excess volumes vary linearly with temperature over nearly the whole range of composition; the results of $(\partial V^E/\partial T)_p$ present asymmetrical curves vs. the composition with a maximum value of 0.0023 $cm^3\ mol^{-1}\ K^{-1}$ near $x_1 = 0.6$ for benzene + 1-hexanol and 0.0058 $cm^3\ mol^{-1}\ K^{-1}$ near $x_1 = 0.6$ for benzene + 3-M-3-P mixtures.

**Registry No.** 3-M-3-P, 77-74-7; benzene, 71-43-2; 1-hexanol, 111-27-3.

### Literature Cited

(1) Riddick, J. A.; Bunger, W. B. "Organic Solvents. Techniques of Chemistry"; Wiley-Interscience: New York, 1970; Vol. II.
(2) Paz Andrade, M. I.; Garcia, M.; Garcia, Fente, F. *Ann. Quim. Esp.* **1975**, *71*, 451.
(3) Ortega, J. *J. Chem. Eng. Data* **1982**, *27*, 313.
(4) Kiyohara, O.; Halpin, C. J.; Benson, G. C. *J. Chem. Thermodyn.* **1978**, *10*, 721.
(5) Kimura, F.; Benson, G. C. *J. Chem. Eng. Data* **1983**, *28*, 157.
(6) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965; Vol. 2.
(7) Ocón, J.; Ortega, J. *An. Quim.* **1980**, *76*, 147.
(8) Ocón, J.; Ortega, J. *An. Quim.* **1981**, *77*, 161.
(9) Ocón, J.; Ortega, J. *Rev. Latinoam. Ing. Quim. Quim. Apl.* **1981**, *11*, 131.
(10) Myers, R. S.; Clever, H. L. *J. Chem. Thermodyn.* **1970**, *2*, 53.
(11) Brown, I.; Fock, W.; Smith, F. *J. Chem. Thermodyn.* **1969**, *1*, 273.

Received for review October 3, 1983. Accepted March 20, 1984.

# NEW COMPOUNDS

## Magnetic and Spectral Studies of *S*-Benzyl-*N*-phenylthiocarbamoylthiobenzamide Complexes with Some Bivalent Metal Ions

**B. Singh, B. P. Yadava, and R. C. Aggarwal***

*Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India*

**The complexes with chemical compositions $VOL_2SO_4$, $ML_2Cl_2$ [M = Cu(II), Cd(II), Hg(II)], and $M'(L-H)_2$ [M' = Cu(II), Co(II), Ni(II)], L = *S*-benzyl-*N*-phenylthiocarbamoylthiobenzamide, $PhC(SCH_2Ph){=}NC({=}S)NHPh$ (BPTT, L), have been prepared and characterized by analytical data, molar conductance, molecular weight, magnetic susceptibility, electronic, infrared, ESR, and X-ray powder diffraction studies. The complexes have been screened for antifungal activity.**

### Introduction

Metal complexes of sulfur donor ligands have received great attention recently (*1*) due to their versatile use as pesticides (*2*) and fungicides (*3*, *4*). The toxicological importance of the -N-C-S- moiety has been well established in a number of fungicides and pesticides (*5*). The complete absence of previous work on transition-metal complexes of BPTT and the possibility of these complexes having antifungal activity prompted us to undertake synthesis and structural studies of $V^{II}O$, Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) complexes of the above ligand.

### Experimental Section

***Materials.*** All the chemicals used in the present study were of British Drug House (BDH) or equivalent grade. The ligand was prepared following the procedure described earlier (*6*).

***Synthesis of the Complexes.*** The complexes $VOL_2SO_4$ and $ML_2Cl_2$ were prepared by adding a methanolic/ethanolic solution of metal salt to the acetone solution of the ligand in 1:2 molar ratio.

All the complexes precipitated almost immediately except $VOL_2SO_4$, which was obtained by heating the reaction mixture on a water bath for a few minutes and keeping it overnight.

The deprotonated complexes, $M'(L-H)_2$, were synthesized by mixing ethanolic solutions of appropriate metal acetate and ligand in 1:2 molar ratio with constant stirring. The resulting complexes were digested on a water bath for $^1/_2$ h to ensure complete deprotonation.

The complexes thus obtained were suction filtered and repeatedly washed with water (in the case of deprotonated complexes only), with ethanol/methanol to remove unreacted metal salt and ligand (if any), and then with ether and finally dried in vacuo.

