Gallium–Gallium Bonds in Hexahalogenodigallate(II) Ions

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Summary The ions $Ga_2X_6^{2-}$ (X = Cl, Br, or I), which contain a metal–metal bond and probably have ethane-like structures, are formed when gallium dissolves in halogen acids and have been isolated as crystalline Me_4N^+ salts.

MIXED-VALENCE gallium dihalides, $Ga^+GaX_4^-$, are well characterised in the melt,[1] solid state,[2] and in nonaqueous solutions;[3] however, the species responsible for the reducing properties of freshly prepared solutions of gallium have remained in doubt.

Solutions of powdered gallium in aqueous HCl, HBr, or HI, and solutions prepared electrolytically from the metal, show several Raman bands[4] associated with oxidisable complexes. We now find that anodic dissolution of gallium (75 mA for 2 hr.), in an electrolyte of 6M-HCl or -HBr at 0°, followed by addition of Me_4NX solution, precipitates a white solid. This contains only a small amount of Me_4NGaX_4 (i.r. bands at 374 cm.$^{-1}$ for X = Cl and 274 cm.$^{-1}$ for X = Br) which is removed by recrystallisation from nitromethane, yielding colourless crystals stable under normal conditions.

The products analyse for all elements as $(Me_4N)_2Ga_2X_6$ (X = Cl or Br), with the dimeric formulation established by absence of paramagnetism, conductivity as 2 : 1 electrolytes in nitrobenzene, and vibrational spectra (Table). The ν(Ga–X) frequencies of the anion (I) are identified by position, intensity, and shift on change of halogen. An additional very intense polarised Raman band has no counterpart in i.r. spectra and strongly supports the presence of the gallium–gallium bond. The frequencies of this band in (I) are below that of ν(Ge–Ge) (273 cm.$^{-1}$) in the structurally related molecule Ge_2Me_6,[5] and are in the established range[6] of 120—240 cm.$^{-1}$ for metal–metal bonds. The marked shift of the band with change of halogen is not unreasonable allowing for coupling with ν(M–X), as is found[7] for ν(Hg–Hg) in mercurous chloride (169 cm.$^{-1}$), bromide (136 cm.$^{-1}$), and iodide (113 cm.$^{-1}$).

Spectra of hexahalogenodigallate(II) *ions* (*cm.*$^{-1}$)

		ν(Ga–X)		ν(Ga–Ga)
$Ga_2Cl_6^{2-}$	Raman[a]	327 w	375 s	233 vs
	i.r.[b]	302 s	330 vs	
$Ga_2Br_6^{2-}$	Raman[a]	247 w	311 s	162 vs
	i.r.[b]	200 m	242 vs	
$Ga_2I_6^{2-}$	Raman[a]	190 w	286 s	122 vs
	i.r.[b]	153 m	199 vs	

[a] Aqueous acid solutions and ether extracts of $H_2Ga_2X_6$.

[b] Petroleum jelly mulls of $(Me_4N)_2Ga_2X_6$. I.r. and Raman bands of these compounds were also measured in nitromethane solutions.

$$Ga \xrightarrow[\text{anodic oxidation}]{HX(aq)} \underset{(I)}{[X_3Ga\text{–}GaX_3]^{2-}} \xrightarrow{\text{ether extraction}} \underset{(II)}{H_2Ga_2X_6}$$

X = Cl, Br, or I

Ether extraction is an alternative method of isolating the gallium halide complexes from the aqueous phase to retard further oxidation. Analytical ratios X : Ga = 3·0, and Raman and i.r. spectra of extracts in Et_2O or Pr^i_2O show the species to be complex acids (II). Bands due to these compounds diminish over several days and are replaced by bands of known tervalent gallium complexes $HGaX_4$ and solvated GaX_3.[8] Previously noted changes[4] in the Raman spectra of species prior to oxidation can be explained by replacement of halide ligands by solvent molecules.

The formal oxidation state of +2 for gallium in (I) is consistent with coulombic measurements during the anodic dissolution. The mean valence found in this way was 1·8 to 1·9 during preparative runs and approached 2·0 in 1M-HCl or -HBr and at reduced current densities, in agreement with an earlier investigation[9] of anodic dissolution of gallium in HCl. This oxidation state is also encountered in the substance $Na_2[Ga_2Me_6]$ first prepared in 1933.[10] Preparation of hexahalogenodigallate(II) ions without disproportionation, suggests that it may be possible to form the isomeric "gallium dihalide" structures, $X_2Ga{-}GaX_2$, originally assigned[11] to these compounds.

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