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Solution and Solid State Behavior of Co^{2+}, Ni^{2+} and Zn^{2+} Tosylaminoacidate Systems: Crystal and Molecular Structure of Bis(N-tosylglycinato)tetraaquocobalt(II) and Bis(N-tosyl-β-alaninato)tetraaquozinc(II) Complexes

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Abstract

The interactions between N-tosylamino acids and cobalt(II), nickel(II) and zinc(II) ions in aqueous solution and in the solid state have been investigated. From concentrated aqueous solutions, compounds of general formula $[M(II)(N\text{-tosylaminoacidato})_2(H_2O)_4]$(M = Co(II), Ni(II) and N-tosylaminoacidato = N-tosylglycinate ($Tsgly^-$), N-tosyl-α- and -β-alaninate (Ts-α- and Ts-β-ala^-); M = Zn(II) and N-tosylaminoacidate = $Tsgly^-$, Ts-β-ala^-) and $[Zn(II)(N\text{-tosylaminoacidato})_2(H_2O)_2]$ were isolated and characterized by means of thermogravimetric, electronic and infrared spectra. For two of them: $[Co(Tsgly)_2(H_2O)_4]$ (I) and $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$ (II) the crystal and molecular structures were also determined. Both compounds crystallize in the monoclinic space group $P2_1/c$, with two formula units in a cell of dimensions: a = 13.007(6), b = 5.036(2), c = 18.925(7) Å, β = 102.33(3)° for (I) and a = 14.173(6), b = 5.469(2), c = 17.701(7) Å, β = 106.63(3)° for (II). The structures were solved by the heavy-atom method and refined by least-squares calculations to R = 0.031 and 0.064 for (I) and (II) respectively. The cobalt and zinc atoms lie in the centers of symmetry, each bonded to two amino-acid molecules through a carboxylic oxygen atom and four water molecules in a slightly tetragonally distorted octahedral geometry. The second carboxylic oxygen atom is not involved in metal coordination. Electronic and X ray-powder spectra suggest that the tetrahydrate complexes of Co^{2+}, Ni^{2+} and Zn^{2+} ions of the same amino acids are isomorphous and isostructural. No coordinative interactions between ligand and metal ions were found in aqueous solution on varying the pH values before hydroxide precipitation.

Introduction

Among N-protected amino acids such as N-acetyl, N-benzoyl, N-benzyloxycarbonyl and N-toluensulphonyl amino acids, only the latter class of derivatives has been proved to coordinate in aqueous and alcoholic solution to the copper(II) ion, undergoing amide nitrogen deprotonation as a function of pH [1, 2]. In the complexes separated in the solid state a square-pyramidal geometry of the copper(II) ion seems to be preferred [1b].

Since similar features were observed for oligoglycines with other metal ions such as Ni(II) and Co(II) [2, 3], in an attempt to quantify the role of both the ligand and the metal ion in favouring the behavior described above, in this paper we report the results of an investigation on the coordinative interactions between N-toluensulphonyl-amino acids and Co(II), Ni(II) and Zn(II) in aqueous solution and in the solid state. Some data on these systems in aqueous solution are also reported in ref. 4.

Experimental

Preparation of the Complexes

All the complexes of formula $ML_2(H_2O)_4$, (M = Co(II), Ni(II) and Zn(II); L = N-tosylglycinate, N-tosyl-α- and N-tosyl-β-alaninate) were obtained by slow evaporation of an aqueous or aqueous–

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methanolic (1:1) solution containing metal(II) acetate salt and amino acid in a 1:2 molar ratio.

From the above solution a complex of formula $Zn(Ts\text{-}\alpha\text{-}ala)_2(H_2O)_2$ was separated by adding diethyl ether.

The bis(N-tosylglycinato)diaquo zinc(II) and bis-(N-tosyl-β-alaninato)diaquo zinc(II) complexes were prepared by dehydrating the tetraaquo analogues at 70–80 °C.

Analysis of the compounds, within experimental error, are available as supplementary material.

