

Chapter 2

Definition of “Heavy Metals” and Their Role in Biological Systems

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2.1 Introduction

At first glance, it would appear to be a rather simple matter to define a “heavy metal” – it is a metal that is “heavy”. Unfortunately, a more in-depth consideration reveals a huge amount of problems with this simple definition. This definition is meant to suggest that the density of a heavy metal is high, but this physical property is quite meaningless in the context of plants and other living organisms. Plants do not deal with metals in their elemental (valence state of 0) forms; they are not accessible to plants. Metals are only available to them in solution, and it is necessary for metals to react with other elements and form compounds before they can be solubilised. Once such a chemical compound is formed (e.g. a salt), the density of the metal does not play any role. We do not know of any correlation between the density of a metal and its physiological or toxicological effects, or even the chemical properties of its compounds. Therefore, let us leave the question of how to define a “heavy metal” until later, and first consider the definition of a “metal”.

2.2 The Definition of Heavy Metals in Plant Science

2.2.1 *Metals*

Metals are often characterised and distinguished from nonmetals by their physical properties – the ability to conduct heat, and an electrical resistance that is directly proportional to temperature, malleability, ductility and even lustre (Housecroft and Sharpe 2008; Müller 2007). These properties, especially that of a temperature-dependent conductivity, at least allow us to define what a metal is in contrast to

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nonmetals and metalloids. However as mentioned above, all of these physical properties are lost after the metal has been chemically transformed into a chemical compound that can be taken up by plants (Shaw et al. 2004). It is well known that the properties of chemical elements can be determined from their positions in the periodic table of the elements (Fig. 2.1). In general, the chemical elements become more metallic as we move towards the lower left corner of the table and nonmetallic towards the upper right corner. In other words, metallic character decreases from left to right and from the bottom to the top of the table. Metalloids (elements with properties intermediate between metals and nonmetals) occur close to the diagonal border between metals and nonmetals in the table. A metal can be categorised according to the last electronic subshell in its atom. There are s-elements, which can be subdivided into alkaline elements (first main group) and alkaline earth elements (second main group). All s-elements are metals except for H (the first element in the first main group). The first element in the second main group, Be, is also somewhat special (its oxides are amphoteric), but it is still considered to be a metal. Among the other groups of the periodic table, d-group elements (transition elements) are all metals. Many of them form compounds with different valence states, which is an important factor in their toxicity. Some of the oxides of transition elements have slightly amphoteric properties, but they are still all considered to be metals. Then there are the f-group elements, also known as the rare earth elements, which are subdivided into the lanthanide series (including La) and the actinide series (including Ac). All of these rare earth elements are also metals and so are sometimes called rare earth metals. The next group, the p-group, occurs towards the right hand side of the periodic table and thus represents a mixed group of

Alkali elements

Alkali earth elements																2	
1 H															He		
3 Li	4 Be	Transition elements										Lead group					
11 Na	12 Mg	IIIa	IVa	Va	VIIa	← VIIIa →		VIa	VIIa	VIIIa	IXa	Xa	XIa	XIIa	10 Ne		
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116		

Lanthanide	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 2.1 Periodic table of the elements. Metals and some metalloids are indicated. The transition elements, the rare earth elements (lanthanide series, actinide series) and the lead-group elements on the right hand side of the table are relevant to the definition of “heavy metals” provided in this chapter

metals, metalloids and nonmetals. This includes the elements of the third to seventh main groups of the periodic table, but excludes the rare gases (the eighth main group). Metallic members of this group include Al, Ga, In, Tl, Sn, Pb, Bi, Te and Po. All of them (except Bi) form amphoteric oxides. Si, Ge, As and Te are considered to be metalloids; sometimes B and Sb are included too (Fig. 2.1). Since there is no common name for the metal/metalloid members of the p-group, we suggest that these metals and metalloids should be termed “lead-group elements”, as lead is the representative of this group that has been studied in the greatest depth in plant science.

