

“SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITIES OF BIOSENSITIVE SCHIFF BASE LIGANDS WITH Cr, Mo, W METAL CARBONYL COMPLEXES”

Amit Singhal^{1*}, Manish Kaushik², Munesh Kumar³, Manoj Agarwal⁴

¹ Department of Chemical Sciences, Jagdishprasad Jhabarmal Tibrewala University, Jhunjhunu, Rajasthan

² Department of Applied Sciences, Accurate Institute of Management & technology, Gr. Noida (U.P.)

³ Department of Chemistry, Agrasen P.G. College, Sikandrabad, Bulandshahr (U.P.)

⁴ Department of Applied Sciences, Accurate Institute of Management & technology, Gr. Noida (U.P.)

* Author for correspondence

Abstract

We have synthesized twelve polynuclear complexes $\{M(CO)_4[SB]\}$ 1a-1c, 2a-2c and 3a-3c, (1a, $M = Cr$, $SB=L^1$, $X = NH_2$; 1b, $M = Mo$, $SB=L^1$, $X = NH_2$; 1c, $M = W$, $SB=L^1$, $X = NH_2$; 2a, $M = Cr$, $SB=L^2$, $X = NO_2$; 2b, $M = Mo$, $SB=L^2$, $X = NO_2$; 2c, $M = W$, $SB=L^2$, $X = NO_2$; 3a, $M = Cr$, $SB=L^3$, $X = OCH_3$; 3b, $M = Mo$, $SB=L^3$, $X = OCH_3$; 3c, $M = W$, $SB=L^3$, $X = OCH_3$; 4a, $M = Cr$, $SB=L^4$, $X = H$; 4b, $M = Mo$, $SB=L^4$, $X = H$; 4c, $M = W$, $SB=L^4$, $X = H$) by photochemical displacement of two CO group from $M(CO)_6$ by 3-aminobenzilidene-2-amino phenol [L^1], 3-nitrobenzilidene-2-amino phenol [L^2], 4-methoxybenzilidene-2-amino phenol [L^3] and benzilidene-2-amino phenol [L^4]. The synthesized complexes exhibit variable degree of antibacterial activity. The complexes have been characterized by elemental analysis, IR, [1H]-NMR spectroscopy and magnetic studies. The spectroscopic studies suggest a bidentate behavior of the ligand via phenolic-O and imine-N donor atoms with the metal (0).

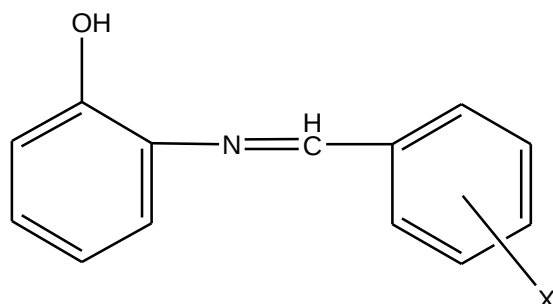
Keywords- Schiff bases, coordination chemistry, N-donor Schiff bases, antibacterial activity.

Introduction

A Schiff base is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases are of the general formula $R_1R_2C=N-R_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine. Monodentate Schiff's bases are less known to form stable complexes, probably due to the insufficient basic strength of the imino nitrogen of the C=N group.

