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# Synthesis, Characterization and Antitumor Activity of Manganese(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Platinum(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones

M. MOHAN*, A. KUMAR, M. KUMAR

*Department of Chemistry, N.R.E.C. College, Khurja-203 131 (U.P.), India*

and N. K. JHA

*Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi-110 016, India*

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## Abstract

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pt(II) with 3- and 5-substituted salicylaldehyde benzoylhydrazones (XSBH, X = H, 3-$NO_2$, 3-$CH_3O$, 5-Br, 5-Cl, 5-$CH_3$ or 5-$NO_2$) were prepared and characterized by elemental analyses, conductance measurements, magnetic moments (300–78 K) and spectral studies. On the basis of these studies the following structures are suggested: distorted octahedral for $Mn(XSBH)_2$, dimeric, low-spin, five-coordinate for $Ni(XSBH)Cl\cdot 2H_2O$, dimeric, high-spin, five-coordinate for $Co(XSBH)Cl\cdot 2H_2O$, dimeric four-coordinate for Zn(XSBH) and a square-planar structure for $M(XSBH)Cl\cdot H_2O$ (M = Cu(II) or Pt(II)). The polycrystalline ESR spectra of Cu(II) complexes are isotropic and indicate a $d_{x^2-y^2}$ ground state in square-planar stereochemistry. All the metal(II) complexes were screened for their antitumor activity against the P388 lymphocytic leukaemia test system in mice and were found to possess no significant activity at the dosages used.

## Introduction

Aroylhydrazones have been shown to possess modest bacteriostatic properties *in vitro* against micro-organisms such as *Mycobacterium tuberculosis*, *Mycobacterium smegmatis*, *Candida albicans* and *Aspergillus niger* [1, 2] and were found significantly to mobilize iron from $^{59}$Fe-labeled reticulocytes in mammals [3, 4]. Thus, they are potentially of use in the treatment of iron overload in man [3, 4]. Recently, preliminary studies have shown that aroylhydrazones, particularly salicylaldehyde benzoylhydrazone (SBH) and pyridine-2′-carboxaldehyde-2-pyridylhydrazone (PCPH) are potent inhibitors of DNA synthesis in a variety of cultured human and rodent cells, and their copper(II) complexes produce significant inhibition of tumor growth when given to mice bearing a transplanted fibrosarcoma [4, 5]. Although the bioactive forms and the mechanisms of action of SBH and PCPH and their copper(II) complexes are uncertain, their cytotoxic activity is equal to or greater than that of many chelators previously known to possess such properties, including compounds used clinically [5]. Moreover, these compounds are relatively non-toxic to mice and show some measure of selectivity in their effects on different cell types [5]. Because of these promising results, we have synthesized some metal(II) complexes of 3- and 5-substituted salicylaldehyde benzoylhydrazones to get more active antitumor compounds. All these compounds have been characterized by elemental analyses and various spectral studies and screened for their antitumor activity against the P388 lymphocytic leukaemia test system in mice at the National Cancer Institute, Bethesda, Md. It is highly surprising that none was found to possess significant activity.

## Experimental

Salicylaldehyde, 3-methoxysalicylaldehyde (*O*-vanillin) benzoylhydrazide and $K_2PtCl_4$ were obtained from Aldrich Chemical Co., Milwaukee, Wis., and used without further purification. 5-Chlorosalicylaldehyde and 3- and 5-nitrosalicylaldehydes were purchased from Eastman Chemical Co., Rochester, N.Y. 5-Bromosalicylaldehyde and 5-methylsalicylaldehyde were prepared according to reported methods [6]. All other chemicals and solvents were of reagent grade or equivalent.

3- and 5-Substituted salicylaldehyde benzoylhydrazones were prepared according to the reported procedure [6]. The authenticity of the compounds was proved by m.p. and infrared spectra.

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*Author to whom correspondence should be addressed.

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*Synthesis*

All the metal(II) chelates were obtained by the following general method. A hot solution of 3- or 5-XSBH (1 mmol) in 95% ethanol (20 ml) was added to a hot solution of the metal(II) salt (1 mmol) in the minimum amount of ethanol or an aqueous solution of $K_2PtCl_4$ (0.415 g, 1 mmol) and the resulting dark colored solution was refluxed for 2–3 h. The boiling solution was then allowed to cool at room temperature and stand overnight. Dark colored crystalline solids were separated from the solution and were filtered off, washed with ethanol and diethyl ether and dried over $P_2O_5$ under vacuum.

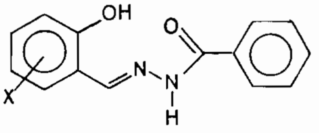
*Physical Measurements*

Conductance measurements were carried out in ethanol at $10^{-3}$ M on a Toshniwal conductivity bridge type CL01/01. All magnetic susceptibilities were measured on polycrystalline samples with a vibrating sample magnetometer. ESR spectra were recorded on a Varian spectrometer in the solid state as polycrystalline samples using DPPH as a reference material. The diffuse reflectance spectra of the compounds were measured on a Cary 14 spectrophotometer equipped with a diffuse reflectance accessory, using MgO as a reference. The infrared spectra in the 4000–200 $cm^{-1}$ range of the free ligands and their complexes were measured on a Perkin-Elmer 337 spectrophotometer in CsI.

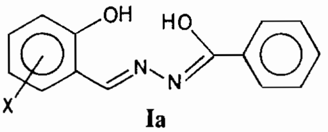
Elemental analyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory of CDRI, Lucknow, India. Metal analyses were by standard gravimetric procedures. The analytical data of the compounds are reported in Table I.

## Results and Discussion

The infrared spectra of the free ligands 3- and 5-XSBH exhibit strong $\nu$(N–H) absorption bands at *ca.* 3276 and *ca.* 3210 $cm^{-1}$ and $\nu$(C=O) at *ca.* 1670 $cm^{-1}$, suggesting that the ligands are in the keto form **I** in the solid state. However, in solution and in the presence of metal ions, the ligands may exist in equilibrium with the tautomeric enol form **Ia**. On the loss of the enolic and phenolic protons, tautomer **Ia** may act as a doubly charged tridentate ligand coordinating through the phenolic oxygen, the azomethine nitrogen and the carbonyl oxygen atoms. When a hot solution of 3- and 5-XSBH in ethanol is refluxed with ethanolic or aqueous solution of the metal(II) salt, colored shining crystals of the compounds of general formula $Mn(XSBH)_2$, $M(XSBH)Cl \cdot 2H_2O$ (M = Co(II) or Ni(II)), Zn(XSBH) and $M(XSBH)Cl \cdot H_2O$ (M = Cu(II) or Pt(II)) are formed. The Mn(II), Cu(II) and Pt(II) complexes are soluble in water and in a variety of organic solvents, while the remaining complexes are insoluble in all solvents tested. The molar conductances of Mn(II), Cu(II) and Pt(II) complexes in ethanol at *ca.* $10^{-3}$ M at 27 °C are in the range 7.5–10.5 $ohm^{-1}$ $cm^2$ $mol^{-1}$, indicating their non-electrolytic behavior in solution [7].



