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Review

α-Amino acids: Natural and artificial building blocks for discrete polymetallic clusters

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ABSTRACT

In this report we attempt to describe and review the employment of α-amino acid ligands for the construction of metallic complexes. We focus our interest on the synthesis of discrete polynuclear M_n ($n \geq 3$; M = *d*–, *f*– and 3*d*–4*f* metal ions) complexes containing natural occurring or artificial α-amino acid ligands, and we briefly discuss their magnetic properties, where this is feasible. Polymeric species, coordination polymers and chains are not included in this review, due to space limitations. Finally, metallic clusters with macrocyclic ligands, and poly-peptides ligands are not included in this survey.

Contents

1. Introduction

The field of coordination chemistry has witnessed a major growth in the recent years; this is mainly due to both the exciting phenomena displayed by metallic complexes and their sophisticated applications that are already available, or that will be developed in the near future. Scientific areas such as magnetism, photovoltaics, catalysis, sensors, imaging and gas storage are based on the use of metallic compounds, either oligonuclear, $\{M_n\}$ (n = 1–2), polynuclear species ($n \geq 3$) or polymeric ($n = \infty$). This is particularly true for 3*d*-homometallic, 3*d*–4*f* heterometallic,

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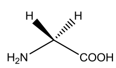
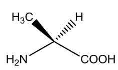
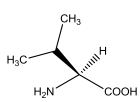
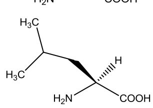
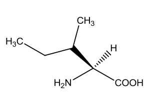
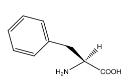
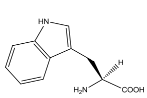
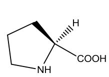
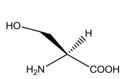
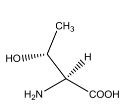
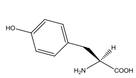
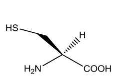
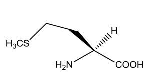
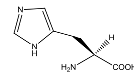
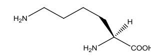
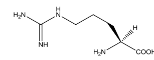
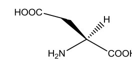
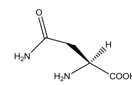
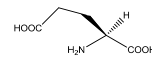
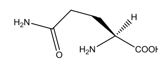
and 4*f*-complexes. For instance, in magnetism the field of *Molecular Magnetic Refrigeration* is emerging [1]; recent studies of isotropic high-spin molecules with an enhanced magnetocaloric effect (MCE; that is, the change of the magnetic entropy, ΔS_m, upon an applied-field change) suggest potential technological application at low temperatures, since MCE and the associated principle of adiabatic demagnetization can be efficiently exploited for cooling. In addition, molecular nanomagnets with extremely high energy barriers (>1000 K) for the re-orientation of the magnetization have been reported [2–4], and species now remain magnetized upon the removal of an external magnetic field at temperatures as high as T_b = 60 K [5,6]. In bioinorganic chemistry, Dismukes et al. reported the sustained water oxidation photocatalysis by a bioinspired manganese cluster [7], and studies on heterometallic Ru–Mn complexes have shown that accumulative light-induced electron transfer in a synthetic system can occur, mimicking the proton-coupled oxidation of the Ca–Mn cluster of PSII [8–10]. Thus, it becomes evident that coordination chemistry has evolved a lot in the last two decades, leading the way for advanced technological applications.

Table 1
[a,b,c,d]The twenty primary amino acids.

Name	Code	Structure	Side chain	pk_a[1]	pk_b[2]	pI[3]
Glycine	Gly		Nonpolar	2.34	9.60	5.97
Alanine	Ala		Nonpolar	2.34	9.69	6.0
Valine[4]	Val		Nonpolar	2.32	9.62	5.96
Leucine	Leu		Nonpolar	2.36	9.60	5.98
Isoleucine	Ile		Nonpolar	2.36	9.60	6.02
Phenylalanine	Phe		Nonpolar	1.83	9.13	5.48
Tryptophan	Trp		Nonpolar	2.83	9.39	5.89
Proline	Pro		Nonpolar	1.99	10.60	6.30
Serine	Ser		Polar	2.21	9.15	5.68
Threonine	Thr		Polar	2.09	9.10	5.60
Tyrosine	Tyr		Polar	2.20	9.11	5.66
Cysteine	Cys		Polar	1.96	10.28	5.07
Methionine	Met		Nonpolar	2.28	9.21	5.74
Histidine	His		Polar	1.82	9.17	7.59
Lysine	Lys		Polar	2.18	8.95	9.74
Arginine	Arg		Polar	2.17	9.04	10.76
Aspartic acid	Asp		Polar	1.88	9.60	2.77
Asparagine	Asn		Polar	2.02	8.80	5.41
Glutamic acid	Glu		Polar	2.19	9.67	3.22
Glutamine	Gln		Polar	2.17	9.13	5.65

[1]pK_a is the negative of the logarithm of the dissociation constant for the —COOH group.
[2]pK_b is the negative of the logarithm of the dissociation constant for the —NH_3 group.
[3]*pI* is the pH at the isoelectric point.
[4]All the essential amino acids are in colour red.
[a] D. R. Lide, Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1991.
[b] J. Clayden, N. Greeves, S. Warren, Organic Chemistry, Oxford University Press, Oxford, 2012, pp. 554–555.
[c] E. Gammon, General Chemistry, Houghton Mifflin College Div, Boston, MA, 1998, pp 1079–1082.
[d] N. V. Bhagavan, Medical Biochemistry, Academic Press, 2002, pp 331.

Among the numerous *Lewis*-base organic ligands that have been employed for the formation of metallic complexes, α-amino acids consist a very important family of ligands, due to their versatility regarding the coordination mode and binding properties towards metal ions. Such species, termed simply amino acids hereafter, have the general formula $H_2NCH(R)COOH$ (R = various organic groups, consisting the *side-chain* of the amino acid) with both the amine and the carboxylic acid group attached on the *alpha* carbon atom (Table 1). In addition, amino acids can adopt the $H_2NC(R_1)(R_2)COOH$ general formula, with two *side-chains* on the *alpha* carbon atom. Very often, amino acids are found in their *zwitterionic* form, in which the amine groups is protonated and positively charged, and the carboxylic acid group is deprotonated and negatively charged (Scheme 1), yielding an overall neutral charge for the amino acid, depending of course on the pH of the solution and pK_α values of the amino acids. Furthermore, depending on