Transition Met Chem (2011) 36:417–424
DOI 10.1007/s11243-011-9485-z

Synthesis, spectroscopic characterization, and antimicrobial activity of cobalt(II) complexes of acetone-*N*(4)-phenylsemicarbazone: crystal structure of $[Co(HL)_2(MeOH)_2](NO_3)_2$

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Received: 19 December 2010 / Accepted: 17 March 2011 / Published online: 9 April 2011

Abstract Four Co(II) complexes, $[Co(HL)_2](OAc)_2$, $[Co(HL)_2Cl_2]$, $[Co(HL)_2(MeOH)_2](NO_3)_2$, and $[Co_2(HL)_4(SO_4)_2]$ (HL = acetone-*N*(4)-phenylsemicarbazone) were synthesized and characterized by physicochemical and spectroscopic methods. The magnetic susceptibility measurements indicate that the complexes are paramagnetic with three unpaired electrons. In all the complexes, the semicarbazone is coordinated as a neutral bidentate ligand. The structure of $[Co(HL)_2(MeOH)_2](NO_3)_2$ was confirmed by single crystal X-ray crystallography. The ligand is neutral and bidentate, being coordinated to the cobalt atom through the carbonyl oxygen and the azomethine nitrogen. Intermolecular hydrogen bonding and C–H···π interactions combine to stabilize the crystal structure. The ligand and its two complexes $[Co(HL)_2Cl_2]$ and $[Co(HL)_2(MeOH)_2](NO_3)_2$ were screened for their antibacterial and antifungal activities using disk diffusion methods.

Introduction

Semicarbazones are very promising compounds from the view of point of coordination chemistry because of their interesting range of pharmacological properties including antimicrobial [1], anticonvulsant [2], and antitumor [3] activities. A significant advantage of semicarbazone derivatives over their thiosemicarbazone analogues seems to be their lower toxicity [4]. The synthesis and reactivity of cobalt complexes of Schiff base ligands have long attracted the attention of inorganic chemists [5]. The cobalt complexes of tetradentate Schiff base ligands have been extensively used to mimic cobalamin (B_{12}) coenzymes [6], and as dioxygen carriers and oxygen activators [7]. They are also used for enantioselective reduction [8] and as antimicrobial agents [9]. Some cobalt complexes of pyridine-2-carbaldehyde thiosemicarbazone have been found to show cytotoxic activity [10], while the conformationally rigid cobalt-based molecular square of tetra(2-pyridyl)-thiosemicarbazone revealed interesting magnetic properties [11].

The coordination possibilities derived from the many potential donor atoms in the semicarbazones are increased if the substituents include additional donor atoms and they can also be modified by placing substituents on the backbone donor atoms. The π-delocalization and the configurational flexibility of their molecular chains can give rise to a great variety of coordination modes [12]. These classes of compounds usually react with metals to give complexes in which the semicarbazones behave as chelating ligands. Semicarbazones exist in two tautomeric forms, keto and enol [13], and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Currently, there are only very few reports on cobalt complexes of *N*(4)-substituted semicarbazones [14]. Keeping in view the above points and with the aim of elucidating the coordination behavior of acetone-*N*(4)-phenylsemicarbazone (HL), its Co(II) complexes were synthesized and characterized. The keto form of HL is given in Scheme 1.

Electronic supplementary material The online version of this article (doi:10.1007/s11243-011-9485-z) contains supplementary material, which is available to authorized users.

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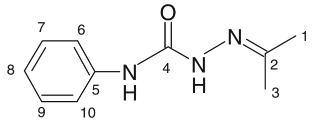

Scheme 1

Experimental

Acetone (Merck), *N*(4)-phenylsemicarbazide (Sigma–Aldrich), $Co(OAc)_2 \cdot 4H_2O$ (Merck), $CoCl_2 \cdot 6H_2O$ (Merck), $Co(NO_3)_2 \cdot 6H_2O$ (Merck), and $CoSO_4 \cdot 6H_2O$ (Merck) were of analar grade and used as received. Methanol (Merck) was used without further purification. All the test microorganisms were obtained from the Microbial Type Culture Collection and Gene Bank (MTCC), Institute of Microbial Technology, Chandigarh, India.