The coordination chemistry of Schiff bases as multidentate ligands gained much importance for more than two decades because of their use as models in biological systems[1-4]. There is enormous interest presently in the field of coordination chemistry of later '3d' transition metals with Schiff bases. They have also been used as biological models [5], oxygen carriers and drugs [6]. Transition metal complexes of 1, 10-phenanthroline (phen), 2,2-bipyridyl (bpy) or their modified variants are widely employed in several research areas including bioinorganic and biomedical chemistry [7-14]. Metal complexes of the Schiff bases have been widely studied due to their unusual magnetic properties, novel structural features and relevance to biological systems [15]. We have synthesized polynuclear complexes of the type 1a-1c, 2a-2c, 3a-3c, 4a-4c and 5a-5c (1a, $M = Cr$, $L=SB^1$, $R = H$; 1b, $M = Mo$, $L=SB^1$, $R = H$; 1c, $M = W$, $L=SB^1$, $R = H$; 2a, $M = Cr$, $L=SB^2$, $R = Me$; 2b, $M = Mo$, $L=SB^2$, $R = Me$; 2c, $M = W$, $L=SB^2$, $R = Me$; 3a, $M = Cr$, $L=SB^3$, $R = Eth$; 3b, $M = Mo$, $L=SB^3$, $R = Eth$; 3c, $M = W$, $L=SB^3$, $R = Eth$; 4a, $M = Cr$, $L=SB^4$, $R = n-pr$; 4b, $M = Mo$, $L=SB^4$, $R = n-pr$; 4c, $M = W$, $L=SB^4$, $R = n-pr$; 5a, $M = Cr$, $L=SB^5$, $R = Ph$; 5b, $M = Mo$, $L=SB^5$, $R = Ph$; 5c, $M = W$, $L=SB^5$, $R = Ph$) has been synthesized by photochemical displacement of two CO groups in group-6 metal carbonyls with by 3-aminobenzilidene-2-amino phenol [L^1], 3-nitrobenzilidene-2-amino phenol [L^2], 4-methoxybenzilidene-2-amino phenol [L^3] and benzilidene-2-amino phenol [L^4]. Both the ligands & their complexes were characterized on the basis of physical properties, elemental analysis data, magnetic studies, infrared and nuclear magnetic resonance spectroscopy. It was found

that the ligands have bidentate nature coordinating through phenolic-O and imine-N donor atom. Thus replacing two CO group to maintain charge density on metal centre.



3/4 substituted benzylidene -2- aminophenol

Experimental

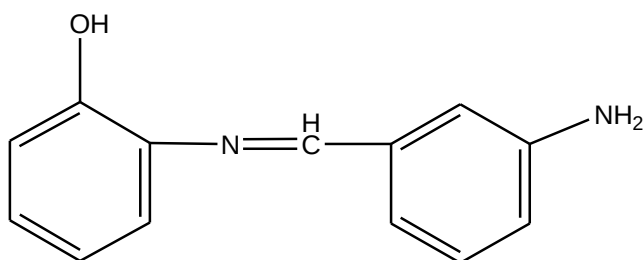
Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and CH_2Cl_2 . All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120°C , molecular weight of the complexes were determined cryoscopically in benzene, cyclooctadiene (COD), n-hexane, n-pentane, benzene were purchased from E. Merck, and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), dichloromethane were purchased from Aldrich and were used as supplied.

Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation were performed with a medium pressure 400W mercury lamp through a quartz bulb.

Synthesis of the ligands-

Synthesis of ligand 3-aminobenzilidene-2-amino phenol [L^1]

The ligand 3-aminobenzilidene-2-amino phenol [L^1] was prepared by literature method [16] as followed. A mixture of 3-amino benzaldehyde (1.21 g, 0.01M) with 2-aminophenol (1.09g, 0.01M) in 50 mL of ethanolic medium. The solid product formed was removed by filtration and recrystallized from ethanol. Yield 72%.