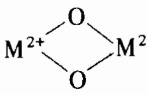
**I**



**Ia**

X = H, $3\text{-}CH_3O$, $3\text{-}NC_2$, 5-Cl, 5-Br, $5\text{-}CH_3$, $5\text{-}NO_2$

The assignments of some of the important bands observed in the spectra of the free XSBH ligands and their metal(II) complexes are reported in Table II. The infrared spectra of the free ligands exhibit bands at *ca.* 3440s, 3380s and *ca.* 2800 $cm^{-1}$ which are assigned to $\nu_{as}$(OH), $\nu_s$(OH) and intramolecular H-bonded (OH) of the phenolic group, respectively [8]. In the spectra of the metal(II) complexes, these absorption bands disappear and the phenolic (C–O) stretching and bending vibrations, observed at *ca.* 1520 and *ca.* 1280 $cm^{-1}$, respectively, in the free ligands, are displaced to higher frequencies in the Co(II), Ni(II) and Zn(II) complexes (*ca.* 1540–1550 $cm^{-1}$ and 1290–1310 $cm^{-1}$), while in the Mn(II), Cu(II) and Pt(II) complexes these are not much perturbed. The trend of the displacement of these bands is a reliable criterion of the mono- or polymeric nature of the complexes. The upward shift is definite proof of the dimeric nature of the Co(II), Ni(II) and Zn(II) complexes, involving phenoxide bridging [9, 10]. The displacement of these bands to higher frequencies is probably due to the increase in C–O bond strength on extended delocalization of the $\pi$ system of the azine moiety. The dimeric nature of the Co(II), Ni(II) and Zn(II) complexes is also supported by the appearance of new bands at 720–735 $cm^{-1}$. These bands originate from



ring vibrations [11, 12].

In the NH stretching frequency region, the high frequency spectral band $\nu_{as}$(NH) remains practically unchanged on coordination with a metal ion, relative to that of the free ligands, while the low frequency spectral band $\nu_s$(NH) is displaced to higher frequency by approximately 50 $cm^{-1}$ in the Mn(II), Cu(II) and Pt(II) complexes. This suggests that the ligands exist

TABLE I. Analytical Data of Metal(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones

| Compound | Color | Found (%) | | | | Calculated (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | M | C | H | N | M |
| H-SBH | white | 69.85 | 4.98 | 11.49 | | 70.00 | 5.00 | 11.67 | |
| 3-$NO_2$SBH | white | 58.85 | 3.95 | 14.80 | | 58.95 | 3.86 | 14.74 | |
| 3-$CH_3$OSBH | white | 66.62 | 5.26 | 10.45 | | 66.67 | 5.19 | 10.37 | |
| 5-BrSBH | white | 52.59 | 3.39 | 8.70 | | 52.68 | 3.45 | 8.78 | |
| 5-ClSBH | white | 61.15 | 4.10 | 10.15 | | 61.20 | 4.01 | 10.20 | |
| 5-$CH_3$SBH | white | 70.87 | 5.57 | 11.10 | | 70.87 | 5.51 | 11.02 | |
| 5-$NO_2$SBH | white | 59.10 | 3.90 | 14.82 | | 58.95 | 3.86 | 14.74 | |
| Mn(H-SBH)$_2$ | light yellow | 63.14 | 4.10 | 10.47 | 10.50 | 63.04 | 4.13 | 10.51 | 10.31 |
| Mn(3-$CH_3$OSBH)$_2$ | yellow | 60.80 | 4.80 | 9.32 | 9.18 | 60.71 | 4.72 | 9.44 | 9.27 |
| Mn(3-$NO_2$SBH)$_2$ | light yellow | 54.10 | 3.28 | 13.56 | 8.90 | 53.94 | 3.21 | 13.48 | 8.82 |
| Mn(5-ClSBH)$_2$ | yellow | 55.75 | 3.60 | 9.20 | 9.18 | 55.82 | 3.65 | 9.30 | 9.13 |
| Mn(5-BrSBH)$_2$ | dark yellow | 48.59 | 2.95 | 8.17 | 7.86 | 48.63 | 2.89 | 8.10 | 7.95 |
| Mn(5-$CH_3$SBH)$_2$ | yellow | 64.10 | 2.92 | 9.90 | 9.88 | 64.18 | 2.85 | 9.98 | 9.79 |
| Mn(5-$NO_2$SBH)$_2$ | yellow | 53.82 | 3.17 | 13.52 | 8.90 | 53.94 | 3.21 | 13.48 | 8.82 |
