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Potentiometric Studies and Modelization of Ternary Complexes of Nickel(II) with a Tetradentate Schiff-base and Its Reduced Form as the Primary Ligand and Methionine and Cysteine as the Secondary One

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The stability constants of binary and ternary complexes of nickel(II) with two tetradentate ligands: bis(2-hydroxyacetophenone) ethylenediimine (H_2BS) and N,N'-bis(2-hydroxyacetophenyl)-1,2-diaminoethane (H_2BSR) as primary ligands and two amino acids: methionine (Met) and cysteine (Cys) as secondary ones, were determined by potentiometric measurements at constant temperature (25.0 ± 0.1°C) and ionic strength (0.2 mol L^{-1}, NaCl) in water-ethanol (90 : 10 w/w) medium. Two species are formed for which the molar ratio of metal to BS or BSR and Met or Cys are 1 : 1 : 1 and 1 : 1 : 2. The binary and ternary complexes of BSR are more stable than those of BS. The values of Δ log K constants show that ternary complexes have a higher stability than the corresponding binary ones in the case of methionine but not for cysteine.

The geometry of all the species formed have been optimized by molecular mechanics using the EMO program. It was found that there is a direct correlation between the stability constants of the ternary complexes and their steric energy.

***Key words*: Ternary complexes, Schiff-base, Amino acids, Stability constants, Modelization.**

INTRODUCTION

The role of nickel as an active oligo element was recently revealed. The fact that chemotropic H_2-utilizing anaerobic bacteria required Ni to grow and the subsequent identification of Ni as a component of hydrogenases provided definitive proof of the biological role of nickel[1, 2]. The coordination chemistry of nickel with ligands of biological interest has generated much attention because of the ability of nickel to bind hard and soft donor ligand, which allows its

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coordination chemistry to encompass a variety of geometries and oxidation states, with a different reactivity in biological systems and in organometallic chemistry[3a]. In addition, nickel(II) can interact with various biological species like proteins and nucleic acids and plays an important role in their association. Ternary complexes of metal ions represent the simplest models to study this type of interaction.

Amino acids have a great complexing ability and their complexes were widely studied[3b], particularly the ternary ones[4, 5]. In fact, the interactions between the different ligands in these ternary complexes are analogous to the metal enzyme-substrate interactions in metalloenzymes. The confirmation of the coordination of the thioether sulfur atoms of methionyl residues in various blue copper proteins gave a large impetus to the study of transition metal complexes of thioether ligands. Among these ligands, methionine and cysteine are the most common thioether donors in biological systems[6].

Schiff bases deriving from *o*-phenylenediamines and salicylaldehyde with N_2O_2 donor set have been widely studied because of their interesting biological activity. Their complexes are used as models to study biological systems[7, 8]. In our laboratory, transition metal complexes with tetradentate Schiff base (H_2BS) and its reduced form (H_2BSR) (Fig. 1) have been synthetized and characterized[9].

The present work reports the

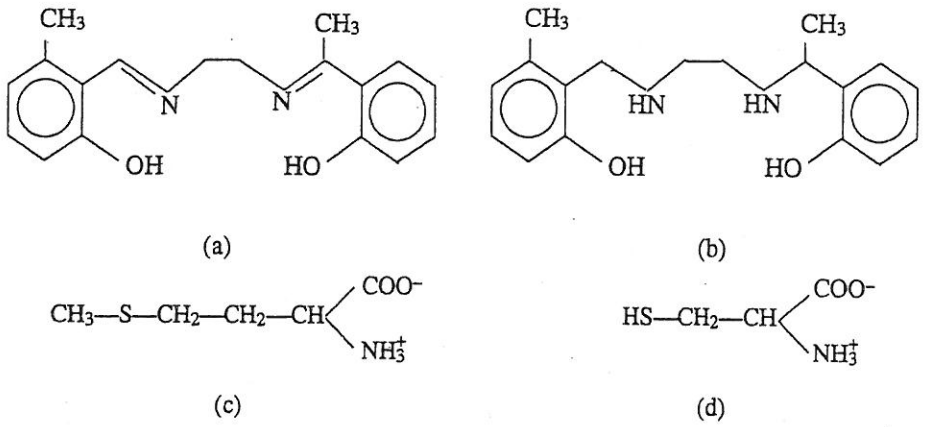


Fig. 1. Structure of ligands: (a) H_2BS: N,N′-bis(2-hydroxy acetophenon0)ethylenediimine, (b) H_2BSR: N,N′-bis(2-hydroxy acetophenyle)-1,2-diaminoethane, (c) Met: Methionine, (d) Cys: Cysteine

