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Dicobalt(II) complexes of a triazolate-containing Schiff-base macrocycle: synthesis, structure and magnetism

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A new Schiff-base macrocycle is obtained by the lead(II) ion templated [2+2] condensation of 3,5-diacetyl-1*H*-1,2,4-triazole and 1,4-diaminobutane in the presence of sodium hydroxide. Transmetallation of the resulting dilead complex, $Pb_2(L2)(ClO_4)_2$ **1**, in acetonitrile with two equivalents of $CoCl_2{\cdot}6H_2O$ leads to the isolation of an orange, six-coordinate complex, $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2{\cdot}H_2O{\cdot}2CH_3CN$ **2**. Subsequent reaction of **2** with two equivalents of NaOCN or NEt_4Cl yielded red–purple five-coordinate $[Co^{II}_2(L2)(NCO)_2]$ **3** and red five-coordinate $[Co^{II}_2(L2)(Cl)_2]{\cdot}1.5CH_3CN$ **4**, respectively. In all three air-stable dicobalt complexes the macrocycles contain two high-spin cobalt(II) centers which are weakly antiferromagnetically coupled ($2J = -3.0, -0.4, -3.5\ cm^{-1}$ for **2**, **3** and **4**, respectively). Complexes **2**–**4** have been characterized by X-ray diffraction and are the first structurally characterised complexes of a triazolate-containing macrocycle to date.

Introduction

A wide range of transition metal complexes of L1 (formed by [2+2] condensation of 3,6-diformylpyridazine[1,2] and 1,3-diaminopropane) with interesting redox and magnetic properties[2–6] have been isolated. Currently, there is considerable interest in utilising substituted 1,2,4-triazoles as ligands for transition metal ions,[7,8] for example in efforts to develop new magnetic materials[9] and photochemically driven molecular devices.[10] Triazoles are of particular interest because of their ability to mediate magnetic exchange interactions and their correct ligand field strength range to produce spin crossover complexes with iron(II).[8] So we decided to incorporate this moiety into Schiff-base macrocycles which are related to L1 (*e.g.* $L2^{2-}$, Fig. 1). Torres and co-workers have successfully isolated some related triazolate-containing macrocyclic complexes prior to our work, although none have been structurally characterised to date.[11,12] We report here on the formation and characterisation of three cobalt(II) complexes, $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2{\cdot}H_2O{\cdot}2CH_3CN$ **2**, $[Co^{II}_2(L2)(NCO)_2]$ **3** and $[Co^{II}_2(L2)(Cl)_2]{\cdot}1.5CH_3CN$ **4** of the new Schiff-base macrocycle $L2^{2-}$ (Fig. 1) which is derived from 3,5-diacetyl-1*H*-1,2,4-triazole[11] and 1,4-diaminobutane. These are the first examples of structurally characterised triazolate-containing macrocyclic complexes, and as such they represent a significant step forward in the development of the coordination chemistry of this and related ligand systems.[13]

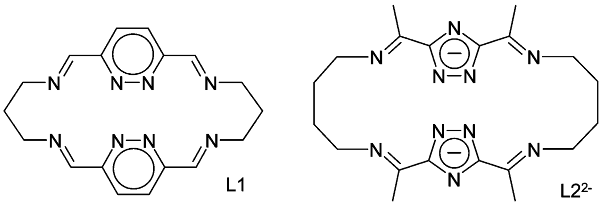
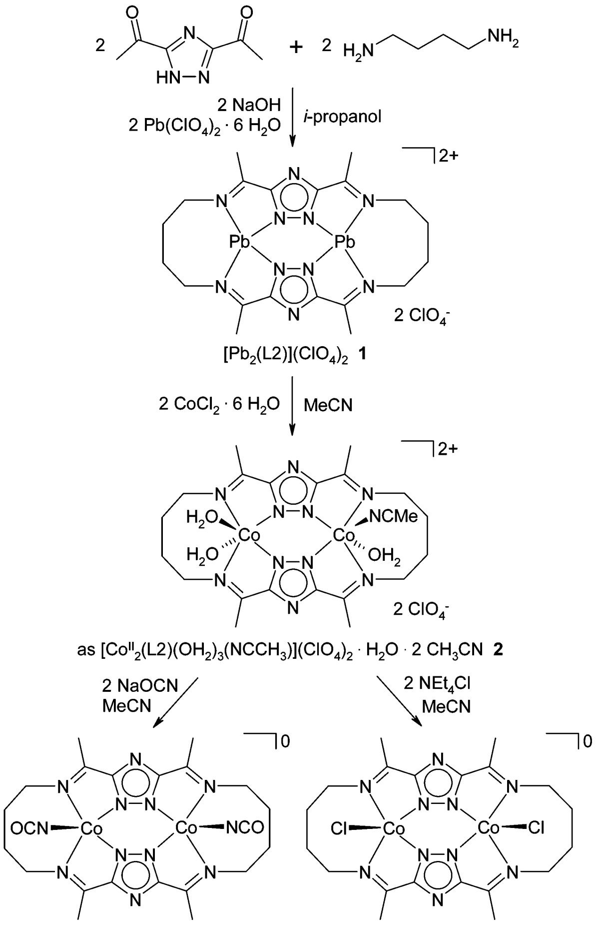


Fig. 1 The ligands L1 and $L2^{2-}$.

