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# The preparation and characterization of bis-chelated nickel(II) complexes of the 6-methylpyridine-2-carboxaldehyde Schiff bases of S-alkyldithiocarbazates and the X-ray crystal structure of the bis{S-methyl-*β*-*N*-(6-methylpyrid-2-yl)-methylenedithiocarbazato}nickel(II) complex

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**Abstract**—New nickel(II) complexes of general formula, [Ni(NNS)$_2$] (NNS$^-$ = uninegatively charged tridentate ligands formed by condensation of 6-methyl-2-formylpyridine with S-methyl- and S-benzyldithiocarbazates) have been prepared and characterized by a variety of physico-chemical techniques. Magnetic and spectroscopic evidence support a distorted octahedral structure for these complexes. The crystal and molecular structure of the bis{S-methyl-*β*-*N*-(6-methylpyrid-2-yl)methylenedithiocarbazato}nickel(II) complex has been determined by X-ray diffraction studies. The complex has a distorted octahedral structure with the ligands coordinated to the nickel(II) ion as uninegatively charged tridentate chelating agents *via* the pyridine nitrogen, the azomethine nitrogen and the mercaptide sulphur atoms. The distortion from the regular octahedral geometry is ascribed to the stereochemical limitations imposed by the planar tridentate ligands. © 1997 Elsevier Science Ltd

*Keywords*: nickel(II) complexes; Schiff bases; S-alkyldithiocarbazates; crystal structure; 6-methylpyridine-2-carboxaldehyde Schiff bases; octahedral nickel complexes.

Transition metal complexes of Schiff base ligands derived from S-alkyl esters of dithiocarbazic acid have been the subject of a large number of publications [1–10]. Interest in these complexes has been stimulated by their interesting physico-chemical properties [9,10] and potentially useful biological activities [11]. Thus the nickel(II) complex of the 2-acetylpyridine Schiff base of S-methyldithiocarbazate, [Ni(NNS)Cl] has been shown to display marked activity in the P388 Lymphocytic Leukaemia test system [12]. Several Schiff bases of S-alkyldithiocarbazates and some of their transition metal complexes have also been shown to possess a range of antifungal and antibacterial properties [8]. Past work on metal–dithiocarbazate complexes focused mainly on the synthetic and spectral characterization of the complexes. Structural work by X-ray crystallography on this type of compounds is very limited. As part of our ongoing work on metal–dithiocarbazates, we report here the synthesis and

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characterization of two bis-ligand nickel(II) complexes of the 6-methyl-2-formypyridine Schiff bases of S-methyl- and S-benzyldithiocarbazate together with the X-ray crystal structure of the bis{S-methyl-*β*-*N*-(6-methylmethylpyrid-2-yl)methylenedithiocarbazato}nickel(II).

## EXPERIMENTAL

All physical measurements and analytical procedures were similar to those described previously [5].

### *Synthesis of the ligands*

The ligands were synthesized by boiling a mixture of the appropriate S-alkyldithiocarbazate (2 mmol) in abs. ethanol (50 $cm^3$) and 6-methyl-2-formylpyridine (2 mmol) in the same solvent (50 $cm^3$) for about 3 min. On cooling, the Schiff bases crystallized out of the reaction mixture as shining pale yellow crystals. These were recrystallized from methanol to obtain beautiful shining pale yellow needles.

*HNNSBz* (*the Schiff base of S-benzyldithiocarbazate*): m.p. 152°C; Found: C, 59.8; H, 5.1; N, 14.1. Calc. for $C_{15}H_{16}N_3S_2$: C, 59.6; H, 5.3; N, 13.9%.

*HNNSMe* (*the Schiff base with S-methyldithiocarbazate*): m.p. 155°C; Found: C, 47.8; H, 4.9; N, 18.7; Calc. for $C_9H_{11}N_3S_2$: C, 48.0; H, 4.9; N, 18.7%.

