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A simple method for identifying and distinguishing between the diastereoisomers that result from wrapping polydentate ligands around octahedral metal ions

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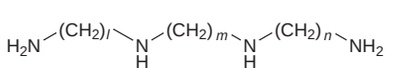
Polydentate ligands can be wrapped around octahedral centres in many different ways. This presents chemists with the challenge of being able to identify or distinguish between all the available isomers, in a straightforward manner, without necessarily having to draw them. Some of the existing nomenclature systems have been reviewed and elements of some of them extended and systematised so that they can readily be used as parts of a descriptive shorthand for the wrapping of a ligand around a metal ion.

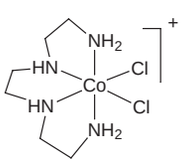
Alfred Werner's classic publication concerning the stereochemistry of octahedral cobalt(III) complexes is now past its centenary.[1] The theory described therein explains the existence of and the relationship between the 1,2 (*cis*) and 1,6 (*trans*) isomers of the $[CoCl_2(en)_2]^+$ ion. Since then co-ordination chemists have exercised their imagination in extending Werner's ideas, through new ligand design, to probe the more subtle aspects of octahedral stereochemistry.

Obvious extensions of the bis(1,2-diaminoethane) system are to bridge the adjacent ends of the two didentates with $(CH_2)_m$ units ($m \geqslant 2$), and to extend the link within the didentates, to give the general ligands represented by **I** (often represented by the abbreviations *l*,*m*,*n*-tet, where *l*,*m*,*n* are integers greater than or equal to 2). Linear tetraamines of this sort were synthesized, became commercially available in the 1960s, and the co-ordination chemistry was explored actively.[2,3] Substituents can be added, nitrogen atoms can be replaced by other donor atoms to produce ligands such as ethylenediiminodiacetic acid (edda), and the diversity of possible ligands is limited only by the imagination.



I

The ligands *l*,*m*,*n*-tet (*l*,*m*,*n*≥2)



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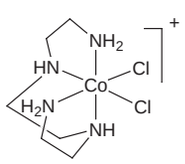

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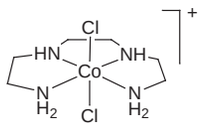

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As investigations into the chemistry of complexes such as $[CoX_2(trien)]^{n+}$ developed it became obvious that isomers were formed. Without a knowledge of the exact stereochemistry, chemists usually devise a working nomenclature to identify or distinguish between isomeric complexes (which may have been produced by different synthetic routes), *e.g.* red/pink; α/β; π/κ; A/B *etc.* Thus the two violet *cis* isomers of $[CoCl_2(trien)]^+$, **1** and **2**, produced by Sargeson and Searle,[4] had characteristically different spectroscopic properties, and were called α and β. The green *trans* isomer, **3**, was readily identified by analogy with the green *trans*-bis(1,2-diaminoethane) system.

The next phase of the research is to assign structural representations to the isomers that have been produced. The α isomer was shown to be **1** and the β form to be **2**. This nomenclature has since been extended so that complexes with fully folded linear tetradentate ligands are known as the α isomer, and all those with only one fold are assigned as the β isomer.[5] Thus the trivial names α and β became structural descriptions.

A further extension of these kinds of system involves linking the 1,2-diaminoethane units at both ends, so that the donor groups form part of a macrocyclic ring. Octahedral complexes of N_4 macrocyclic ligands such as cyclam[6] and Me_6cyclam (Curtis macrocycles)[7] were also synthesized in the 1960s, and the isomeric complexities enumerated (Fig. 1).[6,8] Both *cis* (folded) and *trans* (planar) macrocycle topologies have been observed, and the various isomers described either by the sequence of absolute configurations around the secondary nitrogen atoms in the macrocyclic ring[6,7] or by Roman numerals.[6] Thus a cyclam complex could be named as the *trans*-(*RSSR*) or *trans* type III isomer. The Roman numerals began as labels for the isomers, but they have become structural descriptors.

A unified system of notation for describing isomers of mononuclear complexes has been proposed, is recommended by IUPAC[9] and is in use in the Indexes to Chemical Abstracts.[10] The system encompasses a range of different co-ordination numbers and geometries using a symmetry site term, and provides for the representation of diastereoisomers using numerical sequences which are derived from the locations of donor atoms and groups of differing priority. The priority of a group relative to others in the molecule is determined using the Cahn, Ingold, Prelog (CIP) Rules.[11] This means that the numerical sequence used to describe, for example, two α isomers may well differ, depending on the relative priorities of the donor groups either in the tetradentate ligand or the remaining two sites. Determining just which isomer is being discussed requires decoding of the numerical sequence.

Another well recognised structural nomenclature is *mer* and *fac*, which can be used to describe the geometry adopted by tridentate ligands (Fig. 2) of which dien is a typical example. This nomenclature is well known, perhaps better than α and β, as it is used to describe examples of isomerism in metal complexes that are commonly presented in undergraduate classes.[12] Tetraamines, like those described above, and other linear tetradentate ligands can be envisaged as arising from extension of one end of a tridentate ligand. This idea leads to the approach proposed by Saito[13] for hexadentate ligands, where tridentate segments of the co-ordinated polyamine chain are labelled *mer* (*m*) or *fac* (*f*), depending on whether the segment is wrapped around the edge (meridian) or face of the octahedron. Thus **1**

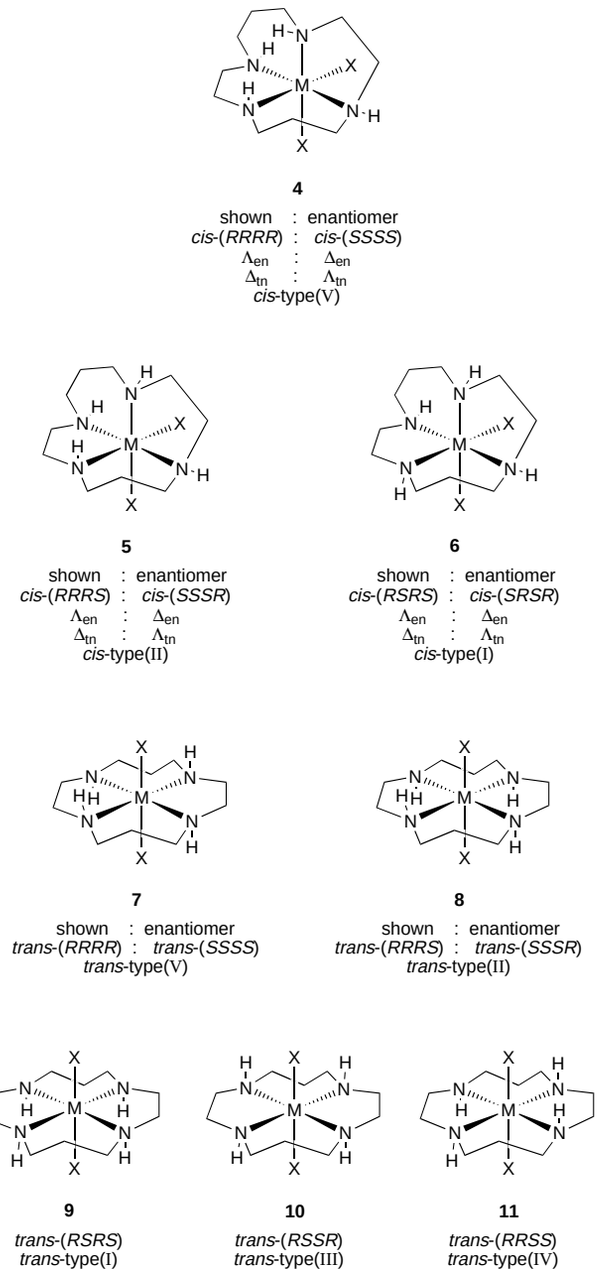

Fig. 1 The isomers resulting from wrapping cyclam in different ways about an octahedral centre

would be *fac*,*fac*-$[CoCl_2(trien)]^+$ (or *ff*-$[CoCl_2(trien)]^+$) and **2** would be the *fac*,*mer* (or *fm*) isomer. *trans*-Tetraamines such as **3** would be assigned *mer*,*mer* (or *mm*). A similar kind of approach has been used to describe complexes of pentadentate ligands as combinations of tetradentate structural descriptions, for example as αα or αβ.[14]

The Saito system is an attractive starting point for an octahedral nomenclature system because it is directly related to octahedral topology, leads to easy visualisation of isomers, and can be readily extended to longer chain linear pentadentate and hexadentate ligands, and (with some minor modifications) to tripodal and macrocyclic systems, without reference to model systems. This extension of the Saito system forms the basis of the general system we propose for the description of the diastereoisomers that result from wrapping polydentate ligands around an octahedral metal ion.

Shortcomings of the Existing Nomenclatures

The 'steering wheel' system that is recommended by IUPAC,

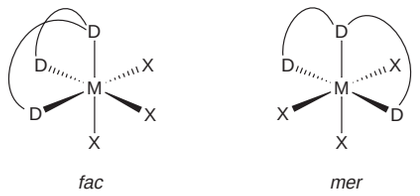

Fig. 2 Facial (*fac*) and meridional (*mer*) isomers in complexes of a linear tridentate ligand

and employed in the Indexes to Chemical Abstracts, is able to describe all possible isomers of a complex in a unique way which is presumably well suited to the establishment of a computer searchable database. It achieves this through a combination of terms which describe, in turn, the co-ordination geometry, the relative locations of the donor atoms or groups, and the absolute configurations of the central metal ion and the ligands which surround it. Unfortunately, the numerical sequence which is used to identify a particular geometrical isomer of a polydentate ligand depends not only on the CIP priority of the donor groups in the polydentate ligand, but also on the CIP priorities of any other ligands in the molecule. This means that while the label for a particular isomer of a compound may be unique to it, it requires some analysis before it can be determined exactly which isomer is being represented. The topological information, while there, is rather deeply embedded in the numerical code, making it difficult to visualise the complex on reading its code. It is presumably for this reason that this notation is not widely used by chemists when discussing or analysing chemical reactions or structures.