Results and discussion

Synthesis and characterisation

Attempts to prepare the metal-free macrocycle H_2L2 were unsuccessful, as was found to be the case with the analogous ligand L1, so the template method was followed to synthesise it from the 3,5-diacetyl-1*H*-1,2,4-triazole head unit and 1,4-diaminobutane (Scheme 1). Somewhat surprisingly, experiments attempting to synthesise a copper complex directly from the triazole and amino components, *i.e.* using copper(II) ions as templates, were not successful. Rather, the use of lead(II) ions



Scheme 1 Synthesis of the complexes **1**–**4**.

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as templates proved to be the best way to obtain comparatively good yields of macrocyclic complex in sufficient purity. Specifically, the addition of lead(II) perchlorate hexahydrate followed by 1,4-diaminobutane to a solution of 3,5-diacetyl-1*H*-1,2,4-triazole, in the presence of stoichiometric amounts of base to deprotonate the triazole head unit, yields $[Pb_2(L2)](ClO_4)_2$ **1** as a white, crystalline material. The band at 1630 cm^{-1} in the infrared spectrum shows that an imine bond has formed and an intense band at 1089 cm^{-1} provides clear evidence of the presence of perchlorate anions. The FAB mass spectrum indicates that the product is a dilead complex of the [2+2] Schiff-base macrocycle $L2^{2-}$.

The air stable, six-coordinate dicobalt(II) macrocyclic complex $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2\cdot H_2O\cdot 2CH_3CN$ **2** is crystallised as orange blocks in 54% yield, by adding two equivalents of $CoCl_2\cdot 6H_2O$ to $[Pb_2(L2)](ClO_4)_2$ **1** in refluxing acetonitrile, filtering to remove the resulting $PbCl_2$, and finally diffusing diethyl ether into the filtrate. The transmetallation reactions of $[Pb_2(L2)](ClO_4)_2$ **1** are unusual in our experience: we have found that the lead ions must be removed (in this case by precipitation as $PbCl_2$), otherwise as attempts are made to precipitate the transition metal complex from the reaction solution the colour slowly fades and white, lead-containing products precipitate instead. A band at 1638 cm^{-1} in the infrared spectrum of **2** shows that the imine bonds remain intact and the FAB mass spectrum shows that a dicobalt complex of $L2^{2-}$ has formed. The complex is a 2 : 1 conductor in acetonitrile.

The addition of two equivalents of NaOCN to **2** results in the formation of red–purple crystals of $[Co^{II}_2(L2)(NCO)_2]$ **3** in 30% yield. Again the imine stretch is observed at 1638 cm^{-1} and there is no evidence of either amine or carbonyl absorptions. The presence of NCO^- is confirmed by a strong band at 2217 cm^{-1}. The complex is a non-conductor in acetonitrile.

Similarily, the addition of two equivalents of NEt_4Cl to **2** leads to the formation of $[Co^{II}_2(L2)(Cl)_2]\cdot 1.5CH_3CN$ **4** as red crystals, in 36% yield. The imine stretch in the IR spectrum of **4** is observed at 1637 cm^{-1} and the electrospray mass spectrum indicates that it is a dicobalt complex of the ligand $L2^{2-}$ containing chloride. Again, it is a non-conductor in acetonitrile. After about two weeks time at room temperature in air, a red sample of **4** turned into a dull orange powder. An elemental analysis of the orange powder was in excellent agreement with hydration of the complex having occurred (Found: C, 35.90; H, 5.30; N, 21.18. $C_{20}H_{28}N_{10}Co_2Cl_2\cdot 4H_2O$ requires C, 35.88; H, 5.38; N, 20.93%). However, an attempt to remove the water in high vacuum failed and the red colour did not return. Also, the elemental analysis figures were retained, so we here propose the formulation of the orange powder as six-coordinate $[Co^{II}_2(L2)(OH_2)_2(Cl)_2](H_2O)_2$. Consistent with this, the orange complex is a non-conductor in acetonitrile.

