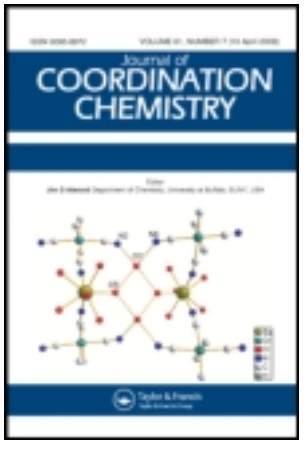
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:31
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of chloro-bis(quinoline-2-carboxylato-κ^2N,O)gallium(III)

Danuta Dobrzyńska [a], Lucjan B. Jerzykiewicz [b], Joanna Bejczak [a], Joanna Wietrzyk [c] & Marta Świtalska [c]

[a] Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[b] Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

[c] Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Rudolfa Weigla 12, 53-114 Wrocław, Poland

Published online: 10 Mar 2011.

To cite this article: Danuta Dobrzyńska, Lucjan B. Jerzykiewicz, Joanna Bejczak, Joanna Wietrzyk & Marta Świtalska (2011) Synthesis and characterization of chloro-bis(quinoline-2-carboxylato-κ^2N,O)gallium(III), Journal of Coordination Chemistry, 64:6, 1082-1090, DOI: 10.1080/00958972.2011.563383

To link to this article: http://dx.doi.org/10.1080/00958972.2011.563383

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [Renmin University of China] at 10:31 13 October 2013

Journal of Coordination Chemistry
Vol. 64, No. 6, 20 March 2011, 1082–1090

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of chloro-bis(quinoline-2-carboxylato-κ^2N,O)gallium(III)

DANUTA DOBRZYŃSKA*†, LUCJAN B. JERZYKIEWICZ‡, JOANNA BEJCZAK†, JOANNA WIETRZYK§ and MARTA ŚWITALSKA§

†Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
‡Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland
§Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Rudolfa Weigla 12, 53-114 Wrocław, Poland

(*Received 16 November 2010; in final form 10 January 2011*)

The preparation and characterization of a new gallium(III) complex with quinoline-2-carboxylate, of formula [Ga(quin-2-c)$_2$Cl], are described. The crystal structure of the complex has been determined by X-ray diffraction, crystallizing in monoclinic space group $P2_1/n$ with Ga(III) adopting a distorted tetragonal pyramid. Gallium(III) coordinates two quinoline-2-carboxylates and one chloride with a Cl,N$_2$,O$_2$ donor set. In the crystal the 2-D supramolecular structure is generated by weak intermolecular interactions, C–H$\cdots$O, C–H$\cdots$Cl, and C–H$\cdots\pi$. The cytotoxicity assays against several human cancer cell lines (Du145, A549, MCF-7, A498, HT-29) and against mouse fibroblasts (BALB/3T3) revealed moderate antiproliferative activity of the complex.

Keywords: Quinoline-2-carboxylate; Gallium(III) complex; Crystal structure; Cytotoxic activity

Downloaded by [Renmin University of China] at 10:31 13 October 2013

1. Introduction

The tumor-inhibiting properties of gallium(III) have been recognized for a number of years [1, 2]. The unfavorable pharmacokinetics of simple gallium salts, mainly gallium nitrate, prevented its use in systematic chemotherapy of cancer patients. The next generation of anticancer gallium compounds, tris(8-quinolinato)gallium(III) (KP46) [3, 4] and tris(3-hydroxy-2methyl-4H-pyran-onato)gallium(III) (gallium maltolate) [5], with improved bioavailability are selected for clinical studies. Studies on structure–activity relationship of gallium semicarbazones have suggested that anti-tumor activity directly correlates with chelating activity [6]. Several new chelate complexes, with N,O and rarely S donors, have been reported to have high cytotoxic potency [7–10].

*Corresponding author. Email: danuta.dobrzynska@pwr.wroc.pl

ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.563383

The use of gallium salts and complexes as radiopharmaceuticals for clinical utility in positron emission tomography (PET) studies of myocardial perfusion or other physiological processes is well-established [11]. Examples of gallium compounds which have found use in human studies are ^{68}Ga-DOTA-D-Phe^{1}-Tyr^{3}-octreotide (DOTATOC, DOTA = 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraaceticacid) [12] and ^{68}Ga-DOTA-PEG$_2$-D-Tyr^{6}-b-Ala^{11}-Thi^{13}-Nle^{14}-BN(6-14) amide (PEG = 2-ethylene glycol 2-aminoethyl-carboxymethyl ether) [13]. New promising Ga(III) chelates with naphtol Schiff base [14] and *N,N′*-bis-aminipropyl-*N,N′*-dimethylenediamine ligands have been applied [15].

