International Journal of Chemistry and Applications.
ISSN 0974-3111 Volume 3, Number 1 (2011), pp. 35-47

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# Photochemical Reactions of $[M(CO)_6]$ (M=Cr, Mo & W) with Mono- and Bi-dentate Schiff base Ligands

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## Abstract

Some new noble Schiff bases viz; 2-{[(Z)-phenylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^1$); 2-{[(Z)-(3-methoxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^2$) and 2-{[(1Z)-1-phenylethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^3$) react with G-6 metal hexacarbonyl in benzene to give monosubstituted derivatives while 2-{[(Z)(2-hydroxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^4$); 2-{[(Z)(2-hydroxy-3-methoxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^5$); 2-{[(Z)-(2-hydroxynaphthalen-1-ylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^6$); 2-{[(2Z)-4-oxo-4-phenylbutan-2-ylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^7$) and 2-{[(E)-furan-2-ylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^8$) react with G-6 metal hexacarbonyl in benzene to give disubstituted derivatives. The synthesized ligands exhibit variable degree of antibacterial activities. The complexes were characterised on the basis of physical properties, elemental analysis, IR and NMR spectroscopic data.

**Keywords:** Schiff base, G-6 metal carbonyl, benzenesulphonamide and antibacterial activity

## Introduction

Compounds having sulphonamide group have long been used as drug for diseases like cancer, tuberculosis, diabetes, malaria and leprosy. It has now been observed that some of these drugs show increased biological activity when administered in the form of metal complexes (1-7). Numerous references are now available to show that the condensation products of sulpha drugs with aldehydes, ketones or their derivatives are biologically very active, besides having good complexing ability. Their activity has also been shown to increase on complexation with metal ions, (8-9). Numerous compounds containing a sulphonamide group or hydrazine residue, or their combination in one molecule, show cytostatic and antibacterial activity (10-12). The compounds bearing thiazole moiety have been found to possess antibacterial, antitubercular and anti-inflammatory activity (13).

However, from literature survey it appears that no G-6 metal carbonyl complexes with these Schiff bases have yet been reported. In search of more biologically effective agent and industrial utility led to explore a variety of chemical entities with biological properties. In this paper we have used eight schiff bases (fig-I) namely 2-{[(Z)phenylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^1$); 2-{[(Z)-(3-methoxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^2$); 2-{[(1Z)-1-phenylethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^3$); 2-{[(Z)(2-hydroxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^4$); 2-{[(Z)(2-hydroxy-3-methoxyphenyl)methylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^5$); 2-{[(Z)-(2-hydroxynaphthalen-1-ylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^6$); 2-{[(2Z)-4-oxo-4-phenylbutan-2-ylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^7$) and 2-{[(E)-furan-2-ylmethylidene]amino}-N-(1,3-thiazol-2-yl)benzenesulphonamide ($SB^8$) as ligand in the CO displacement reaction of $M(CO)_6$ (where M=Cr, Mo & W) have been investigated. We describe the preparation and characterization of new complexes $\{M(CO)_5[SB^1]\}$; $\{M(CO)_5[SB^2]\}$; $\{M(CO)_5[SB^3]\}$; $\{M(CO)_4[SB^4]\}$; $\{M(CO)_4[SB^5]\}$; $\{M(CO)_4[SB^6]\}$; $\{M(CO)_4[SB^7]\}$and $\{M(CO)_4[SB^8]$, (where M=Cr, Mo & W) which were prepared by photochemical reaction between $M(CO)_6$ with $[SB^1]$- $[SB^8]$.The complexes were characterised by physical, elemental, IR and $^1H$ NMR analyses. The spectroscopic studies suggest mono-dentate coordination of ligands in $\{M(CO)_5[SB^1]\}$; $\{M(CO)_5[SB^2]\}$; $\{M(CO)_5[SB^3]\}$and bidentate coordination of the ligands in $\{M(CO)_4[SB^4]\}$; $\{M(CO)_4[SB^5]\}$; $\{M(CO)_4[SB^6]\}$; $\{M(CO)_4[SB^7]\}$and $\{M(CO)_4[SB^8]$, (where M=Cr, Mo & W).

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. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120ºC, molecular weight of the complexes were determined cryoscopically in benzene. Organic solvent and silica gel were purchased from E. Merk and $M(CO)_6$ (M=Cr, Mo & W) were purchased from Aldrich, 2-Aminobenzene sulphonamide and sulpha drugs sulphathiazole were purchased from Sigma, USA and used as supplied.

The schiff's bases $SB^1$, $SB^2$, $SB^3$, $SB^4$, $SB^5$, $SB^6$, $SB^7$ and $SB^8$ were prepared by following the literature procedure [14]. Magnetic susceptibity measurements of the complexes were carried out by Gouy method. $^1H$ NMR data were recorded in $CDCl_3$ or DMSO on a 500MHz Brucker FT-NMR at Tata Institute of fundamental Research, Mumbai, India .UV irradiation were performed with a medium pressure 400W mercury lamp in a quartz bulb.

