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Review

Metal Complexes with Schiff Bases as Antimicrobials and Catalysts

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Abstract: Complexes of Schiff bases (SBs) with metals are promising compounds exhibiting a broad range of applications, such as catalysts, polymers, dyes, and several biological activities, including antimicrobial, anticancer, antioxidant, antimalarial, analgesic, antiviral, antipyretic, and antidiabetic actions. Considering the crisis that the whole world is now facing against antimicrobial-resistant bacteria, in the present review, we chose to focus on the activity of SBs as antimicrobials, particularly underlying the most recent studies in this field. Finally, some interesting catalytic applications recently described for metal complexes with SBs have also been discussed.

Keywords: Schiff bases; antibacterials; imines; antimicrobials; metal complexes; antifungals

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1. Introduction

The widespread usage of SBs in chemistry, industry, medicine, and pharmacy has notably enhanced the interest in these intriguing compounds [1,2]. The functional feature of SBs is represented by the azomethine group -C=N-, where the substituents may be alkyl, aryl, or heterocyclic groups. The carbon atom of the imine bond is predisposed to nucleophilic addition, whereas the nitrogen atom holds an extremely reactive free electron pair, able to form stable complexes with metals. The catalytic activity of SBs [3], their corrosion inhibition behavior [4], as well as the action as photosensitizers [5], and fluorescent chemo-sensors tools for the detection of Cu^{2+} and Fe^{3+} metal ions [6] have been reported. Moreover, numerous biological activities were described in the literature for these compounds [7–9], such as antitumoral [10–12]; antimicrobial [13]; antimalarial [14]; antioxidant; neuroprotective; antidiabetic; antidepressant [15]; anti-inflammatory [16]; and acetylcholinesterase (AChE)-, butyrylcholinesterase (BChE)- [17–19], and carbonic anhydrase-inhibiting [20] ones. Moreover, coatings made of SBs have been shown to improve the bioactivity of materials, suggesting the use of these compounds in medicine [21]. In a biological context, the azomethine nitrogen of SBs represents a site for the binding of metal ions with numerous biomolecules, including proteins and amino acids, responsible for its biological activities. The highly stable complexes formed by SBs with transition metals often lead to compounds with strongly enhanced activities in inorganic [22,23] and bioinorganic chemistry [24], materials science [25], and pharmacology for biomedical applications [26–30]. The most described biological activities regarding the SBs complexes are antitumoral [31–35], antioxidant [36,37], antidiabetic [38–41], antimalarial [42], antiarthritic [43], antimicrobial [44–48], neuroprotective, catalase-like and catecholase-like

enzymatic [49,50], and DNA-binding [51,52]. Recently, Aggarwal et al. (2022) [53] underlined the potential applicability of some SBs and their metal complexes for the treatment of COVID-19 [54], which may represent valid alternatives to the classic treatments for this disease [55,56]. Moreover, the liposomal formulation of an SBs complex with arsenic has been described as an agent for drug delivery for the treatment of acute promyelocytic leukemia [57]. The importance of hybrid materials of SB complexes with metals and laccase, an oxygen-reducing enzyme, has also been studied [58]. Recently, stilbene-derivatized SB ligands and their Cu(II) complexes have been suggested as radio-imaging agents for the diagnosis of Alzheimer's by positron emission tomography when prepared with the positron-emitting radioisotope Cu-64 [59]. Among metals, the coordination chemistry of SBs with inner transition metals, such as lanthanide(III) ions, has promptly progressed in the last decade because of its vast range of applications, specifically in physical applications such as magnetic, luminescence, lasers, optical glasses, telecommunications, biosciences, and numerous biological activities [60,61]. Given the numerous properties of complexes of SBs with metals, we decided to focus on a single activity exerted by this class of compounds. Antimicrobial resistance (AMR) has been declared by the World Health Organization (WHO) to be one of the major global health problems, specifically one of the top ten public health threats worldwide [62,63]. Several studies address the most clinically important pathogens, called ESKAPE pathogens, represented by both Gram-positive and Gram-negative bacteria, namely, *Enterococcus faecium* and *Staphylococcus aureus* (Gram-positive bacteria) and *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, and *Enterobacter* spp. (Gram-negative bacteria) [64]. In this context, the purpose of this review was to highlight the antimicrobial activity exerted by SBs complexed with metals dwelling specifically on the most recent studies in this field. Moreover, some interesting studies regarding the catalytic activity of these compounds have been described.

2. SBs Complexes with Metals as Antimicrobials

The antimicrobial activity of some SBs complexes with transition metals is described in this paragraph. Generally, the data refer to the lowest concentration of the tested antimicrobial agent (minimal inhibitory concentration, MIC) that is able to inhibit the visible growth of the bacterium being investigated. Microbes were generally referred to as the American Type Culture Collection (ATCC), the National Collection of Industrial Microorganisms (NCIM), and the Microbial Type Culture Collection (MTCC). Some authors determined the antimicrobial activity by measuring the diameter (as mm) of the zone showing the complete inhibition (inhibition zone diameter, IZD) determined by using the agar well diffusion method. In one article by Kargar et al. (2022) [65], Percentage Mean Mycelial Inhibition (PMMI) is reported against *Aspergillus brasiliensis*.

2.1. SBs Complexes with Transition Metals

The antimicrobial activities of some SBs complexes with transition metals recently described are reported in Table 1.

Aroua et al. (2023) [66] described the synthesis and characterization of diverse complexes derived from SBs and the evaluation of their antitumoral, antimicrobial, and insecticide activities. The antibacterial activity was studied against Gram-negative *Escherichia coli* and Gram-positive *Bacillus subtilis* (standard drug: tetracycline, IZD = 35 mm and 38 mm, respectively), whereas the antifungal activity was studied against *Aspergillus niger* (standard drug: nystatin, IZD = 32 mm). Complexes Cl_2Cr (**1**) and ClMn (**2**) with Cr(III) and Mn(II), respectively, were the most active of the study as antimicrobials.

Alorini et al. (2023) [67] described the synthesis and antitumoral and antimicrobial activities of 2-((E)-(4-((E)-4-chlorobenzylidene)amino)phenyl)imino)methyl)naphthalen-1-ol as SB ligand complexed with Mn(II), Co(III), Ni(II), Cu(II), and Zn(II). The antibacterial and antifungal activities were studied against *Salmonella enterica* serovar *Typhi* and *Candida albicans*, respectively, using gentamycin (IZD = 17 mm against *S. enterica* ser. *Typhi* at 10 mg/mL) and clotrimazole (IZD = 21 mm against *C. albicans* at 10 mg/mL) as standards.

Complex $Co(L)(Cl)_2(H_2O)_2$ (**3**) with Co(III) was the most active against the microbial strains used.

Al-Janabi et al. (2023) [68] recently reported an interesting study on metal complexes (Ni(II), Pd(II), Pt(II), Zn(II), and Hg(II)) SBs derived from 4-chloro-3-methyl phenyl hydrazine as dual inhibitors of SARS-CoV-2 and antibacterials. The antibacterial activity was evaluated against *S. aureus* and *P. aeruginosa*, and compound **4** showed an interesting activity in comparison to the reference amoxicillin (IZD = 29 ± 1.0 mm and 31 ± 0.61 mm against *S. aureus* and *P. aeruginosa*, respectively). Interestingly, the compound was also an inhibitor of the main protease (Mpro) of the virus SARS-CoV-2 [69].

Devi et al. (2022) [70] reported the synthesis of sixteen complexes of four SB ligands with transition metals, namely Co(II), Ni(II), Cu(II), and Zn(II), deriving from 4-(benzyloxy)-2-hydroxybenzaldehyde and their in vitro antioxidant, antimicrobial activity, and molecular docking studies. In vitro antimicrobial activities were studied against four bacterial strains (*S. aureus*, *B. subtilis*, *P. aeruginosa*, and *E. coli*) and two fungal strains (*A. niger* and *C. albicans*). Ciproxacin (MIC = 0.0047 µmol/mL) and fluconazole (MIC = 0.0051 µmol/mL against *C. albicans* and MIC = 0.0102 µmol/mL against *A. niger*) were used as references. Complexes with Ni and Cu (**5**–**8**) were the most active against bacteria and fungi. They showed comparable activity to standard drugs against *C. albicans*. The potential mechanism of action was suggested through molecular modeling studies. Docking of complex **6** with enzyme *C. albicans* sterol 14-alpha demethylase suggested a hydrophobic binding.