The chemical properties of gallium(III) ion are very similar to those of iron(III) with the exception of redox functions. Gallium binds effectively to iron-transporting protein transferrin and is delivered to the cell mainly *via* endocytosis. The main target of gallium in the cell is iron-dependent enzyme ribonucleotide reductase (RR). Replacement of iron by gallium causes enzyme inactivity [16–18].

Here we report the synthesis, X-ray diffraction structure, and cytotoxic activity studies of a new gallium complex with quinoline-2-carboxylate. Quinoline-2-carboxylic acid (Hquin-2-c) is a biological ligand with its role in tryptophan metabolism [19] and some pharmaceutical applications reported [20]. Hquin-2-c itself provides a donor set similar to the coordination center in the pyrroloquinoline quinone (PQQ) cofactor of quinoproteins, consisting of pyridine nitrogen and carboxylate in ortho positions [21]. Quinoline-2-carboxylate usually forms N,O chelates with metal ions [22]; only one gallium(III) complex with quin-2-c ion, $[Ga_2(\text{quin-2-c})_2(\mu\text{-OH})_2]\cdot 4\text{py}$, has been isolated and characterized to date [23].

Downloaded by [Renmin University of China] at 10:31 13 October 2013

2. Experimental

2.1. *Materials and methods*

Gallium chloride and quinoline-2-carboxylic acid were purchased from Aldrich and used as received.

IR spectra were recorded as KBr pellets or nujol mulls using Perkin-Elmer FTIR-2000 and Perkin-Elmer FTIR-1600 spectrophotometers from 50 to 4000 cm^{-1}. Elemental analyses (C, H, N, Cl) were obtained with a Perkin-Elmer 2400 analyzer.

2.2. *Synthesis*

To a solution of 0.40 mmol of Hquin-2-c in the mixture methanol–ethanol–propan-1-ol (1 : 1 : 1) was added 0.25 mmol of $GaCl_3$. After 1 week, colorless crystals were formed. These crystals were collected, washed with the alcohol mixture, and air dried (yield 30%). The complex is soluble in DMSO.

Elemental analysis Calcd for $C_{20}ClGaH_{12}N_2O_4$ (%): C, 53.44; H, 2.69; N, 6.23; Cl, 7.89. Found (%): C, 52.84; H, 3.19; N, 6.64; Cl, 7.41. IR (cm^{-1}) 3113 (m), 1654 (vs), 1616 (m), 1594 (m), 1572 (m), 1516 (m), 1467 (s), 1390 (vs), 1367 (s), 1353 (s), 1275 (m), 1217 (w), 1188 (m), 1163 (m), 1050 (w), 974 (m), 906 (m), 822 (m), 806 (s), 775 (vs), 645 (m), 629 (w), 614 (m), 575 (w), 523 (w), 503 (m), 431 (w), 408 (m), 394 (m), 374 (m), 350 (m), 295 (m), 261 (m), 252 (m), 241 (m), 177 (m).

2.3. *Crystal structure determination*

Preliminary examination and intensity data collections were carried out on a KUMA KM4 κ-axis diffractometer with graphite-monochromated Mo-Kα radiation and with a CCD camera. All data were corrected for Lorentz, polarization, and absorption effects [24]. The structures were solved by direct methods and refined by full-matrix least-squares on all F^2 data using the SHELXTL (version 6.14) program [25]. Carbon-bonded hydrogens were included in calculated positions and refined in the riding mode using SHELXTL default parameters.

2.4. *Cell lines*

Human A-549 (lung), Du145 (prostate), MCF-7 (breast), A498 (renal), HT-29 (colon) cancer cell lines, and BALB/3T3 (mouse fibroblast) were obtained from American Type Culture Collection (Rockville, MD, USA).

