Stability and structure of copper(II), nickel(II) and zinc(II) heterobinuclear complexes containing some biologically important ligands

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The stability constants of heterobinuclear complexes formed in aqueous solution for the biologically important ligands, viz., (i) dopa, (ii) dopamine (dopm) and (iii) L-histidine (his) with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II) and (iv) L-cysteine (cys) and (v) d-penicillamine (pen) with Ni(II)-Zn(II) have been evaluated by computer based analysis of the pH titration data. The binary systems Ni(II)/Zn(II)-dopa and dopm have also been studied. The heterobinuclear species of the types MAM' or MA2M' have been detected with dopa, dopm, cys and pen ligands, while in the his ligand systems MA2HM', MA2M', MA2H-1M' and MA2H-2M' mixed metal species have been found to be present. A qualitative attempt has been made on the comparison of the log β values, to study the Irving-Williams order of stabilities. The higher stabilities of mixed metal complexes over the mixed ligand system is also discussed.

The complexes of amino acids and peptides are important in the study of biofluids, particularly when hyper accumulated metal ions are present for physiological or pathological reasons. In vivo, the effective metal ion concentrations are interrelated and their mutual influence may be one of antagonism or stimulation. However, the causes of these influences are not yet satisfactorily understood. In view of these observations and also by considering the fact that investigations on the mixed metal systems compared to the mixed ligand systems are sparse, we report in this paper the heterobinuclear complex formation of (i) dopa, (ii) dopamine (dopm) and (iii) L-histidine (his) with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II) and (iv) L-cysteine (cys) and (v) d-penicillamine with Ni(II)-Zn(II) in aqueous solution. The ligands L-dopa and dopm are well known for their use in neuro-transmission processes and in the treatment of Parkinson disease. The imidazole group of histidine plays a fundamental role in several metal protein and metal-enzyme reactions in living organisms. Through the soft mercapto sulphur atom, penicillamine and cysteine participate in a variety of redox and acid-base reactions with metal ions. This paper is in continuation of our earlier work on mixed metal complex systems.

Materials and Methods

All the ligands used were of Fluka products of puriss quality. The metal(II) perchlorate stock solutions were prepared and estimated as described earlier. The ionic strength was adjusted to 0.15 mol dm⁻³ with NaClO₄. Other details on the potentiometric pH titrations, and data analysis and calculations have been earlier reported. All the calculations have been done with the aid of MINIQUAD-75 computer program on a HCL-MAGNUM II computer and the species distribution plots have been obtained using the computer program AUTOGRAPH. The auxiliary binary stability constant data under the present experimental conditions (Table 1) required for the computation of the mixed metal complex stability have been taken from our earlier work on Ni(II)/Zn(II)-dopa systems have been reinvestigated under the present experimental conditions.

Results and Discussion

Binary Ni(II)/Zn(II)-dopm and dopa systems

From the computer analysis of the pH titration data, the binary species NiAH, NiA and NiA₂H in the Ni(II)-dopm(A) system, and ZnAH and ZnA types of species in the Zn(II)-dopm(A) system have been detected in addition to HA, H₂A and H₃A species. The log β values of MA species in the
Table 1—Stability constants for the proton-ligand and Cu(II)/Ni(II)/Zn(II)-ligand (ligand = dopa, dopm, his, pen and cys) binary systems