results of a study in solutions of ternary complexes of nickel(II) with a tetradentate Schiff base and its reduced form as the primary ligand and methionine or cysteine as the secondary one. The resurgent interest in these systems is mainly due to the results of previous studies showing that complexes of copper(II) with the ligand H_2BSR present an anticancer activity[10]. Moreover, the l-methionine plays an important role in the metabolism of platinum anticancer drugs: the Pt_{II}-l-Met complexes are formed instantaneously in plasma after injection of cisplatin into rats[11].

The aim of this study is to determine the influence of both steric and electronic effects on the stability of the complexes.

EXPERIMENTAL

Methionine and cysteine were purchased from Riedel De Haen, while hexahytrated nickel chloride was obtained from Merck and used without further purification. The ligands H_2BS and H_2BSR were synthesized and purified as previously described[9]. Exact concentration of metal solution was determined by titration with EDTA.

The potentiometric titrations were carried out in water-ethanol (90 : 10 v/v) solution at a 0.2 mol L^{-1} ionic strength (NaCl) in a thermostated vessel at 25.0 ± 0.1°C under a nitrogen atmosphere. All the solutions were titrated with carbonate free NaOH, (0.1 mol L^{-1}). The pH values were measured with a Tacussel PN81 pH-meter. The pH-meter readings in water-ethanol (90 : 10 v/v) mixture pH(r) differs by an amount from the corrected reading in aqueous medium pH*, according to the equation pH* = pH(r) – δ[12], the value in water-ethanol (90 : 10 v/v) mixture as reported to be 0.02. Accordingly the presence of 10% of ethanol in the solvent has a minor influence on the protonation or complexes stability constants obtained.

Potentiometric measurements were carried out as follows:

(i) For the solution of only the ligands, methionine and cysteine, their concentration were $5 \cdot 10^{-3}$ mol L^{-1} in water.

(ii) For both the solutions of H_2BS and H_2BSR, the concentration in water-ethanol (90 : 10 v/v) were $5 \cdot 10^{-3}$ mol L^{-1}.

(iii) For the binary complexes nickel-amino acid in 1 : 2 molar ratio, $[Ni^{2+}] = 5 \cdot 10^{-3}$ mol L^{-}, $[AA] = 10^{-2}$ mol L^{-1} (AA = Met or Cys).

(iv) For the binary complexes nickel-Schiff base in 1 : 1 molar ratio, $[Ni^{2+}] = [L] = 10^{-4}$ mol L^{-} (L = H_2BS or H_2BSR) in water-ethanol (90 : 10 v/v).

(v) For the ternary complexes in 1 : 1 : 2 molar ratio ($[Ni^{2+}] = [L] = 10^{-4}$ mol L^{-1}, $[AA] = 2 \cdot 10^{-4}$ mol L^{-1}) in water-ethanol (90 : 10 v/v).

The Sirko program[13] was used to calculate both protonation and stability constants of the ligands and their binary and ternary complexes. Computer-refined values of the constants corresponding to the minimum standard deviation were retained and used for the calculation of species distribution.

Molecular modelization

Molecular modelization was carried out by molecular mechanistics using the Emo program[14] which allows the determination of an optimised geometry and of a minimized steric energy for all complexes formed in solution. The minimized value of the steric energy enables to determine the positions of atoms in the complex corresponding to the minimum energetic contributions.