A-549, A498, and HT-29 cells were cultured in RPMI 1640 + Opti-MEM (1 : 1) (both from Gibco, Scotland, UK) supplemented with 5% fetal bovine serum (from Sigma-Aldrich Chemie GmbH, Steinheim, Germany), MCF-7 cells in Eagle medium (IIET, Wroclaw, Poland) supplemented with 2 mmol L^{-1} l-glutamine, 1% mem-non-essential amino acid solution, 0.8 mg L^{-1} of insulin, and 10% fetal bovine serum (all from Sigma-Aldrich Chemie GmbH, Steinheim, Germany). Du145 and BALB/3T3 cells were cultured in Dulbecco medium (IIET, Wroclaw, Poland) supplemented with 2 mmol L^{-1} l-glutamine and 1.0 mmol L^{-1} sodium pyruvate, 10% fetal bovine serum (all from Sigma-Aldrich Chemie GmbH, Steinheim, Germany). All culture media were supplemented with 100 units mL^{-1} penicillin and 100 μg mL^{-1} streptomycin (both from Polfa Tarchomin S.A., Warsaw, Poland). All cell lines were grown at 37°C with 5% CO_2 humidified atmosphere.

2.5. In vitro *antiproliferative assay*

Twenty-four hours before addition of the tested compounds, the cells were plated in 96-well plates (Sarstedt, Germany) at a density of 1×10^4 cells per well. An assay was performed after 72 h of exposure to verify the concentrations of the tested agents. Each compound at each concentration was tested in triplicate in a single experiment, which was repeated 3–7 times. DMSO which was used as a solvent (in a dilution corresponding to its highest concentration applied to the tested compounds) did not exert any inhibitory effect on cell proliferation ($p < 0.05$). In the antiproliferative assays to evaluate cytostatic effect, the SRB method was applied as described previously [26]. The results were calculated as the IC_{50} (50% inhibitory concentration), that is, the dose of tested agent which inhibits 50% of the proliferation of the cancer cell population. IC_{50} values were calculated for each experiment separately and mean values ± SD are presented.

3. Results and discussion

3.1. *Crystal structure*

The structure of [Ga(quin-2-c)$_2$Cl] consists of neutral molecules of the complex. The crystal data and refinement parameters are given in table 1, whereas the

Downloaded by [Renmin University of China] at 10:31 13 October 2013

Table 1. Crystallographic data for [Ga(quin-2-c)$_2$Cl].

Empirical formula	$C_{20}H_{12}ClGaN_2O_4$
Formula weight	449.49
Temperature (K)	100
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions (Å, °)	
a	10.913(4)
b	15.074(5)
c	10.964(4)
β	103.60(3)
Volume (Å^3), Z	1753.0(2), 4
Calculated density (g cm^{-3})	1.703
Linear absorption coefficient (mm^{-1})	1.753
F(000)	904
Crystal size (mm^3)	0.193 × 0.132 × 0.089
θ range for data collection (°)	2.73–27.60
Reflections collected	14617
Independent reflection	4042 [R(int)0.0202]
Goodness-of-fit on F^2	1.051
Final R indices [$I > 2\theta(I_0)$]	$R_1 = 0.0249$; $wR_2 = 0.0662$
R indices (all data)	$R_1 = 0.0312$; $wR_2 = 0.0695$
Largest difference peak and hole (e nm^{-3})	522 and −265

Table 2. Selected interatomic distances (Å) and bond angles (°) for [Ga(quin-2-c)$_2$Cl].

Interatomic distances (Å)		Bond angles (°)	
Ga–Cl(1)	2.181(1)	Cl(1)–Ga–O(11)	110.43(4)
Ga–O(11)	1.899(2)	Cl(1)–Ga–O(21)	118.41(4)
Ga–O(21)	1.879(2)	Cl(1)–Ga–N(1)	97.43(4)
Ga–N(1)	2.078(2)	Cl(1)–Ga–N(2)	99.85(4)
Ga–N(2)	2.067(2)	O(11)–Ga–O(21)	131.10(5)
O(11)–C(11)	1.304(2)	O(11)–Ga–N(1)	82.20(5)
O(12)–C(11)	1.220(2)	O(11)–Ga–N(2)	91.22(5)
O(21)–C(21)	1.310(2)	O(21)–Ga–N(1)	89.10(5)
O(22)–C(21)	1.211(2)	O(21)–Ga–N(2)	83.21(5)
		N(1)–Ga–N(2)	162.71(5)

Downloaded by [Renmin University of China] at 10:31 13 October 2013

interatomic distances and bond angles are presented in table 2. The ORTEP drawing with atom numbering scheme shows the structure of the complex molecule (figure 1).