**Synthesis-1**

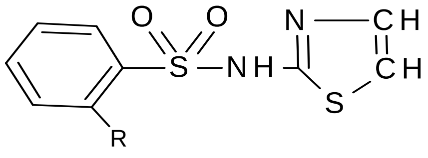
The complexes, (1a)-(3c) were prepared by the photochemical reactions of metal carbonyls M(CO)$_6$ (M=Cr, Mo & W) with SB$^1$, SB$^2$ and SB$^3$ and were obtained in70 to 78% yield by the method given below.

The complex Cr(CO)$_6$ (0.330g, 1.5 m mole) and SB$^1$ (0.560g; 1.5 m mole) were dissolved in DMF (50 cm$^3$). The solution was irradiated for 5h. During the irradiation the colour of the reaction mixture changed from off white to yellow. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a dark yellow solid. After dissolving in $CH_2Cl_2$ (15 cm$^3$), petroleum ether (55cm$^3$) was added, resulting in the precipitation of a dark yellow solid which was washed with petroleum ether and dried under vacuum. Yield of [Cr(CO)$_5$[SB$^1$]}; 73%. The other penta carbonyl complexes of Cr, Mo and W with SB$^1$, SB$^2$ and SB$^3$ were prepared similarly.

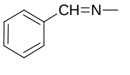
**Synthesis-2**

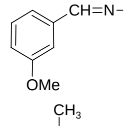
The complexes, (4a)-(8c) were prepared by the photochemical reactions of metal carbonyls M(CO)$_6$ (M=Cr, Mo & W) with SB$^4$, SB$^5$ , SB$^6$, SB$^7$ and SB$^8$ and were obtained in60 to 68% yield by the method given below.

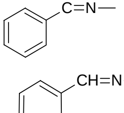
The complex Cr(CO)$_6$ (0.220g, 1.0 m mole) and SB$^4$ (0.359g; 1.0 m mole) were dissolved in Toluene (50 cm$^3$). The solution was irradiated for 9h. During the irradiation the colour of the reaction mixture changed from off white to dark yellow or brown. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a deep brown solid. After dissolving in $CH_2Cl_2$ (10 cm$^3$), petroleum ether and hexane (50:50cm$^3$) was added, resulting in the precipitation of a brown solid which was washed with petroleum ether and hexane mixture (1:1) and dried under vacuum. Yield of [Cr(CO)$_4$[SB$^4$]}; 64%. The other tetra carbonyl complexes of Cr, Mo and W with SB$^4$, SB$^5$, SB$^6$, SB$^7$ and SB$^8$ were prepared similarly.

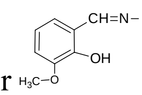


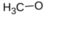
I

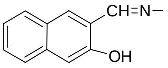
1. SB$^1$; R=$C_7H_6N$ or 

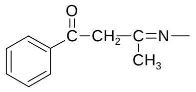
2. SB$^2$; R=$C_8H_8ON$ or 

3. SB$^3$; R=$C_8H_8N$ or 

4. SB$^4$; R=$C_7H_6ON$ or 

5. SB$^5$; R=$C_8H_8O_2N$ or 

6. SB$^6$; R=$C_{11}H_8ON$ or 

7. SB$^7$; R=$C_{10}H_{10}ON$ or 

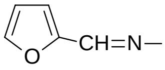
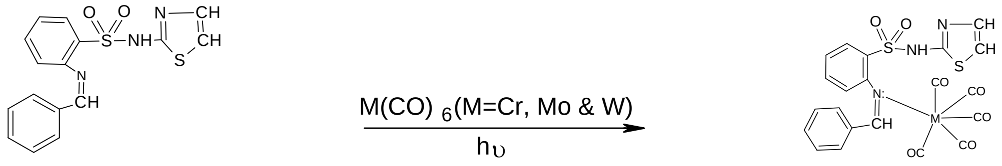
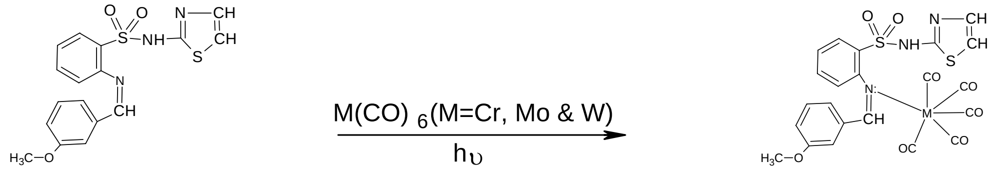
8. SB$^8$; R=$C_5H_4ON$ or 