| Co(H-SBH)Cl·2$H_2O$ | brown | 45.37 | 4.18 | 7.44 | 15.87 | 45.48 | 4.06 | 7.58 | 15.94 |
| Co(3-$CH_3$OSBH)Cl·2$H_2O$ | brown | 45.00 | 4.58 | 7.10 | 14.82 | 45.06 | 4.51 | 7.01 | 14.75 |
| Co(3-$NO_2$SBH)Cl·2$H_2O$ | dark brown | 40.62 | 3.44 | 10.25 | 14.42 | 40.54 | 3.38 | 10.13 | 14.22 |
| Co(5-ClSBH)Cl·2$H_2O$ | brown | 41.50 | 3.65 | 13.92 | 14.50 | 41.59 | 3.71 | 6.93 | 14.59 |
| Co(5-BrSBH)Cl·2$H_2O$ | dark brown | 37.50 | 3.07 | 6.32 | 13.26 | 37.46 | 3.12 | 6.24 | 13.14 |
| Co(5-$CH_3$SBH)Cl·2$H_2O$ | dark brown | 46.89 | 4.39 | 7.25 | 15.42 | 46.94 | 4.43 | 7.30 | 15.37 |
| Co(5-$NO_2$SBH)Cl·2$H_2O$ | brown | 53.82 | 3.17 | 13.52 | 8.90 | 53.94 | 3.21 | 13.48 | 8.82 |
| Ni(HSBH)Cl·2$H_2O$ | green | 45.42 | 4.10 | 7.62 | 15.98 | 45.50 | 4.06 | 7.58 | 15.89 |
| Ni(3-$CH_3$OSBH)Cl·2$H_2O$ | yellowish-green | 45.00 | 4.48 | 7.18 | 14.68 | 45.09 | 4.51 | 7.01 | 14.71 |
| Ni(3-$NO_2$SBH)Cl·2$H_2O$ | green | 40.70 | 3.45 | 10.20 | 14.25 | 40.56 | 3.37 | 10.14 | 14.17 |
| Ni(5-ClSBH)Cl·2$H_2O$ | green | 41.70 | 3.80 | 13.78 | 14.65 | 41.61 | 3.72 | 6.94 | 14.54 |
| Ni(5-BrSBH)Cl·2$H_2O$ | greenish-yellow | 37.57 | 3.08 | 6.19 | 13.15 | 37.48 | 3.12 | 6.25 | 13.09 |
| Ni(5-$CH_3$SBH)Cl·2$H_2O$ | green | 46.89 | 4.50 | 7.38 | 15.45 | 46.97 | 4.44 | 7.31 | 15.32 |
| Ni(5-$NO_2$SBH)Cl·2$H_2O$ | green | 40.48 | 3.29 | 10.05 | 14.07 | 40.56 | 3.37 | 10.14 | 14.17 |
| Cu(H-SBH)Cl·$H_2O$ | black | 47.25 | 3.72 | 7.95 | 17.98 | 47.19 | 3.65 | 7.86 | 17.85 |
| Cu(3-$CH_3$OSBH)Cl·$H_2O$ | black | 46.58 | 4.08 | 7.19 | 16.39 | 46.65 | 4.15 | 7.26 | 16.47 |
| Cu(3-$NO_2$SBH)Cl·$H_2O$ | black | 41.90 | 3.10 | 10.52 | 15.92 | 41.89 | 2.99 | 10.47 | 15.84 |
| Cu(5-ClSBH)Cl·$H_2O$ | dark green | 43.10 | 3.25 | 7.10 | 16.35 | 43.02 | 3.33 | 7.17 | 16.27 |
| Cu(5-BrSBH)Cl·$H_2O$ | black | 38.69 | 2.80 | 6.52 | 14.69 | 38.62 | 2.76 | 6.44 | 14.61 |
| Cu(5-$CH_3$SBH)Cl·$H_2O$ | black | 48.70 | 4.12 | 7.62 | 17.20 | 48.64 | 4.05 | 7.57 | 17.17 |
| Cu(5-$NO_2$SBH)Cl·$H_2O$ | black | 41.79 | 2.89 | 10.39 | 15.88 | 41.89 | 2.99 | 10.47 | 15.84 |
| Zn(H-SBH) | yellow | 55.26 | 3.72 | 9.32 | 21.62 | 55.19 | 3.61 | 9.20 | 21.53 |
| Zn(3-$CH_3$OSBH) | light yellow | 53.79 | 4.26 | 8.30 | 19.49 | 53.83 | 4.19 | 8.37 | 19.55 |
| Zn(3-$NO_2$SBH) | light yellow | 48.00 | 2.94 | 12.10 | 18.82 | 48.09 | 2.86 | 12.02 | 18.71 |
| Zn(5-ClSBH) | light yellow | 49.50 | 3.20 | 8.35 | 19.20 | 49.58 | 3.25 | 8.26 | 19.29 |
| Zn(5-BrSBH) | yellow | 43.88 | 2.70 | 7.25 | 16.98 | 43.82 | 2.61 | 7.30 | 17.05 |
| Zn(5-$CH_3$SBH) | yellow | 56.60 | 4.12 | 8.84 | 20.60 | 56.53 | 4.08 | 8.79 | 20.53 |
| Zn(5-$NO_2$SBH) | yellow | 48.12 | 2.92 | 12.12 | 18.76 | 48.09 | 2.86 | 12.02 | 18.71 |
| Pt(H-SBH)Cl·$H_2O$ | dark red | 34.50 | 2.72 | 5.08 | 40.12 | 34.46 | 2.67 | 5.74 | 40.01 |
| Pt(3-$CH_3$OSBH)Cl·$H_2O$ | red | 34.69 | 3.00 | 5.34 | 37.50 | 34.78 | 3.09 | 5.41 | 37.69 |
| Pt(3-$NO_2$SBH)Cl·$H_2O$ | black | 31.60 | 2.20 | 8.00 | 36.70 | 31.54 | 2.25 | 7.89 | 36.63 |
| Pt(5-ClSBH)Cl·$H_2O$ | black | 32.25 | 2.35 | 5.40 | 37.28 | 32.18 | 2.48 | 5.36 | 37.37 |
| Pt(5-BrSBH)Cl·$H_2O$ | black | 29.58 | 2.08 | 5.06 | 34.50 | 29.65 | 2.11 | 4.94 | 34.43 |
| Pt(5-$CH_3$SBH)Cl·$H_2O$ | dark red | 35.92 | 3.08 | 5.64 | 38.93 | 35.89 | 2.99 | 5.58 | 38.89 |
| Pt(5-$NO_2$SBH)Cl·$H_2O$ | black | 31.61 | 2.30 | 7.92 | 36.70 | 31.54 | 2.25 | 7.89 | 36.63 |

