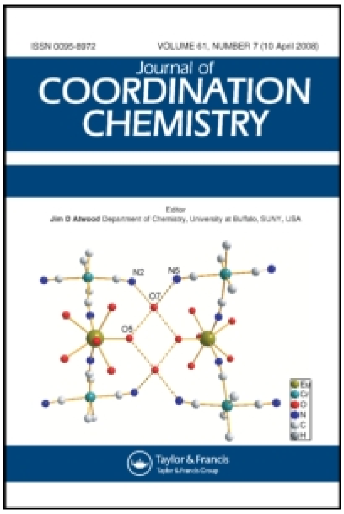

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M. Sivasankaran Nair[a]; S. Suda Kumari[a]; M. A. Neelakantan[b]
[a] Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli-627 012, India [b] Department of Chemistry, National Engineering College, Kovilpatti-628 503, India

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Studies on some novel Schiff-base complexes in solution and solid state

M. SIVASANKARAN NAIR*†,
S. SUDA KUMARI† and M. A. NEELAKANTAN‡

†Department of Chemistry, Manonmaniam Sundaranar University,
Tirunelveli – 627 012, India
‡Department of Chemistry, National Engineering College,
K.R. Nagar, Kovilpatti – 628 503, India

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In solution Schiff-base complexes of stoichiometry MAB, MAB_2 or MA_2B_2 have been detected in the Co(II), Ni(II), Cu(II) and Zn(II)-o-vanillin (o-van) [A]-L-valine (val), L-glutamine (gln) and L-histidine (his)(B) systems. The results suggest that in the M-o-van-val/gln systems, the Schiff-base ligand (AB) is tridentate in M(AB) complexes, while (AB) is tetradentate in his systems. MAB_2 species can be represented as M(AB)(B), where the mode of coordination of (AB) would be similar to that in the M(AB) species. The MA_2B_2 complex can be represented as $M(AB)_2$, where (AB) is tridentate in all the systems. The stabilities of complexes follow the Irwin–Williams order of stability. MAB complexes were isolated and conformed by characterization data. Conductance studies indicate that all complexes are non-ionic. Magnetic susceptibility and electronic spectral data suggest a tetrahedral structure in Co(II) and Ni(II)-o-van-val/gln and Ni(II)-o-van-his systems and square-planar structure in Co(II)-o-van-his and Cu(II)-o-van-val/gln/his systems for the MAB species. The IR spectral data indicate the tri and tetradentate binding of (AB) in the M(AB) complexes, respectively, in M(II)-o-van-val/gln and M(II)-o-van-his systems. Antimicrobial activity of the ligand and its Cu(II) complexes has been studied; Cu(II) complexes have higher activity than that of the ligand and control.

Keywords: Schiff base complexes; Potentiometry; Stability constant; o-Vanillin; Amino acids; Magnetic susceptibilities; Spectral studies; Antimicrobial activity

1. Introduction

Metal complexes of Schiff bases derived from substituted salicylaldehyde and amino acids are of interest both as simple structural models of more complicated biological systems such as SOD–mimic and for their antimicrobial, antifungal, antipyretic and immuno protective activities [1, 2]. Also, transition metal complexes of Schiff bases play an important role in the catalysis of drug interactions [3]. These roles and their potential application in fields such as oxidation catalysts [4], and electrochemistry [5] stimulated our interest in the investigation of amino acid Schiff-base complexes.

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*Corresponding author. Email: maneels@rediffmail.com

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In the present article, the solution equilibria involved in the Co(II), Ni(II), Cu(II) and Zn(II)-o-vanillin (o-van) (A)-L-valine (val)/L-glutamine (gln)/L-histidine (his)(B) systems were studied at 25°C and 0.1 M KNO_3 ionic strength by a batch-wise titration method [6, 7]. The M(AB) Schiff-base complexes were isolated and characterized. The biological activity of the Schiff base and its Cu(II) complexes *in vitro* were tested against the Gram positive bacteria *Streptococcus aureus* and Gram negative bacteria *Escherichia coli* and *Salmonella typhi*.