Al-Shboul et al. (2022) [71] described the synthesis, characterization, computational, and biological activity of four SBs derived from 2,2′-diamino-6,6′-dibromo-4,4′-dimethyl-1,1′-biphenyl or 2,2′-diamino-4,4′-dimethyl-1,1′-biphenyl, and 3,5-dichloro- or 5-nitro-salicylaldehyde, and their complexes with Fe(II), Cu(II), and Zn(II), obtained by reaction with copper-, iron-, and zinc-acetate. The compounds were tested for their antibacterial activity against Gram-positive (*Micrococcus luteus*, *S. aureus*) and Gram-negative (*E. coli*) bacteria, using amoxicillin as a reference drug (IZD: 25, 35, and 10 mm, respectively). The complexes with Zn (Z2Zn, **9**) and Fe (Z4Fe, **11**) showed slight activity against *S. aureus*, even though lower than the reference. The complex with Zn (Z3Zn, **10**) showed the same antibacterial activity of the reference against *M. luteus*. Only complexes with copper (Z1Cu, **12** and Z3Cu, **13**) were active against Gram-negative *E. coli*, with Z3Cu (**13**) exerting higher activity than the reference.

Abdel-Rahman et al. (2022) [72] described five complexes with Co(II), Ni(II), VO(II), Cr(III), and La(III) synthesized from a tridentate NNO monobasic chelating SB ligand (Z)-2-((pyridin-2-ylimino)methyl)phenol. The complexes were tested for their antimicrobial, antioxidant, and antitumoral activities. Antimicrobial activities were studied against *S. aureus*, *K. pneumoniae*, *E. coli*, and *Streptococcus mutans*, a pathogen of dental caries [73]. All the complexes showed slight to high antimicrobial activity, with the exception of the complex with V and La against *K. pneumoniae.* The most interesting activity was observed for the NiL complex (**14**), which showed antibacterial activity similar to or higher than the references gentamicin and ampicillin. Gentamicin was used as a standard for Gram-negative bacteria (*E. coli*, IZD = 27 ± 0.5 mm; and *K. pneumoniae*, IZD = 25 ± 0.5 mm) and ampicillin for Gram-positive bacteria (*S. aureus* IZD = 22 ± 0.1 mm and *S. mutans*, IZD = 30 ± 0.5 mm). The IZD value of NiL complex (**14**) against *E. coli* was even higher than the reference gentamicin. Both complexes NiL (**14**) and LaL (**15**) showed slight activity with respect to ampicillin against *S. aureus*.

Daravath et al. (2022) [74] reported a study on three SBs complexes with copper (**16**–**18**) and their antimicrobial activities against bacteria and fungi not generally investigated, namely Gram-positive *Bacillus amyloliquefaciens* and *Sclerotium rolfsii* and *Macrophomina phaseolina* fungal strains. The study was also carried on against Gram-negative *E. coli*. Streptomycin was used as the reference against bacteria (IZD = 25 ± 0.17 mm and 25 ± 0.15 mm against *B. amyloliquefaciens* and *E. coli*, respectively), whereas mancozeb was used as the reference against fungi (IZD = 24 ± 0.14 mm and 25 ± 0.15 mm, respectively).

Kargar et al. (2022) [65] described the synthesis of two complexes formed between mono and dinuclear SBs and Zn(II) (Z1, **19** and Z2, **20**, respectively) and their biological activities as antimicrobial agents against two Gram-positive (*S. aureus* and *B. cereus*) and two Gram-negative (*E. coli* and *P. aeruginosa*) bacterial strains. The two compounds showed slight activity against Gram-positive bacteria compared with standard chloramphenicol (IZD = 30 mm) and Gram-negative *E. coli* (chloramphenicol, IZD = 33 mm), whereas they demonstrated interesting activity against the Gram-negative bacterium *P. aeruginosa*, being more active than the reference (chloramphenicol, IZD = 11 mm). The complexes showed significant antifungal activity against *C. albicans* (clotrimazole, IZD = 25 mm), while they were inactive against *A. brasiliensis*.

Hajari et al. (2022) [75] described the synthesis and biological activity of several 15-membered ring symmetrical pentaaza macrocyclic SBs complexed with Zn(II), Mn(II), and Cd(II), namely [ZnLBr]ClO_4, [MnLBr]ClO_4 and [CdLBr]ClO_4 (**21**–**23**) and their cytotoxicity, antibacterial, and antioxidant activities. The antibacterial activity was studied against Gram-positive (*S. aureus*, *B. subtilis*, and *Listeria monocytogenes*) and Gram-negative (*E. coli*, *Klebsiella oxytoca*, and *Salmonella typhimurium*), and the complexes showed moderate effectiveness against all the tested bacteria. The references used were penicillin, ampicillin, vancomycin, and tetracycline. The most active were vancomycin (IZD = 14, 18, 24 mm against *S. aureus*, *B. subtilis*, and *L. monocytogenes*, respectively, and IZD = 22, 20, and 18 mm against *E. coli*, *K. oxytoca*, and *S. typhimurium*, respectively) and tetracycline (IZD = 27, 23, 27 mm against *S. aureus*, *B. subtilis*, and *L. monocytogenes*, respectively, and IZD = 29, 29, and 24 mm against *E. coli*, *K. oxytoca*, and *S. typhimurium*, respectively). *S. aureus* was the most resistant bacterium, whereas, interestingly, high activity was found for all three complexes against Gram-negative *E. coli*.

Jyothi et al. (2022) [76] described the study of Co(II) complexes with *N*-methyl thio semicarbazide SBs for their cytotoxicity, DNA binding, and antimicrobial studies. The most interesting results were found for complex II (**24**) against Gram-positive *B. subtilis* and fungus *Fusarium Oxysporium Lycopersicum*, even though with lower activity than references in both cases (penicillin, IZD between 15 and 16 mm against *B. subtilis* and ketoconazole, IZD between 15 and 16 mm against *F.O. Lycopersicum*).

Li et al. (2022) [77] described the design, synthesis, and biological evaluation of dinuclear Bi(III) complexes with isoniazid-derived SBs. *The antibacterial activity was tested against Gram-positive S. aureus* and *B. subtilis* (references vancomycin: MIC = 2 and 0.5 μg/mL; kanamycin, MIC = 2.5 and 1.125 μg/mL; tetracycline, MIC = 0.125 and 0.125 μg/mL against *S. aureus* and *B. subtilis*, respectively) and Gram-negative *E. coli* and *P. aeruginosa* (references kanamycin, MIC = 8 and >128 μg/mL; tetracycline, MIC = 4 and 32 μg/mL against *E. coli* and *P. aeruginosa*, respectively). Complexes 4a and 5a (**25** and **26**) were the most interesting of the series.

Saroya et al. (2022) [78] described a study on organotin(IV) complexes derived from tridentate SBs and their antimicrobial and antioxidant activities. The antibacterial activity was studied against Gram-positive *B. subtilis* (MTCC 441) and *S. aureus* (MTCC 2901) and two Gram-negative *E. coli* (MTCC 732) and *P. aeruginosa* (MTCC 424) (ciprofloxacin, MIC = 0.00471 μmol/mL against all bacteria). The antifungal potency was examined against two fungal strains: *C. albicans* (MTCC 227) and *A. niger* (MTCC 9933) (fluconazole, MIC = 0.01020 μmol/mL against both fungi strains). Compound **27** was the most active, casually showing the same MIC value of 0.01080 μmol/mL against bacteria and fungi.

Table 1. SBs metal complexes with transition metals with antibacterial activities.

