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SYNTHESIS AND STRUCTURAL STUDIES OF MIXED-LIGAND COMPLEXES

Benzoylacetone and *L*-proline, 2-pyrrolidone-5-carboxylic acid or *L*-thioproline

A. M. Donia[1]*, *T. Y. Al-Ansi*[2] *and M. Q. Othman*[2]

[1]Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-kom, Egypt
[2]Department of Chemistry, Faculty of Science, Sana'a University, Sanaa, Yemen

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Abstract

Seven mixed-ligand complexes of cobalt(II), nickel(II) and copper(II) containing benzoylacetone and *L*-proline (HL^1), 2-pyrrolidone-5-carboxylic acid (HL^2) or *L*-thioproline (HL^3) were prepared and characterized by means of elemental analysis, IR, electronic spectra, magnetic moment measurements and molar conductance. Both HL^1 and HL^2 coordinate with these metal ions in a neutral zwitterionic form $(-\overset{+}{N}H_2-\overset{|}{C}H-COO^-)$, whereas HL^3 coordinates as a monobasic chelating agent (O/N). The continuous thermochromism of the nickel(II) complex of HL^1 (2) was attributed to a geometry change; it was investigated by DTA, TG, electronic spectra and X-ray powder diffraction techniques.

Keywords: mixed-ligand complexes of cobalt(II), nickel(II) and copper(II)

Introduction

Mixed-ligand metal complexes find numerous applications in the fields of improvement of lubrication oil [1], photosensitizers for photooxidation reactions [2], selective production of colours in photoimaging [3] and extraction of metal ions [4]. Different mixed-ligand complexes have been studied by different authors [5–8]. Recently, we prepared and characterized metal (Co, Ni and Cu) complexes of *L*-proline and *L*-thioproline [9]. The preparation was carried out from mixed solutions containing the ligand and acetylacetone or dibenzoylmethane (in attempts to obtain the mixed-ligand complexes). The results obtained showed that acetylacetone did not take part in the reactions, whereas dibenzoylmethane did, and its complexes were formed. The present work was devoted to a study of the complexes obtained from mixed solutions containing

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* Author to whom all correspondence should be addressed.

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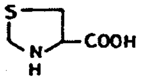
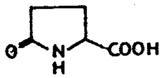
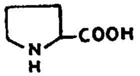
benzoylacetone (which has properties intermediate between those of acetylacetone and dibenzoylmethane) and *L*-proline (HL^1), 2-pyrrolidone-5-carboxylic acid (HL^2) or *L*-thioproline (HL^3).


L-Thioproline (HL^3)


2-pyrrolidone - 5 - carboxylic acid (HL^2)


L-proline (HL^1)

Experimental

Preparation of complexes

All chemicals were of reagent grade, and were obtained from Aldrich. The complexes 1–7 were prepared by mixing equimolar amounts (10 mmol) of benzoylacetone and HL^1 or HL^2 dissolved in ethanol or HL^3 dissolved in water. An appropriate amount of a 2 *M* solution of Na_2CO_3 was added to the ligand mixture. The solution was stirred with heating until effervescence ceased. The metal chloride (10 mmol) solution in ethanol was added dropwise to the reaction mixture with heating and stirring. The precipitates obtained were filtered off and recrystallized from ethanol to remove the inorganic salt (NaCl) formed during the reaction. The isolated complexes were dried over $CaCl_2/P_4O_{10}$.

Working procedures

Elemental analyses (C and H) were carried out at the Micro-Analytical Centre, Cairo University, Egypt. The metal content was estimated with a Perkin-Elmer 2380 Atomic Absorption Spectrometer. IR spectra were recorded in KBr discs on a Perkin-Elmer 1430 spectrometer. Electronic spectra were measured in nujol mulls, using a Perkin-Elmer Lambda 4B spectrophotometer. Magnetic susceptibility measurements were carried out at room temperature on a modified Gouy-type magnetic balance. The molar conductivity measurements were made in DMF with a WTW LF90 conductance bridge. The thermal analyses (DTA and TG) were carried out in air with Shimadzu XD-30 and TGA-50 thermal analysers at a heating rate of $10^{\circ}C\ min^{-1}$. X-ray powder diffraction patterns were recorded on a Philips PW 1728 diffractometer with CuK_{α} radiation.

Results and discussion

The complexes display thermal stability up to 100–220°C, as indicated by their DTA and TG data (Table 2). The DTA curves contain endothermic peaks in the temperature range 17–220°C, which may be assigned to the loss of solvent molecules (H_2O/EtOH) from both the inner and the outer spheres. The curves also exhibit a number of exothermic peaks after desolvation, characteristic of material decomposition. These assignments were confirmed by the TG mass losses, and the IR spectra of the complexes before and after heating up to the corresponding temperature ranges. The molar conductances of complexes 2 and 3 in DMF (Table 1) are consistent with those of 1:1 electrolytes in that solvent [10]. The values for the other complexes indicate a non-electrolytic nature [11]. The complex of nickel(II) with HL^2 (5) displays considerable dissociation, which is responsible for the higher conductance [11]. The analytical and spectral data (Table 1) confirm the formation of mixed-ligand complexes.