2. Experimental

All chemicals and solvents used were chemically pure or analytical reagent grade. The chemicals and solvents were obtained from BDH (AnalaR) except o-van, val, gln and his, which were obtained from Fluka (Puriss). The solvents for physical measurements were purified according to literature methods [8]. The pH measurements were carried out at 25°C and 0.1 mol dm^{-3} KNO_3 ionic strength under nitrogen with a Systronics pH meter (system 361, accuracy ± 0.01 pH unit) as described earlier [9–13]. All solutions were prepared with double-distilled water using grade A glassware. In the Schiff-base complex systems, some time is required before equilibrium is reached and hence a batchwise titration procedure was used [6, 7]. In the Co(II) systems, the bottles were purged with oxygen-free nitrogen gas in order to prevent oxidation of Co(II) to Co(III). The pH data have been analyzed using a computer program designed for the evaluation of Schiff-base complex equilibria [14].

IR-spectra were recorded in KBr with a FT-IR spectrophotometer (Perkin Elmer, Spectrum 1000) in the 4500–450 cm^{-1} region. Magnetic susceptibility measurements on powder samples were carried out with a Gouy balance at room temperature using mercuric tetra(thiocyanato)cobaltate(II) as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant [15]. The molar conductances of the complexes were measured using a Systronics 304 conductivity bridge. Electronic spectra were recorded using a Perkin-Elmer UV-visible spectrophotometer (Lambda 3b) with methanol as solvent in the range of 190–900 nm, using PECSS software.

The Schiff bases were obtained by condensation of o-van with equimolar amounts of val, gln and his. The various complexes were prepared by addition of 5 mmol of metal nitrate, dissolved in ~20–30 mL of water, into the appropriate Schiff base (5 mmol) (1 : 1 molar ratio) with constant stirring. The colors of the solutions change within minutes. The mixture was then refluxed for 2 h. The precipitated solids were filtered off and washed with water, methanol and finally with ether. The product was dried in vacuum over fused calcium chloride.

3. Results and discussion

3.1. *Solution studies*

The M(II)-o-van binary system was re-investigated under the present experimental conditions, while for other systems the binary stability constant data under the present experimental conditions were taken from the literature [13]. In the Co(II), Ni(II) and Cu(II)-o-van systems, MA and MA_2 complexes were detected, while in the corresponding Zn(II) system only MA was found. The $\log\beta$ values (table 1) in these systems are comparable with the corresponding M(II)-salicylaldehyde system (table 1A) [16, 17]. This suggests that o-van coordinates the metal ion in a bidentate manner via aldehydic and phenolic oxygen atoms forming a six-membered ring.

Schiff-base complexes of stoichiometry MAB, MAB_2 and MA_2B_2 have been detected in the Co(II)/Ni(II)/Zn(II)-o-van(A)-val, gln or his(B) systems, while MAB and MAB_2 species have been found to be present in the Cu(II) systems (table 2).

3.2. *Stability and structure of MAB complexes*

The preferential formation of Schiff-base complex over binary species can be illustrated by considering stepwise formation constants of the various species formed (tables 1 and 2). Scheme 1 gives the stepwise formation constants in the Co(II)-o-van-val system.

If the MAB species in the title systems are considered as a mixed ligand complex, then the overall formation constant could be calculated using the formula [18] $(1/2\log K_{MA_2} + 1/2\log K_{MB_2} + 0.3010)$. But the experimental $\log\beta_{M(AB)}$ values (table 2) are higher than the calculated values by more than 2 log units. This indicates different mode of binding in M(AB) i.e. the amino acid(B) reacts with o-van to form a Schiff base (AB), which coordinates the metal ion. In the M(II)-o-van-val/gln systems, the $\log\beta_{M(AB)}$ values are comparable, suggesting a similar mode of binding of the Schiff-base ligand in these two systems, possibly in a tridentate manner through imino-N, phenolic-O and carboxylato-O atoms. The fourth position in M(AB) could be completed by a water molecule. The enhanced stability can be attributed in part to fusion of two ring systems. Multi ring formation by the same ligand leads to greater stability than chelation by two bidentate ligands due to enhanced entropy.