### *Preparation of the complexes*

The complexes were prepared by heating a solution of nickel(II) nitrate hexahydrate (2 mmol) in ethanol (50 $cm^3$) with a solution of the appropriate Schiff base (4 mmol) in the same solvent (50 $cm^3$). The reaction mixture, on being left to cool slowly, deposited crystals of the complexes. These were collected, washed several times with ethanol and dried in a vacuum desiccator over silica gel. Found: C, 42.3; H, 4.1; N, 16.2; Calc. for $C_{18}H_{20}N_6S_4Ni$: C, 42.6; H, 3.9; N, 16.6%. Found: C, 54.2; H, 4.1; N, 8.6; Calc. for $C_{28}H_{28}N_6S_4Ni$: C, 54.6; H, 4.3; N, 8.9%.

### *X-ray crystal structure analysis*

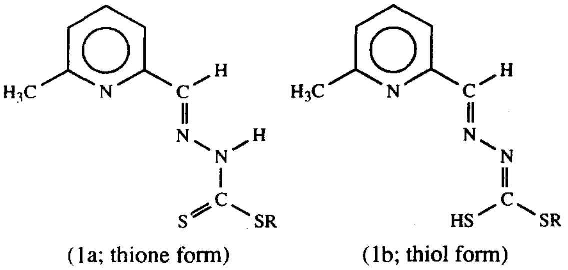
A dark prism crystal of the [Ni(NNSMe)$_2$] complex having an approximate dimension 0.20 × 0.10 × 0.50 mm was mounted on a glass fibre and used for data collection on a Rigaku AFC6S diffractometer with graphite monochromated Mo-$K_\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from a least squares refinement of the diffraction data from 25 carefully centred reflections in the range $20.87 < 2\theta < 29.74°$. The data were collected at $296 \pm 1$ K using the $\omega$ scan technique to a maximum $2\theta$ value of 50.0°. The structure was solved by direct methods [13]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1657 observed reflections [$I > 3.00\ \sigma(I)$] and 343 variable parameters. Neutral atom scattering factors were taken from Cramer and Waber [14]. Anomalous dispersion effects were included in $F_{calc}$ [15]. A summary of crystal data, experimental details and refinement of results are listed in Table 1. All calculations were performed using the TEXSCAN crystallographic software package of the Molecular Structure Corporation [16]. The data were corrected for Lorentz and Polarization effects.

Table 1. Crystal data, data collection and structure refinement parameters for the [Ni(NNSMe)$_2$] complex

| | |
|---|---|
| Compound | [Ni(NNSMe)$_2$] |
| Chemical formula | $C_{18}H_{20}N_6S_4Ni$ |
| Formula weight | 507.34 |
| Crystal class | monoclinic |
| Space group | $P2_1/n$(#14) |
| $a$ (Å) | 8.415(4) |
| $b$ (Å) | 14.200(4) |
| $c$ (Å) | 18.800(3) |
| $\beta$ (°) | 102.36(3) |
| $V$ (Å$^3$) | 2194(2) |
| $Z$ | 4 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.535 |
| $\mu$ (Mo-$K_\alpha$) (cm$^{-1}$) | 12.70 |
| $F$(000) | 1048 |
| $2\theta_{max}$ (°) | 50.0 |
| Total no. of reflections measured | 4322 |
| No. of observations | 1657 [$I > 3.00\ \sigma(I)$] |
| $R$ | 0.046 |
| $R_w$ | 0.045 |
| Largest peak (e Å$^{-3}$) | 0.38 |
| Smallest peak (e Å$^{-3}$) | −0.31 |

## RESULTS AND DISCUSSION

The Schiff bases (Fig. 1), hereinafter abbreviated as HNNSMe and HNNSBz, have protons adjacent to the thiocarbonyl group and consequently, they can exhibit thione–thiol tautomerism. Their IR spectra do not display any $\nu$(S—H) band at *ca.* 2700 cm$^{-1}$ but, exhibit $\nu$(NH) bands in the range 3100–3150 cm$^{-1}$ indicating that, in the solid state, they remain as the



(1a; thione form) (1b; thiol form)