Physical Measurements

The electronic spectra of the solid compounds were recorded as mull transmission spectra with a SHIMADZU MPS 50L spectrophotometer. The infrared spectra were recorded with a PERKIN ELMER 180 spectrophotometer as KBr pellets or in nujol mull on KBr pellets as support in the 4000–250 cm^{-1} spectral range. Room temperature magnetic moments were measured by the Gouy method with $Ni(en)_3S_2O_3$ as calibrant and corrected for diamagnetism with the appropriate Pascal constants. Thermal analyses were performed on a METTLER TA 3000 instrument with a scan speed of 5 °C/min. The polarographic measurements were performed at 25 ± 1 °C and at a dropping time of 2s using an AMEL MULTIPOLAROGRAPH MODEL 471; all half-wave potential values were referred to a saturated calomel electrode (SCE) which was used as reference. The solutions were prepared by adding an aqueous solution of the metal(II) perchlorate hexahydrate (10^{-4} mol/dm^3) to an aqueous solution of N-tosylamino-acidate ($2 \times 10^{-4} \div 10^{-3}$ mol/dm^3), varying the pH value; sodium perchlorate (0.1 mol/dm^3) was used as base electrolyte and the ionic strength was kept constant (μ = 0.1). The pH solution values were obtained by adding an aqueous NaOH solution (0.1 mol/dm^3). The pH-metric measurements were determined with a Prazious pH-meter KNICK.

X-Ray Data Collection and Structure Determination

The structures were determined using a Siemens AED single-crystal diffractometer. Precise lattice constants were determined by least-squares refinement of the angular setting of 24 reflections having $18 < \theta < 24°$ for (**I**) and $50 < \theta < 60°$ for (**II**). Crystal data details of the refinement of structure are summarized in Table I: Intensities were collected in the $\theta - 2\theta$ scan mode, with the use of Mo-Kα radiation for (**I**) and Cu-Kα radiation for (**II**). The intensities of 2248 reflections for (**I**) and 2857 for (**II**) were measured. A total of 1405 for (**I**) and 2209 for (**II**) reflections having $I > 2\sigma(I)$ were considered significant. The measured intensities were corrected for Lorentz and polarization effects, but not for absorption, given the low value of μ and the crystals' dimensions. The structures were solved using the heavy-atom method and refined by full-matrix least-squares calculations using anisotropic thermal para-

TABLE I. Crystal Data.

	$[Co(Tsgly)_2(H_2O)_4]$ (**I**)	$[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$ (**II**)
molecular formula	$C_{18}H_{28}CoN_2O_{12}S_2$	$C_{20}H_{32}ZnN_2O_{12}S_2$
mol wt	587.48	621.784
a, Å	13.007(6)	14.173(6)
b, Å	5.036(2)	5.469(2)
c, Å	18.925(7)	17.701(7)
β, deg	102.33(3)	106.69(3)
V, $Å^3$	1211.1(9)	1314.2(9)
d_{obs} (by flotation) (g cm^{-3})	1.59	1.52
d_{calc} (g cm^{-3})	1.61	1.56
Z	2	2
space group	$P2_1/c$	$P2_1/c$
crystal dimens. (mm)	0.13 × 0.26 × 0.48	0.07 × 0.36 × 0.51
radiation ($\bar{\lambda}$, Å)	MoKα ($\bar{\lambda}$ = 0.71069)	CuKα ($\bar{\lambda}$ = 1.54178)
2θ limits (deg)	6–48	6–120
temp. (°C)	20	20
abs. coeff. (cm^{-1})	9.33	33.27
$F(000)$, electrons	610	640
reflections collected	2248	2857
unique data used $(I) > 2\sigma(I)$	1405	2209
no. of variables	216	198
R	0.031	0.064
R_w	0.034	0.067

TABLE II. Final Fractional Atomic Coordinates (×10^4) with e.s.d.s in Parentheses for $[Co(Tsgly)_2(H_2O)_4]$.

