

**Synthesis, and structural characterization of  
[(CH<sub>3</sub>(C<sub>5</sub>H<sub>4</sub>N))Ga(SCH<sub>2</sub>(CO)O)][(4-MepyH)]<sup>+</sup>, a novel Ga(III) five coordinate  
complex.**

Kulbinder K. Banger<sup>a,d</sup>, Stan A. Duraj<sup>b</sup>, Philip E. Fanwick<sup>c</sup>,  
Aloysius F. Hepp<sup>d\*</sup>, Robert A. Martuch<sup>b</sup>

<sup>a</sup> Ohio Aerospace Institute, 22800 Cedar Point Road, Cleveland, OH,  
44142, USA. Fax: 440.962.3057; Tel: 440.962.3000; E-mail:  
[KulbinderBanger@oai.org](mailto:KulbinderBanger@oai.org)

<sup>b</sup> Dept. of Chemistry, Cleveland State University, Cleveland, OH 44115,  
USA. Fax: 216 687 906; Tel: 216 687 2451; E-mail: [s.duraj@csuohio.edu](mailto:s.duraj@csuohio.edu)

<sup>c</sup> Department of Chemistry, Purdue University, West Lafayette, IN, 47907,  
USA. Fax: 765 494-0239; Tel: 765 494 445725; E-mail:  
[fanwick@xray.chem.purdue.edu](mailto:fanwick@xray.chem.purdue.edu)

<sup>d</sup> National Aeronautics and Space Administration, (NASA), Glenn Research  
Center, MS 302-1, 21000 Brookpark Road, Cleveland, OH, 44135 USA. Fax 216  
433 6106; Tel 216 433 3835; E-mail: [Aloysius.F.Hepp@grc.nasa.gov](mailto:Aloysius.F.Hepp@grc.nasa.gov)

(\*Corresponding author)

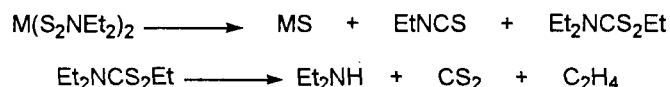
This report is a preprint of an article submitted to a journal for publication. Because of changes that may be made before formal publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

## Abstract

The synthesis and structural characterization of a novel ionic Ga(III) five coordinate complex  $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2][(\text{4-MepyH})]^+$ , (4-Mepy =  $\text{CH}_3(\text{C}_5\text{H}_5\text{N})$ ) from the reaction between  $\text{Ga}_2\text{Cl}_4$  with sodium mercapto-acetic acid in 4-methylpyridine is described. Under basic reaction conditions the mercapto ligand is found to behave as a  $2e^-$  bidentate ligand. Single crystal X-ray diffraction studies show the complex to have a distorted square pyramidal geometry with the  $[(\text{SCH}_2(\text{CO})\text{CO})^-]$  ligands in a *trans* conformation. The compound crystallizes in the  $\text{P2}_1/\text{c}$  (No. 14) space group with  $a = 7.7413(6) \text{ \AA}$ ,  $b = 16.744(2) \text{ \AA}$ ,  $c = 14.459(2) \text{ \AA}$ ,  $V = 1987.1(6) \text{ \AA}^3$ ,  $R(F_o) = 0.032$  and  $R_w = 0.038$ .

## Introduction

Metal chalcogenide semiconductors display very high radiation tolerance and high optical absorption coefficient,<sup>1</sup> consequently Metal Organic Chemical Vapor Deposition (MOCVD) precursors to III/VI materials have received considerable interest for fabrication of optoelectronic devices and thin-film solar cell arrays.<sup>2</sup> One major advantage of metal chalcogenide complexes is their ability to behave as binary single-source precursors.<sup>3-6</sup> The mechanism for decomposition yields metal sulphide type moieties, which can be incorporated into thin-film coatings during fabrication, e.g. dithiocarbamates (Scheme 1).<sup>7</sup> More recently, O'Brien *et al* have demonstrated the ease in which binary single source precursor can serve as excellent reagents for the preparation of semiconducting nanoparticles.<sup>8</sup>



**Scheme 1** Suggested decomposition pathway of metal chalcogenides.

Therefore, the facile syntheses of these single source precursors, which readily decompose to afford the desired semiconductors with the correct stoichiometry are highly desirable. Previously we have reported the preparation of a number of novel gallium(III) dithiocarbamate complexes and recently an indium(III) thioglycolic derivative.<sup>9</sup> Further to this series, we now report the facile preparation of  $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2][(\text{4-MepyH})]^+$  **1** as a possible precursor to the semiconductor GaS, or Ga<sub>2</sub>S<sub>3</sub>.

