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Complexing Ability of some γ-Lactone Derivatives. Thermal, Magnetic and Spectral Studies on Cobalt(II), Nickel(II) and Copper(II) Complexes and their Base Adducts

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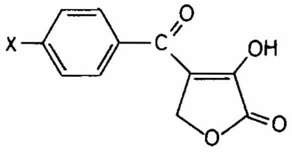
Abstract

The complexes of some γ-lactone derivatives with cobalt(II), nickel(II) and copper(II) have been synthesized and formulated as $[ML_2]\cdot nH_2O$, $M = Co^{2+}$, Ni^{2+} or Cu^{2+}, $n = 2$ or 3 and L = anion of the corresponding ligand. Their structures have been suggested on the basis of analysis, spectral (UV–Vis, IR) and magnetic susceptibility data. The thermal analysis revealed the non-coordinated water among these complexes. The infrared spectra show the existence of water molecules involved in a hydrogen-bonding with the coordinated ligands and the γ-lactones are mono-basic bidentate coordinated to the metal ion via the benzoyl carbonyl and the deprotonated hydroxylic oxygen atoms. The bulkiness and the electronic properties of the lactones on the structure of the complexes are rationalized from the electronic spectral data. The interaction of the complexes with different Lewis basis is studied spectrophotometrically. The ligand field parameters are calculated and related to the bulkiness effect of the ligand molecules. These parameters indicate the axial ligation of the base molecules and that the equatorial plane is occupied by the MO_4, $M = Co^{2+}$, Ni^{2+} or Cu^{2+}, chromophore. The interelectronic repulsion parameter indicates the ionic nature of these complexes. The extent of distortion from the idealized structure is also discussed.

Introduction

The coordination chemistry of heterocyclic ketones and keto-compounds has been investigated in considerable detail [1–7]. Our interest in the coordination chemistry of biologically active compounds led us to study the ligating properties of some γ-lactones (I) whose coordination chemistry is less developed in the literature. These compounds were found to have a wide application as drugs and pharmaceutical preparations [8]. Also, these kinds of molecules display a quite varied coordination behaviour. We report herein the preparation and characterization of copper(II), cobalt(II) and nickel(II) complexes of these γ-lactones either in their solid or solution states.



I

X = H, benzoyl-γ-lactone (HL′),
= Me, *p*-methylbenzoyl-γ-lactone (HL″) and
= OMe, *p*-methoxybenzoyl-γ-lactone (HL‴).

Experimental

Preparation of the Organic Ligands and Metal Complexes

The γ-lactone derivatives were prepared and characterized by Amer [8].

The metal complexes were prepared according to the following general method. An ammoniacal solution of hydrated cobalt(II), nickel(II) or copper(II) chloride (0.01 mol) was added to an ethanolic solution of the corresponding lactone (0.025 mol). The reaction mixture was stirred under reflux on a water-bath for 20–30 min and cooled to room temperature. The solid products were filtered off, washed several times with diethylether and recrystallized from a chloroform–ethanol mixture, then dried under vacuum over P_4O_{10}.

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TABLE I. Analytical Data of the γ-Lactone Derivatives of Metal(II) Chelates

Compound[a]	Calculated(found) (%)			
	C	H	M	H_2O[b]
$[CoL'_2]2H_2O$	52.5(52.1)	4.0(4.0)	11.8(11.9)	7.2(7.0)
$[NiL'_2]3H_2O$	50.7(50.2)	4.2(4.1)	11.3(11.2)	10.4(10.1)
$[CuL'_2]2H_2O$	52.0(51.7)	3.9(4.0)	12.5(12.5)	7.1(7.3)
$[CoL''_2]3H_2O$	52.5(52.4)	4.7(4.6)	10.7(10.8)	9.8(9.9)
$[NiL''_2]2H_2O$	54.2(53.8)	4.5(4.5)	11.1(11.0)	6.8(6.7)
$[CuL''_2]2H_2O$	53.8(53.3)	4.5(4.4)	11.9(12.0)	6.7(6.6)
$[CoL'''_2]2H_2O$	51.3(51.0)	3.9(4.0)	10.5(10.6)	6.4(6.5)
$[NiL'''_2]3H_2O$	49.8(49.4)	4.1(4.0)	10.1(10.0)	9.3(9.2)
$[CuL'''_2]2H_2O$	50.9(50.7)	3.9(4.0)	11.3(11.3)	6.4(6.5)

[a] L′, L″ and L‴ are the anions of the ligands given in I.
[b] Obtained from the thermal analysis.

