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Scientific paper

Syntheses, Characterization, Crystal Structures and Antimicrobial Activity of 4-Bromo-*N*'-(pyridin-2-ylmethylene)benzohydrazide and Its Cobalt(III) and Manganese(II) Complexes

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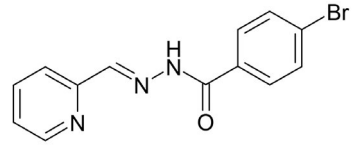
Abstract

A new hydrazone compound 4-bromo-*N*'-(pyridin-2-ylmethylene)benzohydrazide (HL) and its cobalt(III) and manganese(II) complexes, $[CoL_2]NO_3 \cdot 2H_2O$ (**1**) and $[MnL_2]$ (**2**) were prepared. They were characterized by a variety of physicochemical techniques. Molecular structures of the compounds were further confirmed by single crystal X-ray crystallography. The coordination geometry around the cobalt atom in complex **1** and the manganese atom in complex **2** are octahedral, with two pyridine N atoms, two imino N atoms, and two enolate O atoms from the ligands. The compounds were evaluated for their antibacterial (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescence*) and antifungal (*Candida albicans* and *Aspergillus niger*) activities by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) method.

Keywords: Hydrazone; Cobalt complex; Manganese complex; Crystal structure; Antimicrobial activity

1. Introduction

Schiff bases and their metal complexes have been the subject of extensive investigations because of their potential pharmacological properties and a wide variation in their modes of bonding and stereochemistry whereas their hydrazone type complexes received much less attention. Hydrazones prepared by the condensation reaction of carbonyl-containing compounds with hydrazides, have attracted considerable attention for their wide range of biological activities.[1] In recent years, transition metal complexes with various ligands have shown interesting biological especially antibacterial activities.[2] Also, some metal complexes with hydrazones often exhibit diverse biological and pharmaceutical activities.[3] Recent research indicated that hydrazone compounds bearing halido-substituted groups are efficient antimicrobial materials.[4] However, the studies on the antimicrobial activities of metal complexes derived from 4-bromo-*N*'-(pyridin-2-ylmethylene) benzohydrazide (HL) have not been explored. Aiming at exploring new hydrazone based antimicrobial material, a cobalt(III) complex $[CoL_2]NO_3 \cdot 2H_2O$ (**1**) and a manganese(II) complex $[MnL_2]$ (**2**) are reported.



HL

2. Experimental

2. 1. Materials and Physical Methods

2-Pyridinecarboxaldehyde and 4-bromobenzohydrazide were purchased from Merck and used as received. $Co(NO_3)_2 \cdot 6H_2O$ and $MnBr_2$ were purchased from Fluka with AR grade. The solvents and other chemical reagents were commercially available and used without further purification. Analysis of C, H and N were done on Elementar Vario EL III CHNOS elemental analyzer. IR spectra were recorded as KBr discs on Shimadzu IR spectrophotometer. Electronic spectra were recorded on Lambda 35 spectrometer. X-ray diffraction was carried out on a Bruker Smart 1000 CCD diffractometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 using DMSO-d_6 as

solvent and TMS as standard. Solution electrical conductivities were measured on a DIGISUN DI-909 conductivity meter.

2. 2. Synthesis of 4-bromo-*N*'-(pyridin-2-ylmethylene)benzohydrazide (HL).

HL was prepared by mixing 2-pyridinecarboxaldehyde (0.100 mol, 10.7 g) and 4-bromobenzohydrazide (0.100 mol, 21.5 g) in methanol (100 mL). The solution was heated to boiling for 20 min, cooled to room temperature. The solution was stand still in air to slow evaporate to give well-shaped single crystals. Yield: 31.2 g (93%). Characteristic IR data (KBr, cm^{-1}): 3485 and 3397 (OH), 3231 (NH), 1653 (C=O), 1589 (C=N). UV–Vis data (methanol, λ/nm): 300, 363. Anal. Calcd for $C_{14}H_{14}BrN_3O_2$: C, 50.02; H, 4.20; N, 12.50. Found: C, 50.13; H, 4.16; N, 12.41%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.08 (s, 1H, N*H*), 8.62 (d, 2H, Ar*H*), 8.48 (d, 2H, Ar*H*), 7.98 (d, 1H, Py*H*), 7.90 (m, 1H, Py*H*), 7.88 (d, 1H, Py*H*), 7.77 (m, 1H, Py*H*), 7.43 (s, 1H, C*H*=N). ^{13}C NMR (126 MHz, DMSO) δ 162.36, 153.18, 149.53, 148.35, 136.88, 131.57, 129.79, 128.32, 125.72, 124.78, 119.94.

