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Research Article

EQUILIBRIUM STUDY OF THE MIXED COMPLEXES OF ZN(II), CD(II), NI(II) & CO(II) TRANSITION METAL IONS WITH L-ASCORBIC ACID AND L-PHENYLALANINE IN AQUEOUS SOLUTION

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ABSTRACT

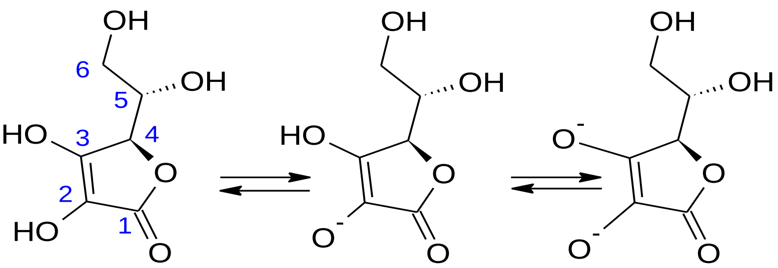
The interaction of Zn(II), Cd(II), Ni(II) & Co(II)transition metal ions with L-Ascorbic acid and L-Phenylalanine have been studiespH metrically at constant ionic strength I =0.1MNaNO$_3$, at 308 K to 318 Ktemperature and potentiometric pH titrations were carried out to determine the stabilities of the binary (1:1) and ternary (1:1:1) complexes, with M(II)= Zn(II), Cd(II),Ni(II) & Co(II) metal ions. The percentage of species distribution curves have been demonstrated with the help of ORIGIN 6.1 software. Stability constant have been determined through (SCOGS) Stability Constant of GeneralizedSpecies computer program. Species distribution curves of complexes have been plotted as a function of pH.The pKa of ligands and log K of ternary metal complexes were determined and correlated with basicity of ligands.

Keywords: L-Ascorbic acid, L- Phenylalanine, Transition metal ions, SCOGS, pH-meter.

INTRODUCTION

An important bio-molecule,L-ascorbic acid (Vitamin C, H_2Asc), acts as pH regulator, an anti-oxidant and a two-electronreductant in vitro and in vivo[1]. It isan essentialnutrient in man due to absence of L-gulonolactine oxidase& found in all foods of plant origin[2],due to deficiency of ascorbic acid causes a disease known as scurvy. A weak acid(L-ascorbic acid) forms mono and di-anionic forms, C (3)–O ($HAsc^-$) &C (2)–O (Asc^{2-}),[3] respectively in the presence of water (Figer 1). Therefore, the role of ascorbic acid is not apparent. On the other hand, presence of two reductants and a number of ascorbic acid roles give systems of considerable complexity. Ascorbic acid, or simply ascorbate[4] (the anion of ascorbic acid), is an essential nutrient for humans and certain other animal species and having antioxidant properties. It is well known that redox chemistry of ascorbic acid plays an important role in human nutrition as well as in the synthesis of advanced nano-materials of noble metal. Thus, the studies on the kinetics and mechanism redox reactions of ascorbic acid in biological systems has become important to bio-, inorganic-, and surface-chemists. Our group is involved for the preparation of colloidal MnO_2[5] and silver nanoparticles[6, 7] in the absence and presence of different stabilizers using ascorbic acid.

L-Ascorbic acid has been proposed to bind a transition metal at two hydroxy groups at the 2- and 3-positions, but in addition to these it also uses the carbonyl C(1)=O group as well as chain OH groups for coordination[8,9]. It means that it utilizes practically all donor oxygen [C(1)–O to C(6)–O] atoms for coordination[8, 9]. In view of this, several studies have been focussed onthe interaction of l-ascorbic acid with transition and inner transition metals[10].

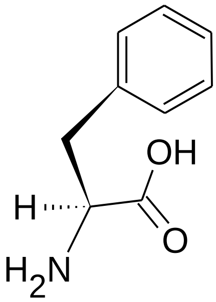


Vitamin C

Figer 1

(L-Ascorbic Acid)

The phenylalanine is aromatic, essential, glycogenic and ketogenic amino acid. In metabolism, it is converted into tyrosine, which forms the hormones like adrenaline, nor adrenaline, melanin pigments. The abnormalities observed in the phenylalanine metabolism are phenylketonaria and alkaptonaria[11].



