



Synthesis, crystal structure and antibacterial activity of a Mn(III)-Co(III) cocrystallized Schiff base complex

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ABSTRACT

A heterobimetallic 1:1 cocrystal, $[Mn(L)Cl][Co(L)Cl] \cdot 2H_2O$ (**1**), where $H_2L = 2,2'$ -[propane-1,2-diybis(nitriloethyl-1-yl-1-ylidene)]diphenol, have been obtained by the reaction of equimolar amounts of $MnCl_2$, $CoCl_2$ and the tetradentate Schiff base ligand (H_2L) in acetone. The complex has been characterized by microanalytical, spectroscopic, thermogravimetric, single crystal X-ray diffraction and other physicochemical studies. Structural studies reveal that **1** comprises two mononuclear units, one of Mn(III) and other of Co(III), both assuming distorted tetragonal pyramidal geometries. The isostructural complex units in **1** and the adduct water molecules are held together by weak intermolecular H-bonding to constitute fascinating supramolecular network in its solid state. The antibacterial activity of the complex has been tested against some Gram(+) and Gram(-) bacteria.

Keywords: Manganese(III); Cobalt(III); Schiff base; Crystal structure; Cocrystal; Supramolecular structure; Antibacterial activity

INTRODUCTION

Cocrystals are considered to be multicomponent crystals with well-defined stoichiometry within the same unit cell. Such crystals are of current interest due to their importance in crystal engineering and drug design [1-6]. Until now, a limited number of inorganic-organic cocrystals containing transition metals have been reported [7-10]. Besides, there has been enhanced interest in the synthesis and characterization of Schiff base complexes of manganese and cobalt due to their important catalytic, magnetic and biological properties. Schiff base complexes of these two metals in +3 oxidation state are very important in these respects [11-14]. Although numerous organic chelating ligands have been used to synthesize complexes of various first row transition metals, any report on synthesis of cocrystal of such complexes containing manganese(III) and cobalt(III) together or along with any tetradentate Schiff base is lacking.

We describe here, the synthesis and characterization of a new co-crystallized complex of manganese(III) and cobalt(III) containing a tetradentate Schiff base (H_2L) derived from propane-1,2-diamine and 2-hydroxyacetophenone. In an earlier communication [15], we reported a synthetic system of the metal chloride, MCl_2 ($M = Mn$ or Co) and H_2L in acetone solvent that yielded on slow evaporation, a mononuclear complex, $[Mn(L)Cl] \cdot H_2O$ in presence of $MnCl_2$ and a binuclear phenoxo-bridged complex, $[Co_2(L)_2Cl_2] \cdot 2CH_3COCH_3$ in presence of $CoCl_2$. With an aim to get a heterobimetallic complex, we repeated the same synthesis in presence of $MnCl_2$ and $CoCl_2$ together. As a result, we have obtained the cocrystal $[Mn(L)Cl][Co(L)Cl] \cdot 2H_2O$ (**1**) which contains two isostructural mononuclear units of both the metal ions. The complex has been characterized by microanalytical, spectroscopic, thermogravimetric and single crystal X-ray diffraction studies. Structural studies indicate that the central Mn(III) or Co(III) ion in the molecular units in **1** adopts tetragonal pyramidal geometry. Such complex units of two different metal ions are arranged alternatively and linked by weak intermolecular H-

bonding in the solid state. In addition to the physicochemical studies, the compound **1** has also been tested *in vitro* to assess its antibacterial activities against some common reference bacteria.

EXPERIMENTAL SECTION

Materials

Commercially available reagent grade propane-1, 2-diamine, 2-hydroxyacetophenone, manganese(II) chloride tetrahydrate and cobalt(II) chloride hexahydrate were used without further purification. All other chemicals and acetone were of analytical grade. The tetradentate Schiff base ligand (H₂L) was obtained by the usual method of condensation of propane-1, 2-diamine with 2-hydroxyacetophenone in 1:2 molar ratio.

Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer 2400-II elemental analyzer. The infrared spectrum was recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer with KBr discs (4000-400 cm⁻¹). Room temperature solid phase magnetic susceptibility was measured by Gouy's method using Hg[Co(NCS)₄] as the calibrant. The diamagnetic corrections were calculated from Pascal's constants. Molar conductance of the complex in dry methanol was measured using a direct reading conductivity meter of Systronics (Type 304). Thermogravimetric analysis was carried out using a Netzsch STA409PC instrument from 30 to 700°C in an atmosphere of dinitrogen at the heating rate of 10°C min⁻¹.