## EXPERIMENTAL

### General.

Air and moisture-sensitive materials were handled under anaerobic conditions using standard Schlenk line techniques, in flame-dried glassware. Solids were manipulated in a Vacuum Atmospheres dry box equipped with a HE-493 dri-train. Heptane and 4-methylpyridine were distilled from CaH<sub>2</sub> under a dinitrogen atmosphere prior to use. Anhydrous gallium(III)chloride and [NaSCH<sub>2</sub>(CO)OH] were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

### Preparation of $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2][(\text{4-MepyH})]^+$

Sodium mercapto-acetic acid (NaSCH<sub>2</sub>(CO)OH) (0.25 mmol) and a small excess of Ga<sub>2</sub>Cl<sub>4</sub>, (0.30 mmol) were reacted in 25 mL of 4-methylpyridine at 0 °C with subsequent warming to room temperature, under Argon. The solution was then allowed to react for 7 days, filtered and then layered with 25 mL of heptane, which afforded colorless white needles suitable for single crystal analysis after 3 days (yield 35%).

### X-Ray Crystal Data Collection.

Single crystal x-ray diffraction data were collected on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. A colorless needle of GaS<sub>2</sub>O<sub>4</sub>N<sub>2</sub>C<sub>16</sub>H<sub>19</sub>, (*M* = 437.19) having approximate dimensions of 0.19 x 0.11 x 0.11 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range  $20 < \theta < 22^\circ$ , measured by the computer-controlled diagonal slit method of centering. The monoclinic cell parameters, calculated volume and density are shown in Table I. Crystal quality was determined by measuring several intense omega reflections, which displayed a half height width of 0.57° with a take off angle of 3.0°, indicating moderate crystal quality. There were no systematic absences; the space group was determined to be P2<sub>1</sub>/c (No. 14). A total of 2562

reflections were collected, of which 2562 were unique.<sup>10</sup> Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $17.0 \text{ cm}^{-1}$  for Mo K radiation. An empirical absorption correction based on the method of Walker and Stuart was applied.<sup>11</sup> Relative transmission coefficients ranged from 0.769 to 1.000 with an average of 0.916.

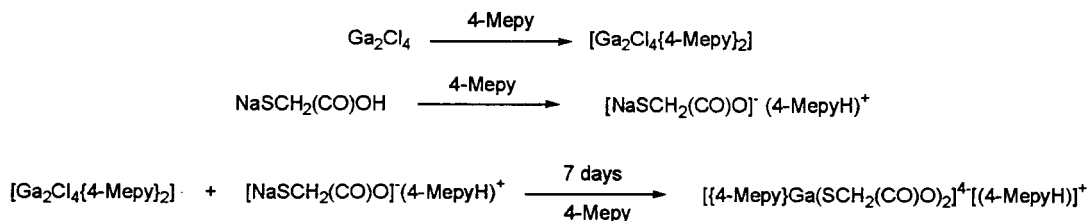
**Table I.** Crystallographic data for  $\text{GaS}_2\text{O}_4\text{N}_2\text{C}_{16}\text{H}_{19}$ , (CCDC 170557).