Atom	*x/a*	*y/b*	*z/c*
Co	0(0)	5000(0)	5000(0)
S	2297(1)	−277(2)	2381(1)
O1	308(3)	2411(7)	4200(2)
O2	1597(3)	4617(8)	3869(2)
O3	2515(3)	991(7)	1756(2)
O4	1828(3)	−2854(6)	2313(2)
O5	−738(4)	7798(9)	4256(3)
O6	−1429(3)	3038(10)	4921(3)
N	1507(3)	1649(9)	2667(2)
C1	956(4)	2798(10)	3798(3)
C2	899(5)	867(11)	3192(4)
C3	3493(4)	−497(10)	3020(3)
C4	3621(4)	−2404(11)	3544(3)
C5	4565(4)	−2573(13)	4039(3)
C6	5383(4)	−907(14)	4016(3)
C7	5238(5)	983(15)	3498(4)
C8	4302(4)	1233(12)	2985(4)
C9	6408(4)	−1179(21)	4551(5)
H1	116(50)	728(106)	2947(32)
H2	1068(46)	−802(122)	3344(32)
H3	1605(42)	3121(127)	2664(31)
H4	4157(42)	2751(117)	2608(31)
H5	5694(47)	1906(111)	3429(31)
H6	4662(42)	−3901(126)	4350(21)
H7	3040(45)	−3741(115)	3558(30)
H8	6887(51)	85(108)	4418(32)
H9	6737(46)	−2889(118)	4552(31)
H10	6274(45)	−978(118)	5007(36)
H11	−623(51)	9252(129)	4117(38)
H12	−1091(49)	7512(122)	3959(35)
H13	−1645(46)	3365(123)	5305(35)
H14	−1382(48)	1347(137)	4879(34)

TABLE III. Final Fractional Atomic Coordinates (×10^4) with e.s.d.s. in Parentheses for $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$.

Atom	*x/a*	*y/b*	*z/c*
Zn	0(0)	5000(0)	5000(0)
S	2600(1)	−2834(2)	2241(1)
O1	165(2)	2548(6)	4146(2)
O2	1430(2)	4261(6)	3821(2)
O3	2514(3)	−5379(6)	2016(2)
O4	2518(2)	−1013(6)	1635(2)
O5	−1321(2)	3212(6)	4933(2)
O6	−698(2)	7697(6)	4130(2)
N	1764(2)	−2333(6)	2678(2)
C1	804(3)	2592(8)	3769(2)
C2	801(3)	436(8)	3231(3)
C3	1773(4)	61(8)	3068(3)
C4	3759(3)	−2395(7)	2936(2)
C5	4302(3)	−313(8)	2919(3)
C6	5210(4)	−12(9)	3485(3)
C7	5572(4)	−1742(12)	4054(3)
C8	6566(4)	−1396(19)	4663(4)
C9	5016(4)	−3875(12)	4055(3)
C10	4111(4)	−4198(10)	3508(3)
H1	626(30)	−1201(80)	−3504(30)
H2	244(30)	743(80)	2677(30)
H3	2358(40)	99(80)	3616(30)
H4	1891(40)	1493(80)	2685(30)
H5	1718(20)	−3800(60)	2980(20)
H6	4018(30)	1064(80)	2474(30)
H7	5639(40)	1610(90)	3471(30)
H8	6706(50)	−3006(190)	5032(40)
H9	6575(50)	201(190)	5024(40)
H10	7129(50)	−1224(190)	4365(40)
H11	5303(50)	−5280(120)	4489(30)
H12	3671(40)	−5795(100)	3530(30)
H13	−1406(20)	7808(60)	3895(20)
H14	−486(20)	9164(60)	4219(20)
H15	−1334(20)	4474(60)	5186(20)
H16	−1824(20)	3644(60)	4592(20)