Synthesis of [Mn(L)Cl][Co(L)Cl]·2H₂O (**1**)

10 mL solution of MnCl₂·4H₂O (0.1 g, 0.5 mmol) in acetone is mixed with CoCl₂·6H₂O (0.12 g, 0.5 mmol) dissolved in same volume of acetone. The mixture was then added dropwise with constant stirring to a 10 mL solution of H₂L (0.16 g, 0.5 mmol) dissolved in the same solvent. To the resulting brown solution, 20 mL of extra solvent was added and stirring was continued for half an hour. The solution was then covered with parafilm, pierced to form 2-3 small holes and left for very slow evaporation at room temperature. Dark brown crystals of compound **1** appeared within a week. The crystals were collected by filtration, washed with a little acetone and finally dried. Yield: 0.22 g, 52% (based on Mn). Anal. Calc. for C₃₈H₄₄Cl₂CoMnN₄O₆: C, 54.49; H, 5.30; N, 6.69. Found: C, 54.46; H, 5.32; N, 6.67%. FTIR (KBr, cm⁻¹): 3432(s), 1636(s), 1597(s), 1586(s), 1438(s), 1347(m), 1234(m), 749(s). A_M (MeOH, Ω^{-1} cm² mol⁻¹): 6. μ_{eff} (RT, BM): 4.78.

X-Ray Crystallography

For X-ray diffraction studies, suitable single crystal of **1** with dimensions of 0.14 × 0.12 × 0.08 mm³ was mounted on a Bruker-Nonius KAPPA diffractometer, both equipped with CCD area detector and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The reflection data were collected and processed using the Bruker-Nonius program suites Bruker SAINT, COLLECT, DENZO-SMN and related analysis software [16-18]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-square refinements on F^2 , using the program SHELX [19]. All non-hydrogen atoms have been refined with anisotropic displacement parameters. The hydrogen atoms were partially located from the difference Fourier maps, partially placed geometrically and refined in riding mode. Crystallographic data and refinement details for the compounds are summarized in Table 1.

CCDC 1004876 contains the supplementary crystallographic data of **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, 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.

Table 1. Crystallographic data and refinement parameters for **1**

| Parameters | 1 |
|---------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Formula | C ₃₈ H ₄₄ Cl ₂ CoMnN ₄ O ₆ |
| Formula weight (g mol ⁻¹) | 837.54 |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ |
| <i>a</i> (Å) | 7.6040(15) |
| <i>b</i> (Å) | 16.864(3) |
| <i>c</i> (Å) | 14.815(3) |
| <i>α</i> (°) | 90 |
| <i>β</i> (°) | 90.32(3) |
| <i>γ</i> (°) | 90 |
| <i>V</i> (Å ³) | 1899.8(6) |
| <i>Z</i> | 2 |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.464 |
| <i>μ</i> (mm ⁻¹) | 0.961 |
| <i>F</i> (000) | 868 |
| <i>hkl</i> range | ±9, ±21, ±18 |
| <i>T</i> (K) | 293(2) |
| <i>λ</i> (Mo K _α) (Å) | 0.71073 |
| Reflections measured | 30837 |
| Reflections unique | 7839 |
| Data with <i>F</i> _o > 2σ(<i>F</i> _o) | 6227 |
| <i>R</i> _{int} | 0.0675 |
| Parameters refined | 470 |
| <i>R</i> ^a (for <i>F</i> _o > 2σ(<i>F</i> _o)) | 0.0510 |
| <i>wR</i> ^b (<i>F</i> ²) | 0.1465 |
| <i>S</i> | 1.06 |
| Δρ _{max} /Δρ _{min} (e Å ⁻³) | 0.77/ -0.51 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}, w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P], P = (F_o^2 + 2F_c^2)/3.$$

