

Preparation, Crystal Structure and Spectroscopic Characterization of [Ga(OH)(SO₄)(terpy)(H₂O)] · H₂O (terpy=2,2':6',2''-Terpyridine): The First Characterized Gallium(III) Sulfato Complex

Andreas Sofetis^a, Giannis S. Papaefstathiou^b, Aris Terzis^c, Catherine P. Raptopoulou^c, and Theodoros F. Zafiroopoulos^a

^a Department of Chemistry, University of Patras, 265 04 Patras, Greece

^b Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, USA

^c Institute of Materials Science, NCSR Demokritos, 153 10 Aghia Paraskevi Attikis, Greece

Reprint requests to Prof. Th. F. Zafiroopoulos. E-mail: tzafir@upatras.gr

Z. Naturforsch. **59b**, 291 – 297 (2004); received December 4, 2003

In dedication to the late Professor John M. Tsangaris for his important contributions to Inorganic Chemistry

The reaction of Ga₂(SO₄)₃·18H₂O and excess 2,2':6',2''-terpyridine (terpy) in MeOH / H₂O leads to [Ga(OH)(SO₄)(terpy)(H₂O)]·H₂O (1·H₂O) in good yield. The structure of the complex has been determined by single-crystal X-ray crystallography. The Ga^{III} atom in 1·H₂O is 6-coordinate and ligation is provided by one terdentate terpy molecule, one monodentate sulfate, one terminal hydroxide and one terminal H₂O molecule; the coordination polyhedron about the metal is described as a distorted octahedron. There is an extensive hydrogen-bonding network in the crystal structure which generates corrugated layers parallel to *bc*. The new complex was characterized by IR and ¹H NMR spectroscopy. The spectroscopic data are discussed in terms of the nature of bonding.

Key words: Crystal Structure, Gallium(III) Sulfate Complex, Terminal Hydroxo Ligands, 2,2':6',2''-Terpyridine Complexes

Introduction

The coordination chemistry of gallium(III) is of great current interest from several viewpoints, including the rise in commercial importance of semiconductors and biomedical developments. In the former area, binary compounds of Ga(III) with the Group 15 elements have emerged as leading materials for optoelectronic devices such as light-emitting diodes and laser diodes in the blue/UV region [1–3]; recently, Qiu and Gao [4] reported the preparation of wurtzite GaN powder with a controlled particle size at relatively low temperatures (500–600 °C), using complex [Ga(urea)₆]Cl₃ as precursor. In the biomedical arena, the interest arises from the incorporation of Ga(III) radionuclides (⁶⁷Ga, ⁶⁸Ga) into diagnostic radiopharmaceuticals [1, 5], the strong antitumor activity of GaCl₃ and Ga(NO₃)₃, which have been tested in cancer patients [6], and the moderate *in vitro* anti-HIV activity (HIV=human immunodeficiency virus) of Ga(NO₃)₃ and some GaCl₃/L complexes (L=various azoles) [7]. For example, gallium-labelled radiophar-

maceuticals have been used for either γ scintigraphy or PET imaging in a broad range of clinical pathologies. Introduced in 1969 as a tumour imaging agent [8], ⁶⁷Ga-citrate still remains a clinically useful radiopharmaceutical [9, 10]. It has been shown to detect a large variety of tumours as well as inflammation / infection sites and skeletal disorders [11, 12]. Within the last decade there has been an intense interest in labelled monoclonal antibodies and peptides *via* a bifunctional metal chelating agent; this approach may lead to the development of new biospecific ^{67/68}Ga radiopharmaceuticals if suitable chelators are synthesized [9].

Gallium(III) is also valuable in the bioinorganic chemistry of iron(III), the former being the diamagnetic mimic of the latter [1]. For instance, diamagnetic Ga(III) analogues of the microbial Fe(III) chelates (siderophores) have been useful in NMR studies [13], since the native Fe(III) complexes are paramagnetic. The basis for the replacement of Fe³⁺ by Ga³⁺ lies in the similar radii of the two metal ions. In reverse, the knowledge gained from studies of Fe³⁺ transport has

been applied to the development of ^{67}Ga radiopharmaceuticals [14].

