Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1199–1208

Synthesis, Characterisation and Applications of Some New 5-Substituted-4-Thiazolidinone-2-Thioxo Azo Derivatives

RITA BAJPAI, SANJAY TIWARI, K.S. TIWARI and B.M.L. TIWARI*
Department of Chemistry
Government Model (Autonomous) Science College, Rewa-486 001, India

4-Thiazolidinone-2-thioxo **(I)** has been refluxed separately with untried phenylazo-salicylaldehydes to get some new chelating 5-substituted-4-thiazolidinone-2-thioxo azo derivatives **(II–V)**. For comparison the 5-(salicylidene) derivative **(VI)** has also been explored. Their characterisation has been done by chemical and spectral data. The azo derivatives **(II–V)** have been used in dyeing a variety of fabrics and histological staining. The derivatives **(II–VI)** have shown distinctive antimicrobial activity as antibacterial, antifungal and antitubercular; and are capable of acting as specific spot test and chromatographic spray reagents. Their toxicity effect and insecticidal activity have been determined with respect to mortality of mosquito larvae, culex and anopheles sp.

INTRODUCTION

Recently, heterocyclic azo compounds have received much attention.[1–13] However, a literature survey reveals the absence of systematic study on 5-substituted-4-thiazolidinone-2-thioxo azo derivatives **(II–V)** with polydentate coordination sites. These derivatives belong to a class of compounds[10–20] which have versatile analytical and pharmacological properties such as bactericides, insecticides, fungicides, herbicides, aldose reductase, anti-viral, anti-inflammatory and anti-cancerous. On these findings a systematic study of synthesis and applications of some new heterocyclic azo compounds **(II–V)** was of interest.

EXPERIMENTAL

4-Thiazolidinone-2-thioxo **(I)** and used phenylazo salicylaldehydes were prepared.[21–23] M.p.s were determined on Gallen Kamp apparatus and are uncorrected. Carbon, hydrogen and nitrogen were estimated by Heraues Carlo Erba-1108 elemental analyser. Sulphur was estimated by Messenger's method and molecular weights were determined by Rast mehod. the IR (KBr), electronic (DMF + DMSO) and ^1H NMR ($CDCl_3$ + DMSO-d_6/TMS) spectra were recorded on Perkin-Elmer-1800 (FTIR), Shimadzu UV-160-PC-controlled

*For correspondence: 41/187, Near Bichhiya Hospital, Rewa-486 001 (M.P.), India.

and Varian EM-360L spectrophotometers repsectively. All chemicals used were of AR grade.

Synthesis

5-(5′-Phenylazo-salicylidene)-4-thiazolidinone-2-thioxo, (II): A mixture of phenylazo salicylaldehyde (2.25 g) and **(I)** (1.33 g) in glacial acetic acid (15 mL) was refluxed on a water bath for 3 h, then cooled. The resulting solid was crystallised from glacial acetic acid as brown crystals (2.0 g, 58.5%), m.p. 225–226°C. Analysis: Calcd. for $C_{16}H_{11}N_3O_2S_2$: C, 56.30; H, 3.22; N, 12.31; S, 18.68. Found: C, 55.44; H, 3.55; N, 11.72; S, 18.60. m.w.: Required, 341. Found, 342.5. IR (4000–700 cm^{-1}): 3800–3560 (w), 3040 (s), 1720 (s), 1580 (s), 1480 (s), 1440 (s), 1340 (s), 1280 (s), 1240 (s), 1180 (s), 1140 (m), 1060 (m), 1020 (s), 960 (m), 920 (m), 820 (s) and 780 (s); UV (λ, nm) : 271 and 348; ^1H NMR (δ, ppm): 2.0 (s), 6.95 (w), 7.05 (w), 7.15 (m), 7.28 (m), 7.70 (m), 7.75 (m), 7.85 (m) and 8.0 (s).