A major shortcoming of the currently used nomenclatures is that different classes of ligand each have their own notations which, as described above, are often artefacts of trivial names given to prototypal examples, rather than being designed to provide as much information as possible about the given complex. *It would be desirable to have a consistent and meaningful nomenclature with which to describe the nature of the wrapping of polydentate ligands around an octahedral metal ion*.

Deficiencies exist also within the nomenclature systems presently employed for various types of ligands, and it is worthwhile considering the nature of these deficiencies before addressing the question of what kind of system might best be used to describe the diastereoisomers that may arise in studies of octahedral complexes of polydentate ligands.

Linear tetradentate ligands have the potential to wrap around an octahedral metal ion to form three topological isomers (being termed facultative[15] or flexidentate[16]), as discussed above, as well as enantiomers (Λ and Δ configurations around the metal ion). This has long been recognised, but what is less well appreciated is that protons (or other substituents) attached to co-ordinated secondary amine (or other) donors in such ligands may be able to adopt alternate positions in space relative to the rest of the ligand. Fig. 3 shows the potential isomers available for the $[CoCl_2(trien)]^+$ system, with both the existing nomenclature and the anticipated nomenclature system. If the ligand is not symmetrical, extra possibilities become available for the wrapping of it around the metal ion, resulting in different compounds, which cannot be represented or distinguished easily by existing nomenclatures. An example is illustrated in Fig. 4, where two Δ-β-(*S*) isomers are shown which cannot be distinguished by present nomenclature systems, along with the proposed folding description.

For complexes of linear tetraamine ligands, the stereochemistry at the co-ordinated *sec*-N positions can be assigned (*R* or *S*) using the CIP Rules,[11] and this is a commonly accepted practice, which also forms part of the IUPAC system. Often the configuration of the *sec*-N atom in the middle of a *fac* ligand segment is omitted, as the spatial location of the H atom is determined by the direction of the fold of the ligand, which is in

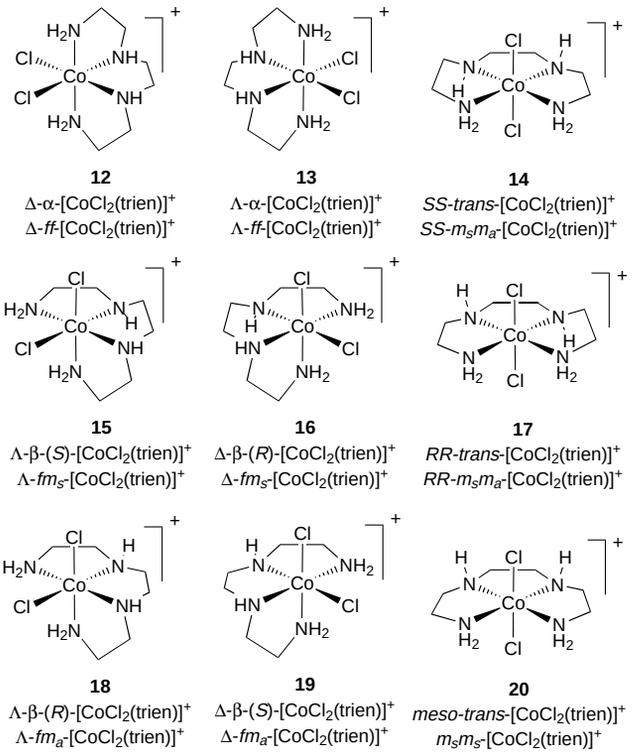

Fig. 3 Potential isomers available for the $[CoCl_2(trien)]^+$ system

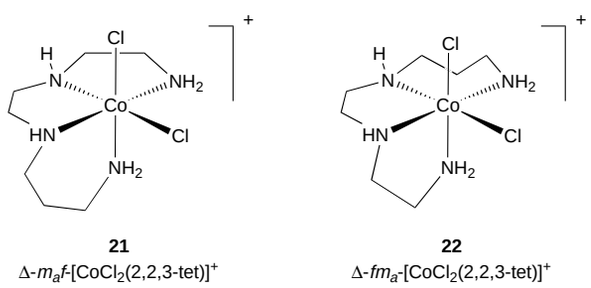

Fig. 4 Example of isomeric complexes which arise from wrapping the ligand 2,2,3-tet in different directions around the same four co-ordination sites

turn related to the absolute configuration around the metal centre. This kind of nomenclature can be applied to complexes of a wide range of related ligands.

One disadvantage of the CIP nomenclature is that it is rather clumsy when dealing with racemates, where the Δ and Λ (or *C* and *A*) forms of the complex are not separated. This results from the fact that the absolute configuration around the *sec*-N atom for a particular position of the proton in space, relative to the rest of the ligand, depends on the configuration of the ligand around the metal ion (Δ/Λ, *C*/*A*). The racemic mixture of **15** and **16** is therefore described as Δ;Λ-β-(*R*;*S*)-$[CoCl_2(trien)]^+$, and its *sec*-NH epimer as Δ;Λ-β-(*S*;*R*)-$[CoCl_2(trien)]^+$. Both the absolute configuration around the metal ion and the *sec*-N atom have to be defined or determined in order fully to describe the wrapping of the ligand around the metal ion. In the nomenclature system we propose, the same notation is used to describe the wrapping of the ligand in **both** enantiomers, so that the racemate can be easily and uniquely described by using the wrapping nomenclature alone. Thus the racemic mixture of **15** and **16** can be simply described as *fm*$_s$-$[CoCl_2(trien)]^+$, and a particular enantiomer identified by putting Δ or Λ (or any other appropriate chiral descriptor) in front of the description as required.

A second disadvantage of the *S*/*R* based nomenclature is that

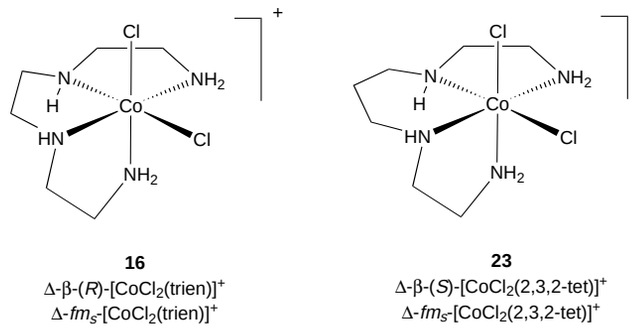

Fig. 5 Two complexes with identical ligand wrapping and *sec*-NH orientation, but with different absolute configurations about the meridional *sec*-nitrogen atom, due to a change in CIP priority

two very similar complexes with identical *sec*-NH spatial arrangements can have different configurational assignments due to a change in priority order of the functional groups bound to the N atom. This is the situation when trien (2,2,2-tet) is replaced with 2,3,2-tet (Fig. 5). It is not immediately clear from the names Δ-β-*R*-$[CoCl_2(trien)]^+$ and Δ-β-*S*-$[CoCl_2(2,3,2\text{-tet})]^+$ that the complexes have essentially identical stereochemistry around the metal ion, and the same would be true if the β description is replaced by the appropriate configuration index in the IUPAC system. Under the proposed system both of these complexes wound be *fm*$_s$ isomers.

Attempts to use descriptions of the absolute configurations (*R*/*S*) of donor groups to identify isomers of *cis* or folded complexes of tetraazamacrocycles, particularly those with irregularly distributed donor groups, come up against similar problems to those described for the complexes of linear ligands, except that there can be an extra twist if the skew line reference system is used for determining the absolute configuration. In the macrocyclic complexes the absolute configuration (Δ or Λ) depends on which of the pairs of chains between the donors are used to set up the skew lines which define the chirality (Fig. 1). Thus, while it is still necessary to work out the configuration of the ligand around the metal ion before the amine substituents can be added, there can also be scope for confusion as to how the absolute configuration is arrived at.

The nomenclature that has been applied to cyclam complexes has another shortcoming when applied to less symmetrical systems. Introduction of substituents on the ring or different donors in place of one or more of the nitrogen donors leads to the possibility of a range of isomers being formed. For example, there may be as many as four different *trans*-type(II) isomers, which differ only in which donor has the hydrogen atom pointing in the opposite direction to the hydrogen atoms on the other three donors. The nomenclature which makes use of the absolute configurations of the donor atoms can be used to identify the isomers of such complexes, but only if it is clear which *R*/*S* symbol refers to each donor atom. This requires that the starting point in the macrocycle be defined, and also that the order in which the donors are considered (*i.e.* the direction taken around the macrocycle) is clear.