in the keto form in these complexes [13], as partly confirmed by the upward shift of the amide-II ($\Delta\nu$(CN) + $\delta$(NH) $\simeq$ 30 $cm^{-1}$) and amide-VI ($\Delta\delta$(CO) $\simeq$ 20 $cm^{-1}$) bands and the downward shift of the amide-I ($\Delta\nu$(C=O) $\simeq$ 35 $cm^{-1}$) and amide-III ($\Delta\delta$(NH) $\simeq$ 15 $cm^{-1}$) bands. However, the spectra of the Co(II), Ni(II) and Zn(II) complexes do not show any characteristic bands of the amide and amino groups, indicating that the ligands are coordinating in the enol form in these complexes [14].

TABLE II. Important Infrared Spectral Data of the Metal(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones

| Compound | $\nu_{as}$(NH) | $\nu_s$(NH) | $\nu$(C=N) | $\nu$(C–O) | $\nu(\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{M})$ | $\nu$(M–O) phenolic | $\nu$(M–O) ketonic/ enolic | $\nu$(M–N) | $\nu$(M–Cl) |
|---|---|---|---|---|---|---|---|---|---|
| H-SBH | 3276s | 3210m | 1630s | 1520s, 1280s | | | | | |
| 3-$CH_3$OSBH | 3276s | 3210m | 1632s | 1518s, 1280s | | | | | |
| 3-$NO_2$SBH | 3272s | 3212s | 1630s | 1518s, 1280m | | | | | |
| 5-ClSBH | 3270s | 3210n | 1630s | 1520s, 1280m | | | | | |
| 5-BrSBH | 3276s | 3208s | 1628s | 1520s, 1276m | | | | | |
| 5-$CH_3$SBH | 3276s | 3212m | 1632vs | 1520m, 1278m | | | | | |
| 5-$NO_2$SBH | 3275s | 3210m | 1630s | 1520s, 1276m | | | | | |
| Mn(H-SBH)$_2$ | 3280s | 3265m | 1590m | 1515m, 1280m | | 440s | 340s | 430m | |
| Mn(3-$CH_3$OSBH)$_2$ | 3275m | 3260m | 1585m | 1520m, 1270m | | 438s | 344m | 425m | |
| Mn(3-$NO_2$SBH)$_2$ | 3275s | 3260s | 1590s | 1516s, 1280s | | 440m | 340s | 430m | |
| Mn(5-ClSBH)$_2$ | 3275m | 3260m | 1588m | 1515m, 1275m | | 440w | 340m | 425m | |
| Mn(5-BrSBH)$_2$ | 3280s | 3260s | 1590s | 1520s, 1270m | | 435s | 342s | 422s | |
| Mn(5-$CH_3$SBH)$_2$ | 3280s | 3258m | 1586m | 1510w, 1274m | | 440m | 337m | 430m | |
| Mn(5-$NO_2$SBH)$_2$ | 3278m | 3260m | 1590s | 1508m, 1270m | | 440s | 335m | 425s | |
| Co(H-SBH)Cl·2$H_2O$ | | | 1586s | 1540m, 1305m | 725s | 447m | 340s | 426m | 415m |
| Co(3-$CH_3$OSBH)Cl·2$H_2O$ | | | 1590m | 1545m, 1310m | 730m | 445m | 340m | 426m | 410s |
| Co(3-$NO_2$SBH)Cl·2$H_2O$ | | | 1585s | 1545m, 1310m | 728s | 448s | 345s | 428m | 408s |
| Co(5-ClSBH)Cl·2$H_2O$ | | | 1580m | 1550s, 1305m | 730m | 445m | 340m | 428s | 415m |
| Co(5-BrSBH)Cl·2$H_2O$ | | | 1585m | 1545m, 1308m | 720s | 448m | 340s | 425m | 410m |
| Co(5-$CH_3$SBH)Cl·2$H_2O$ | | | 1590s | 1550m, 1310m | 730m | 445s | 345m | 425s | 410m |
| Co(5-$NO_2$SBH)Cl·2$H_2O$ | | | 1588m | 1550m, 1300m | 725m | 448m | 340m | 422m | 408w |
| Ni(H-SBH)Cl·2$H_2O$ | | | 1590s | 1545s, 1310m | 730m | 448m | 344m | 420s | 405m |
| Ni(3-$CH_3$OSBH)Cl·2$H_2O$ | | | 1588m | 1545m, 1308m | 728m | 445s | 345s | 428m | 415m |
| Ni(3-$NO_2$SBH)Cl·2$H_2O$ | | | 1590s | 1550m, 1310m | 730m | 445s | 340m | 425s | 415m |
| Ni(5-ClSBH)Cl·2$H_2O$ | | | 1588m | 1550m, 1308m | 725s | 447m | 340s | 420m | 410s |
| Ni(5-BrSBH)Cl·2$H_2O$ | | | 1587m | 1540m, 1300m | 730m | 445m | 340m | 425m | 415s |
| Ni(5-$CH_3$SBH)Cl·2$H_2O$ | | | 1585m | 1545m, 1290m | 728m | 445m | 340m | 420s | 415s |
| Ni(5-$NO_2$SBH)Cl·2$H_2O$ | | | 1588m | 1545m, 1295m | 730s | 448m | 340m | 424m | 415s |
| Cu(H-SBH)Cl·$H_2O$ | 3276s | 3260m | 1585s | 1515m, 1280m | | 435m | 345m | 435m | 330m |
| Cu(3-$CH_3$OSBH)Cl·$H_2O$ | 3278s | 3262m | 1590m | 1510m, 1285m | | 440s | 345s | 438m | 330m |
| Cu(3-$NO_2$SBH)Cl·$H_2O$ | 3280m | 3260s | 1590m | 1506m, 1285m | | 436m | 340s | 438m | 325m |
| Cu(5-ClSBH)Cl·$H_2O$ | 3276m | 3258m | 1580m | 1525m, 1280m | | 440s | 344m | 440s | 324w |
| Cu(5-BrSBH)Cl·$H_2O$ | 3275s | 3255m | 1585s | 1530m, 1280m | | 437m | 345s | 438m | 330m |
| Cu(5-$CH_3$SBH)Cl·$H_2O$ | 3275s | 3260m | 1580m | 1520s, 1280m | | 440s | 340m | 440s | 325w |
| Cu(5-$NO_2$SBH)Cl·$H_2O$ | 3275s | 3262s | 1586m | 1526m, 1285m | | 440m | 340m | 440m | 325m |
| Zn(H-SBH) | | | 1580m | 1540m, 1300m | 730m | 445m | 340s | 420s | |
| Zn(3-$CH_3$OSBH) | | | 1585s | 1545s, 1295m | 720m | 448m | 340s | 425m | |
| Zn(3-$NO_2$SBH) | | | 1585m | 1540m, 1290m | 725m | 450s | 345m | 425m | |
| Zn(5-ClSBH) | | | 1585m | 1545m, 1298s | 730m | 445m | 340s | 425m | |
| Zn(5-BrSBH) | | | 1588s | 1550s, 1295m | 728m | 448m | 338m | 420m | |
| Zn(5-$CH_3$SBH) | | | 1590m | 1545m, 1300s | 725s | 445m | 338s | 428m | |
| Zn(5-$NO_2$SBH) | | | 1586m | 1545s, 1310m | 720s | 445s | 340s | 425s | |
| Pt(H-SBH)Cl·$H_2O$ | 3280m | 3255m | 1590m | 1520m, 1280m | | 440m | 345m | 435m | 325m |
| Pt(3-$CH_3$OSBH)Cl·$H_2O$ | 3276m | 3260m | 1590s | 1525m, 1280m | | 435m | 345m | 435m | 330m |
| Pt(3-$NO_2$SBH)Cl·$H_2O$ | 3280m | 3262m | 1586m | 1530s, 1276m | | 440s | 343m | 438m | 325s |
| Pt(5-ClSBH)Cl·$H_2O$ | 3276m | 3260m | 1585m | 1525m, 1285m | | 437m | 340s | 440s | 330m |
| Pt(5-BrSBH)Cl·$H_2O$ | 3275s | 3265m | 1580m | 1530m, 1285m | | 435m | 340m | 440m | 325m |
| Pt(5-$CH_3$SBH)Cl·$H_2O$ | 3276m | 3260m | 1590m | 1525m, 1280m | | 440m | 340m | 440m | 324w |
| Pt(5-$NO_2$SBH)Cl·$H_2O$ | 3280s | 3260m | 1586m | 1530m, 1285m | | 438m | 340s | 435m | 325m |

The coordination of the azomethine nitrogen atom to the metal(II) ion is indicated by the displacement of the bands chiefly assigned to the $\nu$(N–N) and $\nu$(C=N) stretching vibrations [15]. The spectra of all the complexes exhibit downward shifts of $\nu$(N–N) from *ca.* 980 $cm^{-1}$ for ligands to approximately 970 $cm^{-1}$ and $\nu$(C=N) from *ca.* 1630 $cm^{-1}$ to *ca.* 1590 $cm^{-1}$. These changes in $\nu$(N–N) and $\nu$(C=N) stretching vibrations are typical of coordination of the ligands to the metal ion through the azomethine nitrogen atom [15].

In the far-infrared spectral region, the Mn(II), Cu(II) and Pt(II) complexes exhibit bands at *ca.* 440, *ca.* 430 and *ca.* 340 $cm^{-1}$ which are assigned to $\nu$(M–O) phenolic, $\nu$(M–N), and $\nu$(M–O) ketonic, respectively [16]. In addition to the above bands, the Cu(II) and Pt(II) complexes show a band at *ca.* 330 $cm^{-1}$ which is assigned to the $\nu$(M–Cl) stretching vibration [16]. The complexes of Co(II), Ni(II) and Zn(II) exhibit bands at *ca.* 445, *ca.* 425 and *ca.* 340 $cm^{-1}$ which are assigned to the $\nu$(M–O) phenolic, $\nu$(M–N) and $\nu$(M–O) enolic vibrations, respectively [16]. The Co(II) and Ni(II) complexes also exhibit a band at *ca.* 415 $cm^{-1}$ which is assigned to the $\nu$(M–Cl) stretching vibration [16].

The magnetic susceptibilities data for the metal complexes are reported in Table III. The Zn(II) and Pt(II) complexes are diamagnetic. The $\mu_{eff}$ values of the Mn(II) complexes are typical of the high-spin configurations [17] and are relatively constant at *ca.* 60 ± 0.2 $\mu_B$ except for a drop at lower temperatures. The Curie–Weiss law is obeyed with a relatively small value of $\theta$ (*ca.* –5 K).