Vibrational spectra

The vibrational spectra of the complexes (Table 1) contain bands at 1566–1550 and 1485–1480 cm^{-1}. These bands are assigned to the β-diketone ring (νC–C+νC–O combination) and the phenyl ring, respectively [12, 13], and confirm the presence of the benzoylacetone moiety. The bands observed at 1595–1563 and 1414–1390 cm^{-1} are characteristic of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively [12, 13]. The complexes derived from HL^1 and HL^2 give additional bands at 3200–3190 and 1511 cm^{-1} as (α-amino acids), assigned to $\nu(\overset{+}{N}H_2)$ and $\delta(\overset{+}{N}H_2)$, respectively [13]. The complexes of HL^3 also afford a coordinated ν(NH) band at 3275 –3250 cm^{-1} [12]. The above assignments indicate the formation of mixed-ligand complexes. On the other hand, both HL^1 and HL^2 coordinate in the neutral zwitterionic form $(-\overset{+}{N}H_2-\overset{|}{C}H-COO^-)$ through the carboxylate group, whereas HL^3 coordinates as a monobasic chelating agent through N/O. This coordination behaviour is consistent with our previous data obtained from the optimized structures of the ligands and calculated proton affinity values [9]. The spectra display further bands at 3468–3420, 3115–3070, 2985–2930 and 458–418 cm^{-1}, assigned to ν(OH) of water and/or EtOH, ν(Ar–CH), ν(alph.CH) and ν(M–O), respectively [11, 12]. The possible bridging of the carboxylate group in some complexes was taken from the separation value of the frequencies $\nu(COO^-)$ [8, 12].

Electronic spectra and magnetism

The electronic spectral bands of the complexes in nujol mulls are given in Table 1. The spectral patterns of the cobalt complexes reveal a number of bands within the range 690–500 nm. The bands appear as shoulders of a strong absorption band near 400 nm, which is probably assigned to a charge-transfer transition. The magnetic moment of the cobalt(II) complex of HL^3 (6) coincides with that observed for high-spin five-coordinate Co(II) complexes [14]. The values for complexes 1 and 4 indicate low- and high-spin five-coordinate configurations, respectively [14]. The slight increase in the values may be attributed to the distortion, which predominates in the five-coordinate structures [14]. The nickel(II) complex of HL^1 (2) gives a multiple strong band in the range 800–400 nm, indicating tetrahedral geometry around the Ni(II) [14], while the

Table 1 Elemental analysis magnetic moment, conductance, IR, and electronic spectra of the complexes

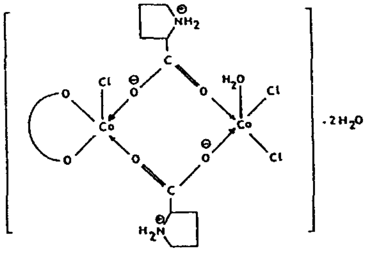
Compound	Color	Elemental analysis*			μ_{eff} (B.M.)	Λ_m in DMF	Electronic spectra/nm in Nujol mulls *d-d* transition
		C	H	M			
(1) $[Co_2(ba)(HL^1)_2(H_2O)Cl_3]\cdot 2H_2O$	green	36.1	4.7	17.4	2.72	46	690(m), 630(w),
		(35.9)	(4.9)	(17.6)			537(broad/sh)
(2) $[Ni_2(ba)(HL^1)_2Cl_2]Cl\cdot 2H_2O$, EtOH	bright	38.5	4.7	16.4	2.09	127.9	800-400(vs/split)
	green	(37.9)	(5.3)	(16.8)			
(3) $[Cu_2(ba)(HL^1)_2Cl_2]Cl\cdot H_2O$,1/2 EtOH	light	37.5	4.4	18.5	1.1	179	660(br)
	blue	(37.9)	(4.8)	(19.0)			
(4) $[Co(ba)_2(HL^2)]\cdot 3/4EtOH$	orange	58.4	5.5	10.9	6.0	16	544(sh), 500(sh)
		(58.3)	(5.4)	(10.8)			
(5) $[Ni_2(ba)(HL^2)Cl(EtOH)(H_2O)]$	light	46.2	4.7	13.4	3.1	103.5	638(br)
	green	(45.5)	(5.1)	(13.1)			
(6) $[Co(ba)(L^3)EtOH]$	pale	48.6	4.6	14.5	5.1	12.8	544(sh), 500(sh)
	red	(48.3)	(5.0)	(14.8)			
(7) $[Cu_2(ba)(L^3)Cl_2]\cdot EtOH\cdot 3H_2O$	dirty	32.4	4.4	20.8	1.13	a	657(br)
	green	(32.5)	(4.4)	(21.5)			