5-(5′-*p*-Methoxy phenylazo-salicylidene)-4-thiazolidinone-2-thioxo, (III): Its preparation method was similar to that of **II** except that *p*-methoxy phenylazo salicylaldehyde (2.56 g) was used and the refluxing time was 45 min; dark brown crystals (2.2 g, 56.69%); m.p. 220–221°C. Analysis: Calcd. for $C_{17}H_{13}N_3O_3S_2$: C, 54.98; H, 3.52; N, 11.32; S, 17.25. Found: C, 54.23; H, 4.09; N, 11.28; S, 16.99. m.w.: Required, 371. Found, 373. IR (4000–700 cm^{-1}): 4000–3360 (w), 3040 (s), 2880 (w), 2800 (s), 1700 (s), 1660 (s), 1580 (s), 1500 (s), 1480 (s), 1445 (m), 1380 (s), 1340 (s), 1275 (s), 1240 (s), 1170 (s), 1120 (s), 1020 (s), 960 (m), 880 (s), 840 (s), 820 (w) and 780 (s); UV (λ, nm): 273 and 348; ^1H NMR (δ, ppm): 2.0 (s), 3.85 (vs), 6.90 (m), 7.0 (s), 7.10 (w), 7.25 (m), 7.75 (m), 7.80 (s), 7.85 (m) and 7.96 (s).

5-(5′-*o*-Methyl phenylazo-salicylidene)-4-thiazolidinone-2-thioxo, (IV): It was obtained by making use of *o*-methyl phenylazo-salicylaldehyde (2.4 g), refluxing time 3 h and processing as for **II**. Brown crystals (2.5 g, 67.02%), m.p. 238–240°C. Analysis: Calcd. for $C_{17}H_{13}N_3O_3S_2$: C, 57.46; H, 3.66; N, 11.83; S, 18.02. Found: C, 56.99; H, 3.82; N, 11.69; S, 17.84. m.w.: Required, 355. Found, 354. IR (4000–700 cm^{-1}) : 4000–3600 (w), 3050 (s), 1700 (w), 1580 (s), 1480 (s), 1460 (s), 1440 (s), 1330 (s), 1280 (m), 1240 (m), 1170 (s), 1120 (w), 1080 (s), 1000 (m), 880 (s), 820 (s) and 780 (s); UV (λ, nm): 273 and 348; ^1H NMR (δ, ppm): 1.25 (m), 2.0 (s), 6.95 (w), 7.05 (w), 7.10 (w), 7.28 (m), 7.70 (m), 7.80 (m), 7.85 (m) and 7.98 (s).

5-(5′-*p*-Methyl phenylazo-salicylidene)-4-thiazolidinone-2-thioxo, (V): It preparation technique was similar to that of **IV** except that *p*-methyl phenylazo-salicylaldehyde was used. Brown crystals (2.45 g, 65.68%), m.p. 227–228°C. Analysis: Calcd. for $C_{17}H_{13}N_3O_2S_2$: C, 57.46; H, 3.66; N, 11.83; S, 18.02. Found: C, 56.97; H, 4.05; N, 11.78; S, 17.95. m.w.: Required, 355. Found, 358. IR (4000–700 cm^{-1}): 4000–3580 (w), 3040 (s), 1700 (s), 1595 (s), 1480 (s), 1460 (s), 1445 (s), 1340 (s), 1275 (m), 1240 (s), 1180 (s), 1140 (m), 1100 (s), 1060 (s), 1020 (w), 960 (w), 920 (w), 880 (s), 820 (s) and 780 (s); UV (λ, nm): 271 and

348; ^{1}H NMR (δ, ppm): 1.25 (m), 2.0 (s), 7.05 (s), 7.15 (w), 7.25 (w), 7.30 (m), 7.70 (m), 7.80 (m), 7.85 (m) and 7.98 (s).