In some cases it is not possible to use absolute configuration to describe the spatial location of substituents on *sec*-N atoms. This will occur whenever the two alkyl substituents on the *sec*-N atom are the same, for example, in dien or 1,4,7,10-tetraazacyclododecane (cyclen). In these cases, the location of the pendant substituent has been described as being *syn*/*anti* or *endo*/*exo* with respect to a particular, defined, ligand in the complex, or even as *up*/*down* with respect to a particular drawing of the complex in question.[17] Clearly the choices of directional references have been rather arbitrary, but one particularly attractive advantage of this kind of approach is that it is independent of the absolute stereochemistry at both the *sec*-N atom and the central metal ion. There is no reason why such a

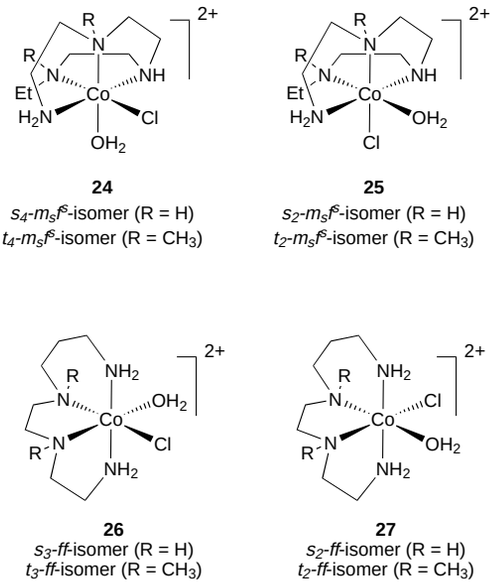

Fig. 6 Examples of pairs of isomers where the monodentate ligands are both *trans* to (inequivalent) secondary (R = H) or tertiary ($R = CH_3$) donor atoms. The donor number subscripts in the new nomenclature allow the isomers to be uniquely described

system cannot be used for molecules where the absolute configuration of the *sec*-N atom can be determined. Indeed, all that is required are some rules by which the directional reference ligand can be identified or determined for each *mer* ligand segment, and the system could then be used for the description of a wide variety of complexes. This idea forms the basis of the second component of the nomenclature system, that of employing subscripts to indicate whether substituents on meridional *sec*-N atoms, or other donor groups, are pointed towards (*syn*) or away (*anti*) from a particular ligand.

The situation becomes even more complex when the remaining co-ordination sites around the octahedral metal ion are occupied by inequivalent donor groups. This information is contained in the configuration number of the IUPAC notation, but again, the code needs to be analysed in detail in order to reveal the information. In most cases, this kind of isomerism is well described by the easily interpreted notation in which the isomers with the substituent of highest priority *trans* to imine, primary, secondary or tertiary nitrogen donors of the polydentate ligand are known as the *i*, *p*, *s* or *t* isomers respectively.[14] However, there are, for example, possible cases of isomeric complexes of linear polyamines (*e.g.* Fig. 6) where there may be more than one type of secondary or tertiary amine to which the higher priority donor group (Cl) could be *trans*. A similar kind of problem can arise with this nomenclature when dealing with complexes of tripodal ligands, like those shown in Fig. 7, where the higher priority ligand (either X or Y) may be defined as being *trans* to either a primary or tertiary amine (using the *p*, *s*, *t* notation) without being able to distinguish between the isomers shown. The third component to the nomenclature system employs a modification of the *p*, *s*, *t* nomenclature to resolve any ambiguities that remain following use of the ligand folding nomenclature.

Generality and Properties of the Proposed Nomenclature System

The need for an easily interpreted system to describe the wrapping of a polydentate ligand around an octahedral metal ion was largely discussed in relation to polyamine ligands. However, the rules described below can be used to label and describe isomers of a wide range of complexes, including those of

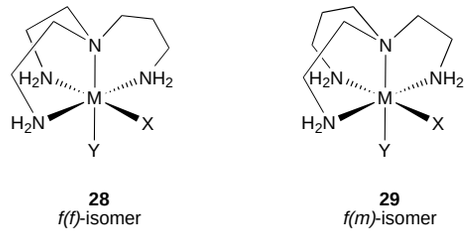

Fig. 7 Isomeric complexes of a tripodal ligand, which would be indistinguishable using only the *p*, *s*, *t* nomenclature, but which could be distinguished using the new nomenclature system

ligands containing donors other than amines. It is worthwhile considering how wide the range of compounds that this system may be applied to is, and what information can be conveyed about relationships between compounds.

A first, general point to note about this new nomenclature system is that the notation for a complex does not change with rotation, inversion or reflection. This means that the description for a particular diastereoisomer does **not** depend on the absolute configuration of the complex. This immediately addresses a number of the problems that exist with the established nomenclature systems. Secondly, it should also be noted that this nomenclature system does rely on the assumption that adjacent donors in a polydentate ligand will co-ordinate in positions that are *cis* to one another in the octahedron. It will therefore break down for any case where a large chelate ring in a polydentate ligand connects donors that are *trans* to one another.

The prefixed series of *m*/*f* symbols that will be used to describe the wrapping of a ligand in an octahedral complex is really a sequence of instructions which allows the geometry of a complex to be either described or drawn in a stepwise manner. This makes it easier to visualise the isomer in question on reading the wrapping code. Conventions (or rules) have been devised which allow the range of isomers that are possible in a mononuclear octahedral complex to be described in distinguishable ways. Essentially, this is done by establishing the order in which the donor groups should be treated and then defining the relative positions of groups within the molecule.

Irrespective of whether one is drawing a structure from the isomer description or describing a known structure, the first step is to identify the backbone chain of the ligand and to determine in which order the donor groups in the backbone chain should be considered. If there is more than one equivalent backbone chain/direction combination, only one of them need be identified for drawing a structure from the wrapping instructions, but all of them need to be identified and checked if one is describing a known structure. This means that, if anything, it is easier to work out a structure from the code than it is to go in the other direction. This is probably desirable in that it is appropriate that fewer demands be placed on the reader of a written piece than are placed on the authors (who should be more familiar with the structure in question and have had the time and opportunity to analyse it fully).

Once one of the backbone chain/direction combinations has been identified, drawing a structure is then simply an exercise of, first, putting the first two donors in the backbone chain into adjacent co-ordination sites on the octahedron, and drawing in the link between them. The *m*/*f* folding description can then be followed in order to locate each subsequent donor in relation to those that are readily there. The ligand framework can be added at each step. Substituents on the donor groups can then be added according to the bracketed, subscript and superscript instructions. Finally, any additional ligands can be placed by decoding the *p*, *s*, *t*, *u*, *x* notation.

Developing the description of a complex of known structure requires that all the backbone chain/direction combinations be identified, as mentioned above. For each of them, the first three

donors in the chain are identified in the structure and determined to be either meridional (*m*) or facial (*f*). Sequential segments are identified and classified until the descriptor sequence for the backbone chain is completed. Sidechains and substituents are then added to the description for each possible combination, before the descriptions are compared using Rule (x). The location of additional ligands can then be specified using the *p*, *s*, *t*, *u*, *x* notation, and Rule (xiii) applied if necessary. This should result in a single description for the geometry of the molecule.

Either enantiomer of a dissymmetric compound can be drawn from the same set of instructions, but the relative stereochemistry in the molecules drawn will, of course, be identical. Just which enantiomer is drawn for a particular compound will depend on which direction the drawer decides to turn when drawing the first facial segment of the polydentate ligand, or, in cases where there are only meridional ligand segments present in the molecule, it will depend on which face of the meridional donor(s) the first axial ligand is placed, which, in turn, will define placement of the substituents on the meridional donor(s) (and therefore their absolute configuration).

An appropriate chiral descriptor can be used with the folding description to identify a particular enantiomer, but it is worth noting that the enantiomer could also be specified by indicating in some way the direction in which the first turn or axial ligand placement should be made. Such a method is closely related to the oriented skew-lines reference system for specifying chirality,[18] and shares the property that it could be used to differentiate between the enantiomers of complexes such as *mer*-$[Co(dien)_2]^{3+}$, which cannot be differentiated using established chiral reference systems [*e.g.* the 'steering wheel' method (*R*/*S*, *C*/*A*), or the skew-lines method (Λ/Δ)].[18,19] In this system the oriented skew-lines can be thought of as arising from the directions of the wrapping before and after the fold or, in the meridional cases, from the direction of the wrapping together with the direction of the substituent (which is the same as that of the chosen axial ligand).

Linear polydentates

This nomenclature allows all isomers of complexes of linear polydentate ligands to be uniquely described, including the spatial location, in relation to the rest of the complex, of protons and other non-co-ordinating substituents attached to secondary and tertiary donor atoms. Thus Δ-m_af-[$CoCl_2$(2,2,3-tet)]$^+$ **21** and Δ-fm_a-[$CoCl_2$(2,2,3-tet)]$^+$ **22** are readily seen to be different isomers because they have different prefixes, as do a wide variety of different kinds of isomers that are drawn and labelled in the various figures that accompany this text.

It is worth noting that the co-ordination geometries around the metal ion in these latter two complexes can readily be seen to be similar by observing that the orders of the descriptors are the exact reverse of each other. This will be true in any case where the two sets of donor atoms are the same as each other, and palindromic. If the sets of donor atoms are the same, but not palindromic, the complexes will not necessarily have the same co-ordination environment around the metal ion when the descriptors are reversed.

Substituents

The spatial location of substituents on donor groups can be described, using the subscript/superscript nomenclature. This system can also readily be used to describe the location of lone pairs, and thus the stereochemistry of donor atoms such as sulfur or oxygen, which can become stereogenic centers upon co-ordination, can also be described if required.

Pendant donors

The location of pendant donors is readily described using this notation, although, depending on whether or not the pendant donor is attached through another donor, different methods are used. Pendant donors attached to the backbone chain of the ligand through a donor group (*i.e.* tripodal ligands where the apex is co-ordinated) are described by placing the tridentate segment descriptor(s) for the pendant donor(s) in brackets after the descriptor for the donor group through which it is attached to the ligand. Pendant donors that are not attached through a donor atom are considered to be part of the backbone chain and will be located using their own unbracketed descriptor.