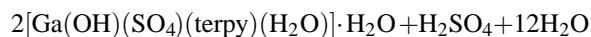
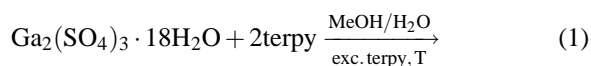
We have recently embarked on a programme aiming at the synthesis, characterization, and evaluation of the antitumour and antiviral activities of gallium(III) chloride, nitrate and sulfate complexes of N-heterocycles. For GaCl_3 and benzotriazoles our studies [15] showed that a variety of structures could be accessed through subtle variations in synthetic parameters and certain complexes exhibit impressive antitumor activity [16]. This paper describes the investigation of the reaction between $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and the tridentate chelating N-ligand 2,2':6',2''-terpyridine (terpy) in MeOH. The obtained mononuclear product possesses four different ligands, *i.e.* sulfato, hydroxo, aqua and terpy ligands. It is worth mentioning that terpy has been used in Ga(III) chemistry only once to date with $[\text{GaCl}_3(\text{terpy})]$ being the only structurally characterized Ga^{III} / terpy species [17]. The title compound is also the first structurally characterized gallium(III) sulfato complex.

There is currently a renewed interest in the coordination chemistry of the sulfate ion [18]. Metal-sulfato species have been studied for their important roles in catalysis [19], in the field of porous-framework materials [20], in stabilizing $\text{Pt}^{\text{III}}\text{-Pt}^{\text{III}}$ species [21], in the chemistry of cisplatin analogues [22] and as models of the active sites of important enzyme systems that have the sulfate anions as substrate, *e.g.* ATP-sulfurylases [1, 23].

Results and Discussion

Synthetic aspects

The complex $[\text{Ga}(\text{OH})(\text{SO}_4)(\text{terpy})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**1**· H_2O) was initially obtained using the 7:1 terpy/ $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ratio in MeOH. The solvent contained a little H_2O to aid dissolution of a slurry formed after mixing the reactants and had to be heated before giving a homogeneous solution. Storage of this solution at $-20\text{ }^\circ\text{C}$ gave crystals of the product in good ($\sim 70\%$) yield. The stoichiometry of the preparation of the complex is summarized in eq. (1):



Employment of the 6:1 and 4:1 terpy/ $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ratios in MeOH/ H_2O has no influence on the identity of the complex. However, an excess of terpy is beneficial to the preparation. Use of the stoichiometric amount of terpy [$\text{terpy}/\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} = 2:1$] does not give **1**; instead, it repeatedly gave a product (or a mixture of products) with poor analytical data and of uncertain nature. We believe that the excess of terpy neutralizes the sulfuric acid produced in the reaction and, thus, the latter does not decompose the hydroxo complex **1**· H_2O .

Description of structure

A drawing of the molecular structure of **1** is shown in Fig. 1. Selected bond distances and angles are given in Table 1.

The crystal of **1**· H_2O contains neutral complex molecules $[\text{Ga}(\text{OH})(\text{SO}_4)(\text{terpy})(\text{H}_2\text{O})]$ and lattice H_2O molecules at a 1:1 ratio. The Ga^{III} atom is coordinated by one tridentate terpy molecule, one monodentate sulfato anion, one terminal hydroxo group and one aquo ligand. The geometry about the metal ion is distorted octahedral, with the H_2O and SO_4^{2-} ligands being in *trans* positions. The terpy ligand occupies meridional sites and exhibits the expected *cisoid* conforma-