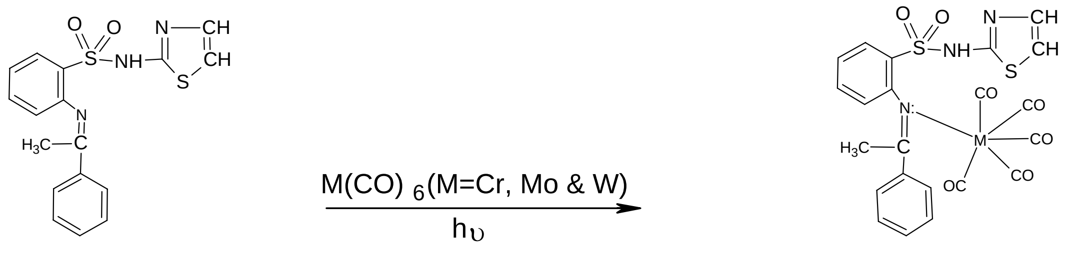
Fig: (I) Structural Representation and abbreviation of the Schiff's bases used in this study.



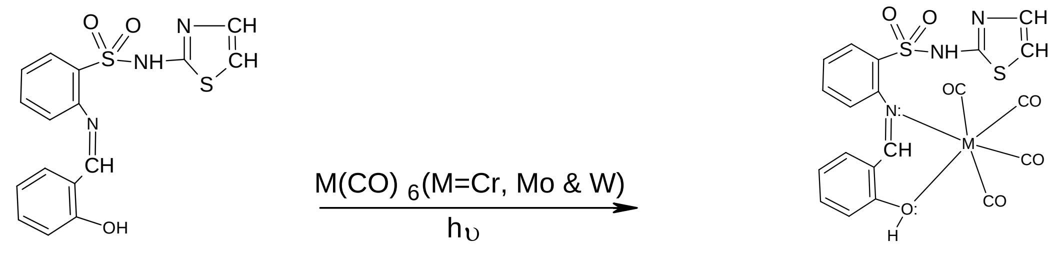
(SB$^1$) Scheme-I (1a-1c)



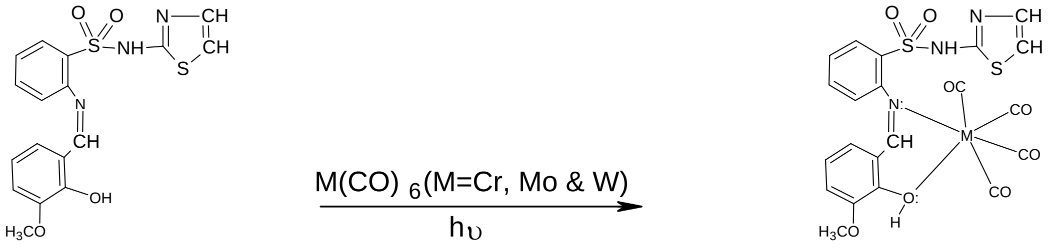
(SB$^2$) Scheme-II (2a-2c)



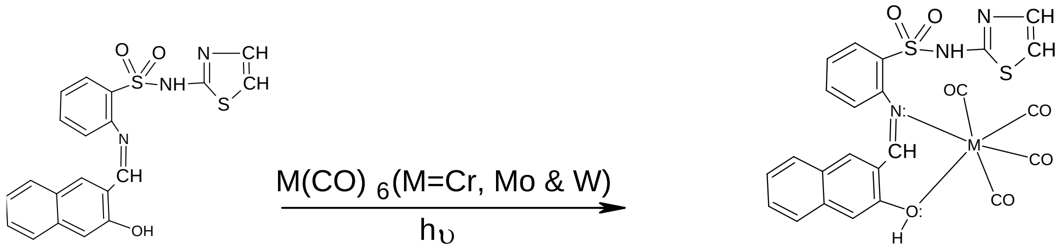
(SB$^3$) Scheme-III (3a-3c)



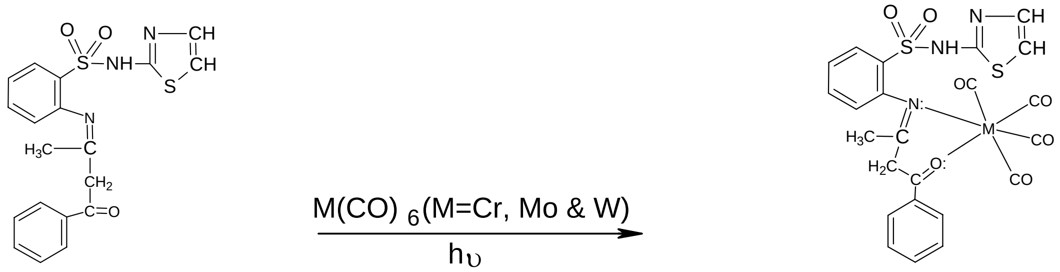
(SB$^4$) Scheme-IV (4a-4c)



