

## Complexes of Benzoylisonicotinic Acid Hydrazide with VO(II), Mn(II), Co(II), Ni(II), Cu(II) & Zn(II)

R. C. AGGARWAL, N. K. SINGH & LAKSHMAN PRASAD  
Department of Chemistry, Banaras Hindu University, Varanasi 221005

Received 9 December 1974; accepted 19 March 1975

Benzoylisonicotinic acid hydrazide  $C_5H_4NC(=O)-N^2H-N^2H-C(=O)-C_6H_5$  (BINH) forms neutral chelates of the compositions  $VO(BINH-H)_2$  and  $M(BINH-H)_2 \cdot 2H_2O$  [where  $M = Mn(II), Co(II), Ni(II), Cu(II)$  or  $Zn(II)$ ]. The magnetic and electronic spectral data indicate that  $Mn(II), Co(II), Ni(II)$  and  $Cu(II)$  form spin-free octahedral complexes while  $VO^{2+}$  forms distorted square-pyramidal complex. Analytical data and infrared spectra of the chelates indicate that BINH behaves as a mononegative bidentate ligand and water molecules are coordinated. The probable bonding sites in the chelates are the enolic oxygen arising from the enolization of the keto group attached to the pyridine ring and  $N^2$  of the  $-NH$  group. Wherever possible, ligand field parameters like  $10 Dq, B', \beta, \beta^\circ$  and LFSE have been evaluated.

IN continuation of our earlier work<sup>1</sup> on the Ti(IV) and Zr(IV) complexes of benzoylisonicotinic acid hydrazide (BINH), we report here the results of our studies on VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of BINH.

### Materials and Methods

*Preparation and analysis of the chelates* — Chelates were prepared by mixing together hot aqueous solutions of the metal nitrates or sulphates and BINH<sup>1</sup> in ~1:2 molar ratio and adding  $NH_4Cl-NH_4OH$  buffer (except for Cu(II) complex till a slight turbidity appeared. The precipitation of the chelates was aided by digestion on a water-bath for about one hr. The chelates were suction filtered, washed successively with water, ethanol and ether and dried at room temperature.

Chelates were analysed for metal contents employing standard literature procedures, after destroying the organic part with a mixture of nitric

and hydrochloric acids and then with concentrated sulphuric acid. Nitrogen was estimated by micro-analysis. Hydrazine was estimated volumetrically using  $KIO_3$  after subjecting the chelates to acid hydrolysis for ~2 hr. The water content was estimated by finding out the loss in weight suffered by the chelates on heating at ~160° for 2-3 hr. The analytical data are given in Table 1.

*Physical measurements* — Magnetic susceptibility of the chelates was measured using a Cahn Faraday Electrobalance employing  $Hg[(Co(CNS)_4)]$  as calibrant. Diamagnetic corrections were estimated by the procedure of Figgis and Lewis<sup>3</sup>. The effective magnetic moments of the chelates are included in Table 1.

Electronic spectra (nujol) of the ligand and the chelates were recorded on a Cary-14 recording spectrophotometer. The values of the spectral parameters like  $10 Dq, B', \beta$  and  $\beta^\circ$  were calculated as described by Lever<sup>4</sup>.

TABLE 1 — ANALYTICAL DATA, COLOUR AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex	Colour	Analysis, calc. (Found)				$\mu_{eff}$ (BM)
		Metal	Nitrogen	$N_2H_4$	$H_2O$	
$VO(BINH-H)_2$	Light brown	9.30 (9.0)	15.35 (14.90)	11.70 (11.60)	—	1.63
$Mn(BINH-H)_2 \cdot 2H_2O$	Light yellow	9.62 (10.01)	14.71 (15.07)	11.21 (11.50)	6.31 (6.52)	6.20
$Co(BINH-H)_2 \cdot 2H_2O$	Yellowish red	10.25 (10.70)	14.61 (14.80)	11.13 (11.50)	6.26 (6.40)	4.73
$Ni(BINH-H)_2 \cdot 2H_2O$	Green	10.21 (10.50)	14.61 (15.00)	11.13 (11.00)	6.26 (6.10)	2.92
$Cu(BINH-H)_2 \cdot 2H_2O$	Deep green	10.96 (10.50)	14.50 (14.70)	—	6.21 (6.30)	2.13
$Zn(BINH-H)_2 \cdot 2H_2O$	Yellowish white	11.17 (11.00)	14.44 (14.60)	11.00 (11.20)	6.19 (6.20)	Diamag.

Infrared spectra (nujol) of the complexes and the ligand were recorded on a Perkin-Elmer spectrophotometer model 621.

### Results and Discussion

The formation of neutral complexes of 1:2 stoichiometry (Table 1) suggests that the ligand coordinates in the enolic form. The probable bonding sites in the chelates are the enolic oxygen arising from the enolization of the keto group attached to the pyridine ring and N<sup>2</sup> of the -NH group.