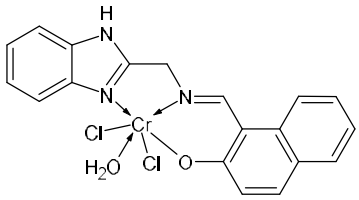
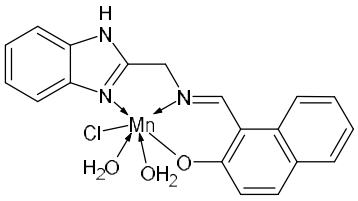
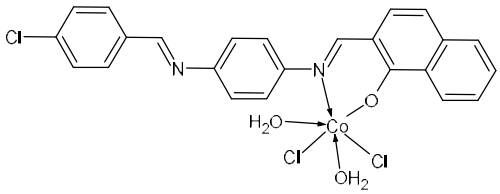
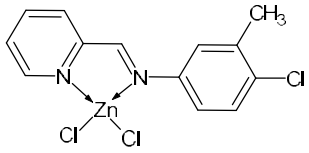
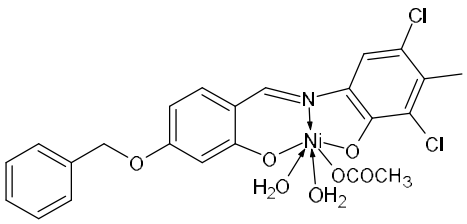
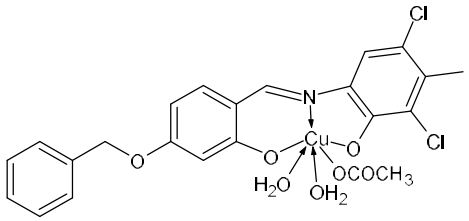
Structure	Compd	MIC or IZD	Ref.
	$C_{19}H_{16}O_2N_3Cl_2Cr$ (**1**)	IZD = 23 mm (*E. coli*) IZD = 24 mm (*S. subtilis*) IZD = 22 mm (*A. niger*)	Aroua et al. (2023) [66]
	$C_{19}H_{18}O_3N_3ClMn$ (**2**)	IZD = 26 mm (*E. coli*) IZD = 24 mm (*S. subtilis*) IZD = 25 mm (*A. niger*)	Aroua et al. (2023) [66]
	$(Co(L)(Cl)_2(H_2O)_2$ (**3**)	IZD = 15 mm (*S. enterica ser. thypi* at 30 mg/mL) IZD = 19 mm (*C. albicans* at 30 mg/mL)	Alorini et al. (2023) [67]
	**4**	MIC = 25 ± 1.10 mm (*S. aureus*) MIC = 28 ± 1.10 mm (*P. aeruginosa*)	Al-Janabi et al. (2023) [68]
	**5**	MIC = 0.0225 µmol/mL (*S. aureus* MTCC 2901) MIC = 0.0112 µmol/mL (*B. subtilis* NCIM 2063) MIC = 0.0225 µmol/mL (*E. coli* MTCC 732) MIC = 0.0112 µmol/mL (*P. aeruginosa* MTCC 424) MIC = 0.0056 µmol/mL (*C. albicans* MTCC 227) MIC = 0.0112 µmol/mL (*A. niger* MTCC 9933)	Devi et al. (2022) [70]
	**6**	MIC = 0.0223 µmol/mL (*S. aureus* MTCC 2901) MIC = 0.0223 µmol/mL (*B. subtilis* NCIM 2063) MIC = 0.0223 µmol/mL (*E. coli* MTCC 732) MIC = 0.0111 µmol/mL (*P. aeruginosa* MTCC 424) MIC = 0.0055 µmol/mL (*C. albicans* MTCC 227) MIC = 0.0111 µmol/mL (*A. niger* MTCC 9933)	Devi et al. (2022) [70]

Table 1. *Cont.*

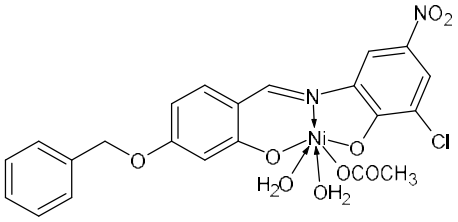
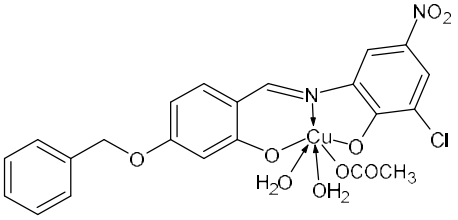
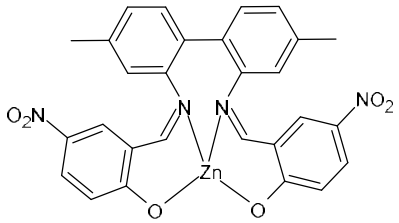
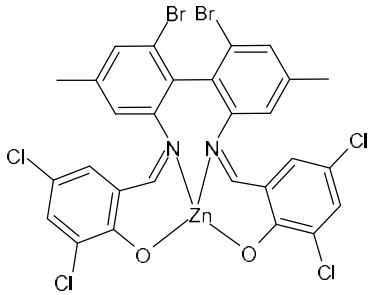
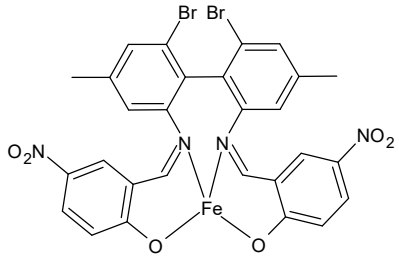
Structure	Compd	MIC or IZD	Ref.
	**7**	MIC = 0.0114 µmol/mL (*S. aureus* MTCC 2901) MIC = 0.0114 µmol/mL (*B. subtilis* NCIM 2063) MIC = 0.0228 µmol/mL (*E. coli* MTCC 732) MIC = 0.0228 µmol/mL (*P. aeruginosa* MTCC 424) MIC = 0.0056 µmol/mL (*C. albicans* MTCC 227) MIC = 0.0114 µmol/mL (*A. niger* MTCC 9933)	Devi et al. (2022) [70]
	**8**	MIC = 0.0113 µmol/mL (*S. aureus* MTCC 2901) MIC = 0.0226 µmol/mL (*B. subtilis* NCIM 2063) MIC = 0.0226 µmol/mL (*E. coli* MTCC 732) MIC = 0.0226 µmol/mL (*P. aeruginosa* MTCC 424) MIC = 0.0055 µmol/mL (*C. albicans* MTCC 227) MIC = 0.0113 µmol/mL (*A. niger* MTCC 9933)	Devi et al. (2022) [70]
	Z2Zn (**9**)	IZD = 15 mm (*M. luteus* ATCC 934) IZD = 21 mm (*S. aureus* ATCC 29213)	Al-Shboul et al. (2022) [71]
	Z3Zn (**10**)	IZD = 25 mm (*M. luteus* ATCC 934) IZD = 18 mm (*S. aureus* ATCC 29213)	Al-Shboul et al. (2022) [71]
	Z4Fe (**11**)	IZD = 20 mm (*S. aureus* ATCC 29213)	Al-Shboul et al. (2022) [71]

