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Cobalt(II) complexes of pyridazine or triazole containing ligands: spin-state control

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Dedicated to Professor George M. Sheldrick (Georg-August-Universität Göttingen) on the occasion of his 60th birthday

Contents

Abstract

Structurally characterised cobalt(II) complexes containing pyridazine, triazole or triazolate ligands are the subject of this review. Firstly a brief introduction to Schiff-base macrocyclic chemistry is given and then the crystal structures and magnetic properties of pyridazine-containing cobalt(II) complexes are discussed, focussing on macrocyclic complexes. There follows a discussion of the crystal structures, as well as the magnetic behaviour where known, of cobalt(II) complexes containing the triazole moiety in a N^1,N^2-bridging fashion. Finally an overview of reported complexes where the triazole unit has been incorporated into a Schiff-base macrocyclic framework is provided. None of these triazole-containing macrocyclic complexes has been structurally characterised.

Keywords: Cobalt(II) complexes; Pyridazine; Triazole; Triazolate; Magnetochemistry

1. Scope

This short overview briefly covers the cobalt(II) coordination chemistry which has resulted from the recent introduction of the new heterocyclic head unit, 3,6-diformylpyridazine [1,2], into Schiff-base macrocyclic chemistry (Section 3). Then triazole- and triazolate-N^1,N^2-bridged cobalt(II) acyclic complexes are reviewed (Section 4.1) as background to Section 4.2 which deals with the recent introduction of the heterocyclic head units 3,5-diformyl-1,2,4-triazole [3] and 3,5-diacetyl-1,2,4-triazole [3–5] into Schiff-base macrocyclic chemistry.

Pyridazine-bridged cobalt complexes have recently been reviewed [6] so the main focus of this paper will be on the triazole- and triazolate-N^1,N^2-bridged complexes. It should be noted that triazole moieties have also been incorporated into phthalacyanine-type monometallic macrocycles [7], and small macrocycles for which no structurally characterised complexes have yet been reported [8], however, these ligand types are not covered here. As there are, to date, no published examples of structurally characterised cobalt (or indeed any other metal) complexes of triazole- or triazolate-containing Schiff-base macrocycles [9], a review of the few related

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acyclic triazole- and triazolate-N^1,N^2-bridged cobalt complexes which have been structurally characterised is provided, before the published examples of *macrocyclic* Schiff-base metal complexes are reviewed. A brief introduction is provided to Schiff-base macrocycle synthesis (Section 2) but the reader is referred to earlier reviews for more detailed introductions to this general area and in depth reviews of pyridine and phenol based head units [10] along with a recent overview of thiophenolate based head units [11]. Macrobicycles, or cryptands, have also been reviewed recently [12].

2. Introduction to Schiff-base macrocycle synthesis

Schiff-base macrocycles are generally prepared by the metal templated reaction of a suitable dicarbonyl head unit and diamine lateral unit (Fig. 1) [10], although there are some metal-free syntheses [13]. The presence of the metal ion promotes the cyclisation reaction by: (a) enhancing the polarisation of the carbonyl bond and thereby facilitating nucleophilic attack by the amine; (b) the kinetic template effect (aiding in directing the steric course of the reaction); and (c) the thermodynamic template effect (draining the equilibrium and stabilising the macrocycle as the metal complex).

The success or otherwise of the cyclisation reaction is usually readily identified by analysis of the infrared spectrum of the product: this should contain no absorptions due to primary amine or carbonyl groups but should have a new band due to the presence of the imine bonds. Depending on the metal ion template used, differing ring sizes can be formed during the cyclisation reaction. If one dicarbonyl moiety reacts with one diamine moiety a [1 + 1] macrocycle results, if two dicarbonyl moieties react with two diamine moieties then a [2 + 2] macrocycle results (Fig. 1), and so on. Unless single crystals suitable for X-ray diffraction can be obtained it can be non-trivial to identify what ring size has been formed (due to ready fragmentation of these complexes, mass spectrometry is not always as helpful as one might expect in this regard).

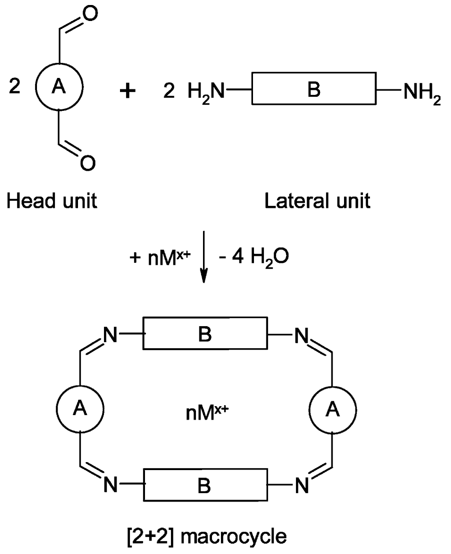


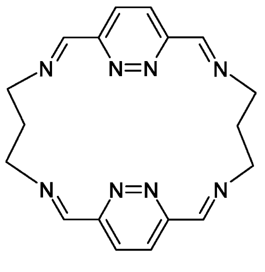
Fig. 1. Schematic representation of a metal ion templated Schiff-base macrocycle synthesis.

The keys to developing new Schiff-base macrocycles are: (a) preparing and/or purchasing suitable dicarbonyl head units and diamine lateral units; (b) finding suitable reaction conditions for the cyclisation reaction; (c) finding suitable reaction conditions for any subsequent transmetallation reactions. In general, much effort must be devoted to the preparation of, usually, the head units, with the diamine lateral components used being commercially available in most cases [14]. Once this has been achieved, the development of suitable cyclisation protocols is of varying difficulty. Usually one can identify a couple of potentially suitable metal ion template(s) on the basis of the macrocycle ring size, donor atoms and the geometry these will provide. Often these template ions will not be transition metal ion(s) but rather metal ions such as lead(II), barium(II) or silver(I), which will be replaced later on, in a transmetallation reaction. In some cases the appropriate metal ion template is readily identified and works well under fairly standard conditions (room temperature or reflux; reagent grade alcohol or acetonitrile reaction solvents; in air) whilst in other cases the required cyclisation conditions are rather demanding. For example, it may be that only one combination of reaction conditions works at all, or that particularly dry conditions are required. In such cases, unless one is fortunate enough to try the winning combination early on, this will require a significant amount of work. Finally, given that usually the cyclisation is carried out on non-transition metal ions, transmetallation reactions are required to replace these metal ions(s) with the transition metal ions of interest. This is usually straightforward, unless the precursor complex is highly insoluble.

3. Cobalt(II) complexes of pyridazine-containing ligands

Cobalt and copper complexes of pyridazine- or phthalazine-containing ligands were reviewed recently [6]. Here our attention will focus on those cobalt(II) complexes featuring bridging pyridazine, or indeed phthalazine, moieties. Of these, those *acyclic* complexes for which magnetic studies have been reported have all been in the *high spin* state and are only weakly antiferromagnetically coupled [15,16]. Prior to our work there were only two examples of cobalt complexes of macrocyclic pyridazine- or phthalazine-containing ligands, neither of them fully characterised [17,18]. Indeed, very few such complexes, cyclic [19–21] or acyclic [16,22], have been structurally characterised to date.

An overview of the introduction of 3,6-diformylpyridazine [1,2,23] into Schiff-base macrocyclic chemistry was published recently [6]. Here attention is focussed on the family



L¹

Fig. 2. The pyridazine-containing Schiff-base macrocyclic ligand L^1.

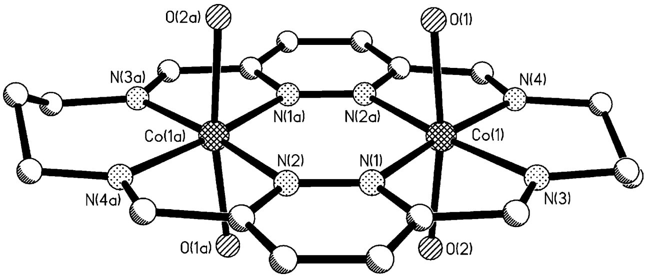


Fig. 4. Perspective view of the $[Co^{II}_2(L^1)(H_2O)]^{4+}$ cation.

of dicobalt(II) complexes of the pyridazine-containing macrocycle L^1 (Fig. 2) as this includes examples of low spin and spin crossover complexes as well as of high spin complexes [19–21].

