

New supramolecular complexes of manganese(II) and cobalt(II) with nucleic bases. Crystal structures of $[M(H_2O)_6(1-Mecyt)_6][ClO_4]_2 \cdot H_2O$, $[Co(1-Mecyt)_4][ClO_4]_2$ and $[M(H_2O)_4(cyt)_2][ClO_4]_2 \cdot 2cyt \cdot 2H_2O$ [$M = Co^{II}$ or Mn^{II} ; $cyt =$ cytosine; 1-Mecyt = 1-methylcytosine]

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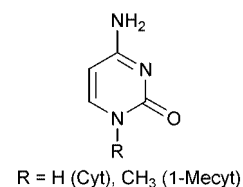
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The reactivity of cytosine [cyt] and 1-methylcytosine [1-Mecyt] towards transition metal ions Mn^{2+} and Co^{2+} has been tested through the analysis of their complexes. Two new compounds have been obtained from 1-Mecyt in aqueous medium, $[M(H_2O)_6(1-Mecyt)_6][ClO_4]_2 \cdot H_2O$ [$M = Mn^{II}$ **1** or Co^{II} **2**], and consist of hexaaqua ions linked to six 1-Mecyt molecules in such a way as to constitute a supramolecular cationic entity. Crystallization water molecules join the supramolecular assemblies by means of hydrogen bonds. Perchlorate anions, which are held in the crystal by electrostatic interactions with the cationic assemblies, insure the electroneutrality of the compounds. Compound **2** (pale pink crystals), when not filtered, over time disappears and gives rise to dark pink crystals of formula $[Co(1-Mecyt)_4][ClO_4]_2$ **3**. Compound **3** contains four 1-Mecyt molecules directly linked through N(3) atoms to Co^{2+} ions in a tetrahedral arrangement. No water molecule is present. The $[Co(1-Mecyt)_4]^{2+}$ cationic units are joined together through hydrogen bonds and form a chain. Perchlorate anions hold these cationic chains together by means of electrostatic forces. The reaction of cyt with Mn^{2+} and Co^{2+} ions leads to compounds of formulae $[M(H_2O)_4(cyt)_2][ClO_4]_2 \cdot 2cyt \cdot 2H_2O$ [$M = Mn^{2+}$ **4** or Co^{2+} **5**] in which base pairs are formed between the two unco-ordinated cytosine molecules and those co-ordinated to the metal ion through the O(2) atom. Each metal ion is six-co-ordinated, being linked also to four water molecules. Perchlorate anions and crystallization water molecules interact with the base pairs and the metal ion through hydrogen bonds to form five-membered rings. The cobalt(II) compound constitutes the first example of cytosine–cobalt(II) co-ordination *via* O(2).

Introduction

The interaction of metal ions with nucleic acids has generated great interest in biochemistry in recent years.^{1–3} Nucleic acids are molecules with a wide spectrum of binding possibilities: *via* nitrogen and oxygen atoms on the bases, *via* hydroxyl groups on the ribose sugar and *via* the negatively charged oxygen atoms on the phosphate groups. This different reactivity depends essentially on the metal ion “hard” acid (class a) or “soft” acid (class b) character.⁴ “Hard” metal ions, such as alkali or alkaline-earth, interact only with the phosphate group and cause stabilization of the double helix. On the contrary, “soft” metal ions, such as Pt^{2+} and Cu^{2+} and several other transition metal ions, prefer to interact with the base moiety and, consequently, in general destabilize the DNA structure. As is known, Mn^{2+} and Co^{2+} are borderline metals and have intermediate properties between a and b class metals.⁵

