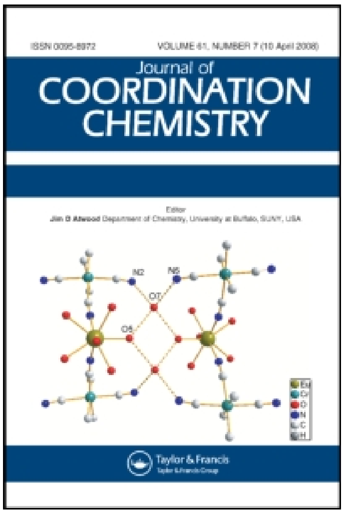

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CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDIES OF A NICKEL(II) COMPLEX OF A LIGAND CONTAINING NITROGEN-SULPHUR DONORS

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CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDIES OF A NICKEL(II) COMPLEX OF A LIGAND CONTAINING NITROGEN-SULPHUR DONORS

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A bis-ligand neutral Ni(II) complex of a Schiff base ligand derived from *S*-benzyldithiocarbazate and *p*-dimethylaminobenzyldehyde was prepared and characterized. Single crystal X-ray diffraction analysis of the nickel(II) chelate established that the Schiff base loses a proton from its tautomeric thiol form and coordinates to Ni(II) *via* the mercapto sulphur and β-nitrogen atoms. The geometry of the Ni(II) ion is square-planar with two equivalent Ni-N and Ni-S bonds; the two dimethylaminobenzyl rings and the coordinated plane are almost in one plane, forming an electronic delocalization system. When the complex crystallizes, benzene molecules are included in the crystal. However, there is no obvious interaction between the complex molecule and the benzene molecule. Magnetic and spectroscopic data support the square-planar structure found in the structure analysis.

The complex crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 7.839(2)$, $b = 10.528(4)$, $c = 10.832(5)$ Å, $\alpha = 100.61(2)$, $\beta = 92.39(2)$, $\gamma = 93.99(2)^\circ$ and $Z = 1$. The structure was refined by full-matrix least-squares to $R = 0.050$ and $R_w = 0.064$, with 2955 reflections having $I > 3\sigma(I)$.

KEYWORDS Nikel(II), crystal structures, Schiff base.

INTRODUCTION

Metal complexes of ligand derived from *S*-alkydithiocarbazic acid have received considerable attention over the past few years.[1–8] This may be attributed to unusual structural features in the resultant metal complexes and their biological activities; some of the metal complexes have anticancer properties.[1] However, there are few examples of structural studies of such complexes containing sulphur-nitrogen ligands.[9,10] Herein, we report the crystal structure and spectroscopic studies of a

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metal complex with a new Schiff base ligand (HL) derived from *S*-benzyldithiocarbazate and *p*-dimethylaminobenzyldehyde.

EXPERIMENTAL

All chemicals used were of analytical grade. Solvents were purified by conventional methods. *S*-benzyldithiocarbazate was prepared by the literature methods.[11]

Physical measurements

IR spectra were recorded on a Nicolet FT-IR-170SX instrument (KBr discs) in the 4000–400 cm^{-1} region. The far-IR spectra (500–100cm^{-1}) were recorded in Nujol mulls between polyethylene sheets. Electronic absorption spectra were obtained on a Shimadzu UV 3100 spectrophotometer in dichloromethane. Solid state electronic spectra were obtained by the reflectance technique on a Shimadzu UV240 spectrophometer using MgO as reference material. Magnetic susceptibility data were collected with a Cahn 2000 magnetobalance. Diamagnetic correction for constituent atoms were made using the Pascal constants. Elemental analyse were performed on a Perkin-Elmer 240C instrument. ^{1}H-NMR spectra were run on a Bruker AM-500 spectrometer using TMS as internal standard and CDU_3 as solvent. Mass spectra were obtained on an ZAB-HS mass spectrometer (FAB sauce).

S-benzyl-β-N-(P-dimethylaminophenyl)methylendithiocarbazate (HL)

A solution of 0.39 g (2mmol) of S-benzyldithiocarbazate in 25 cm^3 of absolute ethanol was added to 25 cm^3 of absolute ethanol containing 0.29 g (2mmol) of *p*-dimethylaminobenzyldehyde. After the mixture was heated under reflux for 2 hours, the solid formed was filtered off, washed with ethanol and recrystallized from benzene. Yellow pyramidal crystals were collected and dried *in vacuo* over P_2O_5; yield 0.56g (85%). IR data (KBr discs, cm^{-1}) 3102, 2975 (N-H, m), 1606 (C = C,s) 1589 (C = N, s), 1018 (C-S, s). Electronic spectra (nm) (dichloromethane, logε): λ_{max} 198 (4.18), 230 (4.19), 278 (4.11), 326 (3.90), 390 (4.69). FAB-MS *m*/z (relative intensity): 330 (5.4, $(M+1)^+$). Mp. 175°C. Anal. calc. for HL ($C_{17}H_{19}N_3S_2$:C, 61.99; H, 5.81; N, 12.76%. Found: C, 62.64; H, 5.85; N, 12.53%.