As plant scientists, we should stress at this point that we never talk about the elemental forms of these elements. We usually only deal with their salts. There are, of course, special cases where the properties of a compound formed from elements from any of the groups defined above are modified (e.g. by organic ligands or substituents). This should then be treated as a special case and does not necessarily have an impact on the divisions and subdivisions of elements. Classifying metals according to their positions in the periodic table of the elements makes sense because the chemical properties of their compounds are related to it.

2.2.2 Heavy Metals

In the fundamental review paper written by Duffus (2002), 13 different works were cited that used lower limits on the density of a “heavy” metal ranging from 3.5 to 7 g cm⁻³. The author stated that the threshold varied depending on the author, and that “it is impossible to come up with a consensus”. Moreover, he concluded that “any idea of defining “heavy metals” on the basis of density must be abandoned as yielding nothing but confusion”. However, this is beside the point; although half of the works cited suggested similar lower limits of 4.5 or 5 g cm⁻³, plants do not have the ability to detect the density of a metal. Thus, “heavy metal” remains an obscure term in the life sciences. It should also be noted that the review paper of Duffus (2002) was commissioned by the International Union of Pure and Applied Chemistry, and certainly represents a chemical point of view that is often neglected by biologists. Apart from the specific weight, the atomic weight, the atomic number, specific chemical properties, and the toxicity were all mentioned as a possible basis for classification – and then rejected for good reasons. So what should we base our definition of “heavy metals” upon? Indeed, is it necessary to use the term at all? Let us now consider what defining “heavy metals” according to the chemical properties of compounds can offer us.

2.2.3 Lewis Acid Strength and Ionic Indices

Any positively charged ion is able to accept electrons, thus defining it as a Lewis acid. In contrast to the physical properties of a metal in its elemental form, the chemical properties of a metal ion determines its ability to form complexes (Pearson 1968),

Table 2.1 Classification of some metals and metalloids according to covalent index (Nieboer and Richardson 1980; Shaw et al. 2004)

Class A elements	Borderline elements	Class B elements
Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Al ³⁺ , Ga ³⁺ , Sc ³⁺ , Y ³⁺	Ga ³⁺ , In ³⁺ , Sn ⁴⁺ , Pb ²⁺ , As ³⁺ , Sb ³⁺ , Ti ²⁺ , V ²⁺ , Mn ²⁺ , Fe ²⁺ , Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺	Tl ⁺ , Tl ³⁺ , Pb ⁴⁺ , Bi ³⁺ , Pd ²⁺ , Pt ²⁺ , Cu ⁺ , Ag ⁺ , Au ⁺ , Hg ²⁺

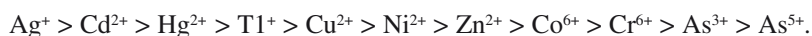
both in vitro and in living systems. Depending on the stability constants of the complexes formed, metal acceptors can be classified in relation to suitable reaction partners as “hard” or “soft”, with some being intermediate between the two. In this way, all metals can be classified as either hard, soft or intermediate. Based on so-called ionic indices and covalent indices, Nieboer and Richardson (1980) classified metals as well as metalloids into three classes: A, B, and borderline (see Table 2.1). Aside from some differences between the categories of “hard” and “soft” on the one side and “A” and “B” on the other side, this categorisation has consequences for possible reaction partners. It follows that “hard” acceptors, or class A group ions (e.g. Mg²⁺, Ca²⁺, Al³⁺, As³⁺), are expected to interact with oxygen-containing ligands, whereas many of the class B group ions that are often very toxic (e.g. Ag⁺, Tl⁺, Hg²⁺, Cd²⁺) form stable bonds with S- and N-containing ligands. The latter are present in the form of SH or imidazo groups in proteins, which could have immediate consequences with respect to toxicity. There is no doubt that quantitative data on the Lewis acid strength are very important for explaining the interactions of different metal ions with specific interaction partners within toxified cells. However, can we explain the toxic effects of specific ions in specific plants on the basis of Lewis acid strengths?

