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Amide nitrogen co-ordination of Co^{II} and Ni^{II} in ternary 2,2′-bipyridine-containing systems. A solution and solid-state study

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The ternary systems 2,2′-bipyridine (bipy)–M–amino acid [M = Co^{II} or Ni^{II}; amino acid (H_2L) = *N*-*p*-tolylsulfonylglycine (tsgly), -β-alanine (ts-β-ala) or *N*-benzoylglycine (H_2hip)] were investigated in aqueous solution by means of polarography, electronic spectroscopy and potentiometry, in order to identify the type, number and stability of complex species, as a function of pH and bipy : M : amino acid ratio. With tsgly the prevailing species are $[M^{II}(bipy)_n(HL)]^+$ and $[M^{II}(bipy)_nL]$ (n = 1 or 2), with pK_{NH} for the deprotonation of sulfonamide nitrogen 7.8(2) and 7.4(2), for Co^{II} and Ni^{II}, respectively and the crystal and molecular structure of $[Co(bipy)_2(tsglyNO)]\cdot 2H_2O$ (NO indicates binding as a N,O-chelating dianion) was determined. The Co^{II} is six-co-ordinated by four nitrogen atoms of the bipy moieties, the deprotonated sulfonamide nitrogen and one carboxylic oxygen of the tsgly dianion. On standing in air, an alkaline solution of bipy–Co^{II}–tsgly turned from orange to wine-red in a few days, indicating the oxidation of Co^{II} to Co^{III}. With ts-β-ala and H_2hip metal hydrolysis prevents the formation of deprotonated complexes.

The co-ordination behaviour of *N*-sulfonylamino acids is closely dependent on the metal-ion type. With Cu^{II}, Cd^{II} [1] and Pd^{II} [2] the binding mode switches from a carboxylate-type co-ordination, at low pH, to an N,O-bidentate co-ordination (*via* a carboxylate oxygen and the deprotonated sulfonamide nitrogen) at higher pH. In the presence of Pd^{II} [3] ion the deprotonated species [PdL] is formed, even at pH < 2. Among these metals only Cu^{II} and Pd^{II} were found effective in the deprotonation of the amide nitrogen in peptides.[4]

Previous studies[5] on Co^{II}–, Ni^{II}– and Zn^{II}–*N*-tosylamino acidate binary systems showed no evidence of metal-promoted sulfonamide deprotonation before metal hydroxide precipitation and the only species isolated in the solid state was $[M(HL)_2(H_2O)_4]$ (M = Co^{II}, Ni^{II} or Zn^{II}; HL = *N*-*p*-tolylsulfonyl-glycinate, -DL-α- or -β-alaninate monoanion); their crystal structures revealed a carboxylate-type co-ordination. The zinc(II) ion normally does not promote peptide-nitrogen deprotonation; with glycylhistidine zinc(II) forms a 1 : 1 complex species where the binding sites are the terminal amino nitrogen, the deprotonated histidine amide nitrogen and the imidazole 1-nitrogen.[6] Nickel(II) and Co^{II} were found effective in the deprotonation of peptides.[4] With Ni^{II}, potentiometric titration reveals that by pH 11 the reaction in each two molecules of glycylglycine is complete and the pK_a value is ≈9.5; with Co^{II} the same reaction shows a pK_a near 10.[7] For Ni^{II} the crystal structure of the corresponding solid species and of that with gly-gly-gly-gly is also known;[8,9] on the contrary no data on solids are reported for the analogous cobalt(II) species. A peculiar feature of the Co^{II}–glygly solution complex is the easy oxygenation and oxidation to the corresponding cobalt(III) species; the crystal structure of the complex anion $[Co(gly\text{-}glyNO)_2]^-$ (gly-glyNO = glycylglycinate dianion) was determined.[10]

In ternary systems an additional compound such as 2,2′-bipyridine (bipy) was found to lower the sulfonamide-nitrogen deprotonation in the presence of Cu^{II} [11] and Cd^{II} [12] and the complexes formed were more stable than the corresponding binary ones. The presence of such an additional compound also enabled Zn^{II} successfully to substitute for a proton bound to a sulfonamide nitrogen. Co-ordination of bipy allowed Pd^{II} to promote this reaction even in RCO substituted amino acids such as hippuric acid.[13]

