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Synthesis of Metal Complexes of 1-Phenyl-3-methyl-4benzoylpyrazole-5-one Semicarbazone by Solid-State and Solution Reactions

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1-Phenyl-3-methyl-4-benzoylpyrazole-5-one semicarbazone (HL) and its complexes have been prepared and characterized on the basis of elemental analyses, IR spectra, ¹H NMR spectra, mass spectra, molar conductivity, thermal analyses and X-ray powder diffraction. The spectral data show that the complexes obtained by solution reactions have the general formulas $[ML_2] \cdot nH_2O$ [M = Mn(II), Co(II), Ni(II), Zn(II)] in which the ligand chelates to the metal ion in a mononegative O,N,O-tridentate fashion. On the other hand, the complexes obtained by solid-state reactions have the formulas $[M(HL)(OAc)_2] \cdot nH_2O$, in which the ligand acts as a neutral bidenate entity that coordinates through the carbonyl oxygen of the pyrazolone ring, the azomethine nitrogen and the two acetate groups that are monodenate.

Keywords complex, pyrazolone, semicarbazone, solid-state reaction

INTRODUCTION

Much effort has been expanded recently to study pyrazolone thiosemicarbazones because these compounds have photochromic properties (Liu et al., 2002; Tang et al., 2000). According to the analyses of their crystal structures, an intermolecular proton transfer mechanism has been proposed. In order to further confirm this mechanism and establish a relationship between the photochromic properties and the structures, a series of these derivates have been studied (Liu et al., 2002a, 2002b; Liu et al., 2001). There has been considerable interest in metal complexes of 4-acylpyrazolones due to their remarkable antitumor, antibacterial and antiviral activities (Bukowsky et al., 1992; Mahalakshmi et al., 1998; Mirza, 1978; Radhakrishnan et al., 1998; Umatani et al., 1980).

Similarly, biological activities of complexes derived from hydrazones have been widely studied because of antimalarial and antituberculosis activities (Hueso-Urena et al., 1998; West et al., 1993). Now they also have been the subject of many researcher (Iskander and El-Sayed, 1976; Iskander and El-Aggan, 1975), but few studies of pyrazolone semicarbazone and its complexes, particularly its solid-state complexes, have been reported. In order to understand the coordination behavior of a novel semicarbazone towards bivalent transition metal ions under different reaction conditions, several metal complexes of 1-phenyl-3-methyl-4-benzoylpyrazole-5-one semicarbazone (HL) (Figure 1) have been synthesized by solid-state and solution reactions and characterized by elemental analyses, IR spectra, ¹H NMR spectra, mass spectra, molar conductance, TG-DTA and X-ray powder diffraction.

EXPERIMENTAL

Physical Measurements and Materials

Elemental analyses of carbon, hydrogen and nitrogen were carried out with a model 2400 Perkin-Elmer analyzer. Infrared spectra were measured on a Bio-RAD FTS-40 spectrophotometer on KBr pellets. The molar conductance values were determined in DMF with a model DSS-11A conductivity meter. TG-DTA measurements were carried out on a Netzsch STA 449C thermal analyzer. The ¹H NMR spectrum of HL was recorded on an AC-80 NMR spectrometer using CDC1₃ as solvent and TMS as an internal standard. Mass spectra were obtained on a HP-5988GC/MS spectrometer. X-ray powder diffraction studies were performed on a MAC Science MXP18AHF diffractometer with Cu K*a* radiation ($\lambda = 1.054056$ Å). All chemicals and solvents used were analytical grade reagents.

Synthesis of HL

A methanol solution (100 mL) containing 1-phenyl-3methyl-4-benzoyl pyrazole-5-one (2.78 g, 10 mmol) and semicarbazide (0.75 g, 10 mmol) was boiled with stirring at reflux



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FIG. 1. Structure of the ligand (HL).

temperature for *ca.* 3 h. The resulting solution was concentrated to ca. 30 mL, and then cooled to room temperature. From the light yellow solution, a large amount of yellow solid powder was precipitated. The product was purified by recrystallizing in anhydrous ethanol. Yield, 2.5 g (74.5%); m.p. 190.0–191.0°C. *Anal.* calcd. for $C_{18}H_{17}N_5O_2$ (335.37): C, 64.47; H, 5.11; N, 20.88%; found: C, 64.50; H, 5.12; N,

20.73%. ¹H NMR (CDC1₃, δ): 1.54 (s, 3H, CH₃), 2.09 (s, 1H, CH), 5.09 (s, 1H, NH), 7.25–7.64 (m, 10H, 2C₆H₅), 7.93 (s, 2H, NH₂). MS: [M + 1]⁺ = 336.