5-(Salicylidene)-4-thiazolidinone-2-thioxo, (VI): 1.3 mL of salicylaldehyde, reflux time 4.5 h and earlier followed technique **(II)** was used to obtain orange-yellow crystals (1.5 g, 55.5%), m.p. 210–211°C. Analysis: Calcd. for $C_{10}H_7NO_2S_2$: C, 50.63; H, 2.95; N, 5.90; S, 27.00. Found: C, 50.02; H, 3.10; N, 6.08; S, 26.56. m.w.: Required, 237. Found, 235.5. IR (4000–700 cm^{-1}): 4000–3640 (w), 3040 (s), 1700 (s), 1660 (s), 1540 (s), 1520 (s), 1480 (s), 1445 (s), 1340 (w), 1300 (s), 1280 (s), 1240 (s), 1170 (s), 1100 (m), 1080 (s), 1020 (s), 900 (m), 880 (m), 820 (s) and 780 (s); UV (λ, nm): 269, 302 and 393; ^{1}H NMR (δ, ppm): 2.85 (s), 6.80–7.00 (br m), 780 (m) and 7.95 (s).

Dyeing process[24–26]: For scouring the selected fabric (2 g) was boiled with 1% aq. NaOH (50 mL, 30 min), cooled and washed with water. The scoured fabric was then worked up in dye **(II–V)** bath (1% w/v in dil. CH_3COOH, pH 3–3.5, 40 mL, 25–100°C) for 1 h, washed well with water, dried in air and then subjected to soap and light-fastness tests. The percentage exhaustion study of the dyes was performed using standard procedure. The observed results are given in Table-1.

Histological staining[24]: A small portion of frog's muscle and in turn cardiac fibres were first teased, washed with water, dehydrated (30, 50, 70 and 90% grades; 5 min in each) with ethanol and then treated individually with different stains (0.5% w/v in dil. CH_3COOH) of **II–V** for 10 min. After this the staining materials were washed with 90% ethanol to remove excess stains, dehydrated in absolute ethanol (7 min), treated with xylol (2 min) to have fineness of the stain and mounted in canadabalsam. The slides so obtained were viewed under a microscope to evaluate the quality of stain. The noted results are summarised in Table-1.

TABLE-1
DYEING AND STAINING PROPERTIES OF **II–V**

Deriva-tives	Silk		Cotton		Wool		Nylon		Polyester		Muscle/cardiac fibres	
	a	b	a	b	a	b	a	b	a	b	c	d
II	MB	71	GB	68	SW	68	Iv	68	LB	72	LB	BB
III	OB	72	SW	70	MB	69	Y	70	BR	71	LB	BB
IV	LfB	73	GB	69	SW	70	Iv	68	LB	73	LfB	LB
V	MB	71	LB	8	RB	68	Y	69	BR	72	OB	Purple

Note: (a) Colour of dyed fabric, (b) % exhaustion, (c) stained stripped muscle colour, (d) stained un-stripped muscle colour; BB = bright brown, BR = brownish-red, GB = golden brown, Iv = ivory, LB = light brown, LfB = left brown, MB = mercedeas brown, OB = orange brown, RB = reddish brown, SW = sandal wood, Y = yellow.

Biological screening[10–19]: The antimicrobial activity of **II–VI** was evaluated *in vitro* by using some selected bacterial and fungal species. The inhibitory zone by "Agar diffusion method" [Laben (1950)] was used to determine the potentiality of **II–VI**. To inhibit the growth of selected test organism, the solutions (DMF) of **II–VI** were employed at 10–50 μg mL^{-1} concentrations. For bacterial species the incubation period demanded 24 h (37°C) but for fungal species it required 8 days (27°C). All the experiments were done in triplicate. The average minimum inhibitory concentrations (MIC) were estimated in respect of produced zone of inhibition (> 15 mm). The results are given in Table-2.

TABLE-2
ANTIMICROBIAL ACTIVITY OF **II-VI**

Test species	MIC, μg mL^{-1}				
	II	**III**	**IV**	**V**	**VI**
Bacterial:					
E. Aeruginosa	20.0	30.0	40.0	40.0	25.0
P. Putida	22.5	32.5	40.0	45.0	27.5
Rhz. sp.	25.0	35.0	45.0	45.0	32.5
S. faecalis	12.0	18.5	22.5	22.5	15.0
S. aureus	17.5	22.0	24.5	24.5	20.0
B. subtilis	20.0	30.0	35.0	35.0	25.0
Fungal:					
S. schenckii	25.0	40.0	50.0	50.0	32.5
A. fumigates	25.0	45.0	50.0	50.0	35.0
Tubercular:					
Mycobacterium tuberculosis $H_{37}Ra$	95.0	105.0	108.0	108.0	100.0