In order to investigate the reactivity of metal ions towards nucleic acids, it is useful to analyse their complexes with nucleobases. If we consider, in particular, the nucleobase cytosine (cyt) and its derivative 1-Mecyt, the binding sites of these ligands may behave differently, depending on the nature of the metal ion. Normally the binding modes are (1) through N(3) and (2) simultaneously through N(3) and O(2) atoms, while co-ordination solely through O(2) is rather unusual. Most transition metal ions prefer the first and second co-ordination



mode.^{6–25} Only a few cytosine complexes showing O(2) co-ordination are known: a Mn^{2+} complex of cytidine 5'-monophosphate (CMP)²⁶ and a Ni^{2+} complex of cyt.²⁷ Compounds of cyt and its derivatives with non-transition metal ions, such as the alkaline earth Mg^{2+} , appear particularly interesting.²⁸ In this case the complexes with cyt and 1-Mecyt show co-ordination through O(2),²⁹ but, in addition, a supramolecular assembly,³⁰ of formula $[Mg(H_2O)_6(1-Mecyt)_6]^{2+}$, made up of a $[Mg(H_2O)_6]^{2+}$ unit and of six 1-Mecyt molecules hydrogen bonded to the water molecules, was synthesized. This last compound might be considered a precursor of the compound containing Mg–O(2) bonds,²⁹ formed from the $[Mg(H_2O)_6(1-Mecyt)_6]^{2+}$ unit by removal of two water molecules from the magnesium inner co-ordination sphere together with two hydrogen bonded 1-Mecyt molecules, and subsequent formation of direct metal–base bonds. Only one compound containing Mg–O(2) bonds has been obtained from cytosine solutions.

Table 1 Selected interatomic distances (Å) and angles (°) for compound **1** with e.s.d.s in parentheses^a

Mn(1)–O(3)	2.180(4)	Mn(1)–O(4)	2.195(5)
Mn(1)–O(5)	2.129(6)		
O(3)–Mn(1)–O(4)	90.0(2)	O(3)–Mn(1)–O(5)	90.0(2)
O(4)–Mn(1)–O(5)	91.2(2)	O(3)–Mn(1)–O(4a)	90.0(2)
O(3)–Mn(1)–O(5a)	90.0(2)	O(4)–Mn(1)–O(5a)	88.8(2)

Hydrogen bonds^b

A	D	H	A...D	H...D	A...H–D
N(3)	O(3)	H(2w)	2.737(5)	1.78(2)	176(3)
O(22)	O(3)	H(1w)	2.702(7)	1.76(4)	168(4)
O(2a)	O(5)	H(6w)	2.651(5)	1.70(2)	177(4)
N(32)	O(5)	H(5w)	2.733(6)	1.79(2)	168(4)
N(31)	O(4)	H(3w)	2.733(6)	1.90(2)	145(3)
O(10)	O(4)	H(4w)	2.683(7)	1.80(5)	152(4)
O(21b)	N(4)	H(4A)	2.844(6)	1.98(1)	162(1)

^a Symmetry codes: a $-x, -y, -z$; b $1-x, -y, 1-z$. ^b A = Acceptor, D = donor.

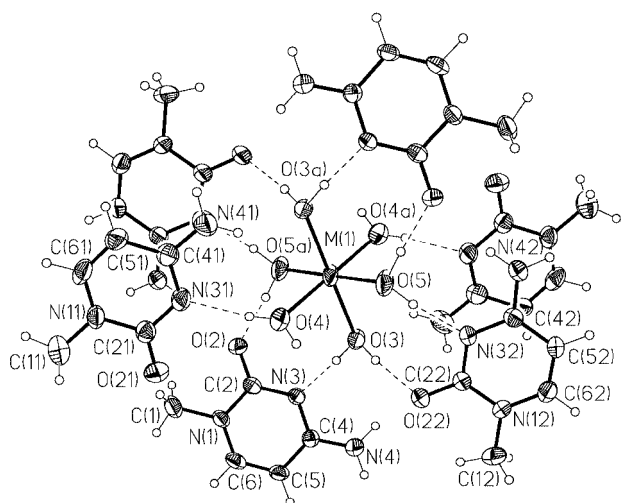


Fig. 1 Crystal structure and atomic labeling of the $[M(H_2O)_6(1-Mecyt)_4]^{2+}$ ion in complexes **1** [$M = Mn^{II}$] and **2** [$M = Co^{II}$].