***Analysis of the Complexes.*** The complexes were analyzed for metal content by standard procedure (*7*). The chloride and sulfur were determined gravimetrically as AgCl and $BaSO_4$, respectively, and nitrogen was determined microanalytically. The analytical data are given in Table I.

***Physical Measurements.*** Molar conductance of the complexes in DMF at $10^{-3}$ M concentration was determined at room temperature on a WTW conductivity meter. The molecular weight of $VOL_2SO_4$, $Co(L-H)_2$, $Ni(L-H)_2$, and $Cu(L-H)_2$ was determined cryoscopically by using nitrobenzene as solvent and that of other complexes could not be determined due to their insolubility. Magnetic susceptibility of the complexes was measured at room temperature on a Cahn-Faraday electrobalance by using $HgCo(NCS)_4$ as calibrant and was corrected for diamagnetism (*8*). The molar conductance, molecular weight, and magnetic moment data are included in Table I. The UV and visible spectra of the ligand and the complexes in Nujol were recorded on a Cary-14 spectrophotometer while IR spectra of the ligand and the complexes were recorded on a Perkin-Elmer spectrophotometer Model 621 in Nujol (4000-200 $cm^{-1}$) and in KBr (4000-400 $cm^{-1}$). The electronic spectral

0021-9568/84/1729-0343$01.50/0

**Table I. Color, Melting Point, Molar Conductance, Molecular Weight, Magnetic Moment, and Electronic Spectral Bands ($cm^{-1}$) and Their Assignments for BPTT Complexes**

| complex | color | mp, °C | $\Delta M$, $\Omega^{-1}$ $cm^2$ $mol^{-1}$ | mol wt found (calcd) | $\mu_{eff}$, $\mu_B$ | electronic bands, $cm^{-1}$ |
|---|---|---|---|---|---|---|
| $VOL_2SO_4$ | green | $140^d$ | 7.8 | 890.0 (887.0) | 1.18 | 11 765 ($d_{xy} \rightarrow d_{yz}$), 16 395 ($d_{xy} \rightarrow d_{zx}$), 23 530 ($d_{xy} \rightarrow d_{x^2-y^2}$) |
| $CuL_2Cl_2$ | pale yellow | 135 | 135.0 | | dia | 15 875 (d → d) |
| $CdL_2Cl_2$ | pale yellow | $190^d$ | 16.6 | | dia | |
| $HgL_2Cl_2$ | pale yellow | $175^d$ | 13.6 | | dia | |
| $Cu(L-H)_2$ | yellow | $115^d$ | 5.32 | 1500.0 (785.50) | 1.50 | 15 385 (d → d) |
| $Co(L-H)_2$ | green | $150^d$ | 5.32 | 1470.5 (780.91) | 1.16 | 15 385 ($d_{xz} \rightarrow d_{xy}$), 21 050 (d → d) |
| $Ni(L-H)_2$ | dark brown | $185^d$ | 5.32 | 817.00 (780.71) | dia | 15 385 ($d_{xz}$, $d_{yz} \rightarrow d_{x^2-y^2}$), 20 535 ($d_{xy} \rightarrow d_{x^2-y^2}$) |

[a] Elemental analyses were submitted for review.

**Table II. Infrared Spectral Bands ($cm^{-1}$) and Their Assignments in BPTT Complexes[a]**

| complex | $\nu$ | | | | |
|---|---|---|---|---|---|
| | (NH) | (C=N) | (M-S) | (M-Cl) | (M-N) |
| ligand | 3200 s | 1635 m | | | |
| $VOL_2SO_4$ | 3225 s | 1635 m | 365 m | | |
| $CuL_2Cl_2$ | 3200 sb | 1620 mb | 320 m | 285 m | 350 m |
| $CdL_2Cl_2$ | 3220 sb | 1645 mb | 300 m | 260 m | |
| $HgL_2Cl_2$ | 3200 s | 1650 m | 305 m | 275 m | |
| $Co(L-H)_2$ | | 1625 mb<br>1635 mb | 360 m | | 300 m |
| $Ni(L-H)_2$ | | 1625 mb<br>1635 m | 370 m | | 310 m |
| $Cu(L-H)_2$ | | 1615 mb<br>1635 m | 350 m | | 290 m |

[a] $Co(L-H)_2$ shows bands due to thioamides I-IV at 1545, 1340, 1300, and 695 $cm^{-1}$, respectively. Other complexes have similar bands within ±15, ±10, ±10, and ±30 $cm^{-1}$, respectively.

