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Original scientific paper

Structural and antimicrobial studies of coordination compounds of VO(II), Co(II), Ni(II) and Cu(II) with some Schiff bases involving 2-amino-4-chlorophenol

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Abstract: Complexes of tailor-made ligands with life essential metal ions may be an emerging area to answer the problem of multi-drug resistance (MDR). The coordination complexes of VO(II), Co(II), Ni(II) and Cu(II) with the Schiff bases derived from 2-hydroxyacetophenone/2-chlorobenzaldehyde with 2-amino-4-chlorophenol were synthesized and characterized by elemental analysis, molar conductance, electronic spectra, FT-IR, ESR, FAB mass, thermal and magnetic susceptibility measurements. The FAB mass and thermal data show degradation of the complexes. The ligand **A** (2-hydroxyacetophenone-2-amino-4-chlorophenol) behaved as tridentate and ligand **B** (2-chlorobenzylidene-2-amino-4-chlorophenol) as bidentate, coordinating through O and N donors. The complexes [VO(**A**)(H₂O)]·xH₂O, [M(**A**)(H₂O)_n]·xH₂O for Co and Ni, [Cu(**A**)(H₂O)] and [VO(**B**)₂]·xH₂O, [M(**B**)₂(H₂O)_n] for Co and Cu and [Ni(**B**)₂] exhibited coordination numbers 4, 5 or 6. X-ray powder diffraction data ($a = 11.00417 \text{ \AA}$, $b = 11.706081 \text{ \AA}$ and $c = 54.46780 \text{ \AA}$) showed that [Cu(CACP)₂(H₂O)₂], complex **8**, crystallized in the orthorhombic system. The *in vitro* biological screening effects of the investigated compounds were tested against the bacteria *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus fecalis* and the fungi *Aspergillus niger*, *Trichoderma polysporum* and *Candida albicans* by the serial dilution method. A comparative study of the MIC values of the Schiff base and their [M(**B**)₂(H₂O)₂] complexes (Co(II), complex **6** and Cu(II), complex **8**), indicated that the metal complexes exhibited a higher or lower antimicrobial activity than 2-chlorobenzylidene-2-amino-4-chlorophenol as the free ligand (**B**).

Keywords: Schiff base; 2-amino-4-chlorophenol; 2-hydroxyacetophenone; metal complexes; spectral studies; antimicrobial activity.

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INTRODUCTION

Some transition metals are essential for the normal function of living organisms. Metallo-drugs are becoming an interesting research area after the discovery of cisplatin.¹ Since then, many complexes have been synthesized and tested on a number of biological systems. Copper complexes are known to have a broad spectrum of biological action,^{2,3} but its concentration as free metal ion inside cells should be lower than 10^{-15} M (calculated)/ 10^{-12} M (observed). A concentration higher than 10^{-9} M in the cytoplasm can be poisonous.⁴ The chemistry of vanadium with multidentate ligands has achieved a special status in the last decade because of its catalytic^{5,6} and medicinal⁷ input. Structural and functional models for vanadate-dependent haloperoxidases and nitrogenases have further stimulated vanadium coordination chemistry.⁸

The structures of the active site of the vanadate-dependent haloperoxidases have been revealed by X-ray diffraction studies. Accordingly, the vanadate ion is distorted towards a trigonal pyramid, thus providing a fifth coordination site to be occupied by the $>NH$ of a histidine, thus covalently linking the vanadate ion to the protein.⁹⁻¹¹

The chemistry of nickel Schiff base complexes has obtained a significant place in bioinorganic chemistry and redox enzyme systems.¹¹ Morrow and Kolasala¹² reported the cleavage of plasmid DNA by square planar nickel-salen [*bis*-(salicylidene)ethylenediamine] complex in the presence of either magnesium monoperoxyphthalic acid (MPPA) or iodosulbenzene.

In this paper, the preparation and structures of VO(II), Co(II), Ni(II) and Cu(II) complexes with some synthesized Schiff base ligands, *i.e.*, 2-hydroxyacetophenone-2-amino-4-chlorophenol (HACP) (**A**) and 2-chlorobenzylidene-2-amino-4-chlorophenol (CACP) (**B**), is described (Fig. 1). The antimicrobial activity of these ligands and complexes is also reported.