Antibacterial screening

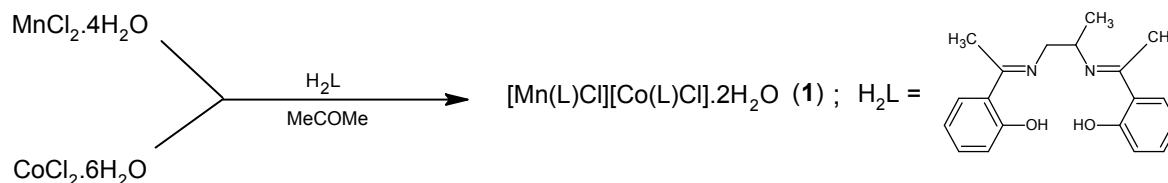
Compound **1** was tested *in vitro* to assess its growth inhibitory activity against two Gram-positive bacteria, viz. *Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441 and two Gram-negative bacteria viz. *Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739 by Kirby Bauer method with necessary modifications [20]. The bacterial strains grown on nutrient agar at 37 °C for 18 h were suspended in a saline solution (0.85%) and adjusted to a turbidity of 0.5 McFarland standards (10⁸ CFU mL⁻¹). The suspension was used to inoculate sterile Petri plates of 9.0 cm diameter in which the test organisms were grown. After solidification, a hole of diameter of 0.6 cm was pierced by a sterile cork borer. Five different concentrations viz. 0.2, 0.4, 0.6, 0.8 and 1.0 mg mL⁻¹ of **1** in dimethyl sulphoxide (dmsO) were used for evaluation of dose response. The discs were placed on the holes of previously seeded plates and incubated at 303 K for *B. subtilis* and at 310 K for all other bacteria. Antibacterial activity of compound **1** was evaluated by measuring the inhibition zone diameters (IZD) and then compared with the experimental data obtained by us earlier [15], for analogous compounds and two antibiotics viz. Gatifloxacin and Ciprofloxacin. Each of the above experiments was repeated thrice along with a control set using dmsO and the mean value was taken for comparison.

RESULTS AND DISCUSSION

Synthesis

In an earlier attempt made by us [15], the reaction of manganese(II) or cobalt(II) chloride with the Schiff base, H₂L in molar ratio of 1:1 in acetone yielded a mixed ligand mononuclear manganese (III) and a binuclear cobalt(III) complex, respectively. In order to see whether any single heteronuclear complex can be synthesized from the same synthetic system, we performed the same reaction using H₂L with both the metal chlorides together. Instead of any common and expected compound, we obtained the cocrystallised complex, **1** containing two discrete mononuclear units of two different metal ions. Although the complex was prepared using manganese(II) and cobalt(II) chloride as starting materials, the bivalent metals underwent aerial oxidation to +3 state in the reaction medium. This fact is commonly observed when harder metal ions combine with ligands containing harder donor atoms to form more stable complexes. The complex **1** has been characterized by microanalytical, spectroscopic and single crystal X-ray diffraction studies. In methanol solvent, **1** behaves as a non-electrolyte as evident from its *Λ*_M value, being 6 Ω⁻¹ cm² mol⁻¹. Room temperature magnetic susceptibility measurements show that **1** possesses a magnetic moment value of 4.78 B.M., close to the spin-only value of high spin Mn(III). In fact, structurally characterized five-coordinate Co(III) complexes are less common and examples of the type [CoL₄]X, where L₄ is a square-planar system and X is a halide group, are found to be square pyramidal as well as diamagnetic [21]. Therefore, it is most likely that the

Co(III) complex unit in **1** is diamagnetic and offers no significant magnetic contribution to **1**. In other words, the experimental magnetic moment of **1** is due only to the presence of a discrete and magnetically non-coupled Mn(III) ion with a d^4 system. All these results including those of the X-ray structural analysis are consistent with the proposed mononuclear formulae of the complex units present in **1**.



FTIR spectroscopy

The infrared spectrum of the complex **1** exhibits strong absorption bands in the region $1586\text{--}1636\text{ cm}^{-1}$ corresponding to the stretching vibrations of the C=N bond [ν_{CN}] of the Schiff base ligand. A broad and strong band at around 3432 cm^{-1} indicates the presence of H_2O molecules in **1**. All other characteristic vibrations including the phenolic C-O stretching of the metal-bound Schiff bases are located in the range $600\text{--}1600\text{ cm}^{-1}$. Thus, the IR spectral data of the compound are in accordance with [22] the respective structural features of **1**.

