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Syntheses and structures of heterobimetallic complexes derived from $[Ga(edt)_2]^-$ as a metalloligand (edt = $^-SC_2H_4S^-$): Potential precursors for ternary materials $MGaS_2$ (M = Cu or Ag)

Yan-Gong Han, Chao Xu, Taike Duan, Qian-Feng Zhang *

Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China

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ABSTRACT

Metathesis reaction between equimolar amount of $[Et_4N][GaCl_4]$ and Na_2edt in methanol resulted in the formation of the dichloro complex $[Et_4N][Ga(edt)Cl_2]$ (**1**), whereas reaction of $[Et_4N][GaCl_4]$ with two equivalents of Na_2edt in methanol gave the complex $[Et_4N][Ga(edt)_2]$ (**2**) which can act as a metalloligand. Treatment of **2** with $M(PPh_3)_2NO_3$ in DMF/CH_2Cl_2 afforded the heterobimetallic complexes $[Ga(edt)_2M\text{-}(PPh_3)_2]$ (M = Cu **3**, Ag **4**) in moderate yields. The structures of **1**–**4** were determined by single-crystal X-ray diffraction analyses. Both $[Ga(edt)Cl_2]^-$ and $[Ga(edt)_2]^-$ anions have a distorted tetrahedral geometry. The former consists of one five-membered ring formed by chelating dithiolate and two terminal chloride atoms while the latter consists of two five-membered rings formed by two the chelating dithiolates. Complexes **3** and **4** consist of metalloligand $[Ga(edt)_2]^-$ anion chelated to $[M(PPh_3)_2]^+$ *via* the sulfur atoms. Both tetrahedrally coordinated Ga and Cu(Ag) atoms are bridged by two sulfur atoms, forming a planar "GaS_2M" (M = Cu, Ag) core. Thermogravimetry analysis revealed that heterobimetallic complexes **3** and **4** decomposed to give the corresponding ternary metal sulfide materials.

1. Introduction

In contrast to a few indium thiolates which are important precursors for sulfur-containing indium compounds, analogous gallium thiolates are extremely rare [1–5]. There are several reports on the use of homoleptic gallium alkylthiolate and arylthiolate complexes as precursors of sulfur-rich gallium sulfide films by chemical vapor deposition [5–9]. Although solid-state thiogallates have been under increased investigation in the past two decades [10–12], the chemistry of soluble molecular gallium thiolate compounds has not been extensively studied to date [13,14]. Similar to analogous indium tetra-thiolates which reacted with coinage-metals to afford bimetallic adducts as single-source precursors to the ternary semiconductors such as $CuInS_2$, $AgInS_2$ and $AgIn_5S_8$ [15–21], gallium tetra-thiolates may be reasonably speculated to coordinate with coinage-metals *via* sulfur atoms of thiolates. Thus, the ability of homolepic $[In(SR)_4]^-$ or $[Ga(SR)_4]^-$ as a metalloligand toward coinage-metals is obviously due to electron-rich sulfur affinity and small steric hindrance in the alkylthiolate moieties. Remarkably, Kanatizidis et al. have shown that indium-tetrathiolates $[In(SR)_4]^-$ reacted with copper- or silver-phosphine species to produce the ternary complexes which are effective single-source precursors to nanocrystalline photovoltaic materials $MInS_2$ (M = Cu, Ag) [15,18–21]. The precursors should have the correct M/In ratio of 1:1 and should decompose in simple steps to the desired products [22,23]. Fenske and coworkers have successfully isolated series of ternary chalcogenide high-nuclear clusters containing groups 11 and 13 metals [24,25]. However, it is very difficult to control the ratio of the two metals in the resulting clusters no matter how the ligands and reaction conditions varied. This may be partly due to the difficulty in obtaining heterometallic precursor complexes with the mixed metals in the proper ratio [26]. In order to prepare complexes with M/Ga (M = Cu, Ag) ratio of 1:1, we selected spirocyclic $[Ga(edt)_2]^-$ anion (edt = $^-SC_2H_4S^-$) as a staring material to coordinate with the cationic $[M(PPh_3)_2]^+$ species which then gave the designed neutral bimetallic complexes. The results and molecular structures of the heterobimetallic coinage-metal/gallium complexes that are potential precursors to $MGaS_2$ (M = Cu or Ag) ternary materials are described in this paper.