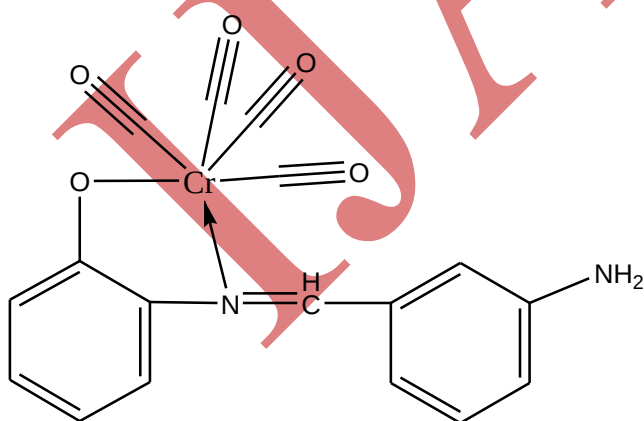
3-aminobenzylidene -2- aminophenol

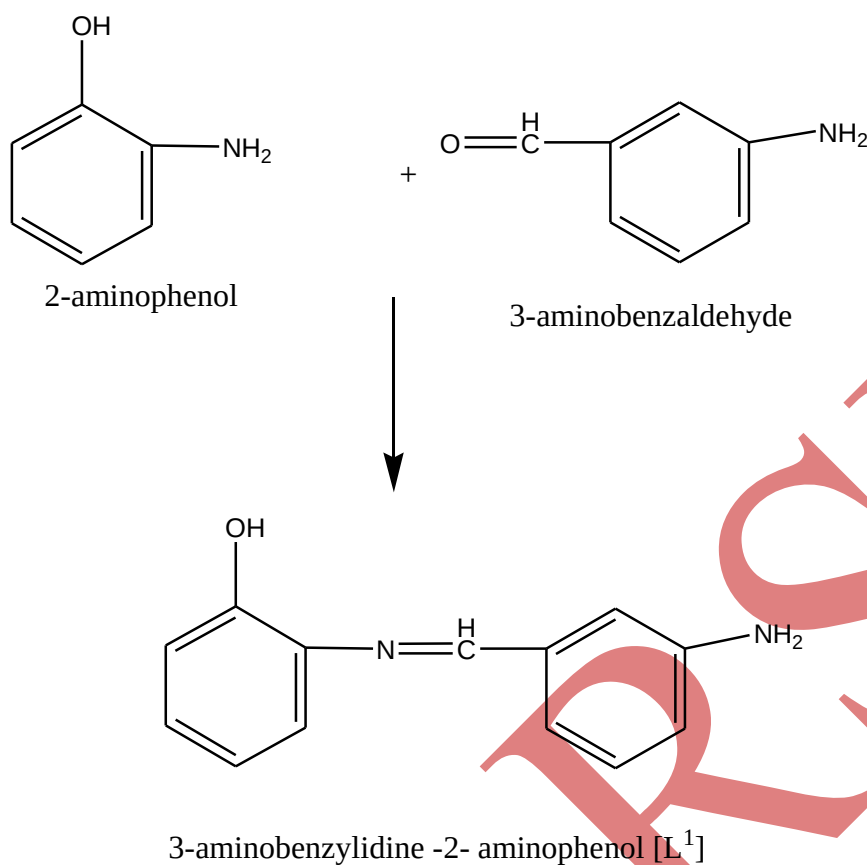
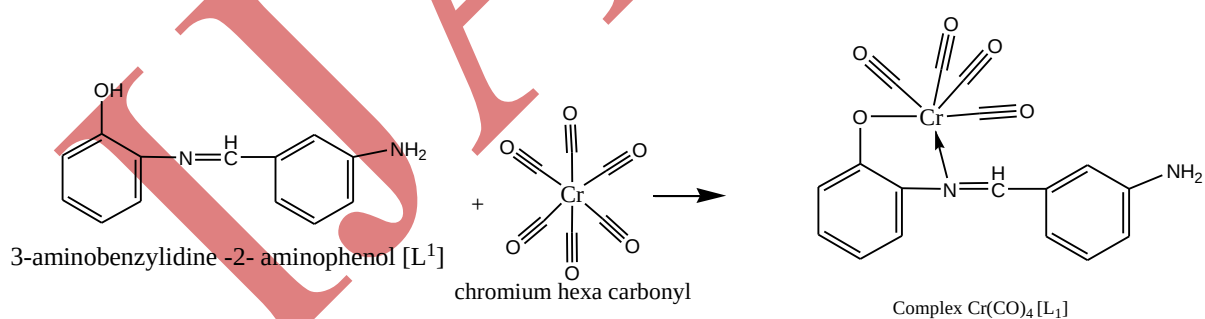
Preparation of complexes

Preparation of complex $\{\text{Cr}(\text{CO})_4[\text{L}^1]\}$

The $\text{Cr}(\text{CO})_6$ (0.110 g, 0.5 mmol) and L^1 (0.10 g, 0.5 mmol) were dissolved in DMF (40-50 cm^3). The solution was irradiated for 3 h. During the irradiation, the color of the reaction mixture changed from colourless to dark yellow. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a dark yellow solid. After dissolving in CH_2Cl_2 (10 cm^3), petroleum ether (50 cm^3) was added, resulting in the precipitation of a dark yellow solid which was washed with petroleum ether and dried under vacuum. Yield of $[\text{Cr}(\text{CO})_4(\text{L}^1)]$: 78%.