Analysis

Carbon and hydrogen contents were estimated at the Microanalysis Unit at UMIST, Manchester, U.K. Metal content was determined titrimetrically using standard EDTA solution in the presence of a suitable metal indicator after the decomposition of a definite weight of the complex with AR HNO_3–HCl. The data are given in Table I.

Physical Measurements

All physical measurements were carried out as previously reported [4–6].

Results and Discussion

γ-Lactone derivatives (I) reacted with hydrated cobalt(II), nickel(II) and copper(II) chloride in the presence of aqueous ammonia to give complexes of stoichiometry $[ML_2]\cdot nH_2O$, $M = Co^{2+}$, Ni^{2+} or Cu^{2+}, $n = 2$ or 3 and L is the anion of the corresponding γ-lactone. The complexes are air stable, soluble in most organic solvents but insoluble in water. Upon heating the complexes in an electric oven at 110–120 °C their colours changed; on cooling in the atmosphere they attained their original colours. This may be due to dehydration and hydration, respectively.

Thermogravimetric Analysis

The thermal decomposition of the complexes was studied by TG and DTG techniques; they unambiguously indicate the absence of coordinated water in all complexes. The TG and DTG curves of the complexes are of two-stage processes. They lose two or three water molecules in the temperature range 66–120 °C characteristic of non-coordinated water molecules. The coordinated water molecules are lost in the 140–190 °C range. This step is followed by the loss of the ligand molecules in the temperature range 360–688 °C, giving the corresponding metal oxide.

Magnetic Moments and Electronic Spectral Data

The room temperature magnetic moments of the solid nickel(II) complexes were found to be 2.47–2.88 BM but as benzene solutions their magnetic moments are 2.56–3.24 BM. This magnetic behaviour is not consistent with tetrahedral, octahedral or high spin five-coordinated nickel(II) complexes. Therefore, these complexes may be present as square planar and tetrahedral structures together in the same crystalline solid and/or they exist in a square planar–tetrahedral equilibrium in the solid state and the tetrahedral configuration predominates in solution [9, 10]. Similar data were reported for nickel(II) complexes having similar magnetic data [11–12]. The polymerization of these complexes in solution to give an octahedral structure is ruled out based on the molecular weight determination (molecular weights were determined by the depression in freezing point using benzene as solvent).

The solid reflectance and chloroform solution spectra of these complexes are shown in Fig. 1 and the data are given in Table II. The spectra in both states are similar with a slight change in the band position. The spectra exhibit a band at 6820–6480 cm^{-1} with energy sequence H > p-Me > p-OMe and a reverse order for its molar extinction coefficient. The second d–d transitional band at 11 000–15 780 cm^{-1} does not shift in a parallel manner. The magnetic moments measured at room temperature (293 K) for benzene solution are used to calculate the tetrahedral percentage in these complexes in solution by the help of the relation, %tetr. = $(\mu_{eff}^2/3.3^2)(100)$, where μ_{eff} is the measured magnetic moment for the samples under investigation and 3.3 is the magnetic moment of pure tetrahedral molecules measured in benzene solution at the same temperature. The values are 60, 86 and 96% for H, p-Me and p-OMe substituents, respectively, in accordance with the fact that as the steric effect increases, the tetrahedral configuration is adopted with certain distortion leading to a drecrease

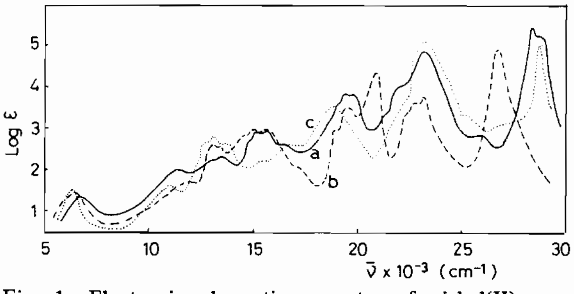

Fig. 1. Electronic absorption spectra of nickel(II) complexes in chloroform at room temperature: (a) $[NiL'_2]3H_2O$; (b) $[NiL''_2]2H_2O$; (c) $[NiL'''_2]3H_2O$.

