes.[4] All the H atoms were located by means of a difference Fourier synthesis. After several further cycles of refinement including all the H atoms, four reflections with $|F_o|-|F_c|>10.0$ were eliminated from the F_o-data set because of the strong imbalances of the background intensities on both sides of each Bragg peak. Refinement was terminated when all the shift/e.s.d. ratios for the non-hydrogen atoms became less than 0.2. The final conventional R index was 0.032 for the 1693 measurable reflections. The final difference Fourier synthesis showed no significant features except for two implausible peaks

Table 2. Fractional atomic coordinates and isotropic thermal parameters[a)]

	x	y	z	B/Å^2
Ni	0	0	0	2.73(0)
S(1)	0.11055(4)	0.26634(21)	0.13102(7)	3.99(3)
S(2)	0.16983(4)	0.54668(18)	0.36153(6)	3.55(3)
N(1)	−0.0179(1)	0.0377(5)	0.1159(2)	2.8(1)
N(2)	0.0340(1)	0.2224(5)	0.2221(2)	2.9(1)
C(1)	0.0948(1)	0.3269(6)	0.2330(2)	2.8(1)
C(2)	0.1352(2)	0.5508(9)	0.4470(3)	4.7(2)
C(3)	−0.0765(2)	−0.0940(7)	0.1058(2)	3.3(1)
C(4)	−0.1023(2)	−0.0779(7)	0.1789(2)	3.2(1)
C(5)	−0.1749(2)	−0.2335(8)	0.1282(3)	4.0(1)
C(6)	−0.2095(2)	−0.2389(9)	0.1827(3)	4.8(2)
C(7)	−0.1717(2)	−0.0724(9)	0.2909(3)	4.7(2)
C(8)	−0.0993(2)	0.0799(10)	0.3442(3)	4.9(2)
C(9)	−0.0645(2)	0.0779(8)	0.2896(3)	4.1(1)
H(2)1	0.174(2)	0.610(8)	0.517(3)	4.9(8)
H(2)2	0.132(2)	0.343(8)	0.457(3)	5.0(7)
H(2)3	0.086(2)	0.641(8)	0.403(3)	4.9(7)
H(3)	−0.109(2)	−0.219(7)	0.035(2)	3.4(6)
H(5)	−0.200(2)	−0.343(7)	0.054(2)	4.2(7)
H(6)	−0.262(2)	−0.352(8)	0.143(3)	4.9(7)
H(7)	−0.203(2)	−0.065(8)	0.320(3)	4.9(8)
H(8)	−0.070(2)	0.170(8)	0.422(3)	5.1(8)
H(9)	−0.018(2)	0.196(7)	0.320(3)	4.2(6)

a) The B's of the non-hydrogen atoms are the equivalent ones of the anisotropic thermal parameters.[15)] The H atoms are labelled in terms of the C atom to which they are attached.

of *ca.* 0.5 eÅ^{-3} in the vicinities of the Ni atom and the center of the chelate ring. The atomic scattering factors for Ni^{2+}, S, N, and C_{cov}, with correction factors for anomalous dispersion for the first two, were taken from International Tables for X-Ray Crystallography.[5)] Those for H atom were adopted from the table of Stewart *et al.*[6)] All the calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University, mainly by the use of the UNICS-II program system.[7)] The drawings were made by the use of the *ORTEP* program.[8)] The final atomic parameters are listed in Table 2, along with their estimated standard deviations. Lists of the structure factors and anisotropic thermal parameters have been deposited with the office of the Chemical Society of Japan as Document No. 8206.

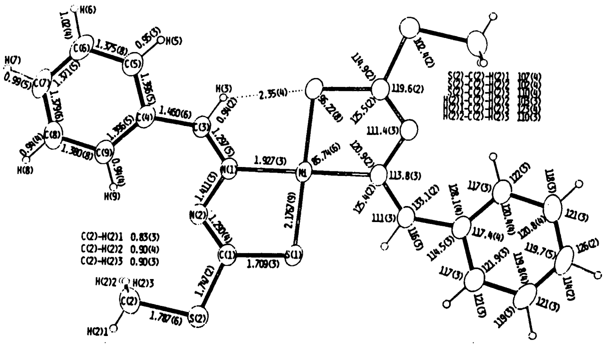

Fig. 1. Bond distances (l/Å) and angles (θ/°) of the molecule. The H atoms are shown as open circles of arbitrary size, and the shapes of the other atoms represent the thermal-motion ellipsoids scaled to enclose 50% probability.