Preparation of the nickel complex

A solution of nickel acetate (0.124 g, 0.5 mmol) in ethanol (20 cm^3) was added to an ethanol solution (20 cm^3) of the ligand (0.329 g, 1mmol). The mixture was refluxed and then stirred for 4 hours. After cooling to room temperature, the crystals which had formed were filtered off, washed with ethanol and dried *in vacuo* over P_2O_5, yield approximately 96%, 0.345 g IR(KBr discs, cm^{-1}) 1552 (C = N), 944 (C-S), 455 (M-N), 371, 356 (M-S). Electronic spectra (nm) (dichloromethane, logε): λ_{max}198 (4.64), 216 (4.51), 292 (4.64), 402 (4.72), 450 (4.66), 540sh (solid), 674sh (solid). Anal. calc. for NiL_2: C, 56.88; H, 5.06; N, 11.74%. Found: C, 57.05; H, 5.31; N, 11.82%.

Brown crystals of $NiL_2 \cdot C_6H_6$ were obtained by slowly diffusing benzene vapour into a DMF solution of NiL_2. Anal. calc. for $NiL_2 \cdot C_6H_6$:C, 60.55; H, 5.34; N, 10.55%. Found: C, 60.23; C, 5.45; H, 5.34; N, 10.58%.

Crystallographic structure determination

A single crystal with dimensions 0.45 x 0.30 x 0.21mm was mounted on a Enraf-nonius CAD4 diffractometer using graphite-monochromated Mo-K_α-($\lambda = 0.71069$ Å) radiation. The scan mode was ω-2τ;3188 independent reflections were collected in the range $2° < 2\tau < 54°$, and 2955 observed reflections with $I > 3\sigma(I)$ were used for further computation. The complex $NiL_2 \cdot C_6H_6$ is triclinic, space group $P1$, mol.wt. 793.75, cell dimensions $a = 7.839(2)$, $b = 10.528(4)$, $c = 11.832(5)$ Å, $\alpha = 100.61(2)$, $\beta = 92.39(2)$, $\gamma = 93.99(2)°$, $V = 956(1)$ Å^3, $Z = 1$, $D_{calc} = 1.38 cm^{-3}$, $F(000) = 416$, $\mu = 8.66$ cm^{-1}.

All calculations were made on a VAX3100 computer using the TEXSAN[12] program package. Intensity data were corrected for Lorentz polarization effects and absorption. The structure was solved by direct methods using MITHRIL.[13] The heavy atom was located in an E map and remaining non-H atoms were located using DIRIF.[14] The structure was refined by full-matrix least-squares methods with anisotropic temperature factors for all the non-hydrogen atoms. The H atoms were fixed geometrically and not refined, but were allowed to ride on those atoms to which they are attached. Data collection used CONTROL[15] software. The final R and R_w $(w = 1/\sigma(F))$ values were 0.050 and 0.064, respectively. The maximum shift/esd and largest peak in the final difference Fourier map were 0.01 and 0.058eÅ^3, respectively.

RESULTS AND DISCUSSION

Synthesis of the Schiff base ligand

The new Schiff base ligand (HL) was obtained in good yield by condensation of *S*-benzyldithiocarbazate with *p*-dimethylamino benzyldehyde.

The important IR bands of the Schiff base together with those of its nickel complex were given above, where the assignments shown are based on assignments made for similar compounds.[16] The Schiff base has a thione group (C = S) and a proton adjacent to the thione group. The thione group is relatively unstable in the monomeric form and tends to a stable C-S single bond by enethiolization, if there is at least one hydrogen atom adjacent to the C = S bond.[17] The IR spectrum of the Schiff base does not display ν(S-H) at about 2570 cm^{-1} indicating that in the solid state the Schiff base remains in the thione forms (I). However, ^{1}H-NMR spectra show that the thione form (I) and the thiolo tautomeric form (II) are in equilibrium in solution, by the presence of the -N = C-SH proton (chemical shift 1.65). The integrated intensity ratio of -NH and -SH protons is about 9:1, respectively.