2.2.4 Toxicity

The term “heavy metal” is linked in many people’s minds to metals (or their compounds) that are toxic. However, this is a feeling rather than a conclusion based on scientific evidence. Two facts should be kept in mind. (1) The effect of any substance on a living system is always dependent on the concentration of it available to cells. Thus, there are no substances that are always toxic. What we need to evaluate toxicity are dose–response data; i.e. quantitative dose–response relationships. (2) Several metal ions are crucial to the metabolism of cells at low concentrations but are toxic at high concentrations, resulting in bell-shaped dose–response relationships (Marschner 1995). These metals are sometimes called micronutrients.

We applied ten different heavy metals (eight transition elements and two lead-group elements) to a system established to biomonitor (based on the ISO 20079 protocol) the higher plant *Lemna minor*, clone St (Naumann et al. 2007). The growth inhibition was quantitatively measured (effective dose required for the inhibition of growth rates by 50%, ErC50) on the basis of multiplication rate, fresh

weight, dry weight, chlorophyll *a*, chlorophyll *b* and total carotenoid content. Based on the averages of all tested parameters, the following phytotoxicity series was obtained:



This toxicity series was compared with the classification of the elements into classes A or B (van Assche and Clijsters 1990). No correlation was found. In this project, the biological objective did not change, and all tests were carried out with exactly the same plant (moreover, under the same standardised environmental conditions). Thus, we would expect the same set of potential ligands for each metal ion applied, i.e. proteins, nucleic acids and low molecular compounds. The situation would be even more complex had we used different biological objects (biomonitoring must be done for algae, fishes, water fleas and higher plants) or different environmental conditions. This was quite a disappointment considering the hope that the toxic effects could be explained, at least in part, by the chemical properties of the salts of these heavy metals. However, on closer inspection this result is less surprising. In a living plant cell there are a large number of different possible target proteins for a specific heavy metal – more precisely for ions of transition elements and lead-group elements (Naumann et al. 2007). These ions belonged to class B or borderline elements. The most sensitive responses were observed for either the water balance of the plants or their chlorophyll contents. In the future, it may be possible to discover whether a certain reaction partner responds in a specific way to a certain ion. However, under *in vivo* experimental conditions, changing the heavy metals is a much more complex task. Class B element ions are able to form complexes with sulfur-containing ligands. This means that all proteins are potential reaction partners. In plants there are approximately 26,000 genes (this is the number in *Arabidopsis thaliana*; there are more in other plant genomes). The number of proteins may be slightly smaller than this, but it can easily reach 10,000 at any given time and under a given set of conditions. If the heavy metal applied is changed (or perhaps only its concentration is modified) in order to compare toxic effects, there is a good chance that the dominant target protein will change as well, e.g. due to an increased or decreased Lewis acid strength. If another target protein becomes the main target, a different metabolic pathway within the complicated network of protein interactions can be affected. Thus, our initial hope, that toxic effects of heavy metal ions in living organisms can be predicted by their chemical properties (e.g. via their Lewis acid properties), is very naive and inadequate. It would be rather a big surprise if quantitative relationships between the chemical properties of heavy metal ions and toxicity held under the complex conditions present in living cells. While the Lewis acid concept remains the best basis for explaining the interactions of metal ions with organic ligands such as proteins, our present underdeveloped knowledge of the network of protein interactions in a living cell means that we cannot predict what will happen when a specific protein is blocked by a toxic concentration of a specific metal ion. A tiny difference in the chemical

properties (Lewis acid strengths) of two different heavy metals may result in a change in the preferred target of interaction. This could easily result in the inhibition of the physiological functions of different proteins. The two proteins involved (in reality it may be different sets of proteins) could have different physiological functions. Nobody can predict the consequences of toxicity in plant cells. Thus, at the moment it is quite impossible to predict the toxicity of a specific heavy metal ion on the basis of its chemical properties (its position within the periodic table of the elements or its Lewis acid properties).