meters for non-hydrogen atoms. At this stage for **(I)**, (R = 4.5%), the hydrogen atoms were located from a ΔF map, excluding those belonging to the methyl group (C(9)), which were fixed in the calculated positions. The R indices for the refinement, including hydrogen atoms with isotropic thermal parameters, were R = 0.031; R_w = 0.034 using the weighting scheme $w^{-1} = \sigma^2 F_o + 0.001346\ F_o^2$. For **(II)** the R index after refinement including Zn, S, O, N and C atoms with anisotropic thermal parameters was 0.071. A subsequent ΔF map provides the positions of hydrogen atoms belonging to amide nitrogen and water molecules; all other hydrogen atoms were fixed in the calculated positions. The final R index including hydrogen atoms with isotropic thermal parameters was 0.064 (R_w = 0.067 using the weighting scheme $w^{-1} = \sigma^2 F_o + 0.002995\ F_o^2$).

Eight reflections, 1 0 0, 4 0 0, 1 1 0, 2 2 0, 0 2 0, −4 0 4, −7 0 6, −5 1 6, affected by extinction or counting error were excluded from the final refinement. Atomic scattering factors, corrected for anomalous dispersion, have been taken from the International Tables [5]. All calculations were performed on the CYBER 76 of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, using the SHELX system [6]. The final atomic coordinates of the atoms are quoted in Tables II and III. Thermal parameters are given in the supplementary material. Analysis: nitrogen, carbon, sulfur and hydrogen were analyzed with a C. ERBA Elemental Analyser Instrument, Mod. 1106, by Mr. G. Pistoni; the water content was determined gravimetrically by thermal analysis.

Results and Discussion

Solid State Behavior

Coordinative interactions between N-tosyl-amino-acids and Co^{2+}, Ni^{2+} and Zn^{2+} ions, only occur in very concentrated solutions (1 M) from which solid compounds of general formula $ML_2(H_2O)_4$ separated. For two of them, $[Co(Tsgly)_2(H_2O)_4]$ and $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$, the crystal structures were also determined.

Description of the Structures

Drawings of the structures showing the atom numbering are given in Figs. 1 and 2. Bond distances and angles are listed in Tables IV and V.

In both structures the heavy atoms lie on the centers of symmetry, each coordinated to two amino acid molecules and four water molecules.

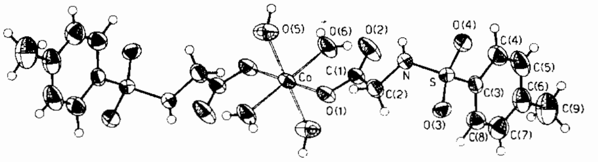

Fig. 1. Perspective view of the complex molecule of $[Co(Tsgly)_2(H_2O)_4]$ showing the numbering scheme and atomic vibrational ellipsoids (40%). The hydrogens are shown as spheres of arbitrary radius.

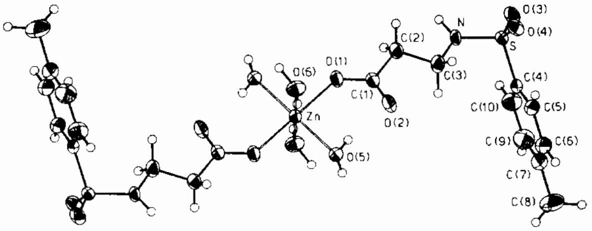

Fig. 2. Perspective view of the complex molecule of $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$ showing the numbering scheme and atomic vibrational ellipsoids (40%). The hydrogens are shown as spheres of arbitrary radius.

The tosyl-aminoacidate molecules are bonded to the metal ions through a carboxyl oxygen atom as has been previously observed in bis(N-tosylglycinato)bis(N-methylimidazole)copper(II) [7], in catena(μ-aqua)bis(N-tosylglycinato)bis(4-methylpyridine)copper(II) [8] and hypothesized for the copper(II)-N-tosylglycinate complex of empirical formula $Cu(Tsgly)_2(H_2O)_4$, identical to those of the complexes under study, obtained under the same experimental conditions (pH < 5) [1a]. A similar coordinative behavior toward metal ions is invariably

TABLE IV. Bond Distances (Å) and Angles (deg) for $[Co(Tsgly)_2(H_2O)_4]$.