Formula Weight	437.19
Crystal size (mm)	0.50 x 0.17 x 0.13
Space group (No.)	P2 <sub>1</sub> /c (No. 14).
A (Å)	7.7413(6)
b (Å)	16.744(2)
c (Å)	14.459(2)
$\beta$ , (°)	90.763(9)
$\gamma$ , (°)	98.983(9)
V, Å <sup>3</sup>	1874.1(6)
Z	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.549
Temperature, K	293
$\lambda$ Radiation (wavelength)	Mo K $\alpha$ (0.71073 Å)
$\mu$ , cm <sup>-1</sup>	16.98
Transmission coeff.	1.000-0.769
Scan method	$\omega$ -2 $\theta$
h, k, l,	-8 to 8, 0 to 18, 0 to 15
No. observed data	2562
No. unique data	2562
Largest shift/esd in final cycle	0.19
R(F <sub>o</sub> )	0.032
R <sub>w</sub>	0.038
F <sub>000</sub>	896.0
Goodness of fit	0.874

The structure was solved using the solution program Mo1EN on a VAX computer.<sup>12</sup> Interpretation of a Patterson heavy atom method revealed the position of the In atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but not refined. The structure was refined in full-matrix least-squares where w is defined as per the Killeen and Lawrence method with terms of 0.020 and 1.0.<sup>13</sup>

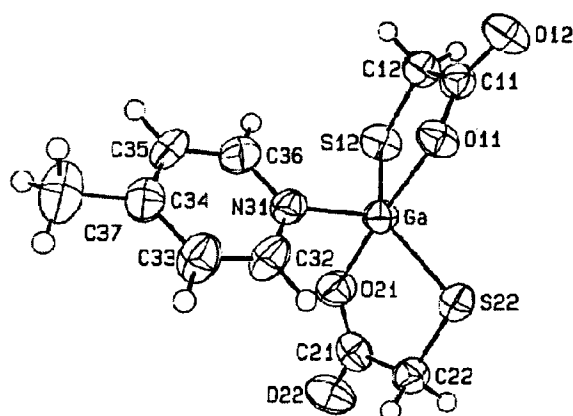
## RESULTS AND DISCUSSION

The use of  $\text{GaCl}_2$  as a starting material for novel main group complexes has also seen a renewed interest. Gallium dichloride is more correctly represented as a  $\text{Ga(I)}$  and  $\text{Ga(III)}$ ,  $([\text{Ga}^+][\text{GaCl}_4^-])$ . The salt comprises a reducing gallium(I) species with the Lewis acidic, tetrahedral  $\text{GaCl}_4^-$  ion. The preparation of **1** can be presumed to occur via the formation of the intermediate, chlorogallium 4-methylpyridine  $[\text{Ga}_2\text{Cl}_4(4\text{-Mepy})_2]$  **2**.<sup>9</sup> The subsequent addition of sodium mecapto-acetic acid ( $\text{NaSCH}_2(\text{CO})\text{OH}$ ) to the basic solution of **2** at  $0^\circ\text{C}$ , followed by warming to room temperature results in the initial deprotonation of the acidic hydrogen to yield the intermediate  $2e^-$  bidentate donor ligand  $(^-\text{SCH}_2(\text{CO})\text{O}^-)$ .<sup>14-17</sup> The reaction then proceeds by the concomitant cleavage of the Ga-Ga bond via disproportionation to Ga metal and  $\text{Ga(III)}$  cation due to the basic reactions conditions,<sup>18</sup> followed by ligation of  $^-\text{SCH}_2(\text{CO})\text{O}^-$  to yield the novel gallium(III) moiety (Scheme 2).



**Scheme 2.** Preparation of  $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N})\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2)][(4\text{-MepyH})_2]^+ \textbf{1}$ .

The reaction is then filtered to remove elemental Ga and the filtrate carefully layered with freshly distilled heptane. Controlled evaporation at room temperature under inert conditions produced a large quantity of colorless crystals, from which one was selected for analysis by single crystal X-ray diffraction. The product was elucidated as the unexpected ionic species  $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N})\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2)][(4\text{-MepyH})]^+ \textbf{1}$  (Figure I, Table II).