Transmetallation of the lead complex, usually the [4 + 4] complex as it is somewhat more readily prepared than the [2 + 2] complex (i.e. L^1, Fig. 2) [2,23], gives the desired dicobalt(II) complex, $[Co^{II}_2(L^1)(CH_3CN)_4](ClO_4)_4$, as red, air stable crystals [19]. The structure determination showed that the pyridazine rings and the cobalt(II) ions are almost co-planar (Fig. 3). Detailed magnetic studies show that the complex is low spin at the low temperature of the X-ray data collection (170 K) with $-2J = -14.2$ cm^{-1} (average Co–N–N = 128.4°), but that there is a gradual incomplete spin transition starting to occur as the temperature is raised [21]. This was the first time that a pyridazine-bridged cobalt(II) complex had been observed to be other than high spin. It should perhaps be noted here that a spin transition had been observed previously, in a pyridazine-coordinated cobalt(II) complex, $[Co(3,3'\text{-bipyridazine})_3]X_2$ (where X = ClO_4 or BF_4), but that in this case the complex is mononuclear, there is no pyridazine bridging and the complex is actually more closely related to complexes such as bis(terpyridine)cobalt(II) [24].

$[Co^{II}_2(L^1)(CH_3CN)_4](ClO_4)_4$ has been used as a precursor complex for the preparation of a family of complexes in which the acetonitrile axial ligands have been replaced by a variety of other anions and molecules [21]. The introduction of four water molecules in place of the four acetonitrile molecules has a dramatic effect on the resulting complex, $[Co^{II}_2(L^1)(H_2O)_4](ClO_4)_4$. The structure of this orange, as opposed to deep red, complex is shown in Fig. 4. As for the acetonitrile adduct, the cobalt ions sit almost exactly in the N_4 basal plane. The complex is high spin at all temperatures studied, with $-2J = 19.2$ cm^{-1} (average Co–N–N = 124.6°).

Switching our attention to the replacement of the acetonitrile solvent molecules by anions, we reacted $[Co^{II}_2(L^1)(CH_3CN)_4](ClO_4)_4$ with NaNCO [21]. Regardless of whether 2, 3 or 4 equivalents of NaNCO were employed, orange crystals of $[Co^{II}_2(L^1)(NCO)_3]ClO_4$ were obtained. In this instance, despite a poor structure determination due to the marginal quality of the crystals, a new macrocycle conformation is clearly seen (Fig. 5). Instead of the very flat macrocycle conformation observed in the previous two structures, here it has folded in order to accommodate a single N-bridging cyanate anion. A similar conformation was observed for a dimanganese(II) complex of L^1 [2]. As expected, the folding of the macrocycle

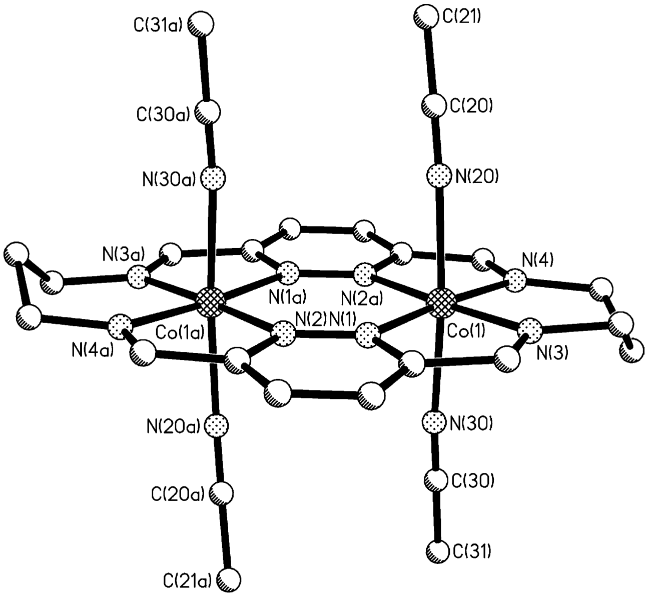


Fig. 3. Perspective view of the $[Co^{II}_2(L^1)(CH_3CN)]^{4+}$ cation.

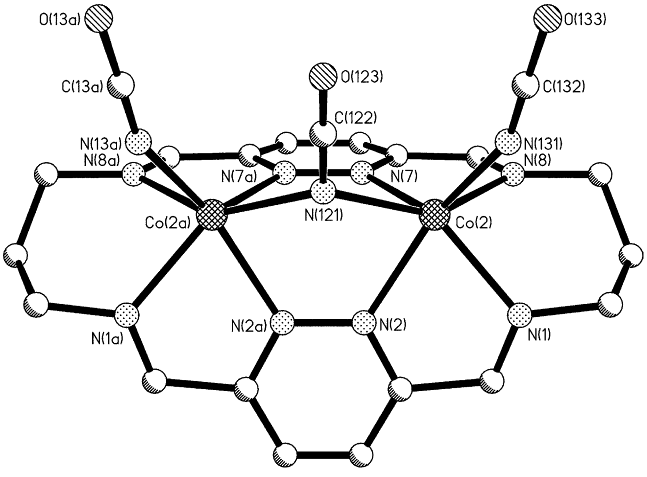


Fig. 5. Perspective view of the $[Co^{II}_2(L^1)(NCO)_3]^{+}$ cation.

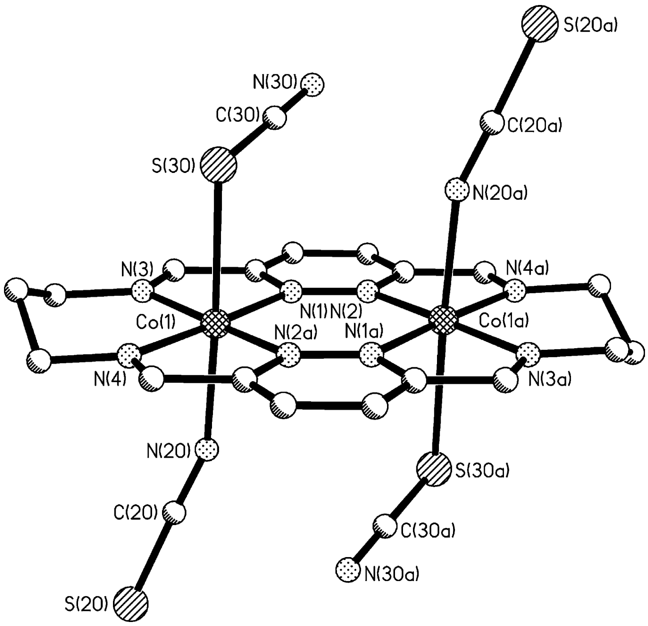


Fig. 6. Perspective view of $[\mathrm{Co}_2^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_2(\mathrm{SCN})_2]$. S-bound NCS^- has been observed once before for cobalt(II), in cobalt(II) thiocyanate trihydrate [51].

impacts on the efficiency of the antiferromagnetic exchange interaction between the two high spin cobalt(II) centres, with the $-2J$ value dropping to 7.5 cm^{-1}.

Finally, diffusion of a solution of $[\mathrm{Co}_2^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{CH}_3\mathrm{CN})_4](\mathrm{ClO}_4)_4$ into a solution of NaSCN results in almost black crystals of $[\mathrm{Co}_2^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_2(\mathrm{SCN})_2]$ [20]. The flat macrocycle conformation is once again observed (Fig. 6). The plane of the pyridazine ring intersects the N_4 basal plane of the cobalt(II) ion at an angle of only 3.3°. Detailed magnetic studies revealed that this complex (average Co–N–N = 128.9°) is low spin at low temperatures ($-2J = -11.7$ cm^{-1}) but at higher temperatures undergoes a gradual and incomplete spin transition [20,21]. This complex, and the acetonitrile adduct, are the first examples of dicobalt complexes which exhibit both a LS⇔HS spin transition and exchange coupling.

In summary, fine tuning of the spin state of the two cobalt(II) ions encircled by the pyridazine-containing Schiff-base macrocycle L^1 is possible, and gives rise to high spin, low spin and spin transition cobalt complexes of this macrocycle. Antiferromagnetic exchange is a feature of all of the complexes. For the flat high spin complexes the $-2J$ values fall in the range 19.2–20.5 cm^{-1}, with the folded high spin complex exhibiting a lower value, 7.5 cm^{-1}. The flat complexes for which the low spin region was fitted gave $-2J$ values in the range 10.2–14.2 cm^{-1}.