The system becomes a bit unwieldy when a pendant arm that is not attached through a donor contains more than one donor group (this will require a hexadentate ligand, because otherwise a backbone chain that included the entire pendant arm would be chosen). The wrapping of such a ligand can be described in this notation by treating the second donor on the pendant arm as if it were attached to the backbone chain through a donor group (the first of the donor groups on the arm). The descriptor for the second donor will therefore appear in brackets immediately after that for the first one (which is not bracketed).

Macrocyclic complexes

Isomers of macrocyclic complexes are also easily described and distinguished using this nomenclature system. The key point in these systems is knowing where in the macrocycle to begin the description from, and being aware that otherwise reasonably similar macrocycles may begin at different places, depending on substitution patterns and so forth. This means that even if all the donors are the same in two different macrocycles, and the co-ordination geometry and wrapping of the ligands is the same, the wrapping notation may be different.

Essentially the process involves 'converting' the macrocycle into a linear ligand by making a virtual cut in it in such a way as to create the highest priority backbone chain. This means that there will be similarities between the wrapping descriptions of macrocyclic ligands and (at least one of) the related linear ligand(s).

Macrobicyclic structures (where all cycles contain three or more donor groups) can also be described using this nomenclature system, although it may not be so easy to identify the backbone chain for the ligand. At least two virtual cuts must be made to 'convert' the ligand into a linear analogue. Of course, difficulties in obtaining the wrapping description for complexes of macrobicycles is unlikely to be a major problem, as the geometrical flexibility of macrobicyclic structures is usually quite restricted, so that the number of geometrical isomers is likely to be quite small.

The Proposed Nomenclature System

The proposed nomenclature system is made up of three components which are necessary in order to describe the diastereoisomers that can occur when a complex is formed between a polydentate ligand and an octahedral metal ion. The location of sequential donor groups in the complex is used to establish the basic ligand framework. The location of substituents on donor atoms is then described in relation to the rest of the complex. Finally, the location of other ligands is specified in relation to the donor groups of the polydentate. Each of these components is dealt with in turn, along with the special case of complexes containing two tridentate ligands.

Description of ligand framework geometry

The proposed nomenclature system is based on the tridentate ligand segment approach introduced by Saito,[13] in which each ligand segment is labelled either *m* or *f* depending on whether it is located on the meridian or face of the octahedron. However, this approach requires some rules in order to allow all possible isomers to be uniquely described. We propose that: **(i)** the wrapping of a polydentate ligand around the metal ion be

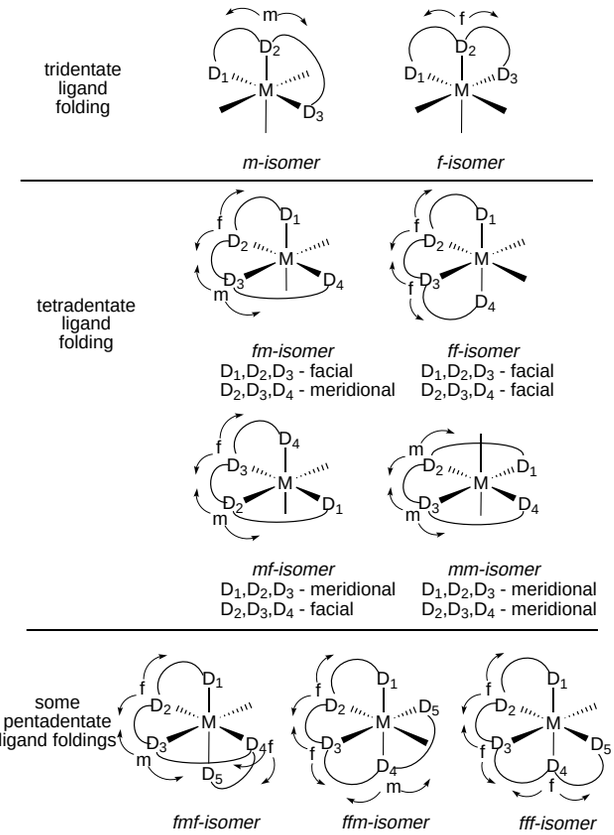

Fig. 8 Sequences of segment descriptors used to describe the wrapping of ligands around a metal ion

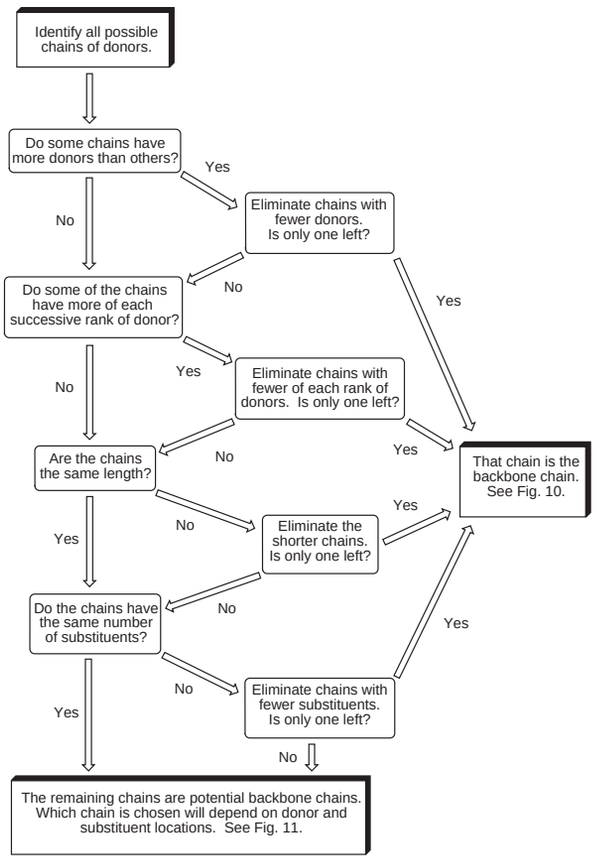

Fig. 9 A decision tree to aid in the identification of the backbone chain of the ligand

described by a sequence of *m*/*f* tridentate segment descriptors. A *m* segment is one which is wrapped around an edge (meridian) of the octahedron, while an *f* segment is wrapped around an octahedral face. Some examples are shown in Fig. 8. A tridentate ligand will be either *m* or *f*. A tetradentate requires two *m*/*f* characters (*e.g. fm*, *mm*, *ff*), a pentadentate three (*e.g. ffm*, *fff*, *fmf*), and a hexadentate ligand four characters (*e.g. ffmf*, *ffff*, *fmmf*).

(**ii**) The description of the folding of the ligand should follow the backbone chain of the ligand, chosen on the basis of numbers, types and locations of donors, and numbers, locations, and types of substituents. A decision tree to aid in determining which chains are potential backbone chains for a ligand is shown in Fig. 9. The backbone chain will be the one which contains the most donor groups. If there is more than one chain with that number of donor groups the one containing the donor of highest elemental seniority should be chosen.[20] Otherwise the longest chain or, failing that, the more substituted chain should be chosen. The location of donors and then the location of substituents nearer one end of the ligand can be used to help choose the backbone chain for a ligand, but these are also involved in the choice of which end of the ligand the folding description should begin from (see below). Some examples of how the chain is chosen can be found in Fig. 10.

Pendant donor groups that are attached to a chain between two donors count as part of that chain and are treated as if they were located at the point of attachment. Thus, the pendant amine in 1,2,3-triaminopropane would be considered to be the middle donor group in the tridentate segment. Pendant donor groups that are attached to a chain through another donor group are part of a different chain.

(**iii**) The description of the wrapping of the ligand around the metal ion should begin from one end of the backbone chain, chosen on the basis of donor location, donor priority, and substituent location and priority. A decision tree to aid in the choice of the end of the backbone chain from which the

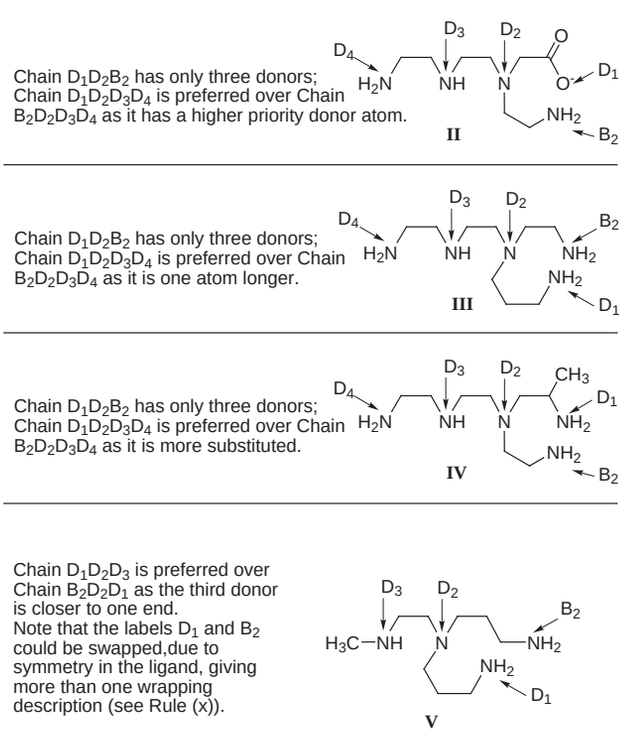

Fig. 10 Some examples of how the backbone chain is chosen

wrapping description should begin (*i.e.* donor order) is shown in Fig. 11. The end of the ligand which has a donor group closest will be chosen. If the donors occur at the same distances from the ends of the ligand the end closer to the higher priority donor atom at the first point of donor difference will be chosen. If the donor groups are symmetrically distributed the number,

