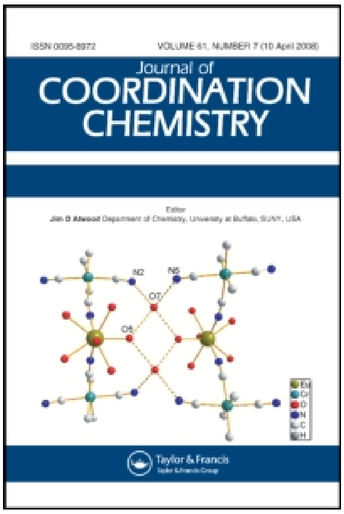

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Synthesis and characterization of Ni(II), Pd(II) and Pt(II) complexes of 2,4-diamino-5-(3, 4, 5-trimethoxybenzyl)pyrimidine complexes

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Synthesis and characterization of Ni(II), Pd(II) and Pt(II) complexes of 2,4-diamino-5-(3, 4, 5-trimethoxybenzyl) pyrimidine complexes

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The Ni(II), Pd(II) and Pt(II) complexes of 2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine (trimethoprim) have been synthesized and characterized by elemental analysis, electronic and IR spectroscopy, and magnetic susceptibility measurements. The single-crystal X-ray structure of the Ni(II) complex is reported. Ni(II) is coordinated to the N(1) atoms of two trimethoprim molecules that act as monodentates. Octahedral coordination around the nickel atom is completed by coordination to two molecules of methanol and two acetate ions. Pd(II) and Pt(II) complexes are square planar and the metal ions coordinate one molecule of trimethoprim, two chloride ions and a molecule of water.

Keywords: Trimethoprim; Pyrimidine; Pd(II); Pt(II); Ni(II); Crystal structure

1. Introduction

The discovery of sulfonamides and the elucidation of their mode of action paved the way for anti-metabolites as potential drugs [1]. Research on nucleic acid biosynthesis with synthetic analogues of purine and pyrimidine bases and observations with anti-thymines led to the realization that 2,4-diaminopyrimidines could inhibit folic acid metabolism in *Lactobacilli*. These observations led to the selection of trimethoprim as an antibacterial agent [2–4]. Trimethoprim is a substituted 2,4-diaminopyrimidine. It is a well-known drug that exhibits antibacterial and antiparasitic activities and is used extensively in medicine [5]. It is used clinically either alone or in combination with a sulfonamide, such as sulfamethoxazole, sulfadiazine or sulfadimethoxine. It is a synthetic, broad-spectrum antimicrobial agent and, like other diaminopyrimidines, acts as an inhibitor of dihydrofolate reductase [6, 7]. Trimethoprim is weakly bactericidal and resistance has emerged due to intensive use and misuse [8]. The emergence of

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resistance to major antibacterial and antiparasitic drugs [9] necessitates urgent need for drugs with novel structures, modes of action, or both. Recent research [10–12] has demonstrated that attaching organic drugs to metal-containing fragments can enhance their activity.

Studies on the interaction of trimethoprim as ligands with metal ions have received attention. Complexes of Co(II) [13], Cu(II) [14, 15], Rh(II) [16] and Cd(II) [17, 18] have been reported. The interaction of Ni(II) with trimethoprim has also been reported [19] and the complex was formulated as $[2NiCl_2 \cdot trimpr]$. It was concluded, from the IR spectrum of the complex, that coordination occurred between Ni(II) and one of the NH_2 groups on the pyrimidine fragment. As part of our studies on metal complexes of malarial drugs as potential chemotherapeutic agents in the management of chloroquine-resistant malaria, we present in this article the synthesis and characterization of Ni(II), Pd(II) and Pt(II) complexes of trimethoprim. We also present the single X-ray crystal structure of an Ni(II) complex of trimethoprim in which the metal is directly bonded to the N(1) atom of the pyrimidine ring.