2. Experimental

2.1. Materials and measurements

All experiments were performed with oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. All reagents, unless otherwise stated, were purchased as

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* Corresponding author. Tel./fax: +86 555 2312041.
E-mail address: zhangqf@ahut.edu.cn (Q.-F. Zhang).

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analysis grade and were used without further purification. $[Et_4N][GaCl_4]$ [27], $Cu(PPh_3)_2NO_3$ [28], and $Ag(PPh_3)_2NO_3$ [29] were prepared according to the literature methods. All elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyzer. Infrared spectra were recorded on a Digilab FTS-40 spectrophoto-meter with use of pressed KBr pellets, and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively, and chemical shift (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Thermogravimetric analysis (TGA) was performed by using a Delta TGA instrument.

*2.2. Preparation of [Et$_4$N][Ga(edt)Cl$_2$] (**1**)*

To a slurry of $[Et_4N][GaCl_4]$ (342 mg, 1.00 mmol) in methanol (10 ml) was added dropwise Na_2edt (145 mg, 1.05 mmol) (obtained from the reaction of H_2edt and MeONa in a 1:2 mol ratio) in 10 ml of methanol with stirring. The mixture was stirred at room temperature for 30 min. Fine white solids were observed. The solution was cooled to 0 °C. The precipitates were collected by suction filtration and washed twice with 10 ml portions of diethyl ether. White air-stable solids were obtained and further recrystallized from DMF/diethyl ether to give colorless block crystals of **1** in 3 days. Yield: 311 mg, 85%. IR (KBr, cm^{-1}): ν(C–S) 644 (m). ^1H NMR (DMSO-d_6, ppm): δ 1.02 (q, J = 6.2 Hz, 12H, CH_3 in Et_4N), 2.75 (br, s, 4H, CH_2 in edt), 2.91 (t, J = 7.8 Hz, 8H, CH_2 in Et_4N). MS (FAB): m/z 233 ($M^+-[Et_4N]$), 163 ($[Ga(edt)]^+$+1). *Anal.* Calc. for $C_{10}H_{24}NCl_2S_2Ga$: C, 33.1; H, 6.66; N, 3.86%. Found: C, 33.0; H, 6.62; N, 3.81%.

*2.3. Preparation of [Et$_4$N][Ga(edt)$_2$] (**2**)*

To a slurry of $[Et_4N][GaCl_4]$ (342 mg, 1.00 mmol) in methanol (10 ml) was added dropwise Na_2edt (290 mg, 2.10 mmol) in 10 ml of methanol with stirring. The mixture was stirred at room temperature for 45 min. Fine white solids were observed. The solution was then stirred for another 30 min. The precipitates were collected by suction filtration and washed twice with 10 ml portions of diethyl ether. Recrystallization from DMF/diethyl ether afforded colorless block crystals of **1** suitable for single-crystal X-ray analysis. Yield: 346 mg, 87%. IR (KBr, cm^{-1}): ν(C–S) 652 (m). ^1H NMR (DMSO-d_6, ppm): δ 1.04 (q, J = 6.4 Hz, 12H, CH_3 in Et_4N), 2.78 (br, s, 8H, CH_2 in edt), 2.93 (t, J = 7.6 Hz, 8H, CH_2 in Et_4N). MS (FAB): m/z 254 ($M^+-[Et_4N]$). *Anal.* Calc. for $C_{12}H_{28}NS_4Ga$: C, 37.5; H, 7.34; N, 3.64%. Found: C, 37.2; H, 7.30; N, 3.64%.

