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Crystal and Molecular Structure of Hexan-2,5-dione bis(4-phenyl-thiosemicarbazonato)nickel(II), ($C_{20}H_{22}N_6S_2Ni$): A Model Study of the Enhancement of the Antibacterial Activity of a Tetradentate N, S Donor Ligand on Metal Complexation

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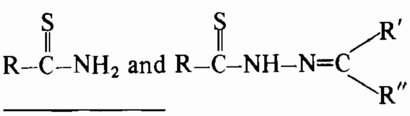
The crystal structure of the nickel(II) complex ($C_{20}H_{22}N_6S_2Ni$) of the N_2S_2 ligand hexan-2,5-dionebis(4-phenyl-thiosemicarbazone) has been solved using diffractometric data. The complex, exhibiting greater antibacterial activity than the free ligand, crystallizes in the space group C2 with $a = 17.414(1)$ Å, $b = 8.485(1)$ Å, $c = 15.129(3)$ Å, $\beta = 104.09(3)°$, $Z = 4$, $d(obsd) = 1.425$ g cm^{-3}, $d(calc) = 1.438$ g cm^{-3} and $\mu(Mo\text{-}K_\alpha) = 10.978$ cm^{-1}. The structure has been refined by full-matrix least squares to a final $R = 0.033$ and $R_w = 0.041$ using 1743 reflections with $I \geqslant 3\sigma(I)$ out of 2049 unique reflections measured ($2° \leqslant \theta \leqslant 27°$). The hydrogens were either located or placed in their calculated positions. The nickel(II) ion lies in the tetrahedrally distorted square planar ligand field of the tetradentate ligand forming two five membered and one seven membered chelate rings. It is observed that the lack of conjugation in the seven membered chelate rings of the present complex and of similar complexes leads to dissymmetry in the ring geometry. The metal ion is coordinatively unsaturated and available for additional coordination in its axial directions.

Introduction

The antitumor and antibacterial activities of thiosemicarbazides and thiosemicarbazones [1–4] have been attributed to their ability to chelate trace metals [5–8]. Jensen has shown that molecules having the general formula



$$R{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH_2 \text{ and } R{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH{-}N{=}C\begin{matrix}\nearrow R' \\ \searrow R''\end{matrix}$$

are capable of forming complexes with transition metal ions [9–11]. More recently it has been found that the thiosemicarbazones are further activated on chelation to some first row transition metal ions [12]. Liebermeister has shown that the copper ion enhances the antitubercular activity of p-acetamidebenzaldehyde thiosemicarbazone [13]. Similarly it has been shown that the active intermediate in the antitumor activity of 3-ethoxy-2-oxybutyraldehyde bis(thiosemicarbazone) is its copper(II) chelate [14, 15]. Several explanations have been suggested for this enhancement in activity on metal complexation [16–18].

The ligand hexan-2,5-dionebis(4-phenyl-thiosemicarbazone) has been found to possess activity *in vitro* against *E. coli* while its nickel(II) complex is about four times more active [19]. Nickel(II) complexes of bidentate thiosemicarbazides and thiosemicarbazones present different structures; in addition to planar four coordinated complexes, complexes with five [20] and six coordination [21, 22] are also known. The X-ray structure analysis of the present complex, hexan-2,5-dione bis(4-phenyl-thiosemicarbazonato)nickel(II) (*1*) was undertaken as a model study to find out the nature of the coordination and the stereochemistry of the Ni(II) chromophore in order to gain insight into the mechanism of its biological activity.

Experimental

Preparation of Hexan-2,5-dione bis(4-phenyl thiosemicarbazone), [$C_{20}H_{24}N_6S_2,LH_2$]

To a solution of 5.7 g (0.05 mol) of 4-phenyl thiosemicarbazide in 200 ml absolute alcohol 5.7 g (0.05 mol) hexan-2,5-dione in 50 ml absolute alcohol was added and the mixture refluxed for 2 hr. A white compound which separated out was filtered,

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TABLE I. Crystallographically Important Data Collection and Processing Information.