Fig. 1. Thione form (1a) and thiol form (1b) of the Schiff bases.

thioketo tautomer (1a). However, when dissolved in ethanol in the presence of nickel(II) salts, they quickly convert to the thiol form with the concomitant formation of complexes of the deprotonated mercaptide forms of the ligand. The related thiosemicarbazones have been shown to coordinate metal ions in both protonated [17] and deprotonated [18] forms. The bis (pyrivic acid thiosemicarbazone)chromium(III) complex is a unique case in which one of the thiosemicarbazones is coordinated as a neutral ligand and the other as a deprotonated ligand [19]. However, the Schiff bases derived from S-alkyl esters of dithiocarbazic acid, which are very similar to the thiosemicarbazones, almost invariably have been found to bind metal ions as the deprotonated mercaptide forms [1–10].

Reaction of the present Schiff bases with nickel(II) salts yield only the bis-ligand complexes of formula, $[Ni(NNS)_2]$. Attempts to prepare the mono-ligated nickel(II) complexes of formula [Ni(NNS)X] (X = Cl, Br, NCS), even with a larger excess of nickel (II) salts than that required for a 1 : 1 metal : ligand complex, always yielded the bis-ligated complexes. This is in marked contrast with the behaviour of the related tridentate Schiff base ligands derived from 2-formylpyridine and S-methyl [19] or S-benzyldithiocarbazate [20] which have been shown to readily yield mono-ligated nickel(II) complexes of formula [Ni(NNS)X] (X = Cl, Br, NCS, I).

The IR spectra of the present nickel(II) complexes do not contain the ν(NH) band of the free ligands indicating that they deprotonate during coordination with the nickel(II) ion. The azomethine ν(C=N) bands of the ligands shift to lower frequencies supporting coordination *via* the azomethine nitrogen atom. Coordination of the azomethine nitrogen atom is further supported by the increase in frequency of the hydrazinic N—N bond as a consequence of the reduction between the lone pairs of electrons on the hydrazine nitrogen atoms. Assignment of other characteristic bands of the ligands and their nickel(II) complexes are given in Table 2.

The nickel(II) complexes reported herein are high-spin with a room-temperature magnetic moment of *ca.* 3.1 B.M., indicating that they are six-coordinate and probably octahedral. Their electronic spectra, in addition to showing the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands of the free ligands at *ca.* 253 and 340 nm, respectively, display a $S \rightarrow Ni^{II}$ charge-transfer transition (LMCT) at *ca.* 460 nm and a *d–d* band at *ca.* 859 nm. The electronic spectra of octahedral nickel(II) complexes are expected to exhibit three spin-allowed transitions in the visible region of the spectrum. In the electronic spectra of the present complexes, however, only one *d–d* band is observed, probably due to the intrusion of tails of intense charge-transfer bands into the visible portion of the spectrum which masks the expected *d–d* bands.

### *The X-ray crystal and molecular structure of* $[Ni(NNSMe)_2]$

The structure of the complex together with the atom numbering scheme adopted is shown in Fig. 2. The bond lengths and bond angles are shown in Table 3.

Table 2. Selected infrared absorption bands and electronic spectral data for the ligands and their nickel(II) complexes.

| | IR spectra (cm$^{-1}$) | | | Electronic spectra[a] | |
|---|---|---|---|---|---|
| Compound | ν(NH) | ν(C=N) | ν(N—N) | State | $\lambda_{max}$ (nm) |
| HNNSMe | 3095m | 1610m | 1062 | Mull | 374, 341 |
| | | | | $CHCl_3$ | 350, 284, 250 |
| | | | | | (4.1) (4.68) (4.52) |
| HNNSBz | 3080s | 1603s | 1070s | Mull | 376, 338 |
| | 3060m | | | $CHCl_3$ | 370sh, 338 |
| | | | | | (4.91) |
| $[Ni(NNSMe)_2]$ | — | 1598m | 1076s | Mull | 850, 430, 338, 290 |
| | | | | $CH_2Cl_2$ | 847, 432, 332 |
| | | | | | (1.77) (4.13) (4.24) |
| | | | | | 300, 250 |
| | | | | | (4.24) (4.20) |
| $[Ni(NNSBz)_2]$ | — | 1600s | 1072s | Mull | 859, 465, 341 |
| | | | | $CHCl_3$ | 852, *ca.* 460sh |
| | | | | | (1.9) |
| | | | | | 342, 254 |
| | | | | | (4.65) (4.53) |

[a] Log ε (litre mol$^{-1}$ cm$^2$) in parentheses.