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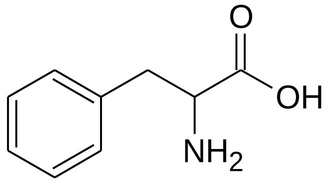

(2*R*)-2-amino-3-phenylpropanoic acid

Phenylalanine (Phe)

It is found in the breast milk of mammals. It is used in manufacture of food and drink products. It isa direct precursor to neuromodulator phenyl ethylamine commonly used dietary supplement. Hence, thestudy of complexes of L-Ascorbic acid and phenylalanine with Co (II), Ni (II) Cd (II) and Zn (II)transition metal ions were carried out in 40% v/v alcohol water media.

EXPERIMENTAL

Potentiometric reagents and solutions

Zn (II), Cd (II), Ni (II) and Co (II) nitrates were obtained from Aldrich Chemical Company and used without purification. The solvents used were of spectroscopic grade. The potentiometric measurements in this study were carriedout in 1: 1 (v: v) aqueous-ethanol media. Ethanol was purchasedfrom Merck and used without further purification.[12]

Doubly distilled and CO_2 free water was used exclusively.Stock solutions of strong acid and strong base were preparedusing analytical reagent grade 0.10M HCl solution(Merck) and 0.10 M NaOH solution (Merck), respectively.The 0.001 M NaOH solution was standardized[11] by titrationagainst the standard oxalic acid dihydrate (Aldrich). During eachtitration the ionic strength was maintained at 0.10 M $NaNO_3$. For eachmixture, the volumewasmade up to 50 $cm^3$with double distilledwater before the titration. These titrations were repeated for the temperaturesof 308 and 318 K. All titrations have been carried out betweenpH 2.0–12.0 and under nitrogen atmosphere.

(i) 5cm^3 $NaNO_3$ (1.0 M) + 5cm^3 HNO_3 (0.02 M) + 40cm^3 H_2O
(ii) 5cm3 NaNO3 (1.0 M) + 5cm3 HNO3 (0.02 M) + 5cm^3 L1 (0.01M) + 35cm^3 H_2O
(iii) 5cm^3 NaNO3 (1.0 M) + 5cm3 HNO_3 (0.02 M) + 5cm^3 L2 (0.01M) + 35$cm^3$$H_2O$
(iv) 5cm^3 NaNO3 (1.0 M) + 5cm^3 HNO_3 (0.02 M) + 5cm3 M(II) (0.01M) + 35cm^3 H_2O
(v) 5cm^3 $NaNO_3$ (1.0 M) + 5cm^3 HNO_3 (0.02 M) +5cm^3 M(II) (0.01M) + 5cm^3L1 (0.01M) +30$cm^3$$H_2O$
(vi) 5cm^3 $NaNO_3$ (1.0 M) + 5cm^3 HNO_3 (0.02 M) + 5cm^3 M(II) (0.01M) + 5cm^3L2(0.01M)+30$cm^3$$H_2O$
(vii) 5cm^3 $NaNO_3$ (1.0 M) + 5cm^3 HNO_3 (0.02 M) + 5cm^3 M (II) (0.01M) + 5cm^3 L1 (0.01M) +5cm^3L2(0.01M) +25cm^3 H_2O.

Where M(II) is Zn(II), Cd(II), Ni(II) & Co(II) transition metal ions and L_1 is L-Ascorbic acid and L_2 L-Phenylalanine. The species distribution curves were obtained by plotting % concentration of the species obtained through Stability Constant of Generalize Species (SCOGS) computer program against pH.

RESULTS AND DISCUSSIONS

The Protonation constants of the ligand were calculated from the potentiometric pH titration data of solutions according to Irving and Rossetti's method[11] and the acid dissociation Constants for the sodium salt of L-ascorbic acid($H_2L_1^-$) are related to the dissociation equilibrium as follows:

$$H_2L_1^- \Leftrightarrow HL_1^{2-} + H^+$$
$$HL_1^{2-} \Leftrightarrow L_1^{3-}$$

Constants for the sodium salt of L-ascorbic acid ($H_2L_1^-$) are related to the dissociation equilibrium as follows:

$$H_2L_2^- \Leftrightarrow HL_2^{2-} + H^+$$
$$HL_2^{2-} \Leftrightarrow L_2^{3-}$$