Empirical formula :	$C_{20}H_{22}N_6S_2Ni$	Molecular weight :	469.28
Crystal dimensions :	0.13 × 0.12 × 0.12 mm	Temperature :	296 K
Crystal parameters[a] :	a = 17.414(1) Å	Crystal system :	Monoclinic
	b = 8.485(1) Å	Space Group :	C2
	c = 15.129(3) Å	Z :	4
	β = 104.09(3)°	D_{cal} :	1.425 g cm^{-3}
		D_{obs} (floatation) :	1.438 g cm^{-3}
Radiation :	Mo-K_α (λ = 0.7107 Å)	Linear absorption coefficient (Mo-K_α) :	10.97 cm^{-1}
Standard for intensity control reflections	(5, 3, −6) (6, −2, −9)	Scan mode[b] :	$\omega/(4\theta/3)$
(measured every one hour of exposure time)		Scan width :	$(0.52 + 0.35\tan\theta)°$
Maximum scan time for a reflection :	60 seconds	Horizontal scan time aperture width :	$(0.75 + 1.0 \tan\theta)$mm

[a] From a least squares fit of the setting angles of 25 selected reflections in the range 17° $\leqslant \theta \leqslant$ 22°. [b] Preliminary scan with the sample crystal indicated that this scan type would be preferable to the $\omega/2\theta$ scan.

washed several times with warm alcohol and dried over fused calcium chloride. Analytical results (C, H, N, S) for the compound agreed well with the values calculated for $C_{20}H_{24}N_6S_2$.

Preparation of Hexan-2,5-dione bis(4-phenyl thiosemicarbazonato)nickel(II), [NiC$_{20}$H$_{22}$N$_6$S$_2$,NiL]

A suspension of 0.4 g (0.001 mol) of the ligand LH_2 and 0.36 g (0.0015 mol) of $NiCl_2 \cdot 6H_2O$ in 100 ml rectified spirit was refluxed for one hour and the clear brown solution was allowed to evaporate slowly at room temperature when brownish-yellow crystals separated out. These were collected by filtration, washed repeatedly with rectified spirit and dried over fused calcium chloride for seventy-two hours. The compound was analysed for Ni, C, H, N and S. The results of Ni, C, H, N and S are 12.54(12.53)%, 51.09(51.20)%, 4.72(4.69)%, 18.01(17.92)% and 13.56(13.65)% respectively; the figures in parentheses represent the calculated results.

Evaluation of Antibacterial Activity

In vitro antibacterial activity of the ligand (LH_2) and its nickel(II) complex (NiL) was determined in the following manner. A culture was grown from a single colony of *E. coli* in a medium containing 2 g NH_4Cl, 6 g $NaHPO_4$, 3 g KH_2PO_4, 3 g NaCl, 0.01 g $MgCl_2$, 0.026 g Na_2SO_4 per litre, supplemented with Ca^{+2} (1 × 10^{-4} *M*), Fe^{+2} (2.5 × 10^{-6} *M*), 0.2% glucose and 0.04% casamino acid placed in an Erlenmeyer flask and incubated in a B.O.D. incubator-shaker at 37 °C. 1% NaCl mixture of the ligand (LH_2) and the metal complex (NiL) were separately prepared by careful grinding of the components in a metal capsule containing stainless steel balls with the help of a vibro mill and 1 mg to 200 mg of these mixtures were added to 10 ml of the medium mentioned before in a 20 ml sterilized test tube. 0.1 ml of the *E. coli* culture was added to it and the test tubes were incubated at 37 °C for 24 hr. The results of this growth inhibition study are presented here in terms of minimum inhibitory concentration (MIC). The MIC values for the ligand (LH_2) and its metal complex (NiL) are 100 μg/ml and 26 μg/ml respectively, indicating a four fold increase in antibacterial activity due to the complexation of the organic ligand with Ni(II).

X-ray Crystallography

Crystallographically important information is presented in Table I. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated radiation in the range 2° $\leqslant \theta \leqslant$ 27°. 1743 out of the 2047 unique reflections measured were considered to be observed [$I \geqslant 3\sigma(I)$]. The data were corrected for Lorentz and polarisation effects but not for absorption.