4. Complexes of triazole-containing ligands

The coordination chemistry of triazole ligands was recently comprehensively reviewed by Haasnoot [25]. The majority of complexes prepared to date are copper complexes. Thompson and co-workers have pointed out that these studies with copper ions indicate that the superexchange capacity of the neutral 4-amino-triazole [26] and the anionic triazolate [27] bridging moieties are similar, with both resulting in dicopper(II) complexes with $-2J$ values in the range 200–244 cm^{-1} [28]. Further, they point out that triazole and triazolate mediate exchange less efficiently than pyrazole, due to ‘the presence of the extra electronegative nitrogen donor in the triazole ring, which has the ability to polarize spin within the triazole ring itself and thus limit exchange’ [28]. Finally, and importantly in the context of this review, they also pointed out that triazole and triazolate bridges diminish the antiferromagnetic exchange in copper(II) complexes in comparison with pyridazine and phthalazine bridged copper(II) complexes (examples of the latter type which were included in this paper have $-2J$ values in the range 489–545 cm^{-1}). The changes in Cu–N–N angles that result from the presence of the five-membered (Cu–N–N ca. 134°) versus six-membered (Cu–N–N ca. 126°) rings also impact in this case. It should be noted that the complexes being compared in drawing the above conclusions all contained fairly flat copper-heterocycle moieties [28].

The ligand field strength of triazoles is just in the right range for iron(II) to give spin-crossover compounds. It has been found that the crossover temperature can be fine-tuned by the other ligands and ranges between 100 and 400 K [25]. Exploiting this fact, Kahn and co-workers have presented some very interesting systems containing polymeric Fe-triazole chains [29]. The iron(II) centers are octahedrally coordinated and the neighbouring metal centers are bridged by three triazole units. These complexes exhibit spin crossover with hysteresis, as is desired for the development of memory devices, as well as a colour change from violet (LS) to white (HS). One particularly interesting complex has a wide hysteresis loop occurring close to room temperature.

Despite this interest in triazole ligands in the development of new magnetic materials, surprisingly few cobalt [30–39], or indeed iron [40], complexes with bridging triazole or triazolate moieties have been reported. In this review we focus on the cobalt complexes which have been structurally characterised [31–38], all of which are of acyclic ligands (Section 4.1). This is followed by an examination of the recent introduction of the triazole head unit, in the form of diformyl- and diacetyl-triazole, into Schiff-base macrocycles (Section 4.2). No reports of structurally characterised complexes of such macrocyclic ligands have been published to date [9] so this section will consider all of the metal complexes reported to date.

4.1. Triazole-bridged cobalt complexes of acyclic ligands

The first structurally characterised dinuclear triazole-containing cobalt complex was described by Engelfriet et al. in 1980 [31]. Single crystals of $[\mathrm{Co}_2^{\mathrm{II}}(\mathrm{L}^2)(\mathrm{NCS})_4]\cdot 2.7\mathrm{H}_2\mathrm{O}$

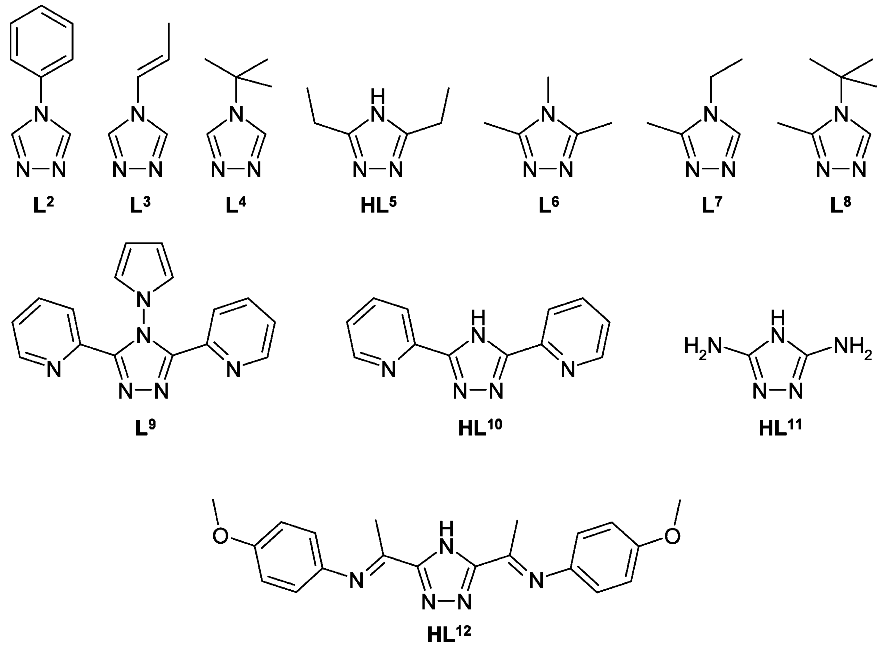


Fig. 7. The triazole-containing acyclic ligands L^2 (4-phenyl-1,2,4-triazole), L^3 (4-allyl-1,2,4-triazole), L^4 (4-*tert*-butyl-1,2,4-triazole), HL^5 (3,5-dimethyl-1,2,4-triazole), L^6 (3,4,5-trimethyl-1,2,4-triazole), L^7 (4-ethyl-3-methyl-1,2,4-triazole), L^8 (4-*tert*-butyl-3-methyl-1,2,4-triazole), L^9 (4-(1H-pyrrole-1-yl)-3,5-bis(pyridine-2-yl)-1,2,4-triazole), HL^{10} (3,5-bis(pyridine-2-yl)-1,2,4-triazole), HL^{11} (3,5-diamino-1,2,4-triazole) and HL^{12}.

were grown from an aqueous solution containing stoichiometric amounts of $Co(NO_3)_2\cdot 6H_2O$, 4-phenyl-1,2,4-triazole (Fig. 7) and NH_4SCN. In the structure the two Co^{II} ions are bridged by three phenyltriazoles (Fig. 8). Each metal ion is also coordinated to one nitrogen atom of an additional, monodentate, triazole and two N-donating thiocyanate anions, forming a slightly distorted octahedral coordination sphere around the cobalt(II) ion. The metal centers are separated by 3.907(1) Å. The water molecules are disordered in between the dimeric units and seem to be necessary to stabilise the structure. The compound is orange–red in colour, turning blue upon powdering as well as on heating up to 460 K, which these authors suggest indicates a change of coordination from octahedral to tetrahedral for the central metal ion. Unfortunately, no magnetic data were reported for this complex.

Replacing the phenyl group with an allyl group, Reedijk and co-workers were able to grow red single crystals of $[Co^{II}_2(L^3)_4(H_2O)(NCS)_4](H_2O)_2$ from a hot, aqueous solution containing the metal thiocyanate and the triazole in a 1:2 stoichiometric ratio (Fig. 7) [32]. Again the two Co^{II} centers are linked by three bridging triazole groups (Fig. 9)

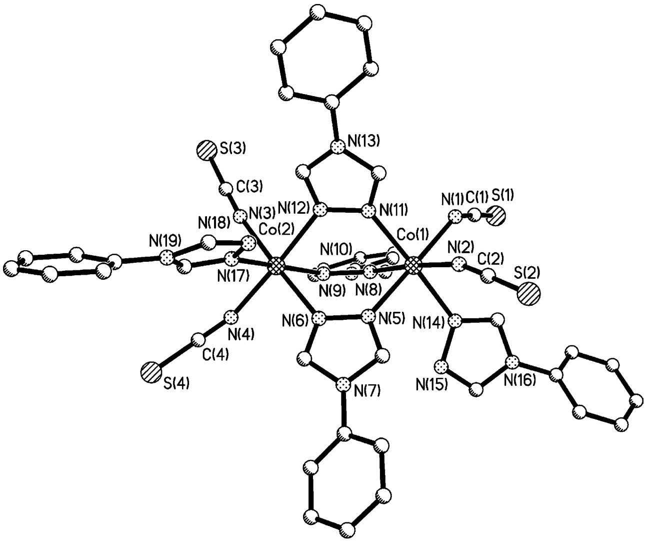


Fig. 8. Perspective view of $[Co^{II}_2(L^2)_5(NCS)_4]$.