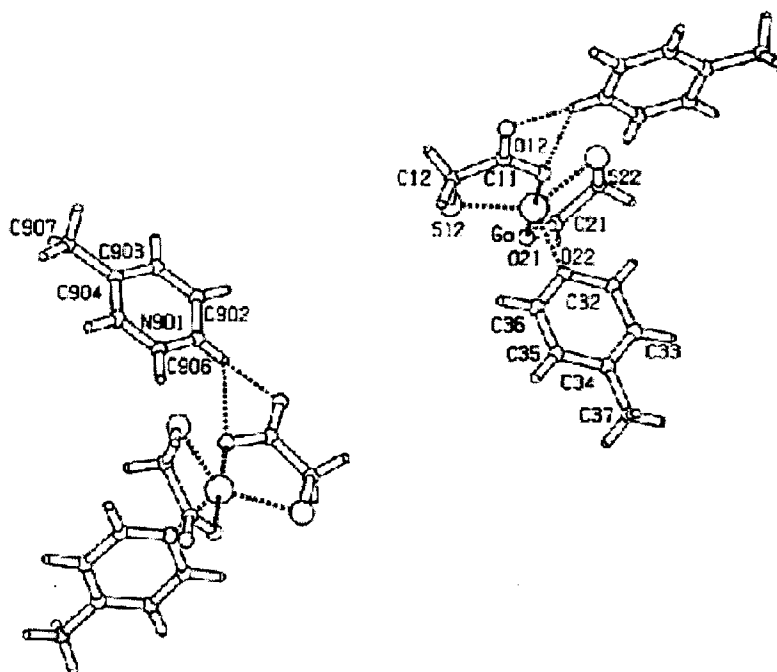
**Fig. 1** X-ray Single Crystal structure for  $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})][(\text{4-MepyH})]^+$  **1**. The  $[(\text{4-MepyH})]^+$  cation has been omitted for clarity .

**Table II.** Selected bond distances (Å) and angles ( $^\circ$ ) for  $\text{GaS}_2\text{O}_4\text{N}_2\text{C}_{16}\text{H}_{19}$ .

Bond	Distance/ Å	Atoms	Angle/ $^\circ$
Ga-S(12)	2.243(1)	S(12)-Ga-S(22)	138.18(6)
Ga-S(22)	2.242(1)	S(12)-Ga-O(11)	86.8(1)
Ga-O(11)	2.039(3)	S(12)-Ga-O(21)	93.8(1)
Ga-O(21)	1.969(3)	S(12)-Ga-N(31)	111.6(1)
Ga-N(31)	2.017(4)	S(22)-Ga-O(11)	88.3(1)
S(12)-C(12)	1.804(5)	S(22)-Ga-O(21)	88.9(1)
S(22)-C(22)	1.805(5)	S(22)-Ga-N(31)	110.1(1)
O(11)-C(11)	1.273(5)	O(11)-Ga-O(21)	176.5(2)
O(11)-H(+)	2.53(7)	O(11)-Ga-N(31)	91.9(1)
O(12)-C(11)	1.239(6)	O(21)-Ga-N(31)	91.1(2)
O(12)-H(+)	1.85(7)	Ga-S(12)-C(12)	97.5(2)
O(21)-C(21)	1.280(6)	Ga-S(22)-C(22)	95.8(2)
O(22)-C(21)	1.217(6)	Ga-O(11)-C(11)	120.0(3)
N(31)-C(32)	1.329(6)	Ga-O(21)-C(21)	121.0(4)
N(31)-C(36)	1.324(6)	Ga-N(31)-C(32)	120.5(3)
N(901)-H(+)	0.88(7)	Ga-N(31)-C(36)	122.8(4)

The thioglycolic ligands are arranged in the expected *trans* geometry, binding through both sulfur and oxygen. In addition, Ga having an underlying  $d^{10}$  configuration allows it to take part in  $d_\pi$ - $d_\pi$  and  $d_\pi$ - $p_\pi$  back bonding with the auxiliary sulfur and oxygen atoms of the bidentate ligand respectively.<sup>19</sup>