In the present contribution we report the preparation and structural characterization of five new compounds with cyt or 1-Mecyt. Two of the 1-Mecyt compounds constitute a rare example of supramolecular assembly containing cobalt(II) and manganese(II) ions. The cyt analogue of Co^{II} is the first example of cytosine–cobalt(II) co-ordination *via* O(2).

Results and discussion

Description of the structures

Compounds **1** and **2** are constituted by cationic supramolecular $[M(H_2O)_6(1-Mecyt)_4]^{2+}$ ($M = Mn^{II}$ **1** or Co^{II} **2**) assemblies, perchlorate anions and crystallization water molecules (Fig. 1). They are isostructural with the related magnesium(II) derivative.²⁹ Each $[M(H_2O)_6(1-Mecyt)_4]^{2+}$ entity is formed by hexa-aquametal ions co-ordinated through ten hydrogen bonds to six 1-Mecyt molecules. In the $[M(H_2O)_6]^{2+}$ units the M–O distances are in the range 2.129–2.195(5) **1** and 2.071–2.096(3) Å **2** (Tables 1 and 2) and their values are similar to those reported for other hexaqua manganese^{31,32} and cobalt compounds,^{33,34} but longer than those of the magnesium derivative. The six 1-Mecyt molecules are not linked in the same way to the hexa-aquametal ions. Four of them form bridges between the water molecules of the best octahedral equatorial plane, through atoms O(3), O(5), O(3a), O(5a). The last two 1-Mecyt molecules are linked to the two axial water molecules through single hydrogen bonds. Different supramolecular entities are joined

Table 2 Selected interatomic distances (Å) and angles (°) for compound **2** with e.s.d.s in parentheses^a

Co(1)–O(3)	2.096(3)	Co(1)–O(4)	2.088(3)
Co(1)–O(5)	2.071(4)		
O(3)–Co(1)–O(4)	88.5(1)	O(3)–Co(1)–O(5)	90.0(1)
O(4)–Co(1)–O(5)	90.5(1)	O(3)–Co(1)–O(4a)	91.5(1)
O(3)–Co(1)–O(5a)	90.0(1)	O(4)–Co(1)–O(5a)	89.5(1)

Hydrogen bonds^b

A	D	H	A...D	H...D	A...H–D
N(3)	O(3)	H(2w)	2.743(4)	1.81(2)	164(4)
O(22)	O(3)	H(1w)	2.722(5)	1.77(3)	174(4)
O(2a)	O(5)	H(6w)	2.636(4)	1.70(2)	167(3)
N(32)	O(5)	H(5w)	2.749(5)	1.80(2)	175(3)
N(31)	O(4)	H(3w)	2.749(5)	1.83(2)	164(4)
O(10)	O(4)	H(4w)	2.778(4)	1.86(4)	162(4)
O(21b)	N(4)	H(4A)	2.848(5)	1.98(1)	161(1)

^a Symmetry codes: a $-x, -y, -z$; b $1-x, -y, 1-z$. ^b A = Acceptor, D = donor.

Table 3 Selected interatomic distances (Å) and angles (°) for compound **3** with e.s.d.s in parentheses^a

Co(1)–N(3)	2.076(2)		
N(3)–Co(1)–N(3a)	101.2(1)	N(3)–Co(1)–N(3b)	113.7(1)

Hydrogen bonds^b

A	D	H	A...D	H...D	A...H–D
O(2d)	N(4)	H(4B)	2.822(3)	1.968(3)	116(1)

^a Symmetry codes: a $1-x, 0.5-y, z$; b $0.25+x, 0.75-y, 0.75-z$; d $x, y-0.5, 1-z$. ^b A = Acceptor, D = donor.