*2.4. Preparation of [Ga(edt)$_2$Cu(PPh$_3$)$_2$] (**3**)*

To a solution of **2** (192 mg, 0.50 mmol) in 10 ml of DMF was slowly added $Cu(PPh_3)_2NO_3$ (326 mg, 0.5 mmol) in 20 ml of CH_2Cl_2, and the mixture was stirred for 2 h. After filtration, the clear solution was layered with 30 ml of diethyl ether. Colorless prism and block crystals of **3** were obtained after 3 days. Yield: 240 mg (57%). Both crystals were suitable for single-crystal X-ray diffraction. Different unit cells of two shape crystals were obtained and two sets of data were collected for structure solution. IR (KBr, cm^{-1}): ν(C–S) 641 (m), ν(P–C) 598 (s), 532 (s), 501 (m). ^1H NMR (CDCl$_3$, ppm): δ 2.76–2.84 (br, s, 8H, CH_2 in edt), 7.26–7.41 (m, 30H, *Ph*). ^{31}P NMR (CDCl$_3$, ppm): δ −1.94. MS (FAB): m/z 842 (M^+), 580 (M^+-PPh_3), 318 (M^+-2PPh_3). *Anal.* Calc. for $C_{40}H_{38}P_2S_4GaCu$: C, 57.0; H, 4.55%. Found: C, 56.8; H, 4.51%.

*2.5. Preparation of [Ga(edt)$_2$Ag(PPh$_3$)$_2$] (**4**)*

Compound **4** was prepared similarly as described for **3** using $Ag(PPh_3)_2NO_3$ (347 mg, 0.5 mmol) instead of $Cu(PPh_3)_2NO_3$. Colorless block crystals were obtained in a yield of 52% (233 mg). IR (KBr, cm^{-1}): ν(C–S) 649 (m), ν(P–C) 596 (s), 530 (s), 499 (m). ^1H NMR (CDCl$_3$, ppm): δ 2.78–2.82 (br, s, 8H, CH_2 in edt), 7.34–7.49 (m, 30H, *Ph*). ^{31}P NMR (CDCl$_3$, ppm): δ 5.31 (d, J = 13.4 Hz). MS (FAB): m/z 886 (M^+), 624 (M^+-PPh_3), 362 (M^+-2PPh_3). *Anal.* Calc. for $C_{40}H_{38}P_2S_4GaCu$: C, 54.2; H, 4.32%. Found: C, 54.1; H, 4.28%.

2.6. X-ray crystallographic study

The structures of $[Et_4N][Ga(edt)Cl_2]$ (**1**), $[Et_4N][Ga(edt)_2]$ (**2**), $[Ga(edt)_2Cu(PPh_3)_2]$ (**3**), and $[Ga(edt)_2Ag(PPh_3)_2]$ (**4**) were determined by single-crystal X-ray diffraction technique. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 296 K using an ω scan mode. The collected frames were processed with the software SAINT [30]. The data was corrected for absorption using the program SADABS [31]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [32]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96, C_{sp2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. The Flack parameter were 0.00 and 0.01(1) for **1** and **2**, respectively, indicating that the correct enantiomorphs have been selected in both structures. Further details of the data determination, crystal data and structure refinement parameters are summarized in Table 1.

3. Results and discussion

A summary of our synthesis was presented in Scheme 1. Metathesis reaction between equimolar amount of $[Et_4N][GaCl_4]$ and Na_2edt in methanol resulted in the formation of the dichloro complex $[Et_4N][Ga(edt)Cl_2]$ (**1**). Treatment of $[Et_4N][GaCl_4]$ with two equivalents of Na_2edt in methanol afforded $[Et_4N][Ga(edt)_2]$ (**2**) in a yield of 87%. The analogous indium complex $[Et_4N][In(edt)_2]$ was previously reported by Kanatzidis and co-workers [4]. Complexes **1** and **2** were stable in both the solid state and solution. Both were soluble in DMF, slightly soluble in THF and MeCN, but sparingly soluble in common solvents. The infrared spectra of both complexes displayed the characteristic ν(C–S) stretching vibration of the coordinated edt^{2-} at 644 and 652 cm^{-1}. The ^1H NMR spectra of **1** and **2** displayed a broad singlet at δ 2.75 and 2.78 ppm, respectively, which are assigned to the protons of the edt^{2-} moiety. The molecular ions corresponding to $[Ga(edt)Cl_2]^-$ and $[Ga(edt)_2]^-$ with the characteristic isotopic distribution patterns can be observed at m/z 233 and 254 in the mass spectra of **1** and **2**, respectively.