TABLE II. Magnetic Moments and Electronic Spectral Data of Nickel(II) Complexes

Compound[a]	μ_{eff}[b]	Solvent	$\bar{\nu}$(cm^{-1}) (ε (mol^{-1} l cm^{-1}))
$[NiL'_2]3H_2O$	2.47	$CHCl_3$	6820(21), 11240(80), 12980(160), 15730(604)
		Py	6888, 8700, 14000
		n-but-NH_2	6905, 8625, 13990
		DMSO	6900, 8320, 14098
		DMF	7000, 8340, 13985
$[NiL''_2]3H_2O$	2.65	$CHCl_3$	6550(30), 12300(55), 13080(370), 14780(342)
		Py	6675, 8260, 14130
		n-but-NH_2	6710, 8235, 14210
		DMSO	6866, 8196, 13898
		DMF	6705, 8200, 13996
$[NiL'''_2]3H_2O$	2.88	$CHCl_3$	6460(38), 11000(42), 12720(583), 13600(500)
		Py	6658, 8210, 14328
		n-but-NH_2	6676, 8206, 14658
		DMSO	6705, 8186, 14265
		DMF	6700, 8208, 14098

[a] L′, L″ and L‴ are the anions of the γ-lactones given in **I**. [b] Measured for solid samples at room temperature (298 K).

TABLE III. Magnetic Ligand Field Parameters of Cobalt(II) Complexes

Compound[a]	μ_{eff}[b]	Solvent	ν (cm^{-1}) (ε(mol^{-1} l cm^{-1}))	10*Dq* (cm^{-1})	*B* (cm^{-1})	*B*′ (cm^{-1})
$[CoL'_2]2H_2O$	4.30	$CHCl_3$	6200(29), 8620(43), 10180(58), 14510(266), 16610(1280)	3655	833.0	0.86
		Py	9680, 16986, 21386	9680	703.8	
		DMSO	9808, 16890, 20986	9808	713.0	
		DMF	9896, 17036, 22080	9896	719.6	0.74
$[CoL''_2]3H_2O$	4.30	$CHCl_3$	6730(19), 8760(36), 10200(62), 13410(287), 14500(282), 16600(20400)	3610	841.0	0.87
		Py	9696, 16990, 20980	9696	705.0	0.73
		DMSO	9786, 17086, 21450	9786	711.6	0.74
		DMF	9886, 17335, 21968	9886	718.9	0.74
$[CoL'''_2]2H_2O$	4.38	$CHCl_3$	6745(14), 8800(24), 10005(32), 12346(700) 13308(510), 16700(20400)	3935	845.0	0.87
		Py	9735, 17026, 22076	9735	707.9	0.73
		DMSO	9820, 17438, 21988	9820	714.1	0.74
		DMF	9886, 17820, 22435	9886	718.9	0.74

[a] L′, L″, L‴ are the anions of the ligands given in **I**. [b] Measured for solid samples at room tempeature (BM).

in the magnetic moment values from that of the regular tetrahedral, and rather consistent with our proposition that the tetrahedral structure predominates in solution. Accordingly, these two bands can be assigned to $^3T_1(F) \rightarrow {}^3A_2(F)$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions, respectively, in a pseudo-tetrahedral ligand field.

Trials to isolate the different solid Lewis base adducts of these complexes failed due to their decomposition upon filtration. On the other hand the solution spectra of these complexes in neat Lewis base solvents (pyridine, dimethylsulphoxode, *N,N*′-dimethylformamide or n-butylamine) are quite different from the original one and exhibit bands at

6658–7000, 8186–8700 and 13 860–14 210 cm^{-1}. In addition, a very intense band at 20 685–22 380 cm^{-1} probably due to M → L charge transfer transition was observed. These spectral data are very consistent with those reported for nickel(II) complexes of octahedral structure [13, 14]. The ν_1 (6658–7000 cm^{-1}) possesses a shoulder in the low energy side (5420–5480 cm^{-1}) suggesting a distortion from the idealized symmetry. Furthermore, the bands are of a splitting nature, consistent with the *trans*-form of the two base molecules [13–15]. The spectral features indicate a $^3B_{1g}$ ground state and the orbital triplets in the tetragonal structure transform into ^3E_g, $^3B_{2g}$, and $^3A_{2g}$, ^3E_g, respectively [15].