(a) in the coordination polyhedron			
Co–O(1)	2.100(4)	O(5)–Co–O(6)	89.8(2)
Co–O(5)	2.077(5)	O(1)–Co–O(6)	87.6(2)
Co–O(6)	2.082(4)	O(1)–Co–O(5)	93.7(2)
(b) in the ligand			
S–O(3)	1.425(4)	C(3)–C(4)	1.365(8)
S–O(4)	1.428(3)	C(3)–C(8)	1.379(8)
S–N	1.590(5)	C(4)–C(5)	1.379(7)
S–C(3)	1.758(5)	C(5)–C(6)	1.363(8)
O(1)–C(1)	1.265(7)	C(6)–C(7)	1.350(10)
O(2)–C(1)	1.227(6)	C(6)–C(9)	1.498(8)
N–C(2)	1.450(9)	C(7)–C(8)	1.391(8)
C(1)–C(2)	1.493(9)		
N–S–C(3)	110.2(2)	S–C(3)–C(8)	120.0(5)
O(4)–S–C(3)	107.6(2)	S–C(3)–C(4)	119.8(4)
O(4)–S–N	106.9(2)	C(4)–C(3)–C(8)	120.2(5)
O(3)–S–C(3)	107.2(2)	C(3)–C(4)–C(5)	119.3(5)
O(3)–S–N	105.5(2)	C(4)–C(5)–C(6)	121.9(5)
O(3)–S–O(4)	119.3(2)	C(5)–C(6)–C(9)	120.7(6)
Co–O(1)–C(1)	126.3(3)	C(5)–C(6)–C(7)	117.9(6)
O(1)–C(1)–O(2)	125.0(5)	C(7)–C(6)–C(9)	121.4(6)
O(2)–C(1)–C(2)	119.4(5)	C(6)–C(7)–C(8)	122.4(6)
O(1)–C(1)–C(2)	115.5(5)	C(3)–C(8)–C(7)	118.2(6)
N–C(2)–C(1)	113.8(5)		

TABLE. V. Bond Distances (Å) and Angles (deg) for $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$.

(a) in the coordination polyhedron			
Zn–O(1)	2.083(4)	O(5)–Zn–O(6)	93.4(1)
Zn–O(5)	2.085(3)	O(1)–Zn–O(6)	92.6(1)
Zn–O(6)	2.157(3)	O(1)–Zn–O(6)	86.7(1)
(b) In the ligand			
S–O(3)	1.443(3)	C(2)–C(3)	1.501(8)
S–O(4)	1.444(4)	C(4)–C(5)	1.380(6)
S–N	1.613(4)	C(4)–C(10)	1.399(6)
S–C(4)	1.763(4)	C(5)–C(6)	1.395(6)
O(1)–C(1)	1.270(6)	C(6)–C(7)	1.370(7)
O(2)–C(1)	1.258(5)	C(7)–C(8)	1.520(7)
N–C(3)	1.479(6)	C(7)–C(9)	1.408(9)
C(1)–C(2)	1.515(6)	C(9)–C(10)	1.379(7)
N–S–C(4)	107.9(2)	N–C(3)–C(2)	109.0(4)
O(4)–S–C(4)	106.5(2)	S–C(4)–C(10)	118.4(4)
O(4)–S–N	109.0(2)	S–C(4)–C(5)	120.7(3)
O(3)–S–C(4)	108.2(2)	C(5)–C(4)–C(10)	120.8(4)
O(3)–S–N	106.3(2)	C(4)–C(5)–C(6)	119.2(4)
O(3)–S–O(4)	118.5(2)	C(5)–C(6)–C(7)	121.3(5)
Zn–O(1)–C(1)	127.9(3)	C(6)–C(7)–C(9)	118.8(5)
S–N–C(3)	117.7(3)	C(6)–C(7)–C(8)	120.7(6)
O(1)–C(1)–O(2)	124.7(4)	C(8)–C(7)–C(9)	120.5(6)
O(2)–C(1)–C(2)	119.0(4)	C(7)–C(9)–C(10)	120.9(6)
O(1)–C(1)–C(2)	116.2(4)	C(4)–C(10)–C(9)	119.0(5)
C(1)–C(2)–C(3)	113.0(4)		

exhibited by other N-protected amino acids, where the protecting group is an acetyl or a benzoyl group [1,9].

