

Structural Studies on Group IV Metal Acetylacetonates

Two types of six-coordinate complexes of acetylacetonate (Hacac) with Group IV elements have been reported previously. They are $[M(\text{acac})_2\text{Cl}_2]$ (M = titanium, germanium, or tin) and $[M(\text{acac})_3]^+$ (M = titanium, germanium, or silicon)¹. The present communication describes the syntheses of other halides of the type $[M(\text{acac})_2\text{X}_2]$, infra-red studies on all the above complexes, and single crystal X-ray investigations on the three complexes $[M(\text{acac})_2\text{Cl}_2]$ (M = titanium, germanium, or tin).

Complexes of the type $[M(\text{acac})_2\text{X}_2]$ (X = fluorine, chlorine, or bromine) have been prepared by direct reactions of the metal tetrahalide with acetylacetonate in an inert solvent. These complexes are diamagnetic, and behave as monomers and non-electrolytes in nitromethane and nitrobenzene. The absence of uncoordinated carbonyl absorption in the infra-red spectra of the complexes indicates that the acetylacetonate groups are bidentate and therefore the metal atoms are six-coordinate. The essential point of interest with these complexes is whether they adopt the *trans* (A) or *cis* (B) configurations (Fig. 1).

The metal-halogen stretching frequencies $\nu(MX)$ for the complexes are given in Table 1. In the spectra of the fluoro-complexes, only one MF stretching frequency is observed near 600 cm^{-1} , and this may indicate that the fluorine atoms are in the *trans*-octahedral positions, as are the methyl groups of the complex $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ (refs. 2 and 3); however, some mixing of MF with MO stretching vibrations is to be expected. Two MX stretching frequencies are observed in the infra-red spectra of the complexes $M(\text{acac})_2\text{Cl}_2$ and $M(\text{acac})_2\text{Br}_2$, suggesting the *cis*-octahedral arrangement of the ligands in these cases. This result is in agreement with the nuclear magnetic resonance results for $\text{Ti}(\text{acac})_2\text{Cl}_2$ (ref. 5) and for $\text{Sn}(\text{acac})_2\text{X}_2$ (X = chlorine, bromine, or iodine)⁶ in organic solvents. The MX stretching frequencies are in the order $\nu(\text{SnX}) < \nu(\text{GeX}) < \nu(\text{TiX})$ consistent with their expected mass dependence.

The complexes of the types $[M(\text{acac})_3]^+ \text{FeX}_4^-$ (M = titanium or germanium; X = chlorine or bromine) absorb at different frequencies, however, namely ~ 377 and $\sim 290\text{ cm}^{-1}$ for the chlorides and bromides respectively. These bands are clearly attributable to the $\nu_3(t_2)$ modes of the FeX_4^- ions⁷, and hence confirm the presence of these ions in the complexes as originally inferred from electronic spectra and other sources of data^{8,9}.

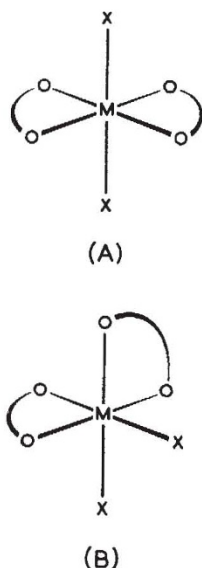


Fig. 1. *Trans* (A) and *cis* (B) forms of $M(\text{acac})_2\text{X}_2$. (Hacac = acetylacetonate, the ring being represented schematically.)

Table 1. METAL-HALOGEN STRETCHING FREQUENCIES IN COMPLEXES OF THE TYPES $M(\text{ACAC})_2\text{X}_2$ AND $[M(\text{ACAC})_3]^+\text{FeX}_4^-$.

