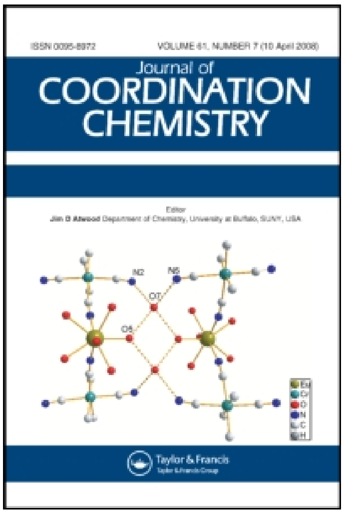

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The coordination properties of aminobenzoate ligands in complexes with alkali metals

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THE COORDINATION PROPERTIES OF AMINOBENZOATE LIGANDS IN COMPLEXES WITH ALKALI METALS

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The crystal structures of sodium 4-amino-2-hydroxybenzoate dihydrate [$NaL \cdot 2H_2O$, $L = C_6H_3(NH_2)(OH)COO$] and potassium 2-aminobenzoate monohydrate [$KL^* \cdot H_2O$, $L^* = C_6H_4(NH_2)COO$] were determined by X-ray diffraction methods. The compound $NaL \cdot 2H_2O$ crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 8.820(2)$, $b = 14.632(3)$, $c = 6.948(2)$ Å, $\beta = 97.88(3)°$. The structure consists of sodium ion pairs joined together by tridentate 4-amino-2-hydroxybenzoate moieties creating a polymeric chain. In the metal centres, two water molecules bridge the sodium atoms. Five oxygen atoms and one nitrogen atom form a distorted octahedral environment. The compound $KL^* \cdot H_2O$ crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 14.684(3)$, $b = 7.618(2)$, $c = 7.512(2)$ Å, $\beta = 96.95(3)°$. The structure consists of octacoordinated potassium atoms bonded with three water molecules and five carboxylate oxygen atoms. Water molecules appear as bridging ligands. The 2-aminobenzoate ligand acts as a pentadentate ligand with the molecular network stabilized by hydrogen bonds. Among the polymeric chains in both structures appear noncovalent interactions of type $N-H \cdots X$.

Keywords: Sodium 4-amino-2-hydroxybenzoate; Potassium 2-aminobenzoate; Crystal structure

INTRODUCTION

The alkali metals and aminobenzoic acids play important roles in biological systems. Na^+ and K^+ ions are responsible for osmotic pressure in cells. They also take part in nerve impulse transmission and stabilization of nucleic acid structures [1,2]. 2-Aminobenzoic acid (anthranilic acid) is the precursor of the α-amino acids tryptophan, phenylalanine and tyrosine [3]. It is also a metabolic product of some bacteria as well as being involved in the biosynthesis of phytohormones. Aminobenzoic acids and their derivatives are also widely investigated with regard to their applications in pharmacy [4]. Aminobenzoic derivatives glafenine and metoclopramide are used as

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an non-narcotic analgesic and an antiemetic drug, respectively [5,6]. The menthyl- and *N*-acetylhomomenthyl anthranilates are described as stable and safe UV filters [7]. 4-Amino-2-hydroxybenzoic acid (PAS) and its sodium, potassium and calcium salts are used for the treatment of tuberculosis and inflammatory bowel disease [8]. Sodium salts of aminobenzoic acids have also been studied with regard to their influence in solubilizing the drugs [9].

The aminobenzoate ligand contains amino and carboxylate groups which may coordinate alkali metals in different ways. In sodium 2-amino-3,5-dichlorobenzoate, coordination through the monodentate carboxylate group occurs [10]. On the other hand, with 3,4-diaminobenzoic acid, sodium salt coordination by a bidentate bridging carboxylate group takes place [11]. In the present work we describe the mode of bonding of sodium ions to 4-amino-2-hydroxybenzoic acid (4-aminosalicylic acid) and potassium ions to 2-aminobenzoic acid.

EXPERIMENTAL

Crystals of the compounds were grown by slow evaporation of aqueous solutions of sodium 4-amino-2-hydroxybenzoate and potassium 2-aminobenzoate. The salt solutions were obtained by adding a solution of sodium (potassium) hydroxide to an aqueous suspension of 4-amino-2-hydroxybenzoic acid (2-aminobenzoic acid) in the molar ratio 1:1.