bands and their assignments are given in Table I. The important IR bands and their assignments are given in Table II. The ESR spectrum of $CuL_2Cl_2$ in DMF solution was recorded at room temperature on a Varian X-band spectrometer Model E-4 by using DPPH as $g$ marker. The X-ray powder photographs of $CuL_2Cl_2$ and $Ni(L-H)_2$ were obtained on a Philips X-ray generator by using nickel-filtered Cu $K_\alpha$ radiation and a Gulenier FR-552 camera. The indexing of X-ray diffraction lines was done by Ito's (*9*) method. The observed and computed $Q$ values along with the corresponding $hkl$ values are listed in Tables III and IV.

The antifungal activity of the complexes and the ligand was determined at 50 and 100 ppm by the food poison technique against *Rhizoctonia solani* Kühn, an omnivorous root pathogen of various crop plants as described by Schmitz (*10*). The number of replications for each concentration was three with suitable control. After 72 h of incubation the percent inhibition was calculated as follows:

$$\text{percent inhibition} = 100(X - Y)/X$$

where $X$ is the diameter of the colony in control plates and $Y$ is the diameter of the colony in test plates at different concentrations. The antifungal activities shown by ligand and complexes are listed in Table V.

## Results and Discussion

Molar conductance values indicate the 1:2 electrolytic nature (*11*) of $CuL_2Cl_2$ and the nonionic behavior of the remaining complexes. The observed molecular weights show the monomeric nature of $VOL_2SO_4$ and $Ni(L-H)_2$ and the dimeric nature of $Co(L-H)_2$ and $Cu(L-H)_2$. Electronic spectra indicate square-pyramidal (*12*, *13*) geometry for $VOL_2SO_4$ and square-planar (*14-17*) geometry for $M(L-H)_2$. Square-planar geometry for $Ni(L-H)_2$ is further supported by its diamagnetic nature. The anomalous $\mu_{eff}$ values of $Co(L-H)_2$ and $Cu(L-H)_2$ may be attributed to a superexchange phenomenon or metal-metal interaction (*18*, *19*) while that of $VOL_2SO_4$ may be due to V=O--V interaction (*20*). The diamagnetism of $CuL_2Cl_2$ is presumably due to the higher polarizability (*21*) of the liganmd, metal-metal interaction and/or superexchange phenomenon. A band at 15 875 $cm^{-1}$ in the electronic spectrum of the above complex is assigned to a d-d transition (*22*) while that at 23 810 $cm^{-1}$ is due to dimeric (*23*, *24*) nature. Although $CuL_2Cl_2$ is diamagnetic in the solid state, it is paramagnetic in solution as is evident from its ESR spectrum at room temperature, $g_{av}$ and $A_{iso}$ values being 2.377 and 56.22 G, respectively. The paramagnetic behavior of the complex in solution is presumably due to weakening (*25*) of electron spin-spin interaction in solution. The X-ray powder diffraction lines of $CuL_2Cl_2$ and $Ni(L-H)_2$ have been indexed assuming tetragonal symmetry. The positive shift (*26*) in thioamide I-III bands in all the complexes, a slight negative shift of $\nu$(C=S) in $VOL_2SO_4$ and $CuL_2Cl_2$, and a comparatively much higher shift in the above mode in the deprotonated complexes indicate bonding through thione sulfur in the first two complexes and through thiolic sulfur in the deprotonated complexes. The lowering in $\nu$(C=N) shows coordination of nitrogen in $M(L-H)_2$ and $CuL_2Cl_2$. The disappearance of $\nu$(N-H) and appearance of an additional $\nu$(C=N) band at 1635 $cm^{-1}$ in deprotonated complexes further supports bonding through thiolic sulfur. This presumably occurs through enoli-