\[
\begin{array}{cccccccccccc}
\text{Parameter} & \text{Cu(II)} & \text{Ni(II)} & \text{Zn(II)} \\
 & \text{dopa}^a & \text{dopm}^a & \text{his}^b & \text{dopa} & \text{dopm} & \text{his}^c & \text{pen}^c & \text{Cys}^c & \text{dopa} & \text{dopm} & \text{his}^d & \text{pen}^e & \text{Cys}^e \\
\log \beta_{\text{HIA}} & 29.73 & 30.34 & 17.37 & - & - & - & - & - & - & - & - & - & - \\
\log \beta_{\text{HIA}} & 32.38 & - & - & 25.93 & (9) & - & - & - & - & - & - & - & - \\
\log \beta_{\text{MAM}} & 23.92 & 22.07 & 14.38 & - & 18.12 & 13.08 & - & (2) & - & - & - & - & - \\
\log \beta_{\text{MAM}} & 18.08 & 15.44 & 10.27 & 10.84 & 9.66 & 8.84 & 11.54 & 9.14 & (6) & (12) & (11) & (6) & (11) \\
\log \beta_{\text{MAH}} & - & - & - & 51.16 & - & - & - & - & - & - & - & - & - \\
\log \beta_{\text{MAH}} & - & - & - & 43.36 & (23) & - & - & - & - & - & - & - & - \\
\log \beta_{\text{MAH}} & - & - & - & 23.25 & 18.49 & - & 15.94 & 23.41 & 20.21 & - & 11.74 & 20.19 & 17.81 \\
\log \beta_{\text{MAH}} & - & - & - & 5.84 & 6.63 & 4.11 & 8.46 & 4.24 & - & 7.46 & - & 4.60 & - \\
\end{array}
\]

\(\text{Ref. 14; } ^b \text{Ref. 13; } ^c \text{Ref. 9; } ^d \text{Ref. 15; } ^e \text{Ref. 16} \)

Ni(II)/Zn(II)-dopm (A) systems (Table 1) are comparable to the values in the Ni(II)/Zn(II)-pyrocatechol(A) systems\(^7\) demonstrating the pyrocatechol-like mode of binding of dopm in the NiA and ZnA (A = dopm) species. In the MAH species in the Ni(II)/Zn(II)-dopm(A) systems, the proton can be attached with the terminal amino group and the protonated ligand binds the metal in a pyrocatechol manner. However, the \(\rho K_{\text{MAH}}^d\) (M = Ni(II)/Zn(II)) values obtained (Table 1) are lesser than the \(\rho K_{\text{NH}}^+\) value of 10.13 for the dopm ligand. This indicates a decrease in basicity of the ligand in presence of the metal ion. The same trend is also observed in the \(\rho K_{\text{MAH}}^d\) values and \(\rho K_{\text{MAH}}^-\) values.

In the NiA(AH)\(^+\) species in the Ni(II)-dopm(A) system, both the ligands bind the metal ion in a pyrocatechol-like manner and the extra proton resides with the terminal amino group of any one of the ligands.

The ligand dopa has four potential coordination sites and at low \(pH\) values, amino acid type (N, O) bonding and at high \(pH\) values, catechol-like (0, 0) bonding with the metal ions have been described\(^17,18\). The present study showed the presence of the binary species of the types NiA-H\(_2\), NiA, NiA-H\(_4\) and NiA-H\(_3\) in the Ni(II)-dopm(A) system, and ZnA-H\(_2\) and ZnA binary species in the Zn(II)-dopm(A) system in addition to HA, H\(_2\)A, H\(_2\)A and H\(_4\)A species. The NiA and ZnA (A = dopa) types of species have been found to favour at higher \(pH\) values demonstrating the catechol-like binding of the dopa ligand with Ni(II)/Zn(II). The comparable log \(\beta_{\text{MAH}}\) values in the Ni(II)/Zn(II)-dopm(A) systems with those values in the Ni(II)/Zn(II)-dopm(A) systems (Table 1) where dopm binds the metal in a pyrocatechol mode supports the argument that dopa binds in a catechol mode in its NiA/ZnA binary complexes. The MAH\(_2\) species has been found to be formed in fairly significant concentration at lower \(pH\) values and amino acid-type bonding is expected with the phenolate oxygens protonated. The M(AH\(_2\))\(^+\) type of species containing amino acid type bonds is formed only with Ni(II) and not with Zn(II). This is in agreement with the observation of Gorton et al.\(^19\) that Ni(II) ion has greater tendency than Zn(II) ion to form bonds with ligand containing (N, O) donor atoms. The NiA-H\(_3\) species is formed by the stepwise deprotonation of the NiA-H\(_4\) species via some structural rearrangement, containing the mixed mode of bonding involving both (N, O) and (O, O) bonds.