X-Ray structure determination

Selected bond distances and angles for complexes **2**–**4** are provided in Table 1. The structure determination on orange crystals of **2** (Fig. 2) reveals that both cobalt atoms are six-coordinate with four equatorial donors supplied by the triazolate macrocycle $L2^{2-}$ and one axial donor provided from a water molecule, however, the remaining axial site is occupied by a further water molecule in the case of Co(1) but an acetonitrile molecule in the case of Co(2). The macrocycle is somewhat domed, with the triazolate mean planes intersecting at 35.8(2)° and the two $(N_{macro})_4$ mean planes of Co(1) and Co(2) intersecting at 22.5(2)°. Both cobalt atoms are raised up out of their respective $(N_{macro})_4$ mean planes, by 0.150(5) Å (Co(1)) and 0.138(4) Å (Co(2)), towards O(31) and O(32), respectively. The bonds to these two water molecules are slightly shorter than those to the axial donors on the opposite side of the macrocycle.

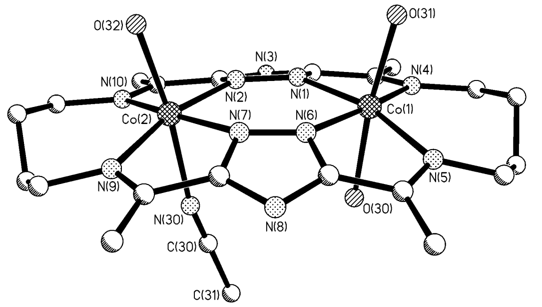

Fig. 2 Perspective view of the cation of **2**, $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)]^{2+}$, solvent molecules and hydrogen atoms have been omitted for clarity.

Red–purple crystals of **3** were grown from the acetonitrile reaction solution by diethyl ether diffusion and the X-ray structure determination carried out (Fig. 3). This reveals that the complex contains five-coordinate cobalt(II) ions. This is in marked contrast to the six-coordinate cobalt(II) ions observed in **2**, and is a first for triazole-bridged dicobalt(II) complexes.[8,14] In each case the four equatorial donors are supplied by the macrocycle whilst the single axial donor is a cyanate ion. Compared with **2**, in **3** the triazolate ring mean planes intersect at a much greater angle (67.77(7)°) whereas the angle between the respective $(N_{macro})_4$ mean planes is only slightly greater (27.30(4)°). As expected, the five-coordinate cobalt ions are displaced from their respective $(N_{macro})_4$ mean planes towards the cyanate ions by a large distance, 0.6215(10) Å and 0.6245(10) Å, for Co(1) and Co(2) respectively. Bonds from the cobalt ions to the cyanate ions are shorter than those to the macrocyclic donors.

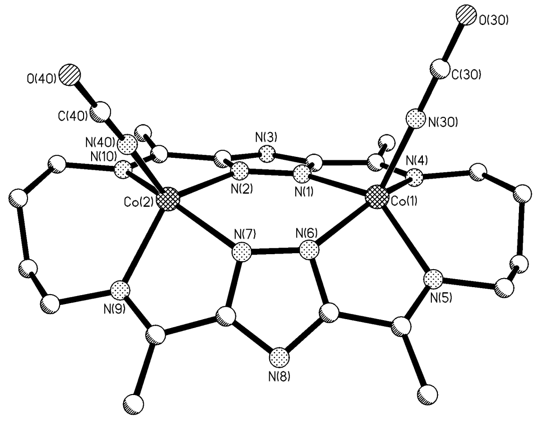

Fig. 3 Perspective view of $[Co^{II}_2(L2)(NCO)_2]$ (**3**), hydrogen atoms have been omitted for clarity.

From a slow diethyl ether diffusion into acetonitrile, red crystals of **4** were obtained (Fig. 4). There are two very similar dicobalt complexes in the asymmetric unit [Co(1)/Co(2), shown; Co(3)/Co(4)], and, like in **3**, the cobalt(II) ions are five-coordinate, however, in this complex the axial positions are occupied by two chloride anions. The two triazolate ring mean planes intersect at angles of 44.1(1) and 44.4(1)° for the Co(1)/Co(2) and Co(3)/Co(4) complexes, respectively, which lie in between those found for **2** and **3**. The intersection angles for the $(N_{macro})_4$ mean planes for the Co(1)/Co(2) and Co(3)/Co(4) complexes in **4** are 32.88(5) and 32.90(5)°, respectively, which are the greatest angles in this series. The cobalt ions are raised out of their respective $(N_{macro})_4$ mean planes towards the chloride anions by 0.367(1) Å [Co(1)], 0.520(1) Å [Co(2)], 0.537 Å [Co(3)] and 0.343 Å [Co(4)]. These values are lower than was observed for the other five-coordinate complex, **3**. This is most pronounced for Co(1) and Co(4), due to the fact that in **4** the nitrogen of an acetonitrile molecule is only 2.635(2) Å from

Table 1 Selected interatomic distances (Å) and angles (°) of $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**), $[Co^{II}_2(L2)(NCO)_2]$ (**3**) and $[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$ (**4**)