Synthesis of acetone-*N*(4)-phenylsemicarbazone (HL)

The synthesis of acetone-*N*(4)-phenylsemicarbazone (HL) has been published by us earlier [15]. An equimolar mixture of *N*(4)-phenylsemicarbazide (0.151 g, 1 mmol) and acetone (1 mmol) was heated at reflux for 3 h in methanol (30 mL) in the presence of three to four drops of dilute acetic acid. On slow evaporation, colorless crystals of HL separated out. These were filtered off, washed with ether, and dried over P_4O_{10} in vacuo, then recrystallized from methanol.

HL: Yield: 80%; M.P.: 152–154 °C. ^{1}H NMR (δ ppm in $CDCl_3$): 8.04 (1H, s), 8.21 (1H, s), 7.02–7.52 (5H, m), 2.03 (3H, s), 1.90 (3H, s), ^{13}C NMR (δ ppm in $CDCl_3$): C(4), 153.69; C(2), 147.72; C(5), 138.25; C(7) & C(9), 128.90; C(8), 123.10; C(6) & C(10), 119.36, C(3), 25.28; C(1), 16.52.

Synthesis of the complexes

A solution of HL (0.382 g, 2 mmol) in methanol (20 mL) was treated with a methanolic solution of 1 mmol quantities of $Co(OAc)_2 \cdot 4H_2O$ (0.249 g) for $[Co(HL)_2](OAc)_2$, $CoCl_2 \cdot 6H_2O$ (0.238 g) for $[Co(HL)_2Cl_2]$, $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g) for $[Co(HL)_2(MeOH)_2](NO_3)_2$, and $CoSO_4 \cdot 6H_2O$ (0.281 g) for $[Co_2(HL)_4(SO_4)_2]$. The solution was heated at reflux for 5 h. The resulting solution was allowed to stand at room temperature and upon slow evaporation crystals separated out, which were collected, washed with methanol and finally with ether, and dried over P_4O_{10} in vacuo.

Microbiological test methods

The in vitro antimicrobial activities were tested using the disk diffusion method [16]. The viable bacterial cells were swabbed onto Muller Hinton Agar (MHA) plates and fungal spores onto Rose Bengal Agar (RBA) plates. The compounds were dissolved in chloroform to a final concentration of 0.1%. The petri plates were incubated for 24 h for bacterial cultures and 76 h for the fungal cultures. The activity of each test compound was assessed by measuring the diameter of the inhibition zone in millimeters. Test substances that produced a zone of inhibition of diameter 9 mm or more were regarded as positive, while in those cases where the diameter was below 9 mm, the sample was considered to have no antimicrobial activity.

Physical measurements

Elemental analyses were carried out using a Vario EL III CHN analyzer. Infrared spectra were recorded on a Thermo Nicolet Avator 370 spectrometer in the range 4,000–400 cm^{-1} using KBr pellets. Electronic spectra were recorded on a Cary 5000 Version 1.09 UV–VIS–NIR spectrophotometer in the range 900–200 nm using solutions in methanol. The room temperature magnetic susceptibility measurements were taken in the polycrystalline state on a Vibrating Sample Magnetometer (VSM) at 5.0 kOe field strength. The molar conductances of the complexes in methanol (10^{-3} M) solutions were measured at 298 K with a Systronics model 303 direct reading conductivity meter.

X-ray crystallography

Single-crystal X-ray diffraction experiments for brown crystals of $[Co(HL)_2(MeOH)_2](NO_3)_2$ were performed on a Bruker AXS Kappa Apex2 CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. A crystal with dimensions $0.25 \times 0.20 \times 0.20$ mm^3 was selected and found to be orthorhombic space group Pbca. The crystallographic data and structure refinement parameters are given in Table 1. The unit cell dimensions and intensity data were recorded at 293 K. The program XPREP in SAINT-Plus was used for data reduction and APEX2/SAINT-Plus for cell refinement [17]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [18]. Anisotropic displacement parameters were refined for non-hydrogen atoms and a weighing scheme of the form $W = 1/\left[\sigma^2\left(F_0^2\right) + (0.\mathrm{ap})^2 + \mathrm{bp}\right]$, where $P = \left(F_0^2 + 2F_c^2\right)/3$.