Thermogravimetric Analysis

The thermogram of TGA (Figure 1) reveals that compound **1** is stable up to 110°C and first stage of weight loss ($\sim 4.3\%$) occurs in the range of $110^\circ\text{--}150^\circ\text{C}$, corresponding to the removal of two molecules of lattice water from **1**. A horizontal portion of the TGA curve in the narrow region $150^\circ\text{--}180^\circ\text{C}$ suggests that no weight loss takes place in this temperature zone. This is followed by a steep decrease in weight up to 310°C and a gradual loss up to the highest temperature of study.

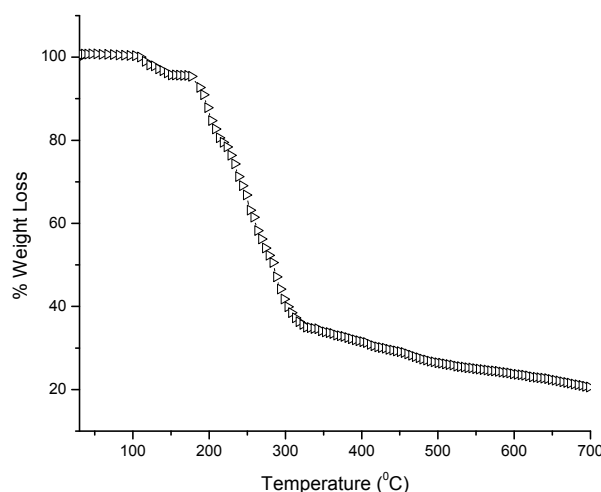


Figure 1. Thermogram of compound **1**

Molecular and supramolecular structures of **1**

The molecular structure of **1** is shown in Figure 2 and few selected bond parameters are listed in Table 2. X-ray diffraction studies reveal that compound **1** crystallizes in the monoclinic space group $P2_1$ and it is a cocrystallized 1:1 complex of discrete $[\text{Mn}(\text{L})\text{Cl}]$ (1A) and $[\text{Co}(\text{L})\text{Cl}]$ (1B) units containing two molecules of water in the lattice. The two heterometallic centers in the cocrystal are quite far apart from each other, the nearest Mn-Co distance being 8.571 \AA . Each of the mononuclear units in **1** has a distorted tetragonal pyramidal geometry with $\text{MN}_2\text{O}_2\text{Cl}$ ($\text{M} = \text{Mn}$ or Co) chromophore. The five-coordination environments around Mn(III) and Co(III) in **1** (Fig. 2) are maintained by a chloride ion (Cl1; Cl2) at the apical position, two imino nitrogen (N1, N2; N3, N4) and two phenolate oxygen (O1, O2; O3, O4) atoms in the basal plane, respectively. The bond dimensions of the two units 1A and 1B are comparable with each other and with similar other Schiff base complexes of Mn(III) and Co(III). As expected, the metal-N bond distances ($1.843\text{--}1.877\text{ \AA}$) are greater than the metal-O bonds ($1.975\text{--}2.008\text{ \AA}$) for both the complex units. Thus, all other bond distances including the metal-Cl ones (2.387 and 2.391 \AA) in both units in **1** agree well with each other as well as with similar other Schiff base complexes of manganese(III) and cobalt(III) [15, 23-25]. Various relevant angles in 1A and 1B are also comparable and have magnitudes in the expected range. Distortion in the coordination sphere of the metal ion from ideal geometry in each mononuclear unit has been noticed due to the

structural constraints imposed by polydentate ligand framework. It is reflected from the wide range of *cisoid* and *transoid* angles, being 83.8-101.9° and 157.7-159.8°, respectively, in **1**.