The magnetic susceptibilities of the dimeric Co(II) complexes in the 300–78 K range are slightly affected by what appear to be very weak antiferromagnetic interactions [18, 19], while the dimeric Ni(II) complexes exhibit anomalous magnetic moments (*ca.* 1.10 $\mu_B$) which are in between the values expected for either high- or low-spin $d^8$ nickel(II) complexes, regardless of the coordination geometry about the metal. Several mechanisms may account for the magnetic moments of these complexes which have a linear tridentate O*–N*–O* ligand system. First, the complexes may be essentially diamagnetic low-spin ones that are contaminated with (or in equilibrium with) a small percentage of some high-spin species (*i.e.*, a low-spin square-planar or 5-coordinate material with a small fraction of a high-spin octahedral, square-planar, tetrahedral or 5-coordinate complex). Precedence for such behavior is known [20–22]. Secondly, a spin-state isomerism [23, 24] between singlet and triplet states for a pseudo-square-planar or 5-coordinate complex may be envisioned [25]. In other words, two energy levels of different multiplicity are positioned with $kT$ of each other (*i.e.*, the complex is near the 'magnetic cross-over point') whereby population of both states

TABLE III. Magnetic Susceptibility Data of the Metal(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones

| | | |
|---|---|---|
| $Mn(H\text{-}SBH)_2$ ($\theta$ = –2 K) | $T$ (K) | 298.7, 270.5, 212.3, 190.0, 154.5, 110.2, 96.2, 78.0 |
| | $\chi_M$ (cgsu) | 15065, 16635, 21126, 23605, 29029, 40563, 46466, 57308 |
| | $\mu_{eff}$ ($\mu_B$) | 6.00, 6.00, 5.99, 5.99, 5.99, 5.98, 5.98, 5.98. |
| $Mn(3\text{-}CH_3OSBH)_2$ ($\theta$ = –2 K) | $T$ (K) | 300.0, 280.0, 258.7, 208.0, 160.3, 109.5, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 14950, 15964, 17337, 21563, 27886, 40822, 45613, 57117 |
| | $\mu_{eff}$ ($\mu_B$) | 5.99, 5.98, 5.99, 5.98, 5.98, 5.98, 5.97 |
| $Mn(3\text{-}NO_2SBH)_2$ ($\theta$ = –1 K) | $T$ (K) | 298.7, 270.5, 242.0, 208.0, 192.3, 148.0, 110.0, 94.5, 78.0 |
| | $\chi_M$ (cgsu) | 15116, 16636, 18595, 21635, 23245, 30304, 40637, 47302, 57308 |
| | $\mu_{eff}$ ($\mu_B$) | 6.01, 6.00, 6.00, 6.00, 5.98, 5.99, 5.98, 5.98, 5.98 |
| $Mn(5\text{-}ClSBH)_2$ ($\theta$ = –3 K) | $T$ (K) | 298.6, 265.5, 240.5, 210.0, 192.0, 150.5, 108.0, 95.0, 78.0 |
| | $\chi_M$ (cgsu) | 15065, 16893, 18649, 21357, 23359, 29801, 41389, 47053, 57308 |
| | $\mu_{eff}$ ($\mu_B$) | 6.00, 5.99, 5.99, 5.99, 5.99, 5.99, 5.98, 5.98, 5.98 |
| $Mn(5\text{-}BrSBH)_2$ ($\theta$ = –1 K) | $T$ (K) | 298.8, 265.5, 238.7, 210.2, 190.5, 110.0, 98.7, 78.0 |
| | $\chi_M$ (cgsu) | 14960, 16836, 18727, 21266, 23386, 40501, 45138, 57117 |
| | $\mu_{eff}$ ($\mu_B$) | 5.98, 5.98, 5.98, 5.98, 5.97, 5.97, 5.96, 5.97 |
| $Mn(5\text{-}CH_3SBH)_2$ ($\theta$ = –4 K) | $T$ (K) | 300.0, 270.7, 240.5, 208.0, 195.0, 150.5, 107.6, 95.8, 78.0 |
| | $\chi_M$ (cgsu) | 15000, 16624, 18649, 21858, 22923, 29701, 39079, 46660, 57308 |
| | $\mu_{eff}$ ($\mu_B$) | 6.00, 6.00, 5.99, 5.98, 5.98, 5.98, 5.98, 5.98 |
| $Mn(5\text{-}NO_2SBH)_2$ ($\theta$ = –2 K) | $T$ (K) | 298.0, 268.5, 242.0, 207.5, 194.5, 152.0, 108.5, 96.0, 78.0 |
| | $\chi_M$ (cgsu) | 15050, 16648, 18471, 21542, 22982, 29408, 41061, 46252, 56926 |
| | $\mu_{eff}$ ($\mu_B$) | 5.99, 5.98, 5.98, 5.98, 5.98, 5.97, 5.97, 5.96, 5.96 |
| $Co(H\text{-}SBH)Cl\cdot 2H_2O$ ($\theta$ = –7 K) | $T$ (K) | 300.0, 280.0, 258.7, 218.5, 190.4, 160.2, 110.4, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 8855, 9446, 9784, 11380, 12710, 14293, 20355, 22286, 27867 |
| | $\mu_{eff}$ ($\mu_B$) | 4.61, 4.60, 4.50, 4.46, 4.40, 4.28, 4.24, 4.18, 4.17 |
| $Co(3\text{-}CH_3OSBH)Cl\cdot 2H_2O$ ($\theta$ = –6 K) | $T$ (K) | 298.8, 270.5, 250.4, 210.0, 190.4, 150.2, 108.8, 97.5, 78.0 |
| | $\chi_M$ (cgsu) | 8929, 9608, 9753, 11524, 12139, 14961, 20267, 22293, 27600 |
| | $\mu_{eff}$ ($\mu_B$) | 4.62, 4.56, 4.42, 4.40, 4.30, 4.24, 4.20, 4.17, 4.15 |
| $Co(3\text{-}NO_2SBH)Cl\cdot 2H_2O$ ($\theta$ = –4 K) | $T$ (K) | 300.0, 268.8, 251.7, 208.6, 192.8, 150.7, 108.6, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 8817, 9627, 10057, 11707, 12044, 15124, 20498, 22286, 27600 |
| | $\mu_{eff}$ ($\mu_B$) | 4.60, 4.55, 4.50, 4.42, 4.31, 4.27, 4.22, 4.18, 4.15 |

