



Table 1. Structural data.

Metal	R	Complex	NE Coord.	Fig.	M-OR	M-OG	M-OW	M-N	k1	k2	N-C-N	N-M-N			
Al(III)	0.50	[H <sub>4</sub> EDTA]	1								67.1				
		K <sub>4</sub> (EDTA)·H <sub>2</sub> O	2	6	OCT	192	201	203		0.09	0.11				
		NH <sub>4</sub> K <sub>4</sub> (EDTA)·2H <sub>2</sub> O(2)	3												
		Rh <sub>4</sub> (EDTA)·2H <sub>2</sub> O(2)	4												
Pd(II)	0.50	[PdH <sub>4</sub> EDTA]Cl <sub>2</sub> ·SH <sub>2</sub> O	5	2+2+2Cl							0.0	53.6			
Ga(III)	0.62	[Ga(H <sub>2</sub> O)(HEDTA)]	6	6+H <sub>2</sub> O	PB	216	181	195	2.06	-0.35	0.25	62.6	80.9		
Co(III)	0.63	[Co(en)(H <sub>2</sub> EDTA)]Cl·3H <sub>2</sub> O	7	4+2EN	OCT	188			2.02			58.2	89.2		
		[Co(en)(H <sub>2</sub> EDTA)]ClO <sub>4</sub> ·3H <sub>2</sub> O	8												
Fe(III)	0.64	NH <sub>4</sub> [Co(EDTA)·2H <sub>2</sub> O	9	6	OCT	192	188	192		-0.04	0.04	52.6	89.9		
		[Co(HEDTA)(H <sub>2</sub> O)·3H <sub>2</sub> O	10	5+H <sub>2</sub> O	OCT	188	191	193	1.98	0.03	0.07		89.6		
		LiFe(EDTA)·3H <sub>2</sub> O	11	6	OCT	192	199		2.19	0.07	0.20				
		LiFe(H <sub>2</sub> O)(EDTA)·2H <sub>2</sub> O	12	6+H <sub>2</sub> O	OPB	201	211	210	2.32	0.10	0.31	57.2	73.4		
		[Fe(H <sub>2</sub> O)(HEDTA)]	13	6+H <sub>2</sub> O	PB	193	201	207	2.22	0.08	0.19	61.0	82.9		
		Rh[Fe(H <sub>2</sub> O)(EDTA)]H <sub>2</sub> O	14	6+H <sub>2</sub> O	PB	199	208	184	2.32	0.09	0.32	54.4	74.9		
		Na[Fe(H <sub>2</sub> O)(EDTA)]·2H <sub>2</sub> O	15	6+H <sub>2</sub> O	PB	198	210	213	2.32	0.12	0.34	52.2	73.6		
		Ag[Fe(H <sub>2</sub> O)(EDTA)]·3H <sub>2</sub> O	16	6+H <sub>2</sub> O	PB	198	209	211	2.34	0.12	0.36	53.4	73.1		
		K[Fe(H <sub>2</sub> O)(EDTA)]H <sub>2</sub> O	17	6+H <sub>2</sub> O	PB	198	212	211	2.33	0.14	0.35	56.7	74.1		
		Tl[Fe(H <sub>2</sub> O)(EDTA)]H <sub>2</sub> O	18	6+H <sub>2</sub> O	PB	196	211	211	2.32	0.15	0.36	56.3	73.8		
Mg(II)	0.65	Ba[Fe(H <sub>2</sub> O)(EDTA)]·4H <sub>2</sub> O	19	6+H <sub>2</sub> O	PB	196	208	208	2.27	0.11	0.31	49.9	73.7		
		C <sub>2</sub> H <sub>10</sub> N <sub>2</sub> [Fe(H <sub>2</sub> O)(EDTA)]	20	6+H <sub>2</sub> O	PB	199	209	213	2.33	0.10	0.34	55.1	74.1		
		(N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> [Fe(H <sub>2</sub> O)(EDTA)]·2H <sub>2</sub> O	21	6+H <sub>2</sub> O	PB	195	209	214	2.33	0.14	0.37	58.2	74.7		
		[Mg(H <sub>2</sub> O) <sub>6</sub> ][Mg(H <sub>2</sub> O)(EDTA)]·2H <sub>2</sub> O	22	6+H <sub>2</sub> O	PB	233	203	206	2.40	-0.30	0.37	57.3	74.1		
		Na <sub>2</sub> [Mg(H <sub>2</sub> O)(EDTA)]·SH <sub>2</sub> O	23	6+H <sub>2</sub> O	MTP	227	208	206	2.38	-0.19	0.30	58.0	75.3		