The structures of **1** and **2** were confirmed by X-ray diffraction analysis. The crystal structure of the $[Ga(edt)Cl_2]^-$ anion in **1** is shown in Fig. 1 and selected bond lengths and angles are summarized in Table 2. Complex **1** crystallized in monoclinic crystal system with non-centro-symmetric space group $P2_1$. **1** consists of well separated cations and anions. There are two perpendicular arrangements for the molecules in the crystal with slightly different conformations, but no significant differences in bonding parameters between two molecules (A and B) were found. The anion in **1** has a distorted tetrahedral geometry that is similar to those of the dichloro anions in $[N(Ph_2PQ)_2GaCl_2]$ (Q = S, Se) [33] and $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_3GaCl_2][GaCl_4]$ [34]. The chelating edt^{2-} ligand in the five-membered gallacycles adopts approximately planar

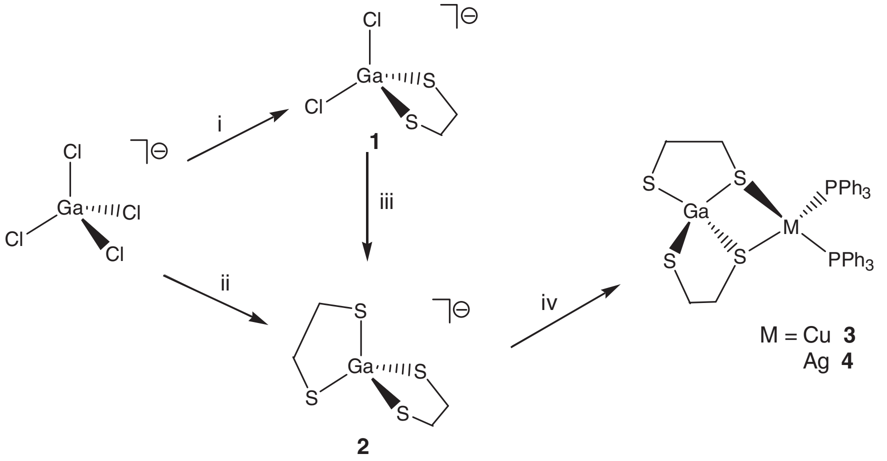
Table 1
Crystal data and structure refinement for complexes $[Et_4N][Ga(edt)Cl_2]$ (**1**), $[Et_4N][Ga(edt)_2]$ (**2**), $[Ga(edt)_2Cu(PPh_3)_2]$ (**3**), and $[Ga(edt)_2Ag(PPh_3)_2]$ (**4**).

Complex	**1**	**2**	**3a**	**3b**	**4**
Formula	$C_{10}H_{24}NCl_2S_2Ga$	$C_{12}H_{28}NS_4Ga$	$C_{40}H_{38}P_2S_4GaCu$	$C_{40}H_{38}P_2S_4GaCu$	$C_{40}H_{38}P_2S_4GaAg$
Formula weight	363.04	384.31	842.14	842.14	886.47
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.3164(3)	8.5777(1)	15.9012(3)	10.5839(1)	10.4472(1)
b (Å)	13.9425(6)	10.4767(2)	16.4144(4)	23.2097(2)	23.3945(2)
c (Å)	14.6567(6)	20.7841(3)	16.7762(3)	15.6176(1)	15.9664(2)
β (°)	92.911(3)		116.563(1)	91.978(1)	91.553(1)
V (Å^3)	1697.27(12)	1867.78(5)	3916.53(14)	3834.16(5)	3900.87(7)
Z	4	4	4	4	4
D_{calc} (g cm^{-3})	1.421	1.367	1.428	1.459	1.509
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
F(0 0 0)	752	808	1728	1728	1800
μ (Mo Kα) mm^{-1}	2.161	1.907	1.554	1.587	1.517
No. reflections measured	17 194	34 161	38 311	37 985	38 675
No. unique reflections	7226	4258	8981	8769	8939
No. observed reflections	5048	3759	6646	6579	7066
No. parameters	197	167	433	433	433
R_{int}	0.0315	0.0271	0.0287	0.0333	0.0274
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0416, 0.0938	0.0289, 0.0692	0.0340, 0.0756	0.0334, 0.0713	0.0293, 0.0674
R_1[a], wR_2[b] (all data)	0.0695, 0.1057	0.0353, 0.0722	0.0554, 0.0837	0.0534, 0.0783	0.0429, 0.0730
Goodness-of-fit (GOF)[c]	1.003	1.054	1.029	1.016	1.015
Flack value	0.00(0)	0.011(10)			
Final difference in peaks (e Å^{-3})	+0.409, −0.254	+0.424, −0.269	+0.675, −0.789	+0.448, −0.240	+0.853, −0.604

[a] $R_1 = \sum || F_o | - | F_c || / \sum | F_o |$.