2. 3. Synthesis of $[CoL_2]NO_3 \cdot 2H_2O$ (1)

To a boiling solution of HL (1.0 mmol, 0.30 g) in methanol (20 mL), a methanolic solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 0.29 g) was added and refluxed continuously for 3 h, and cooled to room temperature. The filtrate was kept in air for a few days, to form crystals suitable for single crystal X-ray diffraction. Yield: 0.16 mg (42%). Characteristic IR data (KBr, cm^{-1}): 3458 (OH), 1588 (CH=N). UV–Vis data (methanol, λ/nm): 290, 335, 383. Anal. Calcd for $C_{26}H_{22}Br_2CoN_7O_7$: C, 40.92; H, 2.91; N, 12.85. Found: C, 40.74; H, 2.86; N, 12.97%. Λ_M (10^{-3} M in acetonitrile): 122 Ω^{-1} cm^2 mol^{-1}.

2. 4. Synthesis of $[MnL_2]$ (2)

To a boiling solution of HL (1.0 mmol, 0.30 g) in methanol (20 mL), a methanolic solution of $MnBr_2$ (1.0 mmol, 0.215 g) was added and refluxed continuously for 3 h, and cooled to room temperature. The filtrate was kept in air for a few days, to form crystals suitable for single crystal X-ray diffraction. Yield: 0.17 g (52%). Characteristic IR data (KBr, cm^{-1}): 1585 (CH=N). UV-Vis data (methanol, λ/nm): 270, 290, 365. Anal. Calcd for $C_{26}H_{18}Br_2MnN_6O_2$: C, 47.23; H, 2.74; N, 12.71. Found: C, 47.45; H, 2.87; N, 12.63%. Λ_M (10^{-3} M in acetonitrile): 20 Ω^{-1} cm^2 mol^{-1}.

2. 5. X-ray Crystallography

Single-crystal X-ray diffraction measurements for HL and the complexes were carried out on a Bruker Smart 1000 CCD area diffractometer equipped with a graphite crystal monochromator for data collection at 298(2) K. The determinations of unit cell parameters and data collections were performed with Mo Kα radiation (λ = 0.71073 Å) and unit cell dimensions were obtained with least-squares refinements. The program SAINT was used for reduction data.[5] All structures were solved by direct

Table 1. Crystal data for HL and the complexes

	HL	**1**	**2**
Formula	$C_{14}H_{14}BrN_3O_2$	$C_{26}H_{22}Br_2CoN_7O_7$	$C_{26}H_{18}Br_2MnN_6O_2$
FW	336.19	763.25	661.22
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*–1	$P2_1/n$	*C*2/*c*
a (Å)	6.5606(12)	14.226(1)	22.006(2)
b (Å)	9.8819(18)	10.9197(7)	14.516(1)
c (Å)	23.238(2)	18.770(1)	17.460(2)
α (°)	91.573(2)	90	90
β (°)	95.122(2)	93.898(1)	112.867(2)
γ (°)	92.684(2)	90	90
V (Å^3)	1498.1(4)	2909.1(3)	5139.1(8)
Z	4	4	8
λ (MoKα) (Å)	0.71073	0.71073	0.71073
T (K)	298(2)	298(2)	298(2)
μ (Mo*K*α) (cm^{-1})	2.748	3.395	3.660
Reflections/parameters	8936/367	15314/388	12849/334
Unique reflections	5547	4060	4767
Observed reflections [$I > 2\sigma(I)$]	3466	5433	3257
Restraints	1	0	0
Goodness of fit on F^2	1.006	1.029	1.030
R_1, wR_2 [$I > 2\sigma(I)$]	0.0498, 0.1370	0.0427, 0.0983	0.0539, 0.1137
R_1, wR_2 (all data)	0.0902, 0.1706	0.0662, 0.1098	0.0877, 0.1253

methods using SHELXS-97 and refined with SHELXL-97,[6] non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms treated by a mixture of independent and constrained refinement. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