The structure was solved by the heavy-atom method and was refined by the full-matrix least squares method using the program ORFLS [23] with anisotropic thermal parameters for the non-hydrogen atoms. Most of the hydrogen atoms were located from difference Fourier syntheses while the remainder were placed in their calculated positions. The hydrogen atoms were included in the structure factor calculation with isotropic temperature factors 1 Å^2 in excess of the equivalent isotropic temperature factors [24] of the atoms to which they were covalently bound. The non-hydrogen scattering factors [25] were corrected for anomalous dispersion [26]. The hydrogen scattering factors were taken from ref. 27. The structure refined to

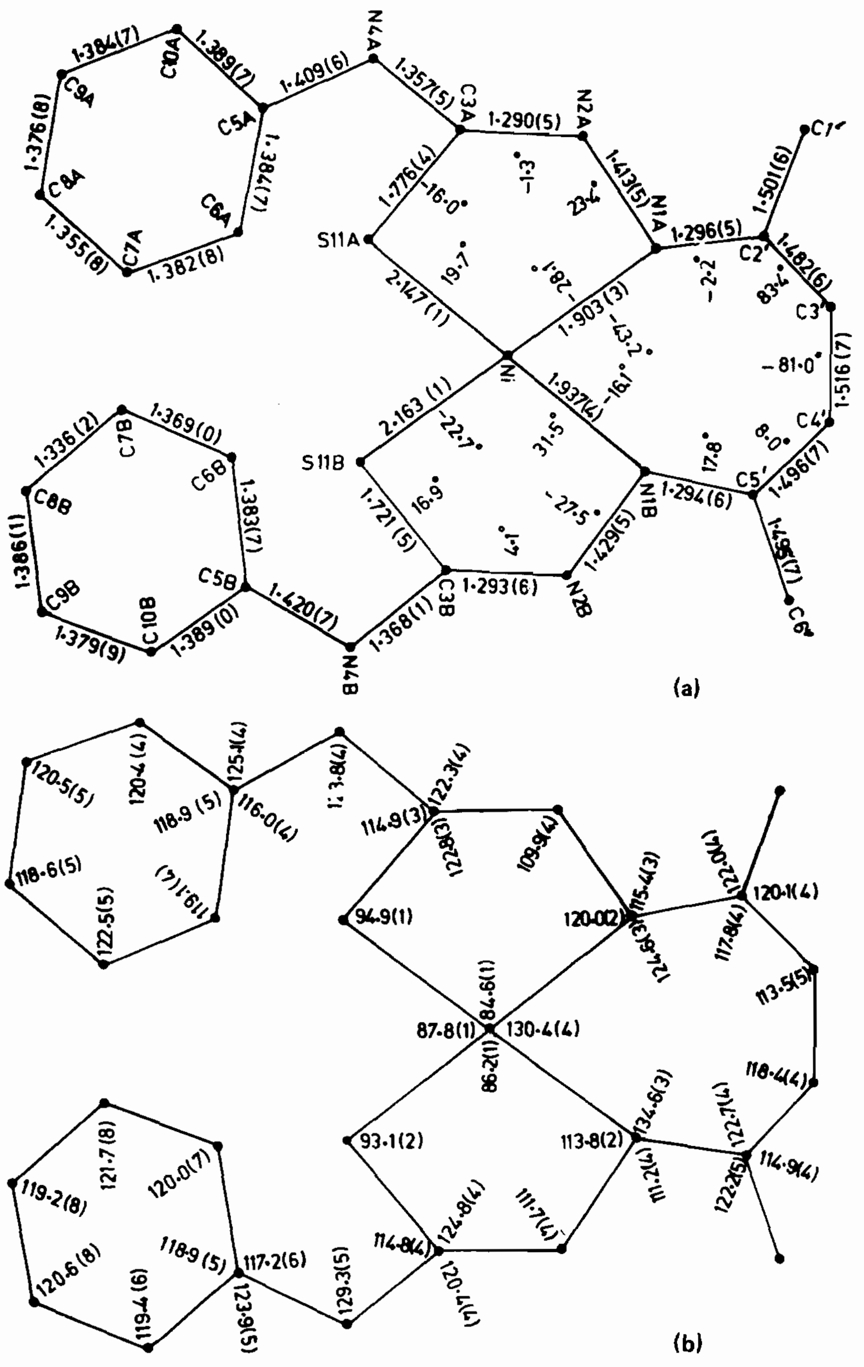

Fig. 1. (a) Bond lengths (Å) and endocyclic torsion angles (°); and (b) bond angles (°) in hexan-2,5-dionebis(4-phenyl-thiosemicarbazonato)nickel(II).

