CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 24, No. 5 May 1976

Regular Articles

[Chem. Pharm. Bull. 24(5) 839—844 (1976)] UDC 547.864'1562.08 : 543.422.4.03

Studies on the Metal Chelate Compounds of Phenazine Derivatives. XII.[1] Far-infrared Spectra of the Metal Chelates of Hydroxyphenazine Derivatives

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(Received May 21, 1975)

The far-infrared spectra of metal chelates of oxine-like ligands, 2,3-dimethyl-5-hydroxyquinoxaline, 1-hydroxyphenazine, 6-hydroxybenzo[*a*]phenazine, 8-hydroxybenzo[*a*]phenazine and 11-hydroxybenzo[*a*]phenazine, with divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) are investigated. The metal–oxygen stretching bands have been assigned tentatively to the 294—219 cm^{-1}. Structure of these metal chelates have been proposed from the magnetic moments, the number of metal–oxygen stretching bands and the spectral pattern in the 600—400 cm^{-1} region. The structure of copper chelates, except for 11-hydroxybenzo[*a*]phenazine copper chelate, is trans square planar. The relationship between the M–O stretching band and atomic number of central metal has been discussed.

In a previous paper, the authors reported on the stability constants of the metal chelates of phenazine derivatives.[3] The purpose of this study is to examine the behavior of the metal-sensitive bands and to propose the structure of these chelates. The far-infrared absorption spectra of the metal chelates derived from 2,3-dimethyl-5-hydroxyquinoxaline (5-DMQx), 1-hydroxyphenazine(1-phz), 6-hydroxybenzo[*a*]phenazine(6-Bphz), 8-hydroxybenzo[*a*]phenazine(8-Bphz), and 11-hydroxybenzo[*a*]phenazine(11-Bphz) have been measured and the M-O stretching bands were assigned tentatively to the 294—219 cm^{-1}, on the basis of the assignments given for metal oxinates.[4,5] Further, in order to aid in determining the structure of these chelates, the magnetic moments were determined.

Experimental

The metal chelates were prepared by mixing metal acetate with the ligand in the ratio of 1: 2.5 in the solvent on Table I. The precipitated metal chelates of 5-DMQx and 1-phz were washed with *n*-hexane. Since the nickel chelate of 5-DMQx does not precipitate in a 50% ethanol, it was prepared in 99.5% ethanol. After ethanol evaporating *in vacuo*, the residue was dissolved in chloroform, filtered, and then *n*-hexane was added to precipitate the nickel chelate. The metal chelates of 6-Bphz and 8-Bphz were washed with water and ethanol. The copper chelate of 11-Bphz was prepared in absolute ethanol and washed with ethanol.

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[1] Part XI: K. Inagaki, Y. Kidani, and H. Koike, *Chem. Pharm. Bull.* (Tokyo), **24**, 156 (1976).

[2] Location: *Tanabe-dori, Mizuho-ku, Nagoya.*

[3] Y. Kidani, K. Inagaki, and H. Koike, *Yakugaku Zasshi*, **93**, 1089 (1973); *idem, Chem. Pharm. Bull.* (Tokyo), **23**, 29 (1975); *idem, Bunseki Kagaku*, **24**, 221 (1975).

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[5] N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, **10**, 798 (1971).