Table 1. *Cont.*

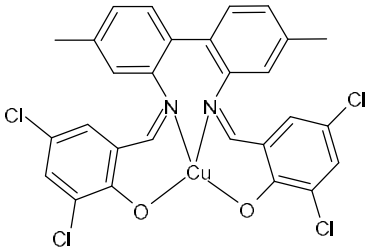
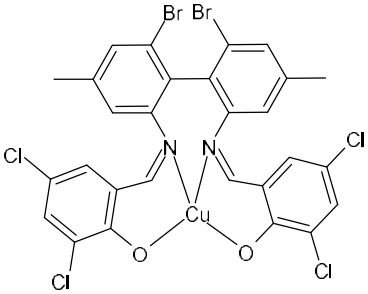
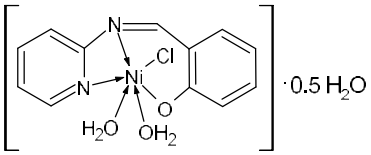
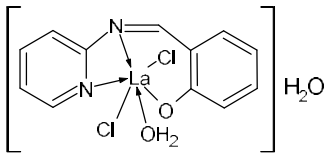
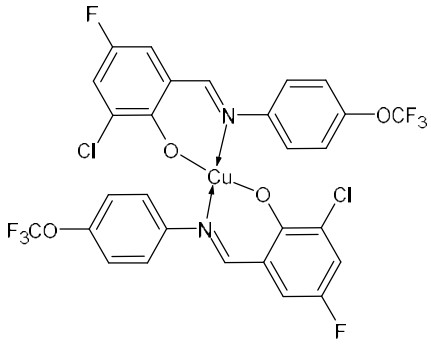
Structure	Compd	MIC or IZD	Ref.
	Z1Cu (**12**)	IZD = 10 mm (*E. coli* ATCC 25922)	Al-Shboul et al. (2022) [71]
	Z3Cu (**13**)	IZD = 20 mm (*E. coli* ATCC 25922)	Al-Shboul et al. (2022) [71]
	NiL (**14**)	IZD = 31.6 ± 0.6 mm (*E. coli* ATCC 10536) IZD = 20.6 ± 0.6 mm (*K. pneumoniae* ATCC 10031) IZD = 20.3 ± 0.6 mm (*S. aureus* ATCC 13565) IZD = 19.6 ± 0.6 mm (*S. mutans* ATCC 25175)	Abdel-Rahman et al. (2022) [72]
	LaL (**15**)	IZD = 21.3 ± 0.6 mm (*E. coli* ATCC 10536) IZD = not active (*K. pneumoniae* ATCC 10031) IZD = 20.3 ± 0.6 mm (*S. aureus* ATCC 13565) IZD = 17.9 ± 0.5 mm (*S. mutans* ATCC 25175)	Abdel-Rahman et al. (2022) [72]
	**16**	IZD = 20 ± 0.21 mm (*B. amyloliquefaciens*) IZD = 19 ± 0.16 mm (*E. coli*) IZD = 18 ± 0.18 mm (*S. rolfsii*) IZD = 18 ± 0.15 mm (*M. phaseolina*)	Daravath et al. (2022) [74]

Table 1. *Cont.*

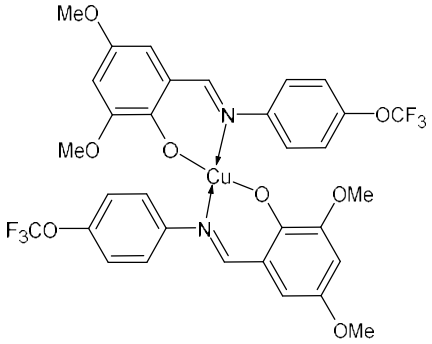
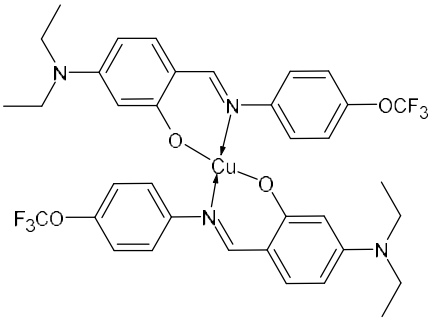
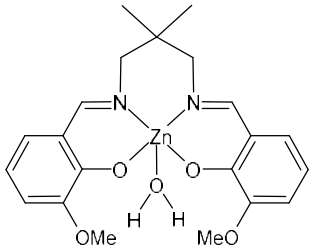
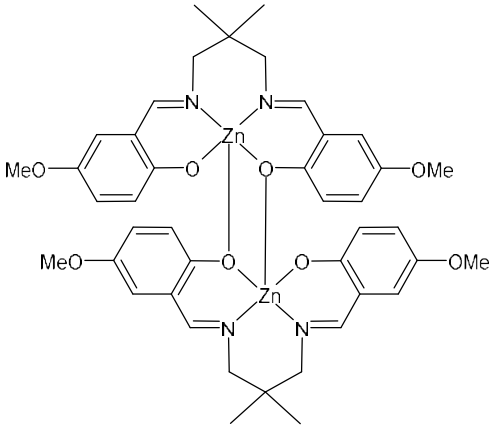
Structure	Compd	MIC or IZD	Ref.
	**17**	IZD = 17 ± 0.14 mm (*B. amyloliquefaciens*) IZD = 16 ± 0.21 mm (*E. coli*) IZD = 15 ± 0.24 mm (*S. rolfsii*) IZD = 16 ± 0.16 mm (*M. phaseolina*)	Daravath et al. (2022) [74]
	**18**	IZD = 16 ± 0.18 mm (*B. amyloliquefaciens*) IZD = 16 ± 0.15 mm (*E. coli*) IZD = 14 ± 0.15 mm (*S. rolfsii*) IZD = 15 ± 0.19 mm (*M. phaseolina*)	Daravath et al. (2022) [74]
	Z1 (**19**)	IZD = 16 mm (*S. aureus* ATCC 25923) IZD = 15 mm (*B. cereus* ATCC 11778) IZD = 11 mm (*E coli* ATCC 25922) IZD = 12 mm (*P. aeruginosa* ATCC 15442) PMMI = 22.8 mm (*A. brasiliensis* ATCC 16404) IZD = 22 mm (*C. albicans* ATCC 10231)	Kargar et al. (2022) [65]
	Z2 (**20**)	IZD = 18 mm (*S. aureus* ATCC 25923) IZD = 14 mm (*B. cereus* ATCC 11778) IZD = 13 mm (*E coli* ATCC 25922) IZD = 12 mm (*P. aeruginosa* ATCC 15442) PMMI = 22.8 mm (*A. brasiliensis* ATCC 16404) IZD = 23 mm (*C. albicans* ATCC 10231)	Kargar et al. (2022) [65]

Table 1. *Cont.*

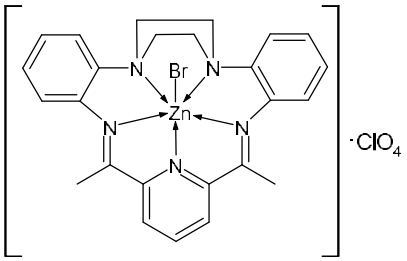
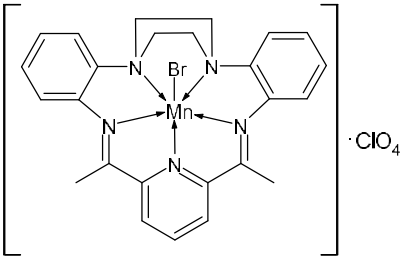
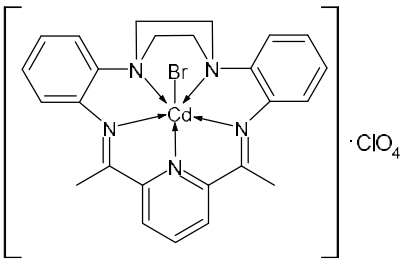
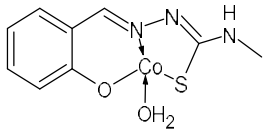
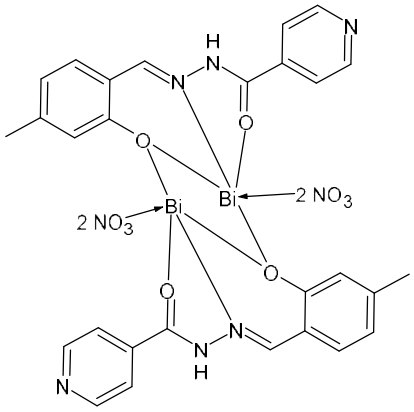
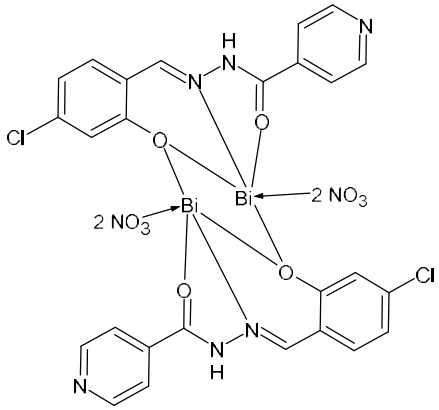
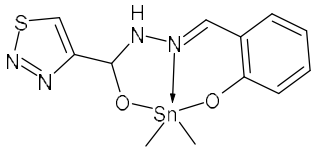
Structure	Compd	MIC or IZD	Ref.
	[ZnLBr]ClO_4 (**21**)	IZD = 14 mm (*S. aureus*) IZD = 15 mm (*B. subtilis*) IZD = 19 mm (*L. monocytogenes*) IZD = 34 mm (*E. coli*) IZD = 28 mm (*K. oxytoca*) IZD = 21 (*S. thypimurium*)	Hajari et al. (2022) [75]
	[MnLBr]ClO_4 (**22**)	IZD = 12 mm (*S. aureus*) IZD = 22 mm (*B. subtilis*) IZD = 17 mm (*L. monocytogenes*) IZD = 29 mm (*E. coli*) IZD = 22 mm (*K. oxytoca*) IZD = 19 (*S. thypimurium*)	Hajari et al. (2022) [75]
	[CdLBr]ClO_4 (**23**)	IZD = 17 mm (*S. aureus*) IZD = 17 mm (*B. subtilis*) IZD = 16 mm (*L. monocytogenes*) IZD = 24 mm (*E. coli*) IZD = 18 mm (*K. oxytoca*) IZD = 21 (*S. thypimurium*)	Hajari et al. (2022) [75]
	II (**24**)	IZD between 11 and 12 mm (*B. subtilis*) IZD between11 and 12 mm *(F.O. Lycopersicum)*	Jyothi et al. (2022) [76]
	4a (**25**)	MIC = 4 µg/mL (*S. aureus*) MIC = 8 µg/mL (*B. subtilis*) MIC = 8 µg/mL (*E. coli*) MIC = 8 µg/mL (*P. aeruginosa*)	Li et al. (2022) [77]