The intention to use chemical properties that are relevant to complex formation in living cells is a good one, but we cannot at present expect this to allow us to make any predictions about the quality or degree of heavy metal toxicity (Duffus 2002; Shaw et al. 2004).

2.3 Toxicity of Heavy Metals in Biological Systems

Before we can describe the toxic effects of heavy metals (given the definition provided in the first part of this chapter), it is necessary to recall two well-known facts. First, a heavy metal is not toxic per se; it is only toxic when its concentration in the plant exceeds a certain threshold (“it is the dose that makes the effect”). This is especially important to the second fact: that some elements, called micronutrients, have essential functions in plant cells. This has been shown for Co, Cu, Fe, Mn, Mo, Ni and Zn. Only when the internal concentration exceeds a certain threshold do they demonstrate toxic effects, and then they are commonly termed “heavy metals”. As far as we know, all of these plant micronutrients are transition elements. No lead-group elements or rare earth elements have been found to be essential for higher plants. Micronutrients are essential for biosynthesis, growth, nucleic acids, growth substances, chlorophyll and secondary metabolites, carbohydrates and lipids, as well as for stress resistance. A supply of micronutrients is also essential for the integrity of membranes (Rengel 2004). The dose–response curves for essential heavy metals have been described by Berry and Wallace (1981), and show deficiency at suboptimal concentrations, tolerance at optimal concentrations (including the potential of the plant to maintain homeostasis) and toxicity at high concentrations (cf. Hagemeyer 2004). There is another not so well-known fact to be considered too. Some of the nonessential heavy metals have a stimulating or inducing effect when they are applied at very low concentrations (these are termed “low concentration stressors”). As an example, Cd produces some stimulating effects at 5×10^{-8} M in barley seedlings, as do Pb and Ti at low levels in detached barley leaves (Kovacs et al. 2009; Nyitrai et al. 2007).

However, let us now consider the toxic effects of heavy metals. Remember that this means the toxic effects of transition element ions, rare-earth (that are not only rare in the environment but are also rarely investigated) element ions and lead-group element ions on plants.

2.3.1 *General Effects*

Sharma and Agrawal (2005) described the general effects of heavy metals on plant physiological processes. Because it can be easily measured, plant growth is commonly used as a general parameter to study the influence of stressors, with growth rate inhibition often being the most obvious plant reaction (Fodor 2002; Hagemeyer 2004). This is especially true of the root system, which is the first plant system to come into direct contact with toxic ions. Leaf chlorosis, disturbed water balance and reduced stomatal opening are characteristic effects of toxic Ni concentrations (Clemens 2006), but they are also caused by many heavy metals (as part of heavy metal toxicity syndrome) and even occur more generally as a stress response.

Fodor (2002) suggested an interesting stepwise model for the action of heavy metals in plants. Initially, there are interactions with other ionic components present at the locus of entry into the plant rhizosphere that subsequently have consequences for the metabolism. This is followed by an impact on the formation of reactive oxygen species (ROS) in the cell wall and an influence on the plasmalemma membrane system (stage 1). At stage 2, the metal ion reacts with all possible interaction partners within the cytoplasm, including proteins, other macromolecules and metabolites. Stage 3 is mainly related to the factors that influence homeostatic events, including water uptake, transport and transpiration. At this stage, symptoms start to develop, and they become visible at stage 4 according to Fodor’s model. As an example, the chlorophyll and, usually to a smaller degree, carotenoid contents decrease, which have obvious consequences for photosynthesis and plant growth (Barcelo and Poschenrieder 2004). The death of the plant cell occurs at stage 5. This model has the advantage that visible effects are linked to metabolic events that are influenced by the metal ion of interest.

