New Synthetic Routes to Sulphur Bridged Group(III) Halide Compounds

ALAN BOARDMAN, SANDRA E. JEFFS, RONALD W. H. SMALL and IAN J. WORRALL

Department of Chemistry, The University of Lancaster, U.K.

Received December 6, 1984

There has been recent interest in the synthesis of the thio-iodides GaI_2SR and InI_2SR [1]. The reported method involves the reaction of R_2S_2 (R = methyl, phenyl) with $PhMI_2$ (M = In, Ga) or GaI_3. The products are formed in moderate yield in the presence of iodine and the reaction times are fairly long. We have found that compounds of this type (MX_2SR) may be prepared in 100% yield by the reaction of the 'dihalides' M_2X_4 (M = Ga, In; X = Cl, Br, I) with the thiols RSH (R = ethyl, n-butyl, cyclohexyl). The methyl derivatives were prepared by the reaction of M_2X_4 with Me_2S_2 and the crystal structure of GaI_2SMe is reported in this letter.

Experimental

Synthesis of GaX_2SR (X = Cl, Br, I; R = Et, n-Bu, cyclohexyl) $Ga_2X_4 + 2RSH = 2GaX_2SR + H_2$

Excess dry thiol was condensed on to cooled solid dihalide (1 g) *in vacuo*. The dihalide readily dissolved to give an orange solution, which on warming evolved hydrogen and after five minutes a clear solution remained. For the ethane thiol reactions, removal of excess thiol yielded white crystalline products; the remainder afforded colourless oils which crystallised on standing. They analysed as GaX_2SR and were soluble in CS_2.

Synthesis of GaX_2SMe (X = Cl, Br) $Ga_2X_4 + Me_2S_2 = 2GaX_2SMe$

Excess dimethyldisulphide was condensed on to cooled solid Ga_2X_4 (1 g) *in vacuo*. After initial dissolution fine white precipitates resulted and the reactions were complete in about one hour. The excess disulphide was removed and white powders, which analysed as GaX_2SMe, remained. They were insoluble in CS_2.

Synthesis of GaI_2SMe

Excess dimethyldisulphide was condensed on to cooled Ga_2X_4 (1 g) *in vacuo*. Rapid dissolution occurred and on removal of excess disulphide a white powder remained which analysed as GaI_2SMe. It was very soluble in CS_2 and Me_2S_2. Good quality diamond-shaped crystals were obtained from these solvents and used in the crystal structure determination. Conversion to $Ga_4I_4(SCH_3)_4S_2$ occurred on heating Me_2S_2 solutions [2].

Synthesis of InX_2SR (X = Cl, Br, I; R = Me. Et, n-Bu, cyclohexyl)

These were prepared by similar methods to those described above but had longer reaction times (12 h). They had similar solubility properties in CS_2, notably all were soluble apart from $InCl_2SMe$ and $InBr_2SMe$.

The Raman spectra of the solids indicate that the compounds soluble in CS_2 are dimers [3] and this is confirmed for GaI_2SMe by the crystal structure described below.

Results

Crystal Structure of $Ga_2I_4(SCH_3)_2$

The structure was solved by a single crystal X-ray study. Crystal data for $[Ga_2I_4(SCH_3)_2]$: triclinic, space group $P\bar{1}$ $a = 8.667(5)$, $b = 9.447(5)$, $c = 7.743(5)$ Å, $\alpha = 51.2(1)$, $\beta = 128.3(1)$, $\gamma = 125.7(1)°$, $\mu = 11.61$ mm^{-1}. Intensity measurements were made on a Stoe STADI-2 diffractometer using Mo-Kα radiation. 1536 reflections were measured and after elimination of those for which $I < 3\sigma(I)$ there remained 1208 unique reflections which were used in the final refinement. The structure was solved using MULTAN [4] and SHELX 76 [5] and refined anisotropically for Ga, I, S and C; currently the R value is 0.0556. Fractional atomic coordiantes are given in Table I*.

The molecule (Fig. 1) is a bridged dimer and is similar to diphenylethylthiogallane [6] with an unsymmetrical planar four membered ring and *trans* methyl groups.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$).

	x	*y*	*z*
Ga 1	5024(3)	1312(3)	7336(3)
I 1	8038(2)	4166(2)	6552(3)
I 2	2068(2)	0652(2)	3689(2)
S 1	3922(7)	1414(6)	9424(8)
C 1	6076(35)	3385(29)	0413(44)

*Lists of structure factors are available on request from the authors.

0020-1693/85/$3.30

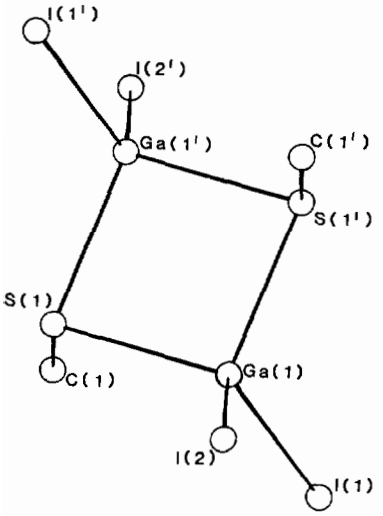

Fig. 1. The molecular structure of $Ga_2I_4(SCH_3)_2$. Bond distances (Å) and angles (°): Ga(1)–I(1) 2.480(2); Ga(1)–I(2) 2.509(2); Ga(1)–S(1) 2.398(5); Ga(1)–S(1') 2.360(5); C(1)–S(1) 1.87(2); I(1)–Ga(1)–I(2) 114.7(1); S(1)–Ga(1)–S(1') 94.5(2); Ga(1)–S(1)–Ga(1') 85.5(1).

We are currently investigating the application of the synthetic method to other elements with bridging potential and have recently prepared $(GaI_2SeMe)_2$.

References

1 G. G. Hoffmann, *Z. Naturforsch., Teil B:, 39,* 352 (1984).
2 A. Boardman, S. E. Jeffs, R. W. H. Small and I. J. Worrall, *Inorg. Chim. Acta, 83,* L39 (1984).
3 A. Boardman, *Ph.D. Thesis,* University of Lancaster, 1984.
4 P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J. P. Declercq, 'MULTAN', A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. University of York, U.K. and Louvain, Belgium, 1977.
5 G. M. Sheldrick, 'SHELX 76', Program for Crystal Structure Determination. University of Cambridge, U.K., 1976.
6 G. G. Hoffmann and C. Burschka, *J. Organomet. Chem., 267,* 229 (1984).