In order to verify the ability of 2,2′-bipyridine to promote amide-nitrogen deprotonation also with cobalt(II) and nickel(II) ions, we report here a solution and solid-state study on ternary 2,2′-bipyridine complexes of such metals with $R\text{–}SO_2$ and R–CO N-protected amino acids such as *N*-tolylsulfonylglycine (tsgly), -β-alanine (ts-β-ala) and *N*-benzoylglycine (H_2hip). Our study enabled the separation of a stable $[Co^{II}(bipy)_2(tsglyNO)]\cdot 2H_2O$ complex, the crystal structure determination of which represents the first example for a Co^{II}-deprotonated bound nitrogen atom.

Experimental

All chemicals were of the highest purity commercially available.

Preparation of the complexes $[M(bipy)_2(tsglyNO)]\cdot 2H_2O$ (M = Co^{II} or Ni^{II})

An aqueous solution (0.05 dm^3) of the corresponding binary complex (0.02 mol dm^{-3}) prepared as in ref. 5 was mixed with an ethanolic solution (0.01 dm^3) of bipy (0.1 mol dm^{-3}) and NaOH was added until pH 10. On slow evaporation in air, the yellow Co^{II}-containing solution turned red and yellow-brown crystals separated, yield 80% (Found: C, 54.9; N, 11.0; H, 4.30. Calc. for $C_{29}H_{29}CoN_5O_6S$: C, 54.85; N, 11.05; H, 4.60%). From the corresponding grey-blue solution containing Ni^{II}, violet crystals separated, yield 75% (Found: C, 54.6; N, 11.35; H, 4.50. Calc. for $C_{29}H_{29}NiN_5O_6S$: C, 54.9; N, 11.05; H, 4.60%).

Polarography

Measurements on ternary systems M^{II}–bipy–amino acid (M = Co or Ni; amino acid = tsgly, ts-β-ala or H_2hip) were carried out on aqueous solutions prepared with a 1×10^{-4} mol dm^{-3} metal concentration and M^{II} : bipy : amino acid molar ratios ranging from 1 : 1 : 2 to 1 : 2 : 20. The pH of the solutions was adjusted by adding small amounts of concentrated aqueous NaOH or HNO_3; $NaNO_3$ was used as base electrolyte, and the ionic strength was kept constant (I = 0.1 mol dm^{-3}). Square-wave voltammetry (SWV) and polarographic measurements were carried out with a PAR model 270A potentiostat/galvanostat at 25 ± 0.1 °C, under a nitrogen atmosphere. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum sheet as the counter electrode. The $E_{\frac{1}{2}}$ values from SWV were calculated from E_p values using the Parry–

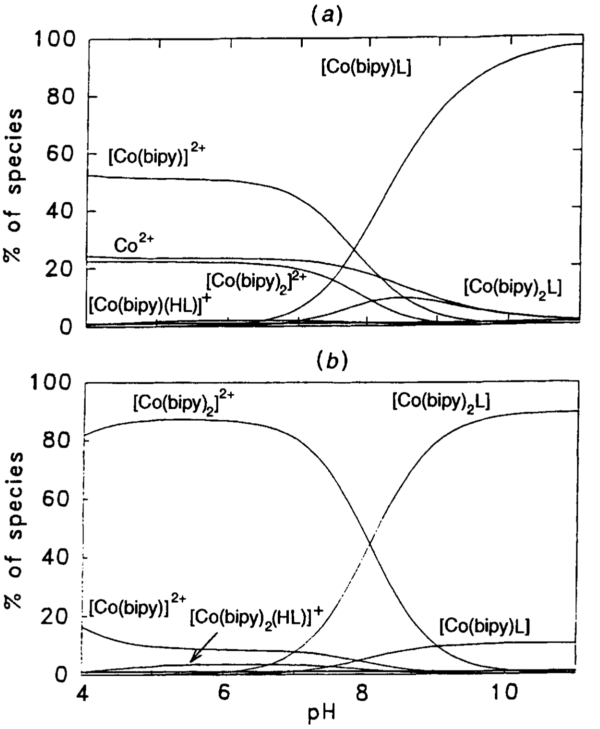

Fig. 1 Distribution curves for the Co^{II}–bipy–tsgly system; (5×10^{-4} mol dm^{-3} Co^{II}) in the molar ratio (*a*) 1 : 1 : 4, (*b*) 1 : 2 : 4