R‡ = 0.033, R_w† = 0.041, goodness of fit = 1.47, using 1743 reflections with I ⩾ 3σ(I) out of a total of 2049 unique reflections measured.

Results and Discussion

The atomic numbering scheme and molecular dimensions are shown in Fig. 1. The atoms of the two 4-phenyl-thiosemicarbazide moiety attached to hexan-2,5-dione are numbered with the suffixes 'A' and 'B'. The atoms in the hexane moiety are primed.

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‡$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.

†$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

TABLE II. Fractional Coordinates of Non-hydrogen Atoms with Their Estimated Standard Deviations and Their B_{eq} (Å^2) (Hamilton, 1959) [24].

Atom	*x*	*y*	*z*	B_{eq}
Ni	0.22966(3)	0.0000(0)	0.08570(3)	3.76
N(1A)	0.2399(2)	−0.0224(5)	−0.0361(2)	3.88
N(2A)	0.1754(2)	−0.0785(5)	−0.1047(2)	4.15
C(3A)	0.1100(3)	−0.0533(6)	−0.0816(3)	3.71
N(4A)	0.0387(2)	−0.0979(6)	−0.1347(2)	4.18
C(5A)	0.0223(3)	−0.1827(7)	−0.2172(3)	4.19
C(6A)	−0.0559(3)	−0.2288(8)	−0.2508(4)	5.20
C(7A)	−0.0779(3)	−0.3141(9)	−0.3310(4)	6.04
C(8A)	−0.0225(4)	−0.3546(9)	−0.3783(4)	6.34
C(9A)	0.0535(4)	−0.3081(10)	−0.3451(4)	6.71
C(10A)	0.0776(3)	−0.2230(10)	−0.2653(3)	5.91
S(11A)	0.10629(6)	0.0351(2)	0.02302(8)	4.29
S(11B)	0.20484(7)	0.0680(2)	0.21374(8)	4.96
N(1B)	0.3289(2)	−0.0822(5)	0.1583(2)	4.04
N(2B)	0.3242(2)	−0.1398(6)	0.2456(3)	4.78
C(3B)	0.2693(3)	−0.0691(7)	0.2748(3)	4.67
N(4B)	0.2606(3)	−0.0970(8)	0.3608(3)	6.00
C(5B)	0.3069(3)	−0.1931(9)	0.4307(3)	5.70
C(6B)	0.3039(4)	−0.1603(10)	0.5193(4)	6.80
C(7B)	0.3472(5)	−0.2486(10)	0.5898(4)	8.92
C(8B)	0.3898(5)	−0.3726(11)	0.5753(4)	9.53
C(9B)	0.3941(4)	−0.4075(12)	0.4871(5)	8.54
C(10B)	0.3519(4)	−0.3202(12)	0.4145(4)	7.81
C(1′)	0.3067(3)	−0.0041(10)	−0.1606(3)	5.81
C(2′)	0.3032(2)	0.0116(8)	−0.0629(3)	4.26
C(3′)	0.3715(3)	0.0777(7)	0.0053(3)	4.88
C(4′)	0.4230(3)	−0.0466(7)	0.0630(3)	4.93
C(5′)	0.3972(3)	−0.1129(7)	0.1427(3)	4.51
C(6′)	0.4587(3)	−0.2071(8)	0.2074(4)	5.75

The positional and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table II*. Table V shows the positional and thermal parameters for hydrogen atoms.

The ligand is tetradentate and nickel(II) is coordinated through the sulphur atoms and the terminal nitrogen atoms of the thiosemicarbazide moieties. The geometries of the two five membered chelate rings differ. The short C–N [1.290(6) Å, 1.293(6) Å] distances show that this bond is essentially a localised double bond in both the five membered rings, implying that the ligand is in the thiol form. This bond length is comparable to the C=N length of 1.285 Å observed in bis(acetophenone thiohydrazonato)nickel(II) [28] and 1.295 Å in [butanedionebis(phenylacetthiohydrazonato)] nickel(II) [29].