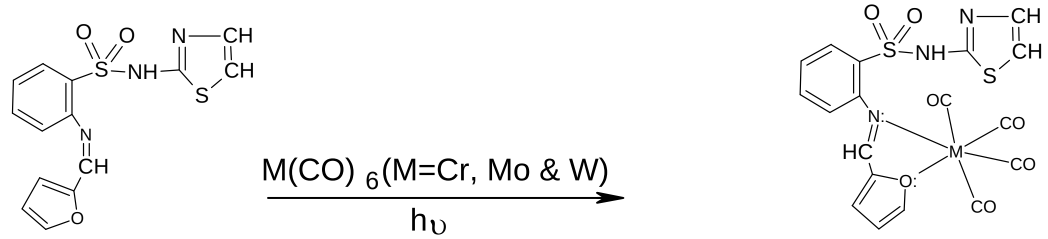
(SB$^5$) Scheme-V (5a-5c)



(SB$^6$) Scheme-VI (6a-6c)



(SB$^7$) Scheme-VII (7a-7c)



(SB$^8$) Scheme-VIII (8a-8c)

**Scheme I to VIII:** Synthesis of complexes (1a)-(8c) from M(CO)$_6$ (M=Cr, Mo & W) and SB$^1$, SB$^2$, SB$^3$, SB$^4$, SB$^5$, SB$^6$, SB$^7$ & SB$^8$ ligands.

**Table1:** Physical & analytical data of Ligands.

| S.No. | Abbreviation of schiff's base | Empirical formula | Color | Yield % | Mol. Wt. | Melting point °C | Found (calculated)% | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | N | S |
| 1 | [SB[1]] | $C_{16}H_{13}N_3O_2S_2$ | Off white | 81 | 343 | 88 | 55.42 (55.98) | 3.75 (3.79) | 12.22 (12.24) | 18.60 (18.66) |
| 2 | [SB[2]] | $C_{17}H_{15}N_3O_3S_2$ | Off white | 79 | 373 | 93 | 54.15 (54.69) | 3.96 (4.02) | 11.16 (11.26) | 17.07 (17.16) |
| 3 | [SB[3]] | $C_{17}H_{15}N_3O_2S_2$ | Light Yellow | 80 | 357 | 97 | 56.40 (57.14) | 4.24 (4.20) | 11.60 (11.76) | 17.80 (17.93) |
| 4 | [SB[4]] | $C_{16}H_{13}N_3O_3S_2$ | Off white | 80 | 359 | 95 | 53.20 (53.48) | 3.66 (3.62) | 11.60 (11.70) | 17.70 (17.83) |
| 5 | [SB[5]] | $C_{17}H_{15}N_3O_4S_2$ | Light Yellow | 82 | 389 | 98 | 52.05 (52.44) | 3.89 (3.86) | 10.72 (10.80) | 16.32 (16.45) |
| 6 | [SB[6]] | $C_{20}H_{15}N_3O_3S_2$ | Off white | 79 | 409 | 93 | 57.30 (58.68) | 3.64 (3.67) | 10.15 (10.27) | 15.53 (15.65) |
| 7 | [SB[7]] | $C_{19}H_{17}N_3O_3S_2$ | Light Yellow | 78 | 399 | 95 | 56.30 (57.14) | 4.20 (4.26) | 11.43 (10.53) | 15.88 (16.04) |
| 8 | [SB[8]] | $C_{14}H_{11}N_3O_3S_2$ | Off white | 83 | 333 | 98 | 49.90 (50.45) | 3.36 (3.30) | 12.53 (12.61) | 19.09 (19.22) |