**Table III. Observed and Computed $Q_{hkl}$ Values for $CuL_2Cl_2$[a]**

| powder pattern lines | $Q_{obsd}$ | $Q_{comp}$ | $hkl$ | powder pattern lines | $Q_{obsd}$ | $Q_{comp}$ | $hkl$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.01215 | 0.01215 | 003 | 12 | 0.0910 | 0.0919 | 108 |
| 2 | 0.03564 | 0.03415 | 203 | 13 | 0.1000 | 0.1001 | 410 |
| 3 | 0.03722 | 0.03925 | 105 | 14 | 0.1026 | 0.1056 | 413 |
| 4 | 0.04055 | 0.0405 | 006 | 15 | 0.1107 | 0.1106 | 404 |
| 5 | 0.0420 | 0.0436 | 204 | 16 | 0.1155 | 0.1154 | 422 |
| 6 | 0.0495 | 0.0495 | 300 | 17 | 0.1181 | 0.1158 | 307 |
| 7 | 0.0537 | 0.0550 | 310 | 18 | 0.1252 | 0.1210 | 317 |
| 8 | 0.0585 | 0.0564 | 311 | 19 | 0.1288 | 0.1273 | 415 |
| 9 | 0.0608 | 0.0612 | 215 | 20 | 0.1594 | 0.1595 | 520 |
| 10 | 0.0647 | 0.0656 | 224 | 21 | 0.1912 | 0.1914 | 532 |
| 11 | 0.0703 | 0.0711 | 304 | 22 | 0.1995 | 0.1992 | 533 |

[a] Lattice parameters: $a$ = 13.47 Å, $c$ = 27.22 Å, $\rho$ = 1.20 g $cm^{-3}$, $\rho$(calcd) = 1.16 g $cm^{-3}$, $z$ = 4.

Table IV. Observed and Computed $Q_{hkl}$ Values for $Ni(L-H)_2$[a]

| powder pattern lines | $Q_{obsd}$ | $Q_{comp}$ | hkl |
|---|---|---|---|
| 1 | 0.0146 | 0.0140 | 101 |
| 2 | 0.0325 | 0.0340 | 112 |
| 3 | 0.0440 | 0.0440 | 400 |
| 4 | 0.0480 | 0.0480 | 004 |
| 5 | 0.0624 | 0.0590 | 104 |
| 6 | 0.0824 | 0.0820 | 212 |
| 7 | 0.0966 | 0.0967 | 115 |
| 8 | 0.1185 | 0.1190 | 205 |
| 9 | 0.1915 | 0.1920 | 008 |
| | | 0.1900 | 411 |
| 10 | 0.2000 | 0.1990 | 412 |

[a] Lattice parameters: $a = 19.08$ Å, $c = 18.24$ Å, $\rho = 0.8$ g cm$^{-3}$, $\rho$(calcd) = 0.78 g cm$^{-3}$, $z = 4$.

Table V. Antifungal Activity[a] for Ligand and Complexes

| | concn | |
|---|---|---|
| compd | 50 ppm | 100 ppm |
| ligand | 13.3 | 31.1 |
| $VOL_2SO_4$ | 6.9 | 19.3 |
| $CuL_2Cl_2$ | 0.0 | 0.0 |
| $CdL_2Cl_2$ | 88.3 | 100.0 |
| $HgL_2Cl_2$ | 37.7 | 42.4 |
| $Co(L-H)_2$ | 12.5 | 13.3 |
| $Ni(L-H)_2$ | 0.0 | 0.0 |

[a] Percent inhibition.

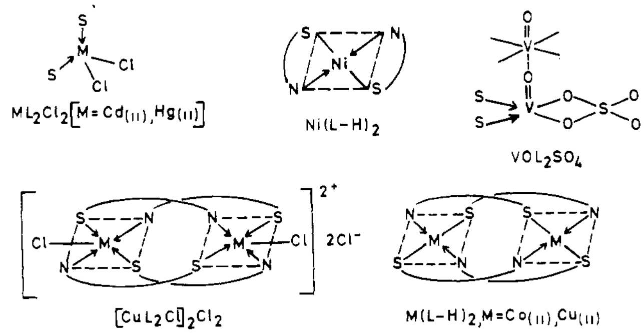

Figure 1.

zation and subsequent removal of the proton by the metal ion. The presence of four bands at 1245, 1150, 1025, and 975 cm$^{-1}$ is indicative of the bidentate chelating (*27*) nature of $SO_4^{2-}$ in $VOL_2SO_4$. Fungitoxicity increases at 100 ppm in the following order: $Co(L-H)_2 < VOL_2SO_4 < HgL_2Cl_2 < CdL_2Cl_2$.

Chemical compositions and physicochemical data suggest the structures in Figure 1 for the complexes.

## Acknowledgment

Sincere thanks are also due to RSIC, IIT Madras, for running ESR spectra of the complexes.

**Registry No.** $VOL_2SO_4$, 89909-15-9; $CuL_2Cl_2$, 89922-01-0; $CdL_2Cl_2$, 89909-16-0; $HgL_2Cl_2$, 89909-17-1; $Cu(L-H)_2$, 89909-19-3; $Co(L-H)_2$, 89909-18-2; $Ni(L-H)_2$, 89909-20-6.

