砷配合物 $As(S_2CNCy_2)_2I$ 和 $As(S_2CNC_6H_{12})_3$ 的合成和晶体结构

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摘要: 合成了 2 种砷的氨荒酸配合物 $As(S_2CNCy_2)_2I$ (**1**)和 $As(S_2CNC_6H_{12})_3$ (**2**)。通过元素分析和红外光谱对其进行了表征,用 X-射线单晶衍射测定了它们的晶体结构。配合物 **1** 的晶体属单斜晶系,空间群为 $P2_1/n$,晶胞参数 a=1.020 9(4) nm,b=1.468 0(5) nm,c=1.521 8(5) nm,β=92.135(5)°和 Z=4。配合物 **2** 的晶体属三方晶系,空间群为 $R\bar{3}$,使用六方坐标,晶胞参数 a=1.622 1(4) nm,c=2.119 4(6) nm,并有 Z=6。测试结果表明,配合物 **1** 为单核结构,中心砷原子为五配位的三角双锥配位构型,此外,在该配合物分子间存在弱的 As…S 相互作用(As…S 0.351 2(4) nm),使得该配合物以弱桥连二聚体存在。在配合物 **2** 中,3 个配体分别以双齿形式与砷原子配位,形成六配位的畸变三棱柱体结构。

关键词: 砷配合物; 晶体结构; 氨荒酸配体
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Synthesis and Crystal Structure of Two Arsenic(Ⅲ) Complexes $As(S_2CNCy_2)_2I$ and $As(S_2CNC_6H_{12})_3$

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Abstract: Two arsenic(Ⅲ) complexes with dithiocarbamate ligands, $As(S_2CNCy_2)_2I$ (**1**) and $As(S_2CNC_6H_{12})_3$ (**2**) were synthesized and structurally characterized by elemental analysed, IR and single crystal X-ray diffraction analysis. Complex **1** crystallizes in the monoclinic system, space group $P2_1/n$, with a=1.020 9(4) nm, b=1.468 0(5) nm, c=1.521 8(5) nm, β=92.135(5)°, and Z=4, while complex **2** crystallizes in the trigonal system, space group $R\bar{3}$, with a=1.622 1(4) nm, c=2.119 4(6) nm, for hexagonal coordinate, and Z=6. Complex **1** has a mononuclear structure, the central arsenic atom is five-coordinated in a distorted trigonal bipyramid. An additional feature was noted in this structure, i.e. the presence of a short intermolecular As…S distance of 0.351 2(4) nm makes the structure as a weakly-bridged dimmer. In complex **2**, The bidentate ligands are chelated to the arsenic atom, forming a coordination polyhedron which can be described as a distorted trigonal antiprism. CCDC: 607955, **1**; 624814, **2**.

Key words: arsenic(Ⅲ) complexes; crystal structure; dithiocarbamate ligands

The chemistry of arsenic (Ⅲ)-1,1-dithiolates has been the subject of considerable research in recent decades[1~5]. It has been stimulated by either the potential applications (e.g. fungicides, herbicides, desiccants and wood preservatives) or their interesting structural behaviour that results from the various coordination patterns of the 1,1-dithiolate ligands[6]. The inhibition action of arsenic(Ⅲ) on the activity of enzymes is a strong field of biochemical investigation[7~12]. Arsenic is cytotoxic and the mechanism of toxicity is believed to be due to the ability of arsenite (As Ⅲ) to bind protein thiols. It can also induce chromosomal damage and

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inhibit DNA repair[13]. In view of above and present of our recent work on bismuth complex and sulfurcontaining ligands, here we report two arsenic(Ⅲ) complexes of dithiocarbamate, $As(S_2CNCy_2)_2I$ and $As(S_2CNC_6H_{12})_3$.

1 Experimental

1.1 General procedure

All chemicals were commercially available and used without further purification. The IR spectra were recorded with a Nicolet-460 spectrometer, using KBr as discs. Elemental analyses were performed on a PE-2400 Ⅱ elemental analyzer. X-ray diffraction measurements were made on a Bruker Smart-1000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ (0.071 073 nm) radiation.