RESULTS AND DISCUSSION

Binary complexes

(a) Complexes of nickel-amino acid (Ni-AA) system: The binary complexes of the system Ni-AA have already been studied extensively; however, we determined their protonation and stability constants in our experimental condi-

tions, in order to test the reliability of the Sirko program. The overall protonation constants of methionine and cysteine and the stability constants (β_{pqr}) of their corresponding binary complexes (defined by equilibrium 1) are reported in Table-1 together with the stepwise constants K_i. Our results are in good agreement with those reported in literature[3b, 15].

$$pNi^{2+} + qH^{+} + rAA^{2-} \rightleftharpoons [Ni_pH_qAA_r]^{2p+q-2r} \quad (1)$$

TABLE-1
PROTONATION CONSTANTS OF Met AND Cys AND STABILITY CONSTANTS OF THEIR BINARY COMPLEXES.

pqr	log β_{pqr}	log K	References	
	Methionine		[3.b]	[12]
011	9.55 (0.05)	9.55	9.06	9.17
021	12.53 (0.10)	2.98	2.10	2.24
101	5.10 (0.10)	5.10	5.33	5.41
102	10.39 (0.04)	5.29	4.56	5.41
103	11.70 (0.08)	1.31	1.71	1.61
	Cysteine			
011	9.39 (0.06)	9.39	10.29	10.36
021	17.73 (0.04)	8.34	8.16	8.18
031	20.04 (0.11)	2.31	1.91	1.90
102	10.08 (0.08)	10.08	9.80	9.82
103	20.96(0.06)	10.88	10.27	10.25

For [Ni-Cys] system, two complexes are formed, the complex Ni-Cys is obtained with a percentage of 35% at pH = 5.7 whereas at pH = 7.5, the complex Ni-Cys_2 is completely formed (100%).

In the case of [Ni-Met] system, three successive complexes are observed. The complex Ni-Met is weakly formed in acidic medium with a maximum of 13% at pH = 3.78. For 4 < pH < 6, the complex Ni-Met_2 is predominant with a percentage of 52% at pH < 5.4. At pH = 8 the only complex observed in solution is Ni-Met_3.

Methionine and cysteine being ambidentate ligands, they can be either monodentate or bidentate, through combinations of (S, N), (N, O) or (S, O) donor atoms. Consequently, all these possibilities were taken into consideration for the modelisation of the binary complexes Ni-AA. As these complexes are formed in aqueous solution, we have also taken into account the two possible coordinence around metal ion (four and six), by completing the coordination sphere with solvent molecules. The values of the calculated minimized steric energy show that: (a) The more stable complexes of 1 : 1 system correspond to monodentate behaviour of the ligand through Ni—S bond. Indeed, the strong affinity of soft metal ions for thiol groups gives rise to monodentate behaviour[3b]. For bidentate behaviour, the more stable complexes correspond to (N, O) donor atoms. (b) For

1 : 2 species all calculations were carried out for a bidentate ligand. The results show that the more stable complexes are formed when N and O are the coordinating atoms, in agreement with literature[3b]. (c) In all cases, the complexes obtained with cysteine are more stable than those of methionine because they show weak steric energy. This result is in agreement with the values of stability constants determined by potentiometry. Compared to cysteine, the extra carbon in the side chain together with the thioether group destabilizes considerably methionine complexes[3b].

All calculations show that lower energy is obtained for a near square-planar geometry for these complexes.

(b) Complexes of the systems Ni-BS and Ni-BSR: The Schiff base H_2BS and its reduced form H_2BSR are tetradentate ligands. The values of the overall protonation constants log β_{qr} according to equilibrium 2 are listed in Table-2.

$$qH^+ + rL^{2-} \rightleftharpoons [H_qL_r]^{q-2r}\ \beta_{qr} \qquad (2)$$

TABLE-2
PROTONATION AND STABILITY CONSTANTS
OF THE SYSTEMS Ni-BS AND Ni-BSR

(a) Protonation constants of ligands

	log β_{qr}			log K_i	
qr	H_2BS	H_2BSR	Equilibria	H_2BS	H_2BSR
11	10.74 (0.06)	9.95 (0.09)	L^{-2}/HL^-	10.74	9.95
21	20.61 (0.04)	18.46 (0.06)	HL^-/H_2L	9.87	8.96
31	28.97 (0.03)	25.86 (0.05)	H_2L/H_3L^+	8.36	7.36
41	35.92 (0.06)	31.67 (0.05)	H_3L^+/H_4L^{+2}	6.95	5.85

