

Formation of Nickel(II) Complexes of 1,3-Bis(tris(hydroxymethyl)methylamino)propane in Aqueous Solution

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The compounds tris(hydroxymethyl)aminomethane (tris), bis(2-hydroxyethyl)iminotris(hydroxymethyl)methane (bis-tris) and 1,3-bis(tris(hydroxymethyl)methylamino)propane (bistrispropane) are often used as buffer materials in biochemical studies. These compounds are also good complexing agents. The equilibrium constants of complexes formed from tris and various metal ions have been reported.¹ Metal complexes of bis-tris have been investigated.²⁻⁴ The complexing properties of bistrispropane (btp) have been first investigated quantitatively with Cu(II) ion.⁵

Experimental Section

The nickel(II) nitrate used in this study was the '99.999%' grade from Aldrich Chemical Company. The stock solution of this salt was standardized by complexometry. The btp used was the '99%+' grade also from Aldrich. An Orion Research EA-940 Expandable Ion Analyzer equipped with a Ross 81-01 combination pH electrode was used. The hydrogen ion concentration was obtained from the measured pH by using the activity coefficient calculated by the Davies equation⁶ at the ionic strength employed here. The hydroxide ion concentration was obtained by using the value of 13.78 for pK_w of water.⁷ Solutions of Ni(NO₃)₂, btp and HCl in appropriate molar ratios were titrated with standard NaOH solution. All titrations were done using 50 mL test solutions at 25.0 ± 0.1 °C. The electronic absorption spectra were obtained with Shimadzu UV-3101PC spectrophotometer using 5-cm quartz cells.

Results and Discussion

The equilibrium data for btp and its Ni(II) complex systems are given in Figure 1. The initial btp-HCl molar ratio is 1 : 2 at the start of the titration for all the systems. Curve 1 is for btp. For Curves 2, 3 and 4, the metal-ligand molar ratio is 1 : 1, 2 : 3 and 1 : 2, respectively. The strong inflection at a=1 for the 1 : 1 system indicates formation of the btp (L) complex NiL²⁺ in large proportion. This complex further reacts with NaOH, undergoing acid dissociation, as in the case of CuL²⁺. However, the final inflection at a=1.75 of Curve 2 of Figure 1 does not coincide with that of the Cu(II)-btp 1 : 1 titration curve⁵ which gives final inflection at a=2. This shows that a totally different type of complex is formed in the Ni(II) system. The value of 1.75 indicates that triply deprotonated dinuclear complex Ni₂L₂H₃⁺ is formed. The final inflection points of Curves 3 and 4 agree with formation of this complex. Curve 3 gives final inflection at

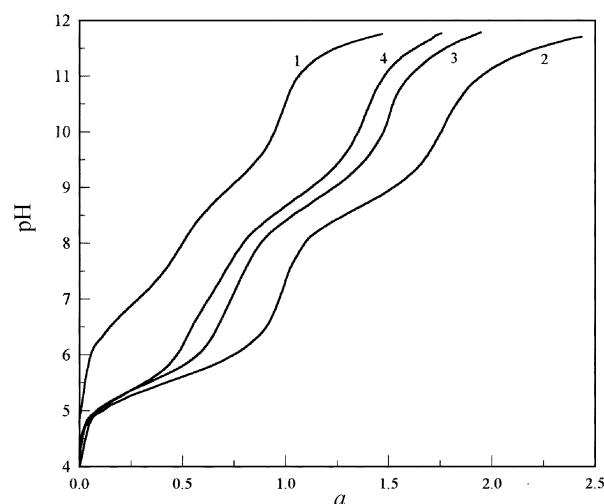
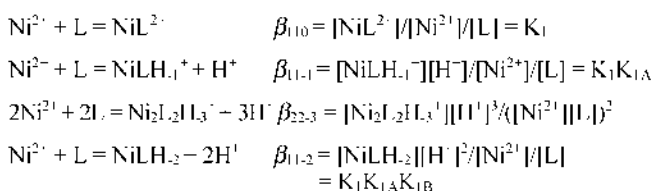


Figure 1. Potentiometric equilibrium curves of bistrispropane and its Ni(II) complex systems. The initial concentrations are: Curve 1: 10.40 mM in btp and 20.80 mM in HCl. Curve 2: 10.06 mM in Ni(NO₃)₂, 10.40 mM in btp and 20.80 mM in HCl. Curve 3: 10.06 mM in Ni(NO₃)₂, 15.60 mM in btp and 31.20 mM in HCl. Curve 4: 10.06 mM in Ni(NO₃)₂, 20.80 mM in btp and 41.60 mM in HCl. Titrated with 1.012 M NaOH, $\mu=0.1$ M KNO₃, a=moles of NaOH / moles of HCl.

a=1.5 and Curve 4 at a=1.375. The reactions taking place between Ni(II) and btp in these solutions are given below.



where K_{1A} and K_{1B} are the successive acid dissociation constants of the complex NiL²⁺. In these expressions, the negative subscript to H indicates the number of protons dissociated from the neutral ligand L. The equilibrium constants were evaluated by the BEST computer program⁸ and are given in Table 1.

