Characterisation of a Binary Transition Metal Complex of a 3′,5′-Cyclic Nucleotide [1]. Preparation and Structure of a Nickel(II) Complex of Guanosine 3′,5′-Cyclic Monophosphate

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Guanosine 3′,5′-Cyclic Monophosphate, Nickel(II) Complex, X-ray

$[Ni(3',5'\text{-cGMP})(H_2O)_5][3',5'\text{-cGMP}] \cdot 5\,H_2O$ (**1**) was isolated from an aqueous solution of $Ni(NO_3)_2$ and guanosine 3′,5′-cyclic monophosphate at a pH of 6.5. **1** is orthorhombic $P2_12_12_1$ with $a = 19.020(4)$, $b = 7.718(1)$, $c = 12.316(2)$ Å, $Z = 2$, $D_c = 1.70$ g·cm^{-3}. The structure was refined to $R = 0.085$ and $R_w = 0.077$ for 1364 independent reflections. The structure of **1** is disordered. The nickel atom has a site occupation factor of 0.5 with the 3′,5′-cGMP moieties of both cation and anion disordered over the same fourfold general positions. Direct metal binding of the purine N(7) is observed with the octahedral coordination of the nickel atom being completed by 5 water oxygens, one of which forms an intramolecular O–H···O hydrogen bond to the guanine O(6). The purine base adopts the *syn* conformation relative to the ribose ring with $\chi_{CN} = -93.3(8)°$. The nucleotide bases are stacked in columns along the *b* screw dyad axes. Parallel to these columns are cavities which are filled by the water molecules and the complexed nickel cations.

Introduction

X-ray structural studies of binary and ternary transition metal complexes of purine nucleotides enjoy considerable current popularity, as evidenced by recent review articles [2, 3]. These investigations have now been extended to ternary metal complexes of ADP [1] and ATP [4, 5]. However, with the exception of one ternary Cu(II) complex of guanosine 3′-monophosphate (3′-GMP) [6] and one binary Cu(II) complex of guanosine 2′-monophosphate (2′-GMP) [7], studies of purine nucleoside monophosphates have been restricted to complexes of 5′-monophosphates, in particular of guanosine 5′-monophosphate (5′-GMP) and inosine 5′-monophosphate (5′-IMP). Direct metal coordination of the purine base nitrogen N(7) has been observed in all characterised binary complexes. In polymeric Cu(II) and Zn(II) complexes, this metal-N(7) binding is augmented by direct metal-phosphate bonding to a second nucleotide molecule. In contrast and contrary to earlier predictions based on solution studies, it is found that the "harder" metals Mn^{2+}, Co^{2+} and Ni^{2+} coordinate only N(7) in their binary complexes, which display the general formula $[M(5'\text{-NMP})(H_2O)_5]$. The octahedral coordination of the metal is completed by five water oxygens. Though no direct metal-phosphate interaction is present, the structure is stabilised by two intramolecular O–H···O hydrogen bonds between two coordinated water molecules and two phosphate oxygens. The purine base is able to adopt its preferred *anti*-orientation relative to the sugar ring with χ_{CN}, the torsion angle C(8)–N(9)–C(1′)–O(1′), in the range $+15 \pm 20°$. Such complexes may be expected to be of biochemical relevance, as conditions *in vivo* would be expected to favour a high degree of hydration of the metal ion. Indeed a similar mode of metal binding has been established crystallographically for Co^{2+} and Mn^{2+} in $^tRNA^{Phe}$ [8].

We have initiated a systematic study of the effect of variation of the sugar substitution in purine nucleotides upon the modes of binding of both "harder" (*e.g.* Ni^{2+}, Co^{2+}) and "softer" (*e.g.* Cu^{2+}) metals. A similar base-phosphate juxtaposition, which would allow the mode of binding described above does not exist for 2′- and 3′-nucleotides or for 2′,3′-cyclic and 3′,5′-cyclic nucleotides. In this context it is interesting to record the recent observation that metal clays very effectively attract the 5′-nucleotides rather than 2′- and 3′-nucleotides [2]. In this paper we present the preparation and first structural characterisation of a metal complex of a 3′,5′-cyclic nucleotide, namely $[Ni(3',5'\text{-cGMP})(H_2O)_5][3',5'\text{-cGMP}] \cdot 5\,H_2O$ (**1**).