2		**3**		**4**	
Co(1)–Co(2)	4.191(3)	Co(1)–Co(2)	4.393(1)	Co(1)–Co(2)	4.2838(8)
Co(1)–N(1)	2.077(8)	Co(1)–N(1)	2.052(2)	Co(1)–N(1)	2.0654(18)
Co(1)–N(4)	2.174(8)	Co(1)–N(4)	2.2186(18)	Co(1)–N(4)	2.175(2)
Co(1)–N(5)	2.172(9)	Co(1)–N(5)	2.1351(19)	Co(1)–N(5)	2.1448(19)
Co(1)–N(6)	2.041(8)	Co(1)–N(6)	2.1036(18)	Co(1)–N(6)	2.055(2)
Co(1)–O(30)	2.162(7)	Co(1)–N(30)	1.958(2)	Co(1)–Cl(1)	2.3415(8)
Co(1)–O(31)	2.083(7)	Co(2)–N(2)	2.0580(19)	Co(2)–N(2)	2.044(2)
Co(2)–N(2)	2.027(8)	Co(2)–N(7)	2.111(2)	Co(2)–N(7)	2.0674(19)
Co(2)–N(7)	2.078(8)	Co(2)–N(9)	2.1686(19)	Co(2)–N(9)	2.180(2)
Co(2)–N(9)	2.164(9)	Co(2)–N(10)	2.167(2)	Co(2)–N(10)	2.185(2)
Co(2)–N(10)	2.192(8)	Co(2)–N(40)	1.965(2)	Co(2)–Cl(2)	2.2827(8)
Co(2)–N(30)	2.209(10)	N(30)–C(30)	1.165(3)		
Co(2)–O(32)	2.091(6)	C(30)–O(30)	1.216(3)		
		N(40)–C(40)	1.152(3)		
		C(40)–O(40)	1.213(3)		
N(6)–Co(1)–N(1)	92.4(3)	N(30)–Co(1)–N(1)	110.29(8)	N(6)–Co(1)–N(1)	89.44(8)
N(6)–Co(1)–O(31)	96.6(3)	N(30)–Co(1)–N(6)	116.68(8)	N(6)–Co(1)–N(5)	77.27(8)
N(1)–Co(1)–O(31)	97.9(3)	N(1)–Co(1)–N(6)	84.69(7)	N(1)–Co(1)–N(5)	158.52(8)
N(6)–Co(1)–O(30)	88.1(3)	N(30)–Co(1)–N(5)	108.60(8)	N(6)–Co(1)–N(4)	156.30(8)
N(1)–Co(1)–O(30)	86.7(3)	N(1)–Co(1)–N(5)	141.11(8)	N(1)–Co(1)–N(4)	76.31(7)
O(31)–Co(1)–O(30)	173.3(3)	N(6)–Co(1)–N(5)	78.07(7)	N(5)–Co(1)–N(4)	109.88(7)
N(6)–Co(1)–N(5)	75.8(3)	N(30)–Co(1)–N(4)	93.73(7)	N(6)–Co(1)–Cl(1)	103.31(6)
N(1)–Co(1)–N(5)	165.4(3)	N(1)–Co(1)–N(4)	75.86(7)	N(1)–Co(1)–Cl(1)	102.51(6)
O(31)–Co(1)–N(5)	92.1(3)	N(6)–Co(1)–N(4)	148.26(7)	N(5)–Co(1)–Cl(1)	96.99(5)
O(30)–Co(1)–N(5)	84.4(3)	N(5)–Co(1)–N(4)	101.71(7)	N(4)–Co(1)–Cl(1)	98.27(6)
N(6)–Co(1)–N(4)	166.6(3)	N(40)–Co(2)–N(2)	124.44(8)	N(2)–Co(2)–N(7)	88.57(8)
N(1)–Co(1)–N(4)	75.6(3)	N(40)–Co(2)–N(7)	102.56(8)	N(2)–Co(2)–N(9)	145.72(8)
O(31)–Co(1)–N(4)	91.1(3)	N(2)–Co(2)–N(7)	84.29(7)	N(7)–Co(2)–N(9)	76.18(8)
O(30)–Co(1)–N(4)	85.2(3)	N(40)–Co(2)–N(10)	104.55(8)	N(2)–Co(2)–N(10)	75.99(8)
N(5)–Co(1)–N(4)	115.1(3)	N(2)–Co(2)–N(10)	76.85(7)	N(7)–Co(2)–N(10)	154.63(8)
N(2)–Co(2)–N(7)	91.3(3)	N(7)–Co(2)–N(10)	152.53(7)	N(9)–Co(2)–N(10)	105.54(8)
N(2)–Co(2)–O(32)	98.1(3)	N(40)–Co(2)–N(9)	98.79(8)	N(2)–Co(2)–Cl(2)	107.04(6)
N(7)–Co(2)–O(32)	95.0(3)	N(2)–Co(2)–N(9)	135.85(8)	N(7)–Co(2)–Cl(2)	104.94(6)
N(2)–Co(2)–N(9)	166.2(4)	N(7)–Co(2)–N(9)	77.34(7)	N(9)–Co(2)–Cl(2)	106.50(6)
N(7)–Co(2)–N(9)	76.8(3)	N(10)–Co(2)–N(9)	102.61(7)	N(10)–Co(2)–Cl(2)	98.84(6)
O(32)–Co(2)–N(9)	90.0(3)	C(30)–N(30)–Co(1)	177.3(2)	N(2)–N(1)–Co(1)	134.92(16)
N(2)–Co(2)–N(10)	76.6(3)	N(30)–C(30)–O(30)	179.4(3)	N(1)–N(2)–Co(2)	135.94(15)
N(7)–Co(2)–N(10)	166.2(3)	C(40)–N(40)–Co(2)	177.4(2)		
O(32)–Co(2)–N(10)	93.1(3)	N(40)–C(40)–O(40)	179.6(3)		
N(9)–Co(2)–N(10)	114.3(3)				
N(2)–Co(2)–N(30)	87.1(3)				
N(7)–Co(2)–N(30)	89.6(3)				
O(32)–Co(2)–N(30)	172.9(3)				
N(9)–Co(2)–N(30)	85.8(3)				
N(10)–Co(2)–N(30)	83.5(3)				
N(2)–N(1)–Co(1)	132.1(7)				
N(1)–N(2)–Co(2)	135.4(7)				
N(7)–N(6)–Co(1)	133.6(7)				
N(6)–N(7)–Co(2)	134.0(6)				