Insecticidal activity[27–30]: Mosquito (anopheles and culex sp.) eggs were collected, identified and kept separately in proper environment for hatching. The ethanolic-DMF (5 : 1) solutions (10 mL), with different concentrations (0.01, 0.02, 0.05, 0.1 and 0.2%), of II–VI were tested for insecticidal activity against twenty mosquito larvae, at subsequent developing stages, in water (100 mL). The best results of toxicity effect were found for 0.1% concentration and the same are recorded in Table-3. The study of metamorphosis, of mentioned mosquito species, revealed that the percent pupation gets markedly reduced at 0.1% concentration solution (ethanol-DMF, 5 : 1) as: *ca.* 95(III); *ca.* 90(IV–V); *ca.* 87–85(II); *ca.* 82–8(VI) % with respect to control.

Spot tests: A drop of derivative's **(II–VI)** solution (0.01%, DMF) was added to few drops of alcoholic solutions (0.01 M) of the respective metal salts (Cl^-, NO_3^-) on a spot plate. Then two drops of NH_4OH (aq. 5%) were added to each of these reaction mixtures. The specific colours so developed have been recorded in Table-4.

TABLE-3
INSECTICIDAL ACTIVITY OF II–VI

Larva in subsequent stages	Time (min) for 100% morality; 0.1% solution; 25°C					
	II	III	IV	V	VI	Control
Anopheles sp.						
Wrigglers	11.0	8.5	10.8	10.8	15.0	80.0
3-day old	12.8	8.5	12.5	12.6	19.0	95.0
6-day old	13.5	11.0	13.4	13.5	21.5	110.0
Full grown	15.2	14.0	14.8	15.0	25.0	125.0
Culex sp.						
Wrigglers	11.4	8.2	11.0	10.8	14.5	79.0
3-day old	12.6	9.5	12.5	12.4	18.5	98.0
6-day old	13.4	10.9	13.5	13.4	22.0	110.0
Full grown	15.5	13.9	14.8	15.0	24.8	124.8

TABLE-4
SPOT-TESTS OF CATIONS BY II–VI

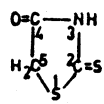
Cations	II	III	IV	V	VI
Ag^{+}	Dark brown*	Brown*	Black*	Blackish*-brown	Reddish-brown*
Mn^{2+}	Light brown	Light brown	Light brown	Light brown	Pinkish-orange
Ni^{2+}	Greenish-yellow	Greenish-yellow	Dark brown	Dark brown	Reddish-brown
Cu^{2+}	Blue*	Bluish-green*	Greenish-brown*	Greenish-brown*	Reddish-brown*
Zn^{2+}	Reddish*	Yellowish-brown*	Light brown*	Light brown*	Orange*
Cd^{2+}	Orange brown	Yellow	Light brown	Light brown	Yellowish-orange
Hg^{2+}	Pinkish-brown*	Canary	Yellowish-brown	Yellowish-brown	Brown*
Pb^{2+}	Yellow	Yellow	Light brown	Light brown	Orange
Cr^{3+}	Bluish-brown	Bluish-brown	Brownish-green	Brownish-green	Reddish-green
Fe^{3+}	Reddish-brown*	Reddish-brown*	Brown*	Brown*	Reddish-brown*
Co^{3+}	Orange	Dark brown	Green	Green	Orange
Ti^{3+}	Yellowish-brown	Yellowish-green	Yellowish-brown	Yellowish-brown	Orange

*Colour with precipitate

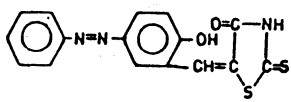
The IR (KBr) spectra of the relevant Ag^+ and Cu^{2+} complexes showed the absence of bands at 3050–3040, 1480, 1340–1330, 1280–1275, 1180–1170 and 780 cm^{-1} which were featuring in **II–VI**. In addition to this a slight lengthening (*ca.* 5 cm^{-1}) of bands orginally present at 1720–1700, 1445–1440 and 1240 cm^{-1} was also observed.