The overall protonation constant (β_{010}) of a polyamine is a measure of its total basicity and therefore a measure of its complex stability. The total basicity (β_{012}) decreases in going from ethylenediamine (en) to *N*-(2-hydroxyethyl)ethylenediamine (hen) to *N,N'*-bis(2-hydroxyethyl)ethylenediamine (bishen). The stability constants (β_{110}) of complexes of these diamines with Ni(II) also decrease in going from en to hen to bishen. However, the decrease in complex stability is substantially smaller than that in total basicity of the ligands.

Table 1. Equilibrium constants for the reaction of btp with metal ions⁴

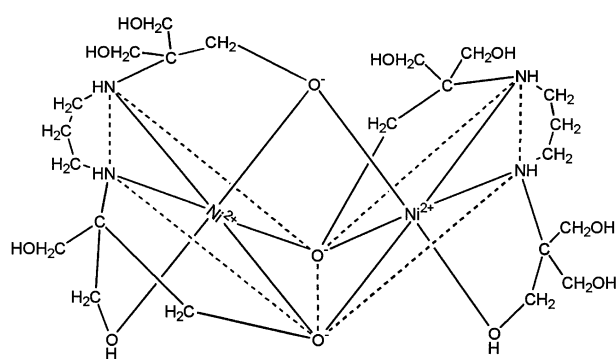
log β , logK	H ⁻	Ni ²⁺	Cu ²⁺
β_{011}	8.89		
β_{012}	15.64		
K_{a1}	-6.75		
K_{a2}	-8.89		
β_{110}		6.97	10.57
β_{11-1}		-1.65	5.12
β_{22-3}		-9.61	
β_{11-2}		-11.20	-3.29
K_{1A}		-8.62	-5.45
K_{1B}		-9.55	-8.41

*At 25 °C and $\mu=0.1$ with KNO₃. The entries for H⁻ and Cu²⁺ are from ref. 5.

This indicates coordination of the hydroxyl groups. The decreasing stability of the complexes is also due to the nature of the fused chelate rings formed by these ligands with Ni(II). The ligands en, hen and bishen form 5, 5-5 and 5-5-5 membered rings, respectively, with increasing ring strain which causes destabilization of the complexes.

However, with 1,3-propylenediamine (pn), *N*-(2-hydroxyethyl)-1,3-propylenediamine (hpn) and btp, the opposite trend was observed. The total basicity (β_{012}) decreases in going from pn¹ to hpn¹ to btp⁵ but the complex stability increases in that order (Table 1). The increasing stability with increasing number of hydroxyl groups in the ligand indicates operation of chelate effect arising from the coordination of these groups. The ligands pn, hpn and btp form 6, 5-6 and 5-6-5 membered chelate rings, respectively. The alternating ring size between 5 and 6 atoms is believed to reduce steric strain which is present in chelates with fused rings of the same size, e.g., 5-5, 6-6, 5-5-5 or 6-6-6 membered rings.^{9,10} The overall protonation constant (log β_{014}) of triethylenetetramine (2,2,2-tet), 1,4,8,11-tetrazaundecane (2,3,2-tet) and 1,5,9,13-tetraazatridecane (3,3,3-tet) are 28.67, 31.67 and 36.03, respectively.¹ The total basicity is largest for 3,3,3-tet. However, 2,3,2-tet forms the most stable chelates; 3,3,3-tet the least stable chelates. 2,2,2-tet, 2,3,2-tet and 3,3,3-tet form 5-5-5, 5-6-5 and 6-6-6 membered chelates, respectively. Thus, the 5-6-5 member chelate is the most stable even though the ligand (2,3,2-tet) that forms this chelate is not the most basic. The 'extra' stability of this chelate has been ascribed to the steric strain in the middle ring which is less strained in 6-atom than in 5-atom ring.¹⁰ The total basicity of btp is about the same as that of bishen. However, Ni(btp)²⁺ is more stable than Ni(bishen)²⁺. This is because the former has 5-6-5 chelate rings while the latter has 5-5-5 rings. Structurally btp resembles 2,3,2-tet and bishen 2,2,2-tet.

Some coordinated hydroxyl groups, due to the inductive effect of the positively charged metal ion, exhibit acidic property. An x-ray study¹¹ on the related Ni(II)-triethanolamine solid complex showed that the metal-triethanolamine oxygen distance is shorter than the metal-coordinated water oxygen distance. This indicates that the former bond is stronger than the latter and therefore that the hydroxyl hydrogen of

**Structure 1.** Ni₂(btp)₂(L₃)₁.

triethanolamine is more acidic than the water hydrogen. Therefore, when this complex reacts with base, the hydroxyl hydrogen of triethanolamine would dissociate before the hydrogen of the coordinated water molecule. A recent x-ray study¹² of Cu(II)-tris solid complexes showed that both the neutral tris and monodeprotonated tris are coordinated to Cu(II) as bidentate and that the Cu-alkoxide oxygen bond is shorter than the Cu-hydroxy oxygen bond. This indicates that the former bond is stronger than the latter. The results of btp complexes of Ni(II) are in agreement with those of the related hydroxyamine complexes.