X-Ray Data Collection and Structure Refinement

Crystallographic data and refinement procedures are given in Table I. X-ray data were collected on a Kuma KM-4 diffractometer. Preliminary Weissenberg photographs gave the crystal system, space group and approximate unit cell dimensions. Data were corrected for Lorentz and polarization effects. The crystal structures were solved by direct methods using the SHELXS-97 program [12] and refined by full-matrix least-squares methods using SHELXL-97 [13]. The positions of all hydrogen atoms were determined from a difference Fourier map and refined. Several cycles of refinement of the coordinates and anisotropic thermal parameters for nonhydrogen atoms reduced R to 0.0340 and 0.0281 for the sodium and potassium salts, respectively. Scattering factors were those incorporated in SHELXL-97. Final parameters and their estimated standard deviations are listed in Tables II and III.

RESULTS AND DISCUSSION

The Crystal Structure of Sodium 4-Amino-2-hydroxybenzoate Dihydrate

The crystal structure of sodium 4-amino-2-hydroxybenzoate dihydrate, $C_6H_3(NH_2)(OH)COONa \cdot 2H_2O$, is shown in Fig. 1. The polymeric structure consists of pairs of sodium ions bridged through tridentate 4-aminosalicylate ligands. Didentate water molecules bridge the sodium atoms in the metal pairs. The Na···Na distance is 3.4780(13) Å. Corresponding distances in polymeric chains of sodium salts of 2-amino-3,5-dichlorobenzoic [10] and 3,4-diaminobenzoic [11] acids are 3.526(2) and

TABLE I Summary of data collection and structure refinement details

Compound	$NaL \cdot 2H_2O$	$KL^* \cdot H_2O$
Formula	$C_7H_{10}NNaO_5$	$C_7H_8KNO_3$
M_r	211.15	193.24
Temperature (°C)	20	20
Radiation	Mo K_α (graphite monochromator, 0.71073 Å)	
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.820(2)	14.684(3)
b (Å)	14.632(3)	7.618(2)
c (Å)	6.948(2)	7.512(2)
β (°)	97.88(3)	96.95(3)
Cell volume (Å^3)	888.2(3)	834.1(4)
Z	4	4
D_{calc} (Mg m^{-3})	1.579	1.539
Absorption coefficient (mm^{-1})	0.173	0.601
Crystal dimensions (mm)	0.2 × 0.25 × 0.40	0.10 × 0.25 × 0.30
Index ranges (h, k, l)	$-10 \rightarrow 10$, $0 \rightarrow 18$, $0 \rightarrow 9$	$0 \rightarrow 20$, $0 \rightarrow 10$, $-10 \rightarrow 10$
2θ range (°)	4.6–55.0	5.5–60.0
Reflections collected/unique	2005/2005	2321
Observed reflections [$I > 2\sigma(I)$]	1324	1777
Goodness-of-fit	1.007	1.098
$R1$; wR_2 [$I > 2\sigma(I)$]	0.0340; 0.0884	0.0281; 0.0811
Extinction coefficient	0.005(3)	0.010(3)
Largest diff. peak and hole (Å^{-3})	0.386; −0.214	0.196; −0.258

TABLE II Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms with e.s.d. values in parentheses for the structure of sodium 4-amino-2-hydroxybenzoate dihydrate

Atom	x/a	Y/a	z/a	U_{eq}
Na	0.3174(1)	0.04461(5)	0.0015(1)	0.0474(2)
O(1)	−0.3738(1)	0.11705(8)	0.5777(2)	0.0437(3)
O(2)	−0.2033(1)	0.07215(9)	0.8235(2)	0.0478(3)
O(3)	0.0808(1)	0.07651(9)	0.8014(2)	0.0427(3)
O(4)	0.4617(1)	−0.00676(9)	−0.2358(2)	0.0369(3)
O(5)	0.5097(2)	0.20213(15)	−0.0537(3)	0.0763(5)
N	0.2458(2)	0.17219(11)	0.2089(2)	0.0432(4)
C(1)	−0.1109(2)	0.11928(9)	0.5371(2)	0.0292(3)
C(2)	0.0428(2)	0.10593(9)	0.6170(2)	0.0303(3)
C(3)	0.1604(2)	0.12402(10)	0.5081(2)	0.0327(3)
C(4)	0.1276(2)	0.15581(9)	0.3197(2)	0.0316(3)
C(5)	−0.0247(2)	0.16896(10)	0.2380(2)	0.0332(3)
C(6)	−0.1405(2)	0.15091(10)	0.3469(2)	0.0314(3)
C(7)	−0.2368(2)	0.10192(10)	0.6535(2)	0.0333(3)

3.1198(5) Å, respectively. The coordination environments of Na ions in the compounds are the same. Each sodium atom is bonded to three different 4-aminosalicylate ions. The first is linked to Na through a carboxylate oxygen atom, the second through a phenolic oxygen O atom and the third by an NH_2 group. Three water molecules complete the coordination sphere. In such a manner the coordination polyhedron of Na takes the form of a distorted octahedron, in which axial positions are occupied by the carboxylate oxygen atom O(2)^{ii} and a water molecule O(5).