**Table2:** Physical & analytical data of Complexes.

| Complexes. | Empirical formula | Color | Yield% | Mol. Wt. | Melting point °C | Found (calculated)% | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | S |
| 1a | $C_{21}H_{13}N_3O_7S_2Cr$ | yellow | 63 | 535 | 153 | 46.86 (47.10) | 2.40 (2.43) | 7.81 (7.85) | 11.92 (11.96) |
| 1b | $C_{21}H_{13}N_3O_7S_2Mo$ | yellow | 68 | 579 | 159 | 43.40 (43.52) | 2.22 (2.25) | 7.23 (7.25) | 11.00 (11.05) |
| 1c | $C_{21}H_{13}N_3O_7S_2W$ | yellow | 66 | 667 | 165 | 37.43 (37.78) | 1.90 (1.95) | 6.28 (6.30) | 9.56 (9.60) |
| 2a | $C_{22}H_{15}N_3O_8S_2Cr$ | yellow | 64 | 565 | 167 | 46.40 (46.73) | 2.63 (2.65) | 7.41 (7.43) | 11.28 (11.33) |
| 2b | $C_{22}H_{15}N_3O_8S_2Mo$ | yellow | 72 | 609 | 162 | 43.03 (43.35) | 2.44 (2.46) | 6.86 (6.90) | 10.47 (10.51) |
| 2c | $C_{22}H_{15}N_3O_8S_2W$ | yellow | 69 | 697 | 170 | 37.56 (37.88) | 2.13 (2.15) | 6.01 (6.03) | 9.16 (9.18) |
| 3a | $C_{22}H_{15}N_3O_7S_2Cr$ | yellow | 66 | 549 | 161 | 37.72 (48.09) | 2.71 (2.73) | 7.63 (7.65) | 11.61 (11.66) |
| 3b | $C_{22}H_{15}N_3O_7S_2Mo$ | yellow | 70 | 593 | 166 | 44.11 (44.52) | 2.52 (2.53) | 7.05 (7.08) | 10.75 (10.79) |
| 3c | $C_{22}H_{15}N_3O_7S_2W$ | yellow | 68 | 681 | 159 | 38.37 (38.77) | 2.19 (2.20) | 6.15 (6.17) | 9.35 (9.40) |
| 4a | $C_{20}H_{13}N_3O_7S_2Cr$ | dark brown | 65 | 523 | 150 | 45.58 (45.89) | 2.45 (2.49) | 8.01 (8.03) | 12.18 (12.24) |
| 4b | $C_{20}H_{13}N_3O_7S_2Mo$ | dark brown | 68 | 567 | 157 | 42.00 (42.33) | 2.28 (2.29) | 7.40 (7.41) | 11.23 (11.29) |
| 4c | $C_{20}H_{13}N_3O_7S_2W$ | dark brown | 72 | 655 | 159 | 36.37 (36.64) | 1.97 (1.98) | 6.39 (6.41) | 9.73 (9.77) |
| 5a | $C_{21}H_{15}N_3O_8S_2Cr$ | dark brown | 71 | 553 | 165 | 45.35 (45.57) | 2.70 (2.71) | 7.56 (7.59) | 11.50 (11.57) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5b | $C_{21}H_{15}N_3O_8S_2Mo$ | dark brown | 66 | 597 | 152 | 42.00 (42.21) | 2.50 (2.51) | 7.02 (7.04) | 10.67 (10.72) |
| 5c | $C_{21}H_{15}N_3O_8S_2W$ | dark brown | 69 | 685 | 170 | 36.38 (36.79) | 2.17 (2.19) | 6.10 (6.13) | 9.30 (9.34) |
| 6a | $C_{24}H_{15}N_3O_7S_2Cr$ | dark brown | 68 | 573 | 158 | 50.00 (50.26) | 2.61 (2.62) | 7.32 (7.33) | 11.10 (11.17) |
| 6b | $C_{24}H_{15}N_3O_7S_2Mo$ | dark brown | 72 | 617 | 157 | 46.35 (46.68) | 2.42 (2.43) | 6.80 (6.81) | 10.25 (10.37) |
| 6c | $C_{24}H_{15}N_3O_7S_2W$ | dark brown | 71 | 705 | 168 | 40.58 (40.85) | 2.11 (2.13) | 5.93 (5.96) | 9.05 (9.08) |
| 7a | $C_{23}H_{17}N_3O_7S_2Cr$ | dark brown | 71 | 563 | 164 | 48.80 (49.02) | 3.01 (3.02) | 7.44 (7.46) | 11.31 (11.37) |
| 7b | $C_{23}H_{17}N_3O_7S_2Mo$ | dark brown | 66 | 607 | 166 | 45.14 (45.47) | 2.81 (2.80) | 6.90 (6.92) | 10.50 (10.54) |
| 7c | $C_{23}H_{17}N_3O_7S_2W$ | dark brown | 69 | 695 | 168 | 39.50 (39.71) | 2.44 (2.45) | 6.05 (6.04) | 9.20 (9.21) |
| 8a | $C_{18}H_{11}N_3O_7S_2Cr$ | dark brown | 65 | 497 | 169 | 43.25 (43.46) | 2.19 (2.21) | 8.40 (8.45) | 12.84 (12.88) |
| 8b | $C_{18}H_{11}N_3O_7S_2Mo$ | dark brown | 68 | 541 | 159 | 39.70 (39.93) | 2.00 (2.03) | 7.70 (7.76) | 11.78 (11.83) |
| 8c | $C_{18}H_{11}N_3O_7S_2W$ | dark brown | 72 | 629 | 158 | 34.17 (34.34) | 1.74 (1.75) | 6.65 (6.68) | 10.15 (10.17) |

**Table 3:** Selected IR bands (cm$^{-1}$) of Schiff's bases.

| S.No. | Schiff's base | ν(NH) sulphonamide group | ν(C-O) phenolic/enolic | ν(C-N) aromatic | ν(C=N) | ν($SO_2$) | ν(C-S-C) Thiazole ring |
|---|---|---|---|---|---|---|---|
| 1 | [SB$^1$] | 3435 bs | - | 1310s | 1610s | 1360,1140 | 743 |
| 2 | [SB$^2$] | 3430 bs | - | 1306s | 1605s | 1356,1135 | 744 |
| 3 | [SB$^3$] | 3440 bs | - | 1308s | 1615s | 1358,1137 | 747 |
| 4 | [SB$^4$] | 2425 bs | 1275m | 1308s | 1612s | 1362,1143 | 748 |
| 5 | [SB$^5$] | 2420 bs | 1270m | 1312s | 1608s | 1352,1132 | 746 |
| 6 | [SB$^6$] | 3425 bs | 1278m | 1309s | 1610s | 1354,1134 | 747 |
| 7 | [SB$^7$] | 3430 bs | 1272m | 1307s | 1608s | 1355,1134 | 748 |
| 8 | [SB$^8$] | 3425 bs | 1278m | 1312s | 1609s | 1359,1140 | 745 |