		Na <sub>2</sub> [Mg(H <sub>2</sub> O)(EDTA)]·3H <sub>2</sub> O	24	6+H <sub>2</sub> O	MTP										
		[Mg(H <sub>2</sub> O) <sub>6</sub> ][H <sub>2</sub> EDTA]	25	0+6H <sub>2</sub> O	OCT			2.07				180.0			
		[Ox(H <sub>2</sub> O)(EDTA)]	26	6+H <sub>2</sub> O	MTP	206	205	205	2.16	-0.10	0.11				
		Cu(II)	0.69	Cu(CuEDTA)·4H <sub>2</sub> O	27	6	OCT	198	234		2.20	0.36	-0.14	58.7	83.6
				[Mn(H <sub>2</sub> O) <sub>6</sub> ][CuEDTA]·2H <sub>2</sub> O	28	6	OCT	225	199		2.04	-0.26	0.05	58.1	81.4
Cu(H <sub>2</sub> O)(H <sub>2</sub> EDTA)	29			5+H <sub>2</sub> O	OCT	247	195	198	2.18	-0.52	0.23	60.3	84.6		
[Cu(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ][CuEDTA]	30			6	OCT	234	196		2.01	-0.38	0.05		89.4		
[Cu(H <sub>2</sub> O) <sub>5</sub> ][CuEDTA]	31			6	OCT	238	196		2.01	-0.42	0.05		89.6		
K <sub>2</sub> [CuEDTA]·3H <sub>2</sub> O	32			6	OCT	230	197		2.07	-0.33	0.10		88.5		
Cr(III)	0.69			NH <sub>4</sub> [Cr(EDTA)·2H <sub>2</sub> O (2)	33	6	OCT								
				K[Cr(EDTA)·2H <sub>2</sub> O (2)	34	6	OCT								
		Rh[Cr(EDTA)·2H <sub>2</sub> O (2)	35	6	OCT										
[Cr(H <sub>2</sub> O)(HEDTA)] (6)	36	6+H <sub>2</sub> O	PB												
Mn(III)	0.70	K[Mn(EDTA)·2H <sub>2</sub> O (2)	37	6	OCT	191	201		2.20	0.10	0.19	56.2	81.6		
Sn(IV)	0.71	[Sn(H <sub>2</sub> O)(EDTA)]	38	6+H <sub>2</sub> O	PB	208	208	2.12	2.31	0.00	0.23				
Zn(II)	0.74	[Mg(H <sub>2</sub> O) <sub>6</sub> ][Zn(EDTA)]·2H <sub>2</sub> O	39	6	OCT	212	205		2.15	-0.07	0.10	54.6	85.00		
		[Mn(H <sub>2</sub> O) <sub>6</sub> ][Zn(EDTA)]·2H <sub>2</sub> O (44)	40												
		[Zn(H <sub>2</sub> O) <sub>6</sub> ][Zn(EDTA)]·2H <sub>2</sub> O (44)	41												
Rh(III)	0.75	Rh(H <sub>2</sub> O)(HEDTA)	42	5+H <sub>2</sub> O	OCT	203	202	210	2.04	0.01	0.02	56.6	87.4		
Co(II)	0.78	Cu[Co(H <sub>2</sub> O)(EDTA)]·4H <sub>2</sub> O	43	6+H <sub>2</sub> O	MTP	210	247	206	2.21	0.37	-0.26	54.9	79.3		
		[Co(H <sub>2</sub> O)(H <sub>2</sub> EDTA)]·2H <sub>2</sub> O	44	6+H <sub>2</sub> O	MTP	237	209	220	2.34	0.28	0.15	57.2	79.1		
		[Mn(H <sub>2</sub> O) <sub>6</sub> ][Co(EDTA)]·2H <sub>2</sub> O	45	6	OCT	209	207		2.15	-0.02	0.08	56.4	84.1		
		[Co(H <sub>2</sub> O) <sub>5</sub> ][Co(EDTA)]·2H <sub>2</sub> O (44)	46	6	OCT	211	206		2.16	-0.05	0.10	58.7	84.3		
		[Mg(H <sub>2</sub> O) <sub>6</sub> ][Co(EDTA)]·2H <sub>2</sub> O (44)	47	6	OCT										

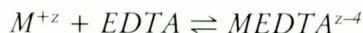
k<sub>1</sub> = M-OR - M-N;      k<sub>2</sub> = M-OR - M-N.