Osteryoung[14] equation $E_{\frac{1}{2}} = E_p - (\Delta E_p/2)$ which relates the peak potential E_p to the half-wave potential for a given pulse amplitude ΔE_p. All the $E_{\frac{1}{2}}$ values refer to the aqueous SCE. A JENWAY 3045 pH-meter equipped with an Ingold HA 405-60-kl pH combined electrode was used for pH measurements. Quasi-reversible reduction processes characterize the ternary systems. The reversible $E_{\frac{1}{2}}$ values for quasi-reversible processes were determined according to Matsuda and Ayabe.[15]

Potentiometry

The potentiometric titrations of the systems M^{II}–bipy–amino acid were performed at M : bipy ratios of 1 : 1 and 1 : 2 and M : amino acid ratios of 1 : 4 and 1 : 6 ($[M^{II}] = 1 \times 10^{-3}$ mol dm^{-3}) using an ORION 8103SC combined ROSS electrode, at 25 ± 0.1 °C, under a nitrogen atmosphere.

Crystallography

The crystal structure of $[Co(bipy)_2(tsglyNO)]\cdot 2H_2O$ was determined using an Enraf-Nonius CAD4 single-crystal diffractometer using Mo-Kα radiation (λ 0.710 69 Å). Lattice constants were determined by least-squares refinement of the angular setting of 25 reflections.

Crystal data. $C_{29}H_{29}CoN_5O_6S$, $M = 634.571$, monoclinic, space group *C*2/*c*, $a = 33.327(3)$, $b = 10.622(2)$, $c = 18.208(3)$ Å, $\beta = 116.31(1)°$, $U = 5778(11)$ Å^3, $D_m = 1.50$ g cm^{-3}, $Z = 8$, $D_c = 1.46$ g cm^{-3}, $F(000) = 2632$, μ(Mo-Kα) = 7.10 cm^{-1}, crystal size 0.20 × 0.15 × 0.30 mm, $T = 25$ °C.

10 502 Reflections [4632 with $I > 2\sigma(I)$] were collected with the ω–2θ scan technique in the range θ 2.5–25.0, scan speed 1.2–8.2° min^{-1}. All data were corrected for Lorentz-polarization effects and absorption based on φ scans[16] (minimum, maximum transmission coefficients 0.98, 1.00). The structure was solved using Patterson and Fourier methods and was then anisotropically refined by full-matrix least squares; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with unit weights for 2677 unique reflections. Hydrogen atoms, excluding those of water molecules, were located from a ΔF map and introduced in the last refinement with isotropic thermal parameters. Final refinement of this model led to $R = 0.052$, $R' = 0.052$. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 17. All calculations were performed on IBM personal computer using SHELX 76,[18] PARST[19] and ORTEP[20] programs.

Crystal data were collected also for the $[Ni(bipy)_2(tsgly\text{-}NO)]\cdot 2H_2O$ complex: $a = 33.221(4)$, $b = 10.830(8)$, $c = 17.900(2)$ Å, $\beta = 117.87(1)°$. 7471 Reflections were collected but only 1669 had $I > 2\sigma(I)$. A tentative isotropic refinement of the model using the same atomic displacement as for the cobalt compound gave an R index of 0.145 using 1021 unique reflections. Owing to the poor quality of the data no structural parameters for the nickel complex are reported, but they are almost equal to those of the cobalt complex.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and reference number 186/223.

Spectroscopic measurements

Electronic spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer (cell length = 1 cm) in the 600–300 nm spectral range on solutions containing 5×10^{-4} mol dm^{-3} M^{II} using M^{II} : bipy : amino acid molar ratios of 1 : 1 : 4 and 1 : 2 : 4. Spectrophotometric pH titrations, under a nitrogen atmosphere, were performed by changing the pH of the samples from 4 to 12 with a known amount of concentrated NaOH. Electronic spectra for microcrystalline complexes were recorded on the same spectrophotometer equipped with a DM60 integration sphere, IR spectra with a Perkin-Elmer FT-IR 1600 instrument as KBr pellets in the spectral range 4000–400 cm^{-1}.