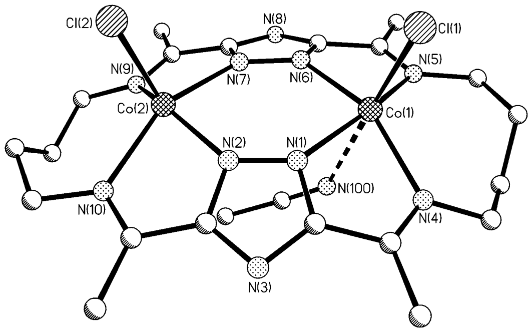

Fig. 4 Perspective view of one of the two independent complex molecules of **4**, $[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$, solvent molecules and hydrogen atoms have been omitted for clarity.

Co(1) [N(100)] and 2.609(2) Å from Co(4) [N(110)], and virtually occupies the other axial position. But these distances are *ca.* 0.4 Å longer than the observed $Co–N_{acetonitrile}$ distance in **2**, so it is reasonable to describe Co(1) and Co(4) in **4** as having a distorted five-coordinate geometry.

There is no significant difference between the average $Co–N_{macro}$ distance in **2**, **3** and **4** (2.116, 2.127 and 2.110 Å for **2**, **3** and **4**, respectively). The $Co–N_{triazolate}$ bonds are shorter than the $Co–N_{imine}$ bonds in all of these complexes. Despite these similarities, interestingly the Co ··· Co separation in **3** is 0.2 Å larger than it is in **2**, whereas the separation in **4** lies in between that of **2** and **3** (0.09 Å larger than in **2**). In all three complexes the cobalt atoms have far from regular geometries. This is in part due to the combination of five- and seven-membered chelate rings which are formed on binding the cobalt(II) ions in the $L2^{2-}$ macrocycle. In all three complexes the five-membered chelate rings have $N_{macro}–Co–N_{macro}$ angles of 77 ± 1°, whereas the $N_{macro}–Co–N_{macro}$ angles in the seven-membered chelate rings differ within the three complexes (114–115° for **2**, 102–103° for **3** and 106–110° for **4**). Again, **4** lies in between **2** and **3** in this respect, the larger angle applying to the pseudo-octahedral site in **4** [on Co(1)], which is closer to the value observed for **2** where both sites are octahedral. The angle on the clearly five-coordinate side of the molecule [Co(2)] resembles more closely the five-coordinate sites in **3**.

Electrochemical studies

In contrast to the rich reversible electrochemistry associated with $[Co^{II}_2(L1)(NCCH_3)_4]^{4+}$,[5] electrochemical studies on **2** reveal only irreversible reduction processes below −1 V and an irreversible oxidation process at approximately +1 V *vs.* 0.01 mol L^{-1} $AgNO_3/Ag$. The cyclic voltammograms of **3** and **4** also show no reversible electron transfer processes. These results, and the observed air stability of complexes **2**–**4**, may well be due, at least in part, to the distorted geometries imposed by the macrocycle (see above) as, for example, cobalt(III) would not be expected to be as accommodating as the high-spin cobalt(II) ions are.[15]

