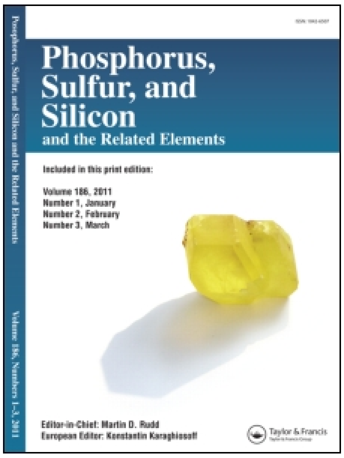

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SYNTHESIS AND CHARACTERIZATION OF Co(II), Ni(II), Cu(II), AND Cd(II) TERNARY COMPLEXESWITH THIOSALICYLIC AND AMINO ACIDS

Said A. Ibrahim[a]
[a] Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

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Communication

SYNTHESIS AND CHARACTERIZATION OF Co(II), Ni(II), Cu(II), AND Cd(II) TERNARY COMPLEXES WITH THIOSALICYLIC AND AMINO ACIDS

SAID A. IBRAHIM
Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

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Twelve mixed ligand Co(II), Ni(II), Cu(II) and Cd(II) complexes involving both thiosalicylic and amino acids have been prepared and characterized by elemental analysis, molar conductivity, electronic and ir spectral measurements. It is found that the monovalent amino- and salicylic acid are coordinated to the metal ions as NO and OS bidentate ligands where five and six membered chelate rings are formed. The ternary complexes formed are found to have a distorted octahedral geometry.

Key words: Mixed ligand complexes; amino acids; thiosalicylic acid.

INTRODUCTION

Ternary transition metal complexes containing an amino acid as a ligand are of significant importance from the biological point of view. Some work is reported for binary complexes using amino acids as ligands,[1–3] but little is reported for ternary complexes involving amino acids.[4–6] This paper reports on the synthesis of ternary complexes of some divalent metal ions, viz Co(II), Ni(II), Cu(II) and Cd(II) with thiosalicylic acid (SO donor ligand) and one of the following amino acids; L-phenylalanine (phe), L-serine (ser) and L-tyrosine (tyr). The study involves also examination of the nature of bonding established between the ligands and the metal ions. The structure of the so obtained mixed ligand complexes is characterized on the basis of elemental analysis, ir and electronic spectra, weight loss as well as conductivity measurements.

RESULTS AND DISCUSSION

Elemental analysis data are consistent with a ratio of 1:1:1 metal ion: amino acid: thiosalicylic acid for all the complexes prepared.

Molar conductivity values of 10^{-3} M solutions of the complexes in DMF lie in the range of 9.3–23.61 $\text{Ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. These values indicate a non-electrolytic nature of all the prepared complexes since the reported range of 1:1 electrolyte in DMF solutions is 65–90 $\text{Ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.[7]

Data of elemental analysis indicate that only two protons from both the amino acid and thiosalicylic acid ligands are liberated during complex formation. The amino acid phenyl alanine acts as monobasic bidentate ligand with the neutral bidentate mode ruled out as we pointed out before.[3] L-Serine and tyrosine although both have an additional OH group as a third bonding site, it does not participate in complexation due to the comparatively weak binding ability of the alcoholic oxygen of the former[3,8] and the weak seven-membered chelate ring to be formed using the latter thus they act also as monobasic bidentate ligands. This is also supported by the results of elemental analysis (cf. Table I) and IR spectra given hereafter. On the other hand, thiosalicylic acid may act as mono- or dibasic bidentate ligand. However the elemental analysis and ir spectra provide ample evidence in favour of its coordination in the monobasic bidentate mode. This can be understood on the basis of high pKa value of its SH group (9.52) relative to the carboxyl one (5.44)[9,10]

Electronic Spectra

The UV-visible spectral bands of DMF solutions of the different complexes are reported in Table II. DMF was used as a solvent because the complexes were insoluble in ethanol and other common solvents. Furthermore, the spectra of metal complexes in DMF solutions exhibited no apparent differences from those recorded on mixing ethanolic solutions of both the metal ions and the ligands. This indicates that DMF does not act as ligand in these complexes. From Table II, three sets of bands could be recognized. The first with ν_{max} in the range 26.31–36.36 kK, is assignable to an intra-ligand CT transition. The second set of bands of the binary chelates comprise a strong band in the range 19.23–25.00 kK. These bands are attributable to a L → MCT transition. This assignment is supported by the dependence of the position and intensity of the band on the nature of the amino acid or thiosalicylic acid moiety.

The third set of bands was found to have ν_{max} in the range 15.87–18.86 kK in the spectra of Co(II) complexes. This band has in most cases shoulders on both sides and may correspond to a distorted octahedral geometry and can be assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions.[11,12] In case of Ni(II) complexes two bands are displayed, the first is located near 15.60 kK and the second appeared at 17.23 kK. These are characteristic of a distorted octahedral geometry around Ni(II)[12] and are due to the spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$.