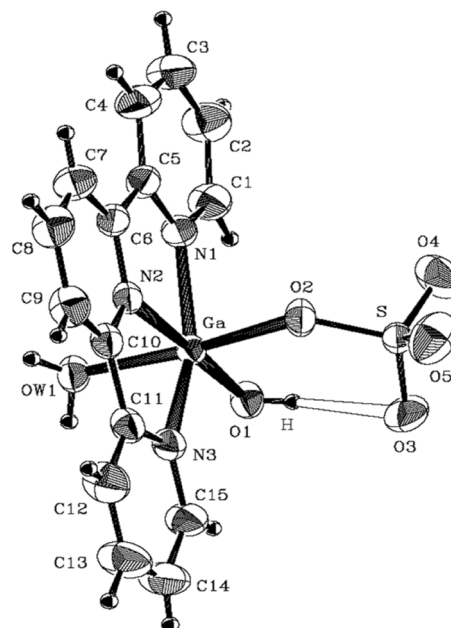


Fig. 1. A labelled ORTEP representation of complex **1**· H_2O ; the lattice H_2O molecule is not shown. Atom O(1) belongs to the hydroxo ligand.

Table 1. Selected bond distances (Å) and angles (°) relevant to the gallium coordination sphere for complex **1**·H₂O.

Ga-O(1)	1.850(2)	Ga-O(2)	1.977(2)
Ga-OW(1)	2.007(2)	Ga-N(1)	2.117(2)
a-N(2)	2.044(2)	Ga-N(3)	2.109(2)
S-O(2)	1.497(2)	S-O(3)	1.453(2)
S-O(4)	1.455(2)	S-O(5)	1.451(2)
O(1)-Ga-O(2)	97.1(1)	O(1)-Ga-OW(1)	88.5(1)
O(1)-Ga-N(1)	104.8(1)	O(1)-Ga-N(2)	178.3(1)
O(1)-Ga-N(3)	101.4(1)	O(2)-Ga-OW(1)	174.1(1)
O(2)-Ga-N(1)	87.0(1)	O(2)-Ga-N(2)	83.7(1)
O(2)-Ga-N(3)	92.2(1)	OW(1)-Ga-N(1)	89.8(1)
OW(1)-Ga-N(2)	90.8(1)	OW(1)-Ga-N(3)	88.5(1)
N(1)-Ga-N(2)	76.7(1)	N(1)-Ga-N(3)	153.7(1)
N(2)-Ga-N(3)	77.0(1)	O(2)-S-O(3)	109.6(1)
O(2)-S-O(4)	107.1(1)	O(2)-S-O(5)	106.3(1)
O(3)-S-O(4)	110.3(1)	O(3)-S-O(5)	112.6(1)
O(4)-S-O(5)	110.7(1)	Ga-O(2)-S	134.3(1)

tion about the interannular C-C bonds necessary for the adoption of the chelating mode.

The Ga-O(1) distance for the hydroxo ligand [1.850(2) Å] is 0.15 Å shorter than the Ga-OW(1) distance for the coordinated H₂O molecule [2.007(2) Å]; this is a consequence of the negative charge on the hydroxo oxygen atom. The Ga-N bond lengths [2.044(2)–2.117(2) Å] are close to those [2.034(7)–2.115(6) Å] in the only other structurally characterized Ga^{III}/terpy complex, *i.e.* [GaCl₃(terpy)] [17]. The Ga-N contact to the central ring of the terpy ligand [Ga-N(2), 2.044(2) Å] is shorter than the Ga-N contacts to the terminal rings [Ga-N(1), 2.117(2) Å; Ga-N(3), 2.109(2) Å], as observed in other complexes containing terdentate terpy ligands [17, 24, 25].

Angular distortions from octahedral geometry are primarily a consequence of the chelating terpy ligand and its restricted bite angles. The «*cis*» N-Ga-N angles are ~ 77°, while the «*trans*» N(1)-Ga-N(3) angle [153.7(1)°] deviates significantly from the ideal value of 180°.

The bond distances and angles within the terpy ligand are typical [24, 25]. The three pyridine rings are not exactly coplanar, and the two N(1)- and N(3)-containing terminal rings make least-squares plane angles of 3.5 and 5.1°, respectively, with the central ring. A slight distortion from planarity is common to complexed terpy [24–28].