Table I. Elementary Analyses of the Metal Chelates

Compounds		C	H	N	Solvent
5-DMQx:	$(C_{10}H_9ON_2)_2Cu$	58.7(58.6)	4.7(4.4)	13.5(13.7)	50% aq-ethanol
	$(C_{10}H_9ON_2)_2Co \cdot 3H_2O$	52.2(52.3)	5.2(5.2)	12.1(12.2)	50% aq-ethanol
	$(C_{10}H_9ON_2)_2Ni \cdot 1/2H_2O$	58.0(58.0)	4.7(4.6)	13.3(13.5)	ethanol
	$(C_{10}H_9ON_2)_2Zn \cdot 2H_2O$	53.7(53.7)	4.8(4.9)	12.3(12.5)	50% aq-ethanol
1-phz:	$(C_{12}H_7ON_2)_2Cu$	63.2(63.4)	3.0(3.1)	12.0(12.3)	50% aq-ethanol
	$(C_{12}H_7ON_2)_2Co\ H_2O$	61.4(61.6)	3.3(3.4)	11.9(12.0)	50% aq-ethanol
	$(C_{12}H_7ON_2)_2Ni\ H_2O$	61.8(61.7)	3.3(3.4)	12.0(12.0)	50% aq-ethanol
	$(C_{12}H_7ON_2)_2Zn$	63.1(63.2)	2.7(3.1)	12.1(12.3)	50% aq-ethanol
6-Bphz:	$(C_{16}H_9ON_2)Cu$	69.5(69.4)	3.1(3.3)	9.8(10.1)	ethanol
	$(C_{16}H_9ON_2)Co \cdot 1/2H_2O$	68.8(68.9)	3.4(3.4)	10.0(10.0)	ethanol
	$(C_{16}H_9ON_2)_2Ni \cdot H_2O$	67.5(67.4)	3.6(3.5)	9.7 (9.9)	ethanol
	$(C_{16}H_9ON_2)_2Zn \cdot 2H_2O$	65.3(65.0)	3.6(3.7)	9.3 (9.5)	ethanol
8-Bphz:	$(C_{16}H_9ON_2)_2Cu$	69.4(69.4)	3.3(3.3)	9.9(10.1)	ethanol
	$(C_{16}H_9ON_2)_2Co \cdot 1/2H_2O$	69.0(68.8)	3.5(3.4)	9.8(10.0)	ethanol
	$(C_{16}H_9ON_2)_2Ni \cdot 1/2H_2O$	69.0(68.9)	3.3(3.4)	9.9(10.0)	ethanol
	$(C_{16}H_9ON_2)_2Zn \cdot 1/2H_2O$	68.3(68.1)	3.3(3.4)	9.7 (9.9)	ethanol
11-Bphz:	$(C_{16}N_9ON_2)_2Cu \cdot 1/4H_2O$	68.7(68.8)	3.3(3.3)	9.9(10.0)	ethanol

The values in parentheses are calculated value.

Magnetic moments were measured with a Shimadzu MB-2 type magnetic balance at room temperature (about 299°K). For the measurements of the far-infrared spectra from 600—200 cm^{-1}, a Nihon Bunko DS-701G spectrophotometer was used. Sample were measured as mulls in nujol; they were placed between two polyethylene films and inserted into a holder.

Result and Discussion

As Table II shows, the magnetic moments of the copper chelates lie in the range 1.70—1.85 B.M. The magnetic moment of the copper chelate of 11-Bphz is a little lower than that of the spin-only formula (1.73 B.M.), and the chelate is considered to be a monomer, because the presence of copper-copper interaction usually produces much larger decrease in the magnetic moment.[6] In the case of the cobalt chelates, their magnetic moments lie in the range 4.71—4.88 B.M. Generally, the values for high spin octahedral and tetrahedral cobalt(II) chelates are 4.4—5.6 and 4.2—4.7 B.M,[7] respectively. Therefore, the configuration of the cobalt(II) chelates can not be defined from the values obtained. In the case of the nickel chelates, their magnetic moments lie within a range of 3.05—3.18 B.M, and these values correspond to two unpaired electrons. Therefore, the nickel chelates may have either tetrahedral or high spin octahedral structure.

Ohkaku, *et al.* concluded that the M-O stretching vibration of the α and β forms of copper oxinates are assigned to the bands at 332 and 324 cm^{-1}, respectively. The far-infrared spectra of copper chelates in the ranges of 400—200 cm^{-1} were shown in Fig. 1. In the spectrum of the copper chelate of 1-phz, band in the ranges of 400—300 cm^{-1} is not observed at all and there is a strong band at 277 cm^{-1}. On the other hand, the spectrum of the potassium salt of 1-phz shows two bands (362 and 227 cm^{-1}) with low intensity. The band at 277 cm^{-1} is metal-sensitive. Therefore, the band may be assigned to the Cu-O stretching vibration. For the same reason, the bands at 294, 278 and 293 cm^{-1} of the copper chelates of 5-DMQx, 6-Bphz and 8-Bphz may be assigned to the Cu-O stretching vibration, respectively.

Billing, *et al.* concluded that the band at 208—246 cm^{-1} observed in copper chelates of substituted quinoxaline is assigned to the Cu-O stretching vibration.[8] Generally, the M-O

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[6] M. Kata, H.B. Jonassen, and J.C. Fanning, *Chem. Revs.*, **64**, 99 (1964).

[7] L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

[8] D.E. Billing, A.E. Underhill, D.M. Adams, and D.M. Morris, *J. Chem. Soc.*, (A), **1966**, 902.