Copper(II) complexes comprised a broad d-d band with maximum absorption at 14.90–18.80 kK. This band is suggestive of a distorted octahedral stereochemistry of Cu(II) and can be assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ electronic transition.[12]

Infrared Spectra

IR spectral bands that can provide conclusive structural evidence for the mode of attachment of the amino acidate and thiosalicylate ligands are reported in Table III.

The broad band appeared in the range 3450–3480 cm^{-1} in the IR spectra of the free amino acids can be assigned to the stretching absorption of the $\overset{+}{N}H_3$ form,[13] since amino acids are known to exist as Zwitter ions (R-$\overset{+}{N}H_3$-COO$^-$). This band disappears in the IR spectra of the complexes. Instead a band at lower frequencies (3100–3280 cm^{-1}) appears, this band can be attributed to the stretching vibration of the coordinated NH_2 group.[3]

TABLE I

Analytical data, color, and molar conductance values of the mixed ligand Co(II), Ni(II), Cu(II) and Cd(II) complexes

No.	Compound	Colour	% Calculated (Found)				Λ_m (Ohm^{-1} cm^2 mol^{-1})
			C	H	N	S	
1	Co(phe)(tsa) . $2H_2O$	deep green	46.60(46.30)	4.64(5.40)	3.39(4.20)	7.77(8.50)	9.29
2	Ni(phe)(tsa) . $2H_2O$	deep green	46.63(45.90)	4.64(4.30)	3.39(3.90)	7.78(8.40)	10.44
3	Cu(phe)(tsa) . $3H_2O$	grey	44.18(45.00)	4.86(4.10)	3.22(3.70)	7.37(7.60)	15.88
4	Cd(phe)(tsa) . H_2O	white	42.91(42.20)	3.82(4.30)	3.12(3.90)	7.15(7.10)	insoluble
5	Co(ser)(tsa).$2H_2O$	black	34.10(34.70)	4.29(4.90)	3.97(4.80)	9.10(9.30)	42.74
6	Ni(ser)(tsa).$3H_2O$	green	32.46(33.10)	4.63(5.10)	3.78(4.30)	8.66(8.30)	9.62
7	Cu(ser)(tsa).$4H_2O$	deep blue	30.57(31.30)	4.87(4.80)	3.56(4.20)	8.16(8.90)	17.75
8	Cd(ser)(tsa).$2H_2O$	white	29.60(30.20)	3.72(3.30)	3.45(4.10)	7.90(7.60)	13.77
9	Co(tyr)(tsa).$3H_2O$	green	43.05(43.60)	4.74(3.80)	3.13(3.80)	7.18(7.60)	17.34
10	Ni(tyr)(tsa).$2H_2O$	white	44.89(44.40)	4.47(4.70)	3.27(3.30)	7.48(6.80)	9.29
11	Cu(tyr)(tsa).$3H_2O$	grey	42.61(43.30)	4.69(4.50)	3.10(2.80)	7.10(6.80)	23.61
12	Cd(tyr)(tsa).$2H_2O$	white	39.88(40.30)	3.97(4.60)	2.90(3.60)	6.65(7.30)	insoluble

TABLE II
Electronic spectral data of the mixed ligand complexes (DMF solutions)

No.*	ν_{max} kK (ε_{max} mol^{-1} cm^{2})
1	15.87(443), 22.22(690), 33.33(1730), 36.36(1793)
2	15.60(55), 17.23(27), 27.02(8275), 33.11(3862)
3	15.38(119), 35.08(3199).
5	18.18(110), 22.22(171), 33.33(1858), 35.71(1884)
6	15.62(19), 17.23(46), 26.31(8148). 32.46(10200)
7	18.86(157), 37.71(2250)
8	27.27(950), 36.36(1204).
9	19.60(82), 25.00(170), 33.33(3409).
10	15.60(129), 17.23(307), 34.48(3181).
11	14.92(81), 25.00(1346), 26.88(871), 34.48(3409).

* Complexes No. 4 and 12 are sparingly soluble in DMF.

The IR spectrum of amino and thiosalicylic acid shows two bands at 1610–1665 cm^{-1} and 1455–1470 cm^{-1} due to ν_{as} OCO and ν_{s} OCO vibrations, respectively. In the complexes, these two bands appear at 1590–1630 cm^{-1} and 1430–1470 cm^{-1}, respectively, indicating the involvement of the carboxylic group in bond formation with metal.[14,15] The separation (ν_{as} – ν_{s}) of the carboxylate stretching vibration and the relative intensities indicate no polymeric configuration of the complexes by bridging carboxylate group.[16]

The S—H stretching frequency band appearing at 2530 cm^{-1} in the spectrum of the free thiosalicylic acid is appeared also in the IR spectra of the complexes. This reveals that coordination of the SH group takes place through the sulfur lone pair and not through proton elimination in all these complexes. This result is consistent with the formulation suggested by the micro-analyses results (Table I) in which thiosalicylic acid appears to function as a mono-carboxylate group where the SH group is coordinated via its sulfur electron lone pair. A convincing evidence for this behaviour can be attained from the high pK$_a$ value of the S—H group (9.52) relative to that of the COOH group (5.44) for thiosalicylic acid.[9,10] However, the observed shift in the ν_{SH} on complexation coordination can be explained on the basis of the expected mesomeric interaction in the six-membered chelate ring formed on complexation of thiosalicylate to the metal ion.