Chromatographic separation[40]**:** It was executed on chromatographic filter paper (30 × 2.5 cm) number one. The n-butyl alcohol mixed with glacial acetic acid 5% w/v) and the same alcohol saturated with 3N HCl were used as developing solvents for Ag^+, Pb^{2+}, and Cu^{2+}, Cd^{2+} separations respectively. The separation time required 12 h in case of the former and 16 h for subsequent metal ion pairs. The spray reagents used were 0.01% solutions (DMF) of **II–VI**. The noted colour of spots and determined R_f values were:

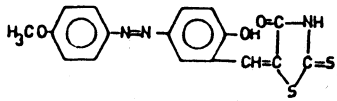
Ag^+ (Brown, **II–VI**; Reddish-brown, **VI**; 0.14–0.16); Pb^{2+} (Yellow; 0.078–0.084); Cu^{2+} (Pink, **II**; Greenish-brown, **III**; Reddish-brown, **II–V**; Brown, **VI**; 0.18–0.22) and Cu^{2+} (Yellow, **II–V**; Orange, **VI**; 0.72–0.77).



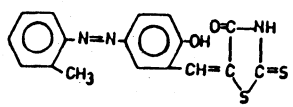
I



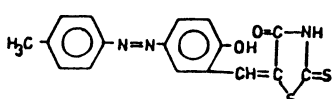
II



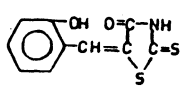
III



IV



V



VI

RESULTS AND DISCUSSION

The given structures of **II–VI** are based on observed analytical data, IR, ^1H NMR and electronic spectra.

Infrared spectra: The IR spectra[31–39] of **II–VI** showed no indication of a –SH band in the region 2600–2500 cm^{-1} but exhibited a strong vibration at 1480 cm^{-1} corresponding to mixed vibration of mercaptomide band. Along with usual absorptions of aromatic rings the derivatives **(II–VI)** showed bands at 1720–1700; 1180–1170 and 780; 3050–3040, 1340–1330 and 1280–1275 and 4000–3360, 1445–1440 and 1240 cm^{-1} pertaining to ν(C=O); ν(C=S); ν(NH) and ν(OH) respectively. The sharp bands observed in the region 1595–1580 cm^{-1} were attributed to ν(N=N) in phenylazo derivatives **(II–V)**. A weak band at 2880 and a sharp band at 2800 cm^{-1}, corresponding to the presence of —OCH_3 group, were noticed in **III**. The existence of a strong band at 1460 cm^{-1} confirmed the presence of —CH_3 group in **IV** and **V**.

The IR spectra of Ag^+ and Cu^{2+} complexes showed the absence of bands at 3050–3040, 1480, 1340–1330, 1280–1275; 1180–1170 and 780 cm^{-1}, while these bands were featuring in **II–VI**. From this it is evident that the coordination of respective metal ions has taken place with thio-carbonyl and nitrogen atoms of 4-thiazolidinone-2-thioxo part of **II–VI**. As a consequence the above bands pertaining to ν(NH) and ν(C=S) were found missing in the respective complexes of Ag^+ and Cu^{2+}. This finding gets further support by the slight lengthening (*ca.* 5 cm^{-1}) of bands corresponding to ν(C=O) (1720–1700 cm^{-1}) and ν(OH) (1445–1440 and 1240 cm^{-1}) on coordination. Hence, it confirms the bidentate nature of these ligands **(II–VI)** with N, S donor set.

Electronic spectra: The electronic spectra[31–39] of the derivatives **(II–VI)** showed characteristic maxima for π-π* transitions, corresponding to the conjugated aromatic rings related to thio-keto structure, in the range 269–302 nm. The brown coloured phenylazo derivatives **(II–V)** exhibited identical λ_{max} value, 348 nm, in respect of n-π* transitions. From this it seems that their brown colour is mainly due to the presence of an independent chromophore (—N=N—) with an auxochrome (—OH). The substitution by —OCH_3 and —CH_3 groups in the terminal benzene ring brought no apparent change in colour and λ_{max} vlaue of these derivatives **(II–V)**. The colour of the remaining derivative **(VI)** is orange-yellow and its λ_{max} appeared at 393 nm. Probably due to absence of —N=N the n-π* transitions of —C=S group have appeared at a longer wavelength and so the colour of **VI** has lightened.