TABLE II. Magnetic Moments of 5-DMQx, 1-phz, 6-Bphz, 8-Bphz and 11-Bphz Metal Chelates

Chelates		Found	Calcd. for the spin-only formula
5-DMQx	Cu	1.77 B.M.	1.73 B.M.
	Co	4.76	3.88
	Ni	3.18	2.82
1-phz	Cu	1.85	1.73
	Co	4.71	3.88
	Ni	3.05	2.82
6-Bphz	Cu	1.81	1.73
	Co	4.85	3.88
	Ni	3.07	2.82
8-Bphz	Cu	1.84	1.73
	Co	4.88	3.88
	Ni	3.05	2.82
11-Bphz	Cu	1.70	1.73

stretching band is more intense than the M-N stretching band. Based on these facts, the band at 229 cm^{-1} of the copper chelate of 5-DMQx may be assigned tentatively to the Cu-N stretching vibration. Likewise, the band appearing at 213 and 216 cm^{-1} may be assigned to the Cu-N stretching vibration for the copper chelates of 1-phz and 6-Bphz, respectively. The M-N stretching vibration of the other metal chelates may appear below 200 cm^{-1}.

Tetracoordinated copper(II) chelate is given either tetrahedral or square planar structure. The number of infrared-active metal-ligand stretching bands is 2 for C_{2h} symmetry (2Bu for trans square planar) and 4 for C_{2v} symmetry ($2A_1+2B_1$ for cis planar and $2A_1+B_1+B_2$ for tetrahedral). The copper chelate of 5-DMQx has one Cu-O and one Cu-N stretching frequencies, so that its structure is expected to have trans square planar configuration. For the same reason, the structure of the copper chelates of 1-phz, 6-Bphz and 8-Bphz is trans square planar. On the contrary, when the copper chelate of 11-Bphz formed L_2M-type chelate, the square planar structure can not be formed because of the large interference of the benzene ring upon chelation. In the spectrum of the copper chelate of 11-Bphz, the two bands at 285 and 256 cm^{-1} may be considered to be due to the Cu-O stretching frequencies.

The Metal Chelates of 5-DMQx

As is evident from the spectra of the metal chelates of 5-DMQx in Fig. 2, when the band at 270 cm^{-1} of cobalt chelate is compared with the Cu-O stretching band at 294 cm^{-1}, the band may be assigned to the Co-O stretching frequency based on the band position and intensity. Likewise the band appearing at 282 and 250 cm^{-1} may be assigned to the M-O stretching frequency for the nickel and zinc chelates, respectively. Generally, zinc chelate possesses either tetrahedral or octahedral structure because zinc ion has not d-orbital available for dsp^2 bonding. If the chelate has the structure that the two 5-DMQx anions coordinate to the metal by forming a trans planar structure and two water molecules occupy the axial position (C_{2h} symmetry), the number of infrared-active metal-ligand bands are 3, that is, metal-oxygen (ligand), metal-nitrogen (ligand) and metal water stretching vibration, respectively. From the report of octahedral metal oxinates, the $M-OH_2$ stretching band appear below 200 cm^{-1}. Elementary analyses and the presence of only one Zn-O stretching frequency suggest an octahedral configuration for the structure of the zinc chelate. In the 600—400 cm^{-1} region, the spectral pattern of the cobalt chelate is similar to that of the zinc chelate, and is somewhat different from that of the copper chelate. Therefore, the structure of the cobalt chelate is probably the same structure as that of the zinc chelate. Further, from the presence of only one Co-O frequency, the structure of the cobalt chelate is probably octahedral, but the magnetic

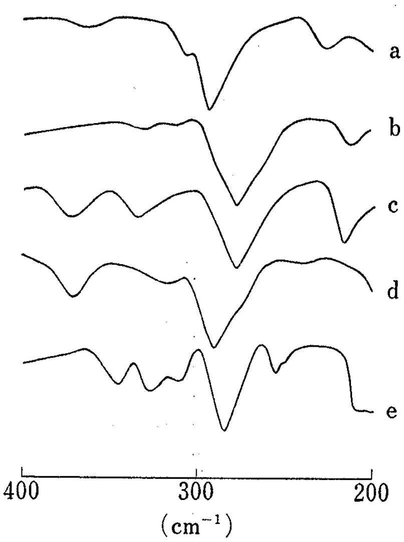

Fig. 1. Far-infrared Spectra of Various Copper Chelates in the Region 400—200 cm^{-1}

a) copper chelate of 5-DMQx,
b) copper chelate of 1-phz,
c) copper chelate of 6-Bphz,
d) copper chelate of 8-Bphz,
e) copper chelate of 11-Bphz

