The Syntheses and Properties of Bis(3-hydroxy-2-methyl-4-pyronato) Complexes of Bivalent Metal Ions

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Bis(3-hydroxy-2-methyl-4-pyronato) complexes of cobalt(II), nickel(II), copper(II), and zinc(II) have been prepared: $CoL_2(OH_2)_2$, $NiL_2(OH_2)_2$, CuL_2, and $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$. The 2,2′-bipyridine-(bpy) and 1,10-phenanthroline(phen) adducts of these complexes were also synthesized: CoL_2(bpy), CoL_2(phen), NiL_2(bpy), ZnL_2(bpy), and ZnL_2(phen). Based on the magnetic, spectral, and thermogravimetric data, the structures of these complexes are proposed: all of the cobalt(II), nickel(II), and zinc(II) complexes are octahedral, and CuL_2 is square planar. The NMR spectra of the zinc(II) complexes are discussed.

3-Hydroxy-2-methyl-4-pyrone occurs naturally is also obtained by the alkaline hydrolysis of streptmycin salts.[1] The pyrone has a caramel-like odor, and is used as a spice in bread and cakes. However, the compound is not harmless, the oral lethal dose (LD_{50}) for rats being 1.48 g/kg.[2] On the other hand, Nickell and Gordon reported on a stimulatory effect of this pyrone on plant growth, and suggested that the effect might be brought about by its metal chelate since methoxylation of the hydroxyl group of pyrone renders it inactive.[3] Thus a detailed study of the metal complexes of the pyrone is desirable.

The stability constants have been determined for a number of metal complexes of this pyrone.[4] Several tervalent metal complexes were isolated,[5,6] but no example of the mixed ligand complex containing another base has been reported.

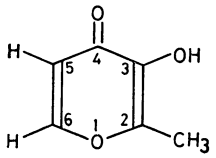

Fig. 1. 3-Hydroxy-2-methyl-4-pyrone.

This paper reports on the syntheses and structural studies of the bivalent metal complexes of 3-hydroxy-2-methyl-4-pyrone (HL, Fig. 1) and their 2,2′-bipyridine and 1,10-phenanthroline adducts.

Experimental

Syntheses of Complexes. Bis(3-hydroxy-2-methyl-4-pyronato)diaquacobalt(II), $CoL_2(OH_2)_2$: A 20 ml portion of 1 M NaOH solution was added to *ca.* 100 ml of warm aqueous ethanol (1:1 by volume) containing 2.54 g (0.02 mol) of 3-hydroxy-2-methyl-4-pyrone and 2.39 g (0.01 mol) of cobalt(II) chloride hexahydrate. The mixture was stirred for *ca.* 30 minutes and then kept standing overnight in a refrigerator. A dull yellow precipitate was obtained by filtration, washed with water and ethanol successively, and air dried. Yield: *ca.* 2.5 g, 72%.

The corresponding nickel(II), copper(II), and zinc(II) complexes, $NiL_2(OH_2)_2$, CuL_2, and $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$, were also prepared by the same method in 81, 80, and 78% Yields, respectively.

Bis(3-hydroxy-2-methyl-4-pyronato)bipyridinecobalt(II), CoL_2(bpy): A mixture containing 1.72 g (0.005 mol) of $CoL_2(OH_2)_2$ and 0.78 g (0.005 mol) of 2,2′-bipyridine in 200 ml of acetone was stirred for *ca.* 5 h and then filtered and washed with acetone. The crude complex was recrystallized from hot acetone and air dried. Yield: *ca.* 2.0 g, 86%.

In a similar fashion, NiL_2(bpy), ZnL_2(bpy), CoL_2(phen) and ZnL_2(phen) were obtained in 60, 85, 86, and 85% yields, respectively.