bs = broad sharp, s = sharp, m=medium

**Table 4:** Selected IR bands cm$^{-1}$ of Complexes.

| Complexes | ν(CO) cm$^{-1}$ | | | | |
|---|---|---|---|---|---|
| 1a | 2072m | 1986m | 1945s | 1932s | 1891m |
| 1b | 2075m | 1991m | 1952s | 1924s | 1880m |
| 1c | 2080m | 1955m | 1955s | 1941s | 1895m |
| 2a | 2075m | 1984m | 1948s | 1939s | 1896m |
| 2b | 2086m | 1994m | 1964s | 1927s | 1889m |
| 2c | 2072m | 1986m | 1948s | 1930s | 1891m |

| | | | | | |
|---|---|---|---|---|---|
| 3a | 2074m | 1990m | 1947s | 1935s | 1890m |
| 3b | 2079m | 1994m | 1959s | 1926s | 1882m |
| 3c | 2075m | 1986m | 1961s | 1930s | 1892m |
| 4a | 2074w | 2023m | 1965m | 1940s | - |
| 4b | 2073w | 2021m | 1963m | 1938s | - |
| 4c | 2077w | 2021m | 1958m | 1940s | - |
| 5a | 2075w | 2019m | 1955m | 1936s | - |
| 5b | 2078w | 2024m | 1965m | 1941s | - |
| 5c | 2078w | 2024m | 1965m | 1941s | - |
| 6a | 2075w | 2025m | 1963m | 1939s | - |
| 6b | 2074w | 2024m | 1964m | 1941s | - |
| 6c | 2080w | 2026m | 1963m | 1942s | - |
| 7a | 2079w | 1982m | 1956m | 1938s | - |
| 7b | 2082w | 1985m | 1953m | 1943s | - |
| 7c | 2087w | 1987m | 1964m | 1942s | - |
| 8a | 2076w | 2022s | 1962m | 1937s | - |
| 8b | 2079w | 2019m | 1956m | 1940s | - |
| 8c | 2084w | 2028m | 1953m | 1942s | - |

s = sharp, m = medium, w = weak

**Table 5:** Selected $^1$H NMR data of Schiff base ligands and complexes.

| Schiff base/ complexes | Azomethine (-CH=N-) 1H | (O-H) 1H | (Ar-H) 4H | ($SO_2NH$) group 1H | ($OCH_3$) 3H | ($CH_3$-C=N-) 3H | (CO-$CH_2$ – C) |
|---|---|---|---|---|---|---|---|
| $SB^1$ | 8.88(s) | - | 6.95-7.55 (d) | 10.15(s) | - | - | - |
| 1a | 9.02(s) | - | 7.02-7.67 (d) | 10.15(s) | - | - | - |
| 1b | 9.01(s) | - | 7.03-7.68 (d) | 10.15(s) | - | - | - |
| 1c | 9.03(s) | - | 7.04-7.70 (d) | 10.15(s) | - | - | - |
| $SB^2$ | 8.90(s) | - | 6.88-7.60 (d) | 10.18(s) | 3.45(s) | - | - |
| 2a | 9.03(s) | - | 6.94-7.74 (d) | 10.18(s) | 3.42(s) | - | - |
| 2b | 9.04(s) | - | 6.93-7.72 (d) | 10.18(s) | 3.41(s) | - | - |
| 2c | 9.04(s) | - | 6.95-7.75 (d) | 10.18(s) | 3.42(s) | - | - |
| $SB^3$ | - | - | 6.85-7.50 (d) | 10.15(s) | - | 1.95(s) | - |
| 3a | - | - | 6.90-7.64 (d) | 10.15(s) | - | 2.10(s) | - |
| 3b | - | - | 6.91-7.63 (d) | 10.15(s) | - | 2.09(s) | - |
| 3c | - | - | 6.92-7.65 (d) | 10.15(s) | - | 2.09(s) | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| SB$^4$ | 8.85(s) | 12.80(bs) | 6.80-7.60 (d) | 10.18(s) | - | - | - |
| 4a | 8.99(s) | 12.86(bs) | 6.85-7.73 (d) | 10.18(s) | - | - | - |
| 4b | 9.00(s) | 12.85(bs) | 6.86-7.74 (d) | 10.18(s) | - | - | - |
| 4c | 8.98(s) | 12.87(bs) | 6.86-7.75 (d) | 10.18(s) | - | - | - |
| SB$^5$ | 8.80(s) | 12.88(bs) | 6.90-7.55 (d) | 10.15(s) | 3.50 | - | - |
| 5a | 8.94(s) | 12.93(bs) | 6.94-7.68 (d) | 10.15(s) | 3.48 | - | - |
| 5b | 8.95(s) | 12.95(bs) | 6.95-7.67 (d) | 10.15(s) | 3.47 | - | - |
| 5c | 8.93(s) | 12.94(bs) | 6.96-7.68 (d) | 10.15(s) | 3.46 | - | - |
| SB$^6$ | 8.85(s) | 12.90(bs) | 6.95-7.50 (d) | 10.17(s) | - | 1.90(s) | - |
| 6a | 8.98(s) | 12.96(bs) | 6.99-7.65 (d) | 10.17(s) | - | 2.05(s) | - |
| 6b | 8.99(s) | 12.98(bs) | 7.00-7.64 (d) | 10.17(s) | - | 2.03(s) | - |
| 6c | 8.97(s) | 12.97(bs) | 6.98-7.63 (d) | 10.17(s) | - | 2.04(s) | - |
| SB$^7$ | - | - | 6.75-7.55 (d) | 10.15(s) | - | 1.90(s) | 5.25(s) |
| 7a | - | - | 6.81-7.68 (d) | 10.15(s) | - | 2.04(s) | 5.29(s) |
| 7b | - | - | 6.82-7.69 (d) | 10.15(s) | - | 2.05(s) | 5.28(s) |
| 7c | - | - | 6.82-7.68 (d) | 10.15(s) | - | 2.06(s) | 5.30(s) |
| SB$^8$ | 8.80(s) | - | 6.98-7.60 (d) | 10.15(s) | - | - | - |
| 8a | 8.93(s) | - | 7.04-7.74 (d) | 10.15(s) | - | - | - |
| 8b | 8.94(s) | - | 7.05-7.75 (d) | 10.15(s) | - | - | - |
| 8c | 8.92(s) | - | 7.05-7.73 (d) | 10.15(s) | - | - | - |

