Supplement

Table 1

The frequency of amino acid residue appearance in the coordination sphere of the metal ions analysed. The analysis is accomplished on the set of non-redundant proteins.

	Ca	Ni	Mg	Fe	Mn	Cd	Zn	Cu	Co
Ala	82	2	18	0	2	1	3	1	0
Arg	26	1	19	0	1	1	2	1	0
Asn	321	2	80	4	15	6	10	1	0
Asp	1179	25	384	55	217	77	325	6	42
Cys	10	29	3	92	3	181	1532	82	18
Glu	483	17	192	113	97	85	236	7	38
Gln	69	2	26	0	4	3	7	5	2
Gly	242	4	26	1	2	2	4	2	0
His	45	96	163	694	143	87	1073	261	60
Ile	62	0	16	3	2	0	2	0	2
Leu	51	0	17	1	0	2	1	0	0
Lys	58	0	11	5	3	4	9	2	0
Met	20	1	8	60	2	2	7	33	1
Phe	42	0	5	0	2	2	1	0	0
Pro	23	0	5	0	0	2	0	0	0
Ser	114	4	90	1	9	6	8	1	4
Thr	121	0	112	0	7	2	9	1	2
Trp	14	0	4	0	0	0	6	0	0
Tyr	65	1	15	44	3	1	3	0	1
Val	61	1	21	0	0	1	0	0	0
H_2O	1489	90	3861	187	330	341	536	38	75

[†] Rel

Table 2

The absolute number of the observed coordination numbers for each of the analysed metal ion.

	Ca	Ni	Mg	Fe	Mn	Cd	Zn	Cu	Co
0	35	2	175	4	3	11	41	6	14
1	18	5	43	1	4	17	39	0	8
2	23	11	62	4	5	29	71	9	3
3	46	10	95	8	12	44	96	47	3
4	66	20	430	25	18	84	615	62	9

5	86	15	630	123	33	28	143	7	30
6	230	19	612	356	118	36	82	0	34
7	334	3	18	27	7	8	9	0	2
8	96	0	4	5	0	2	1	0	0
9	3	0	0	2	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0

Table 3

The total number of quartets (for CN 4 and higher) of amino acid residues (amino acid residues are labelled by normal single-letter codes) found in the coordination sphere of the metal ions with the CN four and higher. The analysis is accomplished on the non-redundant set of proteins; number of structures with a metal ion at the symmetry element is given in parenthesis.

	Ca	Ni	Mg	Fe	Mn	Cd	Zn	Cu	Co
C, C, C, C	0	4	0	9	0	40	195 (4)	0	0
H, H, H, H	0	0	0	5	1	1	0	7	0
D, D, D, D	24	0	2	0	0	0	0	0	0
4 (E/D)	59 (1)	0	3	2	1	2	0	0	3
C, C, C, H	0	0	0	0	0	0	145 (1)	0	0
C, C, H, H	0	0	0	0	0	0	64	0	5
C, H, H, H	0	0	0	0	0	0	3	0	0

Table 4

Atom types by which amino acid residues participate in metal ions coordination. The analysis is accomplished on the set of non-redundant proteins. Hydroxyl stands for the water oxygen and for the Thr, Ser and Tyr side-chain oxygen atoms.

CA	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O CARBOXYL	4	9	35	56	99	394	681	162	4	0	0
N IMIDAZOLE	1	1	0	4	3	3	2	1	0	0	0
S CYSTEINE	0	0	0	0	0	0	0	0	0	0	0
S METHIONINE	0	0	0	0	0	0	0	0	0	0	0
O HYDROXYL	12	21	55	96	136	386	595	225	9	0	0
O (ASN/GLN)	0	3	3	11	24	62	132	50	1	0	0
O BACKBONE	1	8	35	60	119	375	519	112	2	0	0

NI	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O CARBOXYL	1	1	8	11	5	12	4	0	0	0	0
N IMIDAZOLE	3	14	7	18	17	30	3	0	0	0	0
S CYSTEINE	0	0	4	3	10	6	4	0	0	0	0
S METHIONINE	0	0	0	0	0	0	0	0	0	0	0
O HYDROXYL	1	6	1	27	26	25	6	0	0	0	0
O (ASN/GLN)	0	0	0	0	1	3	0	0	0	0	0
O BACKBONE	0	0	0	0	1	1	0	0	0	0	0