Metal	R	Complex	NE Coord.	Fig.	M-OR	M-OG	M-OW	M-N	k1	k2	NCCN	NMN		
Ni(II)	078	$Li_2[Ni(H_2O)(HEDTA)] \cdot 2H_2O$	48	5+H2O	OCT	2.12	2.02	2.08	2.10	0.10	0.08	58.1	86.3	
		$[Ni(H_2O)_4(NiEDTA)] \cdot 2H_2O$ (44)	49	6	OCT	2.05	2.08		2.08	-0.03	0.00	58.3	87.3	
		$[Cu(m)(H_2O)(NiEDTA)] \cdot 3H_2O$	50	6	OCT	2.04	2.08		2.06	0.04	-0.02	59.6	87.6	
		$[Ni(H_2O)(H_2EDTA)]$	51	5+H2O	OCT	2.16	2.03	2.08	2.10	0.12	0.07	59.9	86.5	
		$[Mg(H_2O)_4(NiEDTA)] \cdot 2H_2O$ (44)	52											
		$[Cu(m)(H_2O)(NiEDTA)] \cdot 2H_2O$	53	6	OCT	2.04	2.06		2.08	-0.02	0.02		88.0	
		$[Ca(H_2O)_2(NiEDTA)] \cdot H_2O$	54	6	OCT	2.05	2.06		2.07	-0.01	0.01		87.6	
		$[Cu(H_2O)_4(NiEDTA)]$	55	6	OCT	2.04	2.08		2.08	-0.04	0.00		86.6	
		$[Ni(NH_3)_6(NiEDTA)]$	56	6	OCT	2.05	2.08		2.07	-0.03	-0.01			86.5
		Mn(II)	080	$Li_2[Mn(H_2O)(EDTA)] \cdot 4H_2O$	57	6+H2O	MTP	2.28	2.15	2.23	2.45	0.13	0.30	56.3
$[Mn(H_2O)_4(Mn(H_2O)(HEDTA))] \cdot 2H_2O$	58			6+H2O	MTP	2.25	2.34	2.23	2.38	0.01	0.14	54.8	75.2	
$[Mg(H_2O)_6][Mn(H_2O)(EDTA)] \cdot 2H_2O$	59			6+H2O	PB	2.37	2.14	2.19	2.42	0.23	0.28	60.5	74.4	
$[Mn(H_2O)_4][Mn(H_2O)(EDTA)] \cdot 4H_2O$	60			6+H2O	MTP	2.34	2.16	2.22	2.44	0.08	0.28	45.5	75.2	
$(NH_4)_2[Mn(H_2O)(EDTA)] \cdot 3H_2O$	61			6+H2O	PB	2.26	2.21	2.34	2.36	0.05	0.15	53.6	75.2	
$Na_2[Mn(H_2O)(EDTA)] \cdot 5H_2O$	62			6+H2O	MTP	2.36	2.19	2.15	2.40	0.17	0.21	61.0	76.6	
$Rb_2[Mn(H_2O)(EDTA)] \cdot 3H_2O$	63			6+H2O	PB	2.25	2.19	2.33	2.37	0.06	0.18	54.7	74.1	
$[Zr(H_2O)_2(EDTA)] \cdot 2H_2O$	64			6+2H2O		2.12	2.14	2.27	2.43	-0.2	0.29			
Zr(IV)	080	$[Zr(H_2O)_2(EDTA)] \cdot 2H_2O$												
Sb(III)	090	$[Sb(HEDTA)] \cdot 2H_2O$	65	6+	PB	2.50	2.18		2.35	0.32	0.17			
		$[Tl(H_2O)(EDTA)]$	66	6+H2O	PB	1.92	1.98	2.08	2.30	-0.06	0.32		73.9	
Yb(III)	094	$Cs_2[Yb(H_2O)_2(EDTA)] \cdot 2H_2O$	67	6+2H2O		2.27	2.25	2.37	2.53	-0.02	0.28		69.7	
Na(I)	095	$Na_2[Na(EDTA)]$	68	6+1		2.49	2.44		2.53	0.05	0.09	57.5	70.5	