The metal–oxygen bond distances indicate for both metal ions a slightly tetragonally distorted octahedral geometry. Similar metal–oxygen distances and metal ion environments are present in benzoylglycinate complexes of iron(II), cobalt(II) and nickel(II) ions, although they are involved in polymeric chains [9, 10].

With regard to the Zn(II) complexes, while our $Zn(N\text{-tosylaminoacidato})_2(H_2O)_4$ complexes are isomorphous and isostructural with the analogous Co(II) and Ni(II) complexes, Zn(II)-N-benzoylglycine presents a slightly distorted trigonal bipyramidal geometry [11]. The benzoylglycinate complexes cited above represent the only previously structurally known N-substituted amino acid complexes hitherto reported in the literature.

In the $[Co(Tsgly)_2(H_2O)_4]$ the C^{α}–COO group is planar with amide nitrogen 0.249(2) Å out of plane and forms dihedral angles of 32.2(3)° with sulphonate and 106.0(2)° with the phenyl group. In bis(N-tosylglycinato)bis(N-methylimidazole)copper(II), the corresponding angles are very similar (44.5 and 106.1° respectively) and amide nitrogen is 0.298 Å out of plane. The conformation of the glycinate moiety can be described by using torsion angles around C–C and C–N bonds, O(1)–C(1)–C(2)–N = 169.0(5)° and S–N–C(2)–C(1) = 131.6(5)°.

In the $Zn(N\text{-tosyl-}\beta\text{-alaninato})_2(H_2O)_4$ complex the C^{α}–COO group is planar with C^{β} 0.542(5) Å and N 0.763(3) Å out of the plane and forms an angle of 124.6(2)° and 93.2(1)° with sulphonate and the phenyl group, respectively. The conformation of the β-alaninate moiety can be described by torsion angles around the C'–C^{α} (−156.7(4)°) and C^{α}–C^{β} bonds (168.8(4)°), the corresponding torsion angles in β-alanine are 9.6 and 83.7°.

As found in other tosyl-substituted amino acids [7, 8] the S–N distances, similar in both complexes, are shorter than the corresponding single-bond distances of 1.764 Å in sulphamides [12] and exhibit considerable double-bond character. Moreover the sulphur atoms in both complexes have the usual distorted tetrahedral configuration with bond distances and angles in the range of those found in similar complexes [13].

TABLE VI. Possible Hydrogen Bonds (Å) and Angles (deg).

(a) for $[Co(Tsgly)_2(H_2O)_4]$							
N···O(4)[a]	2.899(6)	N–H(3)	0.75(6)	H(3)···O(4)[a]	2.17(6)	N–H(3)···O(4)[a]	163(5)
O(5)···O(1)[a]	2.706(6)	O(5)–H(11)	0.80(7)	H(11)···O(1)[a]	1.99(6)	O(5)–H(11)···O(1)[a]	149(7)
O(5)···O(3)[b]	2.819(6)	O(5)–H(12)	0.66(6)				
O(6)···O(2)[c]	2.627(7)	O(6)–H(13)	0.85(7)	H(13)···O(2)[c]	1.85(7)	O(6)–H(13)···O(2)[c]	150(6)
(b) for $[Zn(Ts\text{-}\beta\text{-}ala)_2(H_2O)_4]$							
N···O(2)[d]	2.887(5)	N–H(5)	0.98(3)	H(5)···O(2)[d]	1.96(4)	N–H(5)···O(2)[d]	157(3)
O(5)···O(2)[c]	2.645(5)	O(5)–H(15)	0.83(3)	H(15)···O(2)[c]	1.93(4)	O(5)–H(15)···O(2)[c]	144(3)
O(5)···O(4)[b]	2.838(4)	O(5)–H(16)	0.83(3)	H(16)···O(4)[b]	2.12(3)	O(5)–H(16)···O(4)[b]	145(3)
O(6)···O(1)[a]	2.918(5)	O(6)–H(14)	0.86(3)	H(14)···O(1)[a]	2.09(3)	O(6)–H(14)···O(1)[a]	163(3)