Results and Discussion

Solution behaviour

For both the ternary systems involving Co^{II} and Ni^{II} and tsgly three waves are present throughout the pH range investigated. The wave at lower $E_{\frac{1}{2}}$ (wave I) is due to reduction of the free cation and its binary bipy complexes, while the other two (II and III) are attributed to reduction of the ternary complexes containing one and two bipy molecules, respectively. This has been supported by the analysis of $E_{\frac{1}{2}}$ as a function of the logarithm of the bipy concentration (Lingane plot),[21] maintaining the tsgly concentration constant. Up to pH 3.8 only wave I is present. Upon increasing the pH waves II and III appear and their $E_{\frac{1}{2}}$ values are concentration-dependent and shift toward more negative values in two titration steps. The first and second polarographic steps may be assigned to reduction of complexes in which the ligand acts as a simple carboxylate and N,O-bidentate respectively. The Lingane plot performed indicates that the prevailing species are $[M(bipy)(HL)]^+$, $[M(bipy)L]$, $[M(bipy)_2(HL)]^+$ and $[M(bipy)_2L]$, where HL and L refer to the ligand acting as a carboxylate and N,O-chelate, respectively. The overall stability constants, calculated according to Shaap and McMasters,[22] are collected in Table 1 and the distribution curves for Co^{II}, as a function of pH, are shown in Fig. 1.

With ts-β-ala or H_2hip, up to pH 3.7, only wave I is present, indicating the presence of free cation and its binary bipy complexes. On increasing the pH, waves II and III appear. In this case, only one titration step, corresponding to the formation of carboxylate complexes, can be observed. No evidence of the second titration step is present. At pH 6–6.5 the metal hydroxide begins to precipitate and the polarographic signals decrease until they disappear. The overall stability

Table 1 Logarithms of the overall stability constants, β,* determined in 0.1 mol dm^{-3} $NaNO_3$ at 298 K for ternary M^{II}(bipy) complexes with *N*-sulfonyl- and *N*-carbonyl-amino acids

Complex	tsgly		ts-β-ala		H_2hip	
	M = Co	Ni	M = Co	Ni	M = Co	Ni
$[M(bipy)(HL)]^+$	7.37	8.62	7.42	8.67	7.49	8.74
$[M(bipy)_2(HL)]^+$	12.73	15.36	12.79	15.41	12.87	15.48
$[M(bipy)L]$	12.28	14.60				
$[M(bipy)_2L]$	17.50	21.21				

* Corresponding to the equilibria $[M(bipy)_n]^{2+} + HL^- \rightleftharpoons [M(bipy)_n(HL)]^+$ and $[M(bipy)_n]^{2+} + L^{2-} \rightleftharpoons [M(bipy)_nL]$ (n = 1 or 2); estimated standard deviation 0.07. The log β values for $[M(bipy)]^{2+}$ and $[M(bipy)_2]^{2+}$ were respectively 6.06 and 11.42 for Co^{II} and 7.13 and 14.01 for Ni^{II}.[23]

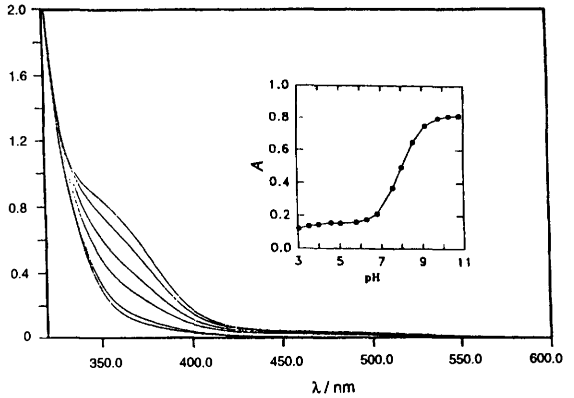

Fig. 2 Electronic spectra of the system Co^{II}–bipy–tsgly in molar ratio 1 : 2 : 4 at different pH, ranging from 3 to 11; 5 × 10^{-4} mol dm^{-3} Co^{II}, cell length = 1 cm. The inset shows the overall pH dependence of the absorbance *A* at 360 nm and 293 K

constants for the ternary carboxylate complexes (ts-β-ala, H_2hip) are reported in Table 1. When the cobalt(II) ternary system is exposed to atmospheric oxygen at alkaline pH a new polarographic wave appears and the colour of the solution changes. The new signal is probably due to the reduction of a cobalt(III) complex, formed upon oxidation of a ternary cobalt(II) complex or of $[Co(bipy)_2]^{2+}$, but no characterization was performed.