		$Na_2^+(H_2O)(H_2EDTA)$	69									180.0		
Er(III)	096	$NH_4[Er(H_2O)_2(EDTA)] \cdot 2H_2O$	70	6+2H2O		2.31	2.23	2.32	2.56				71.9	
Cd(II)	097	$[Mg(H_2O)_6][Cd(H_2O)(EDTA)] \cdot 3H_2O$	71	6+H2O	PB	2.43	2.35	2.25	2.40	0.08	0.05	65.3	76.2	
		$[Mn(H_2O)_4][Cd(EDTA)] \cdot 2H_2O$	72	6+1	PB	2.34	2.33		2.42	0.01	0.09	57.5	75.4	
Hf(III)	097	$Na_2[Hf(EDTA)] \cdot 5H_2O$	73	6+3H2O		2.38	2.35	2.45	2.65	0.03	0.30	62.6	68.7	
Ca(II)	099	$Ca_2[Ca(H_2O)_2(EDTA)] \cdot 7H_2O$	74	6+2H2O		2.53	2.29	2.46	2.66	0.34	0.37	57.8	67.0	
		$Ca_2(H_2EDTA) \cdot 3SH_2O$	75	1+1+1+1+2H2O								67.1		
		$Ca_2(H_2EDTA) \cdot 2H_2O$	76	1+1+1+1+1+H2O								66.4		
Dy(III)	099	$Na_2[Dy(H_2O)_2(EDTA)] \cdot 5H_2O$	77	6+3H2O		2.39	2.46	2.63					68.3	
Tb(III)	100	$Na_2[Tb(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	78	6+3H2O										
Gd(III)	102	$Na_2[Gd(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	79	6+3H2O		2.39	2.47	2.65					67.8	
Sm(III)	104	$Na_2[Sm(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	80	6+3H2O		2.43	2.50	2.67					67.5	
Na(III)	108	$K_2[Na(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	81	6+3H2O		2.43	2.54	2.71					66.9	
Pr(III)	109	$Na_2[Pr(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	82	6+3H2O		2.46	2.53	2.71					67.0	
Sr(II)	112	$Sr_2(SrEDTA) \cdot 2H_2O$	83	6+	PB	2.68	2.37		2.44	0.31	0.07	59.2	74.3	
		$Sr(H_2EDTA)$	84	6+	MTP	2.90	2.27		2.42	0.63	0.15	58.3	73.8	
La(III)	115	$K_2[La(H_2O)_2(EDTA)] \cdot 5H_2O$ (80)	85	6+3H2O										
		$K_2(H_2EDTA)$	86											
Ba(II)	135	$[Ba(H_2O)][Ba(H_2O)(EDTA)] \cdot 0.5SH_2O$	87	6+3+H2O	2.76	2.77	3.08	2.99	-0.01	0.22	41.0	58.1		
Rb(I)	148	$Rb_2(H_2EDTA) \cdot 2H_2O$	88	0									161.8	
Cs(I)	181	$(H_2EDTA) \cdot Cl \cdot H_2O$	89										178.7	
K(I)	216	$(H_2EDTA) \cdot 2H_2O$	90										180.0	
pip		$(C_4H_{10}N_2)(H_2EDTA)$	91										77.3	