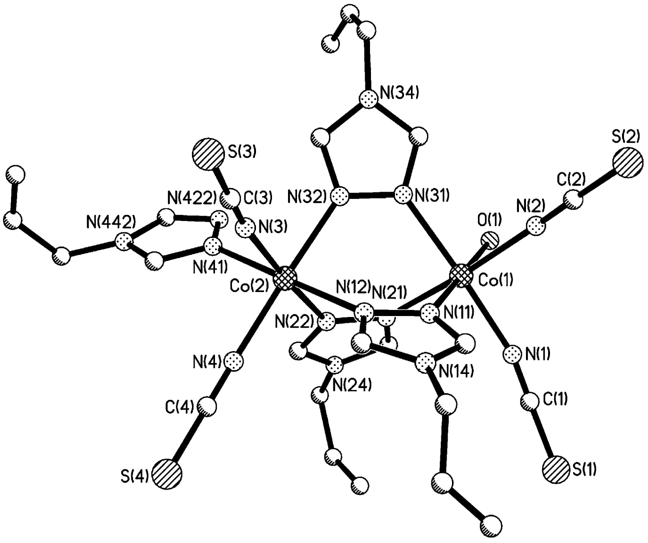


Fig. 9. Perspective view of $[Co^{II}_2(L^3)_4(H_2O)(NCS)_4]$.

and each cobalt center is coordinated by two N-donating thiocyanate groups. To complete the slightly distorted octahedra, one cobalt ion is furthermore coordinated to a monodentate triazole group, whereas the other is coordinated to a water molecule, resulting in unusual asymmetrical coordination. The metal centers are separated by 3.909(2) Å just like in the previous example. Hydrogen bonds to two additional water molecules stabilise the structure. The red complex turns blue on powdering or heating which, in this case, is suggested to be due to the loss of water molecules. The magnetic susceptibility data has been calculated assuming an Ising dimer with $S = {}^{1}/_{2}$. According to this, both high-spin cobalt ions are weakly antiferromagnetically coupled with $J = -10.9$ cm^{-1} ($g_{\parallel} = 7.16$). Also, a very weak ferromagnetic intermolecular exchange may occur, probably via intermolecular hydrogen bonds ($J = +0.02$ cm^{-1}).

The attempt to substitute a *tert*-butyl group in the 4-position of the triazole ring proved successful, and Reedijk and co-workers subsequently grew orange single crystals of $[\mathrm{Co}_3^{\mathrm{II}}(\mathrm{L}^4)_8(\mathrm{NCS})_4](\mathrm{SCN})_2(\mathrm{H_2O})_9$ from an appropriate aqueous reaction mixture (Fig. 7) [33]. This complex is the first example of a trinuclear triazole-bridged cobalt complex (Fig. 10). The cobalt ions are arranged linearly and are octahedrally coordinated, with the terminal ions being slightly distorted. The metal centers are separated by 3.8828(9) Å from each other, the middle one being located on the crystallographic center of inversion. The central cobalt ion is surrounded by six triazole units which provide triple triazole bridges to each of the two terminal cobalt ions. The octahedral coordination of each of the two terminal cobalt centers is completed by a monodentate 4-*tert*-butyl-1,2,4-triazole and two N-donating thiocyanate ions. Five of the nine water molecules in the structure are disordered. Magnetic studies on this compound have been performed in the range 2–35 K. The models used for simulating the experimental data include the Heisenberg model and the Ising model for a trimer. Because of the high zero-field splitting of Co(II), again a $S = {}^{1}/_{2}$ formalism rather than a $S = {}^{3}/_{2}$ is used, assuming that in this temperature range only the Kramers doublet of the lowest energy level is populated. The best fit is given by the Ising trimer equations ($J_{31} = 0$), resulting in $J = -13.2$ cm^{-1} and $g_{\parallel} = 7.8$. Upon applying pressure on the compound, it turns from orange to blue. In the same paper, another trinuclear cobalt compound, formulated as $[\mathrm{Co}_3^{\mathrm{II}}(\mathrm{L}^4)_4(\mathrm{NCS})_6](\mathrm{H_2O})_2$, is described. It has not been structurally characterised, but from the spectral data it is clear that the linearly arranged cobalt centers are now bridged by just two triazole groups each. The octahedron of the central cobalt ion is completed by two N-donating thiocyanate ions. Interestingly, the terminal cobalt ions are tetrahedrally coordinated, with their coordination spheres being completed by two N-donating thiocyanate ions each. This causes the dark-blue colour of the complex. Estimating the exchange coupling constant with the Ising model for this compound yields $J = -8.5$ cm^{-1} ($g_{\parallel} = 9.0$) which is in agreement with the expected weaker exchange when compared to the previous, triply triazole bridged, compound.

In the same year, 1985, Reedijk and co-workers also reported the crystal structure of $[\mathrm{Co}_3^{\mathrm{II}}(\mathrm{HL}^5)_6(\mathrm{NCS})_4(\mathrm{F}_2)](\mathrm{H_2O})_2$, which is the first structurally characterised cobalt complex containing a 3,5-disubstituted triazole (Fig. 7) [34]. Red single crystals were obtained by slow evaporation of the aqueous reaction mixture (Fig. 11). As seen above, the three metal ions are arranged linearly, with the central cobalt centre on the crystallographic inversion center. Here, however, the metal ions are bridged by two triazole units and one fluoride ion, leading to a separation of 3.3726(3) Å between nearest neighbour metal centers. The octahedral coordination sphere of the central Co$^{\mathrm{II}}$ is compressed along the F–Co–F axis. The distorted octrahedral coordination of the terminal Co$^{\mathrm{II}}$ centers is completed by one monodentate N^1-triazole unit and two N-donating thiocyanate ions. The water molecule is well resolved and forms a strong hydrogen bond to the H-N^4 position of one triazole bridge; by symmetry the second water molecule does the same on the other side. Additional hydrogen bonding interactions are present and the sum of all of these interactions is believed to be essential for the stabilisation of the structure. Magnetic studies have been performed between 4 and 80 K. Again, the best fit has been obtained by solving the Ising $S = {}^{1}/_{2}$ type of Hamiltonian yielding $J = -17.4$ cm^{-1} ($g_{\parallel} = 8.23$). Although the analysis of the magnetic behaviour is only

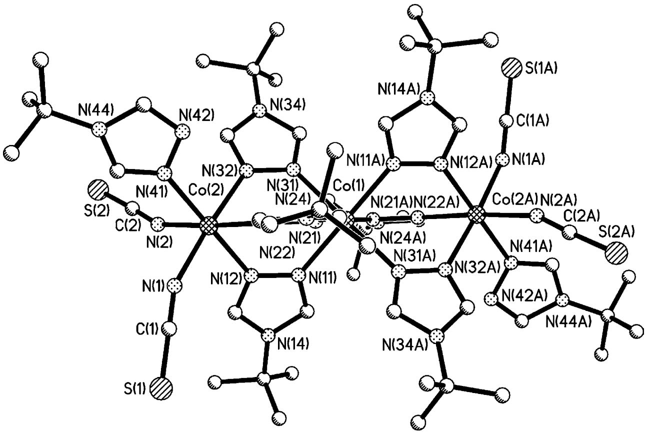


Fig. 10. Perspective view of the $[\mathrm{Co}_3^{\mathrm{II}}(\mathrm{L}^4)_8(\mathrm{NCS})_4]^{2+}$ cation.

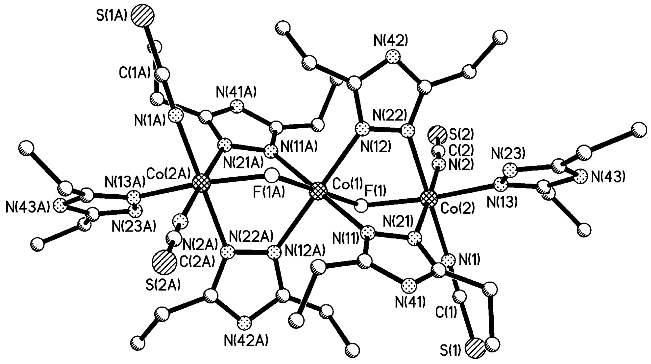


Fig. 11. Perspective view of $[\mathrm{Co}_3^{\mathrm{II}}(\mathrm{HL}^5)_6(\mathrm{SCN})_4(\mathrm{F})_2]$.