The sulfate S-O bond distances display a pattern consistent with its monodentate character. Thus, the S-O(2) bond distance involving the coordinated oxygen atom [1.497(2) Å] is larger than the S-O(3,4,5) distances [average value: 1.453(2) Å] involving the unco-

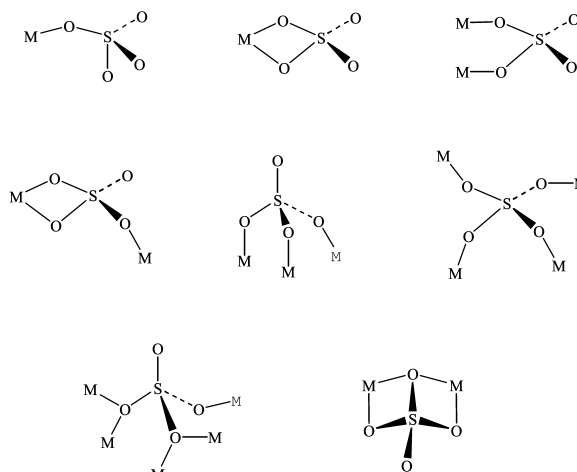


Fig. 2. Crystallographically established coordination modes of the sulfate anion.

ordinated oxygen atoms. The O-S-O bond angles are in the narrow 106.3(1)–112.6(1)° range.

As mentioned in the Introduction, compound **1**·H₂O is the first structurally characterized gallium(III) sulfate complex. Single-crystal X-ray structures of approximately 330 M/SO₄²⁻/L complexes (M=metal, L=any organic ligand) with at least one M-OSO₃ linkage have been reported [18]. The coordination modes established so far by the sulfate ion are presented in Fig. 2.

Complex **1**·H₂O is a rare example of a structurally characterized gallium(III) complex possessing a terminal hydroxo ligand. Other examples include the anionic complex [29] K₂[Ga(EDTA)(OH)]·6H₂O (EDTA⁴⁻ is the ethylenediaminetetra-acetate, N, N',O,O',O'' ligand), the dinuclear compound [Ga₂L(OH)(H₂O)₃]·H₂O, where L⁵⁻ is the N,N'-(2-hydroxylato-5-methyl-m-phenylenedimethylene)bis-(N-(carboxylatomethyl)glycinato) ligand [30], and the neutral mononuclear complex [GaL'(OH)] (L' is the dianion of phthalocyanine) [31]. Barron, Ziller and co-workers [32] have also proposed, based on strong spectroscopic evidences, that the compound [Bu₂^tGa(OH)(thf)] (obtained by hydrolysis of GaBu₃^t in thf) contains a terminal hydroxide; however, a structural proof is lacking because this organometallic compound is a liquid.

The compound **1**·H₂O is extensively hydrogen bonded. Fig. 3 shows the hydrogen bonding (broken lines) and packing arrangement viewed down the α axis, while metric parameters for the hydrogen bonds are listed in Table 2. The water and hydroxo

H Bond ^a	D...A	H...A	D-H...A	Operator of A
O(1)-H(O1)...O(3)	2.880	2.229	154.2	
OW(1)-HA(OW1)...O(1)	2.610	1.755	176.8	$-x, -y, -z$
OW(1)-HB(OW1)...O(4)	2.656	1.856	172.4	$-x, -1/2+y, 1/2-z$
OW(2)-HA(OW2)...O(3)	2.793	2.000	169.9	$1-x, -y, -z$
OW(2)-HB(OW2)...O(5)	2.792	2.071	170.9	$1-x, -1/2+y, 1/2-z$

^a Atom OW(2) is the oxygen atom of the lattice water molecule, while HA(OW2) and HB(OW2) are the two hydrogen atoms of the lattice water molecule; A = acceptor, D = donor.