(b) Stability constants of complexes

	log β_{pqr}	
pqr	H_2BS	H_2BSR
101	6.10 (0.07)	7.31 (0.04)
111	11.53 (0.06)	12.71 (0.04)
121	16.09 (0.08)	18.18 (0.05)

Four successive constants (K_i) were determined for each ligand and the values obtained are in good agreement with those reported for similar ligands[16–18]. In the case of metal-ligand system, the best values for overall stability constants β_{pqr} and the corresponding species are reported in Table-2. β_{pqr} are calculated from equilibrium (3).

$$pM^{2+} + qH^+ + rL^{2-} \rightleftharpoons [M_pH_qL_r]^{(2p+q-\beta_{pqr}\,r)} \qquad (3)$$

Only monomer species are observed. In the $[Ni(H_2L)]^{2+}$ complexes, the phenolic hydroxydes (salicylaldehyde moieties) of the ligand are protonated[17, 18]. The successive deprotonations of these complexes lead to the formation of $[Ni(HL)]^+$ and NiL species respectively. As shown in Table-2, the Ni-BSR complexes are more stable than Ni-BS complexes.

The species distribution diagram of the system Ni-BS (Fig. 2) indicates that in the pH range 4.5–6.5, the protonated species $Ni\text{-}H_2BS$ is obtained with a percentage of 54% at pH = 5.3. Further for 6.5 < pH < 7.5, the complex Ni-HBS is predominant while the main complex Ni-BS appears around pH = 5 and finally becomes the only species observed from pH= 9 onwards.

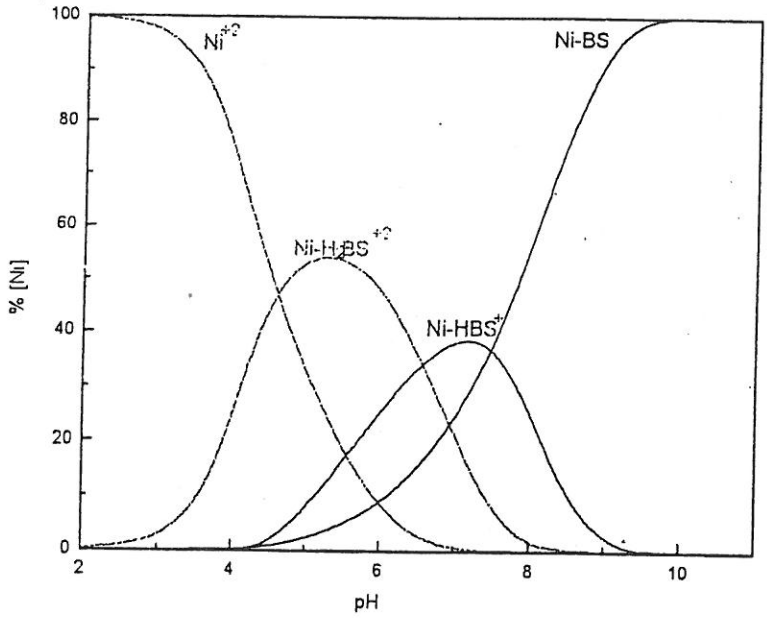


Fig. 2. Species distribution diagrams as function of pH for Ni-BS system

A similar diagram was obtained for the Ni-BSR system. For pH values lower than 7.5, the three species $Ni\text{-}H_2BSR$, Ni-HBSR and Ni-BSR are obtained. At pH = 6, the complex $Ni\text{-}H_2BSR$ is formed (35%) whereas at pH = 7, the complex Ni-HBSR is obtained (40%). The complex Ni-BSR is the main species for pH > 7.5 and becomes the unique compound in solution starting from pH = 9.

The deprotonation constants log K_a and log K_b for the equilibria (4) and (5) are 4.56 and 5.43 respectively for the system Ni-BS and 5.47 and 5.40 for the system Ni-BSR. These values are lower than those of the corresponding deprotonation constants for the free ligands. This fact is due to the presence of the metal ion which enables a proton substitution[19].

$$M(H_2L)]^{2+} \rightleftharpoons [(MHL)]^+ + H^+ \log K_a \quad (4)$$

$$[M(HL)]^+ \rightleftharpoons (ML) + H^+ \log K_b \quad (5)$$

Table-3 lists the values of the steric energy for these binary complexes. The examination of these values shows that the complexes of coordinence four are more stable than those with coordinence six. In fact, most of Ni(II) complexes show a square-planar geometry. The Ni-BSR complex is more stable than Ni-BS.