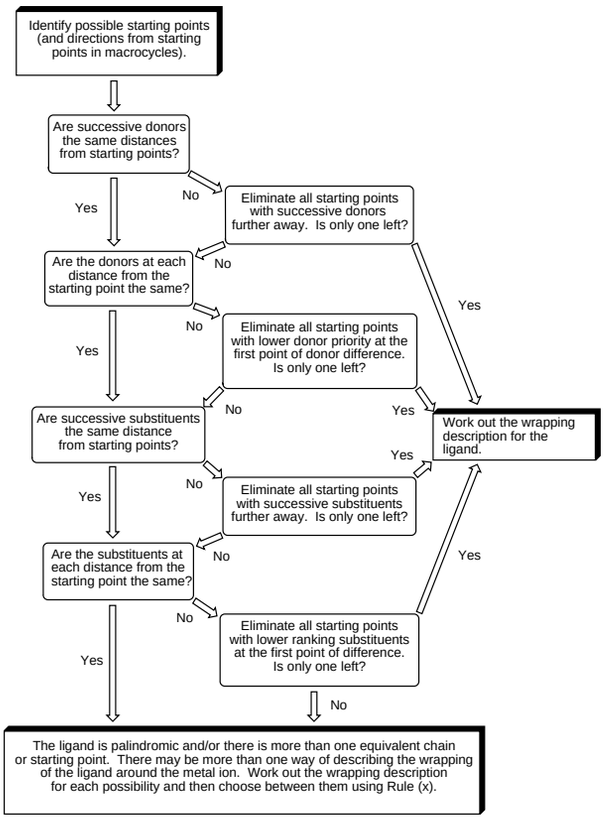

Fig. 11 A decision tree to assist in choosing the starting point (and direction) for the wrapping description

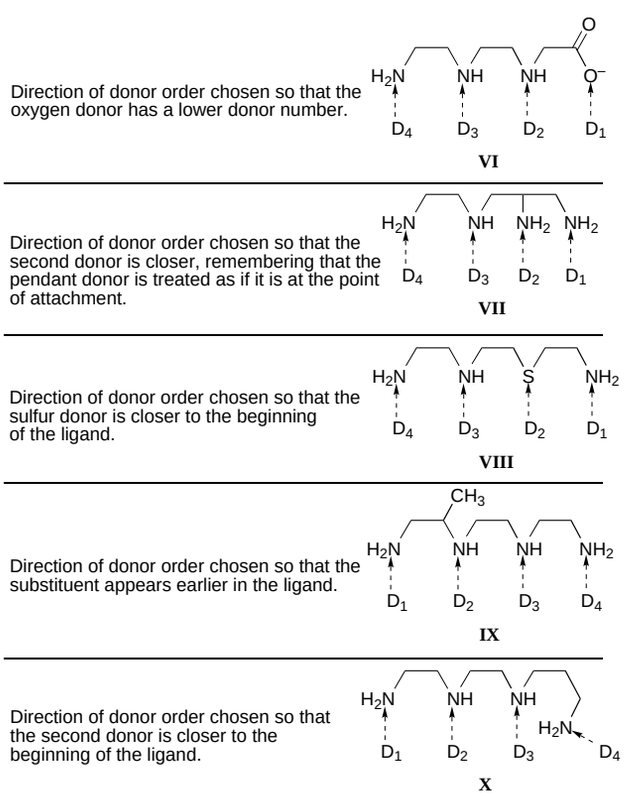

Fig. 12 Examples of donor order choice in backbone chains

locations and sizes of substituents are then considered, so that the chosen end will be closer to substituents (irrespective of their nature), or failing that will be that which is closer to the higher priority sidechain (according to the CIP rules) at the first point of difference. The presence of non-donating heteroatoms

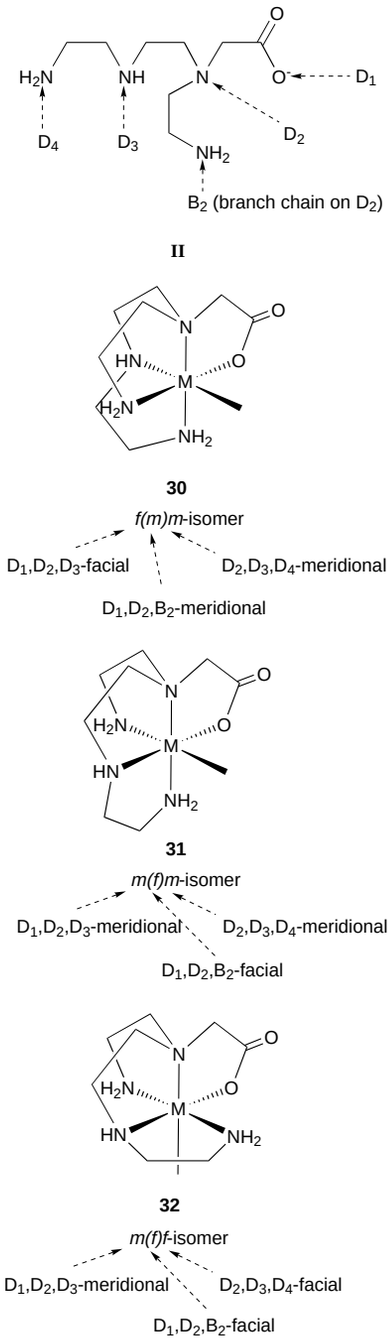

Fig. 13 Wrapping of sidechain donor groups

in a chain should be treated as a kind of substitution, with the assignment of relative priorities based on the CIP priority of the heteroatoms at that position in the structures of the chains being compared.

If the entire ligand (as opposed to just the donor groups) is palindromic, there may be two sequences of *m*/*f* tridentate segment descriptors available to describe the complex using that backbone chain, but if so they will be the reverse of one another [Rule (x) indicates which of the two possibilities should be used to describe the complex]. Some examples of choosing the donor order are shown in Fig. 12.

(**iv**) A pendant donor group attached to the parent chain through a donor group should be represented by the appropriate segment descriptor(s) to describe the location of the branched chain donor. The descriptor should be placed in brackets immediately after the descriptor for the ligand segment in which the point of attachment is the central donor. An example of how a branched chain donor is treated is illustrated in Fig. 13. The spatial relationship between the locations of the

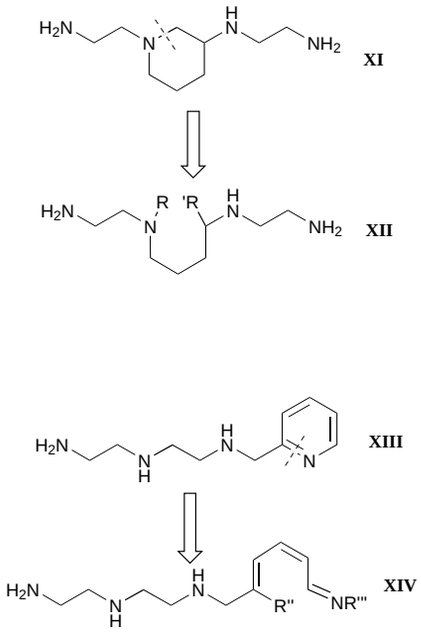

Fig. 14 Treatment of cyclic structures by making a virtual cut across the bonds shown, in order to create the longest possible chain (that contains the greatest number of donors)

branch donor (B_2), the substituted donor (D_2), and the donor immediately preceding it (D_1) is determined as being either meridional or facial, in the usual way, and the symbol (*m* or *f*) placed in brackets after the descriptor associated with the substituted donor.

Ligands containing cyclic structures, including macrocycles, are dealt with by finding (and describing the wrapping of) the longest linear chain of those which contain the largest number of donor atoms (including pendant donors if they are attached to the chain between two other donors). This process amounts to comparing (using Figs. 9 and 11) all the possible linear chains that can result from cutting the cyclic structure at different points. Any remaining fragments are treated as substituents of the appropriate type (*e.g.* in Fig. 14, **XI** is treated as **XII**, and **XIII** as **XIV**).

The backbone chain of macrocyclic ligands where the pendant donors are attached to the macrocycle will start and/or finish at the end of the pendant arm, as this will either include a larger number of donors in the backbone chain, or the backbone chain will be longer (as the arm to which the pendant group is attached now becomes part of a chain). Otherwise, the starting point will be one of the donors in the macrocycle with the highest elemental priority. The two directions of movement around the macrocyclic ring from each possible starting donor must then be compared with each other, based on donor location and type, followed by substituent location and type. The highest ranking direction of movement will define which starting point should be used. The decision tree in Fig. 11 can be used to assist in this process.

After the number of donors and length have been considered, preference is given to the starting point/direction combination which has a second donor (irrespective of what kind) closest to the starting point. The locations of successive donors in each combination can then be used to help choose the one with the highest ranking. If two starting point/direction combinations are equivalent in terms of donor locations, the preference should go to that with the higher priority donor at the first point of donor difference. If the donors are similarly distributed in two or more such combinations, priority goes to the one with the closest substituent, or, if the substituents in each starting point/direction combination are matched in terms of location, towards the higher CIP priority substituent at the first point of difference.