## THE BIMETALLIC COMPLEXES

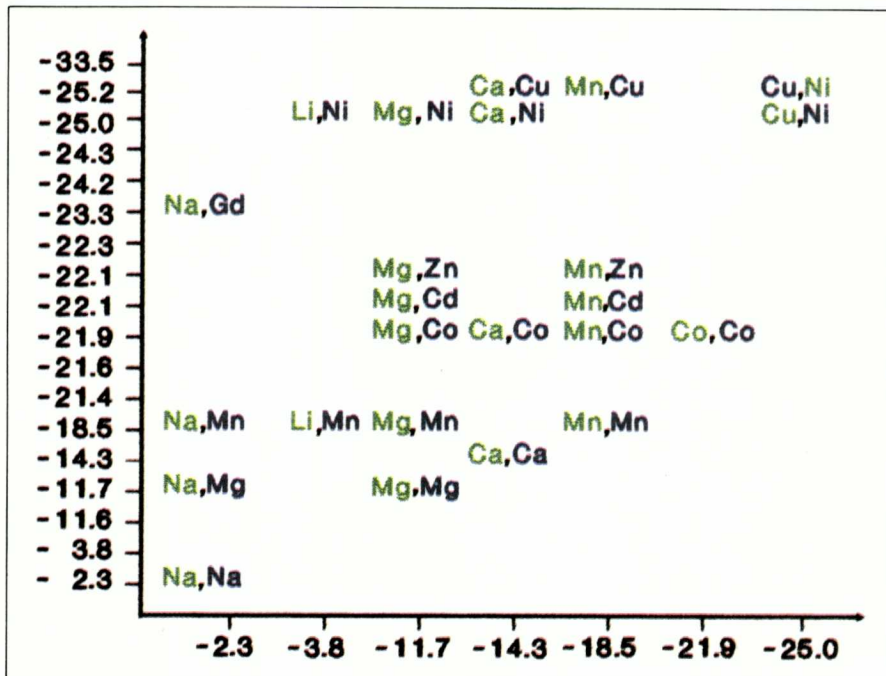
Usually a metal (inner metal) is coordinated to an EDTA ligand by means of six bonds: two bonds to nitrogen atoms of ethylenediamine moiety, and four bonds— to oxygen of carboxylate groups of the same ligand. The first question that we wish to solve is about the metal complexes. When we attempt to introduce two different metals to an EDTA ligand, does a preferential order to occupy the inner position exist? (figure 2).

We have compared the solved structures with the Gibbs energy for the reaction (Table 2):



It is observed that the metals which coordinate with EDTA are those with less Gibbs energies in this reaction, with the exception of the (Cu, Ni) complex, but the Gibbs energies for these two metals are very similar (-25.2 and -25.0 Kcal/mol, respectively) (Table 2).

Table 2. G for  $M^{+z} + EDTA^{4-} \leftrightarrow MEDTA^{z-4} + H_2O$



– left outer metal      – right inner metal

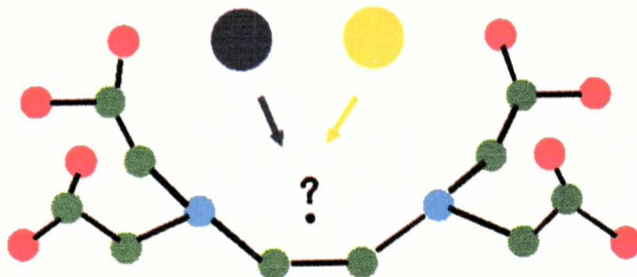


Fig. 2. Which is the atom that has the preferential order?

A similar result is obtained if we compare the pK of hydrolysis of the inner metal. Ions with the lower pK occupy the inner position, so ions with more facility to loose the hydratation molecules, more easily occupy the inner position (figure 3).

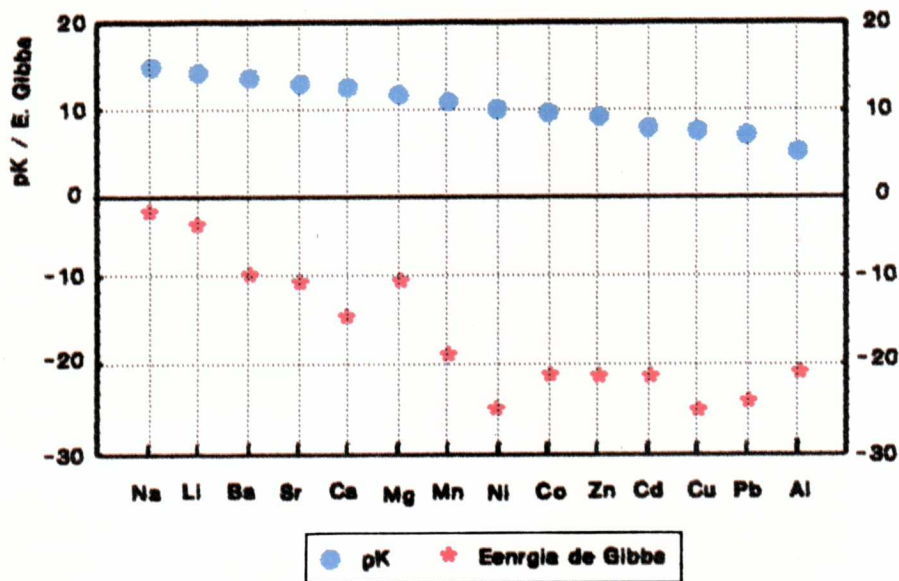


Fig. 3. Hydrolysis pK and Gibbs energy for obtaining of MEDTA.