Compound	MX stretching frequencies (cm^{-1})	
	$\nu(MX)$	$\nu_3(\text{FeX}_4^-)$
$\text{Ti}(\text{acac})_2\text{F}_2$	629 vs	—
$\text{Ti}(\text{acac})_2\text{Cl}_2$	315 m 246 wm	373 vs 304 vs, br
$[\text{Ti}(\text{acac})_3]^+ \text{FeCl}_4^-$	—	379 vs
$[\text{Ti}(\text{acac})_3]^+ \text{FeBr}_4^-$	—	291 vs, 290 sh
$\text{Ge}(\text{acac})_2\text{Cl}_2$	296 s	347 s
$\text{Ge}(\text{acac})_2\text{Br}_2$	241 wm	283 vs, br
$[\text{Ge}(\text{acac})_3]^+ \text{FeCl}_4^-$	—	376 vs, br
$[\text{Ge}(\text{acac})_3]^+ \text{FeBr}_4^-$	—	293 vs, 283 m
$\text{Sn}(\text{acac})_2\text{F}_2$	—	581 vs
$\text{Sn}(\text{acac})_2\text{Cl}_2$	264 m	334 vs
$\text{Sn}(\text{acac})_2\text{Br}_2$	< 200	260 vs

vs, Very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

X-ray powder photographs show that the complexes $[M(\text{acac})_2\text{Cl}_2]$ (M = titanium, germanium, or tin) are not isomorphous with one another, although there is some similarity between the patterns for the germanium and tin crystals. Single crystal studies have given the following results:

Titanium	$a = 11.315$ $b = 8.074$ $c = 9.040$	$\alpha = 96.4^\circ$ $\beta = 99.25^\circ$ $\gamma = 87.0^\circ$	$D_{\text{calc}} = 1.305\text{ g/c.c.}$ $Z = 2$ Space group = $P1$ or $P\bar{1}$;
Germanium	$a = 7.50$ $b = 11.46$ $c = 8.164$	$\alpha = 84.9^\circ$ $\beta = 87.4^\circ$ $\gamma = 88.16^\circ$	$D_{\text{calc}} = 1.678\text{ g/c.c.}$ $Z = 2$ Space group = $P1$ or $P\bar{1}$;
Tin	$a = 14.00$ $b = 7.82$ $c = 13.84$	$\beta = 107.5^\circ$	$D_{\text{calc}} = 1.785\text{ g/c.c.}$ $Z = 4$ Space group = Cc or $C2/c$

It is of interest that the molecular volume of the titanium compound (405 \AA^3) is much larger than that of the germanium and tin compounds (349 and 361 \AA^3 respectively). Owing to the low symmetries of the unit cells, it is not possible to assign molecular symmetries without full structural determinations. Full three-dimensional data have been collected, and are in the process of refinement.

M. COX

Hatfield College of Science and Technology,
Hatfield, Herts.

R. J. H. CLARK
H. J. MILLEDGE

William Ramsay and Ralph Forster Laboratories,
University College,
London, W.C.1.

Received November 4, 1966.

¹ Cox, M., Lewis, J., and Nyholm, R. S., *J. Chem. Soc.*, 6113 (1964).

² McGrady, M. M., and Tobias, R. S., *J. Amer. Chem. Soc.*, **87**, 1909 (1965).

³ Kamasaki, Y., Tanaka, T., and Okawara, R., *Bull. Chem. Soc. Japan*, **37**, 903 (1964).

⁴ Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Complexes* (Wiley, New York, 1963).

⁵ Bradley, D. C., and Holloway, C. E., *Chem. Commun.*, 284 (1965).

⁶ Smith, J. A. S., and Wilkins, E. J., *Chem. Commun.*, 381 (1965).

⁷ Clark, R. J. H., and Dunn, T. M., *J. Chem. Soc.*, 1198 (1963).

⁸ Fackler, J. P., Woodruff, R. J., and Marini, J. C., *Inorg. Chem.*, **3**, 687 (1964).

⁹ Ong, W. K., and Prince, R. H., *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

Effect of Uranium on Catalysts containing Metals of Group VIII of the Periodic System

DURING the course of investigations of catalysts for use in reactions between steam and hydrocarbons, it was found that by introducing uranium to the catalyst formulation a marked improvement in the reaction parameters was obtained.

The catalysts are prepared by impregnation of an inert support with the metal salts, the support being in the form of pure α -aluminium oxide. A preliminary physico-chemical examination of catalysts containing uranium indicates that uranium is probably acting as an electronic promoter.

The first study carried out was on the effect of uranium on the total specific surface area of the catalysts, the surface area being measured by nitrogen adsorption. It was found that the addition of uranium to the nickel-