TABLE III Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms with e.s.d. values in parentheses for the structure of potassium 2-aminobenzoate monohydrate

Atom	*x/a*	*y/a*	*z/a*	U_{eq}
K	−0.01946(2)	0.24974(4)	−0.06580(4)	0.03204(12)
O(1)	0.11539(8)	0.2801(1)	0.2103(2)	0.0366(3)
O(2)	0.10619(7)	0.5294(2)	0.3565(2)	0.0383(3)
O(3)	−0.12654(10)	0.0606(2)	−0.3268(2)	0.0480(3)
N	0.26695(12)	0.6788(2)	0.4978(2)	0.0458(4)
C(1)	0.25086(9)	0.4493(2)	0.2691(2)	0.0253(3)
C(2)	0.30382(10)	0.5723(2)	0.3750(2)	0.0304(3)
C(3)	0.39650(11)	0.5916(2)	0.3519(3)	0.0431(4)
C(4)	0.43507(11)	0.4953(3)	0.2262(3)	0.0505(5)
C(5)	0.38355(13)	0.3748(3)	0.1210(3)	0.0501(5)
C(6)	0.29254(11)	0.3519(2)	0.1445(2)	0.0375(3)
C(7)	0.15044(9)	0.4181(2)	0.2807(2)	0.0254(3)

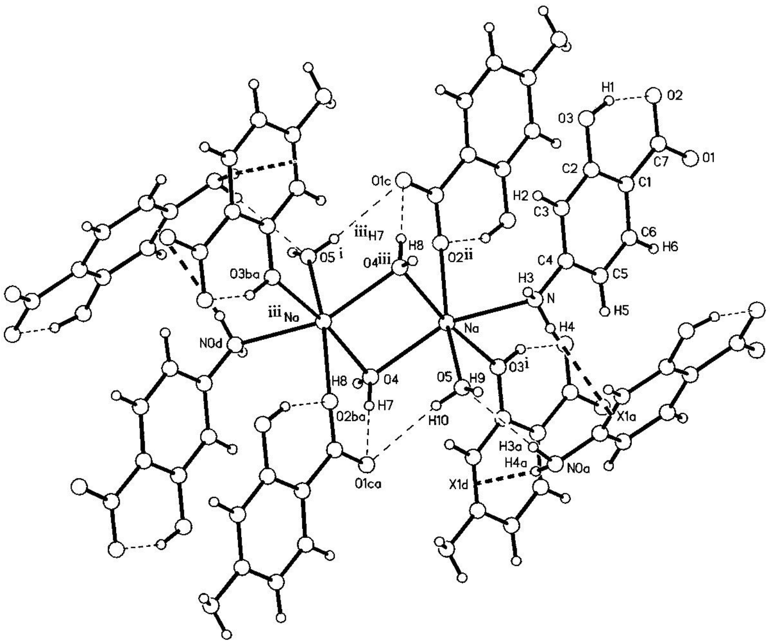

FIGURE 1 Crystal structure of sodium 4-amino-2-hydroxybenzoate.

Octahedral coordination is also observed in sodium salts of 2-amino-3,5-dichlorobenzoic [10], 3,4-diaminobenzoic [11], acetic [14,15] and phthalic acids [16]. Neighboring coordination polyhedra share an edge through the atoms O(4) and O(4)^{iii} from didentate water molecules. Bond lengths in the coordination polyhedron are given in Table IV. The Na–O$_{water}$ distances vary in the range 2.3407(14) to 2.918(2) Å. Na–O$_{carboxyl}$ and Na–O$_{hydroxyl}$ bond lengths are 2.3973(14) and 2.3902(14) Å, respectively. The Na–N bond length is equal to 2.4921(17) Å. Such significant differences in interatomic distances force a considerable distortion in the coordination polyhedron.