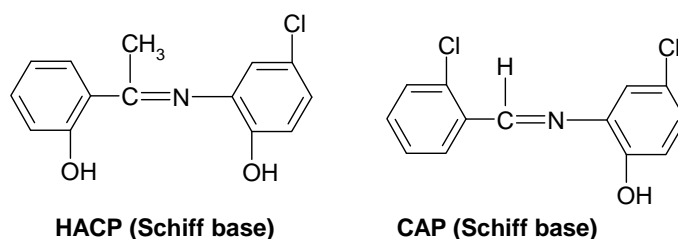


Fig. 1. HACP and CAP Schiff bases.

EXPERIMENTAL

Apparatus and reagents

All the used chemicals and solvents were of Analar grade. Oxovanadium(IV), cobalt(II), nickel(II) and copper (II) chloride/sulphate were obtained from Loba Chemie. Elemental analysis and FAB (Fast Atom Bombardment) mass spectra were realised at SAIF-CDRI,

Lucknow. Molecular weights were determined by the Rast method. Magnetic measurement was made by the Gouy method. Electronic spectra (in MeOH), were recorded on a Perkin-Elmer Lambda-2B-Spectrophotometer. Molar conductance (10^{-3} M) was measured using an Elico-conductivity bridge at room temperature. The FT-IR spectra (in KBr) were recorded at SAIF, IIT, Dehli. X-Ray powder diffraction analysis ($\text{CuK}\alpha$, 1.54060\AA) was performed at SAIF, Punjab University, Chandigarh. The ESR (electron spin resonance) spectra were recorded at SAIF, IIT, Mumbai. Thermal heating of the complexes was performed in a muffle furnace at four temperatures, *i.e.*, 100, 300, 500 and $750\text{ }^{\circ}\text{C}$.

Synthesis of the Schiff bases (ligands)

Two Schiff bases (HACP, CACP) were synthesized by adding a methanolic solution of 2-hydroxy-acetophenone/2-chloro-benzaldehyde (0.060 mol/0.070 mol) to a methanolic solution of 2-amino 4-chlorophenol (0.060 mol/0.070 mol). The reaction mixture was then refluxed on a water bath for about 5–6 h. The condensation product was filtered, washed thoroughly with ethanol and petroleum ether, recrystallized and dried under vacuum. The purity of the synthesized compounds was monitored by TLC (Thin Layer Chromatography) using silica gel (yield **(A)** = 79.5 % and yield **(B)** = 87.6 %).

Preparation of the metal complexes

All the complexes were prepared by mixing a methanolic solution of $\text{MCl}_2/\text{SO}_4 \cdot n\text{H}_2\text{O}$ (5.0 mmol/3.0 mmol) with the methanolic solution of Schiff bases HACP-(**A**)/CACP-(**B**) in a 1:1 or 1:2 molar ratio. The resulting mixture was refluxed on a water bath for 8–9 h. A coloured product appeared on standing and cooling the solution. The complexes were filtered, washed with petroleum ether and dried under reduced pressure over anhydrous CaCl_2 in a desiccator. They were further dried in an electric oven at $60\text{--}70\text{ }^{\circ}\text{C}$.

Antimicrobial activity

The *in vitro* biological screening effects of the investigated compounds were tested against *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus fecalis* by the well diffusion method^{13,14} using agar nutrient as the medium and gentamycin as the control.

The *in vitro* antifungal assay was performed by the disc diffusion method.^{13,14} The complexes and ligand were tested against the fungi *Aspergillus niger*, *Trichoderma polysporum* and *Candida albicans*, cultured on potato dextrose agar as the medium. In a typical procedure, a well was created on the agar medium and nystatin as the control was inoculated with the fungi. The well was filled with the test solution, which diffuses and the growth of the inoculated fungi is affected. The inhibition zone which developed on the plate was measured. The *MIC* values of the complexes were determined by the serial dilution technique.