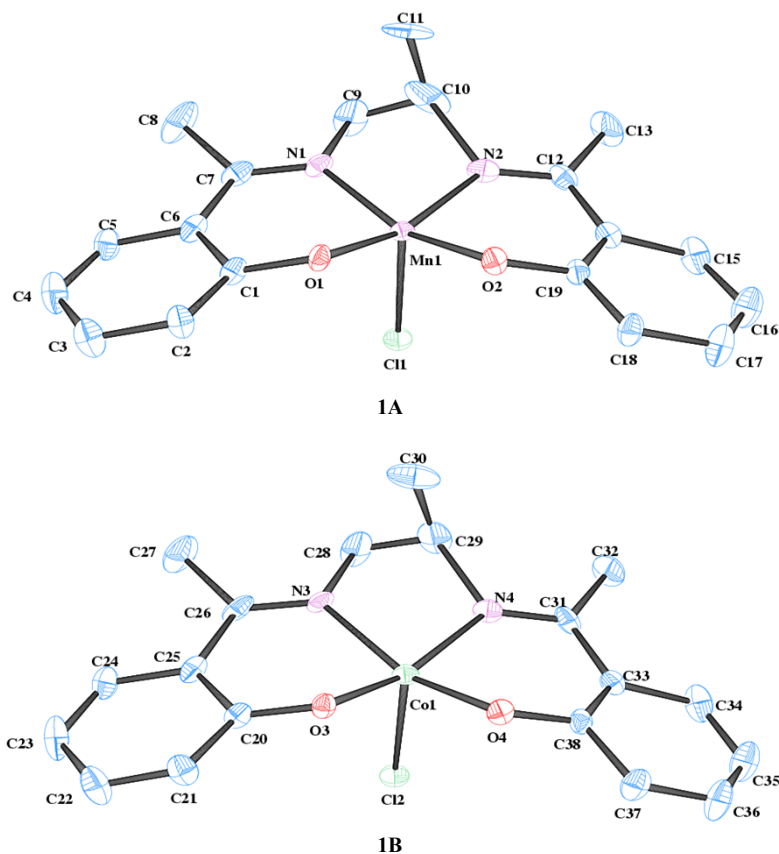


Figure 2. Structures of Mn-moiety (1A) and Co-moiety (1B) in cocrystal **1**

Table 2. Selected bond lengths [Å] and bond angles [°] for the units 1A and 1B in **1**

| 1A | | 1B | |
|---------------------|----------|------------|----------|
| <i>Bond lengths</i> | | | |
| Mn1–Cl1 | 2.387(2) | Co1–Cl2 | 2.391(2) |
| Mn1–N1 | 1.975(6) | Co1–N3 | 1.991(6) |
| Mn1–N2 | 1.990(6) | Co1–N4 | 2.008(6) |
| Mn1–O1 | 1.843(4) | Co1–O3 | 1.854(4) |
| Mn1–O2 | 1.864(5) | Co1–O4 | 1.877(5) |
| <i>Bond angles</i> | | | |
| Cl1–Mn1–N1 | 100.9(2) | Cl2–Co1–N3 | 101.9(2) |
| Cl1–Mn1–N2 | 98.2(2) | Cl2–Co1–N4 | 98.6(2) |
| Cl1–Mn1–O1 | 101.9(1) | Cl2–Co1–O3 | 101.5(1) |
| Cl1–Mn1–O2 | 100.2(2) | Cl2–Co1–O4 | 100.1(1) |
| N1–Mn1–N2 | 83.8(3) | N3–Co1–N4 | 84.4(2) |
| N1–Mn1–O1 | 89.9(2) | N3–Co1–O3 | 89.3(2) |
| N1–Mn1–O2 | 158.4(2) | N3–Co1–O4 | 157.7(2) |
| N2–Mn1–O1 | 159.8(2) | N4–Co1–O3 | 159.8(2) |
| N2–Mn1–O2 | 89.1(2) | N4–Co1–O4 | 88.7(2) |
| O1–Mn1–O2 | 89.8(2) | O3–Co1–O4 | 90.1(2) |

The supramolecular structures and some relevant bond parameters of **1** are presented in Figure 3 and Table 3, respectively. Both the discrete monomeric units 1A and 1B in **1** are connected by supramolecular hydrogen bonding interactions to form 1D supramolecular chain along the crystallographic *a*-axis (Figures 3a and 3b, respectively). These supramolecular chains are further connected by C–H...Cl hydrogen bonding interactions to form 3D supramolecular network (Figure 3c) in the solid state.