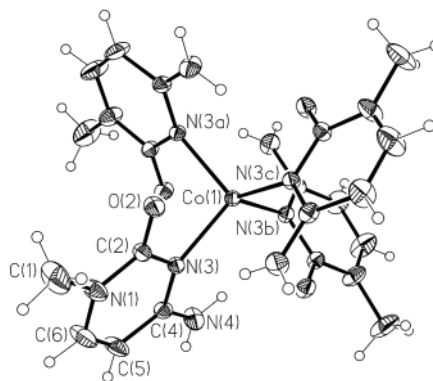


Fig. 2 Crystal structure and atomic labeling of the $[Co(1-Mecyt)_4]^{2+}$ ion in complex **3**.

together by hydrogen bonds in which O(2) of the single bonded 1-Mecyt and N(4) atoms, the linked [O(4)] and crystallization water molecules are involved.

Compound **3** is constituted by $[Co(1-Mecyt)_4]^{2+}$ units and perchlorate anions joined together by electrostatic forces. Each $[Co(1-Mecyt)_4]^{2+}$ unit contains Co^{2+} cations linked to four N(3) atoms of 1-Mecyt molecules in a tetrahedral arrangement (Fig. 2). All four equivalent Co–N distances have a value of 2.076(2) Å (Table 3) and are in agreement with those found in cobalt(II) compounds with the same chromophore.³⁵ The $[Co(1-Mecyt)_4]^{2+}$ units are joined together by hydrogen bonds, in which atoms N(4) and O(2d) ($d = x, y - 0.5, 1 - z$) are involved, in such a way to form a chain.

Compounds **4** and **5** are constituted by $[M(H_2O)_4(cyt)_2]^{2+}$ cations [$M = Mn^{II}$ **4** or Co^{II} **5**], unco-ordinated ClO_4^- anions and nucleobases and crystallization water molecules (Fig. 3). They are isostructural with the related magnesium compound. Co-ordinated and unco-ordinated cytosine molecules are joined

Table 4 Selected interatomic distances (Å) and angles (°) for compound **4** with e.s.d.s in parentheses^a

Mn(1)–O(2)	2.158(5)	Mn(1)–O(3)	2.158(4)
Mn(1)–O(4)	2.219(4)		
O(2)–Mn(1)–O(3)	90.4(2)	O(3)–Mn(1)–O(4)	88.9(2)
O(3)–Mn(1)–O(4)	90.4(1)	O(2)–Mn(1)–O(3a)	89.6(2)
O(2)–Mn(1)–O(4a)	91.1(2)	O(3)–Mn(1)–O(4a)	89.6(1)

Hydrogen bonds^b

A	D	H	A...D	H...D	A...H–D
O(21)	N(4)	H(4A)	3.037(6)	2.13(1)	171(1)
N(3)	N(11)	H(11)	2.804(5)	1.91(2)	175(1)
O(6)	N(41)	H(41B)	3.06(1)	2.19(1)	161(1)
O(61)	N(41)	H(41B)	2.96(2)	2.06(2)	171(1)
O(5)	O(9)	H(6w)	3.06(1)	2.11(3)	170(6)
O(51)	O(9)	H(6w)	2.97(2)	2.02(4)	172(6)
O(9)	O(4)	H(4w)	2.635(8)	1.71(5)	161(4)
O(4a)	N(1)	H(1)	2.934(7)	2.09(1)	154(1)
O(21b)	O(3)	H(1w)	2.817(6)	1.87(6)	173(5)
O(21c)	O(4)	H(3w)	2.749(5)	1.80(4)	169(5)
N(31c)	O(3)	H(2w)	2.759(6)	1.89(5)	150(3)

^a Symmetry codes: a $-x, -y, -z$; b $x, 1+y, z$; c $1-x, -1-y, -1-z$. ^b A = Acceptor, D = donor.