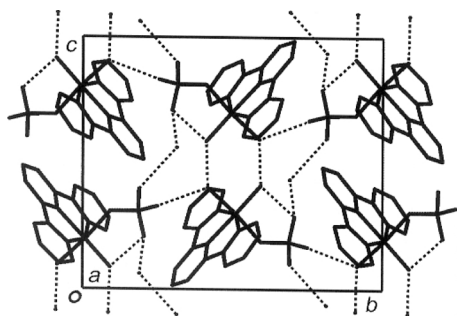


Fig. 3. Hydrogen bonding and packing viewed down the *a* axis for complex **1**·H₂O.

oxygen atoms are involved as donors, while the three uncoordinated sulfate oxygen atoms [O(3), O(4), O(5)] and the hydroxo oxygen atom [O(1)] act as acceptors. It is of interest that the OH⁻ ligand behaves both as a donor and an acceptor. The uncoordinated sulfate atom O(3) is doubly hydrogen bonded to the hydroxo ligand and to the lattice water molecule giving rise to intra- and intermolecular hydrogen bonds, respectively, the latter being stronger. The intermolecular hydrogen bonds generate corrugated layers parallel to *bc*.

The terpy systems of the molecules are piled nearly parallel to each other, and the contact distances are as short as 3.530 Å [for C(2)...C(14)(-1 + *x*, *y*, *z*)], so that the crystal structure is stabilized by stacking interactions between the π systems.

Spectroscopic characterization

In the $\nu(\text{OH})$ region the IR spectrum of **1**·H₂O shows three medium-intensity bands at 3515, 3450 and 3370 cm⁻¹, assignable [32–34] to $\nu(\text{OH})_{\text{hydroxo}}$, $\nu(\text{OH})_{\text{coord. water}}$ and $\nu(\text{OH})_{\text{lattice water}}$, respectively. The broadness and the relatively low frequency of these bands are both indicative of hydrogen bonding.

Two groups of very intense bands assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ appear at 1582–1560 and 1478–1422 cm⁻¹ for free terpy [26, 35]. The two bands of the first group show a ~ 20 cm⁻¹ shift

Table 2. Dimensions of the hydrogen bonds (distances in Å and angles in °) for complex **1**·H₂O.

to higher frequencies in **1**·H₂O due to coordination [26, 32]. The second group shows a shift to higher wavenumbers and also a splitting [26].

The IR bands at 1114 (strong and broad), 1028 (medium), 982 (weak), 656 (medium), 618 (strong) and 445 (weak) cm⁻¹ are due to the sulfato ligand [18, 36]. The IR spectrum of the free, *i.e.* ionic, sulfate (the ion belongs to the *T_d* point group) consists of two bands at ~ 1110 and ~ 615 cm⁻¹, assigned to the $\nu_3(F_2)$ stretching [$\nu_d(\text{SO})$] and $\nu_4(F_2)$ bending [$\delta_d(\text{OSO})$] modes, respectively. The coordination of SO₄²⁻ to metal ions decreases the symmetry of the group and the ν_3 and ν_4 modes are split [26, 36]. Furthermore, the Raman-active $\nu_1(A_1)$ stretching [$\nu_s(\text{SO})$] and $\nu_2(E)$ bending [$\delta_d(\text{OSO})$] modes of the free SO₄²⁻ become IR-active upon coordination, *i.e.* once the symmetry is lowered [36]. In the case the SO₄²⁻-site symmetry is lowered from *T_d* to *C_{3v}* (monodentate coordination), both ν_1 and ν_2 appear in the IR spectrum with weak to medium intensity, while ν_3 and ν_4 each splits into two bands [36]. The structure of **1**·H₂O has local *C_{3v}* symmetry at the sulfato ligand, and the bands at 1114 and 1028 cm⁻¹ are therefore attributable to the ν_3 modes. The bands at 656 and 618 cm⁻¹ are assigned to the ν_4 modes, with the lower frequency band being superimposed by a terpy vibration in this region. The bands at 982 and 445 cm⁻¹ are assigned to the ν_1 and ν_2 modes. Thus, the number and frequencies of the above mentioned bands are consistent with the monodentate sulfato coordination in **1**·H₂O.