Table III shows the deviations of the atoms Ni, S(11A), S(11B), N(1B), N(1A) from the least squares plane through them, and are, respectively, 0.004(0) Å, −0.043(1) Å, 0.038(2) Å, −0.468(4) Å and 0.256(4) Å, indicating that the diamagnetic [19] nickel(II) ion is in a tetrahedrally distorted square planar configuration. This distortion is also evident from the dihedral angle of 16.3° between the planes formed by Ni, N(1A), N(1B) and Ni, S(11A), S(11B). The atoms N(2) and C(3) are found to deviate from the mean planes of the respective five membered chelate rings by −0.123(4) Å and −0.271(5) Å in

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*Tables of anisotropic parameters for non-hydrogen atoms, calculated and observed structure factor amplitudes are available from authors.

TABLE III. Selected Planes and Deviations of Atoms (Å), with E.s.d's in Parentheses from the Least-squares Planes Defined by Them. Atoms marked with asterisks (*) have been excluded from the plane calculations.

	Atoms	Deviations		Atoms	Deviations
Plane 1	S(11A)	0.000(1)	Plane 3	S(11A)	−0.037(1)
	S(11B)	0.000(2)		S(11B)	0.047(2)
	Ni	0.000(0)		N(1A)	0.344(4)
	C(3A)*	−0.334(5)		N(1B)	−0.375(4)
	N(2A)*	−0.190(4)		Ni*	0.058(0)
	N(1A)*	0.288(4)		C(3A)*	−0.372(5)
	N(1B)*	−0.515(4)		N(2A)*	−0.181(4)
	N(2B)*	−1.307(5)		C(3B)*	−0.954(6)
	C(3B)*	−1.062(6)		N(2B)*	−1.159(5)
Plane 2	N(1A)	0.000(4)	Plane 4	S(11A)	−0.043(1)
	N(1B)	0.000(4)		S(11B)	0.038(2)
	Ni	0.000(0)		N(1A)	0.256(4)
	S(11A)*	0.543(1)		N(1B)	−0.468(4)
	C(3A)*	1.115(5)		Ni	0.004(0)
	N(2A)*	0.831(4)		C(3A)*	−0.409(4)
	S(11B)*	−0.245(2)		N(2A)*	0.257(4)
	C(3B)*	0.415(6)		C(3B)*	−0.992(6)

(continued on facing page)

TABLE III. *(continued)*

	Atoms	Deviations		Atoms	Deviations
	N(2B)*	0.552(5)		N(2B)*	−1.235(5)
	C(2′)*	−0.731(6)			
	C(3′)*	−1.668(6)			
	C(4′)*	−1.018(5)			
	C(5′)*	−0.255(6)			
Plane 5	Ni	−0.003(0)	Plane 7	Ni	−0.002(0)
	N(1A)	0.325(4)		N(1A)	0.256(4)
	N(2A)	−0.123(4)		N(1B)	0.081(4)
	C(3A)	−0.271(5)		C(2′)	−0.308(6)
	S(11A)	0.026(1)		C(5′)	0.081(6)
	N(4A)*	−0.712(5)		C(3′)	−1.255(6)
	C(2′)*	0.956(6)		C(4′)*	−0.578(6)
	S(11B)*	−0.046(2)			
	N(1B)*	−0.548(4)			
Plane 6	Ni	0.003(0)			
	N(1B)	−0.364(4)			
	N(2B)	0.193(5)			
	C(3B)	0.317(6)			
	S(11B)	−0.033(2)			
	N(4B)*	0.712(6)			
	C(5′)*	−0.881(6)			
	S(11A)*	0.954(1)			
	N(1A)*	−0.112(4)			

Dihedral angles (°) between planes	1/2	1/4	2/4	3/4	3/5	5/6
	16.3	1.6	14.8	1.2	3.5	27.3

TABLE IV. Shows that the presence of conjugated double bonds in N, S donor tetradentate ligands makes the system symmetric.