Magnetic studies

Magnetic studies show that the cobalt(II) ions in all complexes (**2**, **3** and **4**) are high spin and indicate that the triazolate bridges mediate antiferromagnetic coupling between the two cobalt(II) ions. Fig. 5 shows μ_{eff} and χ_m (per Co) *vs.* temperature for **2**. The susceptibility data showed a characteristic maximum at low temperature due to weak antiferromagnetic coupling. The data were fitted to a simple $S = 3/2$ dimer using an isotropic Heisenberg Hamiltonian ($-2JS_1 \cdot S_2$). The g value of 2.55 for **2** differs significantly from a free $S = 3/2$ ion (2.00) as it incorporates spin–orbit coupling effects. No orbital degeneracy on the Co(II) center ($^4T_{1g}$) or low-symmetry ligand-field effects are taken into account and the effects of zero-field splitting are ignored. The $2J$ value of -3.0 cm^{-1} indicates a very weak antiferromagnetic coupling between the two cobalt centers in **2**. The $2J$ values of **3** (-0.4 cm^{-1}) and **4** (-3.5 cm^{-1}) are of the same magnitude. The g values for **3** (2.23) and **4** (2.24) are very similar to one another due to the similar geometry of the Co(II) centers (five-coordinate). The deviation from the value of the free ion is larger for **3** and **4** than it is for **2** (six-coordinate) indicating different ligand-field splittings in the five-coordinate, as opposed to six-coordinate, complexes. Even though the $2J$ values are small it appears that the extent of antiferromagnetic coupling between the two cobalt centers decreases with an increase of the intersection angle of the triazolate rings which provide the exchange pathway. Complexes **2** (-3.0 cm^{-1}, 36°) and **4** (-3.5 cm^{-1}, 44°) have similar intersection angles and show a similar magnitude of antiferromagnetic coupling. An increase of the intersection angle of the two triazolate units in **3** (-0.4 cm^{-1}, 68°) leads to a decrease in the extent of magnetic exchange. These results clearly show that the triazolate units are the mediator of the magnetic exchange, and also that the exchange is fairly independent of the coordination number (*i.e.* five- or six-coordinate) of the cobalt center. This is furthermore supported by the fact that the extent of magnetic exchange is independent of how far the cobalt centers are either out of their $(N_{macro})_4$ mean plane or the triazolate mean planes. In all three complexes the cobalt centers lie between 0.14 and 0.89 Å beneath the triazolate mean planes and between 0.14 and 0.62 Å above the $(N_{macro})_4$ mean planes.

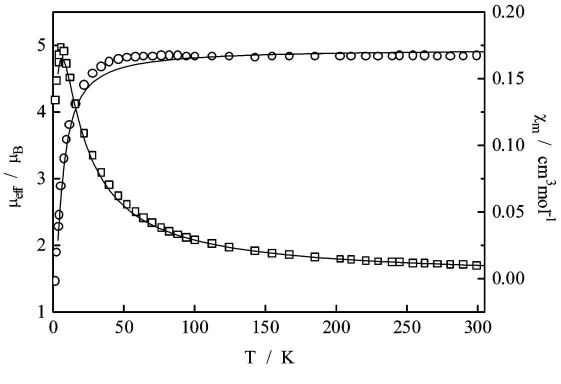

Fig. 5 Experimentally observed temperature dependence of μ_{eff} (○) and χ_m (□), per Co for $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**). The solid lines are the calculated fit for the data to an $S = 3/2$ isotropic Heisenberg model: $2J = -3.0$ cm^{-1}, $g = 2.55$, fraction monomer 0.01.

Studies of dicopper(II) complexes have shown that triazole and triazolate bridges have similar superexchange capacities, but that pyridazine bridges are about twice as effective, other factors (such as co-planarity) being approximately equal.[16] Hence it is no surprise to observe that the degree of antiferromagnetic exchange observed in **2**, **3** and **4** is smaller than the values that were observed for the doubly pyridazine-bridged family of dicobalt(II) complexes of L1, especially given the remarkable co-planarity of the cobalt ions and pyridazine bridging moieties which is observed in this series of complexes of L1 ($2J$ values in the range -10.2 to -20.5 cm^{-1}).[6]

Conclusion

These results, along with those of Torres and co-workers using related triazolate ligands, reveal a bright future for the exploitation of polydentate triazolate-containing ligands. Recently, cobalt(II) complexes of pyridazine or triazole containing ligands have been reviewed by us.[8] We found that no macrocyclic complexes containing a triazole or triazolate moiety, of cobalt or indeed of any other metal ion, had been structurally characterised. In the present paper we describe the first three complexes of a macrocyclic triazolate-containing ligand ($L2^{2-}$) to be structurally characterised. One six-coordinate complex $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**) and two five-coordinate complexes $[Co^{II}_2(L2)(NCO)_2]$ (**3**) and $[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$ (**4**) have been characterised. All complexes contain two high-spin cobalt(II) centers and are weakly antiferromagnetically coupled as has been shown by magnetic susceptibility measurements. We have also found that the magnitude of magnetic exchange is dependent on the intersection angle of the two triazolate rings involved, becoming larger as the intersection angle decreases. Therefore, it would be interesting to develop this ligand system further by varying the lateral units, using alkyl links other than butylene to try and force the two triazolate rings into a more planar geometry and facilitate a larger antiferromagnetic coupling. We are actively pursuing this line of enquiry. In addition, our efforts are directed at varying the transition metal ions (studying iron in particular), axial groups and other aspects of the macrocycle framework itself.[13]

Experimental

3,5-Diacetyl-1*H*-1,2,4-triazole was prepared according to the literature preparation.[11] All reagents and solvents were used as received, without further purification, unless otherwise stated. Acetonitrile was refluxed over calcium hydride and distilled prior to use.