Table 1 Continued

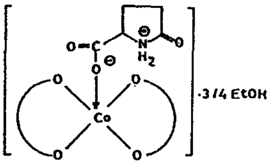
Compound	IR/cm^{-1}										
	ν(OH)	$\nu(\overset{+}{N}H_2)$	ν(Ar–CH)	$\nu_{as}(COO^-)$	$\delta(\overset{+}{N}H_2)$	$\nu_s(COO^-)$	ν(phenyl ring)	ν(aliph CH)	ν(β-diketone chelate ring	ν(NH) coord.	ν(M–O)
(1)	3430(br)	3190(sh)	3070(w)	1595(s)	1511(s)	1390(br)	1480^b	2985(w)	1550(s)		419(m)
(2)	3420(br)	3200(sh)	–	1595(s)	1511(s)	1390(br/s)	1480^b	2950(vw)	1566(s)		
(3)	3430(br)	3200(br)	–	1563s/sh	1515(s)	1414(br)	1480^b	2980(vw)	1552(s)		
(4)	3430(br)	3200	3070(w)	1595(s)	1511(vs)	1405(s/br)	1485^b	2930(w)	1555(s)		425(m)
(5)	3430(br)	3200	3070(vw)	1595(s)	1511(s)	1390(s/br)	1485^b	2950(vw)	1555(s)		425(m)
(6)	3430(br)	–	–	1588(s)	–	1400(s)	1485^b	2930(vw)	1555(m)	3250vw	
(7)	3430(br)	–	3115(w)	1622(s)	–	1390 br/split.	1485^b	2980(w)	1555(sh)	3275–3230 (split.)	418(m)

a: partially soluble, br: broad, m: medium, s: strong, w: weak, b: sharp
Λ_m (cm^2 Ω^{-1} mol^{-1})
*Values in parantheses: (calc.)

magnetic moment of the complex exhibits an anomalous value (2.09 BM). This value is lower than would be expected for purely tetrahedral geometry, suggesting a flattening towards a planar arrangement [15]. The spectrum of complex 5 displays a broad band at 638 nm, assigned to the transition $\nu_2[^3A_{2g} \rightarrow ^3T_{1g}$ (F) in octahedral geometry around the Ni(II) [14]. The magnetic moment of 3.1 BM confirms the octahedral configuration [16]. The broad band observed near 660–650 nm in the spectra of the copper complexes indicates square planar geometry around the Cu(II) [17]. The magnetic moments obtained are much lower than expected for monomeric copper(II) complexes. This indicates that there is a considerable interaction between the copper atoms [18]. On the basis of the above arguments, together with the analytical data (Table 1), the following structures can be suggested:



(1)



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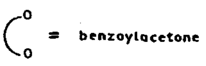
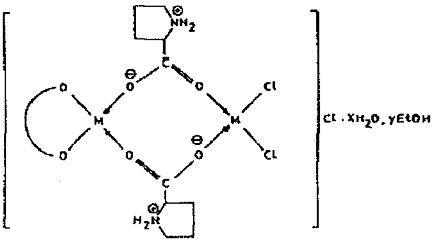
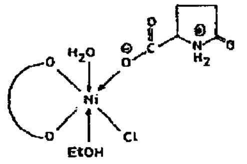
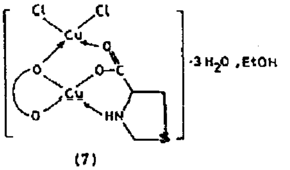




M = Ni, X = 2, Y = 1 (2)
M = Cu, X = 1, Y = 1/2 (3)



(5)



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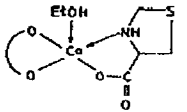

(6)

Thermochromic behaviour of complex 2

The complex undergoes a continuous colour change from bright-green to yellow over the temperature range 50–220°C. The change in colour is irreversible in air at room temperature. The temperature range of the colour change coincides with the endothermic DTA peak (Fig. 1). The TG mass loss (Table 2) corre-