All the complexes show an IR band in the range 3340–3500 cm^{-1}. This band includes ν_{OH} of the hydroxyl group of L-serine and tyrosine in addition to ν_{OH} of coordinated water or water of hydration.

TABLE III

Selected IR bands (cm^{-1}) for the free amino acid ligands and mixed ligand complexes

No.	Assignment				
	ν_{OH}	ν_{NH_2}	ν_{SH}	ν_{as} OCO	ν_s OCO
Free(phe)	-	-	-	1625	1455
1	3340	3250	2510	1590	1455
2	3350	3240	2520	1630	1460
3	3340	3250	2490	1623	1460
4	3500	3100	2510	1620	1470
Free(ser)	3450^a		-	1630	1470
5	3350	-	2510	1620	1430
6	3340	3260	2485	1615	1435
7	3360	3280	2530	1615	1460
8	3460^b		2540	1625	1455
Free(tyr)	3480^a		-	1610	1460
9	3400	3220	2500	1610	1445
10	3220^b		2510	1605	1445
11	3350	3210	2540	1615	1455
12	3450	3210	2520	1615	1435

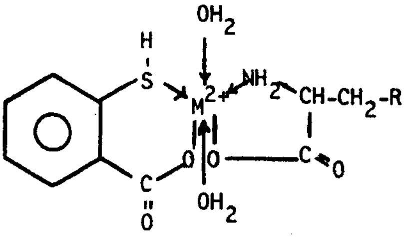
a) broad band, b) ν_{OH} + ν_{NH_2}

The presence of coordinated and lattice water molecules in the prepared complexes has been confirmed by the new band appeared at 3340–3500 cm^{-1} in the IR spectra of the complexes. Also the rocking mode of coordinated water appeared as a weak vibration band in the neighbourhood of 790–960 cm^{-1}.[17] In the other cases, the band observed at about 610–680 cm^{-1} indicates the presence of lattice water molecules.[18] IR spectra of Cd(II) complexes includes ν_{OH} of water of hydration. This is confirmed by the weight loss technique where a weight loss equivalent to one (complex 4) or two (complex 12) water molecules was observed at about 120°C.

Careful examination of the far infrared absorption spectra of the ternary complexes clearly display the M—N, M—O and M—S stretching vibrations in the ranges 460–520 cm^{-1}, 325–345 cm^{-1} and 270–285 cm^{-1} respectively.[18–20]

On the other hand, complexes of Co(II) 1,5-possess a weight loss equivalent to two coordinated water molecules while complex 9 possesses a weight loss equivalent to one water molecule at 120°C and a weight loss equivalent to two water molecules at 180°C. Thus it is suggested that this complex contains two coordinated water molecules and a water molecule as hydration water, nickel(II) complexes 2,10 also have two coordinated water molecules and complex 6 has an additional hydration water molecule as revealed by weight loss measurements. On the other hand, the results of weight loss technique indicated that Cu(II) complexes 3 and 11 have two coordinated and one hydration water molecules whereas complex 7 has two coordinated and two hydration water molecules.

In view of the above findings it is evident that six-coordinate complexes are formed in this investigation except for those of Cd(II) which are four-coordinate chelates. One can deduce the fact that both the monovalent anions of amino and thiosalicyclic acid are coordinated to the metal as N,O and S,O bidentate ligands respectively. The structure of the 1:1:1 ternary complexes studies in this investigation can be represented schematically as below:



R = C_6H_5, phe; = OH, Ser; = $C_6H_4(OH)$ tyr. M^{2+} = Co(II), Ni(II) or Cu(II).

EXPERIMENTAL

Solvents used in this study were of AR grade (BDH or Merck products). All other materials were of G.R. grade.

Synthesis of the mixed ligand complexes. The following general procedure has been adopted for the preparation of the mixed M(II) complexes. The required amount of amino acids (1 mmol) dissolved in the least amount of water-ethanol mixture (1:1) was treated with Cu $(CH_3COO)_2 \cdot H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2 4H_2O$, and $Cd(CH_3COO)_2 2H_2O$ (1 mmol) in the molar ratio 1:1. The reaction mixture was refluxed for 1–3 h, depending upon the type of amino acid. To this solution ethanolic solution of thiosalicylic acid (1 mmol) was added and refluxed for 2 h. The solution was heated till the volume was reduced by approximately half, then cooled, whereby a crystalline product formed. This was filtered off, washed several times with small portions of ethanol and then dried in vacuo over P_4O_{10}.

Physical measurements. IR spectra were recorded on a Pye Unicam SP3-100 spectrophotometer as KBr discs. Electronic spectra were run in a Shimadzu UV 200S spectrophotometer using 1 cm matched silica cells. Conductivity measurements were carried out using an LF Digi 55 conductivity bridge of DMF solutions at 10^{-3} M concentration. All measurements were carried out at room temperature (~25°C).

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