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It is well known that adenosine 3′,5′-cyclic monophosphate plays an essential role in many metabolic processes and that it can influence the activity of certain enzymes. It has also been demonstrated that 3′,5′-cGMP is involved in metabolic control and regulatory functions [9]. 3′,5′-cGMP has been found in a numer of mammalian tissues and body fluids. In the 3′,5′-cyclic nucleotides, the conformation about the C(4′)–C(5′) bond is constrained to be *gauche-trans*. In contrast, a *gauche-gauche* conformation is preferred by 5′-nucleotides and is indeed essential for the formation of intramolecular O–H ··· O hydrogen bonds to the phosphate oxygens in metal complexes of the type $[M(5'\text{-NMP})(H_2O)_5]$.

Experimental

Preparation of $[Ni(3',5'\text{-cGMP})(H_2O)_5][3',5'\text{-cGMP}]\cdot 5H_2O$ (**1**)

The complex **1** was isolated from a 2:1 molar solution of the sodium salt of 3′,5′-cGMP (Sigma Chemical Co) and nickel nitrate in a closed vessel at a pH of 6.5. Very pale green platelets of **1** were harvested after a period of 2–3 weeks. These were filtered and washed with water and methanol. Microanalysis was carried out by Beller (Göttingen).

Analysis for $[Ni(3',5'\text{-cGMP})(H_2O)_5][3',5'\text{-cGMP}]\cdot 5H_2O$

Calcd	C 25.9	H 4.6	N 15.1,
Found	C 25.8	H 4.6	N 15.3.

X-ray structural analysis of **1**

Crystals of **1** were rather small for an X-ray structural analysis. Preliminary photographic studies on a series of these crystals revealed an orthorhombic lattice with the cell constants (as subsequently determined from diffractometer settings) $a = 19.020(4)$, $b = 7.718(1)$, $c = 12.316(2)$ Å, $Z = 2$, $D_{ber} = 1.70\ g\,cm^{-3}$. The X-ray diffraction patterns also revealed very weak diffuse reflections corresponding to an orthorhombic lattice with $c = 24.632$ Å and $Z = 4$, thereby indicating disorder of the structure in the z direction. The relative magnitude of this diffuse scatter varied from crystal to crystal but the average intensity of the diffuse reflections (*i.e.* those with l odd for a lattice with $c = 24.632$ Å) was never more than about 5% of the average intensities of reflections with l even, for similar 2θ values. Systematic absences for $00l$ were observed for $l = 4n + 2$ indicating non-crystallographic symmetry. The relative intensities of the diffuse reflections did not alter with time. The nature of the disorder will be discussed subsequently. Systematic absences for the lattice with $c = 12.316$ Å were in accordance with the space group $P2_12_12_1$.