Compound	Space group	*Z*	Presence of conjugated double bonds	Two halves of the molecules symmetric
Phthalaldehyde bis(4-methylthiosemicarbazone) Ni(II) [30]	$p2_12_12_1$	4	Yes	Yes
Butanedione bis(phenylacetothiohydrazonato) Ni(II) [29]	$p2_1/a$	4	Yes	Yes
Hexane-2,5-dione bis(4-methylthiosemicarbazone) Ni(II) [30]	$p2_1/C$	4	No	No
Present work	C2	4	No	No

fragment A and 0.193(5) Å and 0.317(6) Å in fragment B. The least-squares planes through the two five membered chelate rings are mutually inclined at an angle of 27.3°. In the nickel complex of hexan-2,5-dione bis(4-methyl thiosemicarbazone) and that of phthalaldehyde bis(4-methyl thiosemicarbazone) this inclination is 65° and 33° respectively [30].

The nickel chromophore is dissymmetric. The difference in the Ni–S and Ni–N bonds in the two five membered rings can be attributed to the presence of the saturated carbons, C(3′) and C(4′), which inhibit conjugation in the seven membered chelate ring. From Table IV, which lists a number of similar structures, it is seen that the absence of conjugation in the ligand results in a dissymmetric chromophore.

The large deviations from the ideal values of the bond angles in the seven membered chelate ring indicate a pronounced angle strain. The endocyclic torsion angles in the chelate rings are shown in Fig. 1.

TABLE V. Positional and Thermal Parameters (A^2) of the Hydrogen Atoms.[a]

Name	*x*	*y*	*z*	B
H(N4A)	−0.0060	−0.0668	−0.1143	5.18
H(C6A)	−0.0948	−0.2035	−0.2170	6.17
H(C7A)	−0.1319	−0.3481	−0.3520	7.00
H(C8A)	−0.0352	−0.4125	−0.4333	7.29
H(C9A)	0.0931	−0.3393	−0.3756	7.70
H(C10A)	0.1313	−0.1917	−0.2454	6.93
H(N4B)	0.2161	−0.0502	0.3741	6.97
H(C6B)	0.2727	−0.0733	0.5337	7.74
H(C7B)	0.3437	−0.2247	0.6491	9.83
H(C8B)	0.4156	−0.4351	0.6244	10.48
H(C9B)	0.4241	−0.4969	0.4709	9.39
H(C10B)	0.3576	−0.3403	0.3558	8.75
H1(C4′)	0.4743	−0.0023	0.0849	5.89
H2(C4′)	0.4261	−0.1321	0.0232	5.89
H1(C6′)	0.4844	−0.1406	0.2715	6.68
H2(C6′)	0.5008	−0.2380	0.1819	6.68
H3(C6′)	0.4358	−0.3027	0.2265	6.68
H1(C1′)	0.3652	0.0000	−0.1680	6.7
H2(C1′)	0.2770	0.0717	−0.1966	6.7
H3(C1′)	0.2874	−0.1088	−0.1822	6.7
H1(C3′)	0.3507	0.1495	0.0435	5.87
H2(C3′)	0.4022	0.1391	−0.0268	5.87

[a] Thermal parameters are 1 A^2 in excess of the equivalent isotropic thermal parameters of the parent atoms.

The molecules are packed solely through van der Waals interactions.

Structure–Activity Relationship

From the structural data we find that the Ni(II) ion is present in a distorted square planar ligand field of the N_2S_2 chromophore. This co-ordinatively unsaturated Ni(II) complex may possess a residual tendency to accommodate one or two additional monodentate donors in the available axial positions. Experimental evidence of the formation of such six coordinated complexes was obtained by recording the electronic spectra of this distorted square planar complex (showing only one fairly intense band at 3333 cm^{-1} corresponding to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition [31]) in the presence of heterocyclic donors like pyridine, guanine and cytosine. In such cases the electronic spectra consisted of three bands in the regions 10,000–10,500 cm^{-1}, 12,500–13,000 cm^{-1} and 16,000–16,500 cm^{-1} corresponding to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ respectively [32, 33]. It may, therefore, be suggested that this four coordinated Ni(II) acceptor centre probably binds itself to some suitable nitrogen donor, possibly the N_7 of guanine [34], of a nucleic acid base of bacterial DNA, and thereby inhibits DNA replication [35]. This is manifested by the fourfold increase in antibacterial activity of this Ni(II) complex over its ligand.

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