The crystal structure demonstrates that gallium(III) ion is five-coordinate with two carboxylate oxygens, two quinoline nitrogens, and a chloride. The geometry of gallium can be described as an irregular tetragonal pyramid, with chloride in the apical position and N,O donors defining the basal plane. The carboxylate coordinates monodentate with the Ga–O distances (table 2) very close to median value of such bonds, 1.878 Å, estimated for 84 monodentate gallium carboxylates [27]. The Ga–N bond lengths also fall in the typical range [7, 10].

No classical hydrogen bonds are observed in the crystal. The strongest intermolecular interactions are C–H···O type, creating the 2-D supramolecular

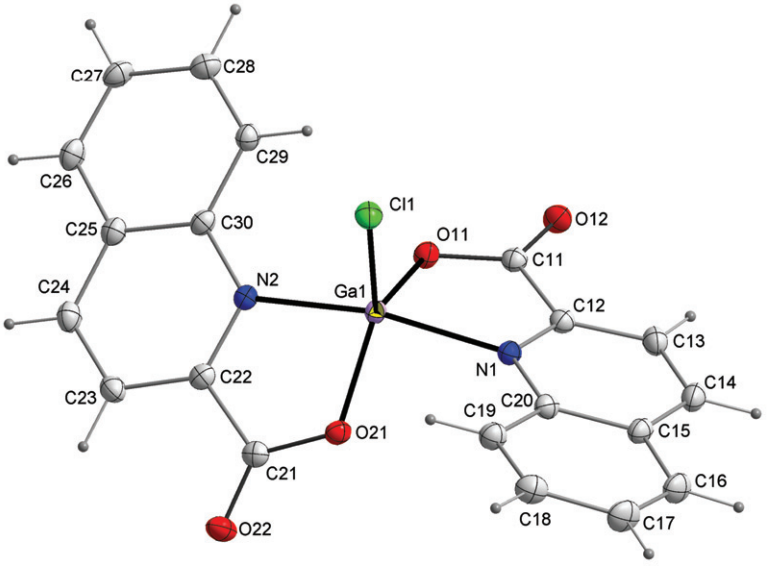


Figure 1. The molecular structure of [Ga(quin-2-c)$_2$Cl] with the atom numbering, plotted with 50% probability of displacement ellipsoids.

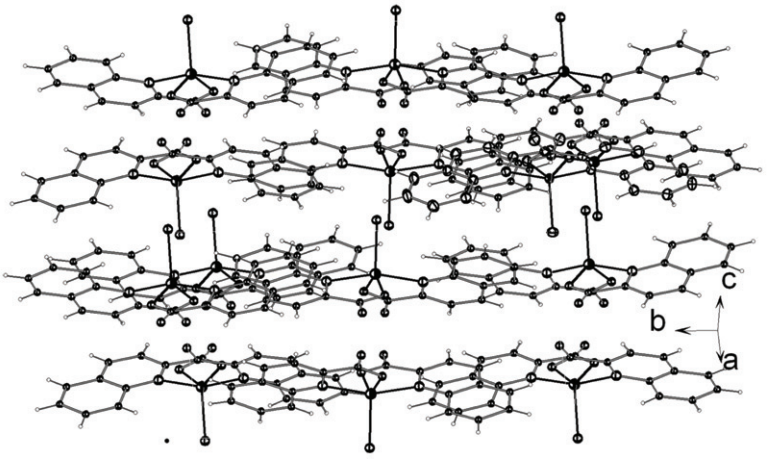


Figure 2. 2-D layers parallel to the [−1, 0, 1] plane of the crystal of [Ga(quin-2-c)$_2$Cl].

layers parallel to [−1,0,1] crystal plane (figures 2 and 3, table 3). Two weak C–H···O intramolecular bonds are also found. The very interesting feature of the crystal of [Ga(quin-2-c)$_2$Cl] is the C–H···Cl interaction (table 3). Similar C–H···Cl contacts have been observed in organic and coordination compounds [28–31]. The chlorides are located within the double layer and shortest Cl···Cl distance equals 3.718(2) Å (figure 2). The supramolecular aggregation is completed by the presence of C–H···π interactions and is as shown in figure 4.