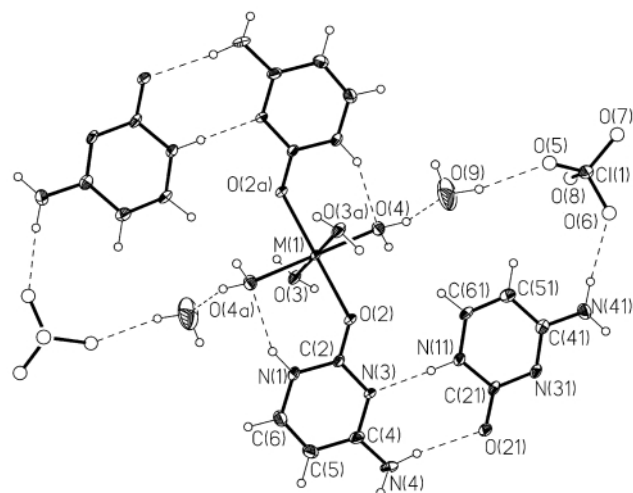


Fig. 3 Crystal structure and atomic labeling of complex **4** [M = Mn^{II}] and **5** [M = Co^{II}].

together by hydrogen bonds in such a way to form base pairs. In both compounds the metal ion is in an octahedral environment, being linked to four water and two cytosine molecules *trans*-coordinated *via* oxygen atoms. The octahedral geometry around Mn^{II} and Co^{II} is slightly elongated with the equatorial plane defined by atoms O(2), O(2a), O(3), O(3a). The M–O(2) and M–O(3) distances [2.158(5) (**4**), 2.097(5) (**5**) and 2.158(4) (**4**), 2.073(5) Å (**5**)] are in the same range found in **1** and **2** for Mn–O and Co–O, while the M–O(4) distances are longer [2.219(4) (**4**) and 2.124(4) Å (**5**)] (Tables 4 and 5) than those in the magnesium compound. Four hydrogen bonds, in which co-ordinated water molecules and nitrogen atoms N(1) and N(1a) are involved, contribute to the stabilization of the structures. Two crystallization water molecules and two perchlorate anions are linked to each other and are also linked to the [M(H₂O)₄–(cyt)₂]²⁺ ion and to the base pairs so as to form two rings (Fig. 3). The formation of base pairs in the complex might favour the co-ordination through the lone pair of O(2) close to N(1).

In all compounds the bond lengths and angles in the cytosine and 1-Mecyt moieties are in agreement with those reported in the literature. The perchlorate anion is tetrahedral, as expected, with mean chlorine–oxygen bond lengths and intra-anion bond angles of 1.387(6) Å and 109.3(4)° (**1**), 1.392(5) Å and 109.5(3)° (**2**), 1.371(7) Å and 109.2(5)° (**3**), 1.42(2) Å and 101(1)° (**4**), 1.41(2) Å and 108(1)° (**5**), respectively.

Table 5 Selected interatomic distances (Å) and angles (°) for compound **5** with e.s.d.s in parentheses^a

Co(1)–O(2)	2.097(5)	Co(1)–O(3)	2.073(5)
Co(1)–O(4)	2.124(4)		
O(2)–Co(1)–O(3)	90.2(2)	O(2)–Co(1)–O(4)	87.3(2)
O(3)–Co(1)–O(4)	91.2(2)	O(2)–Co(1)–O(3a)	89.8(2)
O(2)–Co(1)–O(4a)	92.7(2)	O(3)–Co(1)–O(4a)	88.9(2)

Hydrogen bonds^b

A	D	H	A...D	H...D	A...H–D
O(21)	N(4)	H(4A)	3.055(6)	2.15(1)	170(1)
N(3)	N(11)	H(11)	2.807(6)	1.91(1)	174(1)
O(6)	N(41)	H(41B)	3.07(1)	2.21(1)	160(1)
O(61)	N(41)	H(41B)	2.97(3)	2.08(3)	170(1)
O(5)	O(9)	H(6w)	3.06(1)	2.10(4)	175(6)
O(9)	O(4)	H(4w)	2.647(9)	1.76(6)	152(5)
O(4a)	N(1)	H(1)	2.874(8)	2.05(1)	152(1)
O(21b)	O(3)	H(1w)	2.844(8)	1.91(7)	164(5)
O(21c)	O(4)	H(3w)	2.730(6)	1.78(4)	168(6)
N(31c)	O(3)	H(2w)	2.760(6)	1.91(6)	146(3)