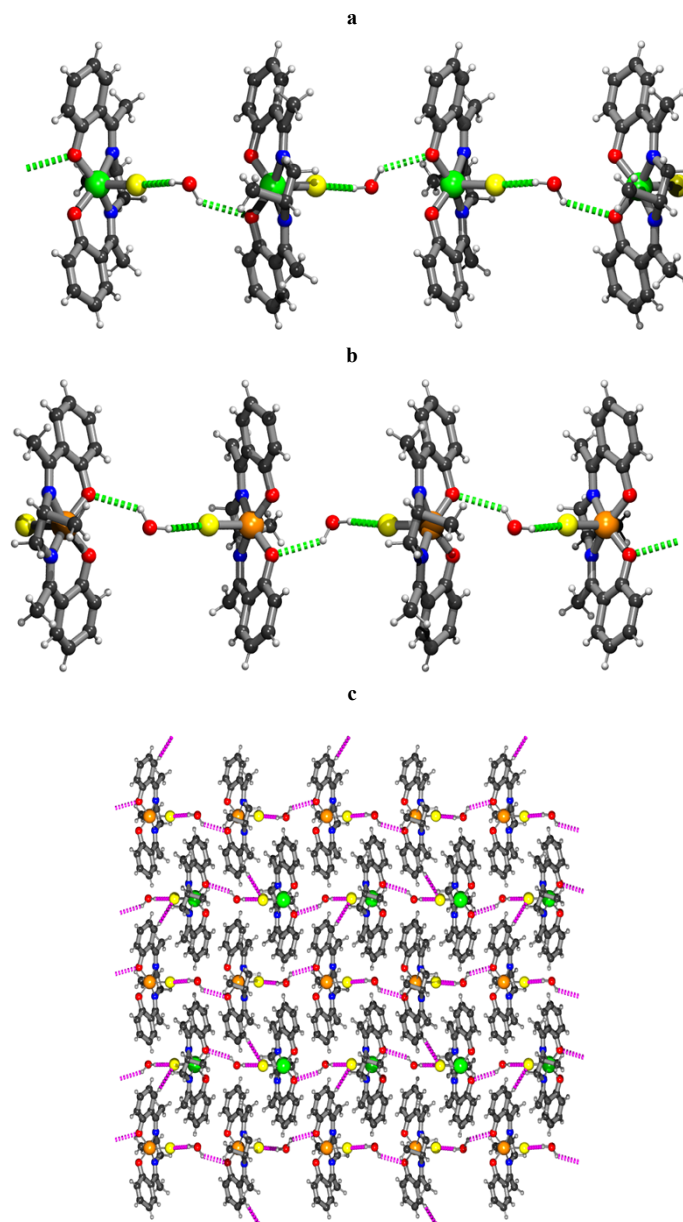


Figure 3. Formation of supramolecular structures through H-bonding interactions in 1: (a) 1D chain in 1A (b) 1D chain in 1B and (c) 3D network

Table 3. Hydrogen bond dimensions in 1

| Donor (D) | Hydrogen (H) | Acceptor (A) | $\angle(\text{DHA})$ ($^\circ$) | D(D-H) (\AA) | D(H...A) (\AA) | D(D...A) (\AA) |
|-----------|--------------|--------------|-----------------------------------|-------------------------|---------------------------|---------------------------|
| O1W | H2W1 | C11 | 168 | 1.01 | 2.27 | 3.264 |
| O1W | H1W1 | O2 | 135 | 1.00 | 2.52 | 3.310 |
| O2W | H1W2 | C12 | 168 | 0.97 | 2.33 | 3.286 |
| O2W | H2W2 | O4 | 132 | 0.96 | 2.50 | 3.221 |
| C11 | H11B | N1 | 100 | 0.96 | 2.42 | 2.754 |
| C30 | H30B | N3 | 102 | 0.96 | 2.30 | 2.663 |
| C34 | H34 | C11 | 158 | 0.93 | 2.82 | 3.703 |

Antibacterial activity of the compounds

The antibacterial activity of compound 1 as IZD is presented in Table 4. The IZD values [15, 25] of few related compounds and two antibiotics viz. Gatifloxacin and Ciprofloxacin are presented for comparison. The results of the antibacterial screening indicate that complex 1 exhibits broad spectrum antibacterial activity against all the reference bacteria. In our earlier studies [25], the tetradentate Schiff base H_2L was found to be mildly active against *B. subtilis* and *E. coli* but inactive against the other two bacteria. But, on complexation with Mn(III) or Co(III), the bactericidal properties were noticed to be appreciably higher than the ligand [15]. The results do not differ much in the cocrystallised complex 1, except that the latter shows a little higher values of IZD against few bacteria. The IZD

data also demonstrate that **1** is more susceptible to both the Gram(+) bacteria and *E. coli* than to *P. aeruginosa*. Thus, the antibacterial properties of **1** are comparable to other analogous Schiff base complexes as well as to the tested antibiotics in some cases. However, the activities are appreciably lower than those of the tested commercial antibiotics at similar doses.