Analyses and Measurements. Metal contents in these complexes were determined by atomic absorption. The results of elemental analysis are shown in Table 1 together with some properties. The visible and ultraviolet absorption and reflection spectra were obtained with Hitachi EPS-3 and Shimadzu MPS-5000 recording spectrophotometers. The infrared spectra (4000—400 cm^{-1}) were obtained with a Hitachi EPI-G2 infrared spectrophotometer by the KBr disk method, and those in the 700—200 cm^{-1} region with a Jasco DS-701G infrared spectrophotometer by the CsI disk method. The magnetic susceptibility was determined at room temperature by the Faraday method with an automatically recording magnetic balance (Shimadzu Seisakusho Co., Ltd.). Mercury(II) tetraisothiocyanatocobaltate(II) was used as a reference

TABLE 1. COLOR AND ANALYTICAL DATA OF THE ISOLATED COMPLEXES

Complex	Color	Found (Calcd), %					Magnetic moment
		C	H	N	M	H_2O	B.M. (K)
$CoL_2(OH_2)_2$	dull yellow	41.44(41.76)	4.52(4.09)		16.93(17.03)	10.1(10.44)	4.74(303)
CoL_2(bpy)	orange	56.19(56.79)	3.97(3.90)	6.22(6.02)			4.56(297)
CoL_2(phen)	reddish orange	58.34(58.91)	3.75(3.71)	5.73(5.72)			4.59(297)
$NiL_2(OH_2)_2$	yellow green	41.55(41.78)	4.39(4.09)		17.29(17.02)	9.9(10.45)	3.21(303)
NiL_2(bpy)	green	56.13(56.81)	4.04(3.90)	6.30(6.02)			3.13(297)
CuL_2	pale green	45.57(45.94)	3.35(3.21)		19.63(20.25)		1.84(297)
$[ZnL_2(OH_2)_2]\cdot 1/2H_2O$	white	39.97(39.94)	4.48(4.19)		18.07(18.13)	11.1(12.49)	
ZnL_2(bpy)	pale yellow	55.72(56.01)	3.92(3.85)	5.93(5.94)	14.08(13.86)		
ZnL_2(phen)	pale yellow	57.85(58.14)	3.62(3.66)	5.64(5.65)	13.15(13.19)		

Table 2. Characteristic IR bands (cm^{-1}) of the isolated complexes

Assignment	ν(C=O)	ν(C=C)	ν(M–O)	Base
HL	1650s	1620vs, 1560s		
$CoL_2(OH_2)_2$	1600s	1570vs, 1500s	466s, 273s	
CoL_2(bpy)	1599vs	1570vs, 1507s	452s, 243s	1022w, 779m, 739w, 422s
CoL_2(phen)	1599vs	1569vs, 1508s	450s, 240s	1419m, 869m, 730m, 423m, 286m
$NiL_2(OH_2)_2$	1598s	1574vs, 1499s	470s, 284s	
NiL_2(bpy)	1598vs	1572vs, 1510s	457m, 272s	1027w, 769m, 740w, 423m
CuL_2	1613vs	1579vs, 1506s	395m, 235s	
$[ZnL_2(OH_2)_2]\cdot 1/2H_2O$	1608s	1576vs, 1508s	472m, 243s	
ZnL_2(bpy)	1602vs	1573vs, 1509s	457m, 230s	1022w, 780m, 740w, 417m
ZnL_2(phen)	1600vs	1572vs, 1510s	457m, 230s	1419m, 870m, 727m, 422m, 286m

substance. Diamagnetic corrections were calculated from Pascal's constants. Thermogravimetric curves were obtained with a Rigaku Denki 8002 H/D differential thermobalance at a heating rate of 3 °C/min in the air. The NMR spectra were measured in $(CD_3)_2SO$ at 100 MHz with a JNM-PS-100 spectrometer (Japan Electron Optics Lab. Co., Ltd.) using tetramethylsilane as an internal reference.