Hydrogen atom positions were calculated for idealized positions and treated with the riding model option of SHELXL, except of those H-atoms that were bound to nitrogen atoms. Their positions were derived from the final Fourier maps and refined. Hydrogen atoms linked to carbon

Table 1 Crystal data and structure refinement parameters of $[Co(HL)_2(MeOH)_2](NO_3)_2$

Parameters	$[Co(HL)_2(MeOH)_2](NO_3)_2$
CCDC no.	802092
Empirical formula	$C_{22}H_{34}CoN_8O_{10}$
Formula weight (M)	629.5
Temperature (T) (K)	293
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a (Å) = 15.7192(5)
	b (Å) = 11.1112(4)
	c (Å) = 16.2768(7)
	α (°) = 90
	β (°) = 90
	γ (°) = 90
Volume V (Å^3)	2,842.89(18)
Z	8
D_{calc} (ρ) (Mg/m^3)	1.471
Absorption coefficient, μ (mm^{-1})	0.671
$F_{(000)}$	1,316
Crystal size (mm^3)	0.25 × 0.20 × 0.20
Color, nature	Brown, block
θ Range for data collection (°)	2.50–28.50
Independent reflections (R_{int})	3,596 (0.0300)
Limiting indices	$-19 \le h \le 21$
	$-13 \le k \le 14$
	$-21 \le l \le 19$
Reflections collected	18,035
Observed reflections [$(I > 2\sigma(I)$]	2,534
Completeness to θ	2,850° (99.9%)
Absorption correction	Semiempirical from equivalents
Maximum and minimum transmission	0.8776 and 0.7903
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3596/2/199
Goodness-of-fit on F^2	1.024
Final R indices [$(I > 2\sigma(I)$]	$R_1 = 0.0339$
	$wR_2 = 0.0833$
R indices (all data)	$R_1 = 0.0566$
	$wR_2 = 0.0935$
Largest difference peak and hole (e Å^{-3})	0.285 and −0.334

$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0$

$wR_2 = \left[\Sigma w\left(F_0^2 - F_c^2\right)^2 \big/ \Sigma w\left(F_0^2\right)^2\right]^{1/2}$

atoms were located via geometrical constraints. All esds, except the esd in the dihedral angle between two least square planes, were estimated using the full covariance matrix. Refinement of F^2 was done against all reflections. A total of 18,035 (3,596 unique, $R_{int} = 0.0300$) reflections form ($-19 \le h \le 21$, $-13 \le k \le 14$, $-21 \le l \le 19$) were collected. Absorption corrections were employed using multi-scan [19] ($T_{max} = 0.8776$ and $T_{min} = 0.7903$). The graphical tool used was DIAMOND Version 3.1f [20].

Results and discussion

The colors, partial elemental analyses, molar conductivities, and magnetic susceptibility values of the complexes are presented in Table 2. In all the complexes, the cobalt is in the +2 oxidation state. In $[Co(HL)_2](OAc)_2$, the Co^{2+} nucleus appears to be four coordinated with two neutral ligand moieties, whereas the acetate ion remained outside the coordination sphere. This stoichiometry was in accordance

Table 2 Analytical data of ligand (HL) and its Co(II) complexes

Compound	Color	Composition % found (calc)			Λ_m^a	μ_m^b (B.M.)
		Carbon	Hydrogen	Nitrogen		
HL	Colorless	62.8 (62.8)	6.6 (6.9)	21.9 (21.9)		
$[Co(HL)_2](OAc)_2$	Brown	51.5 (51.5)	5.8 (5.8)	14.9 (15.0)	87	4.4
$[Co(HL)_2Cl_2]$	Light brown	46.8 (46.9)	5.2 (5.1)	16.4 (16.4)	15	5.2
$[Co(HL)_2(MeOH)_2](NO_3)_2$	Brown	41.6 (41.9)	5.3 (5.5)	17.8 (17.8)	93	5.1
$[Co_2(HL)_4(SO_4)_2]$	Brown	44.6 (44.7)	4.9 (4.9)	15.6 (15.6)	13	4.9

[a] Molar conductivity, 10^{-3} M methanol at 298 K

[b] Magnetic susceptibility per metal atom

with the elemental analyses results. For $[Co(HL)_2(MeOH)_2](NO_3)_2$, a possible stoichiometry with two neutral ligand units coordinated to the metal center along with a nitrate group in the outer sphere was suggested by the elemental analysis, and the structure was confirmed by single-crystal X-ray crystallography. The coordination geometries of the other complexes were deduced from their spectra. Conductivity measurements of the complexes $[Co(HL)_2](OAc)_2$ (Λ_m, 87 $Ohm^{-1}\ cm^2\ mol^{-1}$) and $[Co(HL)_2(MeOH)_2](NO_3)_2$ (Λ_m, 93 $Ohm^{-1}\ cm^2\ mol^{-1}$) show that they are electrolytes, whereas complexes $[Co(HL)_2Cl_2]$ and $[Co_2(HL)_4(SO_4)_2]$ are found to be non-electrolytes in methanol solution.