*(continued)*

TABLE III. *(continued)*

| | | |
|---|---|---|
| Co(5-ClSBH)Cl$\cdot$H$_2$O ($\theta$ = −6 K) | $T$ (K) | 299.7, 270.5, 248.6, 210.5, 190.4, 148.7, 110.2, 97.5, 78.0 |
| | $\chi_M$ (cgsu) | 8825, 9651, 10092, 11237, 12139, 14899, 19630, 21974, 27202 |
| | $\mu_{eff}$ ($\mu_B$) | 4.60, 4.57, 4.48, 4.35, 4.30, 4.21, 4.16, 4.14, 4.12 |
| Co(5-BrSBH)Cl$\cdot$2H$_2$O ($\theta$ = −2 K) | $T$ (K) | 300.0, 270.5, 252.6, 208.8, 190.5, 148.7, 110.2, 97.5, 78.0 |
| | $\chi_M$ (cgsu) | 8971, 9693, 10065, 11537, 12020, 14829, 19914, 22293, 27733 |
| | $\mu_{eff}$ ($\mu_B$) | 4.64, 4.58, 4.51, 4.39, 4.28, 4.20, 4.19, 4.17, 4.16 |
| Co(5-CH$_3$SBH)Cl$\cdot$2H$_2$O ($\theta$ = −7 K) | $T$ (K) | 298.0, 270.2, 252.0, 208.0, 193.0, 148.0, 110.2, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 8953, 9704, 10045, 11741, 12199, 15399, 20200, 22286, 27733 |
| | $\mu_{eff}$ ($\mu_B$) | 4.62, 4.58, 4.50, 4.42, 4.34, 4.27, 4.22, 4.18, 4.16 |
| Co(5-NO$_2$SBH)Cl$\cdot$2H$_2$O ($\theta$ = −6 K) | $T$ (K) | 300.0, 268.8, 250.5, 207.7, 190.5, 148.7, 108.0, 96.5, 78.0 |
| | $\chi_M$ (cgsu) | 8778, 9501, 9926, 11546, 12076, 15112, 20417, 22633, 27600 |
| | $\mu_{eff}$ ($\mu_B$) | 4.59, 4.52, 4.46, 4.38, 4.29, 4.24, 4.20, 4.18, 4.15 |
| Cu(H-SBH)Cl$\cdot$H$_2$O ($\theta$ = −3 K) | $T$ (K) | 300.0, 278.8, 247.5, 210.2, 150.4, 107.5, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 1350, 1452, 1582, 1719, 2345, 3204, 3473, 4363 |
| | $\mu_{eff}$ ($\mu_B$) | 1.80, 1.80, 1.77, 1.70, 1.68, 1.66, 1.65, 1.65 |
| Cu(3-CH$_3$OSBH)Cl$\cdot$H$_2$O ($\theta$ = −4 K) | $T$ (K) | 298.7, 276.0, 250.4, 210.4, 147.9, 107.6, 96.8, 78.0 |
| | $\chi_M$ (cgsu) | 1448, 1500, 1654, 1882, 2618, 3357, 3732, 4577 |
| | $\mu_{eff}$ ($\mu_B$) | 1.86, 1.82, 1.78, 1.76, 1.74, 1.70, 1.70, 1.69 |
| Cu(3-NO$_2$SBH)Cl$\cdot$H$_2$O ($\theta$ = −2 K) | $T$ (K) | 300.0, 280.0, 247.5, 212.0, 148.7, 108.3, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 1320, 1414, 1582, 1785, 2429, 3257, 3473, 4363 |
| | $\mu_{eff}$ ($\mu_B$) | 1.78, 1.78, 1.77, 1.74, 1.70, 1.68, 1.65, 1.65 |
| Cu(5-ClSBH)Cl$\cdot$H$_2$O ($\theta$ = −4 K) | $T$ (K) | 300.0, 278.5, 251.6, 210.3, 149.0, 110.5, 97.6, 78.0 |
| | $\chi_M$ (cgsu) | 1335, 1422, 1556, 1820, 2482, 3269, 3572, 4363 |
| | $\mu_{eff}$ ($\mu_B$) | 1.79, 1.78, 1.77, 1.75, 1.72, 1.70, 1.67, 1.65 |
| Cu(5-BrSBH)Cl$\cdot$H$_2$O ($\theta$ = −6 K) | $T$ (K) | 299.8, 280.3, 251.2, 208.4, 150.5, 108.7, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 1351, 1413, 1559, 1858, 2544, 3442, 3686, 4469 |
| | $\mu_{eff}$ ($\mu_B$) | 1.80, 1.78, 1.77, 1.76, 1.75, 1.73, 1.70, 1.67 |
| Cu(5-CH$_3$SBH)Cl$\cdot$H$_2$O ($\theta$ = −6 K) | $T$ (K) | 300.0, 278.5, 247.6, 210.3, 148.8, 110.0, 97.8, 78.0 |
| | $\chi_M$ (cgsu) | 1335, 1438, 1582, 1841, 2543, 3323, 3607, 4416 |
| | $\mu_{eff}$ ($\mu_B$) | 1.79, 1.79, 1.77, 1.76, 1.74, 1.71, 1.68, 1.66 |
| Cu(5-NO$_2$SBH)Cl$\cdot$H$_2$O ($\theta$ = −5 K) | $T$ (K) | 298.7, 274.5, 248.5, 208.0, 150.2, 108.6, 98.0, 78.0 |
| | $\chi_M$ (cgsu) | 1326, 1427, 1540, 1757, 2405, 3287, 3557, 4416 |
| | $\mu_{eff}$ ($\mu_B$) | 1.78, 1.77, 1.75, 1.71, 1.70, 1.69, 1.67, 1.66 |

becomes probable. The five-coordinate nickel(II) complexes have been shown to exist as high- or low-spin complexes depending upon the $\pi$-bonding character of the ligand donor atoms [26]. A spin-state isomerism between singlet and triplet states for a distorted five-coordinate complex is predicted for Ni(XSBH)Cl$\cdot$2H$_2$O, based on the interpretation of their visible spectra, *vide infra*.

The $\mu_{eff}$ values of the Cu(II) complexes are very close to spin-only for one unpaired electron and are in the range normally observed for copper(II) complexes having an orbitally non-degenerate ground state [17, 27]. The magnitude and slight temperature dependence of the $\mu_{eff}$ values rules out the presence of metal–metal interaction in these complexes. No significant conclusion can be drawn from the magnetic data regarding the stereochemistry of these complexes, since there is little difference between the magnetic moments of various configurations in copper(II) complexes [17, 27].

The X-band ESR spectra of the powdered complexes are axial type with $g_\parallel > g_\perp$ and are consistent with a primarily $d_{x^2-y^2}$ ground state in square-planar structure [27, 28]. Typical examples of these ESR spectra are shown in Fig. 1 and the data are reported in Table IV.

In the UV region (400–200 nm), the free ligands exhibit absorption bands at *ca.* 41 670, *ca.* 38 460 and *ca.* 31 750 cm$^{-1}$ which are assigned to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [6]. The high absorption by the ligands masks any splitting of the bands and only slight wavelength and intensity variations are significant in all metal(II) complexes. The spectra of the complexes are dominated by the ligand absorption bands.

In the visible region, the Mn(II) complexes exhibit two intense absorption bands at *ca.* 18 000 and *ca.* 25 000 cm$^{-1}$ which are assigned to $\pi \rightarrow e_g^*$ and $e_g \rightarrow \pi^*$ transitions, respectively [29].