2. 6. Antimicrobial Assay

The antibacterial activities of the hydrazone compounds and the vanadium complexes were tested against *B. subtilis*, *S. aureus*, *E. coli*, and *P. fluorescence* using MH (Mueller–Hinton) medium. The antifungal activities of the compounds were tested against *C. albicans* and *A. niger* using RPMI-1640 medium. The MIC values of the tested compounds were determined by a colorimetric method using the dye MTT.[7] A stock solution of the compound (150 μg mL^{-1}) in DMSO was prepared and graded quantities (75 μg mL^{-1}, 37.5 μg mL^{-1}, 18.8 μg mL^{-1}, 9.4 μg mL^{-1}, 4.7 μg mL^{-1}, 2.3 μg mL^{-1}, 1.2 μg mL^{-1}, 0.59 μg mL^{-1}) were incorporated in specified quantity of the corresponding sterilized liquid medium. A specified quantity of the medium containing the compound was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 1.0×10^5 cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h and 48 h for bacterial and fungi, respectively. Then the MIC values were visually determined on each of the microtitration plates, 50 μL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH = 7.4) containing 2 mg of MTT mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 μL of isopropanol containing 5% 1 M HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density was measured with a microplate reader at 550 nm.

3. Results and Discussion

3. 1. Chemistry

HL was synthesized from the reaction of pyridine-2-carboxaldehyde and 4-bromobenzohydrazide. The complexes were prepared by reaction of the hydrazone with cobalt nitrate and manganese bromide, respectively. Single crystals of the hydrazone and the complexes were obtained by slow evaporation of the methanolic solution of the compounds. Selected bond lengths and angles are given in Table 2. In both complexes the hydrazones are in deprotonated form. The elemental analyses values are in good agreement with the general formulae of the complexes. Molar conductivities of complexes **1** and **2** measured in methanol at concentration of 10^{-3} mol L^{-1} are 127 and 32 Ω^{-1} cm^2 mol^{-1}, respectively, indicating the 1:1 electrolytic nature of **1** and non-electrolytic nature of **2**.[8]

Table 2. Selected bond lengths (Å) and angles (°) for the complexes

1			
Co1–N1	1.858(3)	Co1–N3	1.938(3)
Co1–N5	1.860(3)	Co1–N6	1.927(3)
Co1–O1	1.919(2)	Co1–O2	1.903(3)
N1–Co1–N3	82.79(12)	N1–Co1–N5	178.94(14)
N1–Co1–N6	97.79(13)	N1–Co1–O1	81.66(11)
N1–Co1–O2	97.58(12)	N5–Co1–N3	96.38(12)
N5–Co1–N6	82.90(13)	N5–Co1–O1	99.16(11)
N5–Co1–O2	81.74(12)	N6–Co1–N3	92.82(12)
O1–Co1–N3	164.43(11)	O1–Co1–N6	90.16(12)
O2–Co1–N3	90.15(12)	O2–Co1–N6	164.59(11)
O2–Co1–O1	91.02(11)		
2			
Mn1–O1	2.144(3)	Mn1–O2	2.133(3)
Mn1–N2	2.179(3)	Mn1–N5	2.205(3)
Mn1–N4	2.298(4)	Mn1–N1	2.362(4)
O2–Mn1–O1	104.52(12)	O2–Mn1–N2	121.25(12)
O1–Mn1–N2	71.89(12)	O2–Mn1–N5	70.93(12)
O1–Mn1–N5	127.79(12)	N2–Mn1–N5	156.08(13)
O2–Mn1–N4	140.41(11)	O1–Mn1–N4	90.64(12)
N2–Mn1–N4	98.12(12)	N5–Mn1–N4	70.93(12)
O2–Mn1–N1	92.71(12)	O1–Mn1–N1	142.55(11)
N2–Mn1–N1	70.75(13)	N5–Mn1–N1	89.09(12)
N4–Mn1–N1	96.89(12)		