The other bisubstituted metalcarbonyl complexes of Cr, Mo, W with L^1 , L^2 , L^3 and L^4 were prepared similarly.

Complex $\text{Cr}(\text{CO})_4 [\text{L}_1]$

Scheme 1 – Preparation of Ligand [L¹]: Reaction of 3-amino benzaldehyde with 2-aminophenol**Scheme 2– Preparation of Complexes:** Reaction of 3-aminobenzylidene-2-amino phenol [L¹] with Cr(CO)₆**Table****1a – Physical and analytical data of Ligands (L¹⁻⁴)**

Ligands	Molecular Formula	Yield (%)	M.p. (°C)	Colour	Found (Calcd.) (%)			Mol. Wt.
					C	H	N	
a (L ¹)	C ₁₃ H ₁₂ N ₂ O	72.0	136	Cream	73.0 (73.5)	5.5 (5.7)	13.0 (13.2)	212.0 (212.3)
b (L ²)	C ₁₃ H ₁₀ N ₂ O ₃	71.5	142	Light yellow	64.1 (64.5)	3.9 (4.2)	11.2 (11.6)	241.6 (242.2)
c (L ³)	C ₁₄ H ₁₃ NO ₂	74.1	146	Light yellow	73.4 (74.0)	5.5 (5.8)	5.9 (6.1)	226.8 (227.3)
d (L ⁴)	C ₁₃ H ₁₁ NO	78.5	127	Yellow	78.5 (79.1)	5.2 (5.6)	6.8 (7.1)	196.8 (197.2)

Table 1 – Physical and analytical data of Complexes

Complexes	Molecular Formula	Yield (%)	M.p. (°C)	Colour	Found (Calcd.) (%)			Mol. Wt.
					C	H	N	
1a	$C_{17}H_{11}CrN_2O_5$	78	146	Light Yellow	53.9 (54.4)	2.5 (2.9)	7.1 (7.5)	374.6 (375.3)
2a	$C_{17}H_{11}MoN_2O_5$	74	154	Yellow	48.1 (48.7)	2.5 (2.6)	6.3 (6.7)	418.3 (419.2)
3a	$C_{17}H_{11}WN_2O_5$	79	165	Yellow	39.5 (40.2)	2.0 (2.2)	5.1 (5.5)	506.2 (507.1)
1b	$C_{17}H_9CrN_2O_7$	76	147	Light Yellow	49.5 (50.4)	2.0 (2.2)	6.5 (6.9)	404.6 (405.2)
2b	$C_{17}H_9MoN_2O_7$	78	155	Yellow	44.8 (45.5)	1.7 (2.0)	6.0 (6.2)	449.2 (451.0)

3b	$C_{17}H_9WN_2O_7$	76	166	Cream	37.3 (38.0)	1.4 (1.7)	4.9 (5.2)	536.3 (537.1)
1c	$C_{18}H_{12}CrNO_6$	75	147	Light Yellow	54.7 (55.4)	2.9 (3.1)	3.7 (3.6)	389.1 (390.3)
2c	$C_{18}H_{12}MoNO_6$	70	156	Yellow	49.2 (49.8)	2.5 (2.8)	3.1 (3.2)	434.9 (436.0)
3c	$C_{18}H_{12}WNO_6$	78	166	Cream	40.8 (41.4)	2.1 (2.3)	2.2 (2.7)	521.2 (522.1)
1d	$C_{17}H_{10}CrNO_5$	78	166	Light Yellow	55.9 (56.7)	2.4 (2.8)	3.5 (3.9)	359.1 (360.3)
2d	$C_{17}H_{10}MoNO_5$	74	164	Yellow	50.0 (50.5)	2.2 (2.5)	3.2 (3.5)	404.2 (406.0)
3d	$C_{17}H_{10}WNO_5$	79	175	Yellow	40.6 (41.5)	1.7 (2.0)	2.2 (2.8)	491.0 (492.1)