The spectra of the Co(II) complexes exhibit five ligand field transitions at *ca.* 6000 [$^4A'_2(F) \rightarrow {}^4E''(F)$], 11 500, 12 300 [$^4A'_2(F) \rightarrow {}^4E'(F)$], *ca.* 16 000 [$^4A'_2(F) \rightarrow {}^4A'_2(P)$] and *ca.* 20 200 [$^4A'_2(F) \rightarrow {}^4E''(P)$] cm$^{-1}$ in addition to the intense intra-ligands

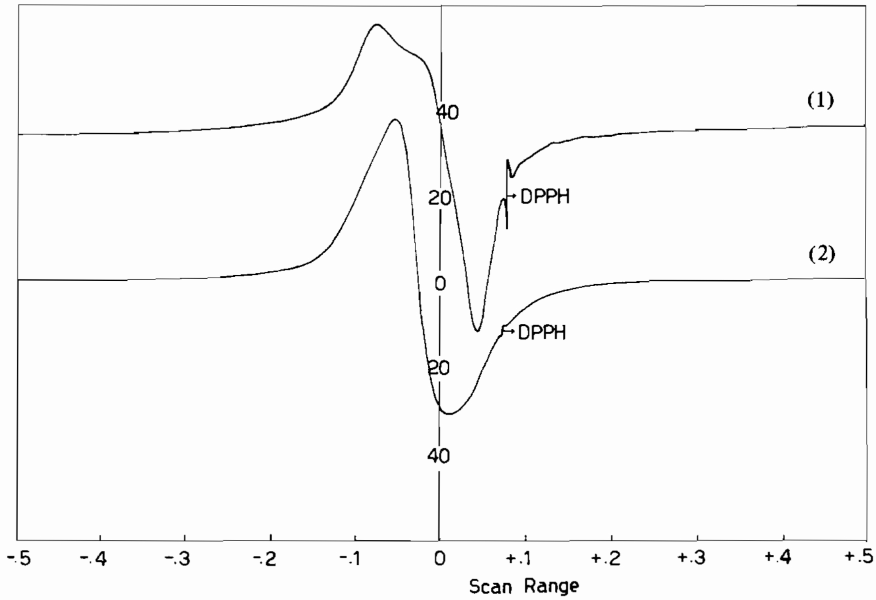


Fig. 1. X-band ESR spectrum of (1) Cu(H-SBH)Cl·$H_2O$; (2) Cu(3-$CH_3O$SBH)Cl·$H_2O$ at room temperature.

bands. The significant splitting of the $^4A'_2(F) \rightarrow {}^4E'(F)$ transition band into two components suggests the intermediate configuration with $C_{2v}$ symmetry for the present Co(II) complexes [30].

The spectra of the Ni(II) complexes exhibit two absorption bands at *ca.* 16 250 and *ca.* 22 750 $cm^{-1}$. The lower energy band is characteristic of low-spin five-coordinate nickel(II) [26] and is assigned in a trigonal bipyramidal environment to the transition $d_{xy}, d_{x^2-y^2} \rightarrow d_{z^2}$. The higher energy band is assigned to the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ transition.

The spectra of the Cu(II) complexes exhibit a broad band at *ca.* 14 500 $cm^{-1}$ which is assigned to the envelope of the $^5B_{1g} \rightarrow {}^2A_{1g}, {}^2B_{2g}, {}^2E_g$ transitions in a square-planar geometry [31].

The spectra of the Pt(II) complexes exhibit two bands at *ca.* 18 000 and *ca.* 20 500 $cm^{-1}$ which are assigned to the metal-to-ligand (Pt(II) → ligand ($\pi^*$)) charge-transfer transition [32].

### *Antitumor Activity*

The antitumor activity of the metal(II) complexes was determined at the National Cancer Institute, Bethesda, Md., according to the standard screening procedure (*cf.* instruction 14) in the P388 lymphocytic leukaemia test system in mice. The P388 lymphocytic leukaemia screen was carried out on $CD_2F_1(CDF_1)$ mice (female). On day 0, $1 \times 10^6$ ascites cells were injected intraperitoneally (ip). The drugs were suspended in saline with Tween-80 and administered ip once daily with the indicated dose (Table V), beginning on day 1 and ending on day 5. Six mice were used per test compound, and a *T*/*C* of greater than 125% was considered significant activity against P388 tumor growth.

All the metal(II) complexes were evaluated for antitumor activity against the P388 lymphocytic leukaemia test system in mice and the results are reported in Table V. None of the complexes shows

TABLE IV. ESR Data of the Copper(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones[a]

| Compound | $g_\perp$ | $g_\parallel$ | $\langle g \rangle$ | $(g)$ |
|---|---|---|---|---|
| Cu(H-SBH)Cl·$H_2O$ | 2.042$g_1$<br>2.144$g_2$ | 2.302$g_3$ | 2.1626 | |
| Cu(3-$CH_3O$SBH)Cl·$H_2O$ | 2.066 | 2.272 | 2.1346 | 4.12 |
| Cu(3-$NO_2$SBH)Cl·$H_2O$ | 2.068 | 2.275 | 2.1370 | 4.04 |
| Cu(5-ClSBH)Cl·$H_2O$ | 2.064 | 2.272 | 2.1333 | 4.25 |
| Cu(5-BrSBH)Cl·$H_2O$ | 2.068 | 2.274 | 2.1366 | 4.02 |
| Cu(5-$CH_3$SBH)Cl·$H_2O$ | 2.067 | 2.272 | 2.1353 | 4.06 |
| Cu(5-$NO_2$SBH)Cl·$H_2O$ | 2.068 | 2.273 | 2.1363 | 4.01 |

[a] $\langle g \rangle = \frac{1}{3}(2g_\perp + g_\parallel)$ or $\frac{1}{3}(g_1 + g_2 + g_3)$; $(g) = (g_\parallel - 2)/(g_\perp - 2)$.

TABLE V. Antitumor Activity of the Metal(II) Complexes of 3- and 5-Substituted Salicylaldehyde Benzoylhydrazones