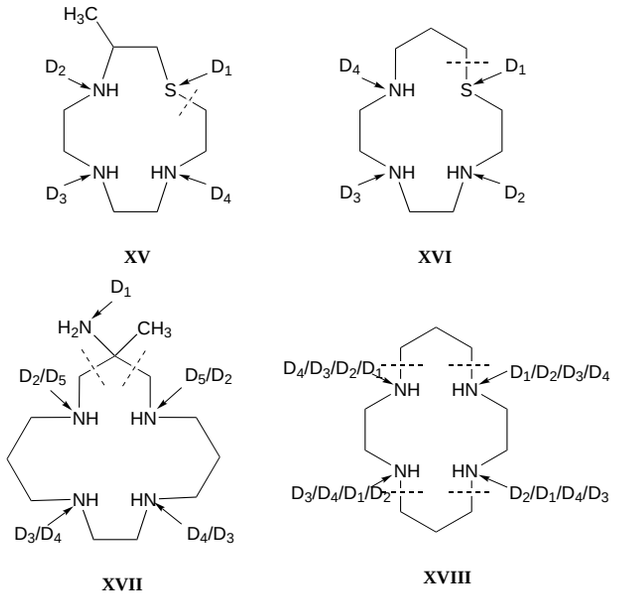

Fig. 15 Determining donor number in macrocyclic ligands. In the last two examples there is more than one equivalent starting point/direction combination. In **XVII** the right hand virtual cut gives rise to the anticlockwise donor sequence. In **XVIII** each of the four possible virtual cuts gives rise to different donor sequences, the donor sequence of the first (top right virtual cut) being given by the left hand symbol in each sequence of four, and the second (bottom right virtual cut) being given by the second donor symbol in the sequence, and so on

If the ligand is sufficiently symmetrical that there is more than one possibility for starting donor and/or direction around the macrocycle, there may be more than one valid sequence of ligand segment descriptors available to describe the wrapping of the ligand around the metal ion. In this case Rule (x) will apply, which requires the full wrapping description to be determined for each possibility.

Examples of choosing donor order and direction are shown in Fig. 15, and some examples of macrocyclic complexes with pendant arms are treated in Fig. 16.

Treatment of non-co-ordinated substituents on interior donor groups

Within the system described above the spatial arrangement of substituent atoms on the central donors of *m*-type segments needs to be described. In this nomenclature system we propose that: (**v**) the symbol *s* (for *syn*) is used as a subscript to indicate that the pendant substituent is pointed towards the higher ranking of the two donor groups that are co-ordinated out of the meridional plane being considered. The symbol *a* (for *anti*) is used as a subscript to indicate that the pendant substituent is pointed away from the higher ranking out-of-plane donor.

(**vi**) For this purpose, any donor that is part of the polydentate ligand will rank higher than a donor which is not. If both out-of-plane donors are part of the polydentate ligand the subscript *s* will refer to the isomer where the substituent points towards the donor group which was considered earlier in the wrapping description.

(**vii**) No subscript should be used when equivalent structures (or an enantiomer) are generated by placing the substituent in each of the two locations. In these cases, a twofold rotation of the complex about the bond between the metal and the substituted donor will often generate the structure with the substituent in the **other** spatial orientation. This kind of situation will occur when both the ligand and the folding sequence are symmetrical about the substituted donor, or when there is a cyclic structure in the ligand which gives rise to two equivalent choices of backbone chain (*e.g.* a ligand containing a piperazine ring where both nitrogen atoms are donor groups).

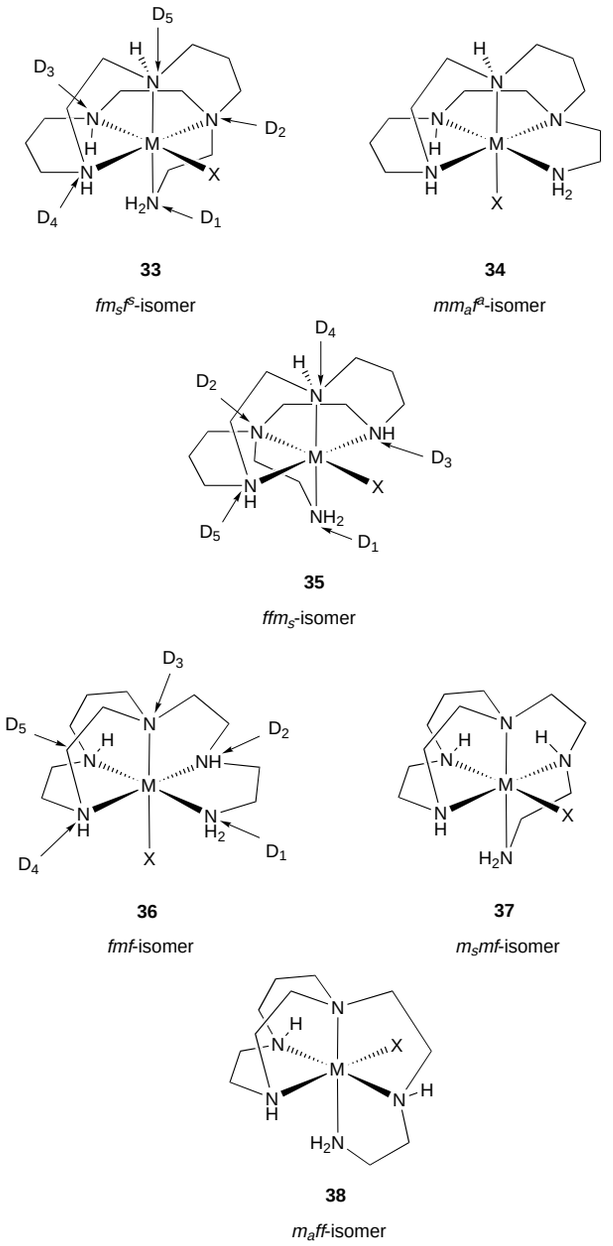

Fig. 16 Wrapping descriptions for pendant arm macrocycles

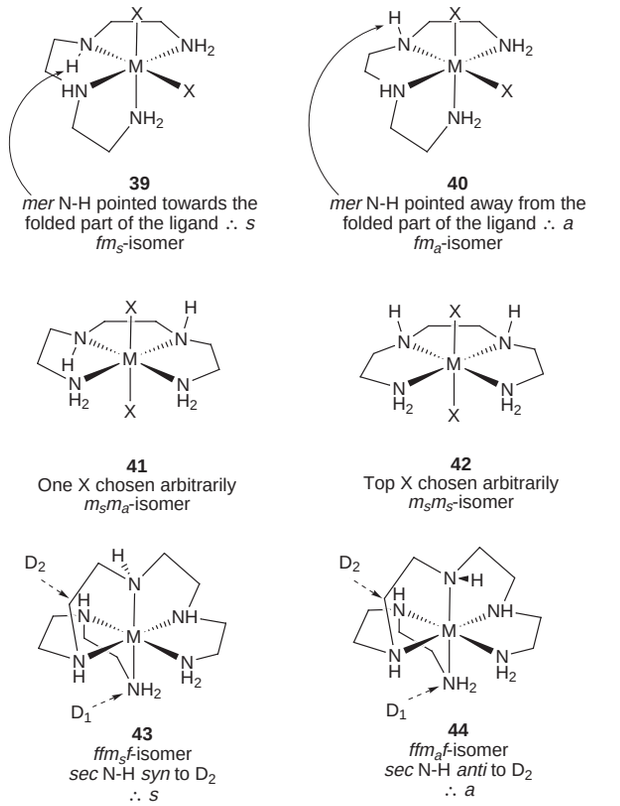

Fig. 17 Choice of *syn*/*anti* subscripts to indicate the locations of substituents on meridional donor groups. Alternative wrapping descriptions are possible for compounds **43**, fm_aff, and **44**, fm_sff, but these are eliminated according to Rule (x)

(**viii**) If the out-of-plane ligands are equivalent, but the different spatial locations of the substituent give different compounds, then the out-of-plane ligand *syn* to the substituent on the first meridional center should be chosen, and all *mer* units in the same plane subscripted with respect to that choice.

Fig. 17 illustrates the use of these subscripts to describe the spatial location of substituents on interior donor groups. Rule (viii) ensures that *meso* compounds, such as **20** and **42**, have only one valid folding description.

Treatment of non-co-ordinated substituents on terminal or pendant donor groups

Inequivalent substituents on the first or last donor groups in a chain, as well as those in pendant donor groups, may also be able to occupy different spatial locations with respect to the rest of the molecule. We propose that: (**ix**) the same symbols, *s* or *a*, be used to describe the position of the **lower** CIP priority substituent on a terminal or pendant donor group, in the same way as described for substituents on interior donor groups, except that they will be written as superscripts before the first and after the remaining descriptors of a chain, as required (Fig. 16, 18). The 'meridional plane' in this case will refer to the plane defined by the terminal donor, the metal ion, and the donor group adjacent to it in the chain or, in the case of a pendant donor, to the plane defined by the pendant donor, the metal ion, and the donor group preceding it in the chain.