Preparation of Metal Complexes

Solution Reaction

A 2 mmol quantity of metal acetate was dissolved in water (10 mL) and warmed to 50° C. Each of the salt solutions was added to a warm ethanol solution (100 mL) of HL (0.67 g, 2.0 mmol) with stirring. The mixture was heated under reflux for 0.5 h and then cooled to room temperature. The resulting product was recrystallized from the mixture of DMF/ethanol (1:4). The precipitate formed was filtered and washed with ethanol, dried in air and stored in a desiccator.

Solid State Reaction

HL (0.6707 g, 2.0 mmol) and the metal acetate [0.4899 g of $Mn(OAc)_2 \cdot 4H_2O$; 0.4982 g of $Co(OAc)_2 \cdot 4H_2O$; 0.4977 g of $Ni(OAc)_2 \cdot 4H_2O$; 0.4390 g of $Zn(OAc)_2 \cdot 2H_2O$] in the mole ratio of 1:1 were mixed in an agate mortar in order to get the best possible homogeneity. The color of the reactants changed immediately with strong acetic acid odors being

 TABLE 1

 Elemental analyses and molar conductivity of the compounds^a

			Color	Elemental analyses (%) found (calcd.)						
Formula	Method	F.W.		С	Н	N	Yield (%)	M.p. or D.p. (°C)	$\Omega^{-1} \cdot \mathrm{cm}^2 \cdot \mathrm{mol}^{-1}$	
HL	L	335.37	Yellow	64.50	5.12	20.73	84	190.0-191.0		
$C_{18}H_{17}N_5O_2$				(64.47)	(5.11)	(20.88)				
$[MnL_2] \cdot H_2O$	L	741.67	Cream	58.59	4.47	19.01	85	>253.0	3.82	
C ₃₆ H ₃₄ MnN ₁₀ O ₅				(58.30)	(4.62)	(18.89)				
$[CoL_2] \cdot H_2O$	L	745.66	Pink	58.19	4.63	18.83	82	>257.0	3.94	
C ₃₆ H ₃₄ CoN ₁₀ O ₅				(57.99)	(4.60)	(18.78)				
$[NiL_2] \cdot 2H_2O$	L	763.44	Reseda	56.32	4.73	17.96	80	>307.0	4.20	
C ₃₆ H ₃₆ N ₁₀ NiO ₆				(56.64)	(4.75)	(18.35)				
$[ZnL_2] \cdot 2H_2O$	L	770.13	Pink	56.14	4.69	17.97	80	>237.0	3.48	
C ₃₆ H ₃₆ N ₁₀ O ₆ Zn				(56.15)	(4.71)	(18.19)				
[Mn(HL)(OAc) ₂] ·	S	562.44	Cream	46.87	5.10	12.39	94	>141.0	12.96	
$3H_2O$				(46.96)	(5.20)	(12.45)				
C ₂₂ H ₂₉ MnN ₅ O ₉										
$[Co(HL)(OAc)_2]$.	S	576.51	Pink	46.46	4.91	12.23	95	>143.0	12.45	
$3H_2O$				(46.56)	(5.16)	(12.37)				
$C_{22}H_{29}CoN_5O_9$										
[Ni(HL)(OAc) ₂].	S	566.19	Green	46.66	5.02	12.40	95	>146.0	11.01	
$3H_2O$				(46.67)	(5.16)	(12.37)				
C22H29N5Ni5O9										
$[Zn(HL)(OAc)_2]$	S	518.83	Buff	50.97	4.37	13.54	96	>260.0	4.62	
$C_{22}H_{23}N_5O_6Zn$				(50.92)	(4.47)	(13.50)				

^{*a*}L: liquid state; S: Solid state.

	Major IK bands of HL and its complexes (cm ⁻¹)												
	Compound	Method	ν(OH)	$\nu(\mathrm{NH}_2)$	$\nu(NH)$	$\nu(C=0)^a$	$\nu(C==0)^{b}$	ν (C==N)	ν(C==O)	$v_{as}(COO)$	$\nu_{s}(COO)$	$\nu(M-O)$	$\nu(M-N)$
271	HL	L		3363 m	3143 m	1718 s	1686 s	1626 s	_	_			_
	$[MnL_2] \cdot H_2O$	L	3654 m	3357 m	—		1653 s	1602 s	1359 s	_		436 w	412 w
	$\frac{[Mn(HL)(OAc)_2]}{3H_2O}$	S	3481 m	3337 m	3157 m	1717 s	1678 s	1592 s	—	1553 s	1329 s	449 w	420 w
	$[CoL_2] \cdot H_2O$	L	3631 m	3286 m			1652 s	1600 s	1364 m	_		431 w	416 w
	$\frac{[Co(HL)(OAc)_2]}{3H_2O}$	S	3477 m	3336 m	3149 m	1717 s	1676 s	1590 s	—	1553 s	1329 s	447 w	428 w
	$[NiL_2] \cdot 2H_2O$	L	3658 m	3298 m			1651 s	1603 s	1364 m	_		443 w	412 w
	$[Ni(HL)(OAc)_2] \cdot 3H_2O$	S	3475 m	3362 m	3146 m	1718 s	1685 s	1624 s	—	1591 s	1372 s	450 w	428 w
	$[ZnL_2] \cdot 2H_2O$	L	3600 m	3287 m			1658 s	1603 s	1363 m	_		440 w	415 w
	$[Zn(HL)(OAc)_2]$	S	_	3357 m	3180 m	1718 s	1665 s	1603 s	_	1552 s	1368 s	455 w	432 w