Downloaded by [Renmin University of China] at 10:31 13 October 2013

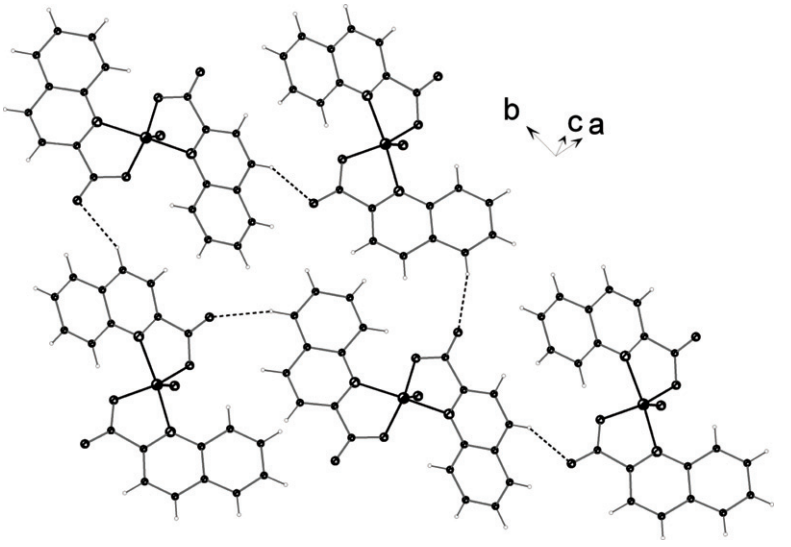


Figure 3. The pattern of the C–H···O interactions forming layers in the crystal of [Ga(quin-2-c)$_2$Cl].

Table 3. Geometrical parameters of C–H···O and C–H···Cl interactions (Å, °) in the crystal of [Ga(quin-2-c)$_2$Cl].

D–H···*A*	*D*–H	H···*A*	D···A	*D*–H···A
C14–H14A···O22^{i}	0.95	2.48	3.355(2)	153
C19–H19A···O21	0.95	2.51	3.066(2)	117
C26–H26A···O12^{ii}	0.95	2.49	3.415(2)	164
C29–H29A···O11	0.95	2.59	3.144(2)	118
C27–H27A···Cl1	0.95	2.96	3.668(1)	132

Symmetry codes: $^{i}x+1/2, -y+1/2, z+1/2$; $^{ii}x-1/2, -y-1/2, z-1/2$.

3.2. *Antiproliferative activity of Ga(quin-2-c)$_2$Cl*

[Ga(quin-2-c)$_2$Cl] was examined for its antiproliferative activity *in vitro* against human cancer cell lines and against mouse fibroblasts. This compound revealed highest antiproliferative activity during 72-h exposure against MCF-7 and A498 and against mouse fibroblast BALB/3T3 with maximal inhibition of proliferation above 50%. For the cell lines mentioned above the IC_{50} values were calculated (table 4). [Ga(quin-2-c)$_2$Cl] was significantly less toxic against cancer cells than cisplatin. Comparing its activity against MCF-7 breast cancer cell line showed IC_{50} value of [Ga(quin-2-c)$_2$Cl] was 0.120 mmol L^{-1} and of cisplatin 0.0128 mmol L^{-1}. Data for other less sensitive (inhibition of proliferation caused by dose of 0.222 mmol L^{-1} ranged from 20% to 50%) cell lines: A549, Du145, and HT-29 are shown as percent of proliferation inhibition in the highest concentration used (table 4). Although [Ga(quin-2-c)$_2$Cl] is not as potent as cisplatin *in vitro*, its antiproliferative activity is comparable to Ga(III) chloride. The cell inhibition induced by $GaCl_3$ is both dependent on the concentration and on the time of exposure as shown by L1210 leukemic cells exposed to gallium