RESULTS AND DISCUSSION

All the metal chelates are coloured, solid and stable towards air and moisture. They decompose at high temperatures ($90\text{--}100\text{ }^{\circ}\text{C}$) and they are more or less soluble in methanol, acetone, ethanol and chloroform as solvents. The analytical data of the complexes are consistent with the proposed molecular formulae (Fig. 2). All the metal chelates have 1:1 and 1:2 (metal:ligand) stoichiometry. The molar conductance values of the complexes in methanol (10^{-3} M) suggest a non-electrolytic nature, due to the low conductivity values.^{15,16} The analytical results of the complexes are presented in Table I.

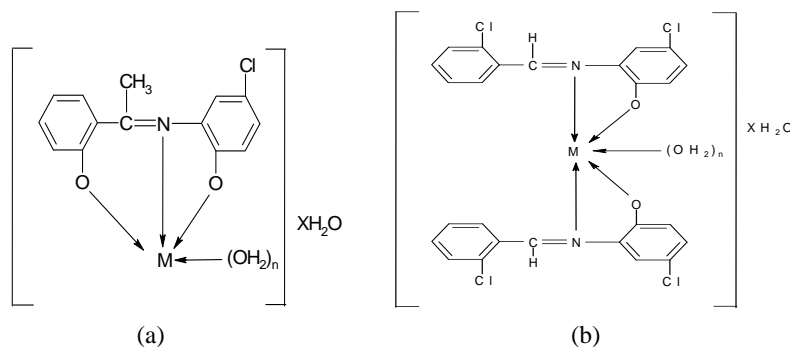


Fig. 2. Structures of the synthesized complexes with Schiff base (ligand):
a) **A** ($n = 1,2,3$; $x = 0,1,2$) and b) **B** ($n = 0,1,2$; $x = 0,1,2$).

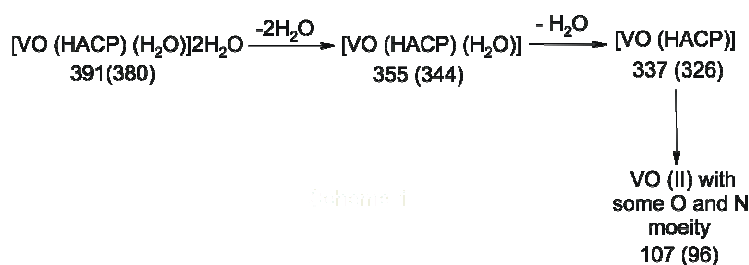
FAB mass spectrum

The FAB mass spectrum of the $[\text{VO}(\text{HACP})(\text{H}_2\text{O})]2\text{H}_2\text{O}$ (**1**) complex was studied as a representative case. Peaks of appreciable intensity were observed at m/z values 391, 355, 337, 259 and 105, suggesting the fragmentation pattern given in Scheme 1.¹⁷ The m/z value 391 corresponds to nearest composition

TABLE I. Physical characterization, analytical, molar conductance and magnetic susceptibility data of HACP (**A**) and CACP (**B**) Schiff base ligands and their metal complexes

Compound	M_r g mol ⁻¹	Colour	Yield %	Elemental analysis				μ_{eff} μ_B	Λ S m ⁻¹ mol ⁻¹
				Found (Calcd.), %					
				C	H	N	M		
(C ₁₄ H ₁₂ NO ₂ Cl) (A)	261.7	Yellow bricks	79.5	64.15 (64.19)	4.53 (4.58)	5.29 (5.34)	–	–	–
[VO(A)(H ₂ O)]·2H ₂ O (1)	380.7	Black	67.7	44.08 (44.12)	4.17 (4.20)	3.62 (3.67)	17.57 (17.59)	1.71	7.3
[Co(A)(H ₂ O) ₃] (2)	372.6	Black	69.9	45.02 (45.07)	4.24 (4.29)	3.71 (3.75)	15.82 (15.80)	5.10	16.2
[Ni(A)(H ₂ O) ₃] (3)	372.4	Light green	69.5	45.06 (45.11)	4.25 (4.29)	3.69 (3.75)	15.75 (15.76)	3.37	14.5
[Cu(A)(H ₂ O)] (4)	341.2	Black	79.7	49.19 (49.23)	3.47 (3.51)	4.06 (4.10)	18.58 (18.61)	1.86	19.3
(C ₁₃ H ₉ NOCl ₂) (B)	265.5	Yellow	87.6	58.71 (58.74)	3.33 (3.38)	5.23 (5.27)	–	–	–
[VO(B) ₂]·2H ₂ O (5)	632.1	Black	67.7	49.31 (49.35)	3.12 (3.16)	4.36 (4.42)	9.98 (10.59)	1.73	14.5
[Co(B) ₂ (H ₂ O) ₂] (6)	624.0	Dark brown	72.6	49.98 (50.00)	3.16 (3.20)	4.42 (4.48)	9.38 (9.43)	5.04	18.9
[Ni(B)] (7)	588.0	Black	74.0	53.02 (53.06)	2.67 (2.72)	4.71 (4.76)	9.95 (9.98)	Diamag- netic	8.1
[Cu(B) ₂ (H ₂ O) ₂] (8)	628.6	Black	75.7	49.59 (49.63)	3.11 (3.18)	4.39 (4.45)	10.08 (10.10)	2.29	17.4