2. Experimental

2.1. *Materials and instrumentation*

All reagents, salts and trimethoprim, were used as obtained from Aldrich. Elemental analyses were performed at the Microanalytical Laboratory of the School of Chemistry, the University of Manchester, UK. IR spectra (KBr disks) were obtained using a Perkin-Elmer paragon 1000 FTIR spectrophotometer equipped with cesium iodide windows (4000–250 cm^{-1}). Electronic spectra were obtained using a Perkin-Elmer Lambda 20 spectrophotometer (190–1100 nm). Magnetic susceptibility measurements were carried out using Sherwood Scientific magnetic susceptibility balance. Diamagnetic corrections were made using Pascal's constants [20].

2.2. *Preparation of metal complexes*

Metal complexes were prepared using the methods outlined below.

2.2.1. Nickel(II) complex of trimethoprim. Some 0.498 g (2 mmol) of $Ni(CH_3COO)_2 \cdot 4H_2O$ was dissolved in 70 cm^3 of methanol followed by a slow addition of 0.586 g (2 mmol) trimethoprim dissolved in 35 cm^3 of methanol. The resulting green solution was refluxed for 1 h and the solution left to evaporate slowly at room temperature. Green crystals suitable for X-ray analysis formed after one week. The complex is formulated as $[Ni(TMP)_2(CH_3OH)_2(OCOCH_3)_2]$ (TMP = trimethoprim). Anal. Calcd for $NiC_{34}H_{50}N_8O_{12}$ (%): C, 49.71; H, 6.14; N, 13.64, Ni, 7.17. Found: C, 49.56; H, 5.94; N, 13.46; Ni, 7.02. Yield: 56%; m.p. 264°C.

2.2.2. Palladium(II) complex of trimethoprim. Some 1.142 g (3.5 mmol) of K_2PdCl_4 was dissolved in 10 cm^3 of deionised water followed by a slow addition of 1.026 g (3.5 mmol) of trimethoprim in 60 cm^3 of methanol. The mixture was stirred at 40°C for 1 h. The yellow product was filtered off under vacuum and washed twice with methanol.

A brownish product was obtained. The complex is formulated as $[Pd(TMP)(H_2O)Cl_2]\cdot H_2O$. Anal. Calcd for $PdC_{14}H_{22}N_4O_5Cl_2$ (%): C, 33.39; H, 4.40; N, 11.12. Found: C, 33.17; H, 4.23, N, 10.97. Yield: 68%, m.p. 237°C.

2.2.3. Platinum(II) complex of trimethoprim. Some 1.453 g (3.5 mmol) of K_2PtCl_4 was dissolved in a minimum amount of deionised water followed by a slow addition of 1.026 g (3.5 mmol) of trimethoprim in 60 cm^3 of methanol. The mixture was stirred at 40°C for 1 h. The yellow product was filtered off under vacuum and washed twice with water. The complex is formulated as $[Pt(TMP)(H_2O)Cl_2]\cdot H_2O$. Anal. Calcd for $PtC_{14}H_{22}N_4O_5Cl_2$ (%): C, 28.39; 3.74; N, 9.46. Found: C, 28.13, H, 3.34, N, 9.30. Yield: 39%, m.p. 214°C.

2.3. *X-ray crystallography*

Data were collected with Mo-Kα radiation at 100 K on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low temperature device. A semi-empirical absorption correction was applied using SADABS [21] with maximum and minimum transmission factors of 0.845 and 0.750 respectively. The structure was solved by direct methods using SHELXS-97 and Fourier syntheses, using the SHELXTL package [21]. Hydrogen atoms were included in calculated positions and the structure was refined using full-matrix least-squares techniques against F^2 [21]. Crystallographic data are presented in table 1.

Table 1. Crystal data and structure refinement details for the nickel complex.