The magnetic moments of the powdered samples of cobalt(II) complexes at room temperature, Table III, were found to be within the range expected for tetrahedral cobalt(II) [16]. The electronic spectra of these complexes as solid samples or in chloroform solution are similar and consistent with those reported for a distorted tetrahedral ligand field. The spectra of all complexes, Table III are similar to each other in the band position but differ in the molar extinction coefficients; representative spectra are shown in Fig. 2. The distortion from ideal symmetry could be rationalized from the presence of three bands at 6200–10 050 cm^{-1}, two bands in the lower energy region and one in the higher energy region at 11 000–16 700 cm^{-1}. The former three bands are assigned to $^2A_2 \rightarrow {}^4T_1(F)$ and the later three bands to $^4A_2 \rightarrow {}^4T_1(P)$ transitions. The baricenters of ν_2 and ν_3 have been evaluated visually as suggested by Cotton *et al.* [17]. The *Dq* values are calculated and given in Table III. The values are in the order *p*-OMe > *p*-Me > H. Furthermore the values of the interelectronic repulsion parameter have been calculated giving values of 833–845 against 971 cm^{-1} for the free cobalt(II) ion. The β' values (B/B_0) are 0.86–0.87 suggesting insufficient metal–ligand orbitals overlap and that the complexes are ionic in nature.

The electronic spectra of these complexes in neat pyridine, dimethylsulphoxide or *N,N'*-dimethylformamide (Table III) exhibit typical octahedral dibasic adducts [CoL_2S_2], S = Py, DMSO or DMF, suggesting a strong interaction with these solvents. The spectra exhibit bands at 9680–9886, 16 986–17 820 and 20 986–22 435 cm^{-1} assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ν_1; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ν_2 and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ν_3, transitions, respectively. The very intense band at 23 468–24 000 cm^{-1} was assigned to M → L charge transfer. These spectral data are used to calculate the different ligand field parameters and the results collected in Table III are in agreement with the values reported for octahedral cobalt(II) complexes with *trans*-axial solvent molecules. The data also indicate the ionic nature of these complexes [18]. The ratio ν_2/ν_1 was found to be in the 1.80–1.74 range suggesting a considerable distortion from the idealized symmetry [19, 20].

The room temperature magnetic moments of copper(II) complexes are in the 2.08–2.14 BM range consistent with a magnetically dilute copper(II) with a large spin-orbit coupling. The electronic spectra of these complexes are shown in Fig. 3 and the data are given in Table IV. The spectra exhibit bands characteristic of a pseudo-tetrahedral symmetry. The bands at 9380–12 720 and that at 14 000 cm^{-1} were found to be in the order H > *p*-Me > *p*-OMe according to their energies but the molar extinction coefficients increase in the opposite order. The solution spectra of these complexes in neat pyridine or acetonitrile exhibit spectral bands characteristic of a square pyramidal ligand field [21–24]. The band at 12 465–12 580 cm^{-1} was assigned to $^2B_1 \rightarrow {}^2A_1$, that at 14 230–15 380 cm^{-1} to $^2B_1 \rightarrow {}^2B_2$ and 17 685–17 890 cm^{-1} to $^2B_1 \rightarrow {}^2E$ transitions in this symmetry. In *N,N'*-dimethylformamide, the spectra display bands at 13 594–13 786 cm^{-1} with a shoulder at 11 210–11 245 cm^{-1}. The band at 18 980–19 356 cm^{-1} which is very intense was assigned to M → L transition. These spectral features suggest a strong tetragonally distorted structure due to the interaction of the complexes with the solvent molecules.

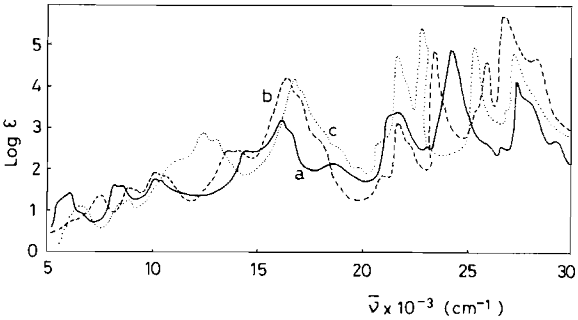

Fig. 2. Electronic absorption spectra of cobalt(II) complexes in chloroform at room temperature: (a) [CoL'_2]·$2H_2O$; (b) [CoL''_2]$3H_2O$; (c) [CoL'''_2]$2H_2O$.