MG	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O CARBOXYL	8	16	43	67	68	309	19	6	0	0	0
N IMIDAZOLE	3	3	9	3	121	13	0	0	0	0	0
S CYSTEINE	1	0	0	0	0	0	0	0	0	0	0
S METHIONINE	0	0	0	0	2	0	0	0	0	0	0
O HYDROXYL	13	45	133	284	1082	2377	52	7	0	0	0
O (ASN/GLN)	1	0	3	6	22	46	3	1	0	0	0
O BACKBONE	4	12	23	24	46	124	3	2	0	0	0

FE	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O CARBOXYL	0	3	8	12	45	80	20	0	0	0	0
N IMIDAZOLE	0	0	6	18	129	515	21	1	0	0	0
S CYSTEINE	1	2	4	44	14	24	3	0	0	0	0
S METHIONINE	0	0	0	0	1	59	0	0	0	0	0
O HYDROXYL	0	0	2	8	61	141	13	1	2	0	0
O (ASN/GLN)	0	0	1	0	0	0	1	0	0	0	0
O BACKBONE	0	0	0	3	3	18	0	0	0	0	0

MN	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O CARBOXYL	0	3	10	29	54	204	14	0	0	0	0
N IMIDAZOLE	0	2	5	13	36	80	6	0	0	0	0
S CYSTEINE	0	0	0	1	2	0	0	0	0	0	0
S METHIONINE	0	0	0	0	0	1	0	0	0	0	0
O HYDROXYL	3	5	10	15	39	263	9	0	0	0	0
O (ASN/GLN)	0	0	1	1	3	12	1	0	0	0	0
O BACKBONE	0	0	2	2	0	15	1	0	0	0	0

CD	1	2	3	4	5	6	7	8	9	10	11
O CARBOXYL	2	17	29	35	21	30	18	4	0	0	0
N IMIDAZOLE	7	5	13	16	13	23	3	0	0	0	0
S CYSTEINE	1	1	1	163	6	2	0	0	0	0	0
S METHIONINE	0	0	0	1	0	0	0	0	0	0	0
O HYDROXYL	5	17	58	75	61	98	13	9	0	0	0
O (ASN/GLN)	0	0	1	1	0	3	2	0	0	0	0
O BACKBONE	2	1	3	4	5	7	8	1	0	0	0

ZN	1	2	3	4	5	6	7	8	9	10	11
O CARBOXYL	14	35	72	158	166	92	12	0	0	0	0
N IMIDAZOLE	18	32	70	562	226	134	11	3	0	0	0
S CYSTEINE	0	7	25	1443	34	0	0	0	0	0	0
S METHIONINE	0	0	0	0	0	0	0	0	0	0	0
O HYDROXYL	5	42	70	167	120	126	12	1	0	0	0
O (ASN/GLN)	0	0	0	7	6	2	1	0	0	0	0
O BACKBONE	0	1	2	10	18	8	3	0	0	0	0

CU	1	2	3	4	5	6	7	8	9	10	11
O CARBOXYL	0	1	3	0	2	0	0	0	0	0	0
N IMIDAZOLE	0	9	90	142	19	0	0	0	0	0	0
S CYSTEINE	0	5	32	43	1	0	0	0	0	0	0
S METHIONINE	0	0	0	32	1	0	0	0	0	0	0
O HYDROXYL	0	0	8	12	4	0	0	0	0	0	0
O (ASN/GLN)	0	0	1	4	0	0	0	0	0	0	0
O BACKBONE	0	0	3	7	1	0	0	0	0	0	0

CO	1	2	3	4	5	6	7	8	9	10	11
O CARBOXYL	1	0	2	4	27	36	3	0	0	0	0
N IMIDAZOLE	0	2	2	16	20	13	1	0	0	0	0
S CYSTEINE	0	0	0	10	4	1	1	0	0	0	0
S METHIONINE	0	0	0	0	0	0	0	0	0	0	0
O HYDROXYL	7	4	2	2	21	34	1	0	0	0	0
O (ASN/GLN)	0	0	0	0	1	0	0	0	0	0	0
O BACKBONE	0	0	1	1	1	1	0	0	0	0	0

Table 5

Distribution of mean distances (metal - electron donor) as a function of coordination number. The analysis is accomplished on the set of structure from PDB (October 2007) with resolution ≤ 1.5 Å. Hydroxyl stands for the water oxygen and for the Thr and Ser side-chain oxygen atoms.