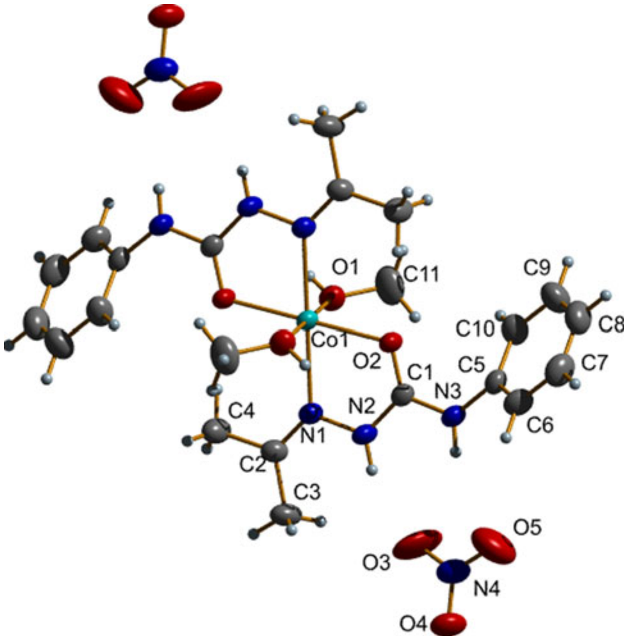

Fig. 1 Molecular structure of $[Co(HL)_2(MeOH)_2](NO_3)_2$ showing the atom numbering scheme

Crystal structure of $[Co(HL)_2(MeOH)_2](NO_3)_2$

A perspective view of the compound showing the crystallographic numbering scheme is shown in Fig. 1 and selected bond lengths and angles are collected in Table 3. The molecule is centrosymmetric and one half of the molecule is related to the other half by a twofold axis passing through the cobalt atom. The complex crystallizes in orthorhombic space group Pbca. The unit cell contains eight molecules. The six-coordinate octahedral Co(II) complex contains two neutral bidentate ligands (HL), two methanol ligands, and two non-coordinating nitrate anions. The semicarbazone ligands constitute the equatorial plane of the octahedron with the metal at the center. The two methanol molecules occupy the remaining two axial positions and hence, they are mutually trans. The Co atom is coordinated by azomethine nitrogen N(1) and carbonyl oxygen O(2) from the semicarbazone, and oxygen O(1) from methanol. The perspective view of the complex shows that the semicarbazone functions as an ON donor ligand, forming two five-membered chelate rings. The compound is centrosymmetric with closely associated crystallographically equivalent molecules, with the Co atom situated on an inversion center in which the bond angles of O(2)–Co(1)–O(2′), O(1)–Co(1)–O(1′) and N(1)–Co(1)–N(1′) are 180°. The semicarbazone fragments {[O(2) and N(1′)], [O(2) and N(1)]} are coordinated to the Co(II) center with angles of O(2)–Co(1)–N(1′) [103.14(5)°] and O(2)–Co(1)–N(1) [76.86(5)°], respectively, which are quite far from a perfect octahedron indicating considerable distortion in the geometry. The terminal aromatic ring is twisted out of the plane as seen in the value of the C(1)–N(3)–C(5)–C(10) torsion angle of −50.7(2)°. The non-coordinating nitrate anions are quite far from a perfect trigonal planar structure, as indicated from their bond angles.