Table 2a. Selected IR bands (cm^{-1}) and (1H)-NMR (ppm) data of L^{1-4} ligands

Ligand	Selected IR bands (cm^{-1})		$^1\text{H-NMR}$ (in CDCl_3) δ ppm
	Imine $\nu(\text{C=N})$	Phenolic OH	
a	1594	3350	7.8 (s, 1H, $-\text{OH}$), 8.4 (s, 1H, $-\text{NH}-$), 7.36 (s, 4H, $-\text{C}_6\text{H}_4$), 1.1 (s, 2H, NH_2)
b	1592	3348	7.9 (s, 1H, $-\text{OH}$), 8.4 (s, 1H, $-\text{NH}-$), 7.34 (s, 4H, $-\text{C}_6\text{H}_4$)
c	1589	3343	7.8 (s, 1H, $-\text{OH}$), 8.3 (s, 1H, $-\text{NH}-$), 7.32 (s, 4H, $-\text{C}_6\text{H}_4$), 1.1 (s, 2H, OCH_3)
d	1594	3356	7.9 (s, 1H, $-\text{OH}$), 8.3 (s, 1H, $-\text{NH}-$), 7.33 (s, 4H, $-\text{C}_6\text{H}_4$)

Table 2b. Selected IR bands (cm^{-1}) and (^1H)-NMR (ppm) data of complexes

Complex	Selected IR bands (cm^{-1})		$^1\text{H-NMR}$ (in CDCl_3) δ ppm
	$\nu(\text{CO})$	Imine $\nu(\text{C=N})$	
1a	2067, 2015, 1957, 1932	1570	8.4 (s, 1H, $-\text{NH}-$), 7.36 (s, 4H, $-\text{C}_6\text{H}_4$), 3.49 (s, 2H, NH_2)
2a	2071, 2015, 1952, 1934	1572	8.4 (s, 1H, $-\text{NH}-$), 7.36 (s, 4H, $-\text{C}_6\text{H}_4$), 3.47 (s, 2H, NH_2)
3a	2069, 2013, 1949, 1930	1574	8.4 (s, 1H, $-\text{NH}-$), 7.36 (s, 4H, $-\text{C}_6\text{H}_4$), 3.52 (s, 2H, NH_2)
1b	2072, 2018, 1959, 1935	1577	8.4 (s, 1H, $-\text{NH}-$), 7.34 (s, 4H, $-\text{C}_6\text{H}_4$)
2b	2072, 2018, 1958, 1935	1570	8.4 (s, 1H, $-\text{NH}-$), 7.34 (s, 4H, $-\text{C}_6\text{H}_4$)
3b	2069, 2019, 1957, 1933	1572	8.4 (s, 1H, $-\text{NH}-$), 7.34 (s, 4H, $-\text{C}_6\text{H}_4$)

1c	2068, 2017, 1958, 1934	1577	8.3 (s, 1H, - <u>NH</u> -), 7.32 (s, 4H, -C ₆ H ₄) , 1.1 (s, 2H, O <u>CH</u> ₃)
2c	2067, 2015, 1957, 1932	1570	8.3 (s, 1H, - <u>NH</u> -), 7.32 (s, 4H, -C ₆ H ₄) , 1.1 (s, 2H, O <u>CH</u> ₃)
3c	2071, 2015, 1952, 1934	1572	8.3 (s, 1H, - <u>NH</u> -), 7.32 (s, 4H, -C ₆ H ₄) , 1.1 (s, 2H, O <u>CH</u> ₃)
1d	2069, 2013, 1949, 1930	1574	8.3 (s, 1H, - <u>NH</u> -), 7.33 (s, 4H, -C ₆ H ₄)
2d	2072, 2018, 1959, 1935	1577	8.3 (s, 1H, - <u>NH</u> -), 7.33 (s, 4H, -C ₆ H ₄)
3d	2072, 2018, 1958, 1935	1570	8.3 (s, 1H, - <u>NH</u> -), 7.33 (s, 4H, -C ₆ H ₄)