In the Co(II), Ni(II), Cu(II), Zn(II)-o-van(A)-gln(B) systems, the $\log\beta_{M(AB)}$ values are higher by ~0.5 log unit compared with the corresponding value in the val(B) system. This increase is not large enough to consider the involvement of the amide group in coordination to the metal ion, and instead can be accounted for by considering intermolecular association via amide groups to an adjacent molecule. Such interactions have also been previously reported [16, 17]. The higher stability constants in the M(II)-o-van-his systems compared with those in the corresponding val and gln(B) systems suggest that in the former system the Schiff-base ligand binds in a tetradentate mode via imino-N, phenolic-O, carboxylate-O and imidazole-N atoms.

3.3. *Stability and structure of MAB_2 complexes*

The $\log\beta_{MAB_2}$ values are given in table 2. It may be noted that the value of 11.39 in the Co(II)-o-van-val system is comparable to that of 11.48 in the Co(II)-salicylaldehyde-val system [16] suggesting similar structures for the MAB_2 species in both systems i.e. MAB_2 species in the former system can also be represented as M(AB)B, where the Schiff base (AB) binds the metal ion in the same mode as in the M(AB) species, and (B) coordinates the metal as in the MB species. The comparable $\log\beta_{MAB_2}$ values in the M(II)-o-van-val/gln systems (table 2) suggest that MAB_2 species in gln systems can also be represented as M(AB)B. Two structures are possible for the MAB_2 species in

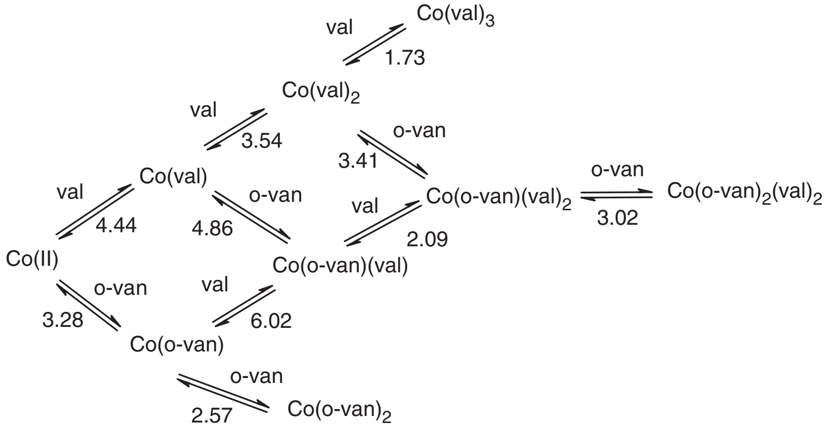
Table 1. Stability constants for Co(II), Ni(II), Cu(II) and Zn(II) with o-van, val, gln and his(A)* (298 K and $I = 0.1\ \mathrm{mol\,dm^{-3}}$ KNO_3).

	Co(II)				Ni(II)				Cu(II)				Zn(II)			
Parameter	o-van	val[a]	gln[a]	his[a]	o-van	val[b]	gln[b]	his[b]	o-van	val[b]	gln[b]	his[b]	o-van	val[b]	gln[b]	his[b]
$\log \beta_{MA}$	3.28	4.44	4.44	6.92	3.51	5.26	5.17	8.57	5.24	8.09	7.74	9.98	2.92	4.75	4.55	6.56
$\log \beta_{MA_2}$	5.85	7.98	8.07	13.86	6.16	9.12	9.45	15.34	9.40	14.38	14.20	17.40	2.74	8.75	8.35	11.77
$\log \beta_{MA_3}$	–	9.71	–	–	–	12.35	–	–	–	–	–	–	–	–	–	–

*val, gln and his become ligand B in Schiff base complex systems.
Ref: [a][13], [b][11].

Table 1A. Stability constants for Co(II), Ni(II), Cu(II) and Zn(II) with salicylaldehyde [16, 17] (298 K and $I = 0.1\,\mathrm{mol\,dm^{-3}}$ KNO_3).

Parameter	Co(II)	Ni(II)	Cu(II)	Zn(II)
$\log \beta_{MA}$	3.48	3.88	5.57	3.00
$\log \beta_{MA_2}$	6.06	6.54	9.83	–



Scheme 1. Stepwise formation constants of binary and ternary complex species.