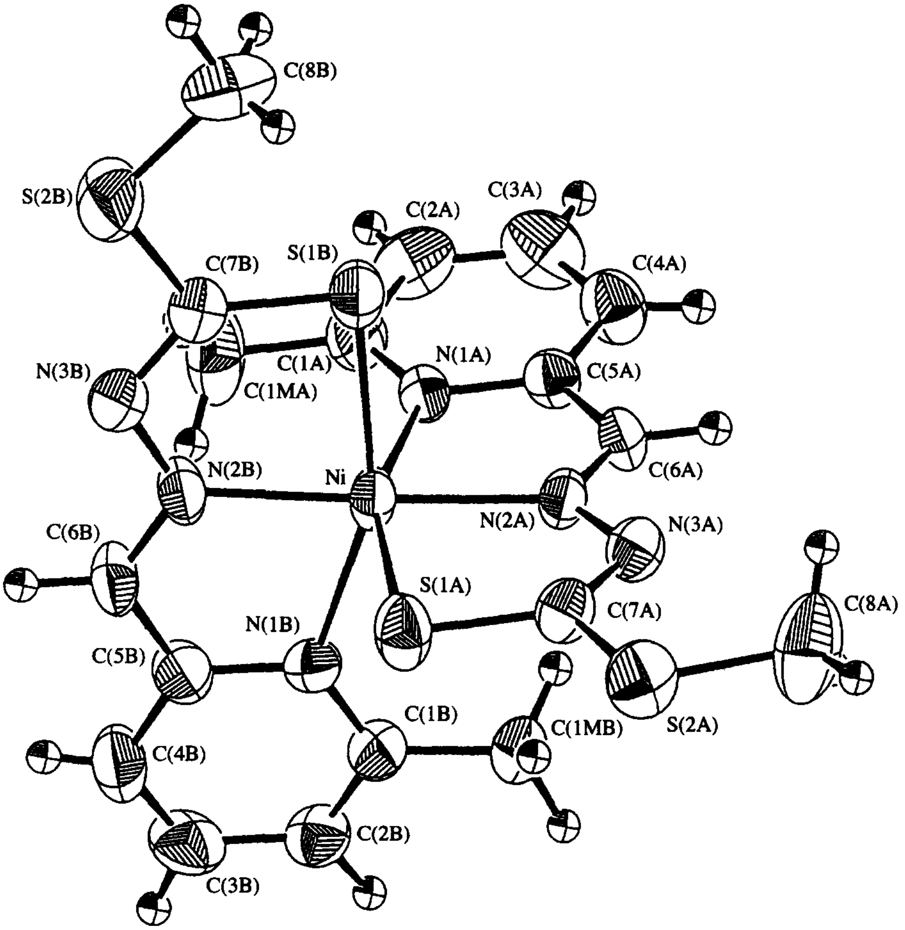


Fig. 2. The structure of [Ni(NNSMe)$_2$], showing the atom numbering scheme.