Stability constants of simple complexes (ML_1, ML_2 and ML_1L_2). SCOGS may also be used to calculate constants for "mixed" complexes containing two different metals and two different ligands. The overall stability constants (ßpqrst) of investigated complexes are expressed by the general equation in aqueous solutions as follows:

$pM_1 + qM_2 + rL_1 + sL_2 + t\,(OH) \rightleftharpoons (M_1)p\,(M_2)q\,(L_1)r\,(L_2)s\,(OH)t$

$$ßpqrst = \frac{[M1]\ p\ [M_2]\ q\ [L_1]r\ [L_2]s\ [OH]\ t}{[M_1]^p\ [M_2]^q\ [L_1]^r\ [L_2]^s\ [OH]^t}$$

In above equation the stoichiometric numbers p, q, r and s are either the zero or positive integer and t is a negative integer for a protonated species, positive integer for a hydroxo or deprotonated species and zero for a neutral species.

Table 1: Proton ligand formation constant, Stability constant and other related constants of the binary and ternary species of Cobalt metal ions with L-Ascorbic acid and L-Phenylalanine at different Ph

pH	H_2L_1	HL_1	HL_2	ML_1	ML_2	ML_1L_2
2.75	18.6	69.2	90.8	8.98	6.04	3.17
2.75	20.3	77.1	98.2	2.4	1.57	3.18
2.77	20.1	78.4	99	1.02	0.65	-
2.78	19.9	79.1	99.3	1.1	0.67	-
2.91	15.5	83.3	99.4	0.94	0.57	-
2.93	15	84.1	99.5	1.42	0.81	-
3.16	9.34	89.2	90.4	1.07	5.83	-
4.21	0.79	84.8	88.1	12.2	6.71	3.73
4.36	0.54	82.1	84.9	14	7.78	7.35
4.52	0.35	78.3	34.7	17.6	1.11	54.1
5.72	-	22.1	27.6	15.7	10	62.2
5.97	-	20.5	25.7	15.1	9.69	64.4
6.07	-	5.18	6.67	6.03	3.96	88.7
7.23	-	3.77	4.69	4.84	3.09	91.3
7.52	-	1.35	1.29	2.86	1.39	95.5
8.36	-	-	-	-	-	-

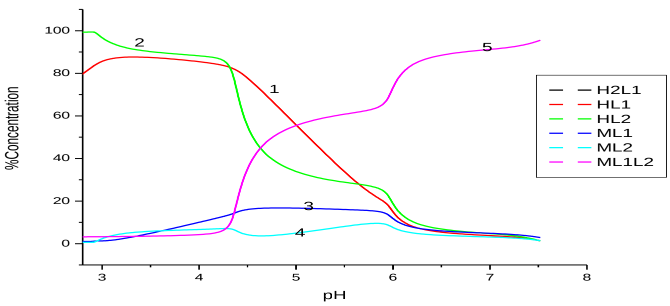

Fig. 1:Species distribution curve of 1:1:1 ternary Co+(II)L1L2-system (1)H3L1 (2)HL1 (3)HL2(4)Cu(II)L1 (5)Co(II)L2 (6)Co(II)L1L2

Table 2: Proton ligand formation constant, Stability constant and other related constants of the binary and ternary species of nickel metal ions with L-Ascorbic acid and L-Phenylalanine at different pH

pH	H_2L_1	HL_1	HL_2	ML_1	ML_2	ML_1L_2
2.76	1.27	4.82	75.2	75.20	6.02	8.00
2.79	1.41	5.73	87.7	87.40	6.86	5.44
2.82	1.37	5. 97	89.7	89.30	6.89	3.38
2.86	1.28	6.12	90.6	90.30	6.83	2.61
2.91	1.16	6.25	91.00	90.60	6.75	2.26
2.95	1.08	6.34	91.30	90.70	6.68	2.02
2.99	0.99	6.42	91.50	90.80	6.63	1.87
3.06	0.85	6.49	91.60	90.80	6.57	1.89
3.12	0.75	6.54	91.20	90.60	6.52	1.91
3.25	0.55	6.55	90.00	90.40	6.48	2.29
3.35	0.44	6.49	89.90	89.60	6.44	2.58
3.54	0.28	6.41	87.10	88.70	6.38	3.58
3.71	0.18	6.27	79.60	86.90	6.31	4.75
3.91	0.11	5.72	11.90	79.80	6.19	6.68
4.36	-	0.86	10.80	12.30	5.68	14.7
6.80	-	0.78	10.40	11.30	0.86	86
6.91	-	0.76	6.20	10.90	0.79	87
6.97	-	0.46	3.34	7.19	0.76	88.3
7.42	-	0.28	1.88	4.90	0.48	92.3
7.89	-	0.18	1.64	3.94	0.29	94.8