A crystal with the dimensions $0.13 \times 0.03 \times 0.18$ mm was used for the data collection. Intensities were collected in the θ–2θ mode ($2\theta \leq 130°$) on a Syntex $P2_1$ diffractometer with graphite-monochromated CuKα radiation ($\lambda = 1.54178$ Å). The data were initially collected for the orthorhombic cell with $c = 24.632$ Å. When the structure solution and refinement revealed the exact nature of the disorder the diffuse reflections with l odd were discarded. The following experimental details refer to the cell with $c = 12.316$ Å. An empirical absorption correction [$\mu(CuK\alpha) = 23.9\ cm^{-1}$] was applied on the basis of azimuthal scan data. Of 1777 unique reflections recorded 1364 with $F_o^2 \geq 2.0\sigma(F_o^2)$ were used for the refinement. The structure was solved by use of Patterson and difference syntheses and refined by blocked full-matrix least squares, $\Sigma w\Delta^2$ being minimised. The refinement established that the nickel atom has a site occupation factor (s.o.f.) of 0.5 but that the 3′,5′-cGMP atom positions display a full occupancy. This means that the 3′,5′-cGMP moieties in the two $[Ni(3',5'\text{-cGMP})(H_2O)_5]$ cations and the two [3′,5′-cGMP] anions in the unit cell are disordered over the same fourfold general positions. Difference syntheses established that the octahedral coordination of the nickel atom is completed by five water oxygens OW(1)–OW(5). One of these OW(2) has a site occupation factor (s.o.f.) of 0.5 with a corresponding non-coordinated water oxygen OW(6) (s.o.f. = 0.5) for the vacant nickel sites. OW(2) and OW(6) occupy positions at a distance of 1.75 Å from one another in the final electron density synthesis. The equivalent isotropic temperature factors U_{eq} for OW(1) and OW(3)–OW(5) (Table I) indicate that these are correctly refined with s.o.f.s of 1.0, thereby confirming a structure formula of $[Ni(3',5'\text{-cGMP})(H_2O)_5][3',5'\text{-cGMP}]\cdot 5H_2O$ for **1**. Refinement of the temperature factor components for OW(4) and OW(5) leads to a very pronounced anisotropy, which suggests that the coordinated and non-coordinated water oxygens must occupy slightly different sites. In view of the averaging of coordinated and non-coordinated water oxygens it is also apparent that the factor components for OW(1) and OW(3) must also be treated with reserve. Surprisingly, with the exception of the proton of the ribose oxygen O(2′), the positions of all 3′,5′-cGMP H atoms could be located in difference syntheses and were included in the final refinement cycles together with group isotropic temperature factors. Bond length constraints $d(C–H) = 1.08 \pm 0.02$, $d(N–H) = 0.99 \pm 0.02$ and $d(O–H) = 0.99 \pm 0.02$ Å were employed. Weights were given by the expression $w = k[\sigma^2(F_o) + 0.0002\ F_o^2]^{-1}$. The terminal R-factor was 0.085 with $R_w = 0.077$. The highest peak in the final electron density synthesis was of $0.65\ aÅ^{-3}$ at 1.00 Å from P. In view of the disorder and small size of the crystal, the final factor may be regarded as satisfactory. Table I lists the final atom coordinates for the non-hydrogen atoms

Table I. Positional parameters ($\times 10^4$).

	x	y	z	U_{eq}
NI	4628(2)	8607(4)	11207(3)	53(2)
N(1)	5713(5)	8353(13)	7599(10)	64(7)
C(2)	5308(6)	8498(15)	6663(10)	59(7)
N(2)	5616(6)	8612(20)	5707(9)	86(9)
N(3)	4610(5)	8505(13)	6729(8)	62(6)
C(4)	4392(7)	8431(14)	7770(10)	55(7)
C(5)	4752(6)	8362(13)	8688(10)	53(7)
C(6)	5477(7)	8233(13)	8624(10)	59(7)
O(6)	5920(5)	8074(11)	9355(7)	78(6)
N(7)	4314(5)	8397(11)	9587(8)	57(6)
C(8)	3687(6)	8480(15)	9163(10)	56(7)
N(9)	3676(5)	8519(11)	8070(8)	48(5)
C(1)′	3048(5)	8522(13)	7414(9)	48(6)
O(1)′	2901(4)	6700(9)	7145(6)	54(4)
C(2)′	3073(5)	9527(12)	6323(9)	47(6)
O(2)′	2464(4)	10631(8)	6236(7)	61(5)
C(3)′	3014(5)	8031(11)	5509(8)	44(6)
O(3)′	2722(4)	8485(8)	4493(6)	53(4)
C(4)′	2571(5)	6756(12)	6128(8)	42(5)
C(5)′	2537(5)	5040(12)	5532(9)	49(6)
O(5)′	2232(4)	5427(7)	4476(6)	46(4)
O(7)	3351(4)	6142(11)	3416(6)	67(5)
O(8)	2149(4)	7288(8)	2834(6)	52(4)
P	2634(2)	6792(3)	3704(2)	47(2)
OW(1)	5275(4)	10862(13)	10867(7)	89(7)
OW(2)	5461(7)	6890(18)	11018(14)	62(10)
OW(3)	4059(4)	6224(14)	11525(7)	93(7)
OW(4)	3857(5)	10322(13)	11741(13)	141(11)
OW(5)	4985(7)	8746(12)	12894(8)	128(9)
OW(6)	6268(10)	7407(20)	11623(14)	84(13)