s = singlet, d = doublet, bs = broad sharp

## Result & Discussion

The complexes, (1a)-(8c) were prepared by the photochemical reaction as shown in scheme (I) to (VIII). Analytical data for {M(CO)$_5$[SB$^1$]}; {M(CO)$_5$[SB$^2$]}; {M(CO)$_5$[SB$^3$]}; {M(CO)$_4$[SB$^4$]}; {M(CO)$_4$[SB$^5$]}; {M(CO)$_4$[SB$^6$]}; {M(CO)$_4$[SB$^7$]}and {M(CO)$_4$[SB$^8$] where M=Cr, Mo & W; complexes are given in Table-2. The photo generation of M(CO)$_5$ from M(CO)$_6$ (M=Cr, Mo & W) has been extensively studied. These 16-electron M(CO)$_5$ fragments react quickly with any available donor to form M(CO)$_5$L species; and if L is a chelating bidentate ligand rapid continuation to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}(\mu\text{-}L)$products may occur [15-20]

In this study photochemical reaction of $M(CO)_6$ (M=Cr, Mo & W) with ($SB^1$)-($SB^8$) Schiff base ligands proceed in this expected manner and gave hither to a unknown series of complexes (1a)-(1c); (2a)-(2c); (3a)-(3c); (4a)-(4c); (5a)-(5c); (6a)-(6c); (7a)-(7c) and (8a)-(8c).

Infrared spectra of all the Schiff bases show a new band in the range 1608-1615 $cm^{-1}$, attributable to the formation of an imino group which was shifted to a lower frequency region about 1590-1595 $cm^{-1}$ in complexes (1a)-(8c) indicating that the ν(C=N) group is taking part in co-ordination to $M(CO)_5$ and $M(CO)_4$ fragment [20-23]. This may be due to decrease in the bond order of ν(C=N) or weakening of the C=N bond resulting from the loss of electron density from the nitrogen to the metal atom (Cr, Mo & W) [20-24]. Which is further supported by the presence of new band in the range 385-395 $cm^{-1}$(s) in the far-IR spectra of the complexes which may be assigned to the ν(M-N) mode[24]. No shifting upon complex formation was observed for the ν asy ($SO_2$), ν sym ($SO_2$), ν(NH) and ν(C-S-C of thiazole ring) stretching vibrations indicating that ($SO_2$), NH and CS groups were not co-ordinated to metal atoms in (1a)-(8c) [19]. OH stretching vibration was not observed for the free ligands $SB^4$, $SB^5$ and $SB^6$ nor for (4a)-(6c) because of hydrogen bonding with the imine nitrogen atom [12, 19, 25]. A strong bond in the range 1270-1278 $cm^{-1}$ in the $SB^4$, $SB^5$, and $SB_6$ may be due to phenolic C-O while in $SB^7$, $SB^8$ may be due to enolic stretching vibrations. In the resulting complexes (4a)-(8c) a shift of this bond to higher frequency in the range 1285-1295 $cm^{-1}$ indicates the bonding of tha ligand through the phenolic or enolic oxygen with metal atom (Cr, Mo, W) without the elimination of hydrogen atom from the OH group, which were also confirmed by the appearance of a new band in the spectra of the metal complexes (4a)-(8c) at 520-583 $cm^{-1}$described to M←O vibrations {26-28], which were not seen in the spectra of ($SB^4$, $SB^5$,$SB^6$, $SB^7$& $SB^8$) ligands.