1.2 Syntheses

1.2.1 Preparation of the *N*,*N*′-dialkyldithiocarbamate sodium [$Na(R_2dtc)$]

To a stirred solution of dialkyl-secondary amine (0.05 mol) in ethanol or methanol (5 mL) was added, at less than 4 ℃, carbon disulfide (3.1 mL, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 mL). After stirring for 4~5 h, evaporation of the volatile was performed without heating. The pure [$Na(R_2dtc)$] was obtained by recrystallization of ethanol (or methanol). Yield: 80%~90%.

$$CS_2 + R_2NH + NaOH \xrightarrow[\text{or } CH_3OH]{CH_3CH_2OH} R_2NCS_2Na + H_2O$$

R_2NCS_2Na: Cy_2NCS_2Na (**1**), $C_6H_{12}NCS_2Na$ (**2**)

1.2.2 Preparation of complex $As(S_2CNCy_2)_2I$ (**1**)

To a stirred solution of AsI_3 (0.2 mmol) in acetonitrile (20 mL), Cy_2NCS_2Na (0.4 mmol) was added. The reaction mixture was stirred for 4 h at 298 K. An orange-red solution was obtained, which was then filtered. The solvent was gradually removed by evaporation under vacuum and a solid product was obtained. The solid was recrystallized from ethanol and orange-red crystals were formed (yield 79%; m.p. 129 ℃). Analysis calculated for $C_{26}H_{44}AsN_2S_4I$(%): C 43.69, H 6.21, N 3.92; found (%): C 43.38, H 6.53, N 3.66. IR (KBr) ν (cm^{-1}): 3 426, 2 976, 2 863, 1 637, 1 508, 1 477, 1 421, 1 272, 1 225, 997, 701.

1.2.3 Preparation of Complex $As(S_2CNC_6H_{12})_3$ (**2**)

To a stirr ed solution of AsI_3 (0.2 mmol) in acetonitrile (20 mL), $C_6H_{12}NCS_2Na$ (0.6 mmol) was added. The reaction mixture was stirred for 4 h at 298 K. An yellow solution was obtained, which was then filtered. The solvent was gradually removed by evaporation under vacuum and a solid product was obtained. The solid was recrystallized from methanol and yellow crystals were formed (yield 79%; m.p. 117 ℃). Analysis calculated for $C_{24}H_{48}AsN_3S_6O_3$ (%): C 41.54, H 6.97, N 6.06; found(%): C 41.38, H 6.63, N 6.24. IR (KBr) ν(cm^{-1}): 3 418, 2 958, 2 845, 1 655, 1 523, 1 465, 1 422, 1 272, 1 229, 985, 715.

1.3 Crystal structure determination and refinement

The crystals having approximate dimensions of 0.35 mm × 0.31 mm × 0.26 mm (**1**) or 0.49 mm × 0.38 mm × 0.35 mm (**2**) were selected for the structural analyses, respectively. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromatized Mo $K\alpha$ (0.071 073 nm) radiation. The structure was solved by direct method and different Fourier syntheses, and refined by full-matrix least-squares on F^2 using SHELX-97 program[14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. Crystallographic data and experimental details of the structure determinations are listed in Table 1.

CCDC: 607955, **1**; 624814, **2**.