M(II)-o-van-his systems: (i) both the Schiff base (AB) and his coordinate in tridentate mode or (ii) the Schiff base (AB) binds in a tetradentate mode and his in a bidentate mode. The $\log K^{MAB}_{MAB_2}$ values (table 2) are ~1 log unit less than the $\log K^{MB}_{MB_2}$ values. This suggests that in M(AB)B species(B), his ligand, coordinates in a bidentate mode and (AB) binds in a tetradentate mode.

3.4. *Stability and structure of MA_2B_2 complexes*

The MA_2B_2 complexes in the M(II)-o-van-val/gln systems are stable with high $\log \beta_{MA_2B_2}$ values (table 2). The CoA_2B_2 species was also reported in the Co(II)-salicylaldehyde-val system [16], where the Schiff base (AB) functions as a tridentate ligand. The comparable $\log \beta_{CoA_2B_2}$ values in the Co(II)-salicylaldehyde/o-van-val systems suggest that the CoA_2B_2 complexes in both these systems are similar i.e. in the M(II)-o-van-val systems also, MA_2B_2 species can be represented as $M(AB)_2$, where (AB) is tridentate. Similar structures can also be assigned for the MA_2B_2 species in the o-van-gln systems (table 2). In the Co(II)/Ni(II)/Zn(II)-o-van-his systems, the $\log \beta_{MAB_2}$ values are much higher than those in the val system. In the former, both Schiff-base ligands cannot bind tetradentate, because it would lead to the improbable coordination number to the metal ion. If the coordination number of six to the metal ion is to be retained, two possible structures are possible. In one structure, one (AB) ligand would be tetradentate and other (AB) will be bidentate. The other possibility is that both the Schiff base ligands would be tridentate utilizing the phenolic oxygen, imino and imidazole nitrogens for coordination. The second structure appears to be

Table 2. Stability constants for the ternary Schiff base complexes in M(II)-o-van(A)-val, gln and his(B) systems (298 K and $I = 0.1\,\mathrm{mol\,dm^{-3}}$ KNO_3).

	Co(II)			Ni(II)			Cu(II)			Zn(II)		
Parameter	val	gln	his	val	gln	his	val	gln	his	val	gln	his
$\log \beta_{\mathrm{MAB}}$	9.30 (7.22)	9.78 (7.25)	12.13 (10.15)	10.45 (7.90)	10.86 (8.11)	14.07 (11.05)	15.30 (12.14)	15.68 (11.80)	17.32 (13.70)	9.10 (7.11)	9.37 (6.47)	10.86 (6.89)
$\log \beta_{\mathrm{MAB_2}}$	11.39	11.51	15.12	13.31	13.69	17.90	19.58	19.63	–	11.24	11.33	14.89
$\log \beta_{\mathrm{MA_2B_2}}$	14.41	14.40	19.50	17.20	17.23	21.36	–	–	–	14.28	14.39	19.10
$\Delta \log K_{11}$	1.58	2.06	1.93	1.68	2.18	1.98	1.97	2.70	2.10	1.43	1.90	1.38

The $\log \beta_{\mathrm{MAB}}$ values in the parentheses are the calculated values assuming the complex to be a mixed ligand complex species.

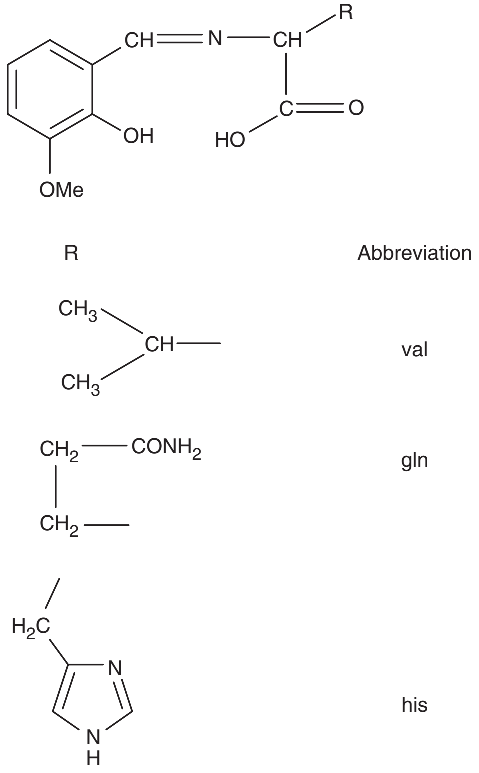


Figure 1. Structure of Schiff base ligands.

more reasonable. The imidazole group is relatively a softer base than the carboxylato group and is known for its high buffering action [17].