**Mixed-metal complex equilibria**

**Dopa with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II)**

From the studies of a number of binary species in the metal-dopa systems, different types of heterobinuclear species are expected and a number of
computer models have been included during computation and the final results showed the presence of MAM' mixed metal species in fairly good concentrations.

In all these mixed metal systems, since the ligand possesses four potential binding sites, there are two possibilities for the binding of dopa with the metal ions. In the CuAZn (A = dopa) species, the first possibility is that Cu(II) binds the ligand in a pyrocatechol-like mode and Zn(II) in a glycine-like manner and vice-versa. The higher stability of CuA complex compared to the ZnA complex suggests the first structure to be more probable. If this is the mode of binding of dopa in the CuAZn species, the log $\beta_{CuAZn}$ (experimental) value of 21.45 (Table 2) should be comparable to the sum of log $\beta$ values of 15.44 in the Cu(II)-dopm (A) system, where the ligand binds the metal ion in a pyrocatechol manner, and the log $\beta$ value of 5.03 for ZnA species in the Zn(II)-glycine (A) system which comes out to be 20.47. Hence the proposed structure is established. The same should be the expected mode of binding of dopa ligand in the CuANi and NiAZn species, where the respective experimental values (20.82 and 15.50) are in close agreement with the calculated values (21.33 and 15.87). Thus in the NiAZn species, dopa binds Ni(II) ion in a pyrocatechol-like mode and Zn(II) in a glycine-like manner. It should be mentioned here that in all the above cases, while calculating the expected log $\beta_{MAM}$, statistical factors resulting from the decrease in number of coordination groups in mixed metal complex species compared to those in the MA and M'A complexes have not been taken into consideration. If this factor is considered, the above calculated values would be lesser by ~ 1 to 2 log units. Thus in all the cases, the experimentally found log $\beta_{MAM'}$ is higher than the theoretically expected values indicating higher stability for the mixed metal complex species.

**Dopm with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II)**

Like dopa containing mixed metal systems, dopm also forms only one type of heterobinuclear species MAM'. In the Cu(II)-dopm-Zn(II) system, the experimental log $\beta_{CuAZn}$ value is 19.87. Considering the higher stability of CuA compared to the ZnA species, in the CuAZn species, it is assumed that dopm binds Cu(II) in a pyrocatechol-like mode. Thus in the log $\beta_{CuAZn}$ value of 19.87 obtained in the Cu(II)-dopm-Zn(II) system, 15.44 log units is accounted for the pyrocatechol mode of binding of dopm with Cu(II) and the remaining value of 4.43 log units is for the binding of dopm ligand with Zn(II). Again by considering the statistical factor mentioned under dopa mixed metal systems above, it can be inferred that the stability constant value for the binding of Zn(II) with dopm ligand in the CuAZn species should be still higher than 4.43 log units. If Zn(II) binds the ligand only through amino nitrogen, the value expected is 3.7 log units as found in the Zn(II)-cysteic acid system where the metal binds the ligand through the N-amino group. This indicates that Zn(II) in the CuAZn dopm species binds the ligand via the amino group and by binding any one of the phenolato oxygen atoms. The bridging of 3-phenolato oxygen with Zn(II) resulting in an 8-membered chelate ring is preferred as compared to that of 4-phenolato oxygen because the latter would result in a sterically unfavourable 9-membered ring. The same type of structural arrangement is expected for the MAM' species in the Cu(II)-dopm-Ni(II) and Ni(II)-dopm-Zn(II) systems.