TABLE IV Selected bond lengths (Å) and angles (°) with standard deviations in parentheses for sodium 4-amino-2-hydroxybenzoate dihydrate and potassium 2-aminobenzoate monohydrate

$NaL \cdot 2H_2O$		$KL^* \cdot H_2O$	
Na–O(2)^{ii}	2.3973(14)	K–O(1)	2.6984(15)
Na–O(4)	2.3407(14)	K–O(2)^{i}	2.7197(13)
Na–O(4)^{iii}	2.4253(14)	K–O(1)^{ii}	2.7583(14)
Na–O(5)	2.918(2)	K–O(2)^{ii}	2.9201(13)
Na–O(3)^{i}	2.3902(14)	K–O(2)^{iv}	2.9238(14)
Na–N	2.4921(17)	K–O(3)	2.7652(16)
		K–O(3)^{iii}	2.9094(16)
		K–O(3)^{v}	3.3577(18)
Na–Na^{iii}	3.4780(13)	K–K^{ii}	3.7560(10)
		K–K^{iii}	3.7560(10)
C(1)–C(6)	1.391(2)	C(1)–C(6)	1.393(2)
C(1)–C(2)	1.406(2)	C(1)–C(2)	1.402(2)
C(1)–C(7)	1.483(2)	C(1)–C(7)	1.506(2)
C(2)–C(3)	1.391(2)	C(2)–C(3)	1.401(2)
C(3)–C(4)	1.382(2)	C(3)–C(4)	1.372(3)
C(4)–C(5)	1.398(2)	C(4)–C(5)	1.376(3)
C(5)–C(6)	1.378(2)	C(5)–C(6)	1.380(2)
C(4)–N	1.3990(19)	C(2)–N	1.387(2)
C(6)–C(1)–C(2)	117.19(11)	C(6)–C(1)–C(2)	118.60(13)
C(3)–C(2)–C(1)	120.60(13)	C(3)–C(2)–C(1)	118.70(14)
C(4)–C(3)–C(2)	120.30(13)	C(4)–C(3)–C(2)	121.17(16)
C(3)–C(4)–C(5)	119.74(14)	C(3)–C(4)–C(5)	120.54(16)
C(6)–C(5)–C(4)	119.59(14)	C(6)–C(5)–C(4)	118.97(17)
C(5)–C(6)–C(1)	121.93(13)	C(5)–C(6)–C(1)	121.99(17)

Symmetry code: $^{i}x, y, z-1$; $^{ii}-x, -y, -z+1$; $^{iii}-x+1, -y, -z$; $^{iv}x, y, z+1$; $^{i}-x, y-0.5, -z+0.5$; $^{ii}x, -y+0.5, z-0.5$; $^{iii}x, -y+0.5, z+0.5$; $^{iv}-x, -y+1, -z$; $^{v}-x, y+0.5, -z-0.5$; $^{vi}-x, y+0.5, -z+0.5$; $^{vii}-x, y-0.5, -z-0.5$.

The angles that would be 90° in a regular octahedral arrangement range from 77.24(6) to 104.25(6)° while angles that would be 180° range from 148.58(6)° to 172.81(5)°. The planar conformation of the 4-amino-2-hydroxybenzoate ligand is stabilized by a short [2.532(2) Å] intramolecular hydrogen bond (O–H···O) between the hydrogen atom of the hydroxyl group and a carboxyl oxygen atom. Both hydrogen atoms of the O(4) water molecule are engaged in two hydrogen bonds. The monodendentate water molecule donates and accepts protons in hydrogen bonds O(5)–H(9)···O^{viii} and N–H(3)···O(5)^{v}, respectively. The NH_2 group participates twice as a proton donor in noncovalent interactions. The first hydrogen atom, H(3), takes part in an N–H···O_{water} hydrogen bond. The second, H(4), forms a contact of the N–H···X type (where X is the center of a C–C bond). Hydrogen bond geometries are given in Table V. The bond lengths in the benzene ring of the ligand lie in the range 1.378(2) to 1.406(2) Å.