Downloaded by [Renmin University of China] at 10:31 13 October 2013

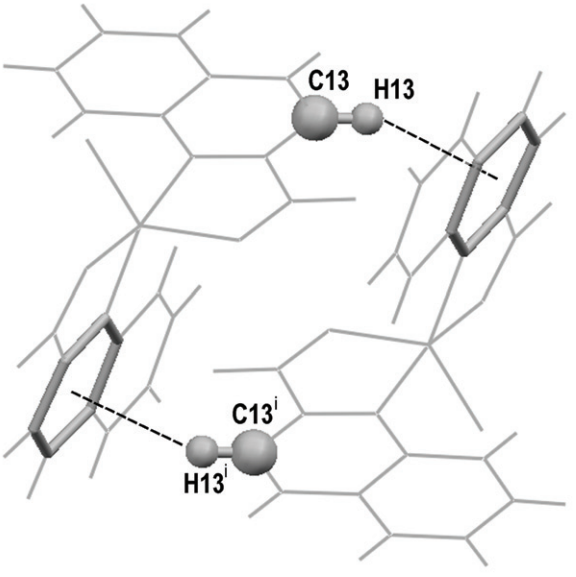


Figure 4. The interlayer interactions of C–H $\cdots \pi$ type in the crystal of [Ga(quin-2-c)$_2$Cl], $^{i} = -x, -y, 1-z$.

Table 4. Antiproliferative activity *in vitro* of [Ga(quin-2-c)$_2$Cl] against cancer cell lines and normal fibroblasts (BALB/3T3).

Cell line	IC_{50} [mmol L^{-1}]		Proliferation inhibition (%) in the highest concentration of [Ga(quin-2-c)$_2$Cl] (0.222 mmol L^{-1})
	[Ga(quin-2-c)2Cl]	Cisplatin	
Du145	–	0.0018 ± 0.0003	17.05 ± 13.78
A549	–	0.0099 ± 0.0024	43.97 ± 6.7
MCF-7	0.120 ± 0.0150	0.0128 ± 0.0015	52.74 ± 20.36
A498	0.174 ± 0.0254	nt	58.22 ± 0.08
HT-29	–	nt	47.64 ± 7.52
BALB/3T3	0.130 ± 0.0284	0.0087 ± 0.00097	72.54 ± 6.44

nt – Non-tested.

chloride during 2–4 days. The IC_{50} was 175 mmol L^{-1} after an exposure time of 48 h, but 35 mmol L^{-1} after an exposure time of 72 h and only 16 mmol L^{-1} after an exposure of 96 h [32].

4. Conclusion

The new gallium complex with quinoline-2-carboxylate ion, [Ga(quin-2-c)$_2$Cl], was prepared and its structure determined by X-ray crystallography. The quinoline-2-carboxylates are bound bidentate to Ga(III) through monodentate carboxylate and quinoline nitrogen. The chloride completes the coordination sphere of the gallium.

Downloaded by [Renmin University of China] at 10:31 13 October 2013

Supramolecular 2-D structures mediated by weak intermolecular interactions are found in the crystal. The antiproliferative activity of [Ga(quin-2-c)$_2$Cl] is much lower than that of cisplatin and comparable to the activity of gallium chloride. Further study on the applicability of the title complex as an imaging agent will be undertaken.

Supplementary material

CCDC No. 720317 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Downloaded by [Renmin University of China] at 10:31 13 October 2013

Acknowledgments

The authors acknowledge financial support from Wrocław University of Technology.