**Stability comparison of mixed metal complexes of dopa and dopm ligands**

It is interesting to compare the stability of the MAM' heterobinuclear species in the Cu(II)-dopa-Zn(II) and Cu(II)-dopm-Zn(II) systems with that in the Ni(II)-dopa-Zn(II) and Ni(II)-dopm-Zn(II) systems, which shows that MAM' species in the former systems are more stable than in the latter systems. This is in accordance with the Irving-Williams order of stabilities. However, in the Cu(II)-dopa/dopm-Zn(II) and Cu(II)-dopa/dopm-Ni(II) systems, the former systems have

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>log $\beta$</th>
</tr>
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<tbody>
<tr>
<td>Cu$^{2+}$ + dopa$^{3-}$ + Zn$^{2+}$ ⇒ [Cu(dopa)Zn]$^{+}$</td>
<td>21.45(9)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + dopa$^{3-}$ + Ni$^{2+}$ ⇒ [Cu(dopa)Ni]$^{+}$</td>
<td>20.88(9)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopa$^{3-}$ + Zn$^{2+}$ ⇒ [Ni(dopa)Zn]$^{+}$</td>
<td>15.50(9)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + dopm$^{2-}$ + Zn$^{2+}$ ⇒ [Cu(dopm)Zn]$^{+}$</td>
<td>19.87(10)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + dopm$^{2-}$ + Ni$^{2+}$ ⇒ [Cu(dopm)Ni]$^{+}$</td>
<td>18.92(10)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopm$^{2-}$ + Zn$^{2+}$ ⇒ [Ni(dopm)Zn]$^{+}$</td>
<td>14.52(9)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + his + Zn$^{2+}$ ⇒ [Cu(his)Zn]$^{+}$</td>
<td>14.61(2)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + dopa + Zn$^{2+}$ ⇒ [Cu(dopa)Zn]$^{+}$</td>
<td>21.96(6)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2his + Zn$^{2+}$ ⇒ [Cu(his)Zn]$^{+}$</td>
<td>16.13(3)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2his + H$^{+}$ + Ni$^{2+}$ ⇒ [Cu(his)H_{2}Ni]$^{3+}$</td>
<td>27.96(3)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2his + Ni$^{2+}$ ⇒ [Cu(his)Ni]$^{+}$</td>
<td>23.30(3)</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2his + Ni$^{2+}$ ⇒ [Cu(his)Zn]$^{+}$</td>
<td>23.30(3)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopa + Zn$^{2+}$ ⇒ [Ni(dopa)Zn]$^{+}$</td>
<td>11.75(3)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopa + Zn$^{2+}$ ⇒ [Ni(dopa)Zn]$^{+}$</td>
<td>19.82(3)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopa + Zn$^{2+}$ ⇒ [Ni(dopa)Ni]$^{2+}$</td>
<td>16.17(4)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopm + Zn$^{2+}$ ⇒ [Ni(dopm)Zn]$^{+}$</td>
<td>13.06(4)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + dopm + Zn$^{2+}$ ⇒ [Ni(dopm)Ni]$^{2+}$</td>
<td>14.21(9)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 2pen + Zn$^{2+}$ ⇒ [Ni(2pen)Zn]$^{+}$</td>
<td>27.18(2)</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 3cys + Zn$^{2+}$ ⇒ [Ni(cys)Zn]$^{+}$</td>
<td>25.15(1)</td>
</tr>
</tbody>
</table>
higher stability than the latter systems. This type of observation against Irving-william series may be accounted for by considering the different geometrical preference of Zn(II) and Ni(II) in their complexes. The tetrahedral arrangement of Zn(II) leads to an increase in flexibility and more favourable molecular arrangement in the mixed metal species unlike in the Ni(II) system which prefers a square planar geometry. Similar trends have also been observed earlier1,6,7.

**His with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II)**

The first study on the heterobinuclear complex formation of His ligand was carried out by Amico et al.22. The present investigation differs from the types of the mixed metal complexes as reported earlier. The $MA_2HM'$, $MA_2M'$, $MA_2H_{-1}M'$ and $MA_2H_{-2}M'$ have been found to be favoured in the Cu(II)-his-Ni(II) system and in the Cu(II)/Ni(II) systems the species of the types $MAM'$, $MA_2M'$ and $MA_2H_{-1}M'$ (in addition $MAH_{-1}M'$ in the Ni(II)-his-Zn(II)) have been detected in the present experimental conditions at an ionic strength of 0.15 (NaClO$_4$) and at 37°C.