[b] $wR_2 = \left[\sum w(| F_o^2 | - | F_c^2 |)^2 / \sum w | F_o^2|^2\right]^{1/2}$.

[c] $\mathrm{GoF} = \left[\sum w(| F_o | - | F_c |)^2/(N_{obs} - N_{param})\right]^{1/2}$.



Scheme 1. Reagents and conditions: (i) Na_2edt/MeOH, (ii) $2Na_2edt$/MeOH, (iii) Na_2edt/MeOH, (iv) $M(PPh_3)_2NO_3$ (M = Cu, Ag)/DMF/CH_2Cl_2.

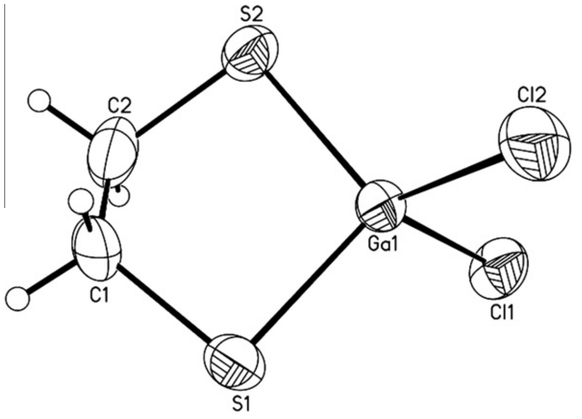


Fig. 1. A view of the $[Ga(edt)Cl_2]^-$ anion in **1**.

Table 2
Selected bond distances (Å) and bond angles (°) for **1**.

Molecule A		Molecule B	
Ga(1)–S(1)	2.2279(14)	Ga(2)–S(3)	2.2209(16)
Ga(1)–S(2)	2.2360(15)	Ga(2)–S(4)	2.2241(16)
Ga(1)–Cl(1)	2.2237(15)	Ga(2)–Cl(3)	2.2185(15)
Ga(1)–Cl(2)	2.1997(16)	Ga(2)–Cl(4)	2.2172(17)
S(1)–Ga(1)–S(2)	99.63(6)	S(3)–Ga(2)–S(4)	100.46(7)
Cl(1)–Ga(1)–S(1)	111.09(6)	Cl(3)–Ga(2)–S(3)	111.17(6)
Cl(1)–Ga(1)–S(2)	115.74(6)	Cl(3)–Ga(2)–S(4)	114.41(7)
Cl(2)–Ga(1)–S(1)	115.51(7)	Cl(4)–Ga(2)–S(3)	115.86(7)
Cl(2)–Ga(1)–S(2)	112.89(7)	Cl(4)–Ga(2)–S(4)	112.21(7)
Cl(1)–Ga(1)–Cl(2)	102.57(7)	Cl(3)–Ga(2)–Cl(4)	103.22(7)

geometry with deviations of 0.17 Å for molecule A and 0.03 Å for molecule B from the least-squares planes. The terminal Ga–Cl bonds in **1** [av. 2.2148(16) Å] are similar to those in $[N(Ph_2PS)_2\ GaCl_2]$

[2.1688(16) Å], $[N(Ph_2PSe)_2GaCl_2]$ [2.1470(15) Å], $[N(Ph_2PS)\{(EtO)_2PO\}GaCl_2]$ [2.1766(6) Å] [33], and $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_3GaCl_2][GaCl_4]$ [2.1853(3) Å] [34]. The crystal structure of $[Ga(edt)_2]^-$ anion in **2** is shown in Fig. 2. The anion in **2** has a highly distorted tetrahedral geometry due to the restricting bite-size of chelating dithiolate, which is similar to that of the anion in $[PPh_4][In(edt)_2]$ [4]. The average Ga–S bond length [2.2612(9) Å] in **2** is in good agreement with those in $[(i\text{-}Pr)_2NH_2][Ga(S\text{-}i\text{-}Pr)_4]$ [2.2678(6) Å] [14], $[i\text{-}Pr_4N][Ga(SEt)_4]$ [2.264(3) Å] [13], and $[Et_4N][Ga(SPh)_4]$ [2.257(3) Å] [13]. The two five-membered chelate rings GaS_2C_2 are non-planar. The average distance between sulfur atoms in different edt^{2-} moieties is ca. 3.8 Å.