This agrees with the values of their stability constants determined by potentiometry.

TABLE-3
STERIC ENERGY FOR BINARY COMPLEXES
Ni-BS AND Ni-BSR

Complexes	C.N.	Steric energy ($kJ\ mol^{-1}$)
Ni-BS	4	90.19
Ni-BS	6	96.04
Ni-BSR	4	85.63
Ni-BSR	6	94.68

The bond distances and the valence angles obtained by optimization of Ni-BS complex are comparable to those obtained by X-ray diffraction[20]. The shortest metal-ligand bonds are observed in more stable complexes as reported below (distances in Å):

	Ni-N	Ni-N	Ni-O	Ni-O
Ni-BS	1.870	1.870	1.820	1.820
Ni-BSR	1.853	1.860	1.815	1.818

In fact, the potentiometric measurement indicated higher stability for Ni-BSR species. The optimized geometry of these complexes is close to a square-planar arrangement and the maximal deviation to square-planar geometry is approximately 10° for Ni-BS and 13° in the case of Ni-BSR.

Ternary complexes

Since the binary complexes of Ni-BS/BSR systems are more stable than those of Ni-AA systems, this suggests that BS and BSR can be considered as primary ligand and Met and Cys as secondary ones.

For all ternary systems only, two complexes are formed with a molar ratio Ni : L : AA equal to 1 : 1 : 1 and 1 : 1 : 2. Table-4 lists the stability constants β_{qr} of these ternary complexes which are defined from the equilibrium (6).

$$NiL + qH^+ + rAA^- \qquad [NiL-(AA)r\text{-}Hq]^{(q-r)} \qquad (6)$$

The complexes containing H_2BSR are more stable than those containing H_2BS. At the same time, complexes with methionine have higher stability than those with cysteine. The relative stability of ternary complexes compared to binary ones is conveniently characterized by the values[21] of Δ log K which is defined for equilibrium (7):

$$NiL_1 + NiL_2 \rightleftharpoons NiL_1L_2 + Ni \qquad (7)$$

where L_1 and L_2 are two different ligands. The value of Δ log K can be obtained by the expressions:

$\Delta \log K = \log \beta_{NiL_1L_2} - \log K_{NiL_1}$ in the case of a complex NiL_1L_2

$\Delta \log K = \log \beta_{NiL_1(L_2)_2} - \log \beta_{Ni(L_2)_2}$ in the case of a complex $NiL_1(L_2)_2$

The $\Delta \log K$ values express the effect on stability of the presence of bonded primary ligand towards the incoming secondary ligand. A positive value of $\Delta \log K$ indicates that ternary complexes are more stable than binary ones.

The $\Delta \log K$ values are reported in Table-4. These results show that the formation of ternary complexes is more favourable for methionine complexes than for those of cysteine. This can be assigned to the fact that binary complexes of cysteine are very stable; so, the approach of another ligand is not favourable[22].