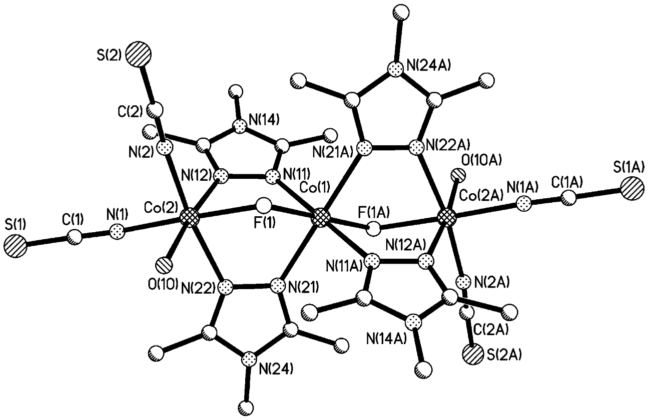


Fig. 12. Perspective view of $[\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^6)_4(\mathrm{SCN})_4(\mathrm{F})_2(\mathrm{H_2O})_2]$.

approximate, one can conclude that by replacing a triazole bridge with a bridging fluoride anion the antiferromagnetic exchange can be increased.

One year later, in 1986, Reedijk and co-workers published a second fluoride bridged cobalt complex, in which they changed the substitution pattern on the triazole ring to 3,4,5-trimethyl [35]. The complex $[\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^6)_4(\mathrm{NCS})_4(\mathrm{F})_2(\mathrm{H_2O})_2](\mathrm{H_2O})_4$ is obtained as dark-red crystalline material from the aqueous reaction mixture (Fig. 7). Again, the structure is centrosymmetric, forming a linear Co···Co···Co chain (Fig. 12). Similar to the previous example, the two neighbouring cobalt ions are bridged by two triazole units and one fluoride anion, causing the octahedral coordination sphere of the central metal to be compressed along the F–Co–F axis. The terminal octahedra are each completed by two N-donating thiocyanate ions and one water molecule. This is the first example in which a monodentate triazole is not coordinated at each of these termini. The Co···Co distance (3.4015(3) Å) is slightly longer than in the, very similar, previous example. Another important difference between the two structures is the hydrogen bonding pattern. In this compound the bridging fluoride anion is strongly hydrogen bonded to an uncoordinated water molecule, whereas in the previous compound the fluoride anions are not involved in the hydrogen bonding. The magnetic behaviour of this compound has been studied. The best fit to the experimental data was again obtained by applying an Ising trimer model ($S = {}^1/_2$), resulting in $J = -7\ \mathrm{cm}^{-1}$ and $g_{\|} = 8.23$. From the plot of both the theoretical fit and the experimental data against temperature it is obvious that the Ising trimer formalism with $S = {}^1/_2$ fails at higher temperatures ($T > 10$ K). As suggested by these authors, possible reasons for this include neglecting the perpendicular magnetic susceptibility, a breakdown of the spin ${}^1/_2$ approach at higher temperatures, or an inappropriate choice of the Hamiltonian set, the last of these being the most likely reason. The Hamiltonian set chosen is only appropriate in the case where the metal centers have equivalent coordination spheres, which is obviously not the case here. Also the $S = {}^1/_2$ approach for Co(II) is only appropriate for a high zero-field splitting (which is usually the case) and at low temperatures. This problem is representative for all of the trinuclear cobalt complexes discussed here.

In 1987 Haasnoot and co-workers introduced the first trinuclear cobalt complex based on an asymmetrically substituted triazole [36]. Orange crystals of $[\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^7)_6(\mathrm{H_2O})_6][\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^7)_8(\mathrm{H_2O})_4](\mathrm{CF_3SO_3})_{12}(\mathrm{H_2O})_8$ were grown from an aqueous solution containing cobalt triflate and the triazole component (Fig. 7). Unfortunately, the quality of the structure is very poor, because of a high level of disorder, yielding a final R_1 value of only 23%. Therefore, bond lengths and angles cannot be discussed. The two trinuclear complexes are independent, but both consist of a linear Co···Co···Co chain with the neighbouring cobalt centers being connected by three bridging triazole units (Fig. 13). All of the cobalt centers are octahedrally coordinated and the two independent complexes differ in the completion of the octahedron for the cobalt centers at the termini. The terminal metal ions are coordinated to three water molecules in one complex, whereas they are coordinated to two water molecules and one monodentate triazole in the other complex. The orientation of the asymmetric triazole units is remarkable: in the complex terminated by two water molecules and one triazole unit, all of the methyl groups of the bridging triazoles point towards the termini of the complex whereas in the other complex two of the six methyl groups of the bridging triazoles

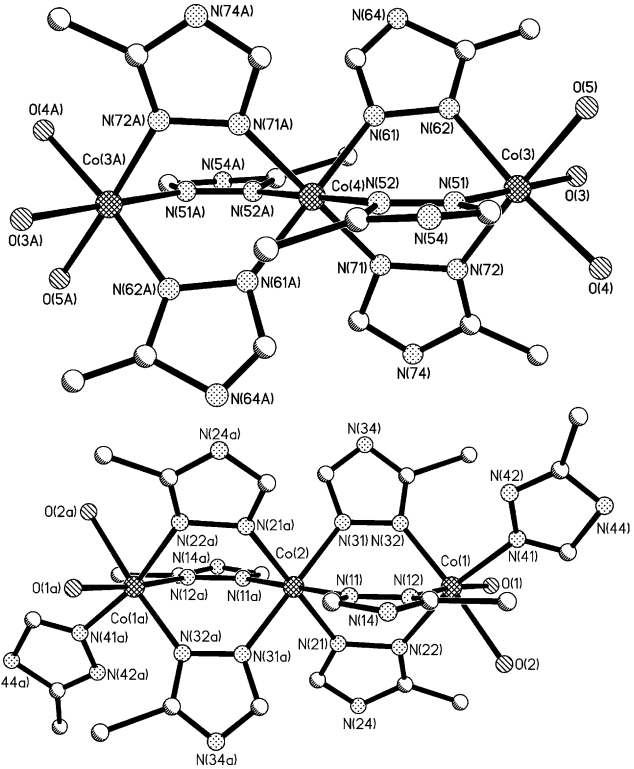


Fig. 13. Perspective view of the $[\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^7)_6(\mathrm{H_2O})_6]^{6+}$ cation (top) and the $[\mathrm{Co}^{\mathrm{II}}_3(\mathrm{L}^7)_8(\mathrm{H_2O})_4]^{6+}$ cation (bottom). The coordinates were typed in from the information given in Ref. [36], the ethyl groups were omitted for clarity.

point towards the central cobalt ion. The two corresponding triazoles are positioned in *trans* sites about the central Co^{II} atom. The triflate anions are highly disordered and this appears to be the main reason for the poor *R* value. The magnetic susceptibility of the compound has also been studied and could be fitted to a Heisenberg Hamiltonian with $S = {}^{1}/_{2}$ resulting in $J = -11$ cm^{-1} and $g = 4.5$ in the temperature range below 40 K. The failure of this model to fit the data obtained at higher temperatures might be due to the fact that the compound consists of two different trinuclear complexes which differ in their magnetic behaviour. But it could also well be that, just like in the other cases presented here, the approximations made in the model are found wanting at higher temperatures. In the same paper the synthesis and investigation of the non-structurally characterised complexes $[Co^{II}_{3}(L^{7})_{12}](CF_{3}SO_{3})_{6}$ and $[Co^{II}_{3}(L^{8})_{7}(H_{2}O)_{5}](CF_{3}SO_{3})_{6}(H_{2}O)_{4}$ is also presented (Fig. 7). Both complexes are orange in colour and consist of a trinuclear unit. In the first one the cobalt ions are proposed to be triply bridged by triazole units and the terminal metal ions to be coordinated to three monodentate triazoles. The magnetic investigation resulted in $J = -12$ cm^{-1} and $g = 4.5$ for an Heisenberg $S = {}^{1}/_{2}$ model. The composition of the second complex closely resembles the structurally characterised one with the 3-methyl-4-ethyl-1,2,4-triazole ligand, but without a crystal structure it cannot be decided for certain whether or not it also consists of two independent trinuclear units. The magnetic susceptibility measurements performed on this compound yielded $J = -14.4$ cm^{-1} and $g = 4.7$ for the Heisenberg $S = {}^{1}/_{2}$ Hamiltonian, which is so far the best description of the magnetic susceptibility of a trinuclear cobalt triazole complex in the range between 4 and 70 K.