Results and Discussion

Infrared Spectra and Thermogravimetric Data. The characteristic IR bands of the metal complexes of 3-hydroxy-2-methyl-4-pyrone and their base adducts summerized are in Table 2. They were assigned in reference to the literature.[7–11] The frequencies of the C=O and C=C stretching vibrations in all these complexes are smaller by *ca.* 50 cm^{-1} than those in the free ligand. This suggests that the 3-hydroxy-2-methyl-4-pyronate ion is coordinated to the metal ion through both oxygen atoms of the carbonyl and hydroxyl groups, and that the delocalization of the olefinic and carbonyl electrons of the 3-hydroxy-2-methyl-4-pyronate ion takes place.[12]

The OH stretching bands of $CoL_2(OH_2)_2$, $NiL_2(OH_2)_2$ and $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$ are shown in Fig. 2. The OH stretching bands of cobalt(II) and nickel(II) complexes are observed at *ca.* 3420 cm^{-1}, both being sharp. In contrast the zinc(II) complex exhibits a very broad band at 3480 cm^{-1}, which might be composed of the OH stretching bands of both the coordinated and lattice water. Thermogravimetric analysis of the three complexes shows that the zinc(II) complex begins to liberate water at around 80 °C, and the nickel(II) and cobalt(II) complexes at around 115 and 105 °C, respectively. The difference in the temperature of water liberation suggests that the zinc(II) complex may contain lattice water, although the thermogravimetric analysis can not discriminate the coordinated and lattice water.

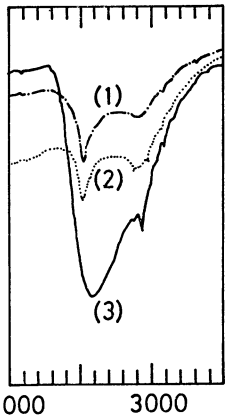

Fig. 2. The IR spectra of: (1) $CoL_2(OH_2)_2$; (2) $NiL_2(OH_2)_2$; and (3) $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$.

The IR spectra of adducts containing heterocyclic diamine (phen or bpy) consist of bands due to the 3-hydroxy-2-methyl-4-pyronate ligand and those of the coordinated diamine. The bands in the 1700—1500 cm^{-1} region are little affected by the coordination of the diamine, no new bands being observed in this region. Thus the bands around 1600 and 1570 cm^{-1} are assigned mainly to the C=O and C=C stretching vibrations, respectively, of the 3-hydroxy-2-methyl-4-pyronate ligand. The coordination of phen to the metal ion is evidenced by the new bands at around 1420, 865, and 725 cm^{-1},[9,10] and the coordination of bpy is also revealed by the shift and split of the characteristic band (751 cm^{-1}) of the free ligand into two bands around 780 and

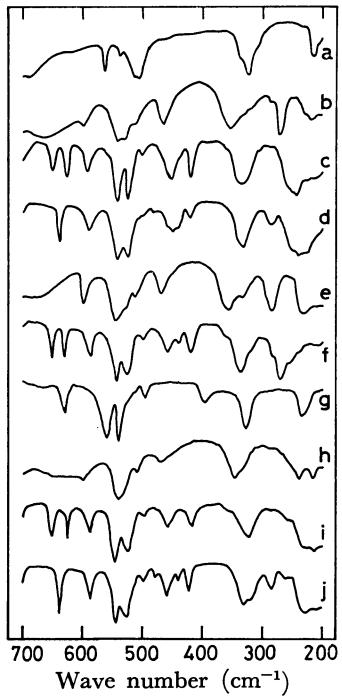

Fig. 3. The far-IR spectra of: (a) HL; (b) $CoL_2(OH_2)_2$; (c) CoL_2(bpy); (d) CoL_2(phen); (e) $NiL_2(OH_2)_2$; (f) NiL_2(bpy); (g) CuL_2; (h) $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$; (i) ZnL_2(bpy); and (j) ZnL_2(phen).

740 cm^{-1},[10,11] and by the appearance of a new band at around 1020 cm^{-1}.[10,11]

The far-IR spectra in the 700—200 cm^{-1} region of the present complexes are shown in Fig. 3. They are assigned tentatively as listed in Table 2 in reference to literature.[8] In the case of adducts containing heterocyclic diamine, the bands assigned to the metal-oxygen stretching are shifted towards the lower-frequency side (around 455 cm^{-1}), the new bands attributable to bpy or phen appearing at *ca.* 420 cm^{-1}. The above shift may be caused by the weakening of the metal-oxygen bond due to the coordination of diamine.