Results and Discussion

The ligands were prepared by condensation reaction of substituted benzaldehyde and 2-aminophenol according to Scheme-1. Complexes (1a-3d) were prepared by photochemical reaction as shown in Scheme-2. Analytical data for {M(CO)₄[L¹]} (1a-3a); {M(CO)₄[L²]} (1b-3b); {M(CO)₄[L³]} (1c-3c) and {M(CO)₄[L⁴]} (1d-3d) where (M= Cr, Mo & W); complexes are given in **Table-1**.

In this study, photochemical reactions of M(CO)₆ (M=Cr, Mo & W) with 3-aminobenzilidine-2-amino phenol [L¹], 3-nitrobenzilidine-2-amino phenol [L²], 4-methoxybenzilidine-2-amino phenol [L³] and benzilidine-2-amino phenol [L⁴] ligands occurs in expected manner, and gave hither to a series of complexes (1a)-(1d); (2a)-(2d) and (3a)-(3d) occur via the displacement of two CO from M(CO)₆ (M=Cr, Mo & W) and co-ordination of metal atom via imine-N and phenolic-O donor atoms yielding M(CO)₄L complexes.

The i.r. spectra of ligands and the corresponding complexes provide information about the metal-ligand bonding. Important IR spectral bands $M(CO)_4SB$ ($SB = 3\text{-aminobenzilidine-2-amino phenol}$ [L^1], $3\text{-nitrobenzilidine-2-amino phenol}$ [L^2], $4\text{-methoxybenzilidine-2-amino phenol}$ [L^3] and $benzilidine-2-amino phenol$ [L^4] and $M=Cr, Mo \& W$) are presented in **Table-2b**. The evidence about metal-imine nitrogen ($M-N$) bond formation is the shifting of $C=N$ vibration found at $1620\text{-}1590\text{ cm}^{-1}$ in free ligand, shifts to lower wavelength $1580\text{-}1550\text{ cm}^{-1}$ in complexes 1a-3d, showing that the ligand coordinate to metal via the imine donor atom [17]. Appearance of a new band around 1580 cm^{-1} in all complexes due to $\nu(C-O-M)$ reveals the participation of phenoxy oxygen in coordination [18, 19]. The IR spectra of the ligands shows a broad band in the region $3250\text{-}3450\text{ cm}^{-1}$ assigned to $-OH$ group. The absence of this band, noted in the spectra of the complexes, indicates the deprotonation of the $-OH$ group. The IR spectra of the metal chelates also shows some new bands in region $305\text{-}450\text{ cm}^{-1}$ which are due to the formation of $M-N$ bond.

In the proton NMR spectra of 1a-3c, the phenolic OH signal disappeared which is in agreement with the formation of metal oxygen bond [20-21]. In addition, the shift of the $C-O$ stretching vibrations in the IR spectrum shows that both imine N and phenolic O donor atoms coordinate to M atom. According to these data, L^1, L^2, L^3 & L^4 ligands behave as bidentate in 1a-3d. The L^1, L^2, L^3 & L^4 ligands must act as a 4-electron donor in order to satisfy the 18-electron rule.

Four bands in the range ($2068\text{-}2072\text{ cm}^{-1}$), ($2013\text{-}2018\text{ cm}^{-1}$), ($1949\text{-}1958\text{ cm}^{-1}$) and ($1932\text{-}1936\text{ cm}^{-1}$) arising from $\nu(CO)$ vibrations are seen which presumably have local C_{2v} symmetry of $M(CO)_4$ unit in $\{M(CO)_4L^1\}$ (1a-3a); $\{M(CO)_4L^2\}$ (1b-3b) and $\{M(CO)_4L^3\}$ (1c-3c) and $\{M(CO)_4L^4\}$ (1d-3d); where ($M=Cr, Mo \& W$); complexes (Scheme-2). These values are in close resemblance to the values of $\nu(CO)$ vibration for other nitrogen containing disubstituted group-6 metal carbonyls [22-25]. The presence of normal ligand bands indicated that these bands were intact

in the complexes. The nature and number of CO bands resemble closely to the bands of other known disubstituted metal carbonyls [26-28].