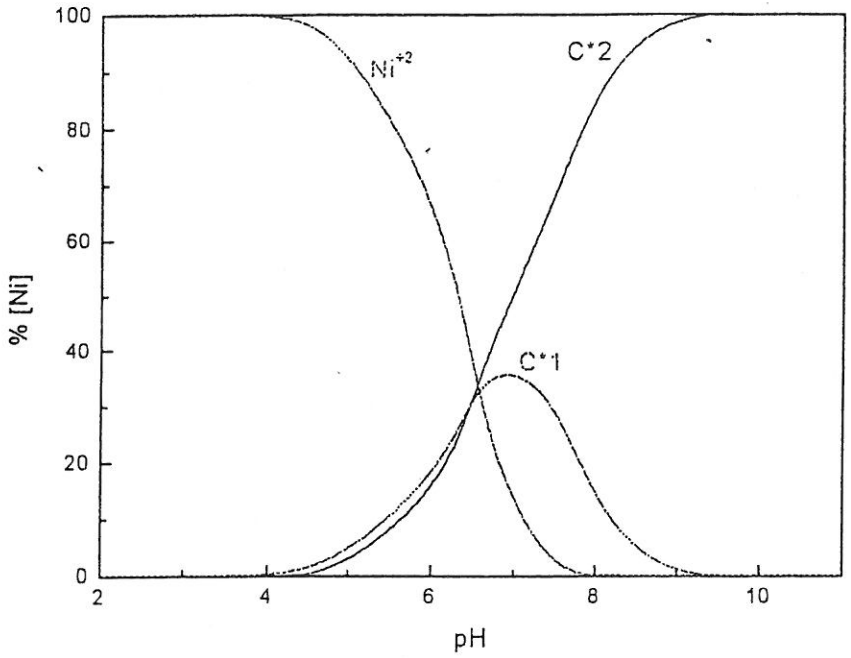
TABLE-4
STABILITY CONSTANTS AND VALUES OF logK
OF THE TERNARY COMPLEXES

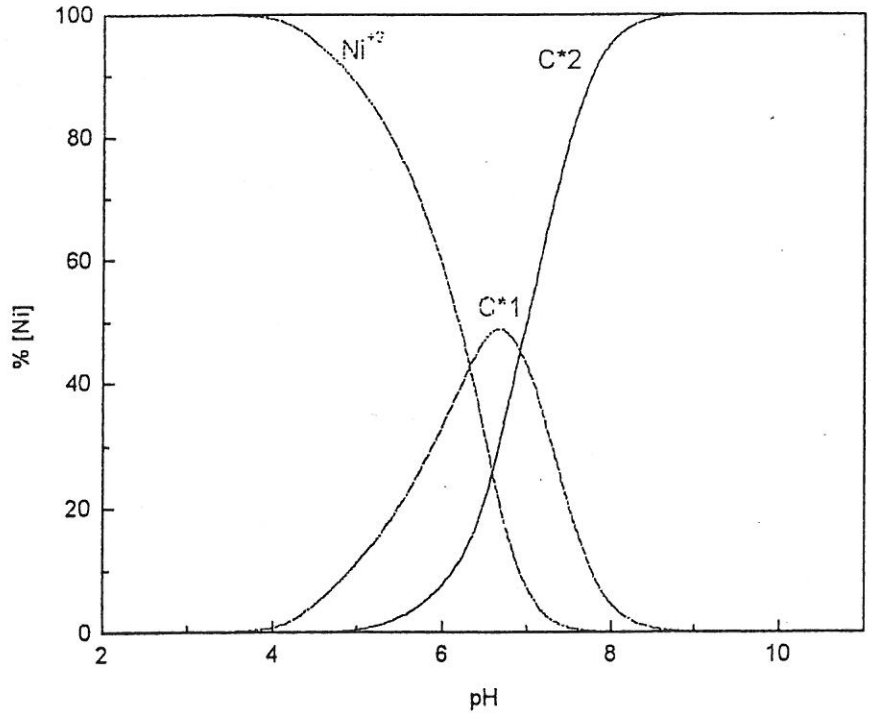
Complexes	$\log \beta_{21}$	$\log \beta_{02}$	$\Delta \log K$
$Ni(H_2BS)(Met)$	21.04 (0.05)	—	2.39
$Ni(H_2BSR)(Met)$	22.03 (0.07)	—	3.22
$Ni(BS)(Met)_2$	—	16.04 (0.07)	5.65
$Ni(BSR)(Met)_2$	—	16.83 (0.10)	6.44
$Ni(H_2BS)(Cys)$	20.31 (0.04)	—	–3.21
$Ni(H_2BSR)(Cys)$	21.50 (0.05)	—	–2.88
$Ni(BS)(Cys)_2$	—	14.80 (0.03)	–6.16
$Ni(BSR)(Cys)_2$	—	15.86 (0.07)	–5.10

For brevity, the species distribution curves (Fig. 3) of only Ni : BS : Met and Ni : BSR : Cys systems are presented. As shown in Fig. 3 the complex 1 : 1 : 1 is formed between pH = 5 and 8 with a maximum at pH = 7. For pH > 7, the complex 1 : 1 : 2 is predominant and remains the only species at pH = 9.