Electronic Spectra and Magnetic Data. Both the absorption (in ethanol) and reflection spectra of the 3-hydroxy-2-methyl-4-pyronate complexes are shown in Figs. 4 and 5, their magnetic moments being listed in Table 1. In the 20000—7000 cm^{-1} region, $CoL_2(OH_2)_2$, CoL_2(bpy) and CoL_2(phen) show absorption bands at *ca.* 18000(sh) (ε=41.8), 8600 (ε=2.6), and 7570 (ε=3.1) cm^{-1}, at *ca.* 19000(sh) (ε=67.2) and 9200 (ε=5.9)

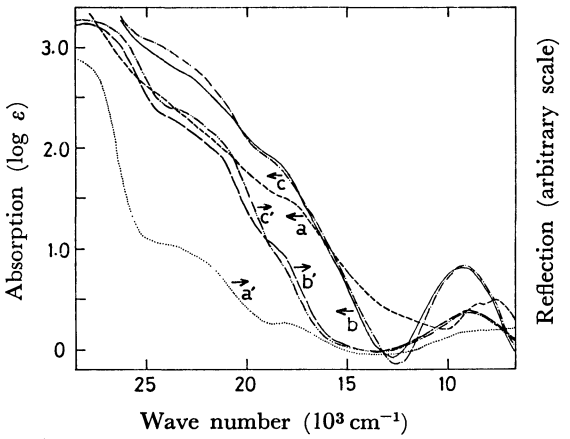

Fig. 4. The absorption and reflection spectra of: (a) and (a'), $CoL_2(OH_2)_2$; (b) and (b'), CoL_2(bpy); (c) and (c'), CoL_2(phen).

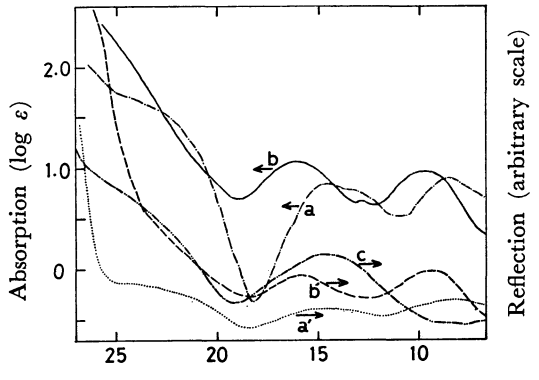

Fig. 5. The absorption and reflection spectra of: (a) and (a'), $NiL_2(OH_2)_2$; (b) and (b'), NiL_2(bpy); (c), CuL_2.

cm^{-1}, and at *ca.* 19200(sh) (ε=65.6) and 9100 (ε=6.1) cm^{-1}, respectively. The reflection spectra of these complexes are similar to the corresponding absorption spectra in solution. The results reveal that all these cobalt(II) complexes are octahedral in the two phases, although the magnetic moments of CoL_2(bpy) and CoL_2(phen) are a little lower than the value usually observed for the octahedral cobalt(II) complexes.[13]

The absorption spectra of $NiL_2(OH_2)_2$ and NiL_2(bpy) in the 20000—7000 cm^{-1} region exhibit bands at 14500 (ε=5.5), 13000 (ε=4.6), and 8500 (ε=7.0), and at 16100 (ε=11.9), 12900 (ε=2.6), and 8800 (ε=7.3) cm^{-1}, respectively. The reflection spectra of these complexes are also similar to the corresponding absorption spectra. The spectra and the observed magnetic moments of $NiL_2(OH_2)_2$ (3.21 B. M.) and NiL_2(bpy) (3.13 B. M.) suggest that both of the nickel(II) complexes are octahedral.