Empirical formula	$C_{34}H_{50}N_8NiO_{12}$
Formula weight	821.53
Temperature (K)	100(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	C_2/c
Unit cell dimensions	
a (Å)	27.080(5)
b (Å)	9.0649(5)
c (Å)	20.416(5)
β (°)	128.663(5)
Volume (Å^3)	3913(2)
Z	4
D_{calc} ($Mg\,m^{-3}$)	1.395
Absorption coefficient (mm^{-1})	0.566
F(000)	1736
Crystal size (mm^3)	0.40 × 0.40 × 0.40
θ range (°)	1.93 to 26.39
Index ranges	$-33 \le h \le 29$, $-8 \le k \le 11$, $-25 \le l \le 25$
Reflections collected	10995
Independent reflections	3993 [R(int) =0.0354]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3993/0/274
Goodness-of-fit on F^2	0.998
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0314$, $wR_2 = 0.0775$
R indices (all data)	$R_1 = 0.0391$, $wR_2 = 0.0796$
Largest diff. Peak and hole (Å)	0.0391 and $-0.231\,e\,Å^{-3}$

3. Results and discussion

Ni(II), Pd(II) and Pt(II) complexes of trimethoprim have been synthesized by reaction between the metal salt and trimethoprim in methanol or methanol/water. The complexes are air-stable. Analytical and spectroscopic data are consistent with the proposed formulation of the complexes.

3.1. *X-ray crystal structure of [Ni(TMP)$_2$(CH$_3$OH)$_2$(OCOCH$_3$)$_2$]*

Single X-ray crystal studies of the compound were undertaken to elucidate the coordination sphere around Ni(II). The molecular structure of the complex with the atom numbering scheme is shown in figure 1 and selected bond length and angles are given in table 2. The Ni(II) atom lies in an octahedral environment formed by two trimethoprim molecules that act as monodentates and coordinate through the pyrimidinyl N(1) atom, two acetate ions that act as monodentate ligands and the octahedral geometry around the Ni(II) ions is completed by coordination to two methanol molecules.

The two Ni–N(1) bond lengths (2.101 Å) are similar and the four other bond lengths from acetates and methanol are essentially the same (2.072 Å) with only very slight variation, but longer than the Ni–N(1) bond. Distortion of the octahedron is confirmed by variations in bond angles. Angles between Ni and the methanol molecules, O(6)–Ni(1)–O(6)#1, are 93.54(8)°. On the other hand, the angle between the Ni atom, methanol and acetate is less than 90° and the angle between Ni, N(1) and methanol is different from the angle involving acetate. O(6)#1–Ni(1)–N(1)#1 is 88.79(6)° whereas O(4)#1–Ni(1)–N(1)#1 is 92.84(5)° O(4)#1–Ni(1)–N(1) is 172.75(6)° while O(6)#1–Ni(1)–N(1)#1 is 177.64(5)°. The crystal structure consists of discrete

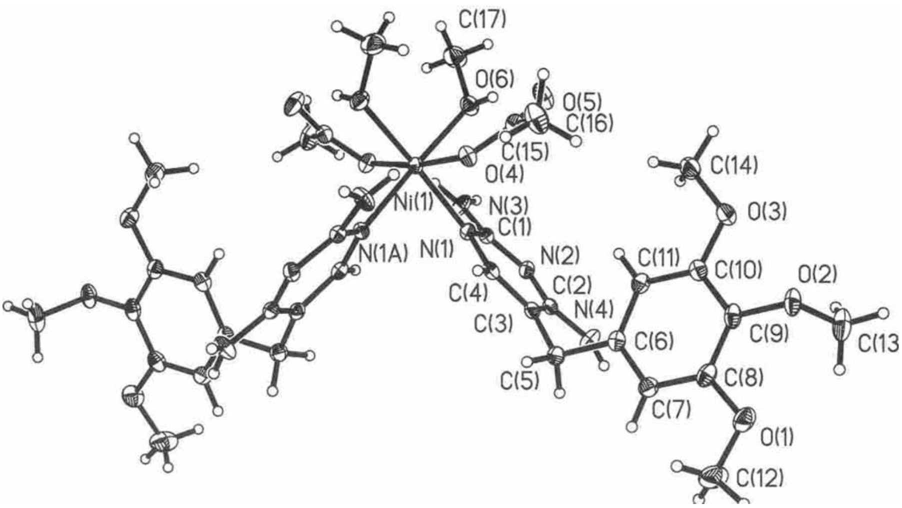

Figure 1. The molecular structure of [Ni(TMP)$_2$(OCOCH$_3$)$_2$(CH$_3$OH)$_2$] showing the atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°) for the nickel complex.