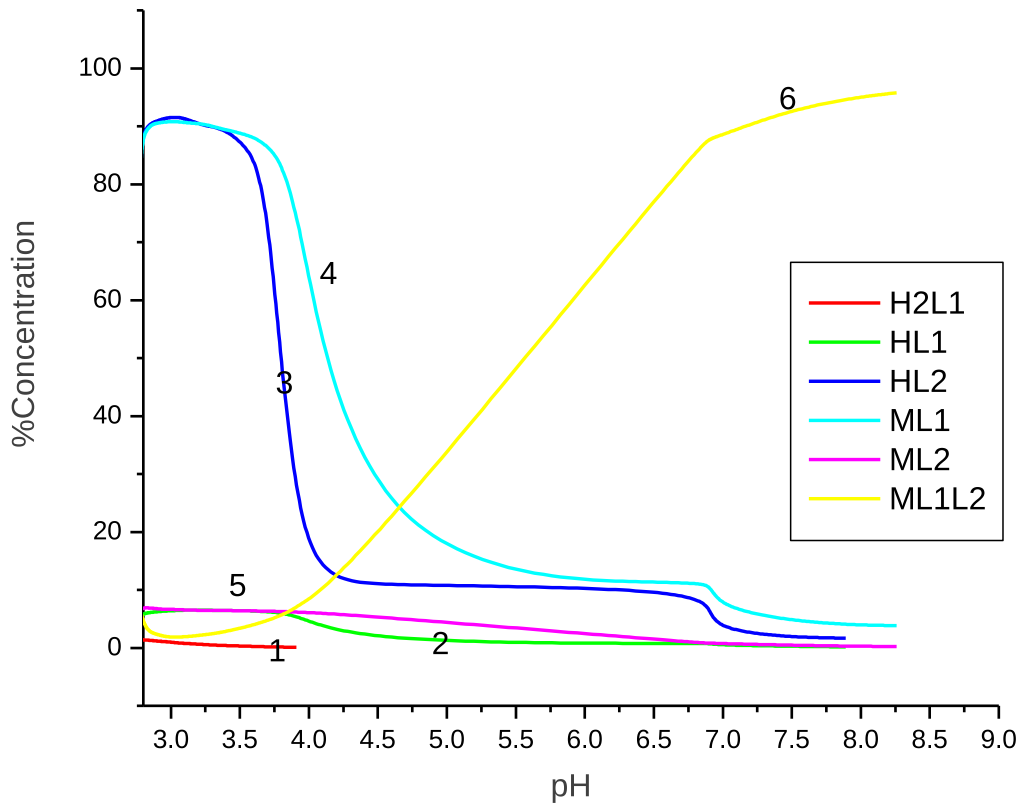

Fig. 2: Species distribution curve of 1:1:1 ternary Ni(II)L1L2-system (1)H3L1 (2)HL1 (3)HL2(4)Ni(II)L1 (5)Ni(II)L2 (6)Ni(II)L1L2

Table 3: Proton ligand formation constant, Stability constant and other related constants of the binary and ternary species of zinc metal ions with L-Ascorbic acid and L-Phenylalanine at different pH

pH	H_2L_1	HL_1	HL_2	ML_1	ML_2	ML_1L_2
2.16	50.9	48.6	50.3	-	49.3	-
2.26	45.4	54.5	73.5	-	26.5	-
2.36	39.8	60.2	78.7	-	21.3	-
2.56	24.4	70.5	77.4	-	22.6	-
3.73	2.68	95	37.8	0.41	60.3	4.25
4.12	1.08	94.1	28.5	0.62	67.3	8.08
4.47	0.46	90	21.4	0.82	70.5	21
5.04	0.1	77.7	12.1	1.19	66.9	43.1
5.67	-	55.6	5.87	1.33	51	55.6
6.04	-	43.1	3.86	1.25	40.6	72
6.23	-	38	3.18	1.19	36	78
6.36	-	35	2.82	1.14	33.4	88.5
7.55	-	10.6	0.59	0.53	10.7	90.8
7.8	-	8.3	0.42	0.46	8.58	91.6
7.96	-	7.12	0.34	0.43	7.53	92
8.97	-	1.86	-	0.31	3.17	---