2.3.2 *Primary Targets of Heavy Metal Toxicity*

Many of the toxic responses induced by heavy metals that have been identified to date have to be classified as being general stress responses, rather than ones that are specific to heavy metals. The question then arises as to whether a specific metal ion actually induces a sensing mechanism in the plant cells for the presence of the toxin at all, or whether it just the damage caused by a heavy metal that induces a signal. According to Clemens (2006), the data that are available to answer this question are “rudimentary at best”. To give an example, proline accumulates under Cd^{2+} stress. However, the accumulation does not occur directly in response to the presence of Cd^{2+} but because of the disturbance to the water balance caused by the excess of Cd^{2+} . One way to investigate the specificity of the stress caused by an excess of a heavy metal ion is to apply the microarray strategy to mRNA-related cDNAs in order to compare the effects of different heavy metals with those of other stress signals, e.g. water deficiency stress. Some data are already available, but we are at a very early stage in this type of research (Clemens 2006; Zimmermann et al. 2004). There is one exception: metal-induced

synthesis of phytochelatins (cf. Clemens 2006). In a posttranslational process, the activity of phytochelatin synthase is upregulated by the heavy metal or a metal–glutathione complex. This response does not need much of a signal transduction chain.

2.3.3 Water Relations

Water relations in higher plants under stress have mainly been investigated in connection with high NaCl concentrations in the submolar or even molar range (Ernst 2004). Concentrations of heavy metals are relevant in the submillimolar or even submicromolar range. Thus, direct osmotic effects can be excluded. Some of the effects mentioned here are common to many heavy metals, such as an influence on membrane transport and an inhibition of root growth and enzyme activities. Early effects may be weakly or strongly connected with water relations. It is relevant to focus here solely on the role of stomata and possible effects of heavy metals. In contrast to earlier results, it is now assumed that the primary effects of heavy metals in whole plants are not directly connected with the induction of stomata closure, but that early effects in roots (e.g. disturbed nutrient absorbance) may be responsible for changes in transpiration (Poschenrieder and Barcelo 2004). In some experiments with both high and low concentrations of heavy metals, enhanced transpiration has been measured. The reason for this is not clear, but it may be caused by damage to the cuticula. In most investigations, however, the application of heavy metals increased the stomatal resistance and in this way decreased the rate of transpiration. It is assumed that stomatal closure after the application of heavy metals is a consequence of stress due to water deficiency. This was concluded from the increased levels of proline and abscisic acid that have been measured, since both are known indicators of drought stress. Proline is evidently not involved in metal detoxification but in membrane stabilisation: K^+ loss and lipid peroxidation were reduced after pretreatment with proline.

New experimental results (see references in Poschenrieder and Barcelo 2004) have revised the old concepts that (i) heavy metals have a direct effect on stomata closure and (ii) that the roots simply act as an osmometer, producing a hydraulic signal. Instead, roots can influence the water content via chemical signals, especially abscisic acid. Moreover, water transport appears to be modulated by an impairment of aquaporins, which is one of the earliest responses to heavy metals in plants. Many well-described physiological (or toxicological) responses may not be direct effects but consequences of fast responses in the roots.

2.3.4 Formation of Reactive Oxygen Species

The bleaching effects of many heavy metals in light have been known for a long time and are connected with the formation of reactive oxygen species (ROS; Asada 1999). The main important ROS are singlet oxygen (1O_2) and the hydroxy radical (HO^*),

because both are highly reactive, carrying out oxidation reactions with many organic molecules at their sites of formation during their short lives. The generation of ROS is a general phenomenon; higher plants developed a highly sophisticated antioxidant system during the course of evolution. This consists of several enzymes (superoxide dismutases, catalases, ascorbate oxidases, glutathione peroxidases and glutathione reductases) and antioxidant substrates (ascorbate, glutathione and α -tocopherol). The main sources of ROS under control conditions (an absence of toxic concentrations of heavy metals) are photosynthetic and respiratory electron transport processes. Only when the capacity of cells to suppress the concentrations of ROS is exceeded do these species then damage cells over a long period. Heavy metals play many roles in this respect (Sharma and Agrawal 2005):

- They directly disturb electron transport, causing electrons to be transferred to oxygen instead of the natural electron acceptors in chloroplasts and mitochondria
- Disturbances to metabolic reactions feed back to electron transport, as just described
- Redox-active metals in different oxidation states under physiological conditions can participate in the Fenton and Haber–Weiss reaction (c.f. Shaw et al. 2004), producing hydroxyl radicals
- Inactivation and downregulation of enzymes of the antioxidant defence system
- Depletion of antioxidant substrates.