3.5. *Species distribution diagrams*

The species distribution diagrams for all the systems indicate that Schiff-base complex formation is favored over binary species. The MAB species is more predominant between pH 5.5 and 6.5, accounting a maximum of ~75% of the total metal ion in the 1 : 1 systems. In 1 : 2 systems, the concentration of MAB was found to occur to a maximum extent of ~60%. The M(AB)B species was found to be favored above pH 6.0 and reaches a maximum of ~30% of the total metal ion at pH 7.0. The $M(AB)_2$ species has been found to be formed only above pH 6.5 and is the predominant species, accounting 70% of the total metal ion at pH 7.5. In order to show the qualitative trends found in the species distribution diagrams, the plot obtained in the Co(II)-o-van(A)-val(B) system is given in figure 3.

3.6. *Stability enhancement in the M(II)-o-van-val, gln/his systems*

The stabilization factor [19], $\Delta \log K_{11}$ ($= \log K_{11} - \log k_{10} - \log K_{01}$) values (table 2) for the systems clearly demonstrate that Irving–William order of stability is followed i.e. Co(II) < Ni(II) < Cu(II) > Zn(II).

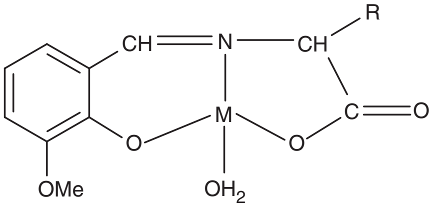


Figure 2. Structure of the AB Schiff base complexes M(II)-o-van(A)-val and gln(B) systems [M(II) = Co(II), Ni(II), Cu(II) and Zn(II)].

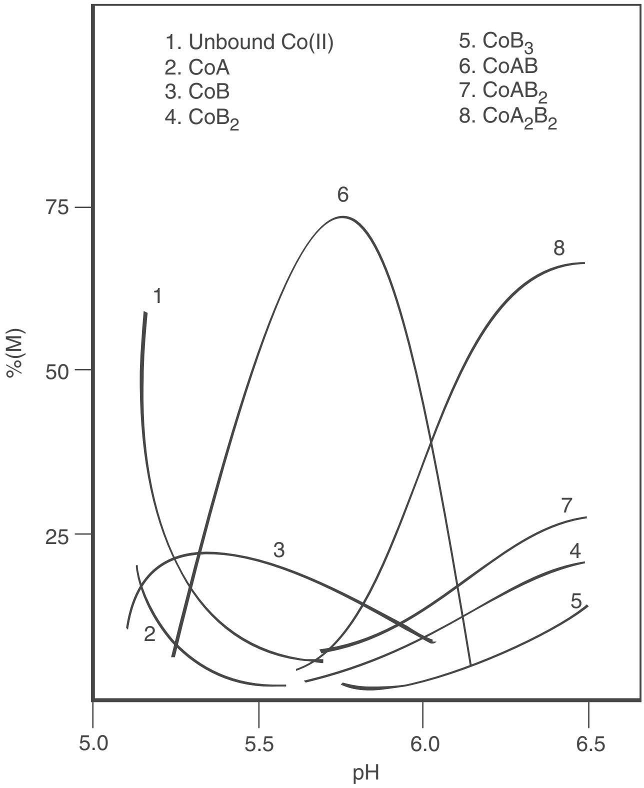


Figure 3. Species distribution diagram for the Co(II)-o-van(A)-val(B)system, $C_M = C_A = C_B = 0.002\,\text{mol}\,\text{dm}^{-3}$. Curve for CoA_2 could not be drawn due to its low concentration.