Results and Discussion

The molecular structure is shown in Fig. 1, together with the bond distances(l), bond angles(θ), and atomic nomenclature scheme. The complex consists of two methyl 3-benzylidenedithiocarbazate groups, each bound to the central Ni atom through the thiol S atom and the hydrazine N atom, to yield a five-membered chelate ring. The NiN_2S_2 moiety is *trans* square planar (coordination plane). This coordination geometry is compatible with the results of the ESR measurement of Cu^{2+} doped in $Ni(bdc)_2$.[1,2)]

The Ni–S bond distance of 2.1767(9) Å is in the range of 2.1—2.3 Å found in the four-coordinated Ni(II) complexes, as has been pointed out by Lopez-Castro and Truter.[9)] The Ni–N bond distance of 1.927(3) Å is comparable with the value of 1.896(7) Å found in bis(ethyldithiocarbazate)nickel(II), in which the environment about the Ni atom is similar to that in $Ni(bdc)_2$.[10)] The bond distances of S–C(1.709 Å), C–N(1.290 Å), and N–N(1.411 Å) in the chelate ring are intermediate between the usual values for single and double bonds. The chelate ring is nearly planar, with the maximum deviation of 0.041 Å, as shown in Table 3. The bond distances and the planarity are indicative of an extensive delocalization of π electrons over the chelate ring. Such a large delocalization of π electrons can be expected to give rise to a large proton hfs. The thiomethyl group has the normal S–C(sp^3) bond distance of 1.787(6) Å and is attached to the ring carbon with the C–S–C bond angle of 102.4(2)° and at

Table 3. Least-squares planes and torsion angles

(a) Coefficient of least-squares plane equations.

Equations are of the form $lu+mv+nw=d$, where u, v, and w are in Å units referred to the a, b, and c* axes respectively.

	Plane	l	m	n	d/Å
I	Coordination	−0.2870	0.8560	−0.4300	0.0
II	Chelate ring	−0.2722	0.8408	−0.4680	−0.0307
III	Benzene ring	−0.2341	0.8364	−0.4957	−0.3623

(b) Deviations (l/Å) from least-squares planes.

Atoms with an asterisk are not included in the calculation of the plane.

I		II		III	
Ni	0	Ni	0.031	C(3)*	0.064
S(1)	0	S(1)	−0.024	C(4)	0.007
N(1)	0	N(1)	−0.041	C(5)	−0.007
N(2)*	0.120	N(2)	0.025	C(6)	0.002
C(1)*	0.099	C(1)	0.010	C(7)	0.003
C(3)*	−0.092	S(2)*	0.005	C(8)	−0.002
		C(2)*	−0.007	C(9)	−0.003
		C(3)*	−0.138		

(c) Selected torsion angles (θ/°).

S(1)–C(1)–S(2)–C(2)	−178.3(2)	Ni–N(1)–C(3)–C(4)	−175.7(3)
N(1)–N(2)–C(1)–S(2)	−177.1(2)	N(1)–C(3)–C(4)–C(5)	173.5(4)
N(2)–C(1)–S(2)–C(2)	1.0(3)	N(1)–C(3)–C(4)–C(9)	−4.9(7)

the normal S–C(sp^2) distance (1.747(2) Å). These bond distances and angle suggest that the delocalization of π electrons is not extended to this part, although the thiomethylic S–C is almost coplanar with the chelate ring. The coordinated N atom is also bonded to the benzylidene group; the N(1)–C(3) distance (1.297(5) Å) falls within the range of 1.29—1.34 Å established for the coordinated N=C bond;[11] it is longer than the generally accepted value for N(sp^2)–C(sp^2) of 1.24 Å.[12] Judging from the planarity and lengthening of the bonds about N(1), the π electrons seem to be delocalized over C(3). An inspection of the bond angle at C(3) reveals that there is a steric repulsion between the chelate ring and the phenyl group. The benzene ring is planar, with a maximum deviation of 0.007 Å. This ring rotates slightly about the C(3)–C(4) bond; the torsion angles about this bond are 173.5(4) and −4.9(7)°. The intramolecular contact of S(1)···H(3) is 2.35(4) Å, where the C···S distance and the C–H···S angle are 3.053(4) Å and 130.4° respectively. The S···H distance is far shorter than the sum of the van der Waals radii of these atoms (3.05 Å);[13] it indicates a definite C–H···S interaction or hydrogen bonding. The large proton hfs of the ESR spectra of Cu^{2+} doped in Ni(bdc)$_2$ is expected to occur also through this H···S short contact. Such a short contact has also been observed in nickel(II) bis(dipropyldithiocarbamate).[14]

Fig. 2. An edge-on view of the molecule. The H atoms have been omitted for clarity.