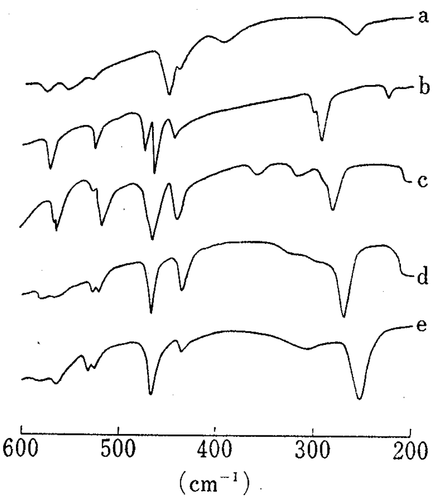

Fig. 2. Far-infrared Spectra of Metal Chelates of 5-DMQx in the Region 600—200 cm^{-1}

a) potassium salt, *b*) copper chelate,
c) nickel chelate, *d*) cobalt chelate,
e) zinc chelate

moment is a little lower than the value expected for high spin octahedral structure. Based on the magnetic moment and elementary analyses, the nickel chelate is expected to have a tetrahedral structure. However, the number of the band due to Ni-O stretching frequency is only one. Therefore, a definite conclusion as to the structure of nickel chelate is difficult to strike.

The Metal Chelates of 1-phz

As is shown in Table III, the cobalt chelate has a strong band at 255 cm^{-1}, with shoulder at 248 cm^{-1}. The nickel and zinc chelates have a strong band at 267 cm^{-1}, with shoulder at 253 cm^{-1} and a strong band at 238 cm^{-1}, with shoulder at 225 cm^{-1}, respectively. These bands are assigned to the M-O stretching frequencies, on the basis of the assignment of the Cu-O stretching band. Similarity in the spectral pattern among the cobalt, nickel and zinc chelates may indicates that these chelates have the same structure. Combining the infrared spectra, elementary analyses and magnetic moments, the tetrahedral structure for these chelates may be considered.

The Metal Chelates of 6-Bphz

As is seen in Fig. 3 and Table IV, the cobalt chelate showns two bands, at 252 and 235 cm^{-1}. We have assigned these bands to the asymmetric and symmetric Co-O stretching vibration, respectively, on the basis of the assignment of the Cu-O stretching band. The nickel chelate gives also two bands at 271 and 245 cm^{-1}. The former is assignable to the asymmetric, and the latter, to the symmetric stretching vibration of Ni-O, respectively. The zinc chelate has a strong band at 230 cm^{-1}, with shoulder at 219 cm^{-1}. The spectral pattern of the cobalt and nickel chelates are similar to each other. Further, the magnetic moment and the presence of two M-O stretching frequencies suggest a tetrahedral configuration for the structure of the cobalt and nickel chelates. In the 600—400 cm^{-1} region, the spectral pattern of the zinc chelate is similar to that of cobalt and nickel chelates. However, it is not possible to clearly differentiate between asymmetric and symmetric stretching vibration. From elementary analyses, the zinc chelate has two water molecules. Therefore, the structure of the zinc chelate can not be proposed from these data.

Table III. Observed Frequencies (cm^{-1}) of Metal Chelates of 5-DMQx and 1-phz

5-DMQx					1-phz				
K	Cu	Co	Ni	Zn	K	Cu	Co	Ni	Zn
553m	576m	578w	570m	562w	579m	609 s	588 s	590 s	587 s
			562m		560 s		570sh	567 s	567m
530m	530m	529w	532w	530w	533m	561 s	554 s	552 s	551 s
		521w	520w	522w	502m	530w	521 s	530m	529m
451 s	476 s	468 s	468 s	467 s	482w	493w	490w	489w	488w
	469 s					485w			
398 s	448m	436m	442 s	436w	420 s	439 s	440 s	443 s	443 s
270w			360w		362w	422 s	428 s	429 s	422 s
262w	307sh		320w		227m				
	294 s	270 s	282 s	250 s		277 s	255 s	267 s	238 s
	229m						248sh	253sh	225sh
					213w				

abbreviation; s, strong; m, medium; w, weak; sh, shoulder

The Metal Chelates of 8-Bphz

The bands based on the Co-O stretching vibration are found at 270 and 256 cm^{-1}. The former may be attributed to the asymmetric Co-O stretching, and the latter, to the symmetric Co-O stretching vibration. The asymmetric and symmetric Ni-O stretching vibrations are found at 275 and 264 cm^{-1}, and the corresponding bands of the zinc chelate are observed at 260 and 247 cm^{-1}, respectively. The spectral patterns among the cobalt, nickel and zinc chelates are similar to each other. From the magnetic moment, the presence of two M-O stretching vibration and the same spectral pattern, the tetrahedral structure for these chelates may be considered.