The magnetic measurements were carried out on a Quantum Design MPMS5 Squid Instrument as described earlier.[3,4,6] Other measurements were carried out as described previously.[2,3]

CAUTION! Whilst no problems were encountered in the course of this work, perchlorate mixtures are potentially explosive and should therefore be handled with appropriate care.

Syntheses

$[Pb_2(L2)](ClO_4)_2$ (1). To a stirred solution of 3,5-diacetyl-1*H*-1,2,4-triazole (153 mg, 1 mmol) and NaOH (40 mg, 1 mmol) in 2-propanol (30 cm^3) was added $Pb(ClO_4)_2 \cdot 3H_2O$ (460 mg, 1 mmol). A solution of 1,4-diaminobutane (88 mg, 1 mmol) in 2-propanol (3 cm^3) was added dropwise, causing the reaction mixture to become instantly cloudy. The reaction mixture was stirred at room temperature for 5 h, prior to heating and stirring on an oil-bath at reflux temperature overnight. The off-white precipitate produced was collected by filtration and dried under vacuum. The solid was added to CH_3CN (10 cm^3 per 100 mg) and subsequently filtered to remove the yellow insoluble powder. The volume of the filtrate was reduced and a large excess of diethyl ether added. The resulting fine suspension was stirred for 1 h, after which time the white precipitate of $[Pb_2(L2)](ClO_4)_2$ (327 mg, 32%) was readily collected by filtration. Found: C, 23.47; H, 2.72; N, 13.50; Cl, 6.93. $C_{20}H_{28}N_{10}Pb_2Cl_2O_8$ requires C, 23.51; H, 2.76; N, 13.71; Cl, 6.94%. IR (KBr disk) ν_{max}/cm^{-1}: 3445, 2927, 1630, 1448, 1416, 1358, 1089, 625. FAB *m*/*z* (rel. intensity) [fragment]: 154 (100) $[C_6H_{12}N_5]^+$, 220 (33), 307 (23) $[C_{12}H_{24}N_{10}]^+$, 923 (18) $[Pb_2(L2)(ClO_4)]^+$.

$[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (2). To a heated, stirred solution of $[Pb_2(L2)](ClO_4)_2$ (**1**) (102 mg, 0.1 mmol) in CH_3CN (60 cm^3) was added dropwise a solution of $CoCl_2 \cdot 6H_2O$ (48 mg, 0.2 mmol) in CH_3CN (5 cm^3). The resulting grey–tan suspension was refluxed for 4 h. Once the mixture had cooled down to room temperature the volume was reduced to about 10 cm^3 *via* rotary evaporation (*ca.* 40 °C) and the precipitate was removed by centrifugation (3000 rpm, 10 min). Vapour diffusion of diethyl ether into the resulting clear orange supernatant yielded orange crystals of $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (43 mg, 54%). Found: C, 30.36; H, 4.49; N, 17.23. $C_{20}H_{36}N_{10}Co_2Cl_2O_{12}$ requires C, 30.13; H, 4.55; N, 17.57%. IR (KBr disk) ν_{max}/cm^{-1}: 3415, 1638, 1601, 1486, 1443, 1416, 1357, 1222, 1188, 1091, 761, 623. FAB *m*/*z* (rel. intensity) [fragment]: 154 (100) $[C_6H_{12}N_5]^+$, 307 (15) $[C_{12}H_{24}N_{10}]^+$, 524 (40) $[Co_2(L2)]^+$, 625 (93) $[Co_2(L2)(ClO_4)]^+$. λ_{max}/nm (MeCN) ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 643 (19.1), 947 (22.3). Λ_m (MeCN) = 289 $mol^{-1}\ cm^2\ \Omega^{-1}$ (*cf.* 220–300 for a 2 : 1 electrolyte in MeCN).[17]