In the CuA$_2$HNi species, since protonated binary species have been detected9,13 in both Cu(II)/Ni(II)-his(A) systems, and from the higher stability of CuA compared to NiA (A = his) species, it can be expected that one histidine binds Cu(II) in a tridentate manner and the protonated his binds Ni(II) through the imidazole nitrogen and carboxylato oxygen atoms as in the NiAH histidine species9, and Cu(II) and Ni(II) can be bridged through the carboxylato groups of both the ligands. By expecting this mode of binding, the log $\beta_{CuA,HNi}$ can be calculated by summing up the log $\beta_{CuA}$ value13 in the Cu(II)-his(A), log $\beta_{NiAH}$ value9 in the Ni(II)-his(A) and log $\beta_{values}$ for the carboxylato binding20 with Cu(II) and Ni(II) and the value comes to be 26.88. Again, if the statistical factors as described under dopa and dopm mixed metal systems are taken into consideration, the calculated value should be still lesser by ~1 to 2 log units. The higher experimentally found value indicates higher stability for the mixed-metal species.

In the $MA_2M'$ [$M$ = Cu(II)/Ni(II) and $M'$ = Ni(II)/Zn(II)] type of species, both His ligands bind M(II) in a glycine like manner and imidazole nitrogen atom of both His ligands can bind M(II). This is in agreement with the findings of Amico et al.22 for the CuA$_2$Ni species in the Cu(II)-his-Ni(II) system. By supposing this mode of coordination, one can obtain the theoretical value for log $\beta_{MA_2M'}$ by summing up twice the value of log $K_{MA}$ in the M(II)-glycine(A) system20 and the value of log $K_{MA}$ in the M(II)-imidazole(A) system9,13 and the values obtained are in agreement with the experimental values. The deprotonation of the pyrrole group in one of the His ligands in MA$_2$M' species gives rise to the formation of MA(AH$_{-1}$)M' in the title systems. As in the MA$_2$M' species, it can be expected that in the above deprotonated species, both the ligands bind the metal ion M (= Cu(II)/Ni(II)) in a glycine-like manner and one His binds M' through imidazole N-atom and the second His(deprotonated) coordinates it through pyrrole N-atom. The deprotonation of the pyrrole group in both the His ligands begins at a pH of 6.5 in presence of the metal ions Cu(II) and Ni(II) and gives rise to the formation of Cu$_2$H$_{-2}$Ni in the Cu(II)-His-Ni(II) system. In this species, both His ligands bind Cu(II) in a glycine like manner, and the pyrrole N atoms of the deprotonated His ligands bind Ni(II) ion.

For the CuA$_2$Zn and NiA$_2$Zn mixed metal species detected in the Cu(II)/Ni(II)-His-Zn(II) systems, it is reasonable to assume that the His ligand binds Cu(II)/Ni(II) in a glycine-like manner and Zn(II) binds through the imidazole N-atom of the ligand. If so, the log $\beta_{MAZn}$ values (M = Cu(II)/Ni(II)) can be calculated by summing up the log $K_{MA}$ values in the Cu(II)/Ni(II)-glycine(A) systems20 and the log $K_{MA}$ value in the Zn(II)-imidazole(A) system13. These values are in agreement with the experimental values. The deprotonation of the ligand His in the pyrrole group in presence of Ni(II) and Zn(II) gave the mixed metal complex NiAH$_{-1}$Zn in which Ni(II) can bind His in a glycine-like manner and Zn(II) binds the deprotonated His ligand through the pyrrole N-atom.

The crystallographic evidence23 for the presence of imidazole as a bridge between Cu and Zn in bovine superoxide dismutase makes this study more important. The detection of MAH$_{-1}$M' and MA$_2H_{-1}M'$ mixed metal complexes in the M-histidine-M' systems in the present study is interesting. The deprotonation of pyrrole group of histidine in the mixed metal systems takes place at pH 5.00 and the maximum concentration of the species has been found in the pH range 6 to 7. But in the binary and mixed ligand systems containing histidine ligand, the deprotonation of pyrrole group does not take place even at pH 10. This demonstrates that the mixed metal complex formation is more preferred as compared to mixed ligand complexes.