Table II. Hydrogen atom positional parameters ($\times 10^3$) with isotropic temperature factors ($Å^2 \times 10^3$).

	x	y	z	U
H(1)	616(3)	787(14)	736(8)	75(19)
H(21)	609(2)	917(15)	585(9)	75(19)
H(22)	537(5)	845(15)	500(5)	75(19)
H(8)	326(4)	851(14)	972(6)	75(19)
H(1)′	252(2)	894(11)	762(7)	61(12)
H(2)′	361(2)	999(12)	627(8)	61(12)
H(3)′	355(2)	754(13)	554(8)	61(12)
H(4)′	203(2)	709(11)	629(8)	61(12)
H(51)′	309(2)	484(12)	540(8)	61(12)
H(52)′	213(3)	499(11)	615(6)	61(12)

Table III. Bond lengths (Å).

Ni–N(7)	2.09 (1)	Ni–OW(1)	2,17 (1)
Ni–OW(2)	2.08 (1)	Ni–OW(3)	2.17 (1)
Ni–OW(4)	2.08 (1)	Ni–OW(5)	2.19 (1)
N(1)–C(2)	1.39 (2)	N(1)–C(6)	1.34 (2)
C(2)–N(2)	1.32 (2)	C(2)–N(3)	1.33 (2)
N(3)–C(4)	1.35 (2)	C(4)–C(5)	1.32 (2)
C(4)–N(9)	1.41 (2)	C(5)–C(6)	1.38 (2)
C(5)–N(7)	1.39 (2)	C(6)–O(6)	1.24 (2)
N(7)–C(8)	1.30 (2)	C(8)–N(9)	1.35 (2)
N(9)–C(1)′	1.44 (1)	C(1)′–O(1)′	1.47 (1)
C(1)′–C(2)′	1.55 (2)	O(1)′–C(4)′	1.40 (1)
C(2)′–O(2)′	1.44 (1)	C(2)′–C(3)′	1.53 (1)
C(3)′–O(3)′	1.41 (1)	C(3)′–C(4)′	1.50 (1)
C(4)′–C(5)′	1.52 (1)	C(5)′–O(5)′	1.45 (1)
P–O(3)′	1.637(7)	P–O(5)′	1.612(7)
P–O(7)	1.497(8)	P–O(8)	1.464(8)

Table IV. Bond angles (°).

OW(1)–Ni	–N(7)	92.3(4)		OW(2)–Ni	–N(7)	93.5(5)
OW(2)–Ni	–OW(1)	93.3(5)		OW(3)–Ni	–N(7)	88.0(4)
OW(3)–Ni	–OW(1)	175.2(4)		OW(3)–Ni	–OW(2)	81.9(5)
OW(4)–Ni	–N(7)	98.6(5)		OW(4)–Ni–	–OW(1)	87.2(4)
OW(4)–Ni	–OW(2)	167.8(7)		OW(4)–Ni	–OW(3)	97.5(4)
OW(5)–Ni	–N(7)	177.8(4)		OW(5)–Ni	–OW(1)	88.2(4)
OW(5)–Ni	–OW(2)	84.3(6)		OW(5)–Ni	–OW(3)	91.4(4)
OW(5)–Ni	–OW(4)	83.5(5)		C(6)	–N(1) –C(2)	126.9(10)
N(2)	–C(2) –N(1)	120.0(11)		N(3)	–C(2) –N(1)	120.1(11)
N(3)	–C(2) –N(2)	119.8(11)		C(4)	–N(3) –C(2)	111.4(10)
C(5)	–C(4) –N(3)	130.8(12)		N(9)	–C(4) –N(3)	123.0(11)
N(9)	–C(4) –C(5)	106.1(10)		C(6)	–C(5) –C(4)	118.1(11)
N(7)	–C(5) –C(4)	111.7(10)		N(7)	–C(5) –C(6)	130.2(11)
C(5)	–C(6) –N(1)	112.4(11)		O(6)	–C(6) –N(1)	117.6(12)
O(6)	–C(6) –C(5)	130.0(12)		C(5)	–N(7) –Ni	126.3(8)
C(8)	–N(7) –Ni	129.8(8)		C(8)	–N(7) –C(5)	103.4(10)
N(9)	–C(8) –N(7)	114.6(11)		C(8)	–N(9) –C(4)	104.3(9)
C(1)′	–N(9) –C(4)	130.6(9)		C(1)′	–N(9) –C(8)	125.0(9)
O(1)′	–C(1)′–N(9)	106.4(8)		C(2)′	–C(1)′–N(9)	117.4(8)
C(2)′	–C(1)′–O(1)′	106.7(8)		C(4′)	–O(1)′–C(1)′	104.9(7)
O(2)′	–C(2)′–C(1)′	109.6(8)		C(3)′	–C(2)′–C(1)′	100.8(8)
C(3)′	–C(2)′–O(2)′	109.7(8)		O(3)′	–C(3)′–C(2)′	114.9(7)
C(4)′	–C(3)′–C(2)′	101.7(8)		C(4)′	–C(3)′–O(3)′	113.0(8)
P	–O(3)′–C(3)′	111.6(5)		C(3)′	–C(4)′–O(1)′	102.8(7)
C(5)′	–C(4)′–O(1)′	115.1(8)		C(5)′	–C(4)′–C(3)′	110.4(8)
O(5)′	–C(5)′–C(4)′	105.7(7)		P	–O(5)′–C(5)′	118.2(6)
O(5)′	–P –O(3)′	102.7(4)		O(7)	–P –O(3)′	108.4(4)
O(7)	–P –O(5)′	110.6(4)		O(8)	–P –O(3)′	106.9(4)
O(8)	–P –O(5)′	107.7(4)		O(8)	–P –O(7)	119.2(5)