The pH-metric titration curves of the M^{II}–tsgly system at M : bipy : tsgly molar ratios of 1 : 1 : 4 and 1 : 2 : 4 show two steps, the first being completed at pH ≈ 5.9 and the second at pH ≈ 9.2. The steps correspond to the number of moles of NaOH which are given by equations (1) and (2). The second

$$m\text{NaOH} = m\text{H}_2\text{L} \qquad (1)$$

$$m\text{NaOH} = m\text{H}_2\text{L} + m\text{M}^{\text{II}} \qquad (2)$$

equivalence point, having pK_a = 7.8(2) for Co^{II} and 7.4(2) for Ni^{II}, may be reasonably attributed to the M^{II}-promoted amide deprotonation of the co-ordinated amino acid molecule. In the ts-β-ala and H_2hip systems the second, not well resolved, equivalence point is observed only at the M : bipy molar ratio of 1 : 1 and is accompanied by metal hydrolysis. At the M : bipy molar ratio of 1 : 2 metal hydrolysis is probably prevented by the formation of the stable $[M(bipy)_2]^{2+}$ species and the second titration step is not observed; the same behaviour is observed in the pH-metric titrations of $M(NO_3)_2$–bipy systems at 1 : 1 and 1 : 2 molar ratios. The pH-metric titrations in air displayed the same behaviour; in any case after some days, the alkaline final solution, on standing in air, turned from orange to wine-red.

In the electronic spectra of the orange solution containing Co^{II} : bipy : tsgly in the molar ratios 1 : 1 : 4 and 1 : 2 : 4 (Fig. 2) at increasing pH a new band appears (λ_{max} = 340 nm) following a typical titration pattern. The calculated pK_a value is 8.0(2), in good agreement with that determined potentiometrically. After standing the solution in air for a few days it turns dark red, the band at 340 nm disappears and the d–d maximum shifts to 510 nm, consistent with the presence of $[Co(bipy)_2]^{3+}$.[24]

The electronic spectra of the corresponding systems with ts-β-ala and H_2hip show a different behaviour almost identical to that of the $Co(NO_3)_2$–bipy system: upon increasing pH the solutions become dark brown and a new band appears (λ_{max} = 380 nm) characteristic of the bridged cobalt(II)–dioxygen complex.[25] After several days the band at 510 nm also appears and the solution turns pink-brown. The oxidation of Co^{II} was observed with dipeptides and the time required varies from a few minutes to about 1 d, depending on their pK_{NH} and on steric hindrance.[7] In our case the reaction rate is intermediate between those of binary peptide complexes and ternary bis(bipyridine) cobalt(II) complexes with O-donors.

The electronic spectra of the Ni^{II}–bipy–tsgly system at the molar ratio of 1 : 2 : 4 show, above pH 7, the appearance of a shoulder at about 340 nm, the intensity of which increases with pH; in the corresponding systems with ts-β-ala and H_2hip no changes are observed.

The log β values of the ternary carboxylates for the three amino acids are very similar to one another and those of nickel(II) complexes are greater than those of Co^{II}, as observed for cobalt(II) and nickel(II) binary and ternary bipy-containing species with simple amino acids,[26] N- and O-donor ligands.[27]