The gallium(III) complex **1**·H₂O is diamagnetic, and we investigated the ¹H NMR properties of this compound in order to probe the metal-ligand interactions in this system. The ¹H NMR spectrum was recorded in CD₃OD/D₂O and data for this compound are presented in the Experimental Part. The spectrum was assigned with the aid of studies of free terpy [24, 26] – also presented in the Experimental Part – and a number of other metal complexes of terpy [24, 26, 27]. H(4,12) [see Fig. 1] experience a very small downfield shift of +0.1 ppm upon coordi-

nation, which is usually attributed to Van der Waals deshielding by H(7,9); it has been suggested that this is a direct consequence of the change from *transoid* to *cisoid* configuration about the interannular C-C bonds upon coordination. However, the downfield shift associated with H(3,13) [+0.45 ppm] suggests that induced charge and π -cloud perturbation with the ligand as a consequence of coordination are equally important [24]. A downfield shift (+0.48 ppm) is associated with H(1,15); this results from positive charge building up upon coordination [24, 26]. A small downfield shift (+0.30 ppm) is associated with H(7,9) on the central pyridine ring. Once again, this shift has a variety of origins [24]. In part it may be attributed to Van der Waals interactions, and in part to the fact that the interaction of the metal with the central ring is greater than that with the terminal rings as it has been observed that a short Ga-N bond distance [Ga-N(2) in Fig. 1] is associated with the central ring of the terdentate terpy ligand.

Concluding Comments

The Ga^{III}/SO₄²⁻/terpy chemistry described in this work has fulfilled its promise as a source of the first structurally characterized gallium(III) sulfato complex. Compound 1·H₂O has a remarkable molecular and crystal structure, and interesting spectroscopic properties. We are now using substituted 2,2':6',2''-terpyridines as terminal ligands in gallium(III) sulfate chemistry to prepare other types of complexes, to control the assembly of polynuclear complexes and coordination polymers possessing specific spatial properties and to investigate the occurrence of the so called «sulfate shift» [18, 37]. The study of the antiviral properties of 1·H₂O is also in progress.

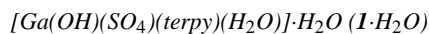
Experimental Section

All manipulations were performed under aerobic conditions using materials (Merck) and solvents as received. Water was distilled in house. Elemental analyses (C, H, N, S) were conducted by the University of Patras, Greece, Microanalytical Service. IR spectra (4000–450 cm⁻¹) were recorded on a Perkin-Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. 400.1 MHz ¹H NMR spectra in CD₃OD/D₂O were recorded on an Avance DPX spectrometer of Bruker at 25 °C. Chemical shifts, quoted on the δ scale and referenced *versus* external TMS, are assigned below according to the atomic labeling scheme of complex 1·H₂O (Fig. 1).

Table 3. Summary of crystal data, data collection and structure refinement for X-ray diffraction study of complex 1·H₂O.

Chemical formula	C ₁₅ H ₁₆ GaN ₃ O ₇ S
Formula weight	452.09
Colour, habit	colourless prism
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.131(5)
<i>b</i> (Å)	14.788(8)
<i>c</i> (Å)	12.911(7)
β (°)	102.60(2)
<i>V</i> (Å ³)	1702(2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.765
μ (mm ⁻¹)	1.787
<i>F</i> (000)	920
Radiation (Å)	Mo-K α (λ = 0.71073)
Temperature (K)	298
Scan mode/speed (° min ⁻¹)	θ – 2 θ /4.0
θ Range(°)	2.29 – 24.99
<i>h, k, l</i> Ranges	–10 → 10, –17 → 0, 0 → 15
Measured reflections	3136
Unique reflections	2.993(Rint = 0.0139)
Reflection used [<i>I</i> > 2 σ (<i>I</i>)]	2.741
Parameters refined	309
[Δ / σ] _{max}	0.006
<i>w</i> ^a	<i>a</i> = 0.0209; <i>b</i> = 0.9046
GoF(on <i>F</i> ²)	1.038
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0265
<i>wR</i> 2 ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.0699
($\Delta\rho$) _{max} /($\Delta\rho$) _{min} (eÅ ⁻³)	0.523/–0.356

^a $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$;
^b $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; ^c $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