CN4

Mean distance

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	2.47	---	2.22	2.33	2.13	2.24	2.03	2.22	---
N IMIDAZOLE	---	2.03	2.27	2.13	2.21	2.24	2.07	2.05	2.02
S CYSTEINE	---	2.26	---	2.3	---	2.52	2.33	2.2	2.19
S METHIONINE	---	---	---	---	---	2.83	---	2.63	---
O HYDROXYL	2.43	2.35	2.21	2.31	2.08	2.35	2.16	2.2	2.11
O Tyr side-chain	---	---	2.79	---	---	---	2.06	---	---
O (ASN/GLN)	2.25	---	2.8	---	2.16	---	2.58	2.23	---
O BACKBONE	2.49	2.05	2.38	2.63	---	2.41	2.46	2.68	---

SD

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	0.17	---	0.28	0.28	---	0.16	0.20	---	---
N IMIDAZOLE	---	0.19	0	0.08	0.07	0.25	0.13	0.1	0.08
S CYSTEINE	---	0.13	---	0.04	---	0.05	0.06	0.05	0.02
S METHIONINE	---	---	---	---	---	0.02	---	0.19	---
O HYDROXYL	0.2	0.26	0.29	0.34	0.29	0.29	0.27	0.13	0.29
O Tyr side-chain	---	---	---	---	---	---	---	---	---
O (ASN/GLN)	0.11	---	---	---	---	---	0.29	0.13	---
O BACKBONE	0.23	---	0.27	---	---	0.24	0.32	0.19	---

Number of observations

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	15	0	22	3	1	5	54	1	0
N IMIDAZOLE	0	20	1	15	4	25	265	102	10
S CYSTEINE	0	41	0	128	0	35	269	45	4
S METHIONINE	0	0	0	0	0	8	0	29	0
O HYDROXYL	85	8	156	5	21	80	155	11	10
O Tyr side-chain	0	0	1	0	0	0	1	0	0
O (ASN/GLN)	3	0	1	0	1	0	2	4	0
O BACKBONE	31	1	19	1	0	9	20	11	0

CN5

Mean distance

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	2.39	2.82	2.15	2.11	2.10	2.17	2.19	2.15	2.20 (2.16)[a]
N IMIDAZOLE	---	2.28	1.79	2.16	2.17	2.23	2.07	2.07	2.09
S CYSTEINE	---	2.27	---	2.43	---	2.44	2.38	---	2.44
S METHIONINE	---	---	---	---	---	---	---	---	---

O HYDROXYL	2.43	1.86	2.16	2.17	2.17	2.39	2.2	2.08	2.17
O Tyr side-chain	---	---	---	1.99	---	---	---	---	---
O (ASN/GLN)	2.44	---	2.28	---	---	---	2.41	---	2.26
O BACKBONE	2.4	2.7	2.3	2.16	2.27	2.37	2.09	2.07	---

SD

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	0.14	---	0.21	0.20	0.09	0.12	0.20	0.01	0.20 (0.11)[a]
N IMIDAZOLE	---	0.1	0	0.12	0.06	0.09	0.12	0.11	0.13
S CYSTEINE	---	0.06	---	0.14	---	---	0.19	---	0.09
S METHIONINE	---	---	---	---	---	---	---	---	---
O HYDROXYL	0.18	0.39	0.21	0.22	0.27	0.21	0.29	0.42	0.21
O Tyr side-chain	---	---	---	0.06	---	---	---	---	---
O (ASN/GLN)	0.25	---	0.19	---	---	---	0.45	---	---
O BACKBONE	0.19	0.15	0.14	0.02	0.08	0.11	0.13	0.09	---

Number of observations

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	36	1	42	17	42	2	57	2	10
N IMIDAZOLE	0	6	1	122	82	18	292	33	16
S CYSTEINE	0	34	0	7	0	2	4	0	3
S METHIONINE	0	0	0	0	0	0	0	0	0
O HYDROXYL	200	11	292	16	50	92	145	23	12
O Tyr side-chain	0	0	0	9	0	0	0	0	0
O (ASN/GLN)	5	0	7	0	0	0	3	0	1
O BACKBONE	70	7	31	4	4	17	12	4	0