Table 3. Bond lengths (Å) and bond angles (°) for [Ni(NNSMe)$_2$]

| | | | |
|---|---|---|---|
| Ni—S(1A) | 2.420(3) | N(3A)—C(7A) | 1.31(1) |
| Ni—S(1B) | 2.412(3) | N(3B)—C(7B) | 1.31(1) |
| Ni—N(1A) | 2.224(7) | N(2A)—N(3A) | 1.385(8) |
| Ni—N(1B) | 2.166(7) | N(2B)—N(3B) | 1.389(9) |
| Ni—N(2A) | 2.004(6) | N(2A)—C(6A) | 1.29(1) |
| Ni—N(2B) | 2.016(6) | N(2B)—C(6B) | 1.26(1) |
| C(7A)—S(1A) | 1.721(9) | C(7A)—S(2A) | 1.734(9) |
| C(7B)—S(1B) | 1.695(9) | C(7B)—S(2B) | 1.761(9) |
| S(1A)—Ni—N(2A) | 80.6(2) | N(2B)—Ni—S(1A) | 94.8(2) |
| S(1A)—Ni—S(1B) | 95.7(1) | N(1B)—Ni—N(1A) | 89.3(2) |
| S(1B)—Ni—N(2A) | 93.8(2) | N(2B)—Ni—N(2A) | 172.8(3) |
| S(1B)—Ni—N(2B) | 81.0(2) | S(1B)—Ni—N(1B) | 158.1(2) |
| S(1B)—Ni—N(1A) | 90.7(2) | N(1A)—Ni—S(1A) | 157.6(2) |
| N(1B)—Ni—N(2B) | 78.2(3) | N(1B)—Ni—S(1A) | 92.5(2) |
| N(1B)—Ni—N(2A) | 107.5(3) | N(1A)—Ni—N(2B) | 107.4(3) |
| N(1A)—Ni—N(2A) | 77.6(3) | | |

The nickel(II) ion in the complex, [Ni(NNSMe)$_2$] is in a six-coordinate environment with the two Schiff base ligands coordinated to the nickel(II) ion as tridentate NNS chelating agents *via* the pyridine nitrogen atom, the azomethine nitrogen atom and the mercaptide sulphur atom. The Schiff bases are present as singly deprotonated tridentate ligands. The deprotonation is accompanied by tautomerisation to the iminothiolate form. While coordinating in the iminothiolate form, the negative charge generated upon deprotonation is delocalized in the C—N—N—C system as indicated by their intermediate bond distances: N(3B)—N(2B) = 1.389(9) Å; N(3A)—N(2A) = 1.385(8) Å; C(6B)—N(2B) = 1.26(1) Å; C(6A)—N(2A) = 1.29(1) Å; N(3B)—C(7B) = 1.31(1) Å; N(3A)—C(7A) = 1.31(1) Å, with the primary effects seen on the C—N bonds. The ligands are coordinated to the nickel(II) ion in the meridional configurations (the sulfur and pyridine nitrogen atoms *cis* to each other and the azomethine nitrogen atoms *trans*). Similar *mer* configurations of NNS tridentate thiosemicarbazone ligands around the nickel(II) ion have also been found in other bis-ligand nickel(II) complexes [21,22]. The Ni—S, Ni—N(imine) and Ni—N(py) distances are 2.420(3), 2.016(6) and 2.166(7) Å, respectively. These values compare well with those of other six-coordinate nickel(II) complexes of related NNS ligands [21,22]. The two Ni—S bonds in the complex are significantly different. Similar differences in the lengths of the two Ni—S bonds have also been observed in the case of bis-chelated nickel(II) complexes of related thiosemicarbazones [21,22]. The C—S bond distances in the complex appear to be longer than those reported for free thiosemicarbazones (1.678 ± 0.0002 Å in 4-formylpyridinethiosemicarbazone [23], 1.684 ± 0.004 Å in 2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone) [24]. This lengthening of the C—S bonds is attributed to the enethiolization process that occurs prior to coordination of the ligands with the nickel(II) ion. The Ni—N(py) bond lengths Ni—N(1B) = 2.166(7) Å and Ni—N(1A) = 2.224(7) Å are close, but are significantly different from the Ni—N distances in the dithiocarbazate chain [Ni—N(2A) = 2.004(6) and Ni—N(2B) = 2.016(6) Å]. It has been pointed out by Curtis [24] that the Ni—N distances appear to be dependent on the nature of the nitrogen donor atom, i.e. amine or imine, and also on the number of atoms in the chelate rings encapsulating the Ni—N bonds. For the purpose of comparison, the nickel-donor atom distances in some other octahedral nickel(II) complexes of analogous ligands, whose structures have been determined by X-ray diffraction, are shown in Table 4. The data show that the two Ni—N distances are different in all the complexes studied so far. The coordination sphere of the nickel(II) atom in the present complex may be considered as a distorted octahedron. The S(1A)—Ni—S(1B) angle is 95.7(1)°, which is larger than the expected ideal value of 90°. The twelve angles subtended at the nickel(II) ion by adjacent donor atoms range from 77.6(3)–89.3(2)°, compared to 90° required for a perfect octahedron. The distortion from the idealized geometry may be attributed to the restricted bite angles imposed by the planar tridentate Schiff bases. For the purpose of comparison, the bond angles of [Ni(NNSMe)$_2$] and