In 1993 Mandal and co-workers reported a dinuclear triazole containing cobalt complex of the tetradentate ligand 4-(1*H*-pyrrole-1-yl)-3,5-bis(pyridine-2-yl)-1,2,4-triazole (Fig. 7) [37]. Orange single crystals of $[Co^{II}_{2}(L^{9})_{2}(H_{2}O)_{4}]Cl_{4}(CH_{3}OH)_{2}(H_{2}O)_{2}$ were grown directly from the reaction mixture containing stoichiometric amounts of $CoCl_{2}\cdot 6H_{2}O$ and the triazole compound in 80% methanol. The authors did not supply the crystallographic details to the CCDC or publish them so only the structural formula is shown in Fig. 14. The two Co^{II} centers are related by a centre of inversion. The metal ions are bridged by two triazoles, from two ligand strands, and are further coordinated to the pyridine nitrogen atoms, resulting in an N_{4} basal plane. In each case the distorted octahedral coordination sphere is completed by two water molecules in the axial positions. This leads to a relatively large Co···Co distance, 4.226(2) Å. No magnetochemical data was reported for this compound. It was designed to perform reductive electropolymerisation on glassy carbon electrodes and, indeed, reduction of CO_{2} in DMSO solution was observed. The closely related triazolate bridged complex cation $[Co^{II}_{2}(L^{10})_{2}]^{2+}$ had been described earlier (Fig. 7), but was not structurally characterised [18].

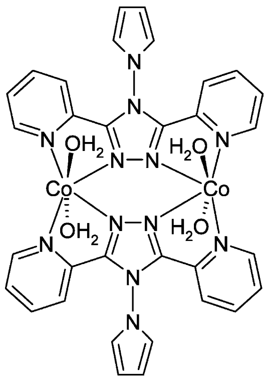


Fig. 14. Line diagram (no coordinates are available from the CCDC or the original paper for this crystal structure) of the $[Co^{II}_{2}(L^{9})_{2}(H_{2}O)_{4}]^{4+}$ cation.

All of the above structurally characterised complexes contain solely triazole units attached to high-spin Co^{II} (d^{7}). However, in 1991 Fabretti, Gatteschi and co-workers published an interesting crystal structure of a *class I mixed-valent* $Co^{II}Co^{III}$ complex formed by employing 3,5-diamino-1,2,4-triazole (Fig. 7) [38]. This is also the first example of a structurally characterised *triazolate*-bridged cobalt complex. Brown single crystals of $[Co^{II}_{2}Co^{III}(HL^{11})_{2}(L^{11})_{4}(H_{2}O)_{6}]Cl_{3}(H_{2}O)_{9}$ were grown by slow evaporation of an aqueous solution containing cobalt(II) chloride and 3,5-diamino-1,2,4-triazole in stoichiometric amounts (Fig. 15). The three cobalt ions are arranged linearly with the central one being located on a crystallographic 3 bar centre. Each of the terminal metal ions are triply bridged, by two triazolate and one triazole unit, to the central metal ion. The coordination sphere of the two terminal Co^{II} ions is completed by three water molecules each, forming a distorted $CoN_{3}O_{3}$ octahedron and giving the whole molecule a C_{3} axis along the Co···Co···Co chain. The central cobalt ion is also octahedrally coordinated, and it is clear from the Co–N bond lengths, which are on average 0.115 Å shorter than those of the terminal metal ions, that the oxidation state of the central cobalt ion is +III rather than +II. The complex is a tri-cation and its positive charge is compensated for by

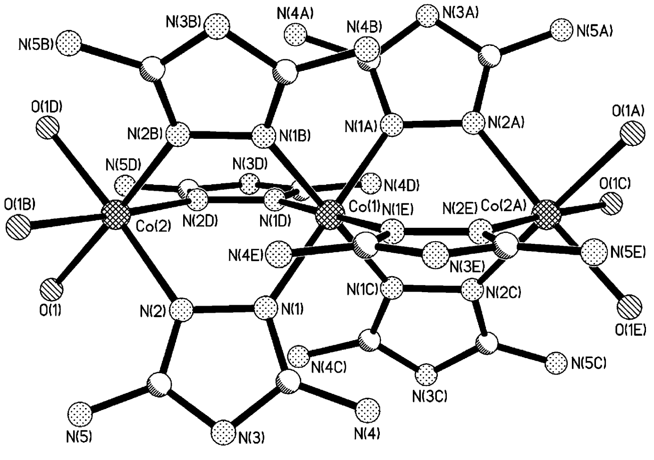


Fig. 15. Perspective view of the $[Co^{II}_{2}Co^{III}(HL^{11})_{2}(L^{11})_{4}(H_{2}O)_{6}]^{3+}$ cation.

three chloride anions, which are disordered as are three of the water molecules. The remaining six water molecules form hydrogen bonds to the triazole moieties. Four of the six bridging triazole units are deprotonated which can be seen from the slightly shorter Co^{II}–N bond length observed for the terminal metal ions, compared to those of the other complexes described here. The $Co^{II}\cdots Co^{III}$ distance is 3.653(3) Å which is considerably smaller than in the other complexes, in full agreement with the mixed-valent nature of this complex. The effective magnetic moment at room temperature for this complex is 7.15 μ_B, which strongly supports the proposal of two uncoupled d^7 high spin (Co^{II}) centers, since it would be too small for three Co^{II} ions. This is furthermore supported by the temperature independence of the magnetic susceptibility from room temperature to 100 K. The EPR spectrum shows only one set of signals, indicating that only one type of Co^{II} species is present.

A further example of a triazolate bridged cobalt complex was presented by Torres and co-workers in 1995 [39]. They condensed 3,5-diacetyl-1,2,4-triazole, a dicarbonyl head unit of interest to us in Section 4.2, with 2 equivalents of *p*-methoxyaniline (HL^{12}, Fig. 7) in the presence of stoichiometric amounts of base and Co^{II} salt. Unfortunately, no crystal structure was reported for of any of the complexes, which analyse as $[Co^{II}_2(L^{12})_2X_2]$ (X being Cl^-, Br^-, BF_4^-, NO_3^- or ClO_4^-), but from the spectroscopic data it is clear that the expected $[1+2]$ condensation has occurred and that two of the resulting Schiff-base ligands bridge two Co^{II} centers as shown in Fig. 16. This results in an N_4 donor set for each metal center. The powder EPR spectrum at 4 K shows an axial spectrum with $g_{\parallel} = 2.16$ and $g_{\perp} = 5.2$, indicative of an octahedral ligand field; so the anions are bound to axial sites (if they are not bridging then an unidentified interaction completes the octahedral coordination). The triazole unit is deprotonated and coordinates as a triazolate anion. Interestingly, attempts to synthesize the free ligand from a stoichiometric mixture of the triazole and amine components proved unsuccessful, instead yielding a mixture of several compounds including the desired one in only 55% yield. Attempts at separation failed to yield the free ligand, as did attempts to demetallate the prepared complexes. Magnetic studies show the presence of antiferromagnetic coupling between the two Co^{II} high-spin centers, of approximate order of $J = -4.3$ cm^{-1} using Lines' theory of Co^{II} cluster complexes [41]. This model describes in a satisfactory manner the magnetic behaviour of the complex between 4.2 and 100 K.

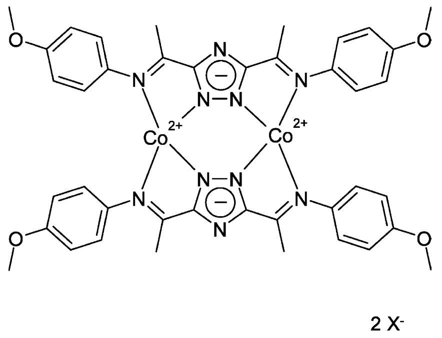


Fig. 16. Line diagram of the proposed structure (based on spectroscopic data) of $[Co^{II}_2(L^{12})_2X_2]$, X being Cl^-, Br^-, BF_4^-, NO_3^-, ClO_4^-.

The examples presented above give an exhaustive overview of structurally characterised bi- and trinuclear triazole-N^1,N^2-bridged cobalt complexes. In all cases the cobalt(II) ions are in the *high spin* state. The complexes mostly contain triazole units attached to the high-spin Co^{II} centers, however, exceptions include a very interesting class I mixed valent $Co^{II}Co^{III}Co^{II}$ complex containing triazole *and* triazolate units, and an acyclic Schiff-base triazolate ligand coordinated to high-spin Co^{II}. The latter complex, whilst not structurally characterised, clearly points out the way to extending this chemistry to include *macrocyclic* ligands, that is by the condensation of diformyl- or diacetyl-triazoles with primary diamines, and this will be addressed in the following section (Section 4.2).