The chelates are insoluble in common organic solvents like benzene, chloroform, carbon tetrachloride, ethanol, acetone, THF, DMF and DMSO etc. and have high decomposition temperature (>250°). The formation of anhydrous chelates from the hydrated chelates with change in colour at relatively high temperatures (~160°) indicates that the water molecules are coordinated. The coordination of water molecules is further confirmed by a comparison of the infrared spectra of the hydrated and anhydrous chelates discussed later.

The corrected magnetic moments of Mn(II), Co(II), Ni(II) and Cu(II) chelates lie well within the range expected for complexes of these metal ions possessing octahedral geometry<sup>3</sup> (Table 1). The magnetic moment of VO(BINH-H)<sub>2</sub> is also normal, being close to the spin only value expected for one unpaired electron in vanadyl complexes<sup>5</sup>.

Ultraviolet spectrum of BINH in nujol shows three bands at 33300, 34800 and 35700 cm<sup>-1</sup>, the last band being similar to that obtained for isonicotinamide and isonicotinic acid<sup>6</sup>.

The UV spectra of all the chelates (Table 2) show one or two bands in the range 34500-37700 cm<sup>-1</sup> which correspond to the ligand bands occurring in the same region. Since no *d-d* transition is expected for Zn<sup>2+</sup> having a *d*<sup>10</sup> configuration, the 28570 cm<sup>-1</sup> band in the Zn(II) chelate corresponds probably to 33300 cm<sup>-1</sup> band observed in the ligand. The red shift in this band is presumably due to a

greater degree of conjugation in the ligand on coordination. Likewise, the above ligand band in Mn(II), Co(II), Ni(II) and Cu(II) chelates also is red shifted and is observed in the range 28600-30700 cm<sup>-1</sup>.

The position of the bands in VO(BINH-H)<sub>2</sub> and their assignment suggest a distorted square pyramidal geometry (C<sub>2v</sub> symmetry) for the chelate<sup>7</sup>.

The visible region spectra (Table 2) of Co(II) and Ni(II) chelates show bands characteristic of octahedral coordination around the central metal ions<sup>8,9</sup>. Also, the  $\nu_2/\nu_1$  ratio (= 1.61) for the nickel chelate lies in the range reported for octahedral Ni(II) complexes<sup>10</sup>. The values of 10 *D<sub>q</sub>* and *B'* (Table 2) in the Co(II) and Ni(II) chelates suggest a place between water and ammonia for the ligand in the spectrochemical series. Further, the values of *B'* show that the metal-ligand orbital overlap is quite appreciable in the two chelates.

A broad band at 14100 cm<sup>-1</sup> in Cu(II)-BINH chelate may be due to the merging of three transitions (Table 2) in a *D<sub>4h</sub>* symmetry<sup>11</sup>. The lowering of the symmetry from *O<sub>h</sub>* to *D<sub>4h</sub>* may be due to Jahn-Teller distortion so common in hexacoordinated Cu(II) complexes.

The bonding sites in the BINH complexes have been established by a careful comparison of their infrared spectra with that of the parent ligand.

BINH shows prominent IR bands at 3270 (νNH), 1680, 1660 (νC=O) and 900 cm<sup>-1</sup> (νN-N). In the spectra of the complexes, the disappearance of one of the two ν(C=O) bands of the ligand, a negative shift in ν(NH) (55-120 cm<sup>-1</sup>), appearance<sup>12</sup> of ν(C-O) in the range 1230-1204; ν(NCO)<sup>13</sup> in the range 1520-1490; ν(C=N)<sup>14</sup> in the range 1640-1605, ν(M-O)<sup>15</sup> in the range 265-240 and ν(M←N)<sup>16</sup> in the range 370-325 cm<sup>-1</sup> and a positive shift of 25-35 cm<sup>-1</sup> in ν(N-N)<sup>17,18</sup> taken together show that BINH acts as a bidentate ligand in all the present chelates, the bonding sites being the enolic oxygen of the isonicotinyl group and N<sup>2</sup> of the -NH group.