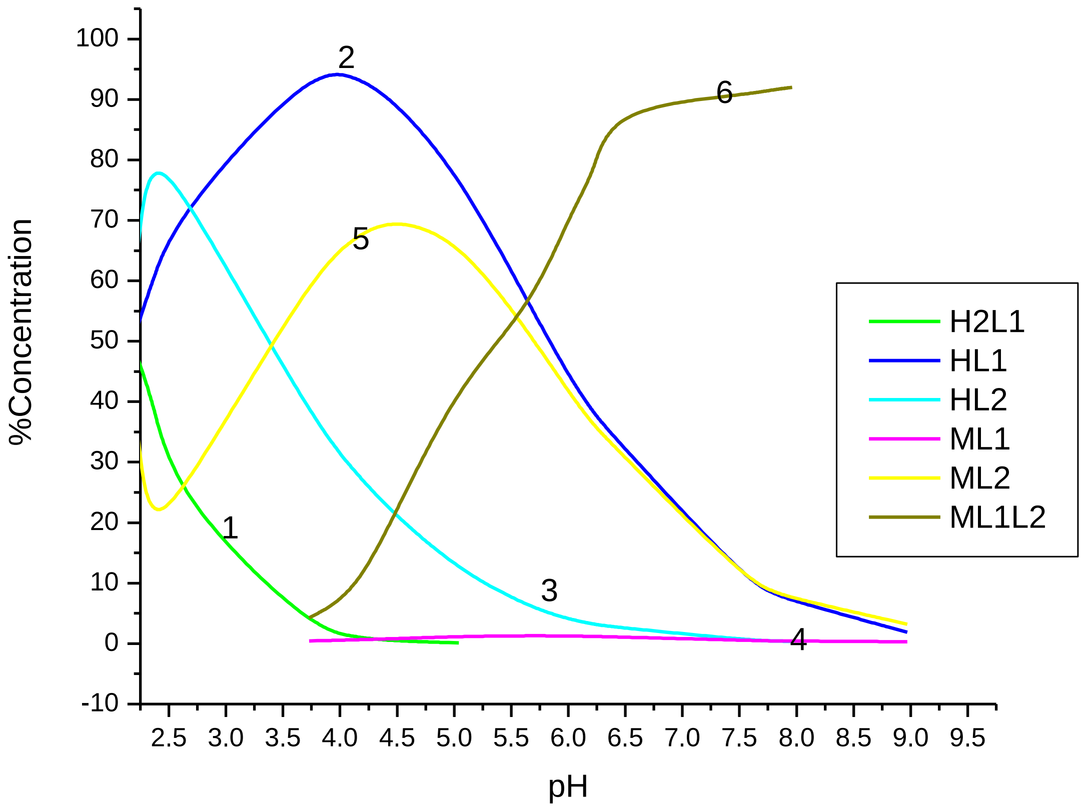

Fig. 3: Species distribution curve of 1:1:1 ternary Zn(II)L1L2-system (1)H3L1 (2)HL1 (3)HL2(4)Zn(II)L1 (5)Zn(II)L2 (6)Zn(II)L1L2