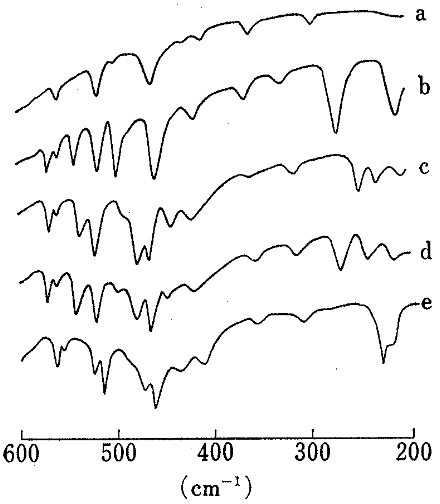

Fig. 3. Far-infrared Spectra of Metal Chelates of 6-Bphz in the Region 600—200 cm^{-1}

a) potassium salt, *b*) copper chelate, *c*) cobalt chelate, *d*) nickel chelate, *e*) zinc chelate

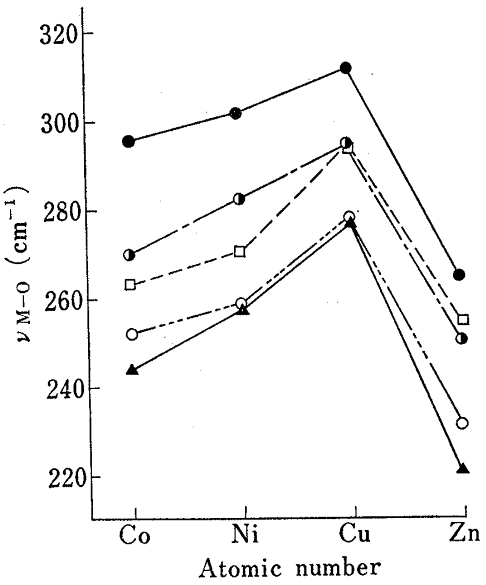

Fig. 4. Relationship between M-O Stretching Bands and Atomic Number of Central Metal

—●—: metal oxinates ($L_2M\ 2H_2O$)
—◐—: metal chelates of 5-DMQx
—□—: metal chelates of 8-Bphz
—○—: metal chelates of 1-phz
—▲—: metal chelates of 6-Bphz

TABLE IV. Observed Frequencies (cm^{-1}) of Metal Chelates of 6-Bphz, 8-Bphz and 11-Bphz

6-Bphz					8-Bphz					11-Bphz	
K	Cu	Co	Ni	Zn	K	Cu	Co	Ni	Zn	K	Cu
560w	573m	568m	570m	568m	573m	564 s	560 s	562 s	568m	592 s	589m
	564w	560w	560w	560w	540 s	545 s	546 s	548 s	541 s	558 s	564 s
	548 s	534m	542m	538sh		538 s					560 s
		530m	536m	532 s			528m	538m	522m	542 s	551 s
500w	522 s	521 s	521 s	520 s	512m	507m	508m	508m	508m	519m	525m
	502 s	493w	500m	493w	460m	451m	461m	461m	459m	485m	507m
464 s	463 s	473 s	479m	482m	438m		452m	453m	448m	439m	458m
		463 s	467 s	463 s			447m	448m		410m	415m
409w	429m	443m	449w	445m		414w	410w	409w	409w	342m	346w
		420m	425m	415m	366w	380sh	369m	369m	368w	308m	327w
362m	372m	367m	370m	365m	321w	370 s	346 s	346 s	341 s	300m	311w
297m	333m	318m	320m	315m		293 s	270 s	275 s	260 s		285m
	278 s	252m	271m	230 s			256m	264m	247m		256w
		235m	245m	219sh							
	216 s										

abbreviation; s, strong; m, medium; w, weak; sh, shoulder

The Relationship between the M-O Stretching Vibration and the Central Metal Ions

Ohkaku, *et al.* have plotted the position of the M-O stretching bands of various metal oxinates *vs.* atomic number of the central metals. These plots gave a straight line (from cobalt to copper). A similar plot has made in the present work using the M-O stretching band (in the case of the chelates having tetrahedral structure, mean value of the asymmetric and symmetric stretching frequencies was used). In spite of the differences of the ligands and chelate structure, a relationship between the M-O stretching frequencies and atomic number show a similarity, as is shown in Fig. 4. The relationship also show a similarity to that of the metal oxinates.

The wave numbers of the M-O stretching bands decreases in the order Cu>Ni>Co>Zn, which is in agreement with Irving-Williams stability order, with respect to each ligand. The order of the stability constants (log K_1 values) of these copper chelates and that of the Cu-O stretching vibration do not coincide each other, in spite of the similarity of the structure among these chelates. It is difficult to deduce a relationship between the Cu-O stretching band and the stability constant.