Complex **2** was isolated in a high yield and may act as a metalloligand that coordinates with the cationic coinage-metal complexes *via* the sulfur atoms, forming the neutral bimetallic complexes $Ga(edt)_2ML_2$ (M = Cu, Ag; L = phosphine ligands). Under this circumstance, treatment of **2** with $M(PPh_3)_2NO_3$ in DMF/CH_2Cl_2 afforded a homogeneous solution from which colorless crystals of $[Ga(edt)_2M(PPh_3)_2]$ (M = Cu **3**, Ag **4**) were isolated in moderate yields. The singlet at δ −1.94 for **3** and the doublet at δ 5.31 ppm for **4** in the $^{31}P\{^1H\}$ NMR spectra were downfield from that of the free PPh_3 ligand. The doublet in the $^{31}P\{^1H\}$ NMR spectrum of **4** is probably due to the coupling with ^{107}Ag and ^{109}Ag. The FAB^+ mass spectra of **3** and **4** exhibited molecular ions corresponding to M^+, $M^+{-}PPh_3$ and $M^+{-}2PPh_3$ with characteristic isotopic distribution patterns.

The solid-state structures of complexes **3** and **4**, as shown in Figs. 3 and 4, respectively, were determined by X-ray crystallography. The bond lengths and angles of the two complexes were compiled in Table 3 for comparison. The two different shaped crystals of **3** analyzed by single-crystal X-ray diffraction have different unit cells but with the same space group $P2_1/n$. As depicted by the views of Fig. 3b and a, the Cu···Ga distance of 2.9892(4) Å in **3b** is slightly shorter than that of 3.056(1) Å in **3a**. Cu(1) or Ag(1) is bonded to two PPh_3 ligands and two edt^{2-} through their sulfur donor sites, forming a tetrahedral P_2CuS_2 or P_2AgS_2 core. Both tetrahedrally coordinated Ga and Cu(Ag) atoms are bridged by two sulfur atoms of two edt^{2-}, forming a planar four-membered "GaS_2M" (M = Cu, Ag) ring. The average Ga–S–Cu angle in **3** (78.89(2)°) is comparable to that in $[(PPh_3)Cu(\mu\text{-}SC\{O\}Ph\text{-}S)(\mu\text{-}SC\{O\}Ph\text{-}S,O)_2Ga(SC\{O\}Ph)]$ (79.39(6)°) [35], but is smaller than the average In-S-Cu angle in $[(PPh_3)_2Cu(SEt)_2In(SEt)_2]$ (85.58(8)°) [15]. The average Ga–S–Ag angle in **4** (79.54(2)°) is also smaller than the average In–S–Ag angle in $[(PPh_3)_2Ag(SMe)_2In(SMe)_2]$ (84.16(3)°) [21]. The average Cu–S bond length in **3** is 2.4482(6) Å and the average Ag–S bond length in **4** is 2.6802(6) Å, which are comparable to those in related bimetallic complexes such as $[(PPh_3)_2Cu(SEt)_2In(SEt)_2]$ (av. Cu–S = 2.418(2) Å) [15] and $[(PPh_3)_2Ag(SMe)_2In(SMe)_2]$ (av. Ag–S = 2.6797(10) Å) [21].

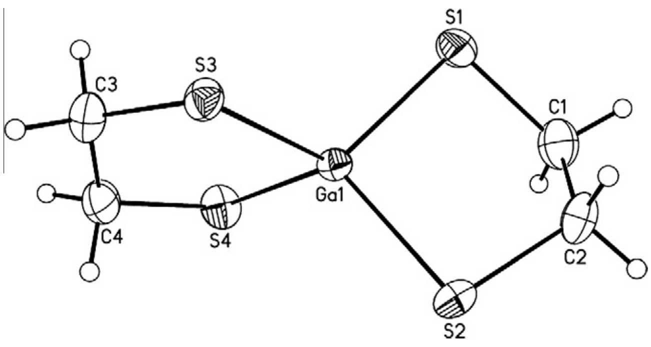


Fig. 2. A view of the $[Ga(edt)_2]^-$ anion in **2**.