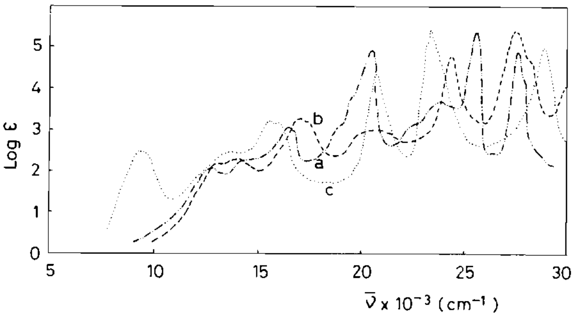

Fig. 3. Electronic absorption spectra of copper(II) complexes in chloroform at room temperature: (a) [CuL'_2]·$2H_2O$ (b) [CuL''_2]$2H_2O$ (c) [CuL'''_2]$2H_2O$.

TABLE IV. Magnetic and Electronic Spectral Data of Copper(II) Complexes

Compound[a]	μ_{eff}[b]	Solvent	ν (cm^{-1}) (ϵ(mol^{-1} l cm^{-1}))
$[CuL'_2]2H_2O$	2.12	$CHCl_3$	12696(128), 14060(170), 16380(1280)
		CH_3CN	12580(37), 14490(21), 14886(162), 17785(24)
		DMF	11210(178), 13594(86), 18980(12380)
$[CuL''_2]2H_2O$	2.08	$CHCl_3$	12720(227), 14040(200), 17080(1750)
		CH_3CN	12580(29), 15380(77), 14660(166), 17890(27)
		DMF	11245(162), 13700(92), 19365(13000)
$[CuL'''_2]2H_2O$	2.14	$CHCl_3$	9380(300), 14030(290), 15680(1580)
		CH_3CN	12465(42), 14380(19), 14730(173), 17754(22)
		DMF	11234(159), 13786(94), 19098(13876)

[a] L′, L″ and L‴ are the anions of the ligands in I. [b] Measured at room temperature for solid samples (BM).

Infrared Spectra

The infrared spectra of γ-lactones and their metal complexes (200–4000 cm^{-1}) with their assignments are studied. The spectra of the free lactones exhibit a strong broad band at 3650–3628 cm^{-1} characteristic of a free hydroxylic group. The spectra of all complexes display a broad band at 3428–3318 cm^{-1}, assigned to hydrogen-bonded OH. This band disappeared when the complexes were heated up to 120 °C. Therefore this band could be due to hydrogen bonded water molecules. This is confirmed by the existence of this band without any position change in the spectra of the complexes upon cooling. Accordingly, the water molecules are not directly coordinated to the metal ion as seen from the prementioned thermal analysis and the following equilibrium could be assumed

$$[ML_2]\cdot nH_2O \xrightleftharpoons{120\,°C} [ML_2] + nH_2O$$

Also the absence of coordinated water molecules was confirmed from the absence of the rocking, twisting and wagging vibrational modes which are activated by coordination in their mormal regions at 970–930 and 660–600 cm^{-1}. The carbonyl stretching frequency in the free lactones are traced at 1740–1760 and 1650–1680 cm^{-1} due to the lactonic and benzoyl carbonyls, respectively. Furthermore the carbonyl overtone frequency was observed at 3020–3100 cm^{-1}. The band at 1650–1680 cm^{-1} in the free lactones was found to be strongly shifted to a lower wavenumber by *ca.* 50–58 cm^{-1} with a reduction in its intensity indicating its bonding to the metal ion. On the other hand, the lactonic band (1740–1760 cm^{-1}) only shifted to a lower frequency by *ca.* 8–12 cm^{-1}, probably due to its bonding with water molecules through hydrogen bonding and not through the metal ion. The vibrational modes of the C–O at 1290–1305 and 546–558 cm^{-1} in the free γ-lactones are shifted to lower and higher energies, respectively, in the metal complexes, indicating the bonding of the deprotonated hydroxylic oxygen to the metal ion. The lactonic C–O vibrational modes at 1260–1248 and 900–880 cm^{-1} in the free ligands are not affected in the complexes molecules. The coordination of these γ-lactones to the metal ion through their benzoyl carbonyl and hydroxylic oxygen atoms is proved from the appearance of bands at 272–300 cm^{-1} which are absent in the free lactones and assigned to ν(M–O). According to the prementioned spectral studies, these γ-lactones are monobasic bidentates coordinated to the metal ion via the benzoyl carbonyl and deprotonated hydroxylic oxygen atoms.

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