Ni–O(6)	2.0719(13)	O(6)–Ni(1)–O(6A)	93.54(8)
Ni–O(6A)	2.0720(13)	O(6)–Ni(1)–O(4A)	87.64(5)
Ni–O(4A)	2.0721(12)	O(6A)–Ni(1)–O(4A)	87.39(5)
Ni–O(4)	2.0721(12)	O(6)–Ni(1)–O(4)	87.39(5)
Ni–N(1)	2.1006(14)	O(6A)–Ni(1)–O(4)	172.75
Ni–N(1A)	2.1006(14)	O(6)–Ni(1)–N(1)	88.79
N(1)–C(4)	1.348(2)	O(6A)–Ni(1)–N(1)	177.64
N(1)–C(1)	1.353(2)	O(4A)–Ni(1)–N(1)	92.33
N(2)–C(2)	1.340(2)	O(4)–Ni(1)–N(1)	92.84(5)
N(3)–C(1)	1.344(2)	O(6)–Ni(1)–N(1A)	177.64(5)
N(3)–C(1)	1.337(2)	O(6A)–Ni(1)–N(1A)	88.79(6)
N(3)–H(3A)	0.86(2)	O(4A)–Ni(1)–N(1A)	92.84(5)
N(3)–H(3B)	0.80(2)	O(4)–Ni(1)–N(1A)	92.34(5)
N(4)–C(2)	1.340(2)	N(1)–Ni(1)–N(1A)	88.88(8)
N(4)–H(4A)	0.818(19)	C(15)–O(4)–Ni(1)	132.64(11)
N(4)–H(4B)	0.87(2)	C(17)–O(6)–Ni(1)	129.47(11)
C(2)–C(3)	1.423(2)	Ni(1)–O(6)–H(60)	105.1(16)
C(3)–C(4)	1.362(2)	C(1)–N(1)–Ni(1)	128.02(11)

Table 3. Hydrogen bond details.

D–H···A	d (D–H)	d (H···A)	d (D···A)	∠(DHA)
N(4)–H(4B)···N(2)#2	0.87(2)	2.24(2)	3.112(2)	179(2)
N(4)–H(4A)···O(3)#3	0.818(19)	2.473(19)	3.1063(19)	135.0(16)
N(3)–H(3B)···O(2)	0.80(2)	2.30(2)	2.925(2)	136(2)
N(3)–H(3A)···O(4)#1	0.86(2)	2.00(2)	2.790(2)	151.1(18)
O(6)–H(60)···O(5)	0.77(2)	1.85(2)	2.5969(18)	164(2)

Symmetry transformations used to generate equivalent atoms are 1: $-x+1$, $y,-z+3/2$; #2: $-x+1/2,-y+1/2,-z+1$; #3:$-x+1/2,-y+1/2,-z+3/2$.

$[Ni(TMP)_2(CH_3OH)_2(OCOCH_3)_2]$ molecules linked to four other molecules by intermolecular hydrogen bonds (table 3).

Packing of $[Ni(TMP)_2(CH_3OH)_2(OCOCH_3)_2]$ molecules in the crystal lattice (figure 2) consists of parallel chains formed by intermolecular H-bonding. Each discrete molecule possesses four intramolecular H-bonding and interacts likewise with four neighbouring molecules. The latter H-bonds involve an oxygen atom of the central methoxy group of each trimethoprim and one of the NH_2 groups. Thus each molecule of trimethoprim acts as an H-bond donor as well as an acceptor. For the intramolecular H-bonds, NH_2 of the trimethoprim and methanol molecules are donors while the acetate O atoms are acceptors.