At acidic pH the metal (Co^{II} or Ni^{II}) is present as the free ion and binary bipy complexes, while the ternary carboxylates are very minor species; this can be justified by considering that log $K^{M(bipy)_n}{}_{M(bipy)_n(HL)}$ (n = 1 or 2) is three orders of magnitude lower than that calculated for cadmium(II) and zinc(II)[12] analogues (Table 2) and the sequence: $Zn^{II} > Cd^{II} > Ni^{II} > Co^{II}$ can be written. Despite the unfavourable value of the above step constant, at neutral pH the deprotonated species begin to form and log $K^{M(bipy)}{}_{M(bipy)L}$ (Table 2) follows the order[2,11–13] $Pd^{II} \gg Cu^{II} > Ni^{II} > Zn^{II} > Co^{II} \approx Pb^{II} > Cd^{II}$ indicating that the metal affinity for N,O-donors is the major factor in determining the complex stability; for L = glycinate and M^{II} = Cu, Zn, Ni or Co the same sequence has been reported.[27] For the pK_{NH} of the sulfonamide nitrogen there is a reverse, quite parallel, order: $Pd^{II} \ll Cu^{II} \ll Ni^{II} \leqslant Cd^{II} \leqslant Zn^{II} \approx Co^{II}$. A well defined pK_{NH} value was not determined[2] for Pb^{II} and can be only roughly estimated as intermediate between those of Cu^{II} and Ni^{II}. The small difference between the step constant for the mono- and bis-bipyridine binary species, probably due to the metal tendency to form octahedral complexes, enables at pH 8.5 a significant percentage of $[M(bipy)_2L]$ also at M : bipy molar ratio of 1 : 1 and is the only species isolated in the solid state. The preference of these metals for octahedral geometry is reflected also in log $K^{M(bipy)_n}{}_{M(bipy)_nL}$ (n = 1 or 2). Indeed the values for n = 1 or 2 are quite similar, both for Co^{II} and Ni^{II}, suggesting that the addition of the tsgly dianion is not hindered by the two bonded bipy molecules.

Table 2 Logarithms of equilibrium constants of M^{II}–bipy and M^{II}–bipy–tsgly systems and pK_{NH} values

M	$\log \beta^{M}_{M(bipy)_n(HL)}$	$\log \beta^{M}_{M(bipy)_nL}$	$\log \beta^{M}_{M(bipy)_n}$ [a]	$\log K^{M(bipy)_n}_{M(bipy)_nL}$	$\log K^{M}_{M(bipy)_n(HL)}$	pK_{NH}	Ref.
Co	7.37(7) [12.73(7)] [b]	12.28(7) [17.50(7)]	6.06 (11.42)	6.22 (6.08)	1.31 (1.31)	7.8	This work
Ni	8.62(7) [15.36(7)]	14.60(7) [21.21(7)]	7.13 (14.01)	7.47 (7.20)	1.49 (1.35)	7.4	This work
Cu		6.1(1)	8.0	8.1		5.5	11
Zn	8.96	11.98	5.30	6.68	3.66	7.8	12
Pd		30.3(1)	19.8	10.5		3.7	13
Cd	7.18	9.90	4.25	5.65	2.93	7.6	12
Pb		9.11(7)	2.9	6.21		*c*	2

[a] Values taken from ref. 23; those corresponding to Pd^{II} were taken from ref. 28. [b] The values in parentheses refer to $n = 2$. [c] See text.

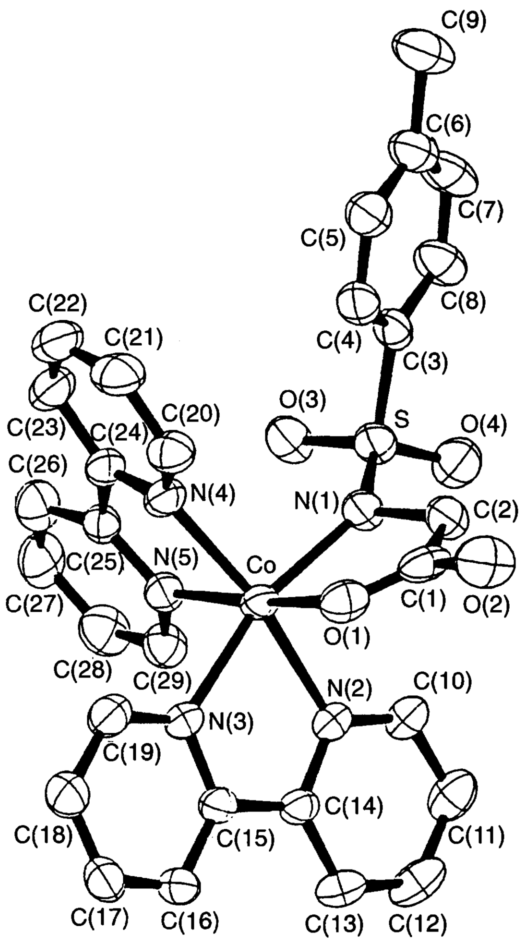

Fig. 3 An ORTEP view of the $[Co(bipy)_2(tsglyNO)]$ moiety, showing the atom numbering and thermal ellipsoids (40%) for the non-hydrogen atoms