with equivalent isotropic temperature factors*. Table II gives the positional parameters for the hydrogen atoms, Tables III and IV the bond distances and angles.

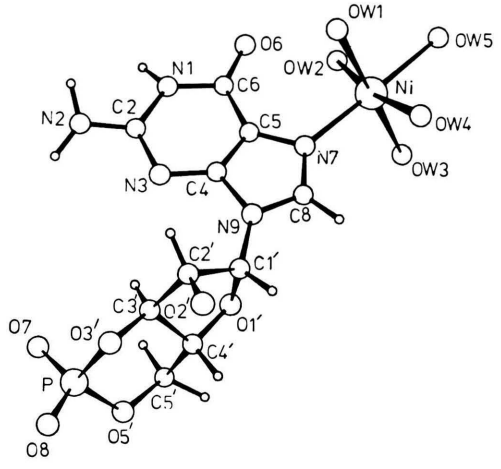

Fig. 1. Structure of the cation $[Ni(3'5'\text{-cGMP})(H_2O)_5]^+$.

Discussion

The principal features of the structure of the cation $[Ni(3',5'\text{-cGMP})(H_2O)_5]^+$ are displayed in Fig. 1. The nickel atoms are directly bonded to the purine base nitrogen N(7) at a distance of 2.09(1) Å, similar to those of 2.12(1) and 2.11(1) Å respectively in the complexes $[Ni(5'\text{-GMP})(H_2O)_5]$ [10] and $[Ni(5'\text{-IMP})(H_2O)_5]$ [11]. As in these complexes, five water molecules of crystallisation complete the slightly distorted octahedral coordination of the nickel atom in **1**. The structure of **1** is stabilised by an intramolecular O–H···O hydrogen bond of length 2.41(1) Å between OW(2) and the guanine O(6). The water molecules of crystallisation are involved in a complex network of hydrogen bonds.

The fact that the structure of **1** is disordered precludes a detailed discussion of bond lengths and angles. The non-crystallographic systematic absences for the diffuse reflections ($l = 4n + 2$) indicate local order in which the nickel cations are related by a 4_1 axis in the z direction ($c = 24.632$ Å). It is perhaps, at first site, remarkable that the nickel cations can be statistically disordered over different sites in the lattice. It is here of considerable relevance to note that sodium guanosine 3',5'-cyclic monophosphate tetrahydrate (**2**) also crystallises in a similar lattice ($P2_12_12_1$) with $a = 18.664$, $a = 7.384$, $c = 12.706$ Å [12]. The 3',5'-cGMP molecules in **2** occupy approximately the same sites as in **1**, although the individual atom positions are considerably shifted. The Na cation is octahedrally coordinated by the four water oxygens and two symmetry related water oxygens. It is not coordinated by N or O atoms of the 3',5'-cGMP moieties. This means that the crystal lattices of both the complex **1** and the salt **2** are determined by the 3',5'-cGMP molecules alone. As may be seen from the projection of a unit cell of **1** (Fig. 2), the