It has been shown on several occasions that lipid peroxidation (Bertrand and Poirier 2005) is just a consequence of oxidative stress, such as that caused by glutathione depletion (Schützendübel and Polle 2002).

As long as the stress is not too high, plants often respond by inducing antioxidant enzymes together with rather unspecific stress proteins, such as heat-shock proteins (Clemens 2006).

2.3.5 Photosynthesis

As already mentioned above, inhibition of photosynthesis is one effect that most of the heavy metals have in common when present at toxic concentrations. It is a very sensitive response. Measuring the photosynthetic activity is a good screening method for detecting possible stress situations, perhaps including those involving heavy metals. Direct effects of heavy metals on light and dark reactions and indirect effects caused by them decreasing the photosynthetic pigment content are involved, as well as changes in stomata function (Mysliwa-Kurdziel et al. 2004). It seems that nearly all of the components of the photosynthetic apparatus are influenced by almost all heavy metals, including chlorophyll and carotenoid content, chloroplast membrane structure, light-harvesting and oxygen-evolving complexes, photosystems and constituents of the photosynthetic electron transport chain (Barcelo and Poschenrieder 2004). Several enzymes involved in the Calvin cycle are also inhibited, especially Rubisco and PEPcarboxylase (Mysliwa-Kurdziel et al. 2004).

2.3.6 Mitochondrial Respiration

Some scientists consider that respiration increases under stress. However, this is more than an oversimplification. It is true that in some plant species the presence of some heavy metals at lower concentrations increases respiration. This is the case, for example, when 1 μM Cd^{2+} was applied to *Vicia faba* (Lee et al. 1976). This, however, is rather the exception to the rule. At toxic concentrations of heavy metals, respiration is usually inhibited (Lösch 2004).

2.4 Conclusion

There seems to be a consensus in the literature that the term “heavy metal” is badly defined and is best avoided (e.g. Duffus 2002; Nieboer and Richardson 1980). However, considering how commonly this term is used in plant science (see the title of this book for example!), it seems hopeless to expect plant scientists to suddenly abandon it. Therefore, we suggest that this term should not be avoided but defined in a better way. Its definition should certainly not be based on the density of the metal in elemental form because it is not relevant to the effects of the metal in plants, whether the defined lower limit on the density of a heavy metal is 3.5 or 7 g cm^{-3} . The term “heavy metal” should be defined in relation to the position of the element in the period table, because this position is related to the chemical properties of compounds that include the element. Although alkali metals and alkaline earth metals are clearly metals, they are not – as common sense already suggests – “heavy metals”. We suggest that three groups from the periodic table should be considered heavy metals: (1) transition elements, all of which are metals, even though some of them form slightly amphoteric oxides (i.e. Ti, Zr, Hf, Rf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os and Zn); (2) rare earth elements, which are subdivided into the lanthanide series (including La itself) and the actinide series (including Ac); (3) some elements from the p-group that are either metals (Al, Ga, In, Tl, Sn, Pb, Sb, Bi and Po) or metalloids/borderline elements. To keep this definition in line with common sense, we suggest that Ge, As and Te should be included, but not B and Si. Since there is a common name for this third group of heavy metals, we suggest calling them the “lead group”, after its most prominent and deeply investigated member. This limitation on the term “heavy metal” clarifies its definition.

The primary targets for the toxicity of heavy metals are still not clear yet. It has been suggested that microarrays could be used to address this issue, but conclusive data is still lacking. Most of the physiological responses are a consequence of heavy metal-induced stress rather than direct effects. An exception is the induction of the synthesis of phytochelatins, which is an example of a direct effect of either heavy metals or glutathione–heavy metal complexes.

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