Table 1 Crystal data and structure refinement details for complexes 1 and 2

Complex	**1**	**2**
Empirical formula	$C_{26}H_{44}N_2S_4AsI$	$C_{24}H_{48}N_3S_6O_3As$
Formula mass	714.69	693.93
Temperature / K	298(2)	298(2)
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	$R\bar{3}$
a / nm	1.440 7(5)	1.622 1(4)

Continued Table 1

b / nm	1.468 0(5)	1.622 1(4)
c / nm	1.521 8(5)	2.119 4(6)
α / (°)	90	90
β /(°)	92.135(5)	90
γ / (°)	90	120
V / nm^3	3.216 3(15)	4.830(2)
Z	4	6
F(000)	1 456	2 196
D_c / (g·cm^{-3})	1.476	1.432
Crystal dimensions / mm	0.18 × 0.16 × 0.13	0.25 × 0.24 × 0.22
θ range / (°)	1.91~25.01	1.74~25.00
Limiting indices	$-12 \leqslant h \leqslant 17, -17 \leqslant k \leqslant 17, -18 \leqslant l \leqslant 17$	$-19 \leqslant h \leqslant 19, -12 \leqslant k \leqslant 19, -25 \leqslant l \leqslant 25$
Reflections collected	16 346	8 453
Independent reflections (R_{int})	5 614 (0.090 5)	1 896 (0.040 8)
Max. and min. transmission / cm^{-1}	0.754 7 and 0.682 9	0.737 3 and 0.709 3
Data / restraints / parameters	5 614 / 246 / 307	1 896 / 46 / 125
Goodness of fit on F^2	1.036	1.058
Final R indices [$I>2\sigma(I)$]	R_1=0.066 2, wR_2=0.157 3	R_1=0.051 7, wR_2=0.130 9
R indices (all date)	R_1=0.166 3, wR_2=0.231 3	R_1=0.084 4, wR_2=0.164 5
Largest diff. peak and hole / (e·nm^{-3})	991 and −680	698 and −792