Table 1. *Cont.*

Structure	Compd	MIC or IZD	Ref.
	5a (**26**)	MIC = 4 µg/mL (*S. aureus*) MIC = 4 µg/mL (*B. subtilis*) MIC = 4 µg/mL (*E. coli*) MIC = 8 µg/mL (*P. aeruginosa*)	Li et al. (2022) [77]
	**27**	MIC = 0.01080 µmol/mL (*B. subtilis* MTCC 441) MIC = 0.01080 µmol/mL (*E. coli* MTCC 732) MIC = 0.01080 µmol/mL (*P. aeruginosa* MTCC 424) MIC = 0.01080 µmol/mL (*C. albicans* MTCC 227) MIC = 0.01080 µmol/mL (*A. niger* MTCC 9933)	Saroya et al. (2022) [78]

2.2. SBs Complexes with Inner Transition Metals (Lanthanides and Actinides) as Antimicrobials

Complexes with inner transition metals, such as lanthanides and actinides, have often shown interesting results. Complex LaL (**15**) by Abdel-Rahman et al. (2022) [72] has been described in the previous paragraph. Other antimicrobial activities of lanthanide complexes with SBs are summarized below (Table 2).

Andiappan et al. (2023) [79] reported the study of several metal complexes of SBs with rare earth (Er, Pr, and Yb) inorganic metals, Schiff-Er (**28**), Schiff-Yb (**29**), and Schiff-Pr (**30**), as antibacterial and antitumoral agents. Complex Schiff-Pr (**29**) with praseodymium showed antibacterial activity against *P. aeruginosa* and *S. aureus*. The complex showed IZD = 24 mm against both bacteria, which was comparable to that of streptomycin used as the standard drug (IZD = 25 mm) against *P. aeruginosa* and higher than that of the standard (IZD = 20 mm) against *S. aureus*. Complexes. Complex Schiff-Er (**28**) and Schiff-Yb (**29**) showed antibacterial activity, even though it was lower than Schiff-Pr (**30**).

Alqasaimeh et al. (2023) [80] described three neutral lanthanides SB coordination complexes with lanthanides (Nd, Tb, and Dy) with (2-((*p*-tolylimino)methyl)phenol) SB. The antimicrobial activity was evaluated in vitro against Gram-positive bacteria *S. aureus*, Gram-negative (*E. coli*) using gentamicin and amikacin as standards against *S. aureus* and against the fungus *C. albicans* using nystatin as the standard. La, Lb, and Lc (**31**, **32**, and **33**) showed activity against bacteria and fungi. It is interesting to note that the free ligand was inactive against bacteria. Particularly, Lc (**33**) was the most active against *C. albicans*.

Table 2. SBs complexes with inner transition metals (lanthanides and actinides) with antimicrobial activity.

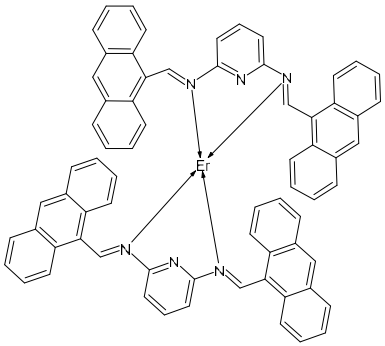
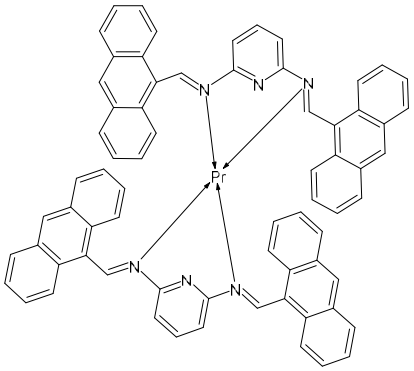
Structure	Compd	MIC or IZD	Ref.
	Schiff-Er (**28**)	IZD = 21 mm (*P. aeruginosa*) IZD = 23 mm (*S. aureus*)	Andiappan et al. (2023) [79]
	Schiff-Pr (**29**)	IZD = 24 mm (*P. aeruginosa*) IZD = 24 mm (*S. aureus*)	Andiappan et al. (2023) [79]

Table 2. *Cont.*

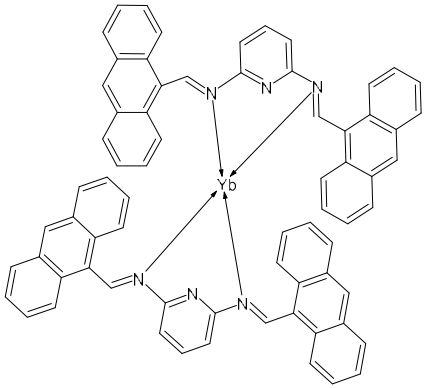
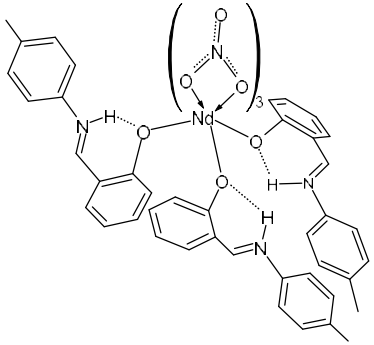
Structure	Compd	MIC or IZD	Ref.
	Schiff-Yb (**30**)	IZD = 22 mm (*P. aeruginosa*) IZD = 20 mm (*S. aureus*)	Andiappan et al. (2023) [79]
	La (**31**)	MIC = 0.75 mg/mL (*S. aureus* ATCC 29213) MIC = 3 mg/mL (*S. aureus* ATCC 33591) MIC = 3 mg/mL (*E. coli* ATCC 25922) MIC = 1.5 mg/mL (*P. aeruginosa* ATCC 27853) MIC = 1.5 mg/mL (*C. albicans* ATCC 10231)	Alqasaimeh et al. (2023) [80]