3. 2. Structure Description of HL · MeOH

The molecular structure of HL·MeOH is shown in Figure 1. The asymmetric unit contains two HL molecules and two methanol molecules. The molecules of HL adopt *E* configuration with respect to the methylidene units. The distances of the methylidene bonds, 1.26 Å, confirm them as typical double bonds. The shorter distances of the C–N bonds and the longer distances of the C=O bonds for the –C(O)–NH– units than usual, suggest the presence of conjugation effects in the hydrazone molecules. The remaining bond lengths in the compound are within normal values.[9] The dihedral angles between the pyridine and benzene rings are 35.6(5)° and 12.2(5)°. The crystal structure of the compound is stabilized by intermolecular hydrogen bonds (Table 3, Figure 2).

3. 3. Structure Description of Complex 1

Molecular structure of complex **1** is shown in Figure 3. The compound contains a mononuclear cobalt(III) complex cation, a nitrate anion, and two water molecules of crystallization. The cobalt center exhibits a distorted octahedral geometry comprising two tridentate ligands coordinated in a meridional fashion and positioned very nearly perpendicularly to each other. The hydrazone li-

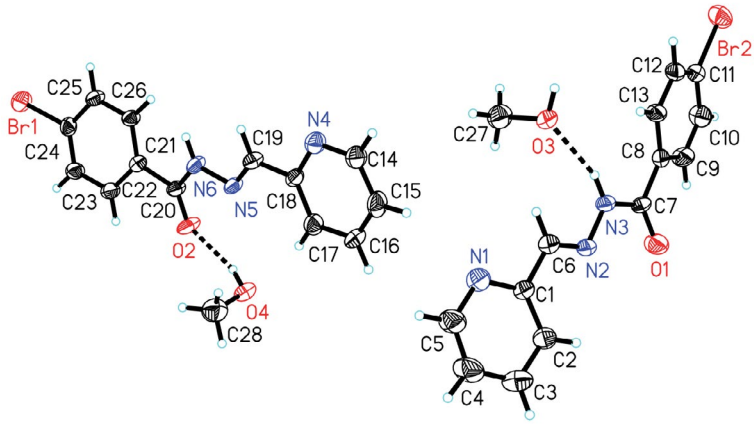


Figure 1. Molecular structure of HL, showing the atom-numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at 30% probability level.

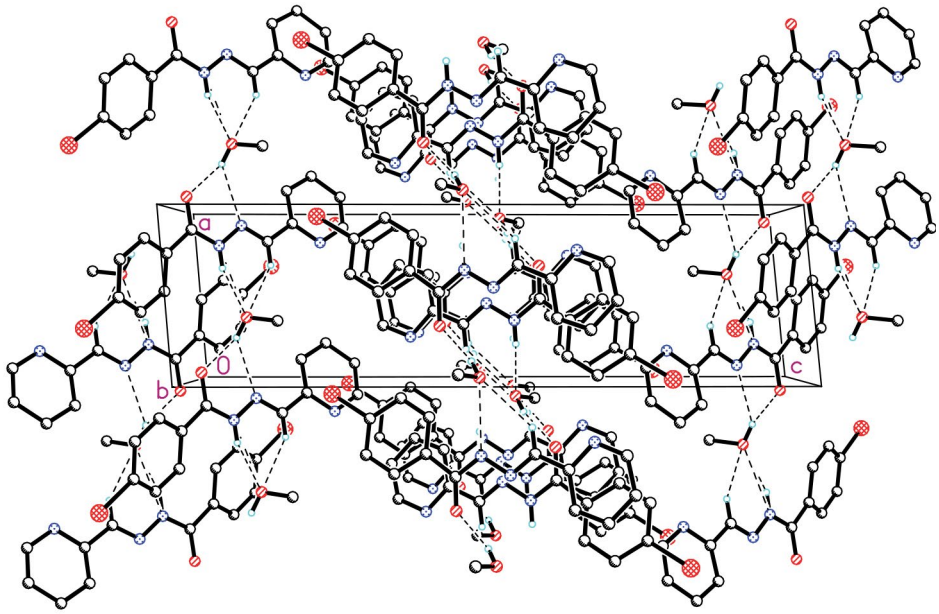


Figure 2. Molecular packing diagram of HL, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