Table 3 Selected bond distances (Å) and angles (°) for $[Co(bipy)_2(tsglyNO)]\cdot 2H_2O$

Co–O(1)	2.098(3)	Co–N(3)	2.164(6)
Co–N(1)	2.054(7)	Co–N(4)	2.141(7)
Co–N(2)	2.151(7)	Co–N(5)	2.126(5)
O(1)–C(1)	1.272(10)	S–C(3)	1.775(8)
O(2)–C(1)	1.235(7)	N(4)–C(20)	1.330(8)
C(1)–C(2)	1.516(9)	N(4)–C(24)	1.345(8)
C(2)–N(1)	1.468(7)	N(5)–C(25)	1.340(11)
N(1)–S	1.562(5)	N(5)–C(29)	1.345(9)
N(4)–Co–N(5)	76.4(2)	N(1)–Co–N(3)	164.3(2)
N(3)–Co–N(5)	90.9(2)	N(1)–Co–N(2)	93.7(3)
N(3)–Co–N(4)	96.5(2)	O(1)–Co–N(5)	173.0(2)
N(2)–Co–N(5)	95.6(2)	O(1)–Co–N(4)	96.6(2)
N(2)–Co–N(4)	168.8(3)	O(1)–Co–N(3)	89.2(2)
N(2)–Co–N(3)	75.6(2)	O(1)–Co–N(2)	91.2(2)
N(1)–Co–N(5)	101.7(2)	O(1)–Co–N(1)	79.4(2)
N(1)–Co–N(4)	95.6(3)	N(2)–C(14)–C(15)	115.3(6)
Co–O(1)–C(1)	115.5(4)	N(3)–C(15)–C(14)	115.8(6)
O(1)–C(1)–C(2)	118.0(7)	Co–N(4)–C(24)	115.2(4)
C(1)–C(2)–N(1)	110.7(6)	Co–N(5)–C(25)	116.3(4)
Co–N(1)–C(2)	112.2(4)	N(4)–C(24)–C(25)	115.5(6)
Co–N(2)–C(14)	116.7(4)	N(5)–C(25)–C(24)	115.3(6)
Co–N(3)–C(15)	116.4(5)		

Crystal structure

The crystal structure is shown in Fig. 3 and the main bond distances and angles are reported in Table 3. The structure consists of monomeric $[Co(bipy)_2(tsglyNO)]$ units and lattice water molecules. The cobalt atom is six-co-ordinated by four nitrogen atoms of the two bipy molecules and by one carboxylic oxygen and the deprotonated sulfonamide nitrogen of the tsgly dianion which forms the usual glycine-like ring.

The co-ordination geometry is a distorted octahedron, as evidenced by the deviation from 90 and 180° of the angles about the central metal ion. This distortion is the result of the constraints imposed by the bipyridine moieties and by the tsgly chelation which forces the 'bite' angle (mean 77.1°) to deviate significantly from the ideal value for a regular octahedron. The best co-ordination least-squares plane is formed by the atoms N(1)N(2)N(3)N(4) (mean deviation 0.06 Å) with an angle O(1)–Co–N(5) of 173.0(2)°. The average $Co–N_{bipy}$ bond distance is 2.145(6) Å with an average N–Co–N 'bite' angle of 76.0(4)°. These values are in line with those found for other Co^{II}–bipy complexes.[29]

As expected, the Co–N(1) bond length [2.054(7) Å] is shorter than those found in cobalt(II)–amino acid complexes [mean 2.15(2)],[30–32] in accordance with the high basicity of the deprotonated sulfonamide nitrogen with respect to the amine one, and is longer than the mean $Co^{III}–N_{amide}$ in $[Co(glyglyNO)_2]^-$ ion (1.90 Å).[10] The Co–O(1) bond distance is almost identical to that found in the binary tetraaquabis(*N*-*p*-tolylsulfonylglycinato)cobalt(II) complex [Co–O(1) 2.100(4) Å].[5]