$[Co^{II}_2(L2)(NCO)_2]$ (3). To a stirred golden solution of $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**) (82 mg, 0.1 mmol) in CH_3CN (50 cm^3) was added NaOCN (33 mg, 0.4 mmol) as a solid. A few drops of water were added to dissolve the salt. Upon the addition of the salt the colour of the solution slowly changed to a pale purple. After stirring for 1 h, the volume of the solution was reduced to 10 cm^3 in vacuo (*ca.* 40 °C). Vapour diffusion of diethyl ether into the solution yielded red–purple crystals of $[Co^{II}_2(L2)(NCO)_2]$ (26 mg, 30%). Found: C, 43.06; H, 4.58; N, 27.50. $C_{22}H_{28}N_{12}Co_2O_2$ requires C, 43.29; H, 4.62; N, 27.54%. IR (KBr disk) ν_{max}/cm^{-1}: 3414, 2217, 1638, 1609, 1501, 1359, 1076, 620. EI *m*/*z* [fragment]: 154 $[C_6H_{12}N_5]^+$, 307 $[C_{12}H_{24}N_{10}]^+$, 568 $[Co_2(L2)(NCO)]^+$. λ_{max}/nm (MeCN) ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 524 (111), 559 (110), 774 (32.6). Λ_m (MeCN) = 3 $mol^{-1}\ cm^2\ \Omega^{-1}$.

$[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$ (4). To a refluxing, stirred golden solution of $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**) (82 mg, 0.1 mmol) in CH_3CN (50 cm^3) was added a solution of NEt_4Cl (33 mg, 0.2 mmol) in CH_3CN. Upon the addition of the salt the colour of the solution changed to a pale purple. After stirring for 30 min, the volume of the solution was reduced to *ca.* 10 cm^3 *in vacuo* (*ca.* 40 °C). Vapour diffusion of diethyl ether into the resulting solution yielded red crystals of $[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$ (23 mg, 36%). Found: C, 38.16; H, 5.52; N, 22.05. $C_{20}H_{34}N_{10}Co_2Cl_2O_2$ requires C, 37.95; H, 5.09; N, 22.12%. IR (KBr disk) ν_{max}/cm^{-1}: 3414, 2933, 1637, 1617, 1486, 1432, 1363, 1239, 1088, 622. EI *m*/*z* [fragment]: 154 $[C_6H_{12}N_5]^+$, 561 $[Co_2(L2)(Cl)]^+$, 602 $[Co_2(L2)(Cl)(CH_3CN)]^+$. λ_{max}/nm (MeCN) ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 513 (169), 561 (142), 820 (49.4). Λ_m (MeCN) = 6 $mol^{-1}\ cm^2\ \Omega^{-1}$.

X-Ray crystallography. Crystal data for $[Co^{II}_2(L2)(OH_2)_3(NCCH_3)](ClO_4)_2 \cdot H_2O \cdot 2CH_3CN$ (**2**) (orange plate, 168 K): $C_{26}H_{45}Cl_2Co_2N_{13}O_{12}$, M = 920.51, monoclinic, space group $P2_1/c$, a = 13.490(5), b = 13.180(6), c = 22.818(9) Å, β = 95.136(16)°, U = 4041(3) Å^3, Z = 4, μ = 1.024 mm^{-1}, 17553 reflections collected. $R1$ = 0.0673 [for 1799 $F > 4\sigma(F)$; $wR2$ = 0.1844 and goodness of fit = 0.698 for all 7340 independent F^2; 483 parameters; all non-H atoms except the triazole C atoms refined anisotropically].

Crystal data for $[Co^{II}_2(L2)(NCO)_2]$ (**3**) (red–purple block, 168 K): $C_{22}H_{28}Co_2N_{12}O_2$, M = 610.42, monoclinic, space group $P2_1/c$, a = 13.286(5), b = 15.836(6), c = 13.262(5) Å, β = 114.294(4)°, U = 2543.1(15) Å^3, Z = 4, μ = 1.351 mm^{-1}, 31449 reflections collected. $R1$ = 0.0293 [for 3099 $F > 4\sigma(F)$; $wR2$ = 0.0644 and goodness of fit = 0.856 for all 5131 independent F^2; 347 parameters].

Crystal data for $[Co^{II}_2(L2)(Cl)_2] \cdot 1.5CH_3CN$ (**4**) (red block, 168 K): $C_{23}H_{32.5}Cl_2Co_2N_{11.5}$, M = 658.86, monoclinic, space group Cc, a = 20.250(4), b = 20.406(4), c = 14.364(3) Å, β = 107.466(3)°, U = 5662(2) Å^3, Z = 8, μ = 1.397 mm^{-1}, 36288 reflections collected. $R1$ = 0.0210 [for 8967 $F > 4\sigma(F)$; $wR2$ = 0.0536 and goodness of fit = 1.030 for all 9372 independent F^2; 734 parameters; racemically twinned BASF = 0.18(1); one MeCN disordered over two sites].

X-Ray data were collected on a Bruker SMART diffractometer (λ = 0.71073 Å) and the structures solved and refined using SHELXS and SHELXL.[18]

CCDC reference numbers 186640, 186641 and 197089.

See http://www.rsc.org/suppdata/dt/b2/b212131j/ for crystallographic data in CIF or other electronic format.

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