gands coordinate to the cobalt center through the pyridine nitrogen, imino nitrogen and enolate oxygens. The coordinate bond lengths in the complex are comparable to those observed in cobalt(III) complexes with hydrazone ligands.[10] Close inspection of the bond distances reveals that the ligands have undergone keto-enol tautomerization. The deprotonation of the ligands enhances the delocalization of electrons across the ligand framework and increases the basicity of the imine nitrogen and pyridine nitrogen. Like most six-coordinate Schiff base complexes, the imine nitrogens in the complex coordinate to the cobalt center in *trans* positions, while the pyridine nitrogens and enolate oxygens occupy *cis* positions.

In the crystal structure of the compound, the complex molecules are linked by nitrate anions and water molecules through intermolecular hydrogen bonds (Table 3), to form a three-dimensional network (Figure 4).

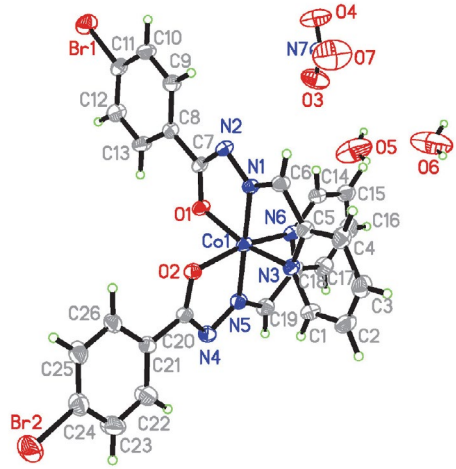


Figure 3. Molecular structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level.

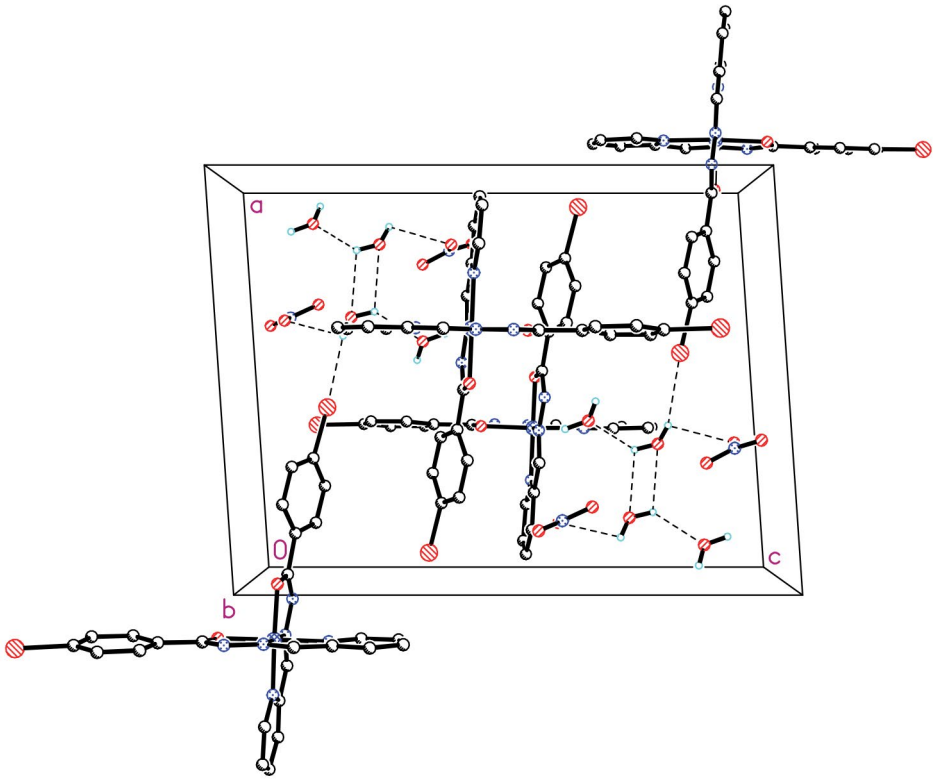


Figure 4. Molecular packing diagram of complex **1**, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