Bond lengths and angles within the bipyridyl ligands are normal. Each bipy molecule is planar [maximum deviation 0.078(9) Å] with an average angle between the planes of the two pyridine rings of 4.4°, and displays a dihedral angle of 97.7(2)°. The four atoms of the glycine chelate ring are fairly planar with deviations from +0.05 to −0.06 Å. Bond distances and angles within the tsgly molecule fall in the range found for the other metal(II) complexes with dianionic *N*-*p*-tolylsulfonylglycine[2] with a shortening of the S–N and S–C bonds with respect to those of free *N*-*p*-tolylsulfonylglycine[33] and its carboxylate complexes.[2]

The crystal packing involves ring stacking interactions (distances in the range 3.46–3.84 Å) involving the N(2)–N(3) bipy molecule and its centrosymmetrically related one, and short O · · · O contacts, ranging from 2.76 to 2.86 Å, involving water molecules and carboxylate oxygen. In addition, the Co^{II} is 3.475(4) Å from sulfonic O(3).

The atoms surrounding the Co^{II} interfere with the binding of dioxygen and slow down the metal oxidation reaction, stabilizing the [Co(bipy)$_2$(tsglyNO)] complex and enabling its isolation in the solid state.

Spectroscopic study

The electronic spectrum of the solid [Co(bipy)$_2$(tsglyNO)]·2H$_2$O complex shows a d–d maximum at 8740 cm^{-1} and two shoulders at 19 770 and 24 500 cm^{-1}, which are consistent with an octahedral geometry.[34] However the calculated B value is not reliable. This electronic spectrum may be the outcome of the high degree of distortion from an ideal octahedron, which is due to the unsymmetrical Co–N bond distances and to the presence of three chelate rings. Although the poor structural data for the nickel(II) complex strongly suggest the same distortion from a regular octahedral geometry to that observed in the cobalt(II) complex, the electronic spectrum can be correctly interpreted in the light of an O_h symmetry and the absorption maxima are assigned as: 9450 cm^{-1}, ν_1, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$; 16 080 cm^{-1}, ν_2, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$; 26 320cm^{-1}, ν_3, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$; $Dq = 945$ cm^{-1} and $B = 936$ cm^{-1}, calculated by using ν_1, ν_2 and ν_3,[34] or $Dq = 1000$ cm^{-1} and $B = 826$ cm^{-1}, calculated from ν_1 and ν_3.[35]

The infrared spectra of the solid complexes are almost identical to one another and to that observed for [Cd(bipy)$_2$(tsglyNO)]·3H$_2$O.[36] Their common feature is the disappearance of the N–H stretching frequency and the shift, with respect to the free amino acid,[33] of the bands due to SO$_2$ and SN groups, in agreement with the presence of the amino acid in the dianionic form.

Conclusion

The ability of 2,2′-bipyridine in promoting amide-nitrogen deprotonation is maintained also in cobalt(II) and nickel(II) systems with N-sulfonylamino acids and the stability of the [M^{II}(bipy)$_n$L] (n = 1 or 2) complexes is unexpectedly high. The deprotonation reaction is preceded by the formation of carboxylate species, although their small stability constant does not allow them to separate in the solid state. The only species isolated in the solid state, even at a M : bipy molar ratio of 1 : 1, is [M(bipy)$_2$L]·2H$_2$O, preventing the formation of bis(deprotonated) [M(bipy)(LNO)$_2$]$^{2-}$ observed for Cu^{II}. The presence of the N,O chelate tsgly makes the oxidation of the cobalt(II) complex faster with respect to ts-β-ala and H$_2$hip. This finding may be attributed to the co-operative effect of the deprotonated amide nitrogen co-ordinated to the cobalt(II) and the lower steric hindrance of the unique amino acid bonded with respect to the two carboxylate ligands in the ts-β-ala and H$_2$hip complexes. In addition, in the electronic spectra, there are no hints of the formation of a bridged cobalt(II)–dioxygen complex as intermediate in the oxidation pathway.

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