[a] $= x, 1 + y, z$. [b] $= -x, \frac{1}{2} + y, \frac{1}{2} + z$. [c] $= -x, 1 - y; 1 - z$. [d] $= x, y - 1, z$.

All the structures are characterized by the presence of alternate layers of hydrophobic and hydrophilic regions. The metal ions lie in the hydrophilic regions, while the phenyl rings lie in the hydrophobic regions. In the complex of Co(II) there are contacts between the benzene rings along the b axis (C(4)–C(8) ($x, y - 1, z$) = 3.54 Å; C(5)–C(7) ($x, y - 1, z$) = 3.54 Å). In the Zn(II) complex the contacts between rings are shorter than 3.6 Å.

The amide nitrogen atom is involved in a hydrogen bond with an oxygen atom of the sulphonil group in the Co(II) complex and with the uncoordinated carboxylic oxygen atom in the Zn(II) complex.

In both complexes, packing is determined by a network of hydrogen bonds involving water molecules, coordinated and uncoordinated carboxylic oxygens and sulphonic oxygens (Table VI).

Spectroscopic Results

The electronic spectra of Ni(II) and Co(II) complexes are typical of slightly distorted octahedral high-spin complexes. Thus the observed bands can be assigned on the basis of the *Oh* symmetry as follows: 8.0×10^3 cm^{-1}, $^4T_{2g} \leftarrow {}^4T_{1g}(F)$; 18.7–19.6×10^3 cm^{-1}, $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ for cobalt(II) complexes and 8.5–8.7×10^3 cm^{-1}, $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$; 13.3–13.7×10^3 cm^{-1} (sh), $^1E_g(D) \leftarrow {}^3A_{2g}(F)$; 14.7–14.8×10^3 cm^{-1}, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$; 24.4–25.0×10^3 cm^{-1}, $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ for nickel(II) complexes. The calculated Dq are 910 and 850–870 cm^{-1} and the B are 780–850 and 850–870 cm^{-1} for Co(II) and Ni(II) complexes [15] respectively, characteristic of octahedral MO_6 chromophores [14–16].

The more relevant IR bands of the tetraaquo complexes, reported in supplementary material, are very similar to one another in band shape and position and are characteristic of N-tosylamino acids coordinated only through the carboxylate group [1, 7, 8]. No significant differences are observed in the IR spectra between tetraaquo and diaquo zinc(II) complexes hindering an unambiguous assignment of the coordination geometry in the latter.

Aqueous Solution Behavior

For all systems the polarographic analysis shows a reduction wave corresponding to the aqueous metal(II) ion reduction [17], the electronic spectra are similar to those of $M(ClO_4)_2(H_2O)_6$ salts in the same experimental conditions and the pH-metric curves are coincident until hydroxide precipitation occurs.

Even after the addition of metal(II) ions to the α-tosylamino acids previously deprotonated (pH > 12), no interaction is observed between metals and ligands before hydroxide precipitation.

However, the presence of metal–ligand coordinative interactions in aqueous solution, before metal hydroxide precipitation, must be excluded. Therefore, for N-tosylaminoacidates, the Co^{2+}, Ni^{2+}, and Zn^{2+} ions are ineffective in promoting amide deprotonation.

Only a little perturbation of the inner solvation sphere of the cations, due to a weakening of the cation solvated–water bonds, is observed at pH greater than 10.

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Supplementary Material Available

Lists of analytical data, observed and calculated structure factors, atomic temperature factors, selected least-squares planes, intermolecular contacts and infrared bands (28 pages) are available on request.

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