IR spectrum of the nikel (II) complex

The spectrum of the Schiff base exhibit strong bands at 2975 and 3102 cm^{-1}, respectively, which can be assigned to ν(N-H) of the free ligand. These bands disappear in the IR spectra of the metal complex, which suggests that the proton on the α-nitrogen atom is lost upon complex formation. A strong band at 1589 cm^{-1} in the IR spectrum of the Schiff base is assigned to ν(C-N). This band is shifted to higher frequencies by about 20 cm^{-1} in the complex. This may be attributed to increasing C(1)-N(1) bond order. The tendency of the Schiff base to deprotonate may be attributed to the stabilization of the deprotonated form by conjugation of the -C = N-N = C-group.[18] A strong band at 1018 cm^{-1} in the IR spectrum of the Schiff base is tentatively assigned to ν(C = S). The band is absent in the spectra of the metal complex. This observation can be explained by the change in the nature of the C = S bond on coordination of the ligand through the sulphur atom, which is proven by crystal structure determination. The two very strong peaks at about 1606 and 1589 cm^{-1} in the IR spectra of the Schiff base may be attributed to the aromatic C = C vibration and the C = N stretching. Although these two vibrational mode may couple to each other, the peak at about 1589 cm^{-1} may be safely assigned to the C = N stretching vibrations of the azomethine group, since the frequency of the band is lowered by about 40 cm^{-1} in the spectra of the metal complex. This may be attributed to decreasing C = N bond order as a result of M-N bond formation.

The Far IR spectra (500 - 100cm^{-1}) of the complex displays a medium to strong band in the 354–371 cm^{-1} region and another in the range 335-356 cm^{-1} which may be assigned to metal-sulphur stretching.[19,20] A band at higher frequencies, 453–477cm^{-1}, can be assigned to metal-nitrogen stretching.[21]

Magnetic properties and electronic spectrum of the Ni(II) complex

The room temperature magnetic moment of the Ni(II) complex suggest that it is essentially diamagnetic. For the d^8 electronic configuration diamagnetism generally implies that the metal ion has a square-planar configuration. The electronic spectra of the complex both in Nujol mull as well as in dichloromethane solution are not very well resolved owing to very intense charge transfer bands extending to the visible portion of the spectrum. However, the absence of any band in the range 1.0 - 15.5 kk is strong evidence that the complex has square planar configuration.[22] Three bands corresponding to the transitions $^1A_{1g} \leftarrow {}^1B_{1g}$ $^1A_{1g} \leftarrow {}^1A_{2g}$ and $^1A_{1g} \leftarrow {}^1E_{1g}$ are expected in the electronic spectrum complex. However, in many instances, especially with sulphur ligands, the bands are submerged under other very intense inter-ligand and charge transfer bands. In the 540–640 nm range only one d-d band is observed, and this is attributed to the square-planar Ni(II) d-d transition.[23] The band around 440 nm is assigned to metal-to-ligand charge transfer; such transition are known in thiosemicarbazide and thiosemicarbazone complexes[24,25] as the S-M(II) transition.

Description of the structure of $NiL_2 \cdot C_6H_6$

An ORTEP drawing of the $NiL_2 \cdot C_6H_6$ complex with the atom numbering scheme is shown in Figure 1. Atomic coordinates for non-hydrogen atoms are listed in Table I and selected bond lengths and angles are given in Table II. It was found that free benzene molecules are incorporated into the crystal. However, there is no obvious interaction between the nickle chelate and the benzene molecules (Figure 1). The nickel is square-planar in configuration with two equivalent Ni-N bonds (1.924(2) Å)

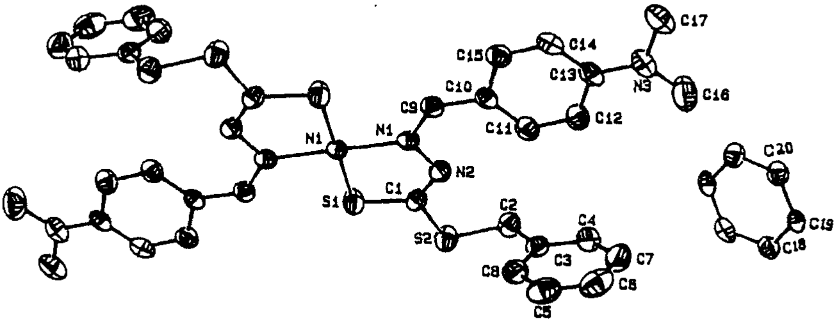

Figure 1 ORTEP drawing of $NiL_2 \cdot C_6H_6$ with the atom numbering scheme.