3.2. *Infrared spectra*

Trimethoprim possesses seven potential donor sites, two pyrimidinyl N atoms, two NH_2 groups on the pyrimidine ring and three methoxy groups. In order to clarify the mode of bonding and the effect of the metal ion on the ligand, IR spectra of the free ligand and the metal complexes were studied (table 4) and bands were assigned based on careful comparison. The N–H stretching frequencies of the pyrimidine NH_2 in the free trimethoprim are assigned at 3471 and 3318 cm^{-1} and are affected by H-bonding as

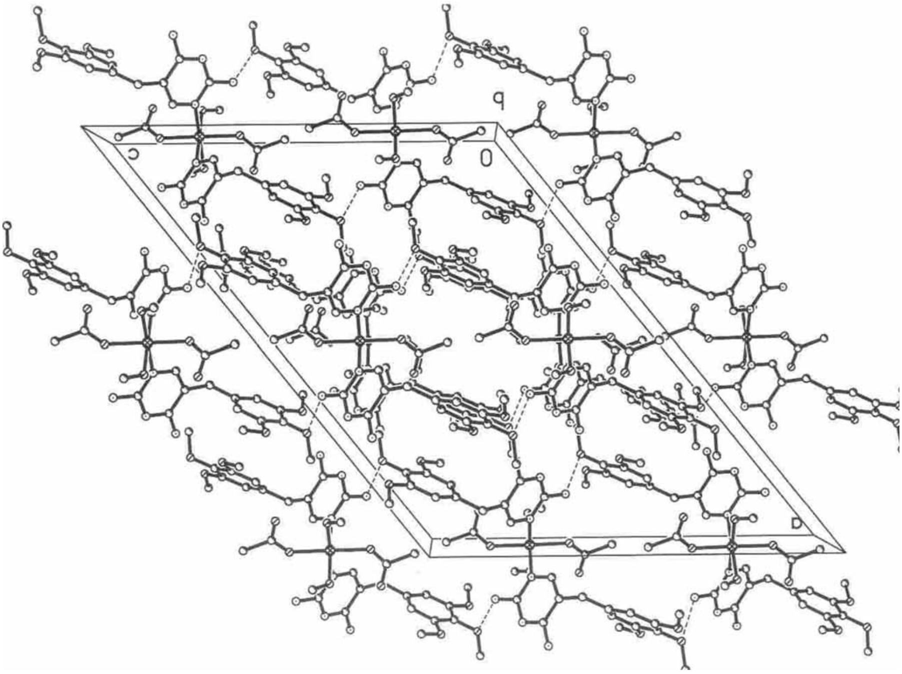

Figure 2. Crystal packing for $[Ni(TMP)_2(OCOCH_3)_2(CH_3OH)_2]$ showing intermolecular H-bonds.

Table 4. Selected IR data (cm^{-1}) for trimethoprim and the complexes.

	$\nu(NH_2)$	$\nu C{=}N$	$\nu M{-}N$	$\nu M{-}O$	$\nu M{-}Cl$
Trimethoprim	3471vs 3318s	1632ms, 1595m 1565m			
$[Ni(TMP)_2(CH_3OH)_2(OCOCH_3)_2]$	3460s 3369ms 3182m	1630s	528s	438ms	
$[Pd(TMP)(H_2O)Cl_2] \cdot H_2O$	3411s 3327ms 3182m	1631vs	589m	528ms	391m
$[Pt(TMP)(H_2O)Cl_2] \cdot H_2O$	3442ms 3182m	1631vs	587m	512ms	368m

shown by a broad band at 3117 cm^{-1} [18, 22]. Bands in the region 3440–3270 cm^{-1} assigned to symmetrical and asymmetrical stretching modes of NH_2 in the spectra of the complexes showed slight changes when compared to trimethoprim. These could be attributed to the overlap of ν(N–H) and ν(O–H) of methanol, lattice water or inter- and intramolecular hydrogen bonding. Medium intensity bands at 3182 cm^{-1} in all complexes are probably associated with ν(O–H) of methanol in the Ni complex and lattice water in the Pt and Pd complexes. This indicates that the NH_2 groups are probably not involved in coordination, as confirmed in the crystal structure of the Ni complexes. Coordination through the quinoline N(1) is confirmed by the shift in ν(C=N) which appears as three bands with medium intensity in trimethoprim but as a single sharp band in all complexes. Thus bands at 1632, 1565 and 1595 cm^{-1} in trimethoprim shift to 1630 cm^{-1} in the complexes.