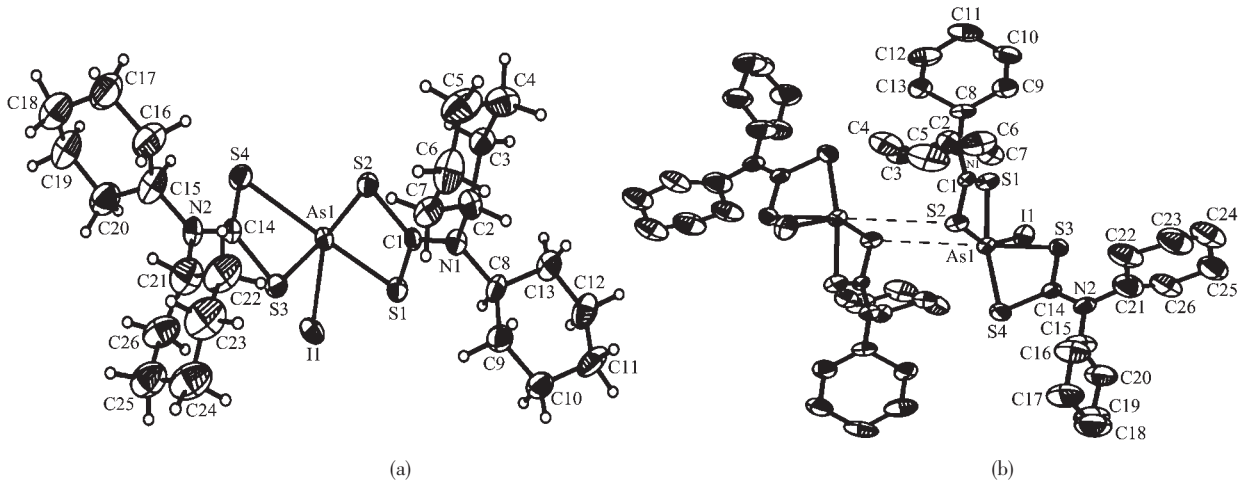
2 Results and discusstion

2.1 Spectroscopic studies

The room temperature (25 ℃) IR spectra displayed a medium intensity band in the region 690~740 cm^{-1} (701 cm^{-1} for **1**, 715 cm^{-1} for **2**), may be assigned to ν(As-C) alkyl/aryl arsenic stretching vibrations. Bands in the region of 1 130~1 220 cm^{-1} may be assigned to the ν(C-N_{sec}) stretching vibrations (1 225 cm^{-1} for **1**, 1 229 cm^{-1} for **2**). The electron donating capacity of the -NR_2-group in dithiocarbamates affects the electronic structure of the complexes and it appears to play an important role in the preference of one form over the others. Since increasing the electron releasing ability of -NR_2-group forces more electron density on to the sulphur atom, via the p-system and, therefore, to the ion of As, it causes greater double bond character in C-N bond. This and, therefore, the contribution to one of the resonance forms are reflected in the shifting of ν(C-N) to higher frequencies. All of the compounds show a set of bands in the region of 1 400~1 500 cm^{-1} (1 421, 1 477, 1 490 for **1**; 1 422, 1 465 for **2**) which falls between the stretching frequencies of C-N single bonds (1 250~1 350 cm^{-1}) and C-N double bonds (1 640~1 690 cm^{-1}). Bands in the region of 2 900~3 000 cm^{-1} can be assigned to C-H stretching vibrations (2 976, 2 863 cm^{-1} for **1**; 2 958, 2 845 cm^{-1} for **2**). In addition, the increased double bond character of the C-S bond is a further evidence for the presence of bidentate dithiocarbamates[15~18].

2.2 Molecular structure of complex 1

The molecular structure of complex **1** is shown in Fig.1. Table 2 gives the selected bond lengths and angles. In complex **1**, the arsenic atom is five-coordinated with lengths: [As(1)-S(3) 0.225 8(3) nm, As(1)-S(1) 0.233 2(4) nm, As(1)-S(2) 0.241 0(3) nm, As(1)-S(4) 0.270 9(4) nm, As(1)-I(1) 0.297 2(2) nm], in a distorted trigonal bipyramid. An additional feature was noted in this structure, i.e. the presence of a short intermolecular As⋯S distance of 0.351 2 (4) nm makes the structure as a weakly-bridged dimmer. The geometry is loosely based on a trigonal bipyramid, with atom S(1), S(3) and S(4) occupying the equatorial positions. As an indication the sum of the equatorial angles (369.22°) at the arsenic atom, so the S(1), S(3), S(4) and As (1) are not co-planner. The I atom occupies approx-



(a) (b)

Fig.1 Structures of the molecule (a) and the dimmer (b) of complex **1**

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

As(1)-S(3)	0.225 8(3)	As(1)-S(1)	0.233 2(3)	As(1)-S(2)	0.241 0(3)
As(1)-S(4)	0.270 9(4)	As(1)-I(1)	0.297 23(17)	As(1)-S(2)#1	0.351 2(4)
S(1)-C(1)	0.172 8(12)	S(2)-C(1)	0.170 7(11)	S(3)-C(14)	0.171 2(12)
S(4)-C(14	0.169 0(12)				
S(3)-As(1)-S(1)	92.08(13)	S(3)-As(1)-S(2)	90.53(13)	S(1)-As(1)-S(2)	74.25(11)
S(3)-As(1)-S(4)	70.41(11)	S(1)-As(1)-S(4)	153.27(12)	S(2)-As(1)-S(4)	85.56(12)
S(3)-As(1)-I(1)	88.29(10)	S(1)-As(1)-I(1)	79.83(9)	S(2)-As(1)-I(1)	153.99(9)
S(4)-As(1)-I(1)	118.26(10)				

imately one apical position of the trigonal bipyramid. Conversely, due to the constraint of the chelating ligand [the angle [S(1)-As(1)-S(2)] is only 74.25(11)°], the S(2) atom can not exactly occupy the corresponding trans axial position of the trigonal bipyramid with the angle I(1)- As(1)- S(2) being 153.99(9)°.