Table 4. IZD values of **1 and some related compounds**

| Compounds | Inhibition zone diameter in cm (Dose in mg mL ⁻¹) | | | |
|-------------------------------|---------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| | Gram-positive bacteria | | Gram-negative bacteria | |
| | <i>S. aureus</i> | <i>B. subtilis</i> | <i>P. aeruginosa</i> | <i>E. coli</i> |
| 1 | 1.4 (0.2), 1.6 (0.4), 1.8 (0.6), 2.1 (0.8), 2.4 (1.0) | 1.3 (0.2), 1.4 (0.4), 1.6 (0.6), 2.2 (0.8), 2.5 (1.0) | 1.2 (0.2), 1.3 (0.4), 1.4 (0.6), 1.7 (0.8), 2.0 (1.0) | 1.4 (0.2), 1.6 (0.4), 1.9 (0.6), 2.1 (0.8), 2.3(1.0) |
| 1A ^a in 1 | -- (0.2), -- (0.4), -- (0.6), 1.2 (0.8), 1.2 (1.0) | -- (0.2), -- (0.4), -- (0.6), -- (0.8), 1.2 (1.0) | -- (0.2), -- (0.4), -- (0.6), 1.0 (0.8), 1.2 (1.0) | -- (0.2), -- (0.4), -- (0.6), 1.4 (0.8), 1.6 (1.0) |
| H ₂ L ^a | --- | 0.8 (0.2), 0.8 (0.4), 0.9 (0.6), 1.0 (0.8), 1.0 (1.0) | --- | 0.9 (0.2), 1.0 (0.4), 1.0 (0.6), 1.1 (0.8), 1.1 (1.0) |
| Gatifloxacin ^a | 1.6 (0.2), 1.9 (0.4), 2.0 (0.6), 2.2(0.8), 2.6 (1.0) | 1.4 (0.2), 1.6 (0.4), 1.9 (0.6), 2.2 (0.8), 2.7 (1.0) | 1.4 (0.2), 1.5 (0.4), 1.8 (0.6), 2.2 (0.8), 2.5 (1.0) | 1.4 (0.2), 1.6 (0.4), 2.0 (0.6), 2.4 (0.8), 2.6 (1.0) |
| Ciprofloxacin ^a | 1.1 (0.2), 1.5 (0.4), 1.8 (0.6), 2.1 (0.8), 2.4 (1.0) | 1.2 (0.2), 1.4 (0.4), 1.8 (0.6), 2.2 (0.8), 2.3 (1.0) | 1.1 (0.2), 1.4 (0.4), 1.7 (0.6), 2.0 (0.8), 2.1 (1.0) | 1.0 (0.2), 1.4 (0.4), 1.9 (0.6), 2.4 (0.8), 2.6(1.0) |
| Control (DMSO) | 0.2 – 1.0 | --- | --- | --- |

^aIZD data were reported by us in a previous communication [15].

CONCLUSION

Synthesis and characterization of a new heterometallic 1:1 cocrystallized complex of manganese(III)-cobalt(III) containing a tetradentate (NNOO) Schiff base ligand have been described in this paper. Both the constituent mononuclear complex units of Mn(III) and Co(III) present in the cocrystal are isostructural and adopt distorted tetragonal pyramidal geometries. Both the moieties are involved in weak intermolecular H-bonding interactions to form 1D supramolecular chain. These alternate 1D chains are further connected by C-H...Cl interactions to constitute 3D supramolecular structure in the solid state. Antibacterial screening of the compound indicates moderately strong bactericidal activities that increase with dose.

In addition to the synthetic know-how, this work enriches the studies on structural and biological aspects of cocrystallized materials with newer Schiff base complexes of first-row transition metals.

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