The mode of coordination of the carboxylate groups can be deduced from the magnitude of the observed separation (Δ) between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$. The presence of acetate in the coordination sphere of the Ni complex is confirmed by $\nu_{as}(CO_2)$

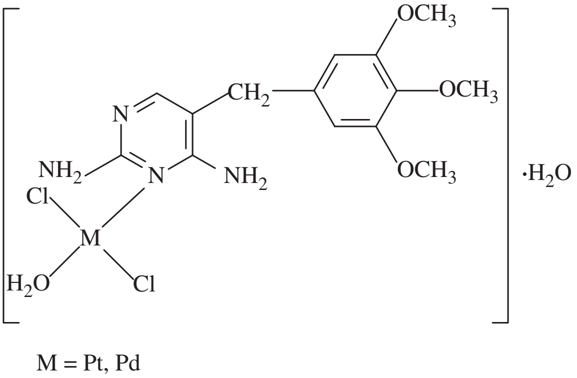

Figure 3. Proposed structure of Pt(II) and Pd(II) trimethoprim complexes.

at 1630 cm^{-1} compared to 1578 cm^{-1} for CH_3COONa [23] and $\nu_s(CO_2)$ at 1471 cm^{-1} compared to 1414 cm^{-1} for CH_3COONa. The band at 528 cm^{-1} is assigned to Ni–N stretching while bands at 438 and 391 cm^{-1} are assigned to Ni–O modes. Spectra of both Pt(II) and Pd(II) complexes are quite similar. Rocking and wagging vibrations of coordinated water, $\rho_r(H_2O)$, occur at 620 cm^{-1} (Pd) and 617 cm^{-1} (Pt) while ρ_w (H_2O) is assigned to the bands at 845 and 810 cm^{-1} in both complexes, respectively. The ν(M–N) mode is assigned to the band at 589 cm^{-1} (Pd) and 587 cm^{-1} (Pt); ν(M–O) bands occur at 528 cm^{-1} (Pd) and 512 cm^{-1} (Pt); ν(M–Cl) is assigned to a single band at 389 (Pd) and 368 cm^{-1} (Pt) as expected for *trans*-M–Cl complexes [24, 25].

3.3. *Electronic spectra and magnetic properties*

Electronic spectra of the complexes were measured using DMF. $[Ni(TMP)_2(CH_3OH)_2(OCOCH_3)_2]$ showed three absorption bands corresponding to partly allowed transitions for a d^8 octahedral environment [26]. The absorption band at 400 nm is assigned to $^3A_{2g}(F) \rightarrow ^3 T_{1g}(P)$; a second band at 662 nm, along with a weak shoulder at about 800 nm, is assigned to $^3A_{2g}(F) \rightarrow ^3 T_{1g}(F)$. The $^3A_{2g}(F) \rightarrow ^3 T_{2g}(F)$ transition is assigned to a broad band that starts at about 1050 nm but could not be fully established due to instrumental limitations [27]. The effective magnetic moments of 2.97 BM are normal.

Due to their electronic requirements, Pt(II) and Pd(II) typically form square planar complexes with electronic spectra dominated by charge-transfer bands [28]. $[Pd(TMP)(H_2O)Cl_2] \cdot H_2O$ and $[Pt(TMP)(H_2O)Cl_2] \cdot H_2O$ spectra are typical of square planar complexes which show no obvious d–d absorption bands but gave a series of fragmented bands between 400 and 300 nm. The fine structure could be attributed to high spin–orbit coupling. The bands in the region 360–310 nm may be attributed to intraligand transitions [29]. Magnetic moments of 0.34 BM for the Pt(II) and 0.24 BM for the Pd(II) complexes respectively confirm the suggested square planar arrangement (figure 3).

Supplementary data

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC 279024. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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