3.7. *Solid state studies*

The solid MAB complexes are found to be soluble in methanol, ethanol and dimethyl sulfoxide. The color, elemental analysis, molar conductance and magnetic susceptibility data of the complexes are given in table 3. Elemental analysis data are consistent with the M(AB) formulae. This is reasonable, because the species distribution diagrams in all the systems demonstrate that M(AB) is the predominant species formed between pH 5.5 and 6.5. The molar conductance of the complexes in methanol for $\sim 10^{-3}$ M solutions

Table 3. Elemental analysis, molar conductivity and magnetic susceptibility of the AB complexes.

				C (%)	H (%)	N (%)	M (%)		
Complex	Color	Empirical formulae	Yield (%)	Calcd (Found)	Calcd (Found)	Calcd (Found)	Calcd (Found)	λ_m (mho cm^{-1} mol^{-1})	Magnetic moment
Co(II)-o-van-val	Yellowish brown	$[Co(C_{13}H_{15}O_4N)(H_2O)]$	64	47.86 (47.50)	5.21 (5.43)	4.29 (4.10)	18.08 (18.23)	6.5	4.70
Co(II)-o-van-gln	Dark brown	$[Co(C_{13}H_{14}O_5N_2)(H_2O)]$	70	43.95 (43.50)	4.50 (4.85)	7.88 (7.53)	16.62 (16.41)	8.2	4.83
Co(II)-o-van-his	Dark brown	$[Co(C_{14}H_{14}O_4N_3)]$	69	48.42 (48.12)	4.04 (4.20)	12.11 (12.30)	16.98 (16.43)	7.2	2.32
Ni(II)-o-van-val	Light green	$[Ni(C_{13}H_{15}O_4N)(H_2O)]$	66	47.89 (47.32)	5.22 (5.46)	4.30 (4.49)	18.02 (18.10)	8.12	3.61
Ni(II)-o-van-gln	Light green	$[Ni(C_{13}H_{14}O_5N_2)(H_2O)]$	72	43.98 (43.78)	4.51 (4.32)	7.89 (7.98)	16.55 (16.66)	6.58	3.53
Ni(II)-o-van-his	Light green	$[Ni(C_{14}H_{14}O_4N_3)]$	70	48.46 (48.23)	4.04 (4.34)	12.11 (12.01)	16.93 (16.41)	8.12	3.75
Cu(II)-o-van-val	Green	$[Cu(C_{13}H_{15}O_4N)(H_2O)]$	71	47.20 (47.54)	5.14 (5.03)	4.23 (4.10)	19.22 (19.04)	10.28	1.81
Cu(II)-o-van-gln	Green	$[Cu(C_{13}H_{14}O_5N_2)(H_2O)]$	78	43.39 (43.56)	4.45 (4.21)	7.79 (7.21)	17.67 (17.11)	8.25	1.85
Cu(II)-o-van-his	Green	$[Cu(C_{14}H_{14}O_4N_3)]$	77	47.79 (47.93)	3.98 (3.46)	11.95 (11.55)	18.07 (18.23)	9.96	1.91

at room temperature are in accord with the expectation of a neutral complex formed by dianionic ligands with a dipositive metal ion.

3.8. *Magnetic measurements*

In Co(II)-o-van-val/gln systems, the μ_{eff} values for MAB complexes fall in the range 4.2 to 4.8 BM, which is characteristic for tetrahedral d^7 complexes [20]. In Ni(II)-o-van-val/gln/his systems the μ_{eff} values are in the range of 3.50–3.75 BM, typical for d^8 Ni(II) complexes in a tetrahedral environment [21–23]. The μ_{eff} values observed in Cu(II)-o-van-val/gln/his and Co(II)-o-van-his systems are 1.81, 1.85, 1.91 and 2.32 respectively, which are characteristic for square-planar complexes [24].