^1H NMR Spectra[31–39]: The ^1H NMR spectra of 4-thiazolidinone-2-thioxo **(I)** displayed sharp resonances at δ 8.0 and 7.45 ppm assignable to —NH and —CH_2 protons, situated at third and fifth positions respectively. All derivatives **(II–VI)** exhibited sharp resonances at *ca.* 7.95–8.0 ppm in their respective ^1H NMR spectra. The presence of this sharp singlet indicates that, on coupling **I** with

other entities to get **II–VI**, there is no appreciable change in the local electron density about the —NH group.

The ^{1}H NMR spectra of **VI** exhibited resonances at δ 7.95 (s; —NH), 7.80 (m; —C=CH), 7.0–6.80 (br m; Ar—H) and 2.85 (s; —OH) ppm. It is interesting to note that the —NH proton virtually remains unaffected upon coupling of salicylaldehyde with 4-thiazolidinone-2-thioxo (**I**). But the downfield shift of the —CH_2 protons clearly suggests that the coupling of salicylaldehyde has taken place at the fifth position of **I**.

Further, **II** resulted through addition of phenylazo entity to **VI**. Due to this coupling the —OH proton experienced an upfield shift and resonated at δ 2.0 ppm. Similarly the resonances corresponding to Ar—H and —C=CH in **VI** have got influenced and appeared in **II** as multiplet in the region δ 6.95–7.85 ppm.

In the ^{1}H NMR spectra of **III–V** the —OH, Ar—H and —C=CH protons resonated at about same position. However, in **III** the methoxy group protons resonated at δ 3.85 (s) ppm while in **IV–V** a medium intensity band was observed at δ 1.25 ppm. It confirmed the presence of —CH_3 protons associated with terminal aromatic ring in **IV** and **V**.

Dyeing of fabrics: The phenylazo derivatives (**II–V**) have successfully been used as azo dye in dyeing silk, cotton, wool, nylon and polyester fabrics. The imparted colours (Table-1), various shades of brown, sandal-wood, yellow and ivory, to fabrics were found stable and passed the soap and light-fastness tests. The percentage exhaustion of the dyes (**II–V**) for fibres containing nucleophilic groups was found *ca.* 68–70% but for fibres devoid of nucleophilic groups it was noted to be *ca.* 71–73%.

Histological staining: The phenylazo derivatives (**II–V**) stain the stripped as well as unstripped muscle fibres (Table-1) of frog to impart brown colours in general. However, the purple colour generated by **V**, in case of unstripped muscle fibres, was adjudged to be of quality grade. The cardiac fibres showed alike proneness to **II–V**.

Biological screening: It was found (Table-2) that solutions (DMF) of all derivatives (**II–VI**) are remarkably active against *S. faecalis* and *S. aureus* with MIC values ranging in between 12.0–22.5 and 17.5–24.5 μg mL^{-1} respectively. The derivatives were also found sensitive against *E. aeruginosa*, *P. putida*, *Rhz.* sp. and *B. subtilis* as their respective MIC values were: 20–25 (**II**), 25–32.5 (**VI**), 30–35 (**III**) and 35–45 (**IV–V**) μg mL^{-1}. Among fungal species the *S. schenckii* and *A. fumigates* were found equally affected and the observed MIC values were: 25.0 (**II**), 32.5, 35.0 (**VI**), 40.0, 45.0 (**III**) and 50.0 (**IV–V**) μg mL^{-1} respectively. The antitubercular screening *in vitro* against *Mycobacterium tuberculosis* $H_{37}Ra$, showed MIC values as: 95 (**II**), 100 (**VI**), 105 (**III**) and 108 (**IV–V**) μg mL^{-1}. From all these findings it is evident that the coupling of phenylazo part with **VI** makes **II** comparatively more sensitive. But the sensitivity of **II** gets gradually reduced on introducing —OCH_3 (**III**) or —CH_3 group (**IV–V**) in the terminal benzene ring.