An edge-on view of the molecule, as shown in Fig. 2, shows that the molecule is, as a whole, roughly planar. The normal to the coordination plane makes an angle of 31.1° with the b axis; also, the directions of the Ni–N(1) and Ni–S(1) bonds make angles of 85.3 and 59.0° with the b axis respectively. These angles correspond to the angles between the b axis and the g_z, g_x, and g_y directions (30.7, 87.1, and 59.3° respectively) determined from the single-crystal ESR measurement of Cu^{2+} doped in Ni(bdc)$_2$.[1]

The molecular packing projected on the ac plane is

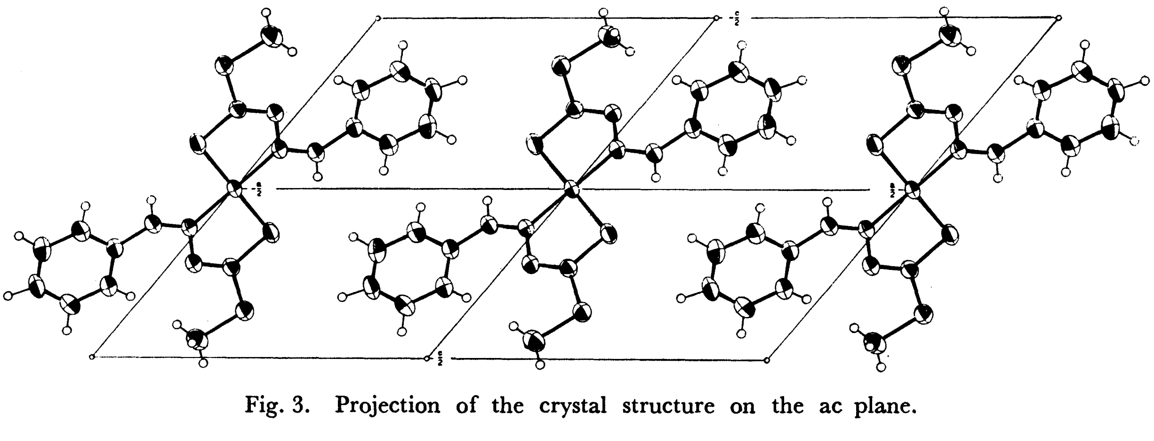

Fig. 3. Projection of the crystal structure on the ac plane.

shown in Fig. 3. There are no unusually close intermolecular contacts; thus, the crystal can be said to be held together primarily by van der Waals forces.

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References

1) T. Oniki, *Bull. Chem. Soc. Jpn.*, **51**, 2551 (1978).

2) T. Oniki, *Bull. Chem. Soc. Jpn.*, **52**, 2584 (1979).

3) G. Bahr and G. Schleitzer, *Z. Anorg. Allg. Chem.*, **280**, 161 (1955).

4) D. W. J. Cruickshank, "Computing Methods in Crystallography," ed by J. S. Rollett, Pergamon Press, Oxford (1965), p. 112.

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

7) T. Sakurai, H. Iwasaki, Y. Watanabe, K. Kobayashi, Y. Bando, and Y. Nakamichi, *Rikagaku Kenkyusho Hokoku* (in Japanese), **50**, 75 (1974).

8) C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL-3794 (1965).

9) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, **1963**, 1309.

10) L. Gastaldi and P. Porta, *Cryst. Struct. Commun.*, **3**, 467 (1973).

11) J. C. J. Bart, I. W. Bassi, M. Calcaterra, and M. Pieroni, *Inorg. Chim. Acta*, **28**, 201 (1978).

12) "International Tables for X-Ray Crystallography," 2nd ed, Kynoch Press, Birmingham (1968), Vol. III.

13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press, Ithaca (1960).

14) G. Peyronel and A. Pignedoli, *Acta Crystallogr.*, **23**, 398 (1967).

15) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).