In addition, magnetic susceptibility measurement shows that (1a)-(8c) complexes were diamagnetic, since these complexes have M(o) (M=Cr, Mo, W)with a low spin $d^6$ configuration . Such diamagnatism might arise from further splitting of the d-orbital in the low symmetry complexes, i.e. $d_x{}^2{}_y$, $d_{xz}{}^2$, $d_y{}^2{}_{z,}$ $d({}_x{}^2{}_{-y}{}^2)^0$, $d_{zz}{}^{0.}$

The number of carbonyl bands provides important clues to the environment of the metal centers [30]. Five carbonyl stretching bands in (1a)-(3c) are attributed to local $C_{4v}$ for $M(CO)_5$ [15-19]. Similarly, four CO stretching absorptions in (4a)-(8c) indicate to local $C_{2v}$ symmetry [19,30]. The ν(CO) modes in (1a)-(8c) move also to lower wave number when compared with the starting carbonyl complexes [16,17, 19].

In the $^1H$ NMR spectra of (1a)-(8c) NH proton of free ligand at 10.27ppm remains approximately unchanged, inferring involvement of the NH group in the complexes. The data also show that NH group does not participate in co-ordination. The small shifting for HC=N proton may be related to decreasing π electron density in C=N bond with complex formation in (1a)-(8c). According to these data, $SB^1$, $SB^2$ & $SB^3$ ligands behave as monodentate in (1a)-(3c).

However in the NMR spectrum of $M(CO)_4[SB^4]$, $M(CO)_4[SB^5]$ and $M(CO)_4[SB^6]$ the phenolic OH signal disappeared which is in agreement with the formation of metal oxygen bond [19, 31, 32]. The NH signal was found 10.27 ppm remains approximately unchanged, inferring the involvement of NH group in complexes. In addition, the shift of the CO stretching vibration in the IR spectrum shows that both imine N and phenolic O-donor atoms co-ordinated to metal atom (Cr or Mo or W). Kinemetic coupling of the CO group with the bonded metal ion would increase the frequencies [33]. According to these data SB$^4$, SB$^5$ and SB$^6$ ligand behave as bidentate in (4a)-(6c). The SB$^4$, SB$^5$ and SB$^6$ ligands must act as a 4-electron donor in order to satisfy the 18-electron rule. Spectroscopic studies show that the SB$^1$, SB$^2$ and SB$^3$ ligands behave as a monodentate ligands via N imine donor atom in (1a)-(3c). While SB$^4$, SB$^5$, SB$^6$, SB$^7$and SB$^8$ ligands are co-ordinated to the central metal as bidentate ligands co-ordinating via their imine N and O donor atoms in (4a)-(8c).

## Antibacterial Activity

The newly synthesized Schiff base ligands (SB$^1$)-(SB$^8$) were screened in vitro for their antibacterial activity against Escherichia coli, Salmonella, para typhi negative bacteria and S.aureas, B. subtile gram positive bacteria in nutrient agar medium by using agar diffusion method [33]. Ciprofloxacin was used as standard drug (control) for comparison.

With the help of activity data it could be observed that synthesized Schiff bases having azomethine group and heteroaromatic moiety exhibit extensive antibacterial activity [34, 35] due to increased liposolubility of the molecules in crossing cell membrane of the microorganism. The antibacterial activity is found to be in the order control >SB$^5$ >SB$^2$ >SB$^8$ >SB$^3$ >SB$^6$ >SB$^7$ >SB$^4$ >SB$^1$ for both positive and negative bacteria under study.

## Summary

In summary SB$^1$, SB$^2$ and SB$^3$ behave as monodentate ligands via N- imine donor atom in complexes (1a)-(1c), (2a)-(2c) and (3a)-(3c) while SB$^4$, SB$^5$, SB$^6$ behave as bidentate ligands via phenolic-O and imine-N donor atom in complexes (4a)-(4c), (5a)-(5c) and (6a)-(6c) and SB$^7$ behave as bidentate ligand via ketonic-O and imine-N donor atom in complexes (7a)-(7c)and also SB$^8$ behave as bidentate ligand via furonoyl-O and imine-N donor atom in complexes (8a)-(8c).

## Acknowledgement

Sincere thanks are due to Head, Department of Chemistry, M.M.H. College, Ghaziabad for providing research facilities. Authors are also thankful to Dr. M.P. Singh, Principal, M.M.H. College, Ghaziabad for his constant encouragement to carry out such research work. Special thanks are also due to CDRI, Lucknow, Intertek, Mumbai for allocation of time for various analyses.

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