^a Symmetry codes: a $-x, -y, -z$; b $x, 1+y, z$; c $1-x, -1-y, -1-z$. ^b A = Acceptor, D = donor.

Conclusions

Useful information can be derived from the analysis of the cobalt(II) and manganese(II) compounds of cyt and 1-Mecyt by comparing these with the magnesium(II) analogues. As far as 1-Mecyt is concerned, both Co^{II} and Mg^{II} form two compounds, while Mn^{II} forms only one. The initial compounds obtained from Mg^{II} or Co^{II} consist of supramolecular assemblies (**1,2**). The other compound (**3**) is characterized by co-ordination metal–base bonds. Significant differences have been encountered in the features of the latter cobalt compound with respect to the magnesium derivative. In fact, the magnesium complex is octahedral while the cobalt one is tetrahedral. Furthermore, even though four base molecules are present in both compounds, in the magnesium complex two of them are linked through co-ordinated water molecules and two are directly bonded to the metal ion *via* O(2), whereas in the cobalt compound all 1-Mecyt are directly bonded to the metal *via* N(3). Tetrahedral co-ordination is not unusual for cobalt(II) compounds: in this case it may be dictated by steric reasons, since the co-ordination of six 1-Mecyt molecules would give an over-crowded assembly. More important than the tetrahedral co-ordination is the involvement of the nitrogen atom, even though the two features are probably correlated. More than on the differences (binding site, number of bases directly linked to the metal) we should focus on the analogies between the two compounds, *i.e.* on their derivation from similar solutions as an evolution of supramolecular assemblies. As for Mg^{II}, also cobalt(II) compounds **2** and **3** coexist in solution and, as previously mentioned, it seems reasonable to suppose that **2** is a precursor of **3**. However, the above mentioned differences imply a transformation mechanism different from that proposed for the magnesium compound. Indeed, in the cobalt(II) case, all six water molecules have to be pushed out from the metal co-ordination sphere in order to allow the bonding of four 1-Mecyt molecules, whereas in the magnesium case there are only two water molecules, which leave the first co-ordination sphere, while the other four remain co-ordinated.

A different behaviour was shown by the Mn²⁺ ion towards the same nucleobase. Only one compound (the supramolecular entity) has been obtained from Mn²⁺ solutions and 1-Mecyt under the same conditions as for Co²⁺ and Mg²⁺. It is noticeable that, in the Mn²⁺ case, the supramolecular assembly does not evolve towards a molecule containing direct metal–base links, as occurs for Co^{II} and Mg^{II}. The complex remains unchanged for several weeks (the reaction mechanism operating for Mg²⁺ and Co²⁺ does not seem to occur).

Table 6 Summary of crystal data for [Mn(H₂O)₆(1-Mecyt)₆][ClO₄]₂·H₂O **1**, [Co(H₂O)₆(1-Mecyt)₆][ClO₄]₂·H₂O **2**, [Co(1-Mecyt)₄][ClO₄]₂ **3**, [Mn(H₂O)₄(cyt)₂][ClO₄]₂·2cyt·2H₂O **4** and [Co(H₂O)₄(cyt)₂][ClO₄]₂·2cyt·2H₂O **5**