#### THE PROTONATED COMPLEXES

In acid medium, the EDTA metal complexes are obtained with protons linked to EDTA ligand. The  $H_4EDTA$  structure shows four protons,

where two are linked to amine groups and the remaining two are linked to two different carboxylate groups. The protonated complexes can be obtained by the substitution of one, two, or three protons of amine or carboxylate group. (figure 4).

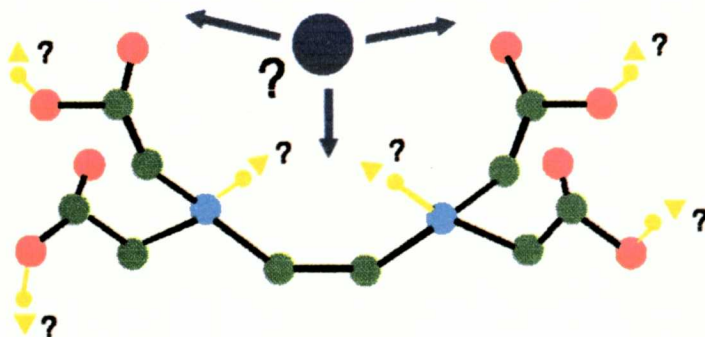


Fig. 4. What groups remain protonated?

The study of the solved crystal structures shows that the hard acid ions are coordinated to four or five oxygen atoms of different protonated EDTA ligands, while the protons of amine groups are not substituted.

Softer acid ions are coordinated to two nitrogen atoms of ethylenediamine moiety and three or four oxygen atoms of carboxylate groups of the same EDTA ligand, while the proton of EDTA is linked to a glycine oxygen atom.

#### THE EDTA CONFORMATION

The  $H_4EDTA$  compound shows a synclinal or cis conformation for the ethylenediamine moiety. This conformation is observed in 92.4% of crystal structures of EDTA metal complexes. A semi-open, or peryplanar, or trans conformation for the ethylenediamine moiety is observed in the protonated complexes of Rb Na,  $Mg(H_2O)_6$ , Cl and I, and the nonprotonated  $Cu_2EDTA \cdot 4(H_2O)$  (figure 5).

#### THE ION COORDINATION NUMBER

A single correlation between the coordination number and, for example, the ionic radii does not exist. Usually, the coordination number increases with an increase of the ionic radii; but, for similar ionic radii, the

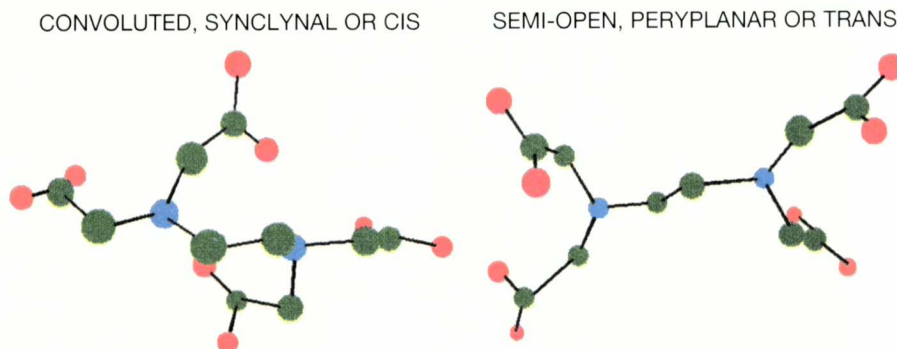


Fig. 5. Different conformations of EDTA ligand.

ion with a higher ionic charge (higher solvation energy or hydrolysis pK) shows also higher coordination number (figure 6).

The influence of ionic radii can be observed from the distortion of six-coordination polyhedra. Thus, an increase of ionic radii, causes an extension of Me-N length and a decrease of the N-Me-N angle. This decreasing results in an increase of N-Me-OR and makes easier the incorporation of a new atom in the opposite site to both nitrogen atoms.