Insecticidal activity: The study of insecticidal activity (Table-3) in respect

of 100% mortality of twenty mosquito larvae (anopheles and culex sp.) revealed that the best results are obtained at 0.1% concentration and the order of toxicity is **III** > **IV** = **V** > **II** > **VI** > > > ethanol-DMF. At similar concentration of **II–VI**, the study of metamorphosis showed a marked reduction in per cent pupation (95–81%) with respect to control and confirmed the above mentioned order of toxicity.

Analytical applications: The treatment of alcoholic solutions (0.01 M) of respective metal ions Ag^{+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Ti^{3+}) with solutions (0.01% DMF) of **II–VI**, in presence of NH_4OH (aq. 5%), generated specific colours and in some cases (Ag^{+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Fe^{3+}) a coloured precipitate was also obtained (Table-4). From this it is evident that these derivatives may be employed as spot-test reagents. It appears that **II–VI** form coloured lakes or soluble metal complexes through their available donor sites. The bidentate nature of these ligands **(II–VI)** have earlier been confirmed by the infra-red study of their respective Ag^{+} and Cu^{2+} complexes.

The paper chromatographic identification[40] of Ag^{+} (R_f: 0.14–0.16) from Pb^{2+} (R_f: 0.078–0.084) and of Cu^{2+} (R_f: 0.18–0.22) from Cd^{2+} (R_f: 0.72–0.77) has successfully been done on the basis of distinctive coloured spots. This justifies that these derivatives **(II–VII)** may be used as good spray (0.01%, DMF) reagents.

Conclusions

The synthesis and characterisation of some new chelating 5-substituted-4-thiazolidinone-2-thioxo azo derivatives **(II–V)** has successfully been achieved. As per expectation these derivatives showed good dyeing, staining, antibacterial, antifungal and insecticidal activity. The **II** appeared to be more active than **VI** but its activity reduced on introducing —OCH_3 **(III)** or —CH_3 group **(IV–V)** in the terminal benzene ring. The derivatives **(II–VI)** have been used as specific spot-test reagents, in the detection of several metal ions, on one hand and as chromatographic spray reagents in the separation of Ag^{+}-Pb^{2+}, Cu^{2+}-Cd^{2+} on the other. In this course of action, the derivatives behave as bidentate ligands with their N, S donor set.

ACKNOWLEDGEMENTS

The authors are grateful ot Dr. S.M. Verma, Prof. Emeritus of BHU, and Dr. V.S. Jolly, Jt. Director, Cancer Research Institute, Gwalior (M.P.), for their interest and valuable suggestions; Director CDRI, Lucknow (U.P.) and Dr. G.K. Jain, Asstt. Director Toxicology Division in particular; Environmental Biology and Chemistry Departments of A.P.S. University, Rewa (M.P.) and Principal Govt. Model (Autn.) Science College, Rewa (M.P.) for facilities. One of us (BMLT) is thankful to UGC, New Dehi, for financial assistance.