The Crystal Structure of Potassium 2-Aminobenzoate Monohydrate

The crystal structure of potassium 2-aminobenzoate monohydrate, $C_6H_4(NH_2)COOK \cdot H_2O$, consists of potassium ions coordinated to 2-aminobenzoate ligands and water molecules. The nearest environment of the potassium ion contains carboxylate oxygen atoms from different anthranilate ligands and three oxygen atoms, achieving coordination number 8 (Fig. 2). K–$O_{carboxyl}$ bond distances

TABLE V Hydrogen bond lengths (Å) and angles (°) with e.s.d's in parentheses for sodium 4-amino-2-hydroxybenzoate dihydrate

D–H···A	*D–H*	*H···A*	*D···A*	<*D–H···A*
O(3)–H(1)···O(2)	0.86(3)	1.74(3)	2.532(2)	151(2)
N–H(3)···O(5)^{v}	0.87(2)	2.42(2)	3.235(3)	157(2)
O(4)–H(7)···O(1)^{vi}	0.91(3)	1.84(3)	2.753(2)	179(2)
O(4)–H(8)···O(1)^{vii}	0.76(2)	2.17(2)	2.889(2)	157(2)
O(5)–H(9)···O(1)^{viii}	0.87(4)	2.07(4)	2.938(2)	174(3)
N–H···X(1A)^{ix}	0.83(2)	2.65(2)	3.473(3)	174(3)

Symmetry codes: $^{v}x, -y+0.5, z+0.5$; $^{vi}x+1, y, z-1$; $^{vii}-x, -y, -z$; $^{viii}x+1, -y+0.5, z-0.5$; $^{ix}x, -y+0.5, z-0.5$; [X(1A) center of the bond C(3)–C(4)].

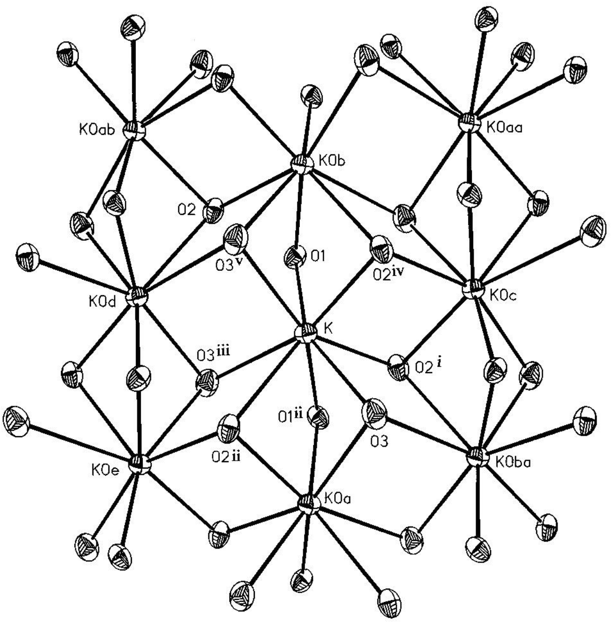

FIGURE 2 Coordination environments of metal atoms in potassium 2-aminobenzoate monohydrate.

vary from 2.6984(15) to 2.9238(14) Å; K–O$_{water}$ bonds are in the range 2.7652(16)–3.3577(18) Å. Such large differences are caused by various coordination modes at the metal atom. The carboxylate group of the 2-aminobenzoate ligand shows polydentate character. The first carboxylate oxygen atom bridges two neighboring potassium ions and the second is connected with three different potassium atoms. Neighboring potassium atoms are bridged by one didentate carboxylate oxygen atom, one tridentate carboxylate oxygen atom and a water molecule, creating a polymeric chain. The distance between K atoms is 3.7450(10) Å. Much longer distances [4.699(1) Å] between neighboring metal atoms along the chain are observed in the case of the polymeric complex calcium 2-aminobenzoate. In this structure two anthranilate ligands bridge two calcium atoms through didentate carboxylate groups [19]. Two water oxygen atoms and a carboxylate group connect neighboring chains in potassium 2-aminobenzoate.

TABLE VI Hydrogen bond lengths (Å) and angles (°) with e.s.d's in parentheses for potassium 2-aminobenzoate monohydrate

D–H···A	*D–H*	*H···A*	*D···A*	*<D–H···A*
N–H(1)···O(2)	0.84(2)	2.15(2)	2.718(2)	125(2)
O(3)–H(7)···N^{iv}	0.83(3)	2.30(3)	3.033(3)	148(2)
O(3)–H(8)···O(1)^{viii}	0.84(3)	1.93(3)	2.738(2)	162(2)
N–H(2)···X(1A)^{ix}	0.89(2)	2.59(2)	3.398(2)	152(2)

Symmetry codes: $^{iv}-x, -y+1, -z$; $^{viii}-x, -y, -z$; $^{ix}x, -y+1.5, z+0.5$; [X(1A) center of the bond C(2)–C(3)].