CN6

Mean distance

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	2.35	2.07	2.10	2.10	2.14	2.35	2.14	---	2.24
N IMIDAZOLE	2.33	2.08	2.17	2.06	2.22	2.29	2.08	2.04	2.06
S CYSTEINE	---	2.37	0	2.34	2.59	2.4	---	---	---
S METHIONINE	---	---	---	2.31	---	---	---	---	2.39
O HYDROXYL	2.4	2.24	2.12	2.18	2.21	2.37	2.15	2.15	2.09
O Tyr side-chain	---	---	---	2.01	---	---	---	---	2.02
O (ASN/GLN)	2.33	2.31	2.19	2.45	---	2.21	2.27	2.19	---
O BACKBONE	2.31	---	2.21	2.77	2.12	2.41	2.24	2.43	---

SD

	CA	NI	MG	FE	MN	CD	ZN	CU	CO

O CARBOXYL	0.11	0.15	0.15	0.08	0.13	0.10	0.16	---	0.13
N IMIDAZOLE	0.03	0.06	0.04	0.09	0.13	0.07	0.08	0.06	0.07
S CYSTEINE	---	0.14	---	0.08	---	---	---	---	---
S METHIONINE	---	---	---	0.07	---	---	---	---	0.01
O HYDROXYL	0.16	0.19	0.15	0.16	0.15	0.19	0.16	0.16	0.16
O Tyr side-chain	---	---	---	0.09	---	---	---	---	---
O (ASN/GLN)	0.1	0.02	0.13	0.41	---	0.02	0.05	---	---
O BACKBONE	0.12	---	0.17	0.33	0.06	0.15	0.19	---	---

Number of observations

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	405	11	207	44	67	22	43	0	6
N IMIDAZOLE	5	25	29	465	42	72	112	18	11
S CYSTEINE	0	6	0	19	1	1	0	0	0
S METHIONINE	0	0	0	47	0	0	0	0	2
O HYDROXYL	592	69	1775	152	135	211	90	18	32
O Tyr side-chain	0	0	0	0	0	0	0	0	1
O (ASN/GLN)	51	4	20	2	0	8	2	1	0
O BACKBONE	473	0	88	27	29	16	13	1	0

CN7

Mean distance

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	2.44	---	---	2.14	---	---	---	---	---
N IMIDAZOLE	2.53	2.04	---	2.1	2.32	2.35	2.1	2.07	2.09
S CYSTEINE	---	---	---	2.34	---	---	---	---	---
S METHIONINE	---	---	---	---	---	---	---	---	---
O HYDROXYL[b]	2.41	2.05	2.21	2.18	2.3	2.22	2.41	---	---
O (ASN/GLN)	2.36	---	2.09	---	2.17	---	---	---	---
O BACKBONE	2.37	---	2.37	2.81	2.09	2.58	2.19	2.05	---

SD

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	0.09	---	---	0.03	---	---	---	---	---
N IMIDAZOLE	0.02	---	---	0.07	0.19	0.07	0.09	0.01	---
S CYSTEINE	---	---	---	0.04	---	---	---	---	---
S METHIONINE	---	---	---	---	---	---	---	---	---
O HYDROXYL	0.14	0.1	0.28	0.25	0.12	0.24	0.17	---	---
O (ASN/GLN)	0.09	---	0.02	---	0.01	---	---	---	---
O BACKBONE	0.08	---	0.14	0.1	0.21	0.29	0.1	---	---

Number of observations

	CA	NI	MG	FE	MN	CD	ZN	CU	CO
O CARBOXYL	5	0	0	4	0	0	0	0	0
N IMIDAZOLE	2	1	0	37	7	3	9	2	1
S CYSTEINE	0	0	0	4	0	0	0	0	0
S METHIONINE	0	0	0	0	0	0	0	0	0
O HYDROXYL	637	3	39	10	6	8	8	0	0
O (ASN/GLN)	119	0	2	0	2	0	0	0	0
O BACKBONE	416	0	3	25	9	4	4	1	0

[a]*Here we replaced the Asp168 rotamer in 1R6X by one that brings the functional group closer to the metal ion.*
[b]*For CN 7, we did not find metal coordinated with the side-chain Tyr.*