	1	2	3	4	5
Formula	C ₃₀ H ₅₆ Cl ₂ MnN ₁₈ O ₂₁	C ₃₀ H ₅₆ Cl ₂ CoN ₁₈ O ₂₁	C ₂₀ H ₂₈ Cl ₂ CoN ₁₂ O ₁₂	C ₁₆ H ₃₂ Cl ₂ MnN ₁₂ O ₁₈	C ₁₆ H ₃₂ Cl ₂ CoN ₁₂ O ₁₈
Formula weight	1130.8	1134.8	758.4	806.4	810.4
Crystal system	Monoclinic	Monoclinic	Tetragonal	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.511(2)	7.674(3)	13.737(2)	6.829(5)	6.756(2)
<i>b</i> /Å	32.346(6)	31.939(6)	13.737(2)	9.997(4)	9.985(2)
<i>c</i> /Å	10.526(3)	10.363(2)	16.131(3)	12.911(5)	12.837(3)
<i>a</i> °				71.65(3)	72.16(2)
<i>β</i> °	104.78(2)	103.96(2)		87.33(5)	87.78(2)
<i>γ</i> °				72.19(5)	72.19(2)
<i>U</i> /Å ³	2473(1)	2465(1)	3044.0(8)	795.3(7)	783.4(3)
<i>Z</i>	2	2	4	1	1
<i>μ</i> (Mo-Kα)/cm ⁻¹	4.68	5.50	8.20	6.79	8.16
Reflections collected/independent	5622/4886	5662/4872	1967/1676	2487/2265	3963/3449
Reflections observed/parameters	2234/346	2718/346	1312/107	2258/238	2155/239
<i>I</i> > <i>nσ</i> (<i>I</i>)	2	3	3	3	3
<i>R</i>	0.055	0.050	0.047	0.069	0.050
<i>R</i> '	0.056	0.054	0.054	0.073	0.056

A comparison of the cyt complexes of Mn^{II}, Co^{II} and Mg^{II} with those of 1-Mecyt allows us to understand the different reactivity of the two bases. With cyt only one type of complex was obtained in all three cases. The structures of these compounds show two cytosine base pairs, which are co-ordinated to the metal ion *via* O(2). The base pair formation is probably responsible for the different way in which the co-ordination proceeds in the cyt complex, for which no supramolecular assembly has been isolated.

Finally, in this work, several new cyt and 1-Mecyt compounds with Mn²⁺ and Co²⁺ metal ions have been prepared and studied by X-ray crystallographic analysis. They point out interesting analogies and differences, regarding both transition and non-transition metal ions, such as Mg²⁺, on the reactivity towards cyt and 1-Mecyt nucleobases. The following conclusions may be drawn: (a) isostructural compounds with cyt (the Co²⁺ case is the first example of O(2) co-ordination) and with 1-Mecyt have been obtained; (b) the supramolecular assembly is probably an intermediate step in the reaction of Mg²⁺ and Co²⁺ with the base which further evolves towards compounds containing Mg–O or Co–N bonds. On the contrary, in the Mn²⁺ case no compound containing co-ordinative covalent bonds was found and only the supramolecular assembly [Mn(H₂O)₆(1-Mecyt)]²⁺ remains remarkably stable for several weeks. (c) The Co²⁺ ion can bind both to atoms N(3) and O(2) of the cytosine moiety, due to its character, which is intermediate between “soft” ions like Cu²⁺ and “hard” ions like Mg²⁺.

Experimental

Materials

Manganese(II) perchlorate hexahydrate, cobalt(II) perchlorate hexahydrate, cyt and 1-Mecyt were obtained from commercial sources and used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Università degli Studi della Calabria (Italy).