[VO(A)(H₂O)]2H₂O, 355 to [VO(A)H₂O], 327 to [VO(A)], 259 to the ligand alone and 107 to VO with a chelated ligand moiety.



Scheme 1.

Infrared spectra

A careful comparison of the spectra of the ligands with those of their complexes resulted in the following information regarding various groups. The IR spectrum of the synthesized HACP (A) Schiff base showed absorption band at 1605 cm⁻¹ due to the azomethine group. It was shifted towards higher frequencies (1617±5 cm⁻¹) in the complexes, suggesting coordination through the azomethine nitrogen.¹⁸ The ligand spectrum showed bands at 3375 and 1360 cm⁻¹ due to the deformation stretching vibration of the phenolic OH group, which were absent in the spectra of the complexes. An intense ligand band at about 1202 cm⁻¹ (phenolic C–O) was shifted to higher frequencies (1235±5 cm⁻¹) in the complexes. This suggests deprotonation of the phenolic OH group after its chelation with the metal ion.^{19,20} The appearance of a broad band around 3344±20 cm⁻¹ in the spectra of the complexes suggests the presence of water molecules. A band of weak intensity at 810–820 cm⁻¹ suggests the presence of coordinated water in all four complexes. The IR spectra of the complexes showed some new bands in the region 525±5 and 475±10 cm⁻¹, which are probably due to the n(M–O) and n(M–N) modes, respectively.^{20–23} A characteristic non-ligand sharp band at 968 cm⁻¹ in the spectra of the VO(II) complex was assigned to (V=O), Table II.

TABLE II. IR spectral data (cm⁻¹) of the metal complexes of HACP (A)

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{C=C})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{V=O})$
HACP (A)	3375 1360	1605	1202	1486	–	–	–
[VO(A)(H ₂ O)]·2H ₂ O (1)	–	1618	1240	1475	520	480	968
[Co(A)(H ₂ O) ₃] (2)	–	1617	1235	1472	525	475	–
[Ni(A)(H ₂ O) ₃] (3)	–	1620	1238	1470	528	467	–
[Cu(A)(H ₂ O)] (4)	–	1615	1240	1476	525	486	–

The IR spectrum of the CACP (**B**) Schiff base showed a band at about 1616 cm^{-1} due to ($>\text{C}=\text{N}$) azomethine group. The complexes displayed lower frequency shift of about 5–10 cm^{-1} , suggesting coordination through the azomethine nitrogen. The ligand spectrum showed bands at 3369 and 1361 cm^{-1} due to the stretching deformation of the phenolic OH. These are absent in the spectra of the complexes. A medium intensity ligand band at about 1266 cm^{-1} (phenolic C–O) shifted to higher frequencies and appeared at 1279 \pm 5 cm^{-1} in the metal complexes. This indicates its involvement in chelation. The appearance of broad bands around 3372 \pm 20 cm^{-1} in the spectra of complexes may be due to water molecules. A band of medium intensity at 835 \pm 10 cm^{-1} (OH rocking) suggests the presence of coordinated water in the VO(II), Co(II) and Cu(II) complexes. This band is absent in the Ni(II) complex. New bands of weak intensity at 528 \pm 5 and 475 \pm 10 cm^{-1} in the metal complexes were tentatively assigned to the $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes, respectively.^{5,19,24–27} A characteristic non-ligand sharp band in the spectra of the VO(II) complex at 984 cm^{-1} was assigned to ($\text{V}=\text{O}$), Table III.