Btp forms monodeprotonated complexes of the form M(LH)₁⁺ with both Cu(II)⁵ and Ni(II). With Cu(II) further increase in pH gives M(LH)₂ but Ni(II) gives the triply deprotonated dinuclear complex M₂(L)₂(H₃)⁺ instead. The probable structure of Ni₂(L)₂(H₃)⁺ is given in Structure 1. While the neutral donor groups may be disposed about the metal ions in several non-critical alternative ways, the presence of the three negatively charged alkoxide oxygen atoms in bridging positions is considered essential for the binding of the two positively charged metal atoms in the dinuclear complex to overcome the coulombic repulsion. The 6-coordinate nature of Ni(II) in its btp complexes is maintained in this dinuclear species. On the other hand, Cu(II) is basically 4-coordinate square in its complexes and therefore can not form triple bridges. This is probably the reason why Cu(II) does not form this type of complex.⁵

The electronic absorption spectra of the Ni(II)-btp complexes are shown in Figure 2. Spectrum 1 is that of the aqua Ni²⁺ ion. Spectra 2, 3, 4, and 5 correspond to Curve 2 of Figure 1 at a=1, 1.375, 1.75, and 2.5, respectively. Spectra 6 and 7 correspond to Curve 3 at a=1.5 and 1.8. Spectra 8 and 9 correspond to Curve 4 at a=1.375 and 1.75. The fact that Spectra 4, 6, and 8 are identical confirms the potentiometric finding that only one and the same species, Ni₂(L)₂(H₃)⁺ is formed at the final inflection points of all three systems. The three strongly basic solutions (Spectra 5, 7 and 9) corresponding to points well past the final inflections of the equilibrium curves also gave the same spectra. These spectra are quite different from Spectra 4, 6 and 8. This shows that complexation reaction continues even after the final inflection points and still different complex species is formed in the alkaline solutions above pH 10. This complex is believed to be Ni(LH)₂.

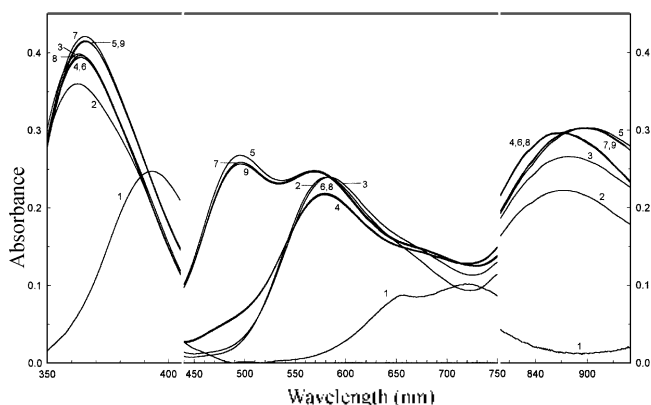


Figure 2. Electronic absorption spectra of Ni(II)-bistrispropane systems. All solutions are 9.73 mM in $\text{Ni}(\text{NO}_3)_2$. Btp concentrations are 10.24 mM (Spectra 2,3,4,5), 15.36 mM (Spectra 6,7), and 20.48 mM (Spectra 8,9). KOH concentrations are 7.69 mM (Spectrum 3), 15.37 mM (Spectra 4,6,8), 24.59 mM (Spectrum 7), and 30.70 mM (Spectra 5,9).

The absorption bands of aqua Ni^{2+} ion shift greatly to shorter wavelengths on btp coordination and one of the twin middle bands of the aqua ion disappears as generally observed on amine coordination. The bands of $\text{Ni}(\text{btp})^{2+}$ occur at considerably shorter wavelengths than the corresponding bands of $\text{Ni}(\text{pn})^{2+}$. This again indicates hydroxyl oxygen coordination in the btp complex. This is in agreement with the conclusions from the potentiometry. The spectra of the related Ni(II)-triethanolamine complexes in aqueous solutions also showed similar trend.¹³ In Figure 2, the 'blue' band (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$) shifts slightly to longer wavelengths on deprotonation. The near ir band (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$) shifts slightly to shorter wavelengths on deprotonation but then shifts in the opposite direction in very basic media. The twin 'red' bands (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F}), {}^1\text{E}_g$) shift to shorter wavelengths and merge on btp

coordination. It is very interesting to note that this middle band splits again in very basic media (NiL_2H_2) as in the aqua Ni^{2+} ion. The structure of NiL_2H_2 is believed to be similar to that⁵ of CuL_2H_2 with additional coordination at the axial positions by the adjacent hydroxyl groups in the ligand btp.

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