A stirred colourless solution of Ga₂(SO₄)₃·18H₂O (0.08 g, 0.11 mmol) in MeOH (20 ml) was added to a pale yellow solution of terpy (0.18 g, 0.77 mmol) in the same solvent (20 ml). The solution was stirred for about 10 min, whereupon a slurry formed. H₂O (10 ml) was added to dissolve the slurry. Storage of the flask containing the homogeneous solution at –20 °C for 1 week yielded colourless prisms (some of them were of X-ray quality), which were collected by filtration, washed with Et₂O (2 × 5 ml), and dried in air. Yield: 0.07 g (71%). IR(KBr pellet): ν = 3515, 3450, 3370, 3063, 2926, 1606, 1580, 1504, 1482, 1458, 1412, 1332, 1258, 1114, 1028, 982, 780, 736, 674, 656, 618, 552, 512, 445 cm⁻¹. – ¹H NMR (400.1 MHz, CD₃OD/D₂O) for the complex: δ = 9.15 [d, 2 H, H(1, 15)], 8.73 [t, 1 H, H(8)], 8.70 [m, 4 H, H(7, 9, 4, 12)], 8.47 [td, 2 H, H(3, 13)], 7.85 [t, 2 H, H(2, 14)], 4.77 (sb, OH⁻/H₂O). – ¹H NMR (400.1 MHz, CD₃OD/D₂O) for free terpy (for convenience, the same labeling scheme used for the coordinated terpy in 1·H₂O is also used for free terpy): δ = 8.67 [d, 2 H, H(1,

15)], 8.62 [d, 2 H, H(4, 12)], 8.40 [d, 2 H, H(7, 9)], 8.07 [t, 1 H, H(8)], 8.02 [td, 2 H, H(3, 13)], 7.47 [m, 2 H, H(2, 14)]. – C₁₅H₁₆N₃O₇SGa (452.09): calcd. C 39.85, H 3.57, N 9.30, S 7.09; found C 39.22, H 3.50, N 9.18, S 7.01.

Crystal structure determination

A colourless prismatic crystal of **1**·H₂O (0.32 × 0.35 × 0.45 mm) was mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo-K_α radiation. Crystal data and full details of the data collection and data processing are listed in Table 3. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 11 < 2θ < 23°. Three stan-

dard reflections, monitored every 97 reflections, showed less than 3% intensity variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic Software.

The structure was solved by direct methods using SHELXS-86 [38] and refined by full-matrix least-squares techniques on *F*² with SHELXL-93 [39]. All H atoms were located by difference maps and refined isotropically. All non-H atoms were refined using anisotropic thermal parameters. One X-ray crystallographic file for complex **1**·H₂O, in CIF format, has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK, under the number 225580. A copy may be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