Preparations

[Mn(H₂O)₆(1-Mecyt)₆][ClO₄]₂·H₂O **1**, [Co(H₂O)₆(1-Mecyt)₆][ClO₄]₂·H₂O **2** and [Co(1-Mecyt)₄][ClO₄]₂ **3**. Single crystals of **1** (colourless parallelepipeds) or **2** (pale pink parallelepipeds) have been obtained by slow evaporation of equimolar aqueous solutions of M(ClO₄)₂·6H₂O (M = Mn²⁺ or Co²⁺) and 1-Mecyt. A small amount of a second compound (polyhedral dark pink crystals) has been obtained in the Co²⁺ solution (compound **3**). The total yield of Co²⁺ reaction was 80% (70 and 10% for **2** and **3**, respectively) and that of Mn²⁺ 55%. When not filtered **2** over

time gradually disappears and gives rise to **3**. Compound **1**, on the contrary, is stable for several weeks: **1** (Found: C, 31.61; H, 4.90; N, 22.65. Calc. for C₃₀H₅₆Cl₂MnN₁₈O₂₁: C, 31.86; H, 4.99; N, 22.30); **2** (Found: C, 32.36; H, 4.85; N, 22.61. Calc. for C₃₀H₅₆Cl₂CoN₁₈O₂₁: C, 31.75; H, 4.97; N, 22.22); **3** (Found: C, 31.68; H, 3.66; N, 22.65. Calc. for C₂₀H₂₈Cl₂CoN₁₂O₁₂: C, 31.68; H, 3.72; N, 22.16%).

Single crystals of [M(H₂O)₄(cyt)₂][ClO₄]₂·2cyt·2H₂O [M = Mn²⁺ **4** (colourless needles) or Co²⁺ **5** (pale pink needles)] have been obtained by slow evaporation of equimolar aqueous solutions of M(ClO₄)₂·6H₂O (M = Mn²⁺ or Co²⁺) and cyt. The yield of the Mn²⁺ reaction was 75 and that of Co^{II} 78%: **4** (Found: C, 23.69; H, 3.87; N, 21.12. Calc. for C₁₆H₃₂Cl₂MnN₁₂O₁₈: C, 23.83; H, 4.00; N, 20.84); **5** (Found: C, 23.75; H, 4.00; N, 20.88. Calc. for C₁₆H₃₂Cl₂CoN₁₂O₁₈: C, 23.71; H, 3.98; N, 20.74%).

IR spectra

The IR spectra of cyt and 1-Mecyt complexes containing water molecules show several strong bands in the 3500–3200 cm⁻¹ region, which may be assigned to co-ordinated and unco-ordinated water and to the NH₂ group. The lower energy bands are assigned to hydrogen bonded ν(O–H_m) and ν(N–H_m) stretching vibrations. The appearance, for the cytosine complexes, of a band near 3600 cm⁻¹ was attributed to the free ν(O–H) stretching vibration of water. In the case of compound **3**, which does not contain water molecules, the strongest band at 3452 cm⁻¹ was assigned to the ν(NH) stretching of the NH₂ group. On the other hand the two weaker bands at 3314 and 3217 cm⁻¹ were assigned to the hydrogen bonded ν(NH) vibrations of the NH₂ group.

Crystallography

Diffraction data were collected at room temperature on a Bruker R3m/V automatic diffractometer by using graphite monochromated Mo-Kα radiation. Lorentz-polarization and analytical³⁶ or semi-empirical (*ψ* scan) corrections³⁷ were applied to the intensity data.

Solutions and refinements were performed with the SHELXTL PLUS system.³⁶ On the Δ*F* map of compounds **4** and **5**, because of two different coexistent orientations of the perchlorate anion, twice as many possible oxygen positions were localized. This disorder was described by assigning to each pair of sites population parameters of 0.7 and 0.3 for **4** and of 0.75 and 0.25 for **5**. All non-hydrogen atoms, except the disordered oxygen atoms of the perchlorate group in **4** and **5**, were refined anisotropically. The hydrogen atoms of the water mole-

cules (except those of the crystallization water molecule in **1** and **2**) were located on a ΔF map and refined with constraints. The nucleobase hydrogen atoms were set in calculated positions and refined as riding atoms. The final geometrical calculations were carried out with the PARST program.³⁸ Crystal data are summarized in Table 6.

CCDC reference number 186/1904.

See <http://www.rsc.org/suppdata/dt/a9/a908901b/> for crystallographic files in .cif format.

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