Table III. IR spectral data (cm^{-1}) of the metal complexes of CACP (**B**)

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{V}=\text{O})$
CACP (B)	3369 1361	1616	1266	1480	–	–	–
[VO(B) ₂] \cdot 2H ₂ O (5)	–	1610	1279	1475	528	475	984
[Co(B) ₂ (H ₂ O) ₂] (6)	–	1605	1282	1476	525	470	–
[Ni(B) ₂] (7)	–	1602	1278	1473	530	482	–
[Cu(B) ₂ (H ₂ O) ₂] (8)	–	1608	1277	1473	530	480	–

Electronic spectra

The electronic spectra of the [VO(**A**)(H₂O)] \cdot 2H₂O (**1**) and [VO(**B**)₂] \cdot 2H₂O (**5**) complexes were recorded in methanol as solvent. They displayed three bands at 666.6–657.8 nm, 588.2–555.5 nm and 454.5–416.6 nm, assignable to the transitions ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ (n_1), ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ (n_2) and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ (n_3), respectively. The suggested geometry for these complexes may be trigonal bipyramidal based on a coordination number five.²⁷ The values of the magnetic moments for these complexes are 1.71 and 1.73 μ_{B} , respectively, indicating the presence of one unpaired electron.^{27,28}

The electronic spectra of the [Co(**A**)(H₂O)₃] (**2**) and [Co(**B**)₂(2H₂O)] (**6**) complexes displayed two main bands at 666.6–625.1 and 526.3–476.1 nm. These were assigned to ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ (n_2) and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ (n_3) transitions, respectively. The various ligand field parameters: $10 Dq$, B , β , $\beta\%$, ν_2/ν_1 , λ and LFSE were calculated to be: 8612 and 8748 cm^{-1} ; 1029 and 957 cm^{-1} ; 0.91

and 0.85; 8.1 and 14.55; 2.2 and 2.2, (-)669 and (-)646 cm^{-1} , 82.31 and 83.61 kJ mol^{-1} , respectively. The ν_1 transition was expected to appear at larger λ (below 10000 cm^{-1}) and hence it could not be observed. The magnetic moment values of the complexes were 5.10 and 5.04 μ_B . The observed transitions are consistent with an octahedral geometry.²⁹⁻³¹

The electronic spectrum of the $[\text{Ni}(\mathbf{A})(\text{H}_2\text{O})_3]$ (**3**) complex, recorded in methanol, showed two bands at 490.0 and 420.0 nm. These bands were tentatively assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (n_2) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{A}_{1g}(\text{P})$ (n_3) transitions, respectively, which are characteristic for hexa-coordinated Ni(II). The value of the various ligand field parameters $10 Dq$, B , β , ν_2/ν_1 , λ and LFSE were calculated to be: 11337 cm^{-1} , 680 cm^{-1} , 0.62, 1.8, (-)540 cm^{-1} and 162 kJ mol^{-1} . Since the value of the magnetic moment is 3.37 μ_B , a high-spin octahedral geometry for Ni(II) is proposed.³²⁻³⁴

The electronic spectrum of the $[\text{Ni}(\mathbf{B})_2]$ (**7**) complex displayed two bands at 710.0 and 460.0 nm, which are assignable to ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ (n_1) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ (n_2) transitions, respectively. This complex is diamagnetic in nature. Therefore, a square-planar geometry is suggested.^{29,35-37}

The electronic spectrum of the $[\text{Cu}(\mathbf{A})(\text{H}_2\text{O})]$ (**4**) complex exhibited two bands at 520.0 and 440.0 nm, assignable to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, respectively. Since the value of the magnetic moment was 1.86 μ_B , square planar geometry is suggested.^{29,35-37}