Table 4. Comparison of nickel-donor atoms bond lengths (Å) in some bis-ligand nickel(II) complexes of NNS ligands

| | Ni—S(1A) | Ni—S(1B) | Ni—N(1A) | Ni—N(1B) | Ni—N(2A) | Ni—N(2B) |
|---|---|---|---|---|---|---|
| [Ni(pytsc)$_2$][a] | 2.440(2) | 2.409(2) | 2.125(7) | 2.106(7) | 2.004(6) | 2.056(6) |
| [Ni(isoqtsc)$_2$][b] | 2.424(2) | 2.412(2) | 2.110(6) | 2.114(6) | 2.013(5) | 2.026(5) |
| [Ni(NNSMe)$_2$][c] | 2.420(3) | 2.412(3) | 2.224(7) | 2.166(7) | 2.056(6) | 2.016(6) |

[a] pytsc = the pyridine-2-carboxaldehydethiosemicarbazone [20],
[b] isoqtsc = the isoquinoline-2-carboxaldehyde thiosemicarbazone [21].
[c] This work.

Table 5. Comparison of selected bond angles (°) for some bis-ligand nickel(II) complexes of NNS ligands

| Angle | [Ni(pytsc)$_2$][a] | [Ni(isoqtsc)$_2$][b] | [Ni(NNSMe)$_2$][c] |
|---|---|---|---|
| S(1B)—Ni—N(2B) | 80.7(0.2) | 81.3(2) | 81.0(2) |
| S(1B)—Ni—N(2A) | 102.8(0.2) | 100.4(2) | 93.8(2) |
| N(2A)—Ni—S(1A) | 79.3(0.3) | 81.2(2) | 80.6(2) |
| N(1A)—Ni—S(1B) | 93.2(0.2) | 91.5(2) | 90.7(2) |
| S(1A)—Ni—S(1B) | 96.1(0.1) | 96.2(1) | 95.7(1) |
| N(1B)—Ni—S(1B) | 158.1(0.2) | 159.0(2) | 158.1(2) |
| N(1A)—Ni—S(1A) | 156.9(0.2) | 159.0(2) | 157.6(2) |
| N(2A)—Ni—N(2B) | 169.0(0.2) | 177.5(2) | 172.8(3) |
| N(1B)—Ni—S(1B) | 158.1(0.2) | 158.9(2) | 158.1(2) |
| N(1A)—Ni—N(2A) | 78.1(0.2) | 78.2(2) | 77.6(3) |

[a] pytsc = the pyridine-2-carboxaldehydethiosemicarbazone [20],
[b] isoqtsc = the isoquinoline-2-carboxaldehyde thiosemicarbazone [21].
[c] This work.

those of other related nickel(II)-thiosemicarbazone complexes previously studied, are compiled in Table 4. It is seen that all the bond angles compare well with each other, but except for the two angles [*viz.* the S(1B)—Ni—N(1A) and N(1A)—Ni—N(1B) angles], no other angles in these six-coordinated nickel(II) complexes are close to the idealized values expected for a regular octahedral geometry, indicating that distortion is a common phenomenon in bis-ligand nickel(II) complexes of planar NNS tridentate chelating agents.

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