Table 2. *Cont.*

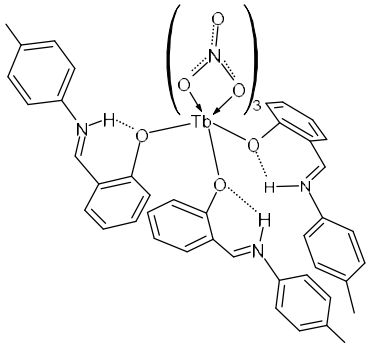
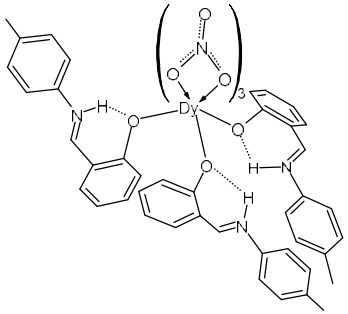
Structure	Compd	MIC or IZD	Ref.
	Lb (**32**)	MIC = 0.75 mg/mL (*S. aureus* ATCC 29213) MIC = 3 mg/mL (*S. aureus* ATCC 33591) MIC = 3 mg/mL (*E. coli* ATCC 25922) MIC = 1.5 mg/mL (*P. aeruginosa* ATCC 27853) MIC = 1.5 mg/mL (*C. albicans* ATCC 10231)	Alqasaimeh et al. (2023) [80]
	Lc (**33**)	MIC = 0.75 mg/mL (*S. aureus* ATCC 29213) MIC = 3 mg/mL (*S. aureus* ATCC 33591) MIC = 3 mg/mL (*E. coli* ATCC 25922) MIC = 1.5 mg/mL (*P. aeruginosa* ATCC 27853) MIC = 0.75 mg/mL (*C. albicans* ATCC 10231)	Alqasaimeh et al. (2023) [80]

Table 2. *Cont.*

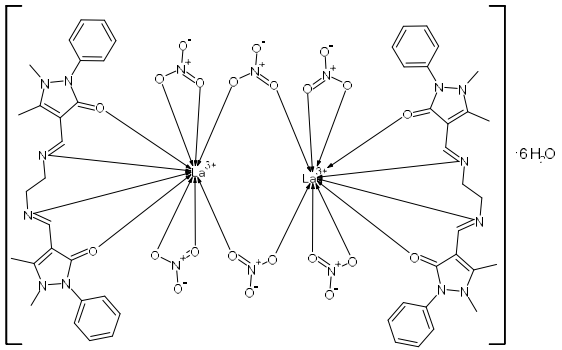
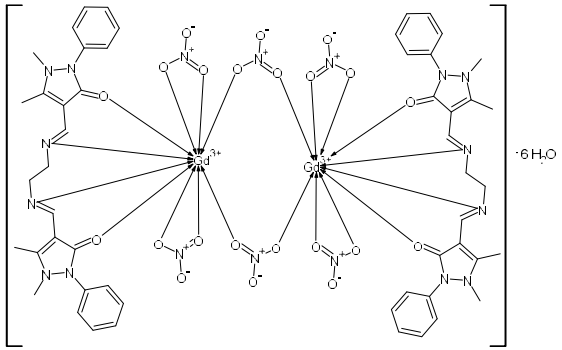
Structure	Compd	MIC or IZD	Ref.
	$[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**34**)	IZD = 32–35 mm (*S. aureus*) IZD = 24–28 mm (*S. subtilis*) IZD = 18–20 mm (*E. coli*) IZD = 18–20 mm (*K. pneumoniae*)	Hussein et al. (2023) [81]
	$[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**35**)	IZD = 21–35 mm (*S. aureus*) IZD = 24–28 mm (*S. subtilis*) IZD = 21–24 mm (*E. coli*) IZD = 21–24 mm (*K. pneumoniae*)	Hussein et al. (2023) [81]

Table 2. *Cont.*

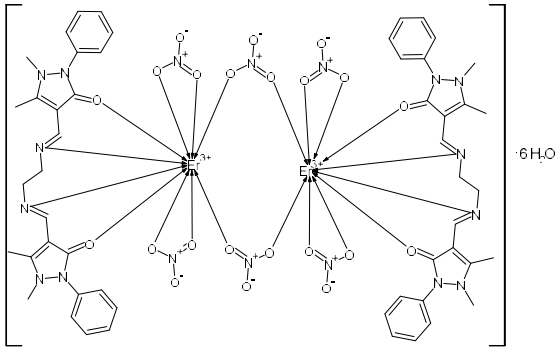
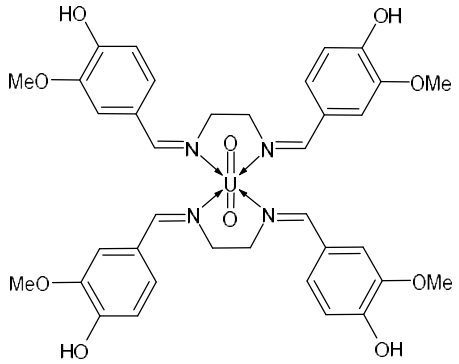
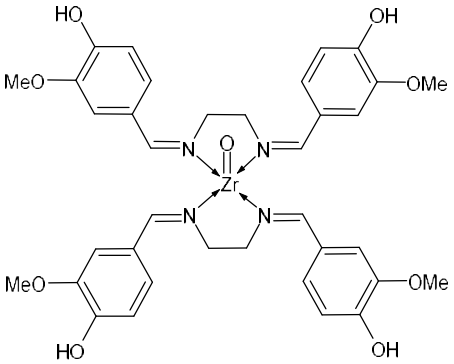
Structure	Compd	MIC or IZD	Ref.
	$[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**36**)	IZD = 28–32 mm (*S. aureus*) IZD = 28–32 mm (*S. subtilis*) IZD = 18–20 mm (*E. coli*) IZD = 24–28 mm (*K. pneumoniae*)	Hussein et al. (2023) [81]
	UrO_2SV (**37**)	IZD = 18 mm (*S. aureus*) IZD = 15 mm (*E. faecalis*) IZD = 20 mm (*K. pneumoniae*) IZD = 15 mm (*P. aeruginosa*)	Awolope et al. (2023) [82]

Table 2. *Cont.*

Structure	Compd	MIC or IZD	Ref.
	ZrOSV (**38**)	IZD = 15 mm (*S. aureus*) IZD = 17 mm (*E. faecalis*) IZD = 17 mm (*K. pneumoniae*) IZD = 16 mm (*P. aeruginosa*)	Awolope et al. (2023) [82]

Hussein et al. (2023) [81] described the synthesis and biological studies of complexes of lanthanides (lanthanum, neodymium, erbium, gadolinium, and dysprosium) with SBs deriving from antipyrine. Antibacterial studies were carried out at concentrations 10^{-3} M against *S. aureus*, *B. subtilis*, *E. coli*, and *K. pneumoniae*. The highest activity against *S. aureus* was found for $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**34**) and $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**35**), whereas $[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6]\cdot 6H_2O$ (**36**) showed activity, lower than the other two, against both *S. aureus* and *B. subtilis*.