The observed magnetic moment (1.84 B. M.) of CuL_2 is normal, indicating that there is no copper-copper interaction. The reflection spectrum of this copper(II)

Table 3. NMR spectra of the zinc(II) complexes in dimethyl sulfoxide solution (δ, ppm)

Complex	HL			Base			
	CH_3	5	6				
	2.22	6.30	7.99				
		($J_{5,6}$=5.1)					
$[ZnL_2(OH_2)_2]\cdot 1/2H_2O$	2.32	6.52	8.11				
		($J_{5,6}$=4.8)					
				bpy			
				3 and 3'	4 and 4'	5 and 5'	6 and 6'
				8.44	7.95	7.45	8.74
				($J_{3,4}$=8.0, $J_{3,5}$=1.2, $J_{3,6}$=1.0,			
				$J_{4,5}$=7.6, $J_{4,6}$=1.7, $J_{5,6}$=4.9)			
ZnL_2(bpy)	2.28	6.39	8.02	8.49	8.05	7.55	8.70
		($J_{5,6}$=5.2)		($J_{3,4}$=8.0, $J_{3,5}$=1.3, $J_{3,6}$=0.8,			
				$J_{4,5}$=7.7, $J_{4,6}$=1.7, $J_{5,6}$=4.9)			
				phen			
				2 and 9	3 and 8	4 and 7	5 and 6
				9.17	7.78	8.51	8.00
				($J_{2,3}$=4.5, $J_{2,4}$=1.5, $J_{3,4}$=8.3)			
ZnL_2(phen)	2.26	6.26	7.91	8.92	7.93	8.72	8.10
		($J_{5,6}$=5.2)		($J_{2,3}$=4.4, $J_{2,4}$=—, $J_{3,4}$=8.4)			

Coupling constants, J, have the unit of Hz.

complex in the 20000—8000 cm^{-1} region shows only one symmetrical d-d band at 14700 cm^{-1}. Troporone and 3-hydroxy-2-methyl-4-pyrone are very similar ligands, both coordinating to a metal ion through oxygen atoms of the hydroxy and carbonyl groups to form a five-membered chelate ring. The absorption spectrum of Cu(troporonato)$_2$ exibits a weak band at 14700 cm^{-1} ($\varepsilon \approx 100$).[14] This complex has the O_4-tetracoordinate planar structure around the copper ion, although the plane including the copper and oxygen atoms makes an angle of 4.9° with the plane of the seven membered ring.[15] The close resemblance of the reflection spectrum of CuL_2 to the absorption spectrum of Cu(troporonato)$_2$ strongly suggests the O_4-tetracoordinate planar structure for CuL_2 in solid.

NMR Spectra of Zn(II) Complexes. The NMR spectra of $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$, ZnL_2(bpy), and ZnL_2(phen) in dimethyl sulfoxide solutions are shown in Table 3. The assingments are based on integration of the peak area in comparison with the NMR spectra of InL_3,[6] 2,2′-bipyridine,[16] and 1,10-phenanthroline and its metal complexes.[17]

In the spectrum of $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$, the resonance peak at 8.81 ppm due to the OH proton of free HL is lost, the resonance peaks of protons 5 and 6 and methyl protons of this ligand being shifted downfield by 0.22, 0.12, and 0.10 ppm, respectively, due to chelation to zinc(II) ion.

In the case of ZnL_2(bpy), the downfield shifts of the protons 5, 6 and methyl protons of the pyronate ligand are much smaller, *i.e.* 0.09, 0.03 and 0.06 ppm, respectively, than those in $[ZnL_2(OH_2)_2]\cdot 1/2H_2O$. Signals of the protons 5 and 6 of this ligand in ZnL_2(phen) are shifted upfield by 0.04 and 0.08 ppm, respectively, while the peak for the methyl protons is shifted down field by 0.04 ppm. This might be caused by a decrease in the electron donation from the chelating oxygen atoms to the metal because of the coligation of bpy or phen to the zinc(II) ion, or by the magnetic anisotropy effect of the ring current of these diamines.

The resonance peaks of the protons 6 and 6′ of bpy in ZnL_2(bpy), and the protons 2 and 9 of phen in ZnL_2(phen) are shifted upfield by 0.04 and 0.25 ppm, respectively, than those of free diamines. Miller and Prince reported that an upfield shift for the 2 and 9 ring protons of phen in the tris-1,10-phenanthroline complexes of Co(III), Fe(II), Ru(II), and Zn(II) and the tetrakis-1,10-phenanthroline complexes of Ca(II) and Mg(II) is probably due to a metal-nonbonded hydrogen interaction.[17] In the present case of ZnL_2(phen), the upfield shift of the 2 and 9 protons of phen may also be due to a similar effect.

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