3.9. *IR-spectra of M(AB) complexes*

The free ligand o-van exhibits a strong band at 1643 cm^{-1} due to the aldehydic group. The strong band in the 1613–1580 cm^{-1} region for the Schiff bases is attributed to the C=N stretching vibration for C=N group due to condensation of the aldehyde group of o-van and the amino group [25]. This band shifts to lower frequencies in the spectra of the metal complexes (1600–1530 cm^{-1}) indicating involvement of azomethine in coordination. The phenolic oxygen stretching vibration that appears at 1298 cm^{-1} in the Schiff bases [26, 27] undergoes a shift to higher frequencies (20–40 cm^{-1}) in the metal complexes. This shift confirms the bonding of the phenolic oxygen with metal [27, 28]. In the low frequency region, the band observed in the complexes in the 438–410 cm^{-1} region is attributed to (M–O) and in the 505–516 cm^{-1} region to (M–N) stretches. A very strong band in the 1625–1595 cm^{-1} range for the complexes is typical for the asymmetric vibration of the coordinated carboxylate group, confirming coordination of the amino acid through the carboxylic oxygen [27]. However, the band in the 1396–1367 cm^{-1} region can be ascribed to the symmetric vibrations of the coordinated carboxylate. To summarize, the IR data suggest that the metal ion is bound to the Schiff base through the phenolic oxygen and the imino nitrogen and carboxylato oxygen in the M(II)-o-van-val/gln systems. In the M(II)-o-van-his system the Schiff base ligand coordinates in a tetradentate mode via imino-N, phenolic-O, carboxylate-O and imidazole-N atoms.

3.10. *Electronic absorption spectra*

The electronic absorption data of Co(II), Ni(II) and Cu(II) Schiff-base complexes were recorded at 300 K using methanol as solvent. The proposed geometries are given in table 4. In the tetrahedral geometry, Co(II) shows one absorption band due to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition in the UV-VIS region [27]. The ${}^4A_2(F) \rightarrow {}^4T_1(F)$ transition occurs in the IR region. The $\lambda_{\max}$ values in Co(II)-o-van-val/gln systems (600–700 nm) are characteristic of tetrahedral complexes. The 482 nm band in Co(II)-o-van-his is characteristic of square-planar Co(II) complexes [29, 30] corresponding to the transition ${}^4A_{1g} \rightarrow {}^4B_{1g}$. In the tetrahedral Ni(II) complexes the transitions are ${}^3T_1(F) \rightarrow {}^3T_1(P)$ [31]. For the CuAB species in the Cu(II)-o-van-val/gln/his systems, the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition is assignable to a square-planar geometry [32, 33].

Table 4. Electronic absorption spectral data of the AB complexes at 300 K.

Complex	Absorption λ_{max} (in nm) in methanol	Band assignments	Geometry
Co(II)-o-van-val	650	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
Co(II)-o-van-gln	659		
Co(II)-o-van-his	482	${}^4A_{1g} \rightarrow {}^4B_{1g}$	Square planar
Ni(II)-o-van-val	625	${}^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral
Ni(II)-o-van-gln	610		
Ni(II)-o-van-his	564		
Cu(II)-o-van-val	625	${}^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar
Cu(II)-o-van-gln	650		
Cu(II)-o-van-his	695		

Table 5. Biological activities of Schiff bases and their Cu(II) complexes (zone formation in mm).

Bases and complexes	*S. aureus*	*E. coli*	*S. typhi*
Ampicillin	11	10	13
o-van-val	7	6	6
o-van-gln	9	8	7
o-van-his	9	10	7
Cu(II)-o-van-val	17	15	15
Cu(II)-o-van-gln	19	19	20
Cu(II)-o-van-his	18	19	16

3.11. *Biological activities*

The biological activity of the Schiff bases and their Cu(II) complexes (50 µg per test) *in vitro* were tested against the Gram positive bacteria *S. aureus* and Gram negative bacteria *E. coli* and *S. typhi* by the disc diffusion method [34] using agar as nutrient and ampicillin as a control. The zone of inhibition against the growth of bacteria for the Schiff bases and their Cu(II) complexes are given in table 5. From the results, it is clear that the inhibition zone of Cu(II) Schiff-base complexes are higher than those of the control and the Schiff bases alone which can be explained by the chelation [35] of the Schiff base with Cu(II). The chelation reduces the polarity of the central metal atom, mainly because of partial sharing of its positive charge with the ligand. Also, the normal cell process may be affected by the formation of hydrogen bonds, through the azomethine nitrogen atom with the active centers of cell constituents [36].

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