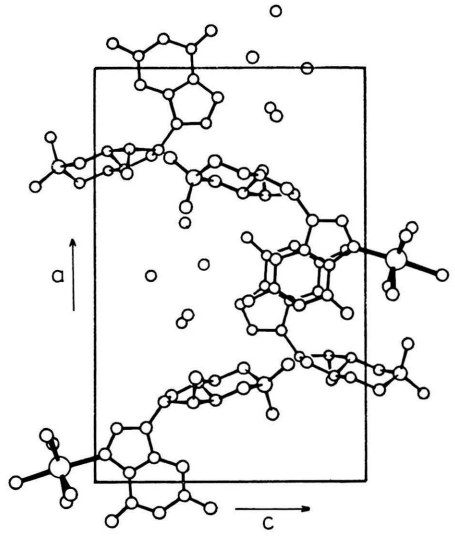

Fig. 2. Projection of the contents of a unit cell of **1**.

nucleotide bases are stacked in columns along the screw dyad axes of the y direction. Parallel to these columns are cavities which are filled by the water molecules and the complexed nickel ations in **1** and by the water molecules and the sodium cations in **2**. The water oxygens adopt different positions in the two structures. It is apparent that dispersion forces between stacked guanine bases and not hydrogen bonding are responsible for the observed crystal structure of **1** and **2**.

The glycosidic torsion angle χ_{CN} [O(1')–C(1')–N(9)–C(8)] is *syn* with a value of −93.3(8)° in **1**, as opposed to −102.4° in **2**. The ribose moiety in **1** displays the C(4')*exo*–C(3')*endo*

* Lists of anisotropic temperature factors and observed and calculated structure factors are available from the Fachinformationszentrum Energie–Physik–Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2. The Registry-Nr., CSD. 50192, the name of the author, and the reference should be given.

conformation, which is characteristic for cyclic nucleotides. For the phosphate ring, which is constrained to adopt a chair conformation, C(4′) is —0.718 and P 0.725 Å from the least squares plane through the remaining four ring atoms. The values of the torsion angles ψ_{OO} [O(5′)-C(5′)-C(4′)-O(3′)] and ψ_{OC} [O(5′)-C(5′)-C(4′)-C(3′)] are respectively —175.4(7) and —59.4(8)°. The exocyclic P–O(7) and P–O(8) distances of 1.50(1) and 1.46(1) Å indicate that the negative charge is delocalised over both these phosphate oxygens. The endocyclic P–O single bonds P–O(3′) and P–O(5′) are respectively 1.64(1) and 1.61(1) Å.

The observed coordination of N(7) but not a phosphate oxygen by the nickel cation in **1**, is of considerable biochemical significance. Inspection of Fig. 2 indicates that the phosphate oxygen O(7) protrudes into the cavities and could, therefore, be binded by the nickel cation instead of N(7) without disturbing the stacking pattern of the nucleotide bases. Furthermore, it should be possible for the nickel cation to directly bind both N(7) and O(7) of a second 3′,5′-cGMP molecule without major reorganisation of the structure. The local organisation of the nucleotides and the water molecules in the crystal lattice may be similar to the situation in solution, where base stacking is also observed. Conditions *in vivo* would be expected to favour a high degree of hydration of the metal ion. Thus it seems likely that binding to N(7) will be preferred over phosphate binding for 3′,5′-cyclic nucleotides. It should be noted in this context that the complex was prepared at approximately neutral pH (= 6.5). A similar mode of metal ion coordination stabilised by only one intramolecular OW–H···O(6) hydrogen bond may also be visualised for complexes of guanosine 2′- and 3′-nucleotides. In the analogous adenosine nucleotides this metal coordination will be stabilised by an intramolecular OW···H–N(6) hydrogen bond. As the binding pattern in complexes of "harder" metals with 5′-nucleotides is stabilised by three intramolecular hydrogen bonds, this could then explain why such metal cations prefer to complex these nucleotides.

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