3. 4. Structure Description of Complex 2

Molecular structure of complex **2** is shown in Figure 5. The manganese center exhibits a distorted octahedral geometry comprising two tridentate ligands coordinated in a meridional fashion and positioned very nearly perpendicularly to each other. The hydrazone ligands coordinate to the manganese center through the pyridine nitrogen, imino nitrogen and enolate oxygens. The coordinate bond lengths in the complex are comparable to those observed in manganese(II) complexes with hydrazone ligands.[11] Close inspection of the bond distances reveals that the ligands have undergone keto-enol tautomerization. The deprotonation of the ligands enhances the delocalization of electrons across the ligand framework and increases the basicity of the imine nitrogen and pyridine

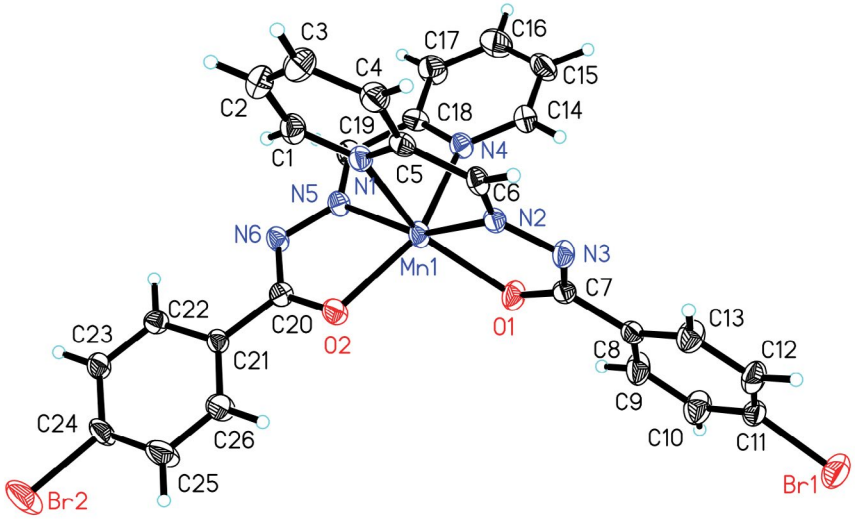


Figure 5. Molecular structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at 30% probability level.

Table 3. Hydrogen bond distances (Å) and bond angles (°) for the compounds

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	Angle (*D*–H···*A*)
HL				
O3–H3B···N2^{i}	0.85(1)	2.48(4)	3.127(5)	133(5)
O3–H3B···O1^{i}	0.85(1)	1.99(3)	2.775(5)	151(5)
O4–H4A···O2	0.82	1.97	2.767(4)	164(5)
N6–H6···O4^{i}	0.86	2.06	2.873(5)	156(5)
N3–H3···O3	0.86	2.05	2.884(5)	162(5)
1				
O5–H5B···Br2^{ii}	0.85	2.75	3.346(5)	129(5)
O5–H5B···O3^{iii}	0.85	2.50	2.924(7)	112(5)
O5–H5A···O6	0.85	2.42	3.031(12)	129(6)

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) –1 + *x*, *y*, *z*; (iii) 1 – *x*, 1 – *y*, 1 – *z*.

nitrogen. Like most six-coordinate Schiff base complexes, the imine nitrogens in the complex coordinate to the manganese center in *trans* positions, while the pyridine nitrogens and enolate oxygens occupy *cis* positions.