In addition, magnetic susceptibility measurement shows that (1a-3e) complexes were diamagnetic. Since these complexes have $M(0)$ [$M=Cr, Mo, W$] with a low spin d^6 configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes i.e. $d_{xy}^2, d_{xz}^2, d_{yz}^2, d_{(x^2-y^2)}^0, d_{z^2}^0$ [29, 30].

Antibacterial Activity

All the synthesized complexes were screened for their antibacterial activity by using agar diffusion method [31] against *S. aureus*, *B. subtilis* gram positive and *E. coli*, *S. paratyphi* gram negative bacteria in nutrient agar medium. Ciprofloxacin was used as standard drug for comparison.

These Schiff's Bases and their metal carbonyl complexes show antibacterial activity against *E. coli*, *S. aureus*, *B. subtilis* and *S. paratyphi*. It is found that benzilidene-2-amino phenol [L^4] studied here follow such a decomposition scheme in the cell, and diazoalkane intermediates further could alkylate the nucleophilic centres of biologically important macromolecules and in particular DNA. 3-aminobenzilidene-2-amino phenol [L^1], 3-nitrobenzilidene-2-amino phenol [L^2] and 4-methoxybenzilidene-2-amino phenol [L^3] shows moderate activity. With the help of activity data it could be observed that complexes $M(CO)_3L^4$ (1d-3d) showed good activity against *E. coli* and *S. paratyphi*. Complexes $M(CO)_3L^1$ (1a-3a), $M(CO)_3L^2$ (1b-3b), and $M(CO)_3L^3$ (1c-3c) exhibited good activity against *S. paratyphi*. A comparative study of Schiff base ligands and its complexes indicate that the metal complexes exhibit higher antibacterial activity than that of free ligand.

Conclusion

The IR spectroscopic data are in well accord with a *cis*-chelating bidentate coordination of the ligand [32] L^1 , L^2 , L^3 & L^4 ligands behave as a bidentate ligand via imine N and phenolic O donor atom in 1a-3d. In view of above, we have now investigated the twelve new complexes 1a-3d, which have been prepared for the first time, by the photochemical reaction of metal carbonyls $M(CO)_6$ ($M=Cr, Mo \text{ \& } W$), with 3/4 substituted benzylidene -2- aminophenol ($L^1, L^2, L^3 \text{ \& } L^4$).

The results show that benzilidene-2-amino phenol [L^4] and its metalcarbonyl derivatives exert a good inhibitory effect on different bacterial activity, thus confirming our previous data about the cytotoxic activity of these compounds.

Acknowledgements

Sincere thanks are due to Head, Dept. of Chemistry, A. I. M. T., Greater NOIDA, Head, Dept. of Chemical Sciences, JJTU, Rajasthan and Gaurav Pharma Limited, Pitampura, New Delhi for providing research facilities. Authors are also thankful to Dr. Vivek Kumar, Professor, IIT Roorkee, (Saharanpur Campus) for his constant encouragement to carry out such research work. Special thanks are also due to CDRI, Lucknow, Intertek, Mumbai, I.I.T., Roorkee, Research Lab, Delhi University and TIFR, Mumbai for allocation of time for various analyses.