TABLE 2 Major IR bands of HL and its complexes (cm^{-1})

 $^{a}\nu$ (C=O) of hydrazide moiety.

 ${}^{b}\nu$ (C=O) of pyrazolone moiety.

discharged. The mixture was ground for 1 h and heated on a water bath at 70°C for 3 h to accelerate the reaction. After further ground at room temperature, the product was dried in a desiccator. It is noticed that the solid-state products should not be washed by water, ethanol, etc.

RESULTS AND DISCUSSION

A summary of the analytical results and some physical properties of HL and its complexes are shown in Table 1. The data obtained show that HL forms 1:2 complexes by the solution reaction and 1:1 complexes by the solid-state reaction. The products are in good agreement with the formulas $[ML_2] \cdot nH_2O$ (M = Mn, Co, n = 1; M = Ni, Zn, n = 2) and $[M(HL)(OAc)_2] \cdot nH_2O$ (M = Mn, Co, Ni, n = 3; M = Zn, n = 0), respectively. The complexes are colored, air-stable solids. They are slightly soluble in DMF and DMSO. The molar conductivities of the complexes are around $3.48 \sim 12.96 \ \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ in DMF, which shows that all complexes are non-electrolytes in DMF (Geary, 1971). It is emphasized that the solid-state products washed with water or ethanol turn into the liquid-state complexes. In order to confirm the conclusion mentioned above, the following experiment was carried out. The solid-state Ni (II) complex was washed with the water/ethanol or suspended in a small amount of ethanol, refluxed for 0.5 h and filtered. The elemental analyses data of the product are C, 57.69; H, 4.59; N, 18.44%, which is consistent with the calculative values (C, 58.01; H, 4.60; N, 18.79%) of NiL₂ \cdot H₂O. Thus, the complex [Ni(HL)(OAc)₂] · 3H₂O was transformed into the product $[NiL_2] \cdot H_2O$, formed by the solution reaction. Moreover, the other solid-state complexes show similar phenomena. These results suggest that the solid-state products are not only unstable in solution, but also cannot be synthesized by solution reactions. They are the intermediates of the solution reaction (Chen et al., 1997; Lei and Xin, 1995; Yao et al., 1995).

Infrared Spectra

The Liquid-State Complexes

The important infrared spectral frequencies are given in Table 2. The v(C=N) band of HL at 1626 cm^{-1} exhibits a bathochromic shift of $23-26 \text{ cm}^{-1}$ for the complexes, which suggests coordination of the azomethine nitrogen. The band at 1718 cm^{-1} for v(C=O) of hyrazide moiety and the band at 3143 cm^{-1} for v(NH) in HL are absent in the complexes and new absorption bands attributed to $v(C-O^-)$ (Niu et al., 1998) are observed at $1359-1364 \text{ cm}^{-1}$. These imply that the semicarbazide undergoes isomerization from the keto form to the enol form during the solution reaction, and then coordinates through a deprotonated oxygen. The shift of v(C=O) of pyrazolone moiety to lower wave numbers shows that the carbonyl oxygen atom of the pyrazolone ring bonds to the metal ion. All of these data confirm the fact that HL behaves

as a mononegative tridentate ligand forming two conjugated chelate rings and existing in the enolized form in the complexes.

The Solid-State Complexes

IR spectral data of the solid-state complexes show that HL acts as a neutral bidenate ligand coordinating through the carbonyl oxygen atom of the pyrazolone ring and the azomethine nitrogen atom forming a six-membered. This mode of chelation is supported by the following evidence. (1) The v(C=N) band shifts to lower wave number. (2) The v(C=O) of pyrazolone moiety band also shifts to lower wave number. (3) The v(C=O) of hydrazide moiety bands remain more or less at the same position, suggesting non-coordination of the carbonyl oxygen of semicarbazide.

The bands in the region of the 1552–1591 and 1329–1372 cm⁻¹ are attributed to v_{as} and v_{sy} frequencies of OAc⁻, respectively. The frequency difference between these two bands indicates monodentate coordination of the acetato group (Nakagawa and Shimanouchi, 1964).