TABLE 2 — ELECTRONIC SPECTRAL BANDS (IN NUJOL) AND THEIR ASSIGNMENTS

Compounds	Bands (cm <sup>-1</sup> )	Assignment	Ligand field parameters
BINH	33300, 34800, 35700	<i>L</i>	
VO(BINH-H) <sub>2</sub>	12000, 16600, 22200 36360	<i>d<sub>xy</sub></i> → <i>d<sub>yz</sub></i> ; <i>d<sub>xz</sub></i> ; <i>d<sub>x<sup>2</sup>-y<sup>2</sup></sub></i>	
Mn(BINH-H) <sub>2</sub> ·2H <sub>2</sub> O	28570, 35100, 37700	<i>L</i>	
Co(BINH-H) <sub>2</sub> ·2H <sub>2</sub> O	8500, 18500, 28600, 34250	<sup>4</sup> <i>T<sub>1g</sub></i> → <sup>4</sup> <i>T<sub>2g</sub></i> ( <i>F</i> ); <sup>4</sup> <i>T<sub>1g</sub></i> ( <i>P</i> )	10 <i>D<sub>q</sub></i> = 9590 cm <sup>-1</sup> ; <i>B'</i> = 740 cm <sup>-1</sup> ; β = 0.763; β° = 23.71%; LFSE = 21.81 kcal/mole
Ni(BINH-H) <sub>2</sub> ·2H <sub>2</sub> O	10100, 16300, 28990, 37700	<sup>3</sup> <i>A<sub>2g</sub></i> → <sup>3</sup> <i>T<sub>2g</sub></i> ( <i>F</i> ); <sup>3</sup> <i>T<sub>1g</sub></i> ( <i>F</i> )	10 <i>D<sub>q</sub></i> = 10100 cm <sup>-1</sup> ; <i>B'</i> = 860 cm <sup>-1</sup> ; β = 0.814; β° = 18.6%; LFSE = 34.56 kcal/mole
Cu(BINH-H) <sub>2</sub> ·2H <sub>2</sub> O	14100, 30770, 34480	<i>L</i> Envelope of three transitions, <sup>2</sup> <i>B<sub>1g</sub></i> → <sup>2</sup> <i>A<sub>1g</sub></i> ; <sup>2</sup> <i>B<sub>2g</sub></i> ; <sup>2</sup> <i>E<sub>g</sub></i>	10 <i>D<sub>q</sub></i> = 14100 cm <sup>-1</sup> ; LFSE = 24.1 kcal/mole
Zn(BINH-H) <sub>2</sub> ·2H <sub>2</sub> O	28570, 35100	<i>L</i>	

*L* = intraligand transition.

The bands observed in the regions 3450-3315 and 720-660  $\text{cm}^{-1}$  in the present chelates are absent in the spectra of ligand and the anhydrous compounds. These may therefore be assigned to coordinated water<sup>19</sup>.

#### Acknowledgement

Authors are thankful to Prof. G. B. Singh, Head of the Chemistry Department, Banararas Hindu University, for providing laboratory facilities and one of them (L.P.) is thankful to ICMR, New Delhi, also for the award of a junior research fellowship.

#### References

1. AGGARWAL, R. C., PRASAD, T. & YADAVA, B. N., *J. inorg. nucl. Chem.*, **37** (1975), 899.
2. VOGEL, A. I., *A text-book of quantitative inorganic analysis* (Longmans, Green, London), 1961, 380.
3. FIGGIS, B. N. & LEWIS, J., in *Modern coordination chemistry*, edited by J. Lewis & R. G. Wilkins (Interscience, New York), 1960, 403.
4. LEVER, A. B. P., *J. chem. Educ.*, **45** (1968), 711.
5. SELBIN, J., *Chem. Rev.*, **65** (1965), 153.
6. STEPHENSON, H. P. & SPONER, H., *J. Am. chem. Soc.*, **79** (1957), 2050.
7. STOCKLOSA, H. J., WASSON, J. R. & MCCORMIK, S., *Inorg. Chem.*, **13** (1974), 592.
8. CARLIN, R. L., *Transition metal Chem.*, **1** (1965), 9.
9. MANCH, W. & FERNILIUS, W. C., *J. chem. Educ.*, **38** (1961), 195.
10. SACCONI, L., *Transition metal Chem.*, **4** (1969), 199.
11. PAOLETTI, P., FABBRIZZI, L. & BARBUCCI, R., *Inorg. chim. Acta Rev.*, **7** (1973), 43.
12. HAMADA, H., *Bull. chem. Soc. (Japan)*, **32** (1959), 1051.
13. MASHIMA, M., *Bull. chem. Soc. (Japan)*, **35** (1962), 338.
14. FREDRICKSON, L. D., *Analyt. Chem.*, **36** (1964), 1349.
15. NAKAMOTO, K., UDOVICH, C. & TAKEMOTO, J., *J. Am. chem. Soc.*, **92** (1970), 3922.
16. LEVER, A. B. P. & MANTOVANI, E., *Inorg. Chem.*, **10** (1971), 817.
17. NICHOLLS, D., ROWLEY, M. & SWINDELLS, R., *J. chem. Soc. (A)*, (1966), 950.
18. BRAIBANTI, A., DALLAVALLE, F., PELLINGHELLI, M. A. & LEOPORATI, E., *Inorg. Chem.*, **7** (1968), 1430.
19. GAMO, I., *Bull. chem. Soc. (Japan)*, **34** (1961), 760; 765; 1430.