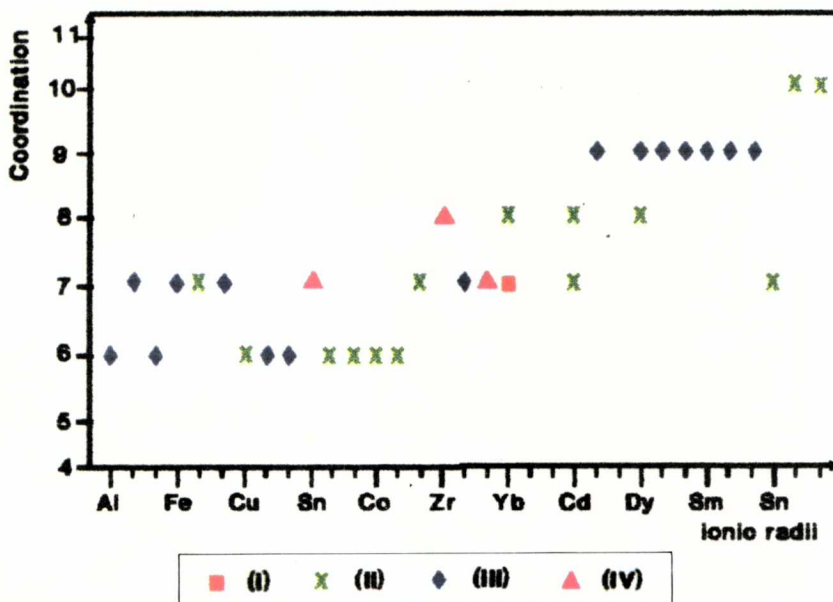


Fig. 6. Correlation between coordination number and ionic radii.

The results obtained from the study of coordination numbers suggest a mechanism for the coordination of metal ions to an EDTA ligand. In aqueous solution the metal ion will be solvated and the EDTA must show the typical convoluted or synclinal conformation as has been observed from spectroscopic analysis (figure 7). The loss of solvation molecules depends on the ionic radii, the acidity of the medium, and the acid character of the metal ion. The metal ion losing more easily the solvation molecules, will be linked to an EDTA ligand, occupying the inner position. It will lose all solvation water molecules or not, according to the solvation energy. In the second case the water molecule occupies the opposite site to the EDTA ligand and causes an increase in the coordination number. For hard acid ions the poor ability in losing the solvation molecules, makes each metal ion bond to different EDTA ligands, and yields a semi-open conformation in the EDTA ligand.

Cu(II) ion shows a large bond length due to the Jahn-Teller effect, this fact causes a behaviour more similar to that observed for hard acid ions.

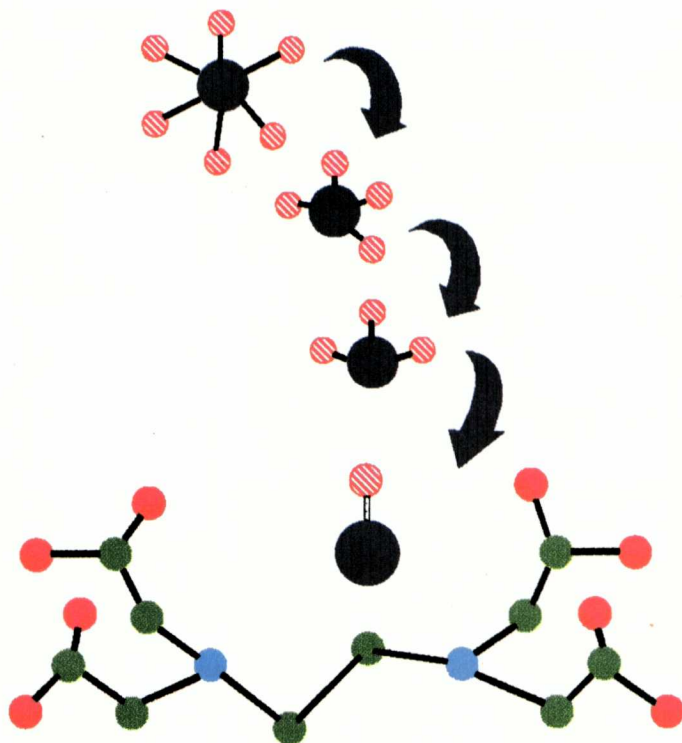


Fig. 7. Lost aqueous solvation of the metal.



## ABSTRACT

A crystallochemical study of metal complexes with the ethylenediaminetetraacetic acid ligand has been carried out. The structural data were obtained from the Cambridge Data Base, University of Barcelona and Lomonosov State University Moscow. The results obtained indicate that the solvation energy, the ionic radii and the acid character determine the coordination number of metal complexes and the conformation of ethylenediaminetetraacetic acid.

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