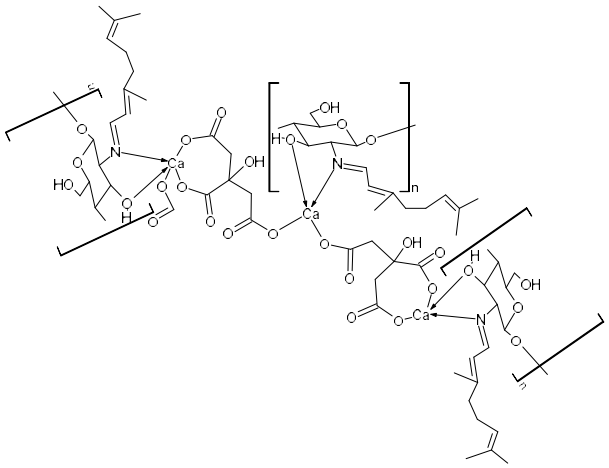
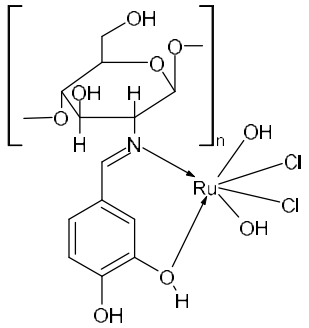
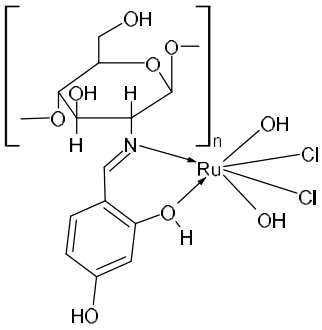
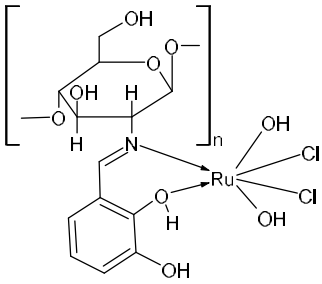
Awolope et al. (2023) [82] reported the synthesis and antibacterial and antioxidant activity of some SBs with transition metals and actinides. The antibacterial activity was evaluated against Gram-positive *S. aureus* and *E. faecalis* and Gram-negative *K. pneumoniae* and *P. aeruginosa*. The most interesting compounds of the study as antibacterials were UrO_2SV and ZrOSV (**37** and **38**). Specifically, UrO_2SV (**37**) showed higher activity against *S. aureus* and *K. pneumoniae* (nystatin was used as standard, IZD = 27 and 23 mm, respectively), whereas compound ZrOSV (**38**) showed slight activity against *E. faecalis* and *P. aeruginosa* (nystatin, IZD = 25 and 22 mm, respectively).

3. Chitosan SBs Complexes as Antimicrobials

Chitosan SBs have shown interesting biological activities [83] as being anticancer [84,85], antioxidant [86–88], antibacterial [89–92], and antidiabetic [93]. Some chitosan-based SBs are used for the removal of toxic metal ions from the aqueous medium, including Fe(III) [94], Pb(II) [95], Cu(II), Cd(II) [96], Cr(III) [97], and Cr(VI) [98,99]. Some authors also describe chitosan SBs complexes with metals and their biological activities as antitumoral and antimicrobial. Specifically, an interesting study describes the synthesis of biopolymeric chitosan-supported SB complexes with Cu(II), Ni(II), and Zn(II) and their biological evaluation as antitumoral agents against MG-63 osteosarcoma cancer cell lines. The complexes were more active than pure chitosan against the cancer MG63 cell line [100]. Recently, some chitosan SBs-based polyelectrolyte complexes with graphene quantum dots have been described, along with their prospective biomedical applications as antibacterials. One compound, namely PE-G-3 (structure not shown), showed interesting activity against *Helicobacter pylori* measured by the in vitro inosine 5′-monophosphate dehydrogenase (IMPDH) inhibitory assay, as long as its activity to enhance wound healing [101]. A recent study by Ignatova et al. (2022) [102] described the synthesis of an SB derivative (Ch-8Q) of chitosan and 8-hydroxyquinoline-2-carboxaldehyde and novel fibrous materials successfully obtained from Ch-8Q and polylactide (PLA) by one-pot electrospinning of their blend solution and the complexes of the mats with Cu(II) and Fe(III). The incorporation of Ch-8Q in the fibrous mats and complexation with Cu(II) and Fe(III) led to the ability to kill all *S. aureus* bacteria within 3 h of contact. Moreover, in contrast to the chitosan-containing mats, which only reduce the adhesion of pathogenic bacteria *S. aureus*, Ch-8Q-containing materials and their complexes inhibit bacterial adhesion.

Tao et al. (2023) [103] have recently reported an interesting study on SB deriving CS-CT-CCa complex (**39**) with natural citral (CT), chitosan (CS), and calcium citrate (CCa) and its activity against *Vibrio parahaemolyticus*, which is defined the "number one killer" of seafood products (Table 3). The complex, which had good dispersion properties and an excellent sustained released ability, was active against *V. parahaemolyticus* and increased the membrane permeability of *V. parahaemolyticus*, also determining the inhibition of biofilm-forming ability in a dose-dependent manner. CT mainly comes from the essential oil of lemon grass and has vigorous antibacterial activity: it was used for comparison against *V. parahaemolyticus* (MIC = 1024 μg/mL) along with CS-CT (MIC = 256 μg/mL) and ciprofloxacin (MIC = 4 μg/mL).

Table 3. Chitosan SBs complexes with metals with antimicrobial activity.

Structure	Compd	MIC or IZD	Ref.
	CS-CT-CCa (**39**)	MIC = 128 µg/mL (*V. parahaemolyticus* ATCC 17802)	Tao et al. (2023) [103]
	$Ru(CVSB)(H_2O)_2]Cl_2$ (**40**)	IZD = 11 mm (*A. flavus*) IZD = 12 mm (A. niger) IZD = 11 mm (P. chryogenum) IZD = 10 mm (*F. oxysporum*) IZD = 12 mm (*T. viride*)	Amirthaganesan et al. (2022) [104]
	$Ru(CSSB)(H_2O)_2]Cl_2$ (**41**)	IZD = 14 mm (*A. flavus*) IZD = 12 mm (A. niger) IZD = 10 mm (P. chryogenum) IZD = 11 mm (*F. oxysporum*) IZD = 10 mm (*T. viride*)	Amirthaganesan et al. (2022) [104]
	$Ru(COSB)(H_2O)_2]Cl_2$ (**42**)	IZD = 12 mm (*A. flavus*) IZD = 12 mm (*A. niger*) IZD = 11 mm (P. chryogenum) IZD = 10 mm (*F. oxysporum*) IZD = 12 mm (*T. viride*)	Amirthaganesan et al. (2022) [104]

Amirthaganesan et al. (2022) [104] reported a study on ruthenium(III) complexes derived from chitosan SBs ($Ru(CVSB)(H_2O)_2]Cl_2$ (**40**), $Ru(CSSB)(H_2O)_2]Cl_2$ (**41**) and $Ru(COSB)(H_2O)_2]Cl_2$ (**42**), and their antifungal activity evaluation against *Aspergillus flavus*, *A. niger*, *Penicillim chryogenum*, *Fusarium oxysporum*, and *Trichoderma viride*, by disc diffusion method.

Amphotericin-B was used as the standard drug (IZD = 22, 26, 20, 22, and 26 mm, respectively). Ruthenium(III) complexes showed higher antifungal activity than their parent ligands.

4. Metal Complexes with SBs with Catalytic Activity

Metal complexes with SBs are often studied and used for their catalytic activities. Table 4 summarizes the compounds endowed with this activity most recently reported. Bikas et al. (2023) [105] described the synthesized and characterization of two dinuclear Zn(II) complexes with SBs, namely $Zn_2(L^1)_2(N_3)_2$ (**43**) and $Zn_2(L^2)_2(N_3)_2$ (**44**), derived from 4-aminoantipyrine. The complexes were demonstrated to be active catalysts in the reaction of benzonitrile and sodium azide for the synthesis of tetrazoles. The model compound for tetrazoles used was 5-phenyl-1*H*-tetrazole. Neshat et al. (2023) [106] reported the synthesis and characterization of a Cu(II) complex CuL_2 (**45**) with a bidentate SB derived from *Ortho*-vanillin. The catalytic activity was studied in the oxidation of selected primary and secondary alcohols. The complex showed higher performance in the oxidations of secondary alcohols under mild reaction conditions. The catalytic activity in the oxidation of secondary aromatic alcohols was shown to be higher with substrates containing electron-withdrawing substituents, whereas it was low in the oxidation of aliphatic primary alcohols. The authors suggested a radical mechanism for the catalytic activity. Rabiei et al. [107] recently described a functionalized metal–organic-framework nanocatalyst, which is an SB complex with Cu and Pd [Cu(BDC-NH_2)@Schiff base Pd(II) (**46**)], for C–N coupling. It was obtained via a two-step post-synthetic modification reaction of Cu(BDC-NH_2) with *N*,*N*′-bis(5-formylpyrrol-2-ylmethyl) homopiperazine followed by Pd ion immobilization. Optimization of the C–N coupling reaction of *p*-tolylboronic acid with 1-(2-oxo-2-phenylethyl)-1H-pyrrole-2-carbonitrile in the presence of this catalyst was studied. The catalyst showed several advantages, being robust and stable under the reaction conditions, easily separated from the mixture, capable of being reused up to seven times, and producing products with high yields. Jabbari et al. [108] described the preparation of a V(O)-SB complex on MCM-41 (Mobil Composition of Matter No. 41) as a stable, efficient, reusable, and chemoselective nanocatalyst for the oxidative coupling of thiols and oxidation of sulfides. The complex, named V(O)-5NSA-MCM-41 (**47**), can be used for the synthesis of disulfide and sulfoxide derivatives using hydrogen peroxide (H_2O_2) as a biocompatibility, inexpensive, and available oxidant. Products were obtained with good yields. Recently, the development of magnetic Fe_3O_4-chitosan immobilized Cu(II) SB catalyst [Fe_3O_4@CS@Schiffbase@Cu (**48**)] has been reported [109]. This heterogeneous catalyst has been demonstrated to be an efficient and reusable catalyst for microwave-assisted one-pot synthesis of propargylamines via the A^3 coupling reaction of aldehydes, alkynes, and amines. The catalyst was efficiently recyclable and reusable even after six cycles and proved its superiority over homogenous catalysts by producing 95% of the desired product.