References

[1] T. Pieper, K. Borsky, B.K. Keppler. *Top Biol. Inorg. Chem.*, **1**, 171 (1999).
[2] M.J. Clarke, F. Zhu, D.R. Frasca. *Chem. Rev.*, **99**, 2511 (1999).
[3] P. Collery, J.L. Domingo, B.K. Keppler. *Anticancer Res.*, **16**, 687 (1996).
[4] M. Thiel, T. Schilling, D. Gey, R. Ziegler, P. Collery, B.K. Keppler. *Contrib. Oncol.*, **54**, 439 (1999).
[5] L.R. Bernstein, T. Tanner, C. Godfrey, B. Noll. *Met.-Based Drugs*, **7**, 33 (2000).
[6] K.C. Agrawal, A.C. Sartorelli. *Prog. Med. Chem.*, **15**, 321 (1978).
[7] V.B. Arion, M.A. Jakupec, M. Galanski, P. Unfried, B.K. Keppler. *Inorg. Biochem.*, **91**, 298 (2002).
[8] K. Mohammadi, K.H. Thompson, B.O. Patrick, T. Storr, C. Martins, E. Polishchuk, V.G. Yuen, J.H. McNeil, Ch. Orvig. *Inorg. Biochem.*, **99**, 2217 (2005).
[9] A. Dobrov, V.B. Arion, N. Kandler, W. Ginzinger, M.A. Jakupec, A. Rufiska, N. Graf von Keyserlink, M. Galanzski, Ch. Kowol, B.K. Keppler. *Inorg. Chem.*, **45**, 1945 (2006).
[10] R. Shakya, F. Peng, J. Liu, M.J. Heeg, C.N. Verani. *Inorg. Chem.*, **45**, 6263 (2006).
[11] R.E. Weiner, M.L. Thakur. In, M.J. Welch, C. Redvanly. *Handbook of Radiopharmaceuticals*, Wiley, New York (2003).
[12] M. Henze, J. Schumacher, A. Dimitrakopoulou-Strauss, L.G. Strauss, H.R. Mäcke, M. Eisenhut, U. Haberkorn. *Eur. J. Nucl. Med. Mol. Imaging*, **31**, 466 (2004).
[13] A. Dimitrakopoulou-Strauss, P. Hohenberger, U. Haberkorn, H.R. Mäcke, M. Eisenhut, L.G. Strauss. *Nucl. Med.*, **48**, 1245 (2007).
[14] S.E. Harpstrite, J.L. Prior, N.P. Rath, V.J. Sharma. *Inorg. Biochem.*, **101**, 1347 (2007).
[15] Y.-M. Hsiao, C.J. Mathias, S.-P. Wey, P.E. Fanwick, M.A. Green. *Nucl. Med. Biol.*, **36**, 39 (2009).
[16] C.R. Chitambar, W.G. Matthaeus, W.E. Antholine, K. Graff, W.J. O'Brien. *Blood*, **71**, 1930 (1988).
[17] C.R. Chitambar, J. Narasimhan, J. Guy, D.S. Sem, W.J. O'Brien. *J. Cancer Res.*, **51**, 6199 (1991).
[18] J. Narasimhan, W.E. Antholine, C.R. Chitambar. *Biochem. Pharmacol.*, **44**, 2403 (1992).
[19] P. Zhou, D. O'Hagan, U. Mocek, Z. Zeng, L.D. Yuen, T. Frenzel, C.J. Unkefer, J.M. Beale, H.G. Floss. *J. Am. Chem. Soc.*, **111**, 7274 (1989).
[20] Kyowa Fermentation Industry, Co. Ltd. *Fr. Demande FR2181563*.
[21] O. Geiger, H. Görisch. *Biochem. J.*, **261**, 415 (1989).
[22] D. Dobrzyńska. *J. Coord. Chem.*, **59**, 921 (2006).
[23] W. Li, M.M. Olmstead, D. Miggins, R.H. Fish. *Inorg. Chem.*, **35**, 51 (1996).
[24] Oxford Diffraction. *CrysAlis CCD and CrysAlis RED (Versions 1.171.31)*, Oxford Diffraction Poland, Wroclaw, Poland (2006).
[25] *Bruker SHELXTL. (Version 6.14)*, Bruker AXS Inc., Madison, WI, USA (2003).

[26] J. Wietrzyk, M. Chodynski, H. Fitak, E. Wojdat, A. Kutner, A. Opolski. *Anti-Cancer Drugs*, **18**, 447 (2007).
[27] R.H. Hocking, T.W. Hambley. *Inorg. Chem.*, **42**, 2833 (2003).
[28] X.-L. You, Ch.R. Lou, Y. Zhang, D.Ch. Zhang. *Acta Cryst. C*, **60**, o69 (2004).
[29] N. Vembu, M. Nallu, J. Garrison, W. Young. *Acta Cryst. E*, **59**, o936 (2003).
[30] C. Janiak, T.G. Scharmann. *Polyhedron*, **22**, 1123 (2003).
[31] R.J. Santos-Contreras, F.J. Martínez-Martínez, N.A. Mancilla-Margalli, A.L. Peraza-Campos, L.M. Morín-Sanchez, E.V. García-Báez, I.I. Padilla-Martínez. *Cryst. Eng. Comm.*, **11**, 1451 (2009).
[32] E.M. Perchellet, J.B. Ladesich, P. Collery, J.P. Perchellet. *Anti-Cancer Drugs*, **10**, 477 (1999).

Downloaded by [Renmin University of China] at 10:31 13 October 2013