Selecting between possible folding descriptions for a complex

The presence of pendant donors that are attached through another donor introduces the possibility that there may be more than one possible backbone chain, each with its own folding description. The same situation can arise with the two possible directions in palindromic ligands. Two examples are shown in Fig. 19, while compounds **43** and **44** are other examples. The folding descriptions for the different chains and/or directions may or may not be the same, so we need a convention by which we can choose a single description for the complex: (**x**) if there is more than one sequence of wrapping descriptions available for a complex, the description having the most *f* descriptors should be chosen. If there are two descriptions with the same number of *f* descriptors the sequence with the *f* descriptors as early as possible in the sequence should be chosen. Finally, if two wrapping descriptions differ only in terms of the subscripts and superscripts that describe substituent location, the one with *s* symbols earliest in the description should be chosen. The convention of using the description with the most facial units (or folds) as early as possible in the sequence is chosen in order to make it easier when dealing with the location of substituents. As described above, substituent location is described relative to folded parts of the ligand, so it may make it more convenient to have drawn such folded parts of the ligand as early as possible.

Fig. 20 provides some good examples of the application of Rule (x), where there are more than one possible starting point/direction combinations. There are four possible starting point/direction combinations available for all of the structures shown,

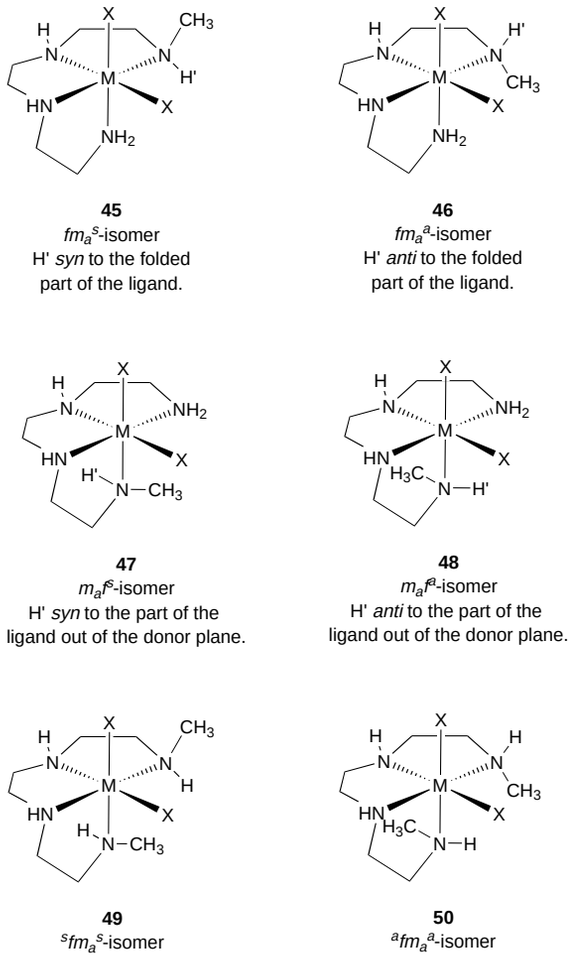

Fig. 18 Choice of *syn*/*anti* subscripts to indicate the locations of substituents on terminal donor groups. Note that the reversal of segment descriptors between, for example, **48** and **19** or **50** is caused by a change in donor order as a result of methylation

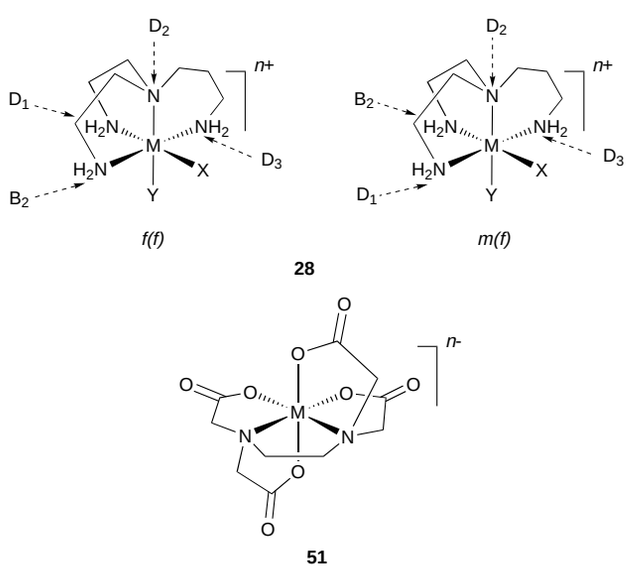

Fig. 19 Choice between multiple sequences. In describing **28**, D_1 and B_2 can be chosen in either way to give the wrapping sequences shown. By convention [Rule (x)] we choose the $f(f)$ designator to describe this complex. The complex $[M(edta)]^{n-}$ **51** could be described by any of the following sequences: $m(f)m(f)$, $m(f)f(m)$, $f(f)m(f)$ or $f(f)f(m)$. By convention, the last of these is chosen. Fewer sequences of ligand segment descriptors are possible if the arms become inequivalent (*e.g.* by replacing one or more acetate groups with propionate groups)

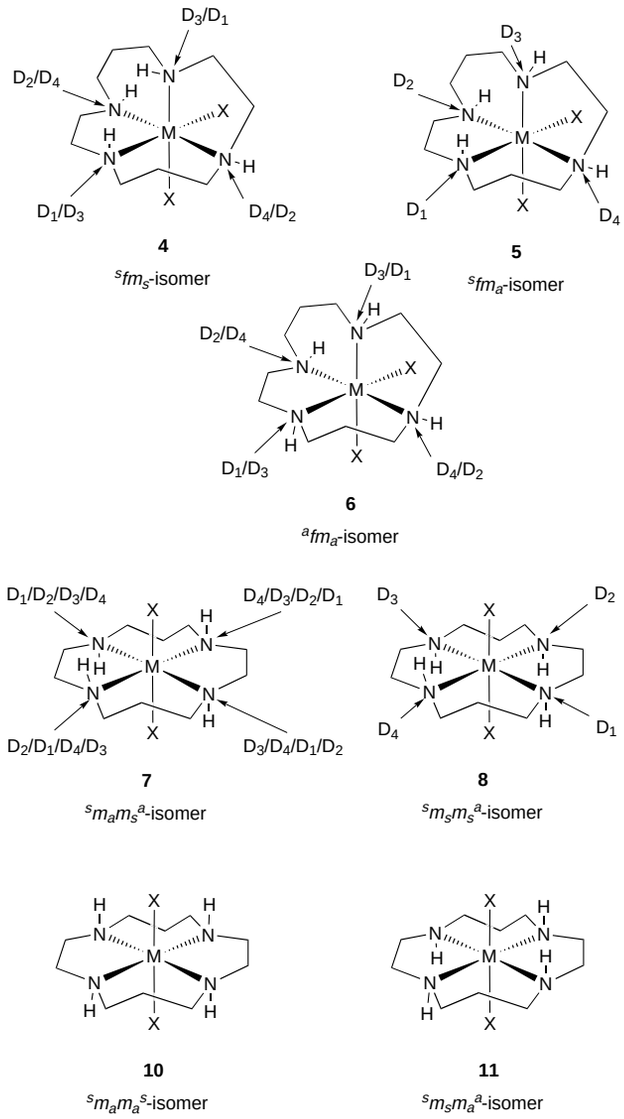

Fig. 20 Wrapping descriptions for macrocyclic complexes

due to the symmetry of the cyclam ligand. In the cases of structures **7**, **10** and **11** all four combinations for each isomer give rise to the same wrapping description. In structure **4**, on the other hand, two of the possible starting point/direction combinations can be described as m_sf^s isomers, and the other two as ^sfm_s isomers. Application of Rule (x) leads us to choose the latter description, which implies either of the two donor orders shown in the structure. All four possible combinations are available to structure **5**, leading to four different candidates for the folding description: m_sf^a, m_af^s, ^sfm_a and ^afm_s. Rule (x) leads us to the third of these as the descriptor for the complex. Finally, **8** is the $^sm_sm_s^a$ isomer, where the other descriptions (which have the *anti* indicator earlier) are eliminated using the rule. If the ligand were made less symmetrical by some form of substitution then some or all of these folding descriptions would represent different isomers.

Location of other ligands in relation to the polydentate

(**xi**) The location of all but the lowest priority of the other ligands in the complex is described, where necessary, by letter codes to indicate the kind of donor to which they are *trans*: *p*, primary donor; *s*, secondary; *t*, tertiary; *u*, unsaturated; *x*, another ligand (l for ligand is not used in order to avoid any confusion with the symbol for a laevorotatory compound). Complexes of pentadentate ligands will have only one extra ligand, and only one site in which it can be placed, so therefore

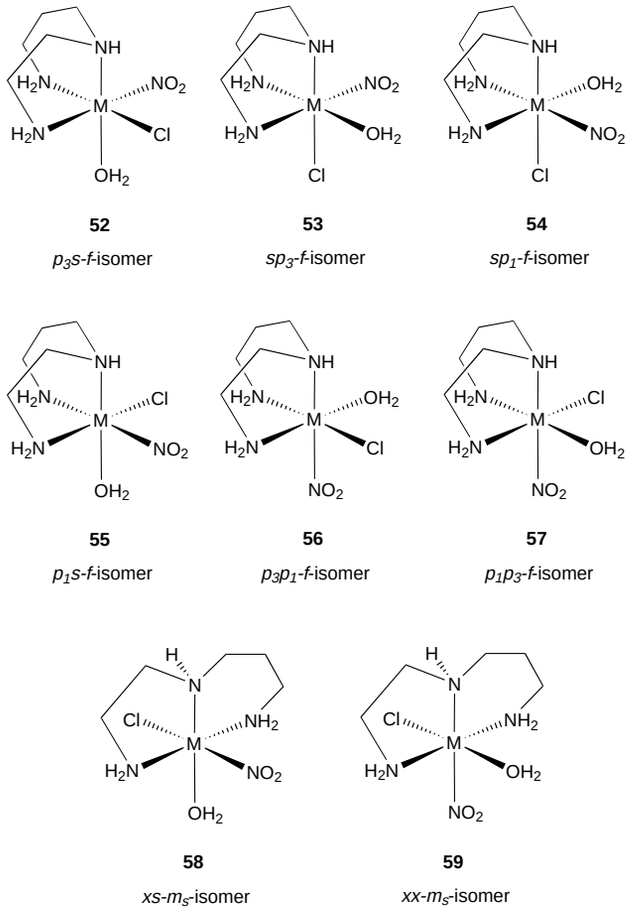

Fig. 21 Some of the isomers available in complexes of a tridentate ligand and three monodentate ligands. The CIP priority order is $Cl > NO_2 > OH_2$, so that the first prefixed letter refers to the location of the Cl ligand and the second to that of the NO_2 ligand. The subscripts in the ligand location portion of the prefix are used in order to resolve any ambiguity that may arise if the donor number of the *trans* ligand is not specified