The results of the modelization of ternary complexes are summarized in Table-5. The values of the steric energy show that 1 : 1 : 1 complexes are more stable when the amino acid acts as a bidentate ligand and this is in good agreement with the chelating effect. The complexes with H_2BSR are more stable than H_2BS ones and this confirms the order of the stability constants determined potentiometrically.

On the other hand, the calculated steric energy shows that cysteine complexes are more stable (lower energy) than similar methionine compounds, whereas for stability constants the reverse order is observed. As ternary complexes lead to many possible interactions, it is very difficult to reach the absolute steric energy for these species. The present values are the best fit obtained, taking into account all known interactions.





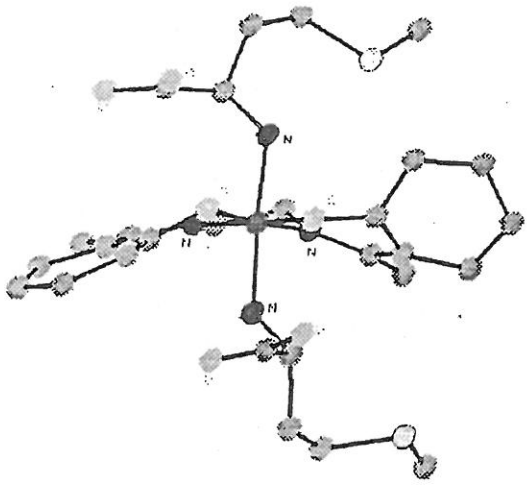
(b)

Fig. 3. Species distribution diagrams as function of pH for ternary complexes:
(a) C_1^*: Ni-BS-Met, C_2^*: Ni-BS-Met_2,
(c) C_1^*: Ni-BSR-Cys, C_2^*: Ni-BSR-Cys_2,

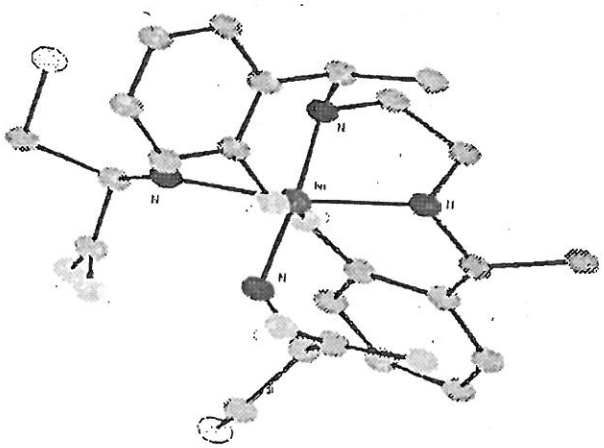
TABLE-5
STERIC ENERGY FOR TERNARY COMPLEXES

Complexes of Ni-BS-AA system	Steric energy (kJ mol^{-1})	Complexes of Ni-BSR-AA system	Steric energy (kJ mol^{-1})
Ni-BS-Met (bidentate)	221.51	Ni-BSR-Met (bidentate)	166.01
Ni-BS-Met (monodentate)	277.57	Ni-BSR-Met (monodentate)	274.01
Ni-BS-Met_2	237.81	Ni-BSR-Met_2	218.07
Ni-BS-Cys (bidentate)	198.27	Ni-BSR-Cys (bidentate)	186.61
Ni-BS-Cys (monodentate)	225.00	Ni-BSR-Cys (monodentate)	289.81
Ni-BS-Cys_2	177.85	Ni-BSR-Cys_2	166.72

Finally, the optimal geometry for these complexes shows an octahedral geometry around the nickel(II) ion (Fig. 4). In addition, the calculations indicate that the two amino-acids molecules are located in *trans* position for Ni-BS-AA system and in *cis* position for Ni-BSR-AA system.



(a)



(b)

Fig. 4. Optimized geometry for ternary complexes:
(a) [Ni-BS-Met_2, (b) [Ni-BSR-Cys_2]

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