Although the triazolate unit should be able to stabilise cobalt in the oxidation state $+$III, to date no complex that contains *only* Co^{III} centers has been structurally characterised or even described [9]. This is true both for acyclic and macrocyclic ligands.

The above examples show that the N^1,N^2-bridging triazole and triazolate units can effectively transmit magnetic interactions between the cobalt centers. Neighbouring metal ions exchange magnetic interactions via antiferromagnetic pathways with the magnitude of exchange, *J*, being in the range of -5 to -20 cm^{-1}. All magnetic data are obtained from a low temperature approximation and no suitable models exist yet to describe the behaviour of trinuclear cobalt complexes for higher temperatures (i.e. $T > 40$ K). It has also been shown that the magnitude of exchange can be altered by replacing some of the bridging triazoles with fluoride anions, increasing the antiferromagnetic exchange.

4.2. Complexes of triazole-containing Schiff-base macrocycles

Triazole moieties were first incorporated into Schiff-base macrocycles by Torres and co-workers in 1993 [5]. Large macrocycles, containing bis(imino)-triazole subunits, are of interest because of their potential ability to, in a controlled way, place the metal centers in a planar N_4 coordination environment and to provide a pathway, via the bridging triazole moiety, for antiferromagnetic exchange to occur between them. If an *N*-unsubstituted 1,2,4-triazole is employed it can be deprotonated to give a triazolate anion within the macrocycle. This facilitates metal coordination and also distinguishes them from diacylpyridine [10] and diformylpyridazine [6] based Schiff-base macrocycles. No reports of structurally characterised complexes of such macrocycles have been published to date [9].

Four small triazolate-containing macrocycles, $[L^{13}]^-$ to $[L^{16}]^-$, have been derived from the condensation of

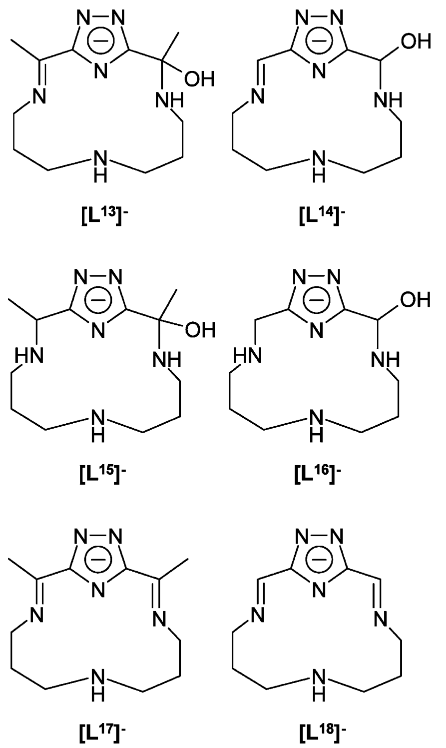


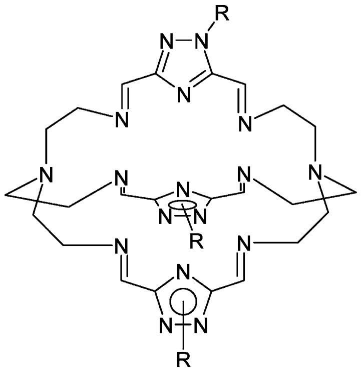
Fig. 17. The triazolate-containing macrocyclic ligands $[\mathrm{L}^{13}]^-$ to $[\mathrm{L}^{18}]^-$. Note that $[\mathrm{L}^{17}]^-$ and $[\mathrm{L}^{18}]^-$ have not been isolated.

bis(3-aminopropyl)amine with 3,5-diformyl-1,2,4-triazole [3] and 3,5-diacetyl-1,2,4-triazole [3–5], respectively, using a variety of metal ion templates (Fig. 17) [5]. In all cases improved yields were obtained when one equivalent of lithium hydroxide was used to promote the deprotonation of the triazole ring. Attempts to obtain the free ligands, without the assistance of at least one metal ion template, have not been successful to date. The first series of macrocyclic complexes prepared by this method has the formula $[\mathrm{M}^{\mathrm{II}}(\mathrm{L}^{13})]\mathrm{ClO}_4$, where M = Ni, Cu, Co, Pb. Only a single example of a macrocyclic complex of $[\mathrm{L}^{14}]^-$ was isolated and characterised, $[\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{14})]\mathrm{ClO}_4$, as the other complexes of this 3,5-diformyl-1,2,4-triazole derived macrocycle were too insoluble to be purified and characterised.

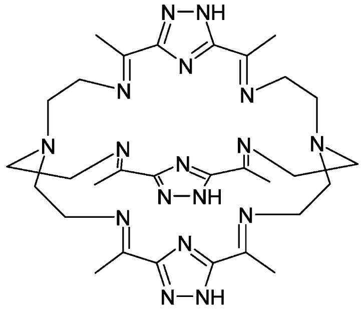
In general no [2 + 2] or higher products or polymeric byproducts were observed, probably due to the strong coordination ability of the triazolate unit, however, in the case of the $[\mathrm{Pb}^{\mathrm{II}}(\mathrm{L}^{13})]\mathrm{ClO}_4$ complex there was some evidence in the mass spectrum for the presence of a low ratio of [2 + 2] product also. The imine complexes, except for the lead complex, can be successfully reduced to the amine analogues, using NaBH_4 in ethanol under reflux conditions, giving complexes of $[\mathrm{L}^{15}]^-$ from those of $[\mathrm{L}^{13}]^-$ and $[\mathrm{L}^{16}]^-$ from those of $[\mathrm{L}^{14}]^-$, respectively (Fig. 17). Again, the resulting compounds have very low solubilities in common solvents other than water.

These complexes are unusual from two points of view, points which may well be inter-related. Firstly, it is uncommon to observe (as is proposed for these macrocycles) the addition of water to an imine bond [42], without the next step, complete hydrolysis, occurring also. This behaviour, addition to an imine bond, has however been observed for the intramolecular addition of an alcohol [43,44] or amine [45] group, or the addition of an alcohol solvent molecule [46]. This usually occurs to relieve steric strain in some of the unsaturated Schiff-base linkages in the macrocyclic ring, forming more flexible, saturated, linkages in their place. The second feature which merits comment is that, on the basis of the mass spectra, the transition metal complexes are proposed to be of the [1 + 1] macrocycles (i.e. as drawn in Fig. 17) and to therefore be bound to the metal ion via the N^4 nitrogen atom of the triazolate ring. This is interesting as the Schiff-base macrocycles derived from the related five-membered heterocycle 2,5-diformylpyrrole have not, to date, coordinated to a single transition metal ion via all three of the donor atoms in the tridentate bis(imino)-pyrrole unit [42,47]. The probable reason for this is the poor metal ion binding geometry which would result (two consecutive $\mathrm{N}_{\mathrm{imine}}$–M–$\mathrm{N}_{\mathrm{pyrrole}}$ angles $\ll 90°$). In one case it has been proposed, on the basis of spectroscopic evidence, that a water molecule has added across one of the four imine bonds in a [2 + 2] macrocycle derived from 2,5-diformylpyrrole and 1,2-diaminoethane, as is proposed to be the case with $[\mathrm{L}^{13}]^-$ and $[\mathrm{L}^{14}]^-$ [42]. Crystals suitable for X-ray diffraction have not been obtained for any of the $[\mathrm{M}^{\mathrm{II}}(\mathrm{L}^{13})]\mathrm{ClO}_4$ or $[\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{14})]\mathrm{ClO}_4$ compounds so the presence of these unusual features has not yet been confirmed. The [1 + 1] di-imine macrocycles $[\mathrm{L}^{17}]^-$ and $[\mathrm{L}^{18}]^-$ (Fig. 17) were not observed.