Bond distances within the semicarbazone ligand, particularly the C(1)–O(2) distance [1.2427(18) Å], which is longer than the standard C=O bond length (1.21 Å) [21], together with the presence of the N–H proton, clearly indicate that the semicarbazone ligand is bound to cobalt in

Table 3 Selected bond lengths (Å) and bond angles (°) of $[Co(HL)_2(MeOH)_2](NO_3)_2$

Bond lengths		Bond angles	
C(1)–O(2)	1.243(18)	C(11)–O(1)–Co(1)	124.48(12)
C(1)–N(3)	1.343(2)	C(1)–O(2)–Co(1)	116.14(10)
C(1)–N(2)	1.348(2)	O(2)–Co(1)–O(2′)	179.99(1)
C(2)–N(1)	1.279(2)	O(2)–Co(1)–O(1)	91.93(5)
C(5)–N(3)	1.414(2)	O(2′)–Co(1)–O(1)	88.07(5)
N(1)–N(2)	1.390(18)		
N(1)–Co(1)	2.176(13)		
N(2)–H(2)	0.838(9)	O(1)–Co(1)–O(1′)	180
N(3)–H(3)	0.831(9)	O(2)–Co(1)–N(1′)	103.14(5)
N(4)–O(5)	1.208(2)		
N(4)–O(3)	1.218(2)		
N(4)–O(4)	1.239(19)		
C(11)–O(1)	1.418(2)	O(2)–Co(1)–N(1)	76.86(5)
O(1)–Co(1)	2.111(12)		
O(2)–Co(1)	2.044(10)	O(1)–Co(1)–N(1)	92.85(5)
		O(1′)–Co(1)–N(1)	87.15(5)
		N(1′)–Co(1)–N(1)	180

the keto form (Fig. 1). The N(2)–C(1) bond length of 1.348(2) Å is considerably shorter than the standard N–C single bond length [1.47 Å]. The azomethine bond, C(2)–N(1) distance 1.279(2) Å, is close to an ideal C=N double bond [1.28 Å], confirming the azomethine bond formation [22]. The N(1)–N(2) [1.3900(18) Å] and N(2)–C(1) [1.348(2) Å] bond distances are intermediate between ideal values of corresponding single [N–N, 1.45 Å, C–N, 1.47 Å] and double [N=N, 1.25 Å, C=N, 1.28 Å] bonds, giving evidence for an extended π-delocalization along the semicarbazone chain [23]. The $Co–O_{(methanol)}$, $Co–N_{(azomethine)}$, and $Co–O_{(carbonyl)}$ bond distances are 2.1114(2), 2.1764(13), and 2.0439(10) Å, respectively. The variations in Co–O bond distances indicate the differences in the strength of the bonds formed by each of the coordinating O atoms and can be attributed to the difference in the π-back bonding capabilities of the oxygen of methanol and the semicarbazone moieties. The Co(1)–N(1) bond distance is greater than the Co–N bond distances reported for other octahedral cobalt complexes [14], which suggests a lack of significant π-bonding in this case. It is evident that there is a significant elongation of the C(1)–O(2) bond distance with a concomitant reduction in N(2)–C(1) (which is a part of the chelate ring) upon coordination of HL. The changes in bond distances are accompanied by changes in the bond angles in HL when the five-membered chelate rings are formed in the complex. It is notable that the N(1)–N(2)–C(1) bond angle contracts by about 3.18° and N(1)C(2)C(4) angle widens by about 1.82° when compared to the previously reported bond angles of HL [15]. The O(2) and N(1) atoms are in *E* conformation with respect to the C(1)–N(2) bond in the free ligand, whereas in the complex they are in the *Z* form. The torsion angles N(2)–N(1)–C(2)–C(4), −179.78 (17)° and N(1)–N(2)–C(1)–O(2) −4.0 (2)° indicate the trans configuration of the C(2)–N(1) bond and the cis configuration of the C(1)–N(2) bond.

The packing diagram of the compound viewed along a axis is shown in the supplementary data. The $\pi \cdots \pi$ interactions are weak as they correspond to a distance greater than 3.8 Å. However, there are appreciable $C–H \cdots \pi$ interactions, of which the interaction at a H···Cg distance of 2.549 Å is the most prominent. The $C–H \cdots \pi$ interactions of the O–H and methyl hydrogens of the methanol with the rings of the neighboring molecules contribute to the unit cell packing. The C(3) and C(4) methyl hydrogen of the semicarbazone are also involved in $C–H \cdots \pi$ interactions with the *N*(4)-phenyl ring Cg(3). The molecules are connected by various intermolecular hydrogen bonds involving the nitrate oxygen atoms (Fig. 2). Oxygen O(1) of the methanol is intermolecularly hydrogen-bonded to O(4) of the nitrate anion, while N(2) and N(3) of the semicarbazone moiety are intermolecularly hydrogen-bonded to O(3) of the nitrate anion to give a six-membered ring comprising of atoms N(3), H(3), O(3), H(2), N(2), and C(1). It is interesting to note that H(3) forms two intermolecular hydrogen bonds with O(3) and O(5) of the neighboring nitrate anion [N(3)–H(3)···O(3); N(3)–H(3)···O(5)] [symmetry code: $1 - x$, $-1 - y$, $1 - z$ with a H(3)···O(3) and H(3)···O(5) distance 2.364(13) and 2.420(13) Å] forming a four-membered ring comprising of atoms H(3), O(5), N(4), and O(3). A weak intermolecular hydrogen bond [C(3)–H(3B)···O(4)] is observed with an angle of 159°, and there is also a weak intramolecular hydrogen bond between C(14)–H(4C) and O(2) with an angle of 150°. Hydrogen bonds and other interactions are summarized in Table 4.