The electronic spectrum of a methanolic solution of the $[\text{Cu}(\mathbf{B})(\text{H}_2\text{O})_2]$ (**8**) complex exhibited a broad band at 490.0 nm, which was assigned to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. The various ligand field parameters, *viz.*: $10 Dq$, λ and LFSE were calculated to be 14492 cm^{-1} , (-)670 cm^{-1} and 103.88 kJ mol^{-1} , respectively. The magnetic moment value was 1.89 μ_B . Based on this, an octahedral geometry is suggested for this Cu(II) complex.^{27,35}

ESR spectra

Based on hyperfine and superhyperfine structures, the ESR spectrum of metal complexes provides information about the environment of the metal ion within the complexes, *i.e.*, the geometry and nature of the ligating sites of the Schiff base and the metal. The ESR spectra of the Cu(II) (**4**) and VO(II) (**5**) complexes were recorded at room temperature. The Cu chelate showed two peaks, one in the low field region and the other in the high field region, from which g_{\parallel} and g_{\perp} were calculated. The g_{\parallel} value (< 2.3) indicates a covalent character of the metal-ligand bond.³⁸ The covalent nature of the metal-ligand bond in the complex is further supported by the G value,³⁹ which was < 4.0 . The value $g_{\parallel} > g_{\perp}$ is well consistent with a primarily $d_{x^2-y^2}$ ground state having an elongated tetragonal or square planar structure, Table IV.^{40,41}

TABLE IV. ESR parameters of the Cu(II) (**4**) and VO(II) (**5**) complexes

Metal complex	g_{\parallel}	G_{\perp}	g_{av}	Δg	G
4	2.2147	2.1206	2.1520	0.0941	1.7934
5	1.9387	1.9665	1.9572	0.0278	–

The x-band ESR spectra of the oxovanadium(IV) (**5**) (d^1 , ^{51}V , $I = 7/2$) complex was not resolved enough at room temperature to exhibit all eight hyperfine lines. The calculated values of g_{\parallel} , g_{\perp} , g_{av} and Δg for the VO(II) (**5**) complex are given in Table IV. The g_{av} value is one-third of $(2g_{\perp} + g_{\parallel})$ value. The values are typical of the spectrum displayed by the square pyramidal VO(II) (**5**) complex with one unpaired electron in an orbital of mostly d_{xy} character. The g_{av} values determined from the spectra are nearer to the spin only value. A slight variation may be the result spin-orbit coupling. In square pyramidal complexes with C_4V symmetry, the V=O band is along the z and the other four donor atoms (O_2N_2) are along the x, y axes. An anisotropic ESR spectrum is expected, exhibiting two g values ($g_z = g_{\parallel} < g_{\perp} = g_x = g_y$).^{42–46}

Powder X-ray diffraction analysis

The X-ray powder diffractogram of the $[\text{Cu}(\mathbf{B})_2(\text{H}_2\text{O})_2]$ (**8**) complex was recorded using $\text{CuK}\alpha$ as the source in the 2θ range $5\text{--}74^\circ$. The data reveal that the complex had crystallized in the orthorhombic system (Table V). Eight reflections of 2θ between 16.10 to 57.53° with a maximum $2\theta = 16.10^\circ$ and $d = 5.50 \text{ \AA}$ were observed. $\sin^2\theta$ and hkl values for different lattice planes were calculated. The crystal data for the $[\text{Cu}(\mathbf{B})_2(\text{H}_2\text{O})_2]$ (**8**) complex are: $a = 11.004173 \text{ \AA}$, $b = 11.706081 \text{ \AA}$, $c = 54.46780 \text{ \AA}$, $D_{\text{obs}} = 1.49680 \text{ gm/cm}^3$ and $D_{\text{cal}} = 1.496015 \text{ gm/cm}^3$. The observed and calculated values of the density and $\sin^2\theta$ show good agreement. The calculated values of the cell volume and particle size are 7016.30 \AA^3 and 1.324 nm , respectively. The number of molecules (n) per unit cell was also calculated using the equation $D = nM/NV$; the value is 10 molecules per unit cell (Fig. 3).