Table 4. SBs complexes with transition metals with catalytic activity.

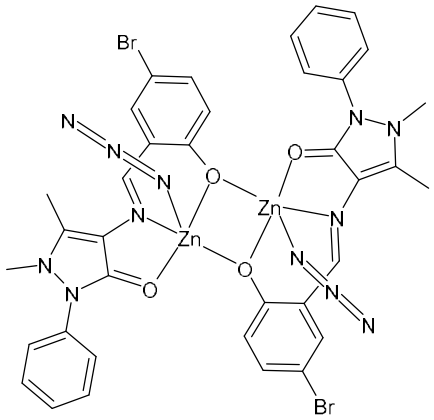
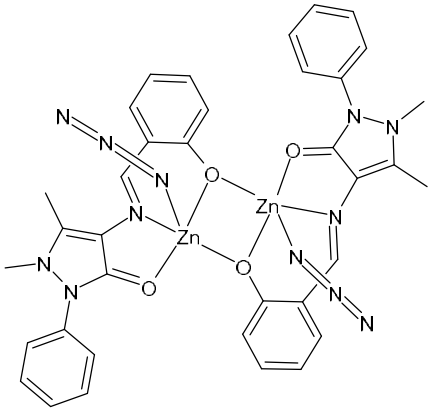
Structure	Compd	Catalyzed Reactions	Ref.
	$[Zn_2(L^1)_2(N_3)_2]$ (**43**)	Synthesis of tetrazoles	Bikas et al. (2023) [105]
	$[Zn_2(L^2)_2(N_3)_2]$ (**44**)	Synthesis of tetrazoles	Bikas et al. (2023) [105]

Table 4. *Cont.*

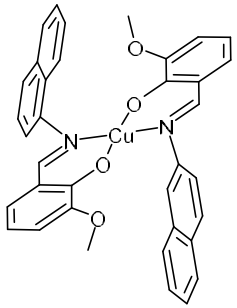
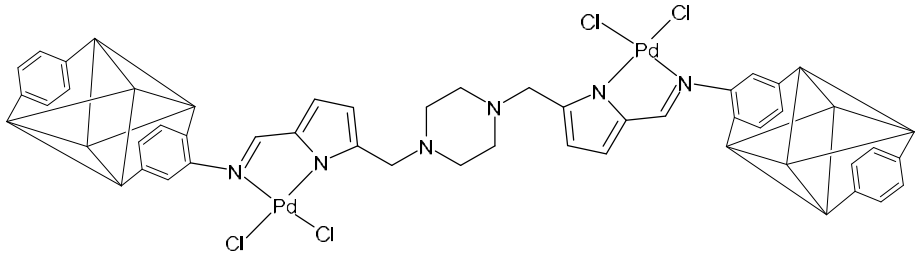
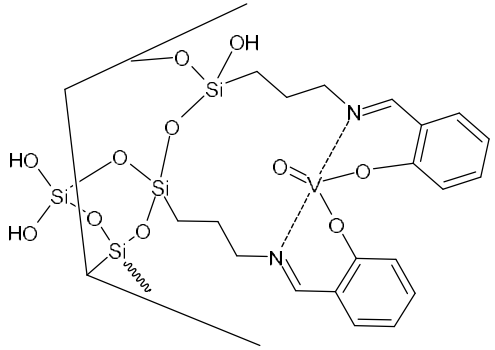
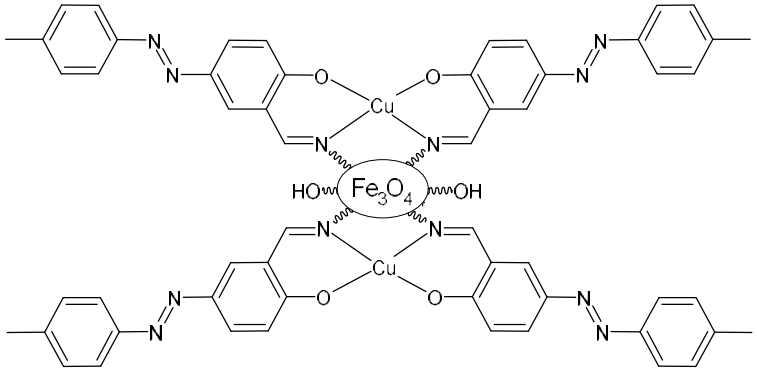
Structure	Compd	Catalyzed Reactions	Ref.
	CuL_2 (**45**)	Oxidation of secondary alcohols	Neshat et al. (2023) [106]
	Cu(BDC-NH_2)@Schiff base Pd(II) (**46**)	C–N coupling reactions	Rabiei et al. (2023) [107]
	V(O)-5NSA-MCM-41 (**47**)	Oxidative coupling of thiols and oxidation of sulfides	Jabbari et al. (2023) [108]

Table 4. *Cont.*

Structure	Compd	Catalyzed Reactions	Ref.
	Fe_3O_4@CS@Schiffbase@Cu (**48**)	A^3 coupling reaction under microwave irradiation	Hasan et al. (2023) [109]

5. Summary

SBs are a well-documented class of ligands able to bind almost all metals of the periodic table. They represent an ideal ligand scaffold since they have shown a large spectrum of biological activities, including antitumor, antiviral, antimicrobial, and anti-inflammatory activities. Complexes of SBs with transition metals have shown numerous applications as catalysts in various biological systems, corrosion inhibitors, polymers, and dyes. Schiff base complexes of transition metal ions catalyze several homogeneous and heterogeneous reactions in which numerous substrates, such as sulfides, aldehydes, phenols, thioanisoles, styrenes, and so on, are converted into the important precursors of drugs and materials. These reactions are usually conducted under mild and stable conditions, giving the desired products in high yields. Furthermore, another advantage that must be considered is that they can be simply separated from the reaction mixture and reused several times.

Interestingly, SBs metal complexes are used in therapeutic or biological applications either as potential drug candidates or diagnostic probes and analytical tools. Their numerous activities, including antitumoral, antimicrobial, antioxidant, and neuroprotective ones, are widely documented. Since AMR is a mounting threat to health and well-being globally, the main aim of this review was to focus, explore, and summarize the most recent available research studies regarding the antimicrobial activity exerted by these compounds. Some of the described compounds showed in vitro antimicrobial activities comparable to, and sometimes higher than, the reference drugs. The antimicrobial activity of metal complexes with SBs and their known anticorrosive potential may have great potential for their future application in several types of surgeries. Finally, the identification of new compounds belonging to this class may represent a new strategy to limit or overcome the occurrence of resistant strains, counteracting antibiotic resistance. The reviewed data clearly suggest that SBs metal complexes deserve particular consideration for their application in different fields, including medicinal chemistry and catalysis.

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