References:

- [1] Panchal P. K. & Patel M. N., *Synth. React. Inorg. Met.-org. Chem.*, **34**, 1277 (2004).
- [2] Thomson K. S., Meneilli J. H. & Orgig C., *Chem. Rev.*, **99**, 2561 (1999).
- [3] Maurya M. R., Agarwal N. & Khurana S., *Indian J. Chem.*, **39A**, 1093 (2000).
- [4] Kumar V. & Dhakarey R., *J. Indian Counc. Chem.*, **20**, 46 (2003).
- [5] Reddy P. R., Mohan S. K., Raju R. M. & Ettaiah P., *Indian J. Chem.*, **45A**, 2381 (2006).
- [6] Biyala M. K., Fahmi N. & Singh R. V., *Indian J. Chem.*, **45A**, 1999 (2006).
- [7] Ji L. N., Zou X. H. & Liu J. G., *Coord. Chem. Rev.*, **216**, 513 (2001).
- [8] Kane-Maguire N. A. P. & Wheeler J. F., *Coord. Chem. Rev.*, **211**, 145 (2001).

- [9] Erkkila K. E., Odom D. T. & Barton J. K., *Chem. Rev.*, **99**, 2777 (1999).
- [10] Xiong Y. & Ji L. N., *Coord. Chem. Rev.*, **185**, 717 (1999).
- [11] Mesmaeker A. K., Lecomte J. P. & Kelly J. M., *Top Curr. Chem.*, **77**, 25 (1996).
- [12] Thorp H. H., *Adv. Inorg. Chem.*, **43**, 127 (1995).
- [13] Sigman O. S., Mazumder A., & Perrin D. M., *Chem. Rev.*, **93**, 2295 (1993).
- [14] Murphy C. J. & Barton J. K., *Method Enzymol*, **226**, 576 (1993).
- [15] Maurya M. R., Bharti N., Naqui F. & Azam A., *Bioinorg. Med. Chem. Lett.*, **10**, 2243 (2000).
- [16] N. Raman and J. D. Raja, *Indian J. of Chem.*, **46A**, 1611-1614 (2007).
- [17] Kovacic J. E., *Spectrochim. Acta* **23A**, 182 (1967).
- [18] Singh B. & Singh U. R., *Synth. React. Inorg. Met.-org. Chem.*, **22**, 791 (1992).
- [19] Singh B., Srivastav A. K. & Singh P. K., *Indian J. Chem.*, **36A**, 72 (1997).
- [20] Duggal H.K., Agarwala B.V., *Spectrosc Lett.*, **21**, 1 (1988).
- [21] Karacan N., Kantarer Z., Akyuz S., *Spectrochim. Acta Part A*, **52**, 771.
- [22] Kirtley S. W., in Eilkinson G., Stone F. G. A, Abel E. W., (eds): "Comprehensive Organometallic Chemistry", Pergamon Press, Oxford, Vol. 3, p 1079, 1255 (1982).
- [23] Cavallo A. S., Solladie G., Tsano E., *J. Organomet. Chem.*, **144**, 181 (1978).
- [24] Lal R., Samanta K. (nee Bera), Banerjee I., *Indian J. of Chem.*, **40A**, 144 (2001).
- [25] Kaim W., Kohlmann S., *Inorg. Chem.*, **26**, 68 (1987).
- [26] Cotton F.A., Kraihanzel, C.S., *J. Am. Chem. Soc.*, **84**, 4432 (1962).
- [27] OZER Zahida, OZKAR Saim., *Turk. J. Chem.*, **23**, 9-14, (1999).
- [28] Timmers, F.J., Wacholtz, W.F., *J. Chem. Ed.*, **71**, 987 (1994), King, R.B., Organometallic Syntheses, **Vol. 1**, Academic Press, New York, 125(1965); Abel E., Bennett, W.M.A., Burton, R. Wilkinson G., *J. Chem. Soc.*, 4559 (1958).
- [29] Senem Karahan, Ploinkose, and Elif Subasi Hamdi Temel; *Synt. and React. in Inorg., Met.-org., and Nano-Met. Chem.*, **38**, 422-427 (2008).
- [30] Singh Ayodhya, Kumar Munesh, Kaushik Manish, Singh Seema and Singh Anjali; *Oriental Journal of Chemistry*, **26(2)**, 601-606 (2010).
- [31] Barry A. L., "The antimicrobial susceptibility Test: Principal and practice", Edited by Illus Lea and Febiges, Philadelphia, Pa. U.S.A., 148-193 (1976).