Compound **1** is significant as it represents a novel thioglycolic five-coordinate Ga(III) ionic complex and the first structurally characterized. The unit cell contains two unique ionic molecules, which show a distorted trigonal pyramidal geometry around the gallium atom. Comparison of the Ga-N bond length of 2.017(4) Å shows it is consistent with that reported for [Ga<sub>2</sub>Cl<sub>4</sub>(4-Mepy)<sub>2</sub>] (2.005(6) Å).<sup>9</sup> The Ga-O(11) bond length of 2.039(3) Å is found to be longer than Ga-O(21) bond length of 1.969(3). The variation in bond lengths may be attributed to the presence of hydrogen bonding observed between both oxygen's and the protonated amine O(12)⋯H(+), O(11)⋯H(+) 1.85(7) and 2.53(7) Å respectively, thus resulting in elongation of the Ga-O(11) (Figure 2). With the absence of hydrogen bonding as associated for the second thioglycolic ligand a Ga-O(21) bond length of 1.969(3) is determined, which is a magnitude similar to those found in gallium carboxylates, (Ga-O = 1.958(5) to 1.984(5) Å).<sup>20</sup> In addition, the Ga-S bond lengths of 2.243(1) and 2.242(1) Å are typical for these family of ligands.<sup>9</sup> Long distance interactions are also observed between the adjacent carbonyl group and the cation of 2.53(7) Å, which would account for the relatively close geometric arrangement of the cation.



**Fig. 2** The crystal structure of  $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N}))\text{Ga}(\text{SCH}_2(\text{CO})\text{O})]^{4+}[(4\text{-MepyH})]^+$  **1**; two molecules are represented displaying ionic interactions.



Comparison of O(11)-C(11) and C(11)-O(12) bond lengths of 1.273(5) and 1.239(6) Å show these are comparable to those reported in literature for C-O and C=O respectively. Thus supporting that the ligand is acting as a 2e<sup>-</sup> donor with the carbonyl group directed away from the metal co-ordination sphere.

## SUMMARY

The thioglycolic ligand represents a bidentate ligand comprising of both auxiliary soft (S) and hard donor (O) atoms. Metal thioglycolic complexes reported in literature demonstrate the ligands ability to serve as either a 1e<sup>-</sup> and/or 2e<sup>-</sup> donor ligand. Reactions reported in neutral conditions illustrate the ligand preferentially behaves as a 1e<sup>-</sup> donor. In addition, the use of sterically demanding groups on the ligand has been shown to reduce ligand to metal association.<sup>14</sup> In basic reaction conditions the acidic proton is readily removed affording the 2e<sup>-</sup> bidentate donor ligand. In this work we demonstrate that 4-methylpyridine can serve as a reaction solvent, in addition to a base and dative ligand by the isolation and characterization of **1**. In conclusion, a novel array of co-ordination chemistry can be invoked by manipulation of the pH of the reaction medium and the steric bulk of peripheral groups of these types of ligands.

## ACKNOWLEDGEMENTS

A. F. H (Director's Discretionary Fund), NASA Cooperative Agreement NCC3-318, S. A. D. (NCC3-162), and P. E. F. (NCC3-246).

## REFERENCES

1. J. Woodyard, G. A. Landis, *Solar Cells*, 1991, **31**, 297.
2. L. L. Kazmerski, S. Wagner, "Current Topics in Photovoltaics", ed. T. S. Coutts and J. D. Meakin, Academic, London, 1985, 41.
3. A. Jones, P. O'Brien, "CVD of Compound Semiconductors: Precursors Synthesis, Development & Application", VCH: Weinheim, 1997
4. M. R. Lazell, P. O'Brien, D. J. Otway, J. Park, *Chem. Mater.*, 1999, **11**, 3430.