Table I Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $NiL_2 \cdot C_6H_6$.

atom	*x/a*	*y/b*	*z/c*	*B*(eq)
Ni	0	0	1.000	2.34(2)
S(1)	0.0095(1)	-0.12497(7)	0.83325(6)	3.61(4)
S(2)	0.1664(1)	-0.07044(8)	0.62659(7)	3.84(4)
N(1)	0.0970(3)	0.1367(2)	0.9290(2)	2.51(9)
N(2)	0.1537(3)	0.1074(2)	0.8158(2)	2.8(1)
N(3)	0.4671(4)	0.7090(2)	0.8704(2)	3.8(1)
C(1)	0.1159(4)	-0.0109(3)	0.7685(2)	2.8(1)
C(2)	0.2555(5)	0.0720(3)	0.5781(3)	3.5(1)
C(3)	0.4386(4)	0.1201(3)	0.6180(2)	2.9(1)
C(4)	0.5150(5)	0.2202(3)	0.5711(3)	4.0(1)
C(5)	0.6991(5)	0.1234(4)	0.7330(3)	4.8(2)
C(6)	0.7718(5)	0.2233(4)	0.6867(4)	5.3(2)
C(7)	0.6794(5)	0.2710(3)	0.6060(3)	4.7(2)
C(8)	0.5344(5)	0.0726(3)	0.6987(3)	3.8(1)
C(9)	0.1251(4)	0.2590(3)	0.9763(2)	2.7(1)
C(10)	0.2114(4)	0.3691(3)	0.9399(2)	2.6(1)
C(11)	0.3010(4)	0.3686(3)	0.8395(2)	3.1(1)
C(12)	0.3839(4)	0.4799(3)	0.8170(3)	3.3(1)
C(13)	0.3816(4)	0.5992(3)	0.8928(3)	2.9(1)
C(14)	0.2916(4)	0.6004(3)	0.9936(3)	3.3(1)
C(15)	0.2112(4)	0.4882(3)	1.0155(3)	3.3(1)
C(16)	0.5466(6)	0.7073(4)	0.7627(4)	5.6(2)
C(17)	0.4687(5)	0.8311(3)	0.9489(4)	4.6(2)
C(18)	-0.1156(6)	0.5607(3)	0.4429(3)	5.2(2)
C(19)	-0.0697(5)	0.6077(3)	0.5576(3)	4.8(2)
C(20)	0.0461(6)	0.5477(4)	0.6141(3)	5.0(2)

and Ni-S bonds (2.168(1) Å). The Schiff base loses a proton from its tautomeric thiol form and act as singly charged bidentate ligand coordinating to nickel ion *via* the mercapto sulphur and β-nitrogen atoms; the dimethylamine phenyl ring is completely planar, and forms a dihedral angle of 10.97° with the coordination plane. The very small dihedral angle indicates the high delocalization of electrons in the π system of the two Schiff base ligands and the nickel ion.

It is interesting to compare the structure of the Schiff base in the free state (Figure 2)[26] and in the nickel complex. The greatest difference concerns bond distances

Table II Selected bond lengths (Å) and angles (°) for $NiL_2 \cdot C_6H_6$.

atom-atom	distance	atom-atom	distance
Ni-N(1)	1.924(2)	C(3)-C(4)	1.390(4)
Ni-S(1)	2.168(1)	C(4)-C(7)	1.377(5)
S(1)-C(1)	1.726(3)	C(5)-C(6)	1.373(6)
S(2)-C(1)	1.752(3)	C(5)-C(8)	1.378(5)
S(2)-C(2)	1.808(3)	C(6)-C(7)	1.363(6)
N(1)-C(9)	1.306(4)	C(9)-C(10)	1.444(4)
N(1)-N(2)	1.416(3)	C(10)-C(15)	1.400(4)
N(2)-C(1)	1.276(4)	C(10)-C(11)	1.404(4)
N(3)-C(13)	1.369(4)	C(11)-C(12)	1.375(4)
N(3)-C(17)	1.439(4)	C(12)-C(13)	1.404(4)
N(3)-C(16)	1.440(5)	C(13)-C(14)	1.409(4)
C(2)-C(3)	1.515(5)	C(14)-C(15)	1.372(4)
C(3)-C(8)	1.377(5)	C(18)-C(20)b	1.373(6)
C(18)-C(19)	1.380(5)	C(19)-C(20)	1.362(6)