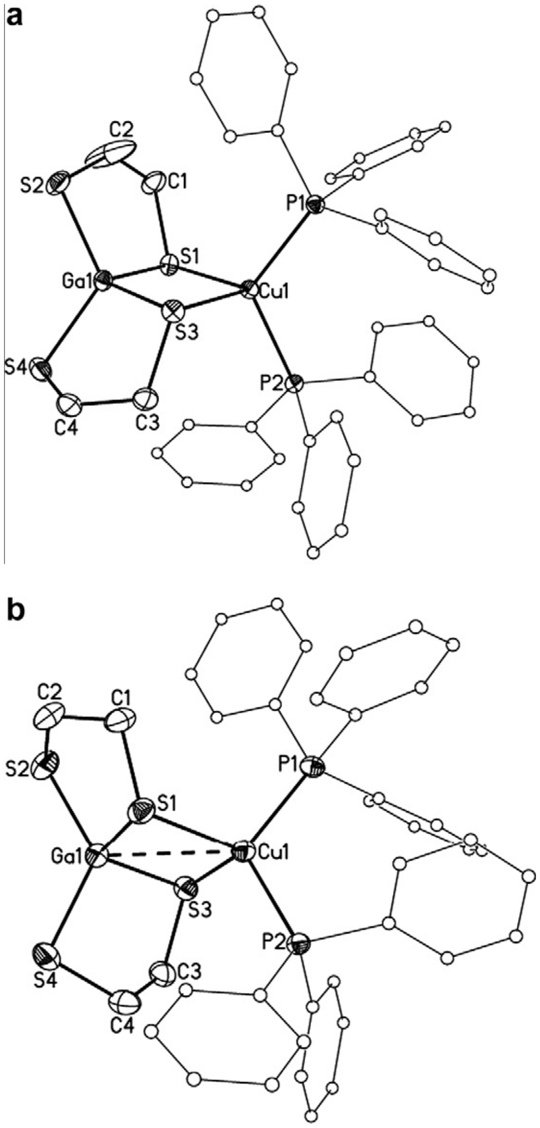


Fig. 3. A perspective view of the structure of $[Ga(edt)_2Cu(PPh_3)_2]$ **3**.

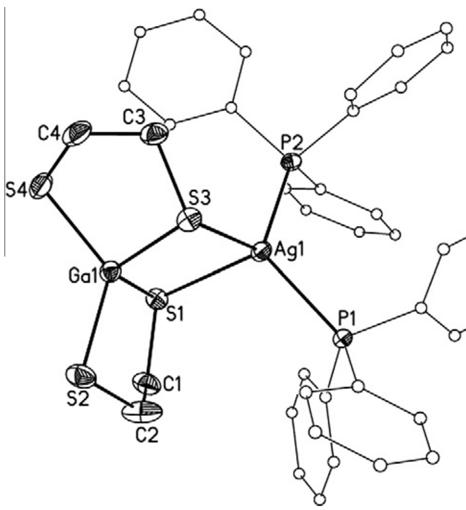


Fig. 4. A perspective view of the structure of $[Ga(edt)_2Ag(PPh_3)_2]$ **4**.

Table 3
Selected bond distances (Å) and bond angles (°) for **2**, **3** and **4**.