## Literature Cited

(1) Satpathy, K. C.; Mishra, H. P. *J. Indian Chem. Soc.* **1981**, *58*, 844.
(2) Johnson, C. W.; Joyner, J. W.; Perry, R. P. *Antibiot. Chemother.* (*Washington, D.C.*) **1952**, *2*, 636.
(3) Gansman, H. W.; Rhykerd, C. I.; Hinderliter, H. R.; Scott, E. S.; Andrieth, L. F. *Bot. Gaz.* (*Chicago*) **1953**, *114*, 292.
(4) Benos, B. G.; Gingras, B. A.; Bayley, C. H. *Appl. Microbiol.* **1961**, *8*, 353.
(5) Das, B. C.; Mahapatra, G. N. *J. Indian Chem. Soc.* **1967**, *44*, 939.
(6) Rai Rameshwar; Verma, V. K. *Indian J. Chem., Sect. B* **1979**, *18*, 284.
(7) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis", 3rd ed.; ELBS and Longmans: London, 1973.
(8) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; p 403.
(9) Azaroff, L. V.; Burger, M. J. "The Powder Method in X-ray Crystallography"; McGraw-Hill: New York, 1958; p 119.
(10) Schmitz, H. *Ind. Eng. Chem. Anal.* **1930**, *4*, 361.
(11) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(12) Stocklosa, H. J.; Wasson, J. R.; McCormic, B. J. *Inorg. Chem.* **1974**, *13*, 592.
(13) Farmer, R. L.; Urbach, F. L. *Inorg. Chem.* **1974**, *13*, 587.
(14) Nishida, Y.; Kida, S. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 325.
(15) Singh, P. P.; Shukla, U. P.; Makhija, R.; Rivest, R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 679.
(16) Lever, A. B. P. "Inorganic Electron Spectroscopy"; Elsevier: Amsterdam, 1964; p 343.
(17) Sacconi, L.; Ciampolini, M. *J. Chem. Soc.* **1964**, 276.
(18) Yamada, S.; Nishikava, H.; Tsuchida, T. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1278.
(19) Hathaway, B. J. *Coord. Chem. Rev.* **1981**, *35*, 231.
(20) Syamal, A. *Coord. Chem. Rev.* **1975**, *16*, 309.
(21) Nyholm, R. S. *Proc. Chem. Soc.* **1961**, 273.
(22) Pignedoli, A.; Peyronel, G. *Gazz. Chim. Ital.* **1962**, *92*, 745.
(23) Khuller, I. P.; Agarwala, U. *Can. J. Chem.* **1975**, *53*, 1165.
(24) Harris, C. M.; Hoskens, B. F.; Martin, R. L. *J. Chem. Soc.* **1959**, 3728.
(25) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Shazly, M.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1980**, *19*, 201.
(26) Peyronel, G.; Pellacani, G. C.; Pignedoli, A. *Inorg. Chim. Acta* **1981**, *58*, 1149.
(27) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978.

Received for review April 25, 1983. Accepted January 9, 1984. B.P.Y. is thankful to the UGC, New Delhi, for the award of a Teacher Fellowship.

---

# Synthesis of Some Dihydroxamic Acid Siderophores

**M. K. Das,* P. Bose, and N. Roy**

*Department of Chemistry, Jadavpur University, Calcutta—700 032, India*

**Twenty-two new dihydroxamic acids having the general formula $(CH_2)_n[CON(R)OH]_2$ ($n$ = 2, 3, 4, 6, 8; R = H, aryl) have been synthesized either by condensation of the acid chlorides with suitable arylhydroxylamines or by the reaction of the esters with hydroxylamine and characterized by elemental analyses and infrared, UV, and proton NMR spectra.**

The importance of hydroxamic acids, RCON(R′)OH, in both biology and medicine is now well recognized (*1–4*), and much of their biological activity seems to be related to their ability to chelate iron specifically (*1*, *2*, *4*). The trihydroxamic acid desferrioxamine B is currently being used for the treatment of iron overload disease (*5*, *6*) and is usually given as the methanesulfonate salt under the trademark Desferal of the Ciba-Geigy Corp. Rhodotorulic acid, a dihydroxamic acid, has also

0021-9568/84/1729-0345$01.50/0 © 1984 American Chemical Society