REFERENCES

1. N.M. Naik and K.R. Desai, *J. Indian Chem. Soc.*, **66**, 35 (1989).
2. R. Jain, D.D. Agarwal and R. Shrivastava, *J. Indian Chem. Soc.*, **66**, 59 (1989).
3. M. Debi, *J. Indian Chem. Soc.*, **66**, 489 (1989).
4. R. Jain and H.K. Pardasani, *Indian J. Heterocycl. Chem.*, **1**, 79 (1991) and *Proc. Indian Natn. Sci. Acad.*, **62**, 317 (1996).
5. B.B. Mahapatra and P.K. Bhoi, *J. Indian Chem. Soc.*, **69**, 14 (1992).
6. P. Majumdar, A.K. Deb and S. Goswami, *Proc. Indian Acad. Sci. (Chem.Sci.)*, **110**, 2 (1998).
7. K. Bag, T.K. Misra and C. Sinha, *J. Indian Chem. Soc.*, **75**, 421 (1998).
8. T.K. Misra, P.K. Santra and C. Sinha, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **110**, 445 (1998).
9. T.K. Misra, D. Das and C. Sinha, *J. Indian Chem. Soc.*, **76**, 125 (1999).
10. P.B. Talukdar, S.K. Sengupta, and A.K. Dutta, *Indian J. Chem.*, **6**, 607 (1971).
11. R.F. Gureva and S.B. Savin, *Zh. Anal. Khim.*, **44**, 2165 (1989).
12. Wang, Zhongyi, Shi, *Yungyong Huaxue*, **15**, 277 (1993).
13. Wang, Lun S. Zhongyi, *Yungyong Huaxue*, **16**, 91 (1994).
14. H.H. Moharram, Elmm Abdel Fattah, Merzabani and S.A. Mansour, *Egypt. J. Chem.*, **26**, 301 (1983).
15. R.R. Mohr and M. Shrivastava, *Indian Drugs*, **26**, 342 (1989).
16. N.N. Roeva S.B. Sewen and M.E. Flyashberg, *Zh. Anal. Khim.*, **95**, 461 (1991).
17. G. Donia Shafie, Ibrahim and M. Tarek, *Bol. Soc. Quim. Peru*, **58**, 90 (1992).
18. Ya Gorishnyv, O.V. Vladzimirskaya and K.M. Ali, *Farm. Zh. (Kiev)*, **2**, 66 (1995).
19. V.H. Shah, N.A. Chauhan and A.R. Parikh, *J. Indian Chem. Soc.*, **74**, 243 (1997).
20. R. Singh, A.K. Choubey and A. Bhattacharya, *J. Indian Chem. Soc.*, **75**, 430 (1998).
21. P.L. Jullian and B.M. Sturgis, *J. Am. Chem. Soc.*, **57**, 1127 (1937).
22. P.N. Mohandas and C.P. Trivedi, *J. Indian Chem. Soc.*, **49**, 739 (1972).
23. K.S. Tiwari, Ph.D. Thesis, APSU (1981).
24. M.C. Patni, Ph.D. Thesis, APSU (1974).
25. N.M. Naik and K.R. Desai, *J. Indian Chem. Soc.*, **66**, 35, 495 (1989).
26. B.R. Modi, B.D. Mistry and K.R. Desai, *J. Indian Chem. Soc.*, **73**, 439 (1996).
27. D.N. Chaudhary and B.P. Das, *Curr. Sci.* (India), **49**, 344 (1979).
28. S.H. Elatmany, I.M. El-deen and M.F. Abdel-Fattah, *J. Indian Chem. Soc.*, **76**, 367 (1996).
29. B.S. Garg, M.B. Aggarwal, R.K. Sharma, V. Kumar and R.K. Seth, *J. Indian Chem. Soc.*, **75**, 4 (1998).
30. R. Vajpai, B.M.L. Tiwari and K.S. Tiwari, *Asian J. Chem.*, **11**, 414 (1999).
31. J. Brown, *Chem. Rev.*, **61**, 476 (1961).
32. F.G. Moers and J.J. Steggerda, *J. Inorg. Nucl. Chem.*, **30**, 3217 (1968).
33. R. Hilal, H. Ead and A. Osman, *Appl. Spectrosc.*, **32**, 557 (1978).
34. T. Allan and R.E. Lenkiski, *Inorg. Chim. Acta*, **L21**, 136 (1987).
35. J.S. Shukla and R. Shukla, *J. Indian Chem. Soc.*, **66**, 209 (1989).
36. A. Jain and A.K. Mukherjee, *J. Indian Chem. Soc.*, **67**, 973 (1990).
37. C.N.R. Rao, Ultraviolet and Visible Spectroscopy and Chemical Applications, Buttrworths, London (1961).
38. R.M. Silverstein and G.C. Bassler, Spectrometric Identification of Organic Compounds, 2nd Edn., J. Wiley, New York (1968).
39. D.H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th Edn., Tata McGraw-Hill, New Delhi (1988).
40. A.I. Vogel, A Text Book of Macro and Semi-micro Qualitative Inorganic Analysis, 4th Edn., Longmans, London, p. 623 (1960).

(*Received:* 15 May 2000; *Accepted:* 17 July 2000) AJC-2076