| Compound | Dose (mg/kg) | Weight difference (*T* – *C*) | *T*/*C* (%) |
|---|---|---|---|
| H–SBH | 400.00 | 0.3 | 95 |
| | 200.00 | –1.0 | 105 |
| | 100.00 | –1.7 | 112 |
| $\mathrm{Mn(H\text{-}SBH)_2}$ | 240.00 | 0.6 | 96 |
| | 120.00 | 0.4 | 104 |
| | 60.00 | 1.1 | 101 |
| $\mathrm{Co(H\text{-}SBH)Cl\cdot 2H_2O}$ | 200.00 | –0.8 | 96 |
| | 100.00 | –0.3 | 91 |
| | 50.00 | –0.3 | 89 |
| $\mathrm{Ni(H\text{-}SBH)Cl\cdot 2H_2O}$ | 240.00 | –0.3 | 86 |
| | 120.00 | 0.4 | toxic |
| | 60.00 | 0.2 | 87 |
| $\mathrm{Cu(H\text{-}SBH)Cl\cdot H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| | 30.00 | –6.2 | toxic |
| | 15.00 | –5.9 | 103 |
| $\mathrm{Zn(H\text{-}SBH)}$ | 240.00 | –6.5 | toxic |
| | 120.00 | –3.1 | 106 |
| | 60.00 | –1.4 | 95 |
| $\mathrm{Pt(H\text{-}SBH)Cl\cdot H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| $\mathrm{3\text{-}CH_3OSBH}$ | 400.00 | | toxic |
| | 200.00 | –1.5 | 97 |
| | 100.00 | –1.0 | 90 |
| $\mathrm{Mn(3\text{-}CH_3OSBH)}$ | 400.00 | | toxic |
| | 200.00 | | toxic |
| | 100.00 | –1.5 | 80 |
| $\mathrm{Co(3\text{-}CH_3OSBH)Cl\cdot 2H_2O}$ | 400.00 | | toxic |
| | 200.00 | | toxic |
| | 100.00 | –2.0 | 90 |
| $\mathrm{Ni(3\text{-}CH_3OSBH)Cl\cdot 2H_2O}$ | 400.00 | | toxic |
| | 200.00 | –1.2 | 98 |
| | 100.00 | –1.0 | 102 |
| $\mathrm{Cu(3\text{-}CH_3OSBH)Cl\cdot H_2O}$ | 400.00 | | toxic |
| | 200.00 | –2.4 | 80 |
| | 100.00 | –1.7 | 94 |
| $\mathrm{Zn(3\text{-}CH_3OSBH)Cl\cdot H_2O}$ | 400.00 | –3.5 | 90 |
| | 200.00 | –2.7 | 90 |
| | 100.00 | –1.2 | 102 |
| $\mathrm{Pt(3\text{-}CH_3OSBH)Cl\cdot H_2O}$ | 400.00 | –2.8 | 88 |
| | 200.00 | –1.6 | 95 |
| | 100.00 | –1.0 | 100 |
| 5-ClSBH | 400.00 | –2.5 | 90 |
| | 200.00 | –1.0 | 85 |
| | 100.00 | –0.5 | 88 |
| $\mathrm{3\text{-}NO_2SBH}$ | 400.00 | | toxic |
| | 200.00 | –1.2 | 98 |
| | 100.00 | –0.5 | 110 |
| $\mathrm{Mn(3\text{-}NO_2SBH)_2}$ | 400.00 | 0.3 | 98 |
| | 200.00 | –1.2 | 102 |
| | 100.00 | –1.2 | 102 |
| $\mathrm{Co(3\text{-}NO_2SBH)Cl\cdot 2H_2O}$ | 400.00 | –2.0 | 90 |
| | 200.00 | –1.4 | 96 |
| | 100.00 | –1.0 | 102 |
| $\mathrm{Ni(3\text{-}NO_2SBH)Cl\cdot 2H_2O}$ | 400.00 | | toxic |
| | 200.00 | –1.4 | 88 |
| | 100.00 | –0.5 | 90 |
| $\mathrm{Cu(3\text{-}NO_2SBH)Cl\cdot H_2O}$ | 400.00 | –2.0 | 90 |
| | 200.00 | –1.7 | 98 |
| | 100.00 | –1.2 | 102 |
| $\mathrm{Zn(3\text{-}NO_2SBH)}$ | 400.00 | | toxic |
| | 200.00 | | toxic |
| | 180.00 | | toxic |
| | 50.00 | –0.3 | 88 |
| | 25.00 | 0.4 | 90 |
| | 12.50 | 0.2 | 100 |
| $\mathrm{Pt(3\text{-}NO_2SBH)}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | –1.2 | 88 |
| $\mathrm{Mn(5\text{-}ClSBH)_2}$ | 400.00 | | toxic |
| | 200.00 | | toxic |
| | 100.00 | –1.2 | 88 |
| $\mathrm{Co(5\text{-}ClSBH)_2Cl\cdot 2H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | –2.0 | 86 |
| $\mathrm{Ni(5\text{-}ClSBH)_2Cl\cdot 2H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | –1.7 | 90 |
| $\mathrm{Cu(5\text{-}ClSBH)Cl\cdot H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | –2.7 | 90 |
| $\mathrm{Zn(5\text{-}ClSBH)}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | –3.0 | 88 |
| $\mathrm{Pt(5\text{-}ClSBH)Cl\cdot H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| | 30.00 | –1.7 | 90 |
| | 15.00 | –1.0 | 102 |
| 5-BrSBH | 240.00 | –2.2 | 90 |
| | 120.00 | –0.9 | 88 |
| | 60.00 | –0.3 | 94 |
| $\mathrm{Mn(5\text{-}BrSBH)_2}$ | 240.00 | –2.4 | 87 |
| | 120.00 | –0.8 | 89 |
| | 60.00 | –0.2 | 90 |
| $\mathrm{Co(5\text{-}BrSBH)Cl\cdot 2H_2O}$ | 240.00 | 0.2 | 112 |
| | 120.00 | –0.1 | 106 |
| | 60.00 | –0.6 | 89 |
| $\mathrm{Ni(5\text{-}BrSBH)Cl\cdot 2H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| $\mathrm{Cu(5\text{-}BrSBH)Cl\cdot H_2O}$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| | 30.00 | | toxic |
| | 15.00 | | toxic |

*(continued)*

TABLE V. *(continued)*

| Compound | Dose (mg/kg) | Weight difference ($T - C$) | $T/C$ (%) |
|---|---|---|---|
| Zn(5-BsSBH) | 240.00 | −0.9 | 99 |
| | 120.00 | 0.4 | 97 |
| | 60.00 | 0.6 | 103 |
| Pt(5-BrSBH)Cl·$H_2O$ | 240.00 | −2.2 | 90 |
| | 120.00 | −0.9 | 88 |
| | 60.00 | −0.3 | 94 |
| 5-$CH_3$SBH | 240.00 | −2.0 | 88 |
| | 120.00 | −1.0 | 90 |
| | 60.00 | −0.5 | 92 |
| Mn(5-$CH_3$SBH)$_2$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | −0.6 | 88 |
| Co(5-$CH_3$SBH)Cl·2$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | −0.2 | 90 |
| Ni(5-$CH_3$SBH)Cl·2$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| Cu(5-$CH_3$SBH)Cl·$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| | 30.00 | −1.0 | 90 |
| | 15.00 | −0.6 | 92 |
| Zn(5-$CH_3$SBH) | 240.00 | −2.0 | 88 |
| | 120.00 | −1.7 | 88 |
| | 60.00 | −0.6 | 95 |
| Pt(5-$CH_3$SBH)Cl·$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | −0.2 | 98 |
| 5-$NO_2$SBH | 240.00 | −3.5 | 89 |
| | 120.00 | −2.5 | 92 |
| | 60.00 | −1.0 | 105 |
| Mn(5-$NO_2$SBH)$_2$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | −1.0 | 88 |
| Co(5-$NO_2$SBH)Cl·2$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| Ni(5-$NO_2$SBH)Cl·2$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| Cu(5-$NO_2$SBH)Cl·$H_2O$ | 240.00 | | toxic |
| | 120.00 | | toxic |
| | 60.00 | | toxic |
| | 30.00 | | toxic |
| | 15.00 | | toxic |
| Zn(5-$NO_2$SBH) | 240.00 | | toxic |
| | 120.00 | −2.0 | 88 |
| | 60.00 | −1.7 | 90 |
| Pt(5-$NO_2$SBH)Cl·$H_2O$ | 240.00 | | toxic |
| | 120.00 | −2.5 | 88 |
| | 60.00 | −1.2 | 95 |

significant activity and they are all toxic at the doses used. These results are highly surprising as the metal chelates of aroylhydrazones, particularly copper(II) complexes, have been shown to be potent inhibitors of DNA synthesis and cell growth in a variety of human and rodent cell lines grown in culture [5]. The antitumor activity of the free ligands is also not enhanced by coordination.

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