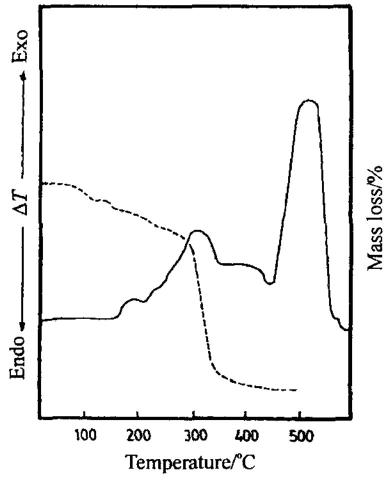

Fig. 1 DTA and TG curves of complex

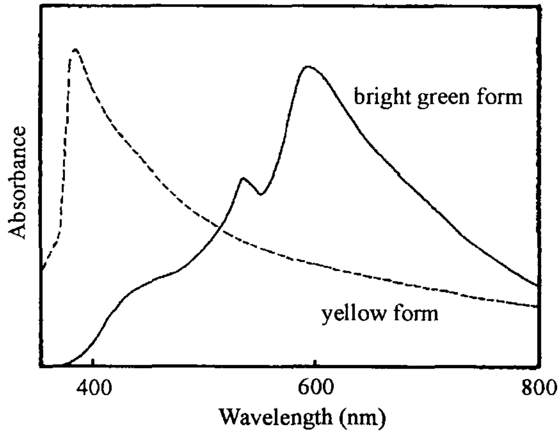

Fig. 2 Electronic spectra of bright green and yellow forms of complex

sponds to $2H_2O$+EtOH. The electronic spectra of the two forms are significantly different (Fig. 2). The characteristic multiple (*d–d*) transition band of the bright-green tetrahedral form disappears from the spectrum of the yellow form, indicating a change in coordination geometry towards the planar configuration. This behaviour confirms the flattening, together with the lower magnetic moment value obtained for the bright-green form. The continuous thermochromism is therefore attributed to a change in geometry, which takes place together with desolvation of the complex. The X-ray diffraction patterns of the two forms are typically the same (Fig. 3), confirming the same packing for the two forms, and therefore the considerable flattening in the bright-green form. The slight changes observed in

Table 2 DTA and TG data of the complexes

Compound	T/°C DTA/TG	Mass loss/% F (calc.)		Assignment
(1)	36–179	7.6 (8.1)	$3H_2O$	a
	180–388	34.4 (35.0)	$2HL^1$	b
(2)	37–220	18.8 (18.8)	$2H_2O$+EtOH	a
	220–374	38.0 (38.2)	$2HL^2$+HCl	b
(3)	19–262	40.7 (40.5)	1/2 EtOH+H_2O+$2HL^1$	a+b
(4)	31–210	6.3 (6.6)	3/4 EtOH	a
	210–350	52.6 (53.3)	mba+HL^2	b
(5)	20–170	4.3 (4.0)	H_2O	a
	170–470	47.3 (46.4)	EtOH+mba	b
(6)	29–189	11.2 (11.6)	EtOH	a
	189–244	32.5 (32.9)	L^3	b
(7)	17–101	2.6 (3.0)	H_2O	a
	101–292	48.2 (47.5)	HCl+mba+ EtOH+$2H_2O$	b

a= loss of solvents, b= decomposition

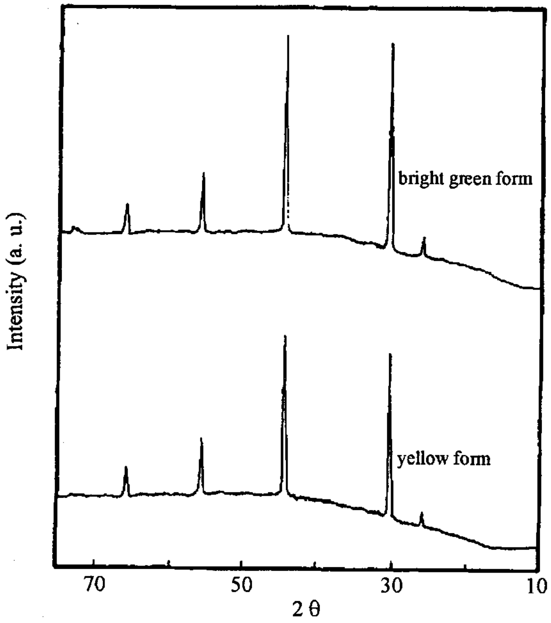

Fig. 3 X-ray powder diffraction patterns of bright green and yellow forms of complex

Table 3 X-ray powder diffraction data of complexes (2)

Bright green form			Yellow form		
2θ degree	I/I_0 a.u.	d/Å	2θ degree	I/I_0 a.u.	d/Å
26.6	8	3.3482	26.6	8	3.3482
31.1	97	2.8732	30.9	93	2.8914
44.8	100	2.0233	44.7	100	2.0256
55.9	28	1.6434	55.8	35	1.6461
66.1	14	1.4123	65.9	17	1.4164
74.8	29	1.2682	74.8	36	1.2682

d=inter-planar spacing

the relative intensities and in the positions of some lines (Table 3) may be attributed to a lattice rearrangement rather than a phase change. Again, the lower temperature of desolvation (wide TG) and the above X-ray result indicate that the solvent of crystallization do not make a significant contribution to the lattice forces [19].

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