Use of tris(2-aminoethyl)-amine (tren), instead of bis (3-aminopropyl)amine, as the amine component in the Schiff-base cyclisation reaction allowed Torres, Vázquez and co-workers to prepare triazole-containing macro*bi*cyclic ligands, or cryptands, in a straightforward manner, without the need for a template metal ion, in good yield [48]. However, initial attempts which employed 3,5-diformyl-1,2,4-triazole as the dicarbonyl head unit were not successful, most likely for solubility reasons. Subsequently, in order to increase the solubility, N^1-substituted derivatives of the triazole dialdehyde head unit were employed, as well as 3,5-diacetyl-1,2,4-triazole, and the three macrobicycles successfully isolated are shown in Fig. 18. The complexes prepared from these ligands are believed to have the following formulae (based on spectroscopic evidence alone): $[\mathrm{Ag}^{\mathrm{I}}_2(\mathrm{L}^{19})](\mathrm{BF}_4)_2$, $[\mathrm{Ag}^{\mathrm{I}}_2(\mathrm{L}^{20})](\mathrm{BF}_4)_2$, $[\mathrm{Cu}^{\mathrm{I}}_3(\mathrm{L}^{19})](\mathrm{PF}_6)_3$ and $[\mathrm{Cu}^{\mathrm{I}}_3(\mathrm{L}^{20})](\mathrm{PF}_6)_3$, $[\mathrm{Ni}^{\mathrm{II}}_3(\mathrm{L}^{21})]\mathrm{Br}_3$ and $[\mathrm{Cu}^{\mathrm{II}}_3(\mathrm{L}^{21})]\mathrm{Br}_3$. Unfortunately no crystallographic data exist for any of these compounds either: the complexes have only been characterised by NMR, IR and MS techniques. A structure determination would be particularly interesting in the case of the $[\mathrm{L}^{21}]^{3-}$ complexes to: (a) determine absolutely whether these complexes are bimetallic, or trimetallic as the mass spectra suggest (elemental analyses would also be interesting in this regard); and (b) reveal whether or not some or all of the triazolate head units are bridging the incorporated metal ions (and hence have the opposite conformation rela-



R = $C_{12}H_{25}$ (**L^{19}**),
CH_2-(C_6H_4)-*p*-(OCH_3) (**L^{20}**)



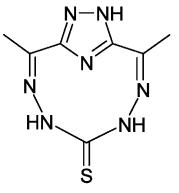
H_3L^{21}

Fig. 18. The triazole-containing macrobicyclic ligands L^{19} (R = $C_{12}H_{25}$), L^{20} (R = CH_2–(C_6H_4)–*p*-OCH_3) and H_3L^{21}.

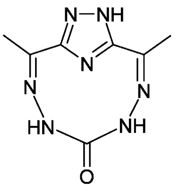
tive to the adjacent imine bonds to that shown in Fig. 18). However, the particularly low solubilities of the complexes of ligand H_3L^{21} may preclude such a study.

More recently authors have focused on 3,5-diacetyl-1,2,4-triazole head unit as the preferred starting material for macrocycle synthesis, probably because of the improved solubility (and stability) over that of the analogous dialdehyde, 3,5-diformyl-1,2,4-triazole. This is despite the fact that in Schiff-base macrocyclic chemistry dialdehydes are usually preferred over diketones for reasons of reactivity combined with the fact that subsequent access to the analogous amine ligands via reduction of the resulting imine bonds to amine bonds does not raise chirality issues in the case of the dialdehyde.

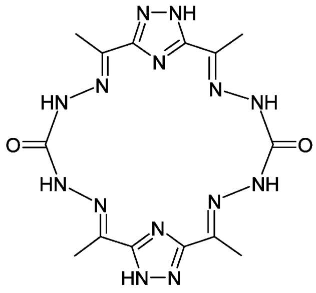
Souza and co-workers were able to obtain two metal-free macrocyclic ligands (Fig. 19) by a 1:1 condensation of 3,5-diacetyl-1,2,4-triazole and carbohydrazide or thiocarbohydrazide, respectively, in the presence of one equivalent of LiOH [49]. However, the yields were modest (below 50%), and the solubility of the macrocycles, presumed to be [1 + 1] macrocycles (m.p., IR and NMR are reported, but critically no MS data), is poor. Only copper complexes have been prepared from these macrocycles so far, obtained by stirring a suspension of the ligand in ethanol containing copper(II) perchlorate. The two resulting green copper complexes have only been characterised by means which



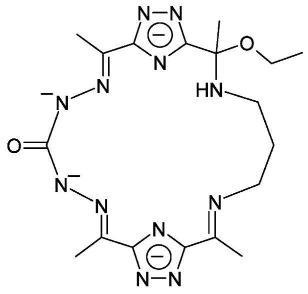
H_3L^{22}



H_3L^{23}



H_6L^{24}



$[HL^{25}]^{4-}$

Fig. 19. The triazole-containing macrocyclic ligands H_3L^{22} (2,8-dimethyl-3,4,6,7-tetraaza-13,5-(1,2,4-triazola)cyclooctaphane-5-thione), H_3L^{23} (2,8-dimethyl-3,4,6,7-tetraaza-13,5-(1,2,4-triazola)cyclooctaphane-5-one), H_6L^{24} and $[HL^{25}]^{4-}$.

do not require dissolution, or at least only require highly dilute solutions of the material, as they too have very low solubilities. The characterisation includes elemental analysis, IR and UV–vis only. It is proposed that the complexes are of [1 + 1] macrocycles, although again no MS data are reported so there is no evidence to support the assumption that the macrocycles are [1 + 1] in size, and that they have the following compositions: $[Cu^{II}(H_3L^{22})](ClO_4)_2(H_2O)_3$ with a neutral ligand and $[Cu^{II}(HL^{23})](H_2O)_4$ with a doubly deprotonated ligand. An X-ray structure determination is needed to identify the true nature of these complexes as the proposed compositions pose many questions about both the macrocycle size and the metal ion coordination environment.

Lead(II) ions are often used as metal ion templates in the synthesis of larger macrocycles [2,23,44,50], and when employed here, with 3,5-diacetyl-1,2,4-triazole and carbohydrazide, initially an acyclic [2 + 1] reaction product is formed as a lead(II) bisthiocyanate complex. When this [2 + 1] lead(II) complex was reacted in ethanol with a further equivalent of either carbohydrazide (H_6L^{24}, Fig. 19) or 1,3-diaminopropane ($[HL^{25}]^{4-}$, Fig. 19), cyclisation occurred and dilead(II) macrocyclic complexes were isolated. Neither complex formed in high yield, however it is not clear whether the yield was calculated based on the limiting reagent, lead(II) ions, or not: no comment was made as to whether adding a further equivalent of lead(II) ions improved the yield of these reactions. It is assumed, not unreasonably, that a $[2+2]$ condensation has occurred in these reactions (Fig. 19), however, as the resulting insoluble solids were only characterised by IR, elemental analysis and melting point (no MS), this is not proven to be the case. The general composition of these complexes was found to be: $[Pb^{II}_2(H_6L^{24})](SCN)_4(CH_3CH_2OH)_2$ for the neutral ligand H_6L^{24} and $[Pb^{II}_2(HL^{25})](CH_3CH_2OH)_2$ for the quadruply negatively charged ligand $[HL^{25}]^{4-}$, which is therefore a further example of a triazolate macrocyclic complex. Once again an X-ray structure determination would be required to answer unequivocably questions such as the actual ring size and whether the triazole moieties in these two macrocycles are in the conformation shown in Fig. 19 or whether the N^1N^2 nitrogen atoms (as opposed to N^4) are pointing into the macrocyclic cavities. However, once again poor solubility is a problem.

The above examples show that there is still much work to do in developing this field. Careful consideration needs to be given to introducing suitable substituents onto the triazole head units in order to increase the solubility of both the ligands and the resulting metal complexes. This would make other means of characterisation more accessible, not least structural characterisation where poor solubility appears to be the main reason why not a single crystal structure has been published yet. Structural studies are important as knowing the exact nature of the macrocycle and metal ion geometries is the key to understanding the properties of transition metal triazolate macrocyclic complexes, which are expected to show interesting behaviour, particularly magnetic behaviour. No magnetic data are available for any of the handful of, rather insoluble, macrocyclic triazole- or triazolate-containing complexes reported to date. This is a challenging field of chemistry and we are working towards contributing to its future development [9].

5. Future directions

There are many interesting avenues remaining to be explored. The pyridazine-containing macrocycle L^1 has yielded a fascinating series of cobalt(II) complexes which range from high spin, to low spin and spin crossover, simply by variation of the axial ligands (Section 3). Clearly the 3,6-diformylpyridazine head unit can also be used in the construction of many more Schiff-base ligands, both cyclic and acyclic, and we are actively working on this [9]. A number of significant issues and challenges in working with triazoles and triazolates have been raised (Section 4). As some of these difficulties are overcome we expect to see this area burgeon also [9], despite the expectation of less efficient mediation of antiferromagnetic exchange relative to both the pyridazines and the pyrazoles. The iron coordination chemistry of both heterocycles, although especially of the triazoles and triazolates, will, of course, also be of very considerable interest.

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