5. M. Lazell, S. J. Norager, P. O'Brien, N. Revaprasadu, *Mater. Sci. Eng.*, 2001, **C16(1-2)**, 129
6. A. Keys, S. G. Bott, A. R. Barron, *Chem. Mater.*, 1999, **11**, 3578.
7. M. A. Bernard, M. M. Borel, G. Lagouche, *Bull. Soc. Chim. Fr.*, 1969, 7066.
8. N. L. Pickett, P. O'Brien, *Chem. Record*, 2001, **1**, 467.
9. E. M. Gordon, A. F. Hepp, S. A. Duraj, T. S. Habash, P. E. Fanwick, J. D. Schupp, W. E. Eckles, S. Long, *Inorg. Chim. Acta*, 1997, **257**, 247.
10. CCDC reference number 170557, full crystal refinement details for (1), see <http://www.ccdc.cam.ac.uk/>
11. N. Walker, D. Stuart, *Acta Crystallogr.*, 1983, **A39**, 158.
12. Mo1EN, "An Interactive Structure Solution Procedure", Enraf-Nonius, Delft, The Netherlands, 1990
13. R. G. Killeen, J. L. Lawence, *Acta Crystallogr.*, 1969, **B25**, 1750.
14. P. Bishop, P. Marsh, A. K. Brisdon, B. J. Brisdon, M. F. Mahon, *J. Chem. Soc. Dalton Trans.*, 1998, 675
15. J. S. Casas, A. Castineiras, M. D. Couce, M. L. Jorge, U. Russo, A. Sanchez, R. Seoane, J. Sordo, J. M. Varela, *Applied Organomet. Chem.*, 2000, **14(8)**, 421.
16. X. Q. Song, Q. L. Xie, N. X. Fang, *Chin. Chem. Lett.*, 1998, **9(10)**, 977.
17. R. M. Khomutov, A. R. Khomutov, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1985, **(11)**, 2649.
18. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, "Advanced Inorganic Chemistry", 6<sup>th</sup> Ed., Wiley-Interscience Press, 1999, Chapter 2, p175
19. (a) I. Toth, L. Zekany, E. Brucher, *Polyhedron*, 1984, **3(7)**, 871, (b) K. Dymock, G. J. Palenik, J. Slezak, C. L. Raston, A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 28.
20. A. Keys, T. J. Barbarich, S. G. Bott, A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 2000, 577.

Figure 1

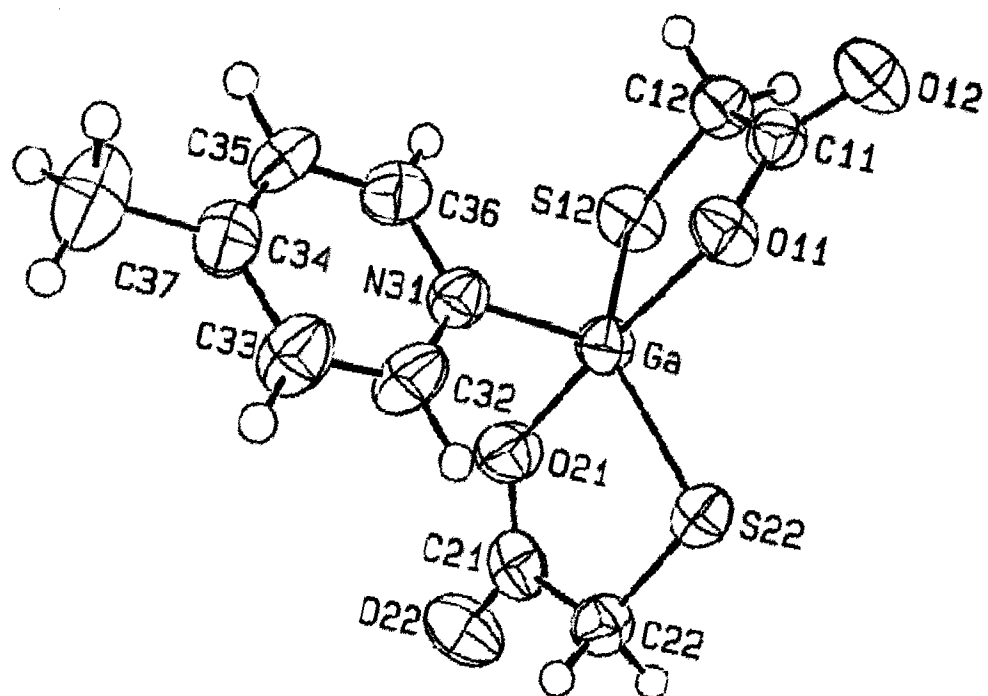


Figure 2