**Pen and Cys with Ni(II) and Zn(II)**

In the Ni(II)-pen-Zn(II) system, heterobinuclear
species of the types NiAZn and NiA2Zn, and in the
Ni(II)-Cys-Zn(II) system, only NiA2Zn species have
been detected. The log β_{NiAZn} value obtained in the
Ni(II)-pen-Zn(II) system is 14.24. The NiA pen
complex has higher stability compared to ZnA pen
complex. The parameter log K_{NiAZn} has been
calculated and the value of 2.74 obtained can be due to
the binding of mercapto sulphur to Zn(II) ion. Hence,
it may be concluded that in the NiAZn species, Ni(II)
binds pen in a bidentate manner through N-amino
and S-mercapto groups, and Zn(II) binds the ligand
through S-mercapto group. Thus, the approximate
log β_{NiAZn} value should be the sum of log β_{NiA}
and log β_{ZnA} value of the bridged binding of mercapto
group of pen with Zn(II) and the value comes to be 14.50,
which compares favourably with the experimental

The log β_{NiAZn} (A = pen and cys) values
obtained in the Ni(II)-pen/cys-Zn(II) systems are
27.18 and 25.15 respectively. The lesser log β value in
the cys containing mixed metal species can be
attributed to the higher basicity of pen compared to the
cys ligand. In these species, pen/cys binds Ni(II) in
a bidentate manner through the mercapto and
N-amino groups and the mercapto group can bridge
Zn(II) ion. The approximate log β value for the
NiA2Zn species in the Ni(II)-pen-Zn(II) system
based on these structural characteristics comes to be
28 units and the experimental value is 27.18. In the
Ni(II)-cys-Zn(II) system, calculated log β_{NiAZn}
value of 24.5 compares favourably with the
experimental value of 25.15.

The distribution of various binary and hetero-
binuclear species of all the eleven systems in the
present study have been drawn (% of [A] versus pH)
and in all the cases concentration of mixed metal
complex species are higher as compared to the binary
analogues. The concentration of the binary species
present in these systems never exceed 20% of the
total ligand present, while the mixed metal species MA2M'
has been found to be present to the extent of more
than 70%. A survey on Zn(II) containing mixed
ligand systems indicates that mixed ligand complex
species of Zn(II) usually never exceeds the
statistically expected value of 50%, but more than
70% of the total ligand has been found to be present in
the form of MAM' species in the Cu(II)-his-Zn(II)
system. Again, these plots indicate that formation of
mixed metal complex starts from very low pH values
and concentration increases with increase of pH
values.

References
1 Amico P, Arena G, Daniele P G, Ostacoli G, Rizzarelli E &
Sammartano S. Environmetal inorganic chemistry, edited by
K J Irgolic & A E Martell (VCH Publishers, Florida) 1985, P
285.
2 An introduction to bio-inorganic chemistry edited by D R
6 Rajathirumoni P, Arasu P T & Nair M S, Indian J Chem. 31A
(1992) 760.
7 Nair M S, Arasu P T, Fernando T L, Pillai M S & Chandran M,
8 Nair M S, Santappa M & Natarajan P, Indian J Chem. 19A
10 Nair M S, Pillai M S & Ramalingam S K, J chem Soc Dalton
237.
14 Arasu P T, Ph D Thesis, Manonmaniam Sundaranar
University, 1993.
16 Nair M S, Arasu P T, Pillai M S & Natarajan C, Talanta, 40
(1993) 1411.
20 Critical stability constants, Vols 1-6 edited by A E Martell & R
22 Amico P, Daniele P G, Arena G, Ostacoli G, Rizzarelli E &
23 Richardson J S, Thomas K A, Rubin B H & Richardson D L,
Proc Natl Acad Sci. USA, 72 (1975) 1349.