- [1] A. R. Barron, A. N. MacInnes, in R. B. King (ed.): *Encyclopedia of Inorganic Chemistry*, Vol. 3, pp. 1249–1269, Wiley, New York (1994).
- [2] S. Nakamura, G. Fasol, *The Blue Laser Diode*, Springer-Verlag, New York (1997).
- [3] F. A. Ponce, D. P. Bour, *Nature* **386**, 351 (1997).
- [4] Y. Qiu, L. Gao, *Chem. Lett.* **32**, 774 (2003).
- [5] S. Jurisson, D. Berning, W. Jia, D. Ma, *Chem. Rev.* **93**, 1137 (1993).
- [6] P. Collery, C. Perchery, in B. K. Keppler (ed.): *Metal Complexes in Cancer Chemotherapy*, pp. 249–258, VCH, Weinheim (1993).
- [7] F. Kratz, B. Nuber, J. Weiss, B. K. Keppler, *Polyhedron* **11**, 487 (1992).
- [8] C. L. Edwards, R. L. Hayes, *J. Nucl. Med.* **10**, 103 (1969).
- [9] M. A. Santos, M. Gil, S. Marques, L. Gano, G. Cantinho, S. Chaves, *J. Inorg. Biochem.* **92**, 43 (2002).
- [10] A. K. W. Stephens, C. Orvig, *Inorg. Chim. Acta* **273**, 47 (1998).
- [11] C. J. Palestro, *Semin. Nucl. Med.* **24**, 128 (1994).
- [12] C. A. Luttrupp, J. A. Jackson, B. J. Jones, M.-H. Sohn, R. E. Lynch, K. A. Morton, *J. Nucl. Med.* **39**, 1405 (1998).
- [13] M. Linas, D. M. Wilson, J. B. Neilands, *Biochemistry* **112**, 3836 (1973).
- [14] S. M. Moerliën, M. L. Welch, K. N. Raymond, F. L. Weigl, *J. Nucl. Med.* **22**, 720 (1982).
- [15] S. Zanas, C. P. Raptopoulou, A. Terzis, Th. F. Zafropoulos, *Inorg. Chem. Commun.* **2**, 48 (1999).
- [16] S. Zanas, Ph.D. Thesis, University of Patras, Greece (2002).
- [17] G. Beran, A. J. Carty, H. A. Patel, G. J. Palenik, *Chem. Commun.* 222 (1970).
- [18] G. Tamasi, R. Cini, *Dalton Trans.* 2928 (2003), and references therein.
- [19] J. Moriyama, H. Nishiguchi, T. Ishihara, Y. Takita, *Ind. Eng. Chem. Res.* **41**, 32 (2002).
- [20] M. I. Khan, S. Cevik, R. J. Doedens, *Chem. Commun.* 1930 (2001).
- [21] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York (1982).
- [22] J. Reedijk, *Inorg. Chim. Acta* **198-200**, 873 (1992).
- [23] I. Boltes, H. Czapinska, A. Kahnert, R. von Bülow, T. Dierks, B. Schmidt, K. von Figura, M. A. Kertesz, I. Uson, *Structure* **9**, 483 (2001), and references therein.
- [24] E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, M. A. M. Daniels, *New J. Chem.* **16**, 855 (1992), and references therein.
- [25] C. Pifferi, M. P. Ricchi, R. Cini, *Polyhedron* **19**, 69 (2000), and references therein.
- [26] A. K. Boudalis, V. Nastopoulos, A. Terzis, C. P. Raptopoulou, *Z. Naturforsch.* **56b**, 122 (2001).
- [27] M. Fréchette, C. Bensimon, *Inorg. Chem.* **34**, 3520 (1995).
- [28] M. G. B. Drew, M. J. Hudson, P. B. Iveson, M. L. Russell, J.-O. Liljenzin, M. Skalberg, L. Spjuth, C. Madic, *J. Chem. Soc., Dalton Trans.* 2973 (1998).
- [29] A. B. Ilyukhin, S. P. Petrosyants, *Kristallografiya* **46**, 845 (2001).
- [30] O. Jarjays, A. D. Moulinet D'Hardemare, A. Durif, M.-T. Averbuch-Pouchot, *Acta Crystallogr., Sect. C* **54**, 931 (1998).
- [31] K. Yamasaki, O. Okada, K. Inami, M. Oka, M. Kotani, H. Yamada, *J. Phys. Chem. B.* **101**, 13 (1997).
- [32] M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, J. W. Ziller, *Polyhedron* **11**, 477 (1992).
- [33] L. S. Gelfand, F. J. Iaconiani, L. L. Pytlewski, A. N. Specca, C. M. Mikulski, N. M. Karayannis, *J. Inorg. Nucl. Chem.* **42**, 377 (1980).
- [34] A. K. Boudalis, N. Lalioti, G. A. Spyroulias, C. P. Raptopoulou, A. Terzis, A. Bousseksou, V. Tangoulis,

- J.-P. Tuchagues, S. P. Perlepes, *Inorg. Chem.* **41**, 6474 (2002).
- [35] S. P. Sinha, *Z. Naturforsch.* **20a**, 552 and 1661 (1965).
- [36] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York (1986).
- [37] C. He, V. Gomez, B. Springler, S. J. Lippard, *Inorg. Chem.* **39**, 4188 (2000).
- [38] G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Germany (1986).
- [39] G. M. Sheldrick, SHELXS-93, Program for Crystal Structure Refinement, University of Göttingen, Germany (1993).