Spectroscopic and magnetic studies

The tentative assignments of the main IR bands of the complexes are presented in Table 5. The characteristic $\nu(^2NH)$ and $\nu(C=O)$ stretches are observed at 3,196 and 1,682 cm^{-1} for free HL, indicative of the ketonic nature of the semicarbazone in the solid state [24]. For all the complexes, the presence of a band assigned to $\nu(^2NH)$ indicates the semicarbazone is coordinated in the neutral form, and the downward shift in the $\nu(C=O)$ stretch for the complexes supports the coordination of the keto form of the ligand, as confirmed by the X-ray crystal structure of the complex $[Co(HL)_2(MeOH)_2](NO_3)_2$. The strong bands in the region 3,206–3,340 cm^{-1} in the spectra of the complexes have been assigned to $\nu(^4NH)$ vibrations [25].

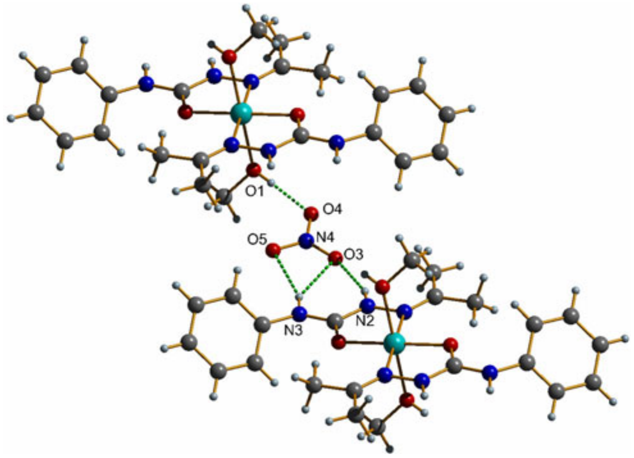

Fig. 2 Intermolecular hydrogen bonding interactions of [Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$

Free HL displays a strong sharp band at 1,591 cm^{-1} ascribed to ν(C=N) of the azomethine group. For the complexes, ν(C=N) shows an upward shift to the region of 1,598–1,610 cm^{-1}, confirming the coordination of azomethine nitrogen [26]. This is further supported by the presence of a band at 415–421 cm^{-1} which corresponds to the ν(Co–N) stretch [27]. The spectra of the complexes exhibit a systematic shift in the positions of the ν(N–N) bands in the 1,140–1,183 cm^{-1} region which gives further evidence of coordination of the ligand through the imine nitrogen [28]. The increase in the ν(N–N) value in the spectra of the complexes is explained by the increase in double bond character. A band at ca. 1,501 cm^{-1} is assigned the interaction between N–H bending and C=N stretching vibration of the C–N–H group of the amide function [29]. A weak band at ca. 1,257 cm^{-1} also results from the N–H bending and C–N stretching interactions. For the complex [Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$, a weak band at 562 cm^{-1} indicates the presence of a Co–O bond resulting from the coordination of methanolic oxygen.

The spectrum of the acetato complex [Co(HL)$_2$](OAc)$_2$ displays strong bands at 1,620 cm^{-1} [ν_a(COO)] and 1,314 cm^{-1} [ν_s(COO)], indicating the ionic nature of the acetate in this compound [30]. For [Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$, the presence of bands at 823 (ν_2), 1,384 (ν_3), and 700 cm^{-1} (ν_4) clearly points to the uncoordinated nature of the nitrate group [31]. For [Co$_2$(HL)$_4$(SO$_4$)$_2$], the ν_1 and ν_2 vibrations, observed as weak bands at 910 and 470 cm^{-1}, suggest the bridged bidentate nature of the sulfate anion in this complex [32]. The symmetry of the sulfate is reduced to C$_{2V}$ when it functions as a bidentate ligand in the complex. The ν_3 vibrations are observed at 1,054, 1,125, and 1,250 cm^{-1}, while the ν_4 vibrations are observed near 610 and 507 cm^{-1}.