The new bands above 3477 cm^{-1} in the all complexes, except for [Zn(HL)(OAc)₂], are assigned to the O–H stretching vibration, which indicates that water molecules are involved in these complexes. This is in agreement with the results of the elemental analyses. In the far-IR region two new bands at 431-455 and $412-436 \text{ cm}^{-1}$ in the complexes are assigned to v(M-O) and v(M-N), respectively (EI-Tabl et al., 2002; Liu et al., 2002a).

XRD Analysis

Figure 2 shows X-ray diffraction patterns of the reaction system of $Zn(OAc)_2 \cdot 4H_2O$ with HL. Obviously, the diffraction peaks of the starting materials disappear and new peaks

FIG. 2. XRD patterns of Zn(II) complexes prepared by the solid-state and the solution-state methods, respectively: (A) HL, (B) $Zn(OAc)_2 \cdot 4H_2O$, (C) $[Zn(HL)(OAc)_2]$, and (D) $[ZnL_2] \cdot 2H_2O$.



				Mass 1	oss (%)	Solid Decomposition product	
Complex	Method	Decomposition stage	Decomposition range (°C)	Found	Calcd.		
$[MnL_2] \cdot H_2O$	L	1	70-253	2.03	2.43	MnL_2	
		2	253-750	87.72	88.01	MnO	
$[Mn(HL)(OAc)_2] \cdot 3H_2O$	S	1	54-141	8.48	9.61	$Mn(HL) \cdot (OAc)_2$	
		2	141-228	10.89	10.50	$Mn(HL) \cdot (OAc)$	
		3	228-689	67.37	67.28	MnO	
$[CoL_2] \cdot H_2O$	L	1	50-257	2.39	2.42	CoL ₂	
		2	257-800	85.74	86.46	Co_2O_3	
$[Co(HL)(OAc)_2] \cdot 3H_2O$	S	1	50-143	8.29	9.54	$Co(HL) \cdot (OAc)_2$	
		2	143-229	10.89	10.42	$Co(HL) \cdot (OAc)$	
		3	229-564	61.95	61.51	CoNO ₂	
$[NiL_2] \cdot 2H_2O$	L	1	80-327	20.57	19.92	NiL ₂	
		2	327-686	67.71	69.15	Ni ₂ O ₃	
$[Ni(HL)(OAc)_2] \cdot 3H_2O$	S	1	54-146	9.27	9.55	$Ni(HL) \cdot (OAc)_2$	
		2	146-307	21.37	20.86	$Ni(HL) \cdot (OAc)$	
		3	307-560	53.61	54.99	Ni ₂ O ₃	
$[ZnL_2] \cdot 2H_2O$	L	1	60-237	4.43	4.68	ZnL_2	
		2	237-800	83.27	84.75	ZnO	
$[Zn(HL)(OAc)_2]$	S	1	60-352	22.25	22.76	Zn(HL)	
, , , ,		2	352-566	60.93	61.55	ZnO	

TABLE 3Thermal analysis data of the complexes

of the product appear in the X-ray diffraction patterns. This reveals that the solid-state product is a new species and not the mechanical mixture of the reactants. The XRD patterns C and D in Figure 2 indicate that the solid-state product is different from the liquid-state product. However, the X-ray diffraction pattern of C is quite broad. This is ascribed to the fact that the solid-state product is not fully crystallized.

Thermal Decomposition Studies

The thermal analysis data of the complexes are summarized in Table 3. All complexes prepared in solution follow a twostep decomposition. The first step, except for $[NiL_2] \cdot 2H_2O$, is consistent with the loss of the water molecules in the temperature range of 50–257°C. The second step occurs in a wide temperature range and corresponds to decomposition of ML₂,



FIG. 3. Suggested structure of the complexes prepared in solution [M = Mn(II), Co(II), Ni(II), Zn(II)].



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FIG. 4. Suggested structure of the complexes prepared in solid-state [M = Mn(II), Co(II), Ni(II), Zn(II)].

leading to the formation of the oxide, M_xO_y . All complexes prepared in the solid state, except for $[Zn(HL)(OAc)_2]$, follow a three-step decomposition. In the first step, the loss of water molecules takes place in the temperature range of $50-146^{\circ}C$ and is attributed to crystal water. In the second stage, the loss of OAc⁻ occurs, while in the third stage, the coordinated oxygen and nitrogen atoms of the Co(II) complex remain bound to the metal ion. The final decomposition product is CoNO₂ (EI-Sayed et al., 2001). All decomposition products of the other complexes prepared in the solid-state are the corresponding oxides.

On the basis of the elemental analyses, spectral and thermal analysis studies, we tentatively propose six-coordinate geometry for the complexes prepared in solution, as shown in Figure 3, and four-coordinate geometry for the complexes prepared in the solid-state, as shown in Figure 4.

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