3. 5. Spectroscopic Studies

The moderate broad bands at 3230 and 3300–3500 cm^{-1} in the IR spectra of HL and complex **1** are ascribed to the stretching vibrations of N–H and O–H, respectively. Characteristic band of ν(C=O) at 1653 cm^{-1} for the free ligand HL is an indication of the *keto*-form in the solid state. For the complexes the absorption bands due to ν(NH) stretching and the amide band ν(C=O) were absent, indicating that the ligands are coordinated in the enolate form.[12] The C=N bonds are represented by intense bands centered at 1588 and 1585 cm^{-1} for complexes **1** and **2**, respectively.[13] In addition, complex **1** shows an intense band at 1383 cm^{-1}, in agreement with the ionic nitrate.[14] The electronic spectra of HL and the complexes show bands centered at 290–340 nm, due to the $n–\pi^*$ transition of the C=N-NH-CO chromophore. The charge transfer LMCT bands are located in the range 360–390 nm.[15]

3. 6. Antimicrobial Activity

The hydrazone HL and the complexes were screened for antibacterial activities against two Gram (+) bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram (–) bacterial strains (*Escherichia coli* and *Pseudomonas fluorescence*) by MTT method. The MIC (minimum inhibitory concentration, μg mL^{-1}) values of the compounds against four bacteria are listed in Table 4. Penicillin G was used as the standard drug. The hydrazone HL shows medium activities against the bacteria *B. subtilis* and *S. aureus*, and no activity against *E. coli* and *P. fluorescence*. The two complexes, in general, have stronger activities than the free hydrazone. Complex **1** has strong activity against *B. subtilis*, *S. aureus* and *E. coli*, and weak activity against *P. fluorescence*. Complex **2** has strong activity against *B. subtilis* and *E. coli*, medium activity against *S. aureus*, and weak activity against *P. fluorescence*. However, both hydrazone and the two complexes have no activity against the two fungal strains (*Candida albicans* and *Aspergillus niger*). It is interesting that complex **1** has even stronger activity against the four bacteria than penicillin G.

Table 4. Antimicrobial activities of the compounds

Minimum inhibitory concentrations (μg · mL^{-1})				
Tested material	***B. subtilis***	***S. aureus***	***E. coli***	***P. fluorescence***
HL	18.8	37.5	> 150	> 150
1	1.2	2.3	4.7	37.5
2	4.7	18.8	9.4	37.5
Penicillin G	2.3	4.7	>150	>150

4. Conclusion

In summary, a new hydrazone compound 4-bromo-*N*'-(pyridin-2-ylmethylene)benzohydrazide and its two new cobalt(III) and manganese(II) complexes were prepared and structurally characterized. The metal centers are in octahedral geometry. Both complexes have interesting antibacterial activities. The cobalt complex has MIC values of 1.2 and 2.3 μg mL^{-1} against *B. subtilis* and *S. aureus*, respectively, which are even better than penicillin G. Further work is required to be carried out to explore new and efficient antibacterial drug based on the present models.

5. Supplementary Data

CCDC 1812949 (HL), 1547397 (**1**) and 1547398 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Povzetek

Sintetizirali smo nov hidrazon 4-bromo-*N*'-(piridin-2-ilmetilen)benzohidrazid (HL) in njegov kobaltov(III) ter manganov(II) kompleks, $[CoL_2]NO_3 \cdot 2H_2O$ (**1**) in $[MnL_2]$ (**2**). Spojine smo okarakterizirali z različnimi fizikalno-kemijskimi metodami. Strukture so bile potrjene z rentgensko monokristalno analizo. Koordinacijska geometrija okoli kobaltovega atoma v kompleksu **1** in manganovega atoma v kompleksu **2** je oktaerična z dvema piridinskima N atomoma, dvema imino N atomoma in dvema enolatnima O atomoma hidrazonskega liganda. Protibakterijske (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas fluorescence*) in protimikotične (*Candida albicans* in *Aspergillus niger*) lastnosti vseh treh spojin smo testirali z MTT (3-(4,5-dimetiltiazol-2-il)-2,5-difeniltetrazolijev bromid) metodo.