TABLE V. XRD data of the $[\text{Cu}(\mathbf{B})_2(\text{H}_2\text{O})_2]$ (**8**) complex

Peak No.	d -Spacing \AA	Relative intensity $I/I_0 \times 100$	$\sin^2\theta$		hkl
			Observed	Cald.	
1	5.504	100.00	0.0916	0.0196	200
2	4.011	59.16	0.0369	0.0369	220
3	3.104	60.02	0.0616	0.0616	320
4	2.752	51.62	0.0784	0.0784	400
5	2.685	96.99	0.0825	0.0827	410
6	2.229	28.90	0.1195	0.1191	433
7	2.000	30.02	0.1485	0.1484	442
8	1.600	22.32	0.2316	0.2314	522

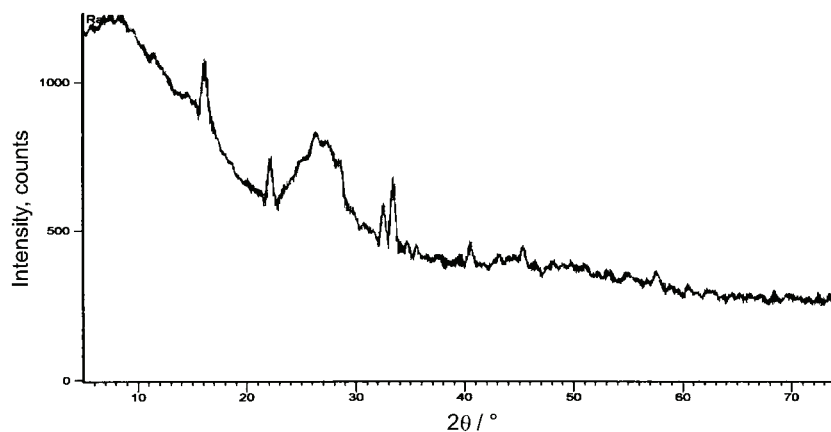


Fig. 3. X-Ray powder diffractogram of the $[\text{Cu}(\mathbf{B})_2(\text{H}_2\text{O})_2]$ (**8**).

Thermal decomposition

The complexes **1–4** of HACP (**A**) and the complexes **5–8** of CACP (**B**) were heated at four temperatures (100, 300, 500 and 750 °C) in a muffle furnace for 20–30 min. The resulting weights were measured. The weight loss at 100 °C corresponds to the loss of lattice water molecules from the complexes.^{17,46,47} The weight measured after heating at 300 °C indicates the loss of coordinated water molecules from the complexes. On heating at 500 °C, the remaining weight indicates the loss of parts of the ligand moiety. The weight of the pyrolysis product after heating at 750 °C corresponds to metal oxide.

Antimicrobial activity

The *in vitro* anti-microbial activity of the investigated compounds was, tested against the micro-organisms *E. coli*, *S. aureus*, *S. fecalis*, *A. niger*, *T. polysporum* and *C. albicans* by the serial dilution method. The minimum inhibitory concentration (*MIC*) values of the compounds against the growth of the micro-organisms are summarized in Table VI. A comparative study of the ligand and its cobalt(II) and copper(II) complexes (*MIC* values) indicated that both complexes **6** and **8** exhibited either higher or lower antimicrobial activity than the free ligand **A**.^{48,49}

The complexes **6** and **8** exhibited better antibacterial activity than their SB-ligand **A** against *E. coli* and *S. aureus*. Against *S. fecalis*, complex **6** showed better activity than its SB-ligand **A** while complex **8** was less active.

The complexes **6** and **8** exhibited better antifungal activity in comparison to SB-ligand **A** against all three fungi, Table VI.

These observations showed that the majority of the complexes were more active than their respective Schiff base ligands. In some cases, Schiff bases are more active than their metal complexes against bacteria. The chelation either enhances or reduces the antimicrobial activity; sometimes it remains neutral. Thus,

TABLE VI. Antimicrobial data (*MIC* value; diameter of inhibition zone, mm) of the investigated compounds