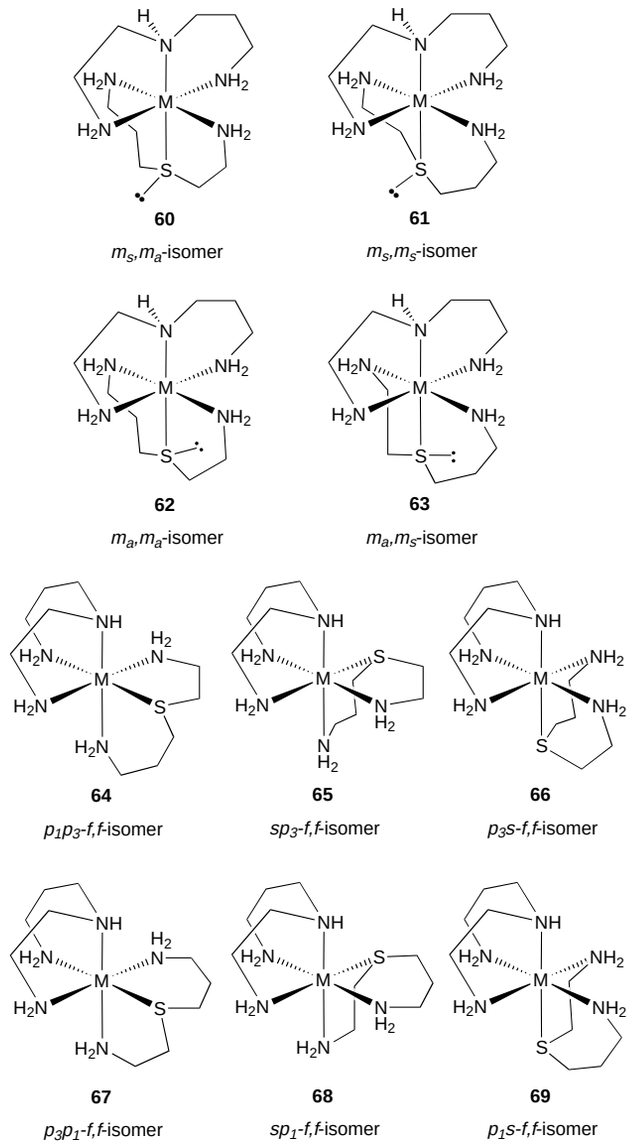

Fig. 22 The special case of complexes containing two tridentate ligands

no notation is required in this case. Usually the locations for the two remaining ligands in a complex of a tetradentate ligand can be unambiguously defined using one letter from the *p*, *s*, *t*, *u* notation. If the other ligands are the same there is no need to define their locations.

Octahedral complexes of tridentate ligands have three coordination sites occupied by other ligands. If the tridentate has the *fac* configuration it is necessary to specify where two of these additional ligands are placed in relation to the rest of the complex. Consistent with the conventions introduced so far, we propose that the *p*, *s*, *t*, *u* notation can be applied for the two highest ranking ligands, in order, as shown in Fig. 21. The possibility that two of the other ligands may be *trans* to one another, rather than *trans* to one of the donors of the polydentate ligand, leads to the need for another letter code, *x* (for extra ligand), in order to describe this situation.[19] If there are two of the lower priority ligands in the complex only one ligand position descriptor will be required, and none is needed if all three are the same.

In some cases, however, both sites that are occupied by the other ligand(s) may be *trans* to donor groups of the same type.

(**xii**) Ambiguity in the *p*, *s*, *t*, *u*, *x* notation can be resolved by adding the donor number of the *trans* group as a subscript, where necessary (Fig. 6). The donor number refers to the order in which the donor is treated in the *m*/*f* folding instructions (which is in turn derived from the rules described above).

If there is more than one possible description for a complex, and Rule (x) does not allow them to be distinguished and prioritised, then the extra ligand location code can be used: (**xiii**) the priority order of the descriptors will be $p > s > t > u > x$. The code which contains more higher priority letters should be chosen. If the same letters are used in the codes for the wrapping descriptions, the one with the higher priority letter first is chosen. If the letter codes for two descriptions are the same, the one with the lowest donor number subscript at each successive place should be chosen.

Special case: complexes containing two tridentate ligands

One other possibility needs to be considered for tridentate ligands, and that is the case where the complex may contain two tridentates, not necessarily the same. Such a complex will either be meridional or facial, so that only one *m*/*f* descriptor is required in theory. However, each of the tridentate ligands may have substituents on the donor atoms for which we may need to specify locations in relation to the rest of the molecule. For this reason, an *m*/*f* descriptor is used for each ligand in the complex, and subscripts and superscripts added to indicate substituent location for each ligand, according to the rules outlined above. The higher priority tridentate ligand should be identified (using the rules, Figs. 9 and 11), and its description placed ahead of that for the other ligand, with the two separated by a comma.

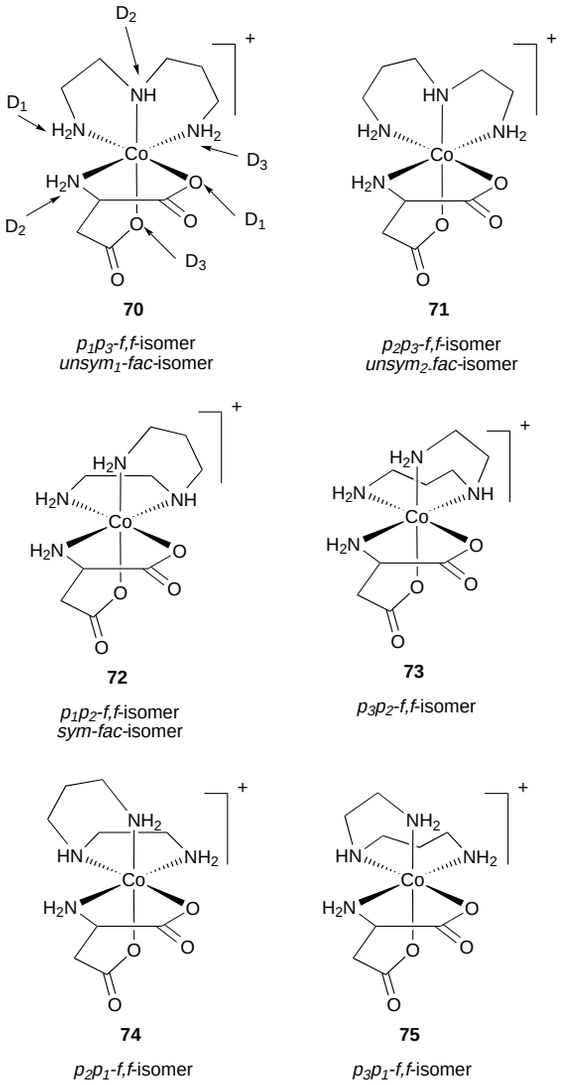

Fig. 23 Isomers of the $[Co(2,3\text{-tri})(S\text{-asp})]^+$ ion

If we ignore the spatial locations of substituents on donor groups, there is only one possible *mer* geometrical isomer, but, depending on the ligands involved, there may be up to six possible *fac* isomers that differ in the relative locations of the donor groups in the two ligands (Fig. 22). In this case it is necessary to choose the higher ranking tridentate ligand (using the chain selection rules outlined above) as the base against which the orientation of other ligand can be described. The *p*, *s*, *t*, *u* notation can then be used to describe the positions of the first and second donors (using the donor order derived using the rules above, Fig. 11) of the second ligand in relation to the donors in the base ligand. If there is more than one possible description, which may occur if either ligand is symmetrical about one of the donors (thereby giving more than one possible donor order), the descriptions should be compared and the one with more high priority descriptors should be chosen, according to Rules (x) and (xiii).

An example of this kind which can be found in the literature is that of the $[Co(2,3\text{-tri})(S\text{-asp})]^+$ ion,[21] for which, since the tridentate *S*-aspartate anion must co-ordinate in a facial configuration, there are six isomers possible (Fig. 23). Three of these have been characterised, and have been described as *sym-fac*, *unsym*$_1$-*fac* and *unsym*$_2$-*fac*, but it is not easy to correlate the isomer descriptors to any particular structure without additional information. The rules we have outlined allow a unique and decodable isomer enumeration. The aspartate ligand is chosen as the backbone chain (owing to the higher elemental priority of the oxygen donor atoms), and the first two donors of the triamine ligand (those of the 1,2-diaminoethane unit) can be located as being *trans* to the first, second or third primary donors of the aspartate ligand (using the donor order that is derived using the rules above).

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