Table 4: Proton ligand formation constant, Stability constant and other related constants of the binary and ternary species of Cadmium metal ions with L-Ascorbic acid and L-Phenylalanine at different pH

pH	H_2L_1	HL_1	HL_2	ML_1	ML_2	ML_1L_2
2.9	14.2	74.6	29.5	0.71	60	0.1
2.98	45.8	2.17	61.2	0.24	37.8	0.09
3.01	12.7	86	67.7	0.19	31.6	0.64
3.06	33.7	0.76	67.8	0.19	31.5	0.65
3.12	10.2	88.9	66.6	0.2	31.7	0.67
3.21	8.46	90.7	64.1	0.21	32.6	0.74
3.29	7.14	92	55.6	0.24	35	0.93
3.38	3.55	93.2	56.8	0.32	41.5	1.69
3.5	4.51	94.3	46.5	0.47	49.9	3.64
3.73	2.69	95.3	37.4	0.63	55.7	6.58
4.03	1.34	94.6	26.5	0.88	59.1	14.4
4.31	0.68	91.8	2.47	0.86	20.6	76.8
4.68	0.26	84.5	0.8	0.51	9.31	89.8
6.48	-	22.2	0.31	0.43	7.07	92.3
7.29	-	9.55	0.21	0.35	4.99	94.5
7.58	-	7.09	0.16	0.31	3.97	95.4
7.94	-	4.79	-	0.3	3.49	96.1
8.19	-	3.63	-	0.28	2.54	97.1
8.35	-	3.04	-	-	2.58	97.2
8.74	-	1.82				
8.75	-	1.83				

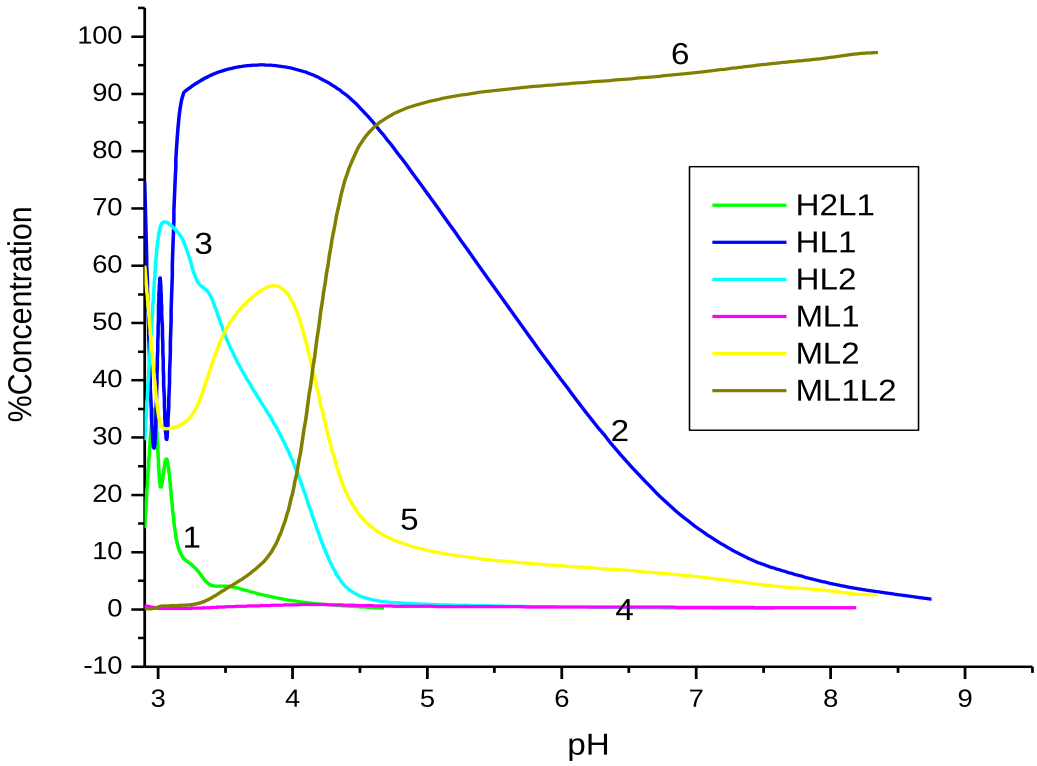

Fig. 4: Species distribution curve of 1:1:1 ternary Cd(II)L1L2-system (1)H2L1 (2)HL1 (3)HL2(4)Cd(II)L1 (5)Cd(II)L2 (6)Cd(II)L1L2

CONCLUSION

On the basis of mention above readings we have to say that, the ternary complex compound of copper is the most stable & their stability constant is in the higher order.

$$L_1\text{-}Cd\text{-}L_2 < L_1\text{-}Cu\text{-}L_2 > L_1\text{-}Ni\text{-}L_2 > L_1\text{-}Co\text{-}L_2$$

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