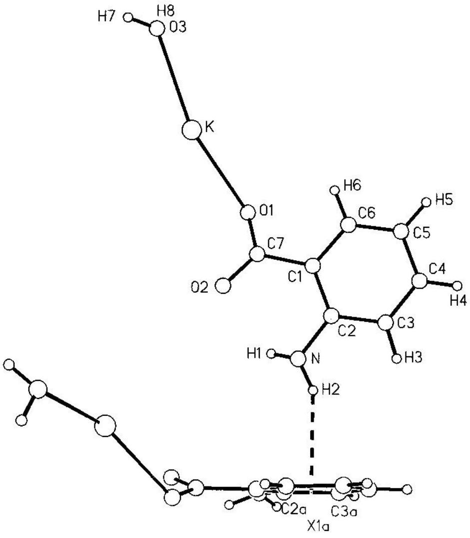

FIGURE 3 Noncovalent interactions in KL* · H_2O.

C–C bond distances and C–C–C angles of the aromatic ring are within normal ranges and are given in Table IV. The C–N bond distance of 1.387(2) Å is very close to that observed for anthranilic acid [17], 3,4- and 3,5-diaminobenzoic acids [18]. C–N–H and H–N–H angles are in the range 111.1(15) to 115(2)°.

The 2-aminobenzoate ligand is stabilized by a strong intramolecular hydrogen bond [N–H(1)···O(2)] between the amino group and a carboxyl oxygen atom. Additionally, the nitrogen atom takes part in an intermolecular noncovalent interaction of the type N–H(2)···X type (X is the centre of a C–C bond) as shown in Fig. 3. Oxygen atoms from water molecules participate as proton donors in hydrogen bonds of the type O(3)–H(7)···N^{iv} and O(3)–H(8)···O(1)^{viii}. Bond lengths and angles are listed in Table VI.

Supplementary Material

Lists of H atom positions, thermal parameters, observed and calculated structure factors are available from the authors on request.

References

[1] S.J. Lippard and J.M. Berg, *Principles of Bioinorganic Chemistry* (PWN: Warszawa, 1998), p. 16.

[2] R.B. King, *Encyclopedia of Inorganic Chemistry* (Wiley: New York, 1995), p. 600.

[3] P. Wiklund and J. Bergman, *Tetrahedron Lett*. **45**, 969 (2004).

[4] A.A. Kamnev, E. Kuzmann, Yu.D. Perfiliev, Gy. Vako and A. Vertes, *J. Mol. Struct*. **482–483**, 703 (1999).

[5] B.A. Moussa, *J. Pharm. Biomed. Anal*. **23**, 1045 (2000).

[6] N.A. el-Ragehy, S.S. Abbas and S.Z. El-Khateb, *Anal. Chim. Acta* **461**, 155 (2002).

[7] A. Beeby and A.E. Jones, *J. Photochem. Photobiol. B: Biol*. **64**, 109 (2001).

[8] C.Y. Panicker, H.T. Varhese, A. John, D. Philip, K. Istvan and G. Keresztury, *Spectrochim. Acta* **A58**, 281 (2002).

[9] R.T. Forbes, P. York and J.R. Davidson, *Int. J. Pharm*. **126**, 199 (1995).

[10] Z. Rzączyńska, R. Mrozek, M. Sikorska-Iwan and T. Głowiak, *J. Coord. Chem*. **49**, 189 (2000).

[11] Z. Rzączyńska, A. Bartyzel and T. Głowiak, *J. Coord. Chem*. **56**, 77 (2003).

[12] G.M. Sheldrick, SHELXS 97; *Program for Solution of Crystal Structures* (University of Göttingen, Germany, 1990).

[13] G.M. Sheldrick, SHELXL 97; *Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1993).

[14] A. Perotti and V. Tazzoli, *J. Chem. Soc., Dalton Trans*. 1768 (1981).

[15] T.S. Cameron, K.M. Mannan and O.R. Mohammed, *Acta Cryst*. **B32**, 87 (1976).

[16] R.A. Smith, *Acta Cryst*. **B31**, 2345 (1975).

[17] C.D.G. Boone, J.L. Derissenand and J.C. Schoone, *Acta Cryst*. **B33**, 3205 (1977).

[18] Z. Rzączyńska, R. Mrozek, J. Lenik, M. Sikorska and T. Głowiak, *J. Chem. Crystallogr*. **30**, 521 (2000).