Table 4 Hydrogen bonds and short contacts in [Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$

(1) H bonding

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(1)–H(1A)···O(4)^{a}	0.82	1.87	2.690(17)	176.4
N(2)–H(2)···O(3)^{b}	0.84(9)	2.07(12)	2.859(2)	157(2)
N(3)–H(3)···O(3)^{b}	0.83(9)	2.36(13)	3.101(3)	148.1(17)
N(3)–H(3)···O(5)^{b}	0.83(14)	2.42(13)	3.212(3)	159.8(16)
C(3)–H(3B)···O(4)^{c}	0.96	2.60	3.510(3)	159
C(4)–H(4C)···O(2)^{a}	0.96	2.27	3.136(2)	150

(2) C–H···π interactions

X–H(I)···Cg(J)	H···Cg (Å)	X–H···Cg (°)	X···Cg (Å)
O(1)–H(1A)···Cg(1)^{a}	2.539	88.42	2.647(13)
O(1)–H(1A)···Cg(2)^{b}	2.539	88.42	2.647(13)
C(3)–H(3A)···Cg(3)^{c}	2.871	135.00	3.614(2)
C(4)–H(4A)···Cg(3)^{d}	3.029	167.88	3.973(2)
C(11)–H(11C)···Cg(1)^{b}	2.999	107.08	3.408(2)
C(11)–H(11C)···Cg(2)^{a}	2.999	107.08	3.408(2)

D Donor, *A* acceptor, *Cg* centroid

Notes

(1) Equivalent position code: ^{a} $1 - x, -y, 1 - z$, ^{b} $1 - x, -1 - y, 1 - z$, ^{c} $x, -1/2 - y, -1/2 + z$

(2) Equivalent position code: ^{a} $1 - x, -y, 1 - z$, ^{b} x, y, z, ^{c} $x, -1/2 - y, -1/2 + z$, ^{d} $-1/2 + x, -1/2 - y, 1 - z$

Cg(1) = Co(1), O(2), C(1), N(2), N(1); Cg(2) = Co(1), O(2′), C(1′), N(2′), N(1′); Cg(3) = C(5), C(6), C(7), C(8), C(9), C(10)

Table 5 Infrared spectroscopic assignments (cm^{-1}) of the ligand (HL) and its Co(II) complexes

Compound	ν^2NH	ν^4NH	νC=O	νC=N	νN–N	νM–N
HL	3,196	3,375	1,682	1,591	1,129	
[Co(HL)$_2$](OAc)$_2$	3,162	3,340	1,657	1,598	1,140	420
[Co(HL)$_2$Cl$_2$]	3,165	3,254	1,651	1,604	1,149	415
[Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$	3,162	3,294	1,655	1,600	1,144	418
[Co$_2$(HL)$_4$(SO$_4$)$_2$]	3,156	3,206	1,658	1,610	1,183	421

The electronic spectrum of free HL shows a maximum at 243 nm assigned to $\pi \rightarrow \pi^*$ transitions of the imine function, while a band at 294 nm is assigned to $n \rightarrow \pi^*$ transitions of the azomethine and carbonyl groups of the semicarbazone moiety [33]. These are shifted to higher energies upon complexation. Bands at ca. 385 nm in the spectra of the complexes are assigned to O → Co^{II} and N → Co^{II} LMCT transitions. The Co(II) complexes [Co(HL)$_2$Cl$_2$], [Co(HL)$_2$(MeOH)$_2$](NO$_3$)$_2$ and [Co$_2$(HL)$_4$(SO$_4$)$_2$] all showed *d–d* bands in the 670–531 nm region. These are assigned to the transitions (^{4}T$_{1g}$ (F) → ^{4}A$_{2g}$ (F)] (ν_2) and (^{4}T$_{1g}$ (F) → ^{4}T$_{1g}$ (P)] (ν_3), consistent with their

Table 6 UV–Vis spectra λ_{max}, nm (ε, M^{-1} cm^{-1}) in methanol solution and assignments