Compound	<i>E. coli</i>		<i>S. aureus</i>		<i>S. fecalis</i>		<i>A. niger</i>		<i>T. polysporum</i>		<i>C. albicans</i>						
	25	50	100	25	50	100	25	50	100	25	50	100					
CACP (6)	13	13	15	i/nm ^a	10	13	17	23	10	14	22	15	17	19	13	16	18
[Co(6) ₂ (H ₂ O) ₂] (6)	20	24	28	11	12	20	17	20	16	12	16	25	18	19	21	15	19
[Cu(6) ₂ (H ₂ O) ₂] (8)	22	25	32	13	15	19	10	15	19	10	15	23	17	20	22	14	18
Nystatin	-	-	-	-	-	-	-	-	-	20	23	24	23	24	20	21	20
Gentamycin	18	20	19	19	22	20	18	21	23	-	-	-	-	-	-	-	-
Standard DMSO	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm	i/nm

^aInactive/not measurable

metal chelation may increase or decrease/suppress the therapeutic value of organic compounds (drugs). It may maintain the property intact by further stabilizing the drug and/or reducing the biodegradability/metabolic decay of the organic ligands through chelation.

CONCLUSIONS

The coordination complexes of VO(II), Co(II), Ni(II) and Cu(II) with two new tridentate and bidentate Schiff base ligands, *i.e.*, 2-hydroxy acetophenone-2-amino-4-chlorophenol (**A**) and 2-chlorobenzylidene-2-amino-4-chlorophenol (**B**), were synthesized and characterized. The ligands coordinated with the metal ions through N or O donors. The complexes exhibited a geometry based on the coordination numbers 4, 5 or 6. A comparative study of the *MIC* value of the ligands and their complexes indicated that the chelation might be helpful in tailoring the structure and monitoring the antimicrobial activity and therapeutic potential of a drug; thus giving a new thrust area in the field of metallo-drugs (bio-inorganic chemistry) through molecular biology. The synthesized metal complexes may also function as single molecule nanoprecursors.

ИЗВОД

СТРУКТУРНО И АНТИМИКРОБНО ПРОУЧАВАЊЕ КООРДИНАЦИОНИХ ЈЕДИЊЕЊА VO(II), Co(II), Ni(II) И Cu(II) СА НЕКИМ ШИФОВИМ БАЗАМА КОЈЕ УКЉУЧУЈУ 2-АМИНО-4-ХЛОРОФЕНОЛ

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Комплекси са есенцијалним металним јонима могу дати одговор на проблем отпорности на више лекова. Координациона једињења VO(II), Co(II), Ni(II) и Cu(II) са Шифовим базама изведеним из 2-хидроксиацетофенон/2-хлоробензалдехида са 2-амино-4-хлорофенилом су синтетисана и окарактерисана елементалном анализом, моларном проводљивошћу, електронским спектрима, FT-IR, ESR, FAB масеним спектрима, термичким мерењима и одређивањем магнетне суспектибилности. FAB масени и термички подаци показују деградацију комплекса. Лиганд **A**, 2-хидроксиацетофенон-2-амино-4-хлорофенол, понаша се као тридентат, а лиганд **B**, 2-хлорбензилиден-2-амино-4-хлорофенол, као бидентат који се координира преко O и N донора. Комплекси [VO(**A**)(H₂O)]·xH₂O, [M(**A**)(H₂O)_n]·xH₂O за Co и Ni, [Cu(**A**)(H₂O)] и [VO(**B**)₂]·xH₂O, [M(**B**)₂(H₂O)_n] за Co и Cu, [Ni(**B**)₂] имају координационе бројеве 4, 5 или 6. Резултати дифракције x-зрака за прах (*a* = 11.00417 Å, *b* = 11.706081 Å и *c* = 54.46780 Å) показују да [Cu(CACP)₂(H₂O)₂] кристалише у орторомбичном систему. *In vitro* биолошка проучавања изучаваних једињења вршена су према бактеријама *Escherichia coli*, *Staphylococcus aureus* и *Streptococcus fecalis* и гљивицама *Aspergillus niger*, *Trichoderma polysporum* и *Candida albicans* серијском методом разблажења. Упоредно проучавање *MIC* вредности Шифове базе и њених [M(**B**)₂(H₂O)₂] (M = Co(II) или Cu(II)) комплекса, указују да метални комплекси имају већу или мању антимикробну активност у односу на 2-хлоробензилиден-2-амино-4-хлорофенол као слободни лиганд (**B**).

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