	2	**3a** (M = Cu)	**3b** (M = Cu)	**4** (M = Ag)
Ga(1)–S(1)	2.2525(9)	2.3050(6)	2.3235(6)	2.2951(6)
Ga(1)–S(2)	2.2618(8)	2.2227(7)	2.2298(7)	2.2410(7)
Ga(1)–S(3)	2.2711(8)	2.2976(6)	2.2998(6)	2.3175(7)
Ga(1)–S(4)	2.2594(9)	2.2452(7)	2.2344(7)	2.2338(7)
M(1)–S(1)		2.4047(6)	2.4230(6)	2.7204(6)
M(1)–S(3)		2.4885(7)	2.4764(6)	2.6399(6)
M(1)–P(1)		2.2800(6)	2.2944(6)	2.4622(6)
M(1)–P(2)		2.2842(7)	2.2776(6)	2.4818(6)
Ga(1)···M(1)			2.9892(4)	
S(1)–Ga(1)–S(2)	96.52(4)	97.59(3)	97.19(3)	96.56(3)
S(1)–Ga(1)–S(3)	115.93(4)	104.08(2)	106.33(2)	110.70(2)
S(1)–Ga(1)–S(4)	115.66(4)	119.10(3)	115.73(3)	114.10(3)
S(2)–Ga(1)–S(3)	116.49(4)	118.82(3)	116.76(3)	114.02(3)
S(2)–Ga(1)–S(4)	117.23(4)	120.46(3)	123.61(3)	125.11(3)
S(3)–Ga(1)–S(4)	96.44(3)	96.96(3)	97.08(2)	96.82(3)
S(1)–M(1)–S(3)		95.72(2)	98.09(2)	90.11(2)
P(1)–M(1)–S(1)		114.42(2)	113.41(2)	109.37(2)
P(2)–M(1)–S(1)		109.86(2)	113.08(2)	104.53(2)
P(1)–M(1)–S(3)		108.37(2)	105.30(2)	116.99(2)
P(2)–M(1)–S(3)		106.60(2)	109.09(2)	115.10(2)
P(1)–M(1)–P(2)		118.98(2)	115.89(2)	116.30(2)
Ga(1)–S(1)–M(1)		80.88(2)	78.04(2)	78.87(2)
Ga(1)–S(3)–M(1)		79.24(2)	77.39(2)	80.20(2)

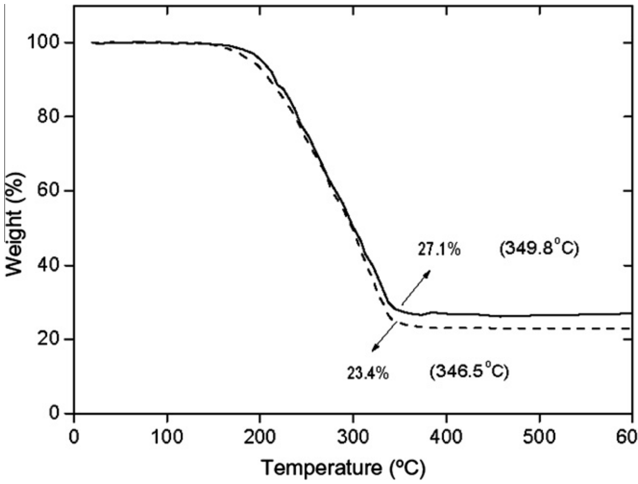


Fig. 5. TGA diagram of complexes [Ga(edt)$_2$Cu(PPh$_3$)$_2$] **3** (dash line) and [Ga(edt)$_2$-Ag(PPh$_3$)$_2$] **4** (solid line).

The potential application of heterobimetallic complexes **3** and **4** as single-source precursors to ternary sulfide materials was investigated by thermogravimetry analysis (TGA). As illustrated in Fig. 5, **3** and **4** gave simple weight-loss decomposition patterns. A single-step weight loss of **3** was observed between 165 and 360 °C, which is attributed to the release of organic ligands with $CuGaS_2$ remaining as a yellow powder (observed 23.2%, calculated 23.4%) [8]. The decomposition temperature of **4** was almost the same as that of **3**. A weight loss of 70.3% (calculated 70.0%) from 180 to 355 °C corresponding to the loss of two PPh_3 and of one dithiolate ligand per formula unit was observed. Further weight loss was observed above 360 °C and the remaining yellow powdery product is again $AgGaS_2$ (observed 27.1%, calculated 27.3%) [36].

In summary, we have successfully synthesized [Et$_4$N][Ga(edt)$_2$] in a relatively high yield which could be used as a metalloligand to coordinate with [M(PPh$_3$)$_2$]$^+$ species, resulting in heterobimetallic complexes [Ga(edt)$_2$M(PPh$_3$)$_2$] (M = Cu, Ag). The potential application of such complexes as single-source precursors for ternary sulfide materials was investigated by thermogravimetry analysis.

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Appendix A. Supplementary material

CCDC 731839, 731840, and 731841 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.044.

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