

A New Organometallic Compound with a Ga-Mn Bond

Satoru ONAKA, Toschitake IWAMOTO and Yuki Yoshi SASAKI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received February 7, 1968)

In this communication, we report a compound having a Ga-Mn bond, $\text{Cl}_2\text{GaMn}(\text{CO})_5 \cdot \text{C}_4\text{H}_8\text{O}$, which was synthesized through a reaction between GaCl_3 and $\text{NaMn}(\text{CO})_5$ in THF (tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$). This compound has a very intense absorption at 149 cm^{-1} in the far-infrared region, which suggests the presence of direct bonding between gallium and manganese. The method of synthesis is as follows: Equimolar amounts of gallium chloride and sodium pentacarbonylmanganate(-I) were separately dissolved in THF, and heated together at $30\text{--}40^\circ\text{C}$ under dry nitrogen for 2 hr, and excess THF subsequently distilled off under reduced pressure. The residue was recrystallized from a mixture (1 : 5) of THF and *n*-pentane. A yellow crystalline powder was

obtained. Yield 80%. Found: Cl, 17.57; Ga, 17.88; Mn, 12.51%. Calcd for $\text{C}_9\text{H}_8\text{O}_6\text{Cl}_2\text{GaMn}$: Cl, 17.42; Ga, 17.11; Mn, 13.48%. mol wt, Found: 441 (osmometry in methyl ethyl ketone). Calcd: 408.

The compound is hygroscopic, but stable in a dry air. It is soluble in several organic solvents, especially in acetone. In solution it was unstable and decomposed in a day or two. Under conditions of 80°C and 0.1 mmHg, it decomposed without melting or sublimation. Thermogravimetry in a nitrogen atmosphere revealed a weight loss of about 60% in a temperature range of $80\text{--}220^\circ\text{C}$. The decrement is in fairly good agreement with the value of 52% calculated for the loss of one THF and five carbon monoxide molecules. The observed infrared absorption bands are shown in Table 1. In the carbonyl region, no absorption band due to bridging carbonyl was observed. The strong absorption band at 149 cm^{-1} can be assigned to a Ga-Mn stretching vibration from its position and intensity. Considering the analytical results, the molecular weight determined, the thermal decomposition behavior and the infrared spectrum, this compound may have the structure shown in Fig. 1. So far, a compound having a Ga-Mn bond has not been obtained. A detailed analysis of the infrared spectrum in the carbonyl region will be reported in following papers.

TABLE 1. INFRARED ABSORPTION BANDS (cm^{-1})*

$\text{Cl}_2\text{GaMn}(\text{CO})_5 \cdot \text{THF}^{**}$	$\text{Mn}_2(\text{CO})_{10}^{1-3)}$	$\text{Ga}_2\text{Cl}_6^{4)}$
2103 ms	2045 s	
2050 w	2012 s	
2035 m sh	1981 m	
2010 s		
1996 vs		
1991 vs		
193 w	120 m	274 vs
149 vs	113 m	123 s
	106 m	73 m

* Only absorption bands below 300 cm^{-1} are listed in the far-infrared region.

** Carbon tetrachloride solution in the carbonyl region, and the Nujol mull in the far-infrared region.

1) T. H. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 97 (1967).

2) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, **1964**, 5560.

3) P. N. Brier, A. A. Chalmers, J. Lewis and S. B. Wild, *ibid.*, **1967**, 1890.

4) A. Balls, J. A. Downs, N. N. Greenwood and B. P. Straughan, *Trans. Faraday Soc.*, **62**, 521 (1966).

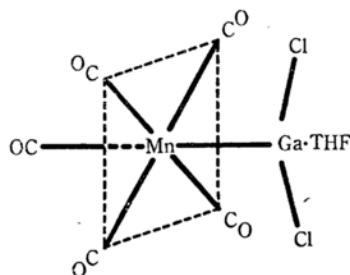


Fig. 1. The estimated structure of $\text{Cl}_2\text{GaMn}(\text{CO})_5 \cdot \text{THF}$.