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	LMCT	*d–d*
HL	243 (27,250)	294 (23,750)	–	–
$[Co(HL)_2](OAc)_2$	215 (29,500)	254 (26,500)	371 (22,000)	720 (11,500), 708 (19,000)
$[Co(HL)_2Cl_2]$	210 (30,000)	265 (29,000)	385 (22,000)	639 (18,900), 551 (19,750)
$[Co(HL)_2(MeOH)_2](NO_3)_2$	233 (29,000)	278 (27,500)	356 (23,000)	644 (17,500), 550 (20,000)
$[Co_2(HL)_4(SO_4)_2]$	212 (28,750)	265 (21,000)	381 (17,500)	670 (14,000), 531 (15,500)

Table 7 Antibacterial and antifungal screening data

Compound	Zone of inhibition (mm)						
	Bacteria					Fungi	
	E. coli	*S. typhi*	*P. vulgaris*	*E. aerogenes*	*B. megaterium*	*A. niger*	*C. albicans*
$[Co(HL)_2Cl_2]$	10.5	–	9	–	7.5	15.5	8
$[Co(HL)_2(MeOH)_2](NO_3)_2$	17	14	–	7	–	–	7
Penicillin	14	10	15	12	20	–	–
Gresiofulvin	–	–	–	–	–	14	10

Concentration 20 μg/disk. The free ligand HL showed no activity against any of the test organisms

octahedral configuration [34]. Electronic spectral data for HL and its complexes are summarized in Table 6.

The observed magnetic moments of the Co(II) complexes are given in Table 2. Both tetrahedral and octahedral Co(II) complexes posses three unpaired electrons, but may be distinguished by the magnitude of the deviation of μ_{eff} from the spin-only value. The magnetic moment of tetrahedral Co(II) complexes with an orbitally non-degenerate ground term is increased above the spin-only value via contribution from higher orbitally degenerate terms and occurs in the range 4.2–4.7 B.M. [35]. Octahedral Co(II) complexes maintain a large contribution due to the $^4T_{1g}$ ground term and exhibit μ_{eff} in the range 4.8–5.6 B.M. [36]. Room temperature magnetic susceptibility studies on $[Co(HL)_2](OAc)_2$ gave a μ_{eff} value of 4.4 B.M., as expected of a four-coordinate tetrahedral Co(II) complex. The μ_{eff} values for $[Co(HL)_2Cl_2]$, $[Co(HL)_2(MeOH)_2](NO_3)_2$, and $[Co_2(HL)_4(SO_4)_2]$ were 5.2, 5.14, and 4.9 B.M., showing that these complexes have an octahedral configuration.

Antimicrobial studies

Free ligand and its two complexes, $[Co(HL)_2Cl_2]$ and $[Co(HL)_2(MeOH)_2](NO_3)_2$, were screened against five bacterial cultures, namely *Escherichia coli* MTCC 585, *Salmonella typhi* MTCC 734, *Proteus vulgaris* MTCC 1771, *Enterobacter aerogenes* MTCC 2990, and *Bacillus megaterium* MTCC 2248 and two fungal cultures, namely *Aspergillus niger* MTCC 281 and *Candida albicans* MTCC 3018. The antimicrobial properties were determined by the standard disk diffusion method [16]. The antibacterial and antifungal screening data of two complexes are presented in Table 7. Chelation often increases the antibacterial activity of a given ligand, due to lipophilic character of the complexes that favor permeation through the bacterial membranes [37]. In the present case, the results reveal that the complexes show some activity, whereas the free ligand is inactive against the tested pathogenic bacteria and fungi.

Supplementary material

All crystallographic data for this paper are deposited with the Cambridge Crystallographic Data Centre (CCDC—802092). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments V. L. Siji is thankful to the Council of Scientific and Industrial Research, New Delhi, India, for financial support in the form of Junior Research Fellowship. The authors are thankful to Dr. M. R. P. Kurup, Department of Applied Chemistry, Cochin University of Science and Technology, for using the software DIAMOND version 3.1f. We are grateful to Dr. Babu Varghese, SAIF, IIT Chennai, India, for providing single-crystal XRD data. The authors are thankful to the SAIF, Cochin University of Science and Technology, Kochi, India, for elemental analyses, IR and electronic spectral data and IIT Roorkee, India, for magnetic susceptibility measurement.

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