atom-atom-atom	angle	atom-atom-atom	angle
N(1)a-Ni-N(1)	180.00	C(4)-C(3)-C(2)	118.0(3)
N(1)-Ni-S(1)	86.32(7)	C(7)-C(4)-C(3)	120.9(3)
N(1)a-Ni-S(1)	93.68(7)	C(6)-C(5)-C(8)	120.3(4)
N(1)-Ni-S(1)^a	93.68(7)	C(7)-C(6)-C(5)	119.2(4)
N(1)a-Ni-S(1)^a	86.32(7)	C(6)-C(7)-C(4)	120.7(3)
S(1)a-Ni-S(1)	180.00	C(3)-C(8)-C(5)	121.3(3)
C(1)-S(1)-Ni	95.9(1)	N(1)-C(9)-C(10)	133.3(3)
C(1)-S(2)-C(2)	103.6(1)	C(15)-C(10)-C(11)	116.7(3)
C(9)-N(1)-N(2)	113.4(2)	C(15)-C(10)-C(9)	116.1(3)
C(9)-N(1)-Ni	126.7(2)	C(11)-C(10)-C(9)	127.1(3)
N(2)-N(1)-Ni	119.9(2)	C(12)-C(11)-C(10)	121.3(3)
C(1)-N(2)-N(1)	112.4(2)	C(11)-C(12)-C(13)	121.6(3)
C(13)-N(3)-C(17)	121.4(3)	N(3)-C(13)-C(12)	121.0(3)
C(13)-N(3)-C(16)	120.4(3)	N(3)-C(13)-C(14)	121.6(3)
C(17)-N(3)-C(16)	118.0(3)	C(12)-C(13)-C(14)	117.3(3)
N(2)-C(1)-S(1)	124.9(2)	C(15)-C(14)-C(13)	120.5(3)
N(2)-C(1)-S(2)	121.3(2)	C(14)-C(15)-C(10)	122.6(3)
S(1)-C(1)-S(2)	113.8(2)	C(20)b-C(18)-C(19)	120.0(4)
C(3)-C(2)-S(2)	117.4(2)	C(20)-C(19)-C(18)	120.1(4)
C(8)-C(3)-C(4)	117.5(3)	C(19)-C(20)-C(18)^b	119.9(4)
C(8)-C(3)-C(2)	124.5(3)		

$^a -x,\ -y,\ 2-z.$ $^b -x,\ 1-y,\ 1-z.$

around atom C(1). In the free ligand, the bond distances C(1)-N(2), 1.324(3) and C(1)-S(1), 1.671(3) Å, suggest a C(1)-N(2) single bond and C(1) = S(1) double bond, while in the complex the bond distances C(1)-N(2), 1.276(4), and C(1)-S(1), 1.726(3) Å, suggest a C(1) = N(2) double bond and a C(1)-S(1) single bond. These results, together with the spectroscopic characterization of the nikel complex, indicate the presence of the C-S-M group, formed by enolisation of -NH-C = S in the free ligand to -N = C-SH coordination of the metal through sulphur after deprotonation. This tendency is so strong that there is no metal complex known containing the neutral ligand which coordinates by the thioketo sulphur atom.

Deprotonation and coordination of the ligand to the metal ion makes the configuration of the ligand quite different. In crystals of the free ligand, the α-nitrogen atom N(2) and the thioketo S atom form intermolecular, hydrogen bonded dimers (Figure 2), and thus the β-nitrogen atom and the thioketo S atom are

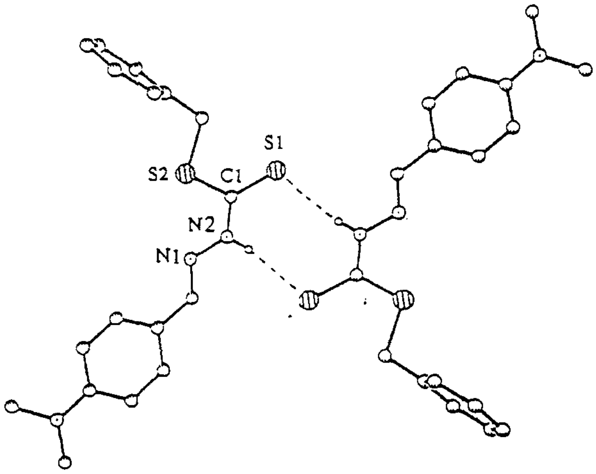

Figure 2 Molecular orientation of the ligand.

in the *trans*-configuration. On the other hand, in the complex, the presence of the metal ion makes the Schiff base coordinate as a bidentate ligand and the thio S and β-nitrogen atoms are *cis* to each other

SUPPLEMENTARY MATERIAL

Tables of hydrogen atoms coordinates, thermal parameters, bond distances and angles, least-squares planars equations, and observed and calculated structure factors are available from the authors on request.

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