2.3 Molecular structure of complex 2

The molecular structure of complex **2** is shown in Fig.2. Table 3 gives the selected bond lengths and angles. The bidentate ligands are chelated to the As atom, forming a polyhedron which can be described as a distorted trigonal antiprism. There are three short As-S bonds and three long As-S bonds. All the three short bonds (mean As-S=0.233 36(16) nm) indicate a strong 'S' coordination, while the other set corresponds to a weak As-S interaction (mean As-S=0.287 57(18) nm). It is noticeable that, in all ligands, the C-S bond associated with the strong As-S bond is significantly longer (mean 0.175 9(6) nm) than that (mean=0.168 5(6) nm) associated with the weak As-S bond, showing clearly the localization of the double bonds.

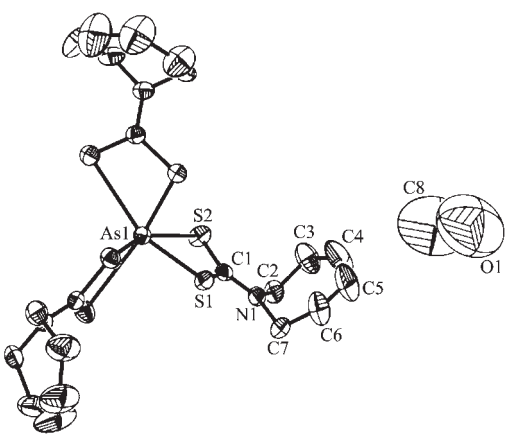


Fig.2 Molecular structure of complex **2**

A diagram of the coordination polyhedron showing the two trigonal faces of the antiprism is depicted in Fig.3. The plane defined by S1, S1A and S1B, which are the strongly coordinated S atoms, is absolutely parallel to that defined by S2, S2A and S2B (the two planes are at an angle of 0° and As is displaced by 0.135(2) and 0.104(3) nm, respectively, from the planes.

Table 3　Selected bond lengths (nm) and bond angles (°) for complex 2

As(1)–S(1)	0.233 36(16)	As(1)–S(1)#1	0.233 36(16)	As(1)–S(1)#2	0.233 36(16)
As(1)–S(2)	0.287 57(18)	As(1)–S(2)#1	0.287 57(18)	As(1)–S(2)#2	0.287 57(18)
S(1)–C(1)	0.175 9(6)	S(2)–C(1)	0.168 5(6)		
S(1)–As(1)–S(1)#1	89.96(6)	S(1)–As(1)–S(2)	68.51(5)	S(1)–As(1)–S(1)#2	89.96(6)
S(1)#1–As(1)–S(2)	93.86(6)	S(1)#1–As(1)–S(1)#2	89.96(6)	S(1)#2–As(1)–S(2)	158.10(6)
S(1)#1–As(1)–S(2)#1	68.51(5)	S(1)–As(1)–S(2)#1	158.10(6)	S(1)#2–As(1)–S(2)#1	93.86(6)
S(2)–As(1)–S(2)#1	107.61(4)	S(1)–As(1)–S(2)#2	93.86(6)	S(1)#1–As(1)–S(2)#2	158.10(6)
S(1)#2–As(1)–S(2)#2	68.51(5)	S(2)–As(1)–S(2)#2	107.61(4)	S(2)#1–As(1)–S(2)#2	107.61(4)

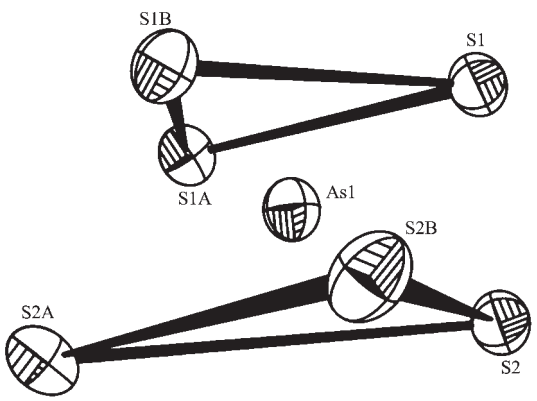


Fig.3　A schematic diagram of the coordination polyhedron in complex **2** showing the two trigonal faces of the antiprism

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