

## Infrared Spectroscopic Evidence for Aluminium Dicarbonyl

By A. J. HINCHCLIFFE, J. S. OGDEN,\* and D. D. OSWALD

(*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR*)

**Summary** Co-condensation of aluminium atoms with carbon monoxide in a krypton matrix at 20 K leads to the formation of an aluminium carbonyl; isotope studies using  $C^{18}O$  suggest that the species has the formula  $Al_2(CO)_2$ .

WE have been carrying out a series of matrix isolation studies on metal carbonyls, and report the existence of a binary carbonyl of the pre-transition metal aluminium. It is generally believed that the only metals which form simple binary carbonyls are those in the three main transition series. However, it has recently been shown that other metals such as uranium<sup>1</sup> or tin<sup>2</sup> yield carbonyls when the corresponding metal atoms are condensed at low temperatures in the presence of carbon monoxide. In our experiments, aluminium was heated to *ca.* 1500 K in tantalum or molybdenum sample holders and the vapour co-condensed with a few mol % CO in a krypton matrix at 20 K; the apparatus is described elsewhere.<sup>3</sup>

The i.r. spectra of these deposits show not only the presence of unchanged carbon monoxide, but additional features in the frequency range 1750–2000  $cm^{-1}$  which can only be assigned to aluminium carbonyls. The Figure shows a spectrum (a) obtained when aluminium atoms are co-condensed with a large excess of krypton containing 3% CO. The two bands at 1988 and 1890  $cm^{-1}$  are always present in the same relative intensity, and are assigned to terminal carbonyl vibrations in a molecular aluminium carbonyl, whilst the feature at *ca.* 2140  $cm^{-1}$  is due to unchanged CO. Figure (b) shows the effect of condensing aluminium in a krypton matrix containing  $C^{16}O$  and  $C^{18}O$ . As expected, two bands are now observed arising from unchanged carbon monoxide, but each of the aluminium carbonyl bands now gives rise to a triplet of peaks with an approximate intensity ratio 2:3:1 in each case.

These results may be interpreted if one assumes that the bands arise from the symmetric and anti-symmetric car-

bonyl vibrations in a structure containing two equivalent CO groups. The molecule  $Al(CO)_2$  will give this pattern of bands if the C–Al–C linkage is bent, but it is not possible at

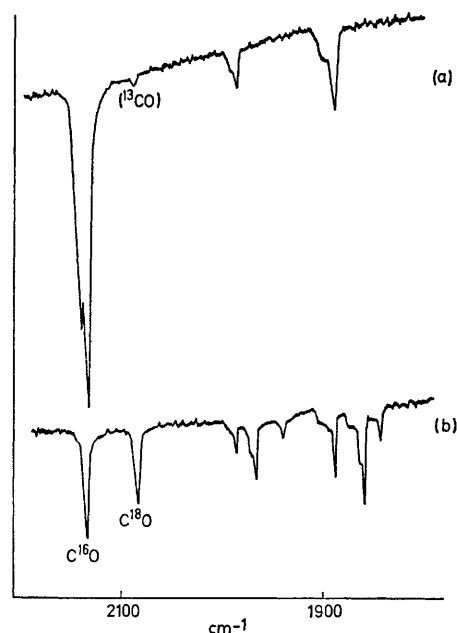


FIGURE. I.r. spectra obtained after co-condensing aluminium atoms in a krypton matrix containing (a) 3%  $C^{16}O$ , and (b) 1.7%  $C^{16}O$  + 1.3%  $C^{18}O$ .

this stage to rule out species such as  $Al_2(CO)_2$  containing more than one atom of aluminium.

This uncertainty, however, does not prevent one from obtaining the two parameters  $K(CO)$  and  $K(CO,CO)$  employed in the Cotton–Kraihanzel force field<sup>4</sup> for a metal dicarbonyl, since in this approximation, the high frequency

CO stretching vibrations are "factored off" from the remaining vibrations of the molecule. The values obtained for  $\text{Al}_x(\text{CO})_2$  are  $K(\text{CO}) = 15.18 \text{ mdyn/\AA}^\dagger$  and  $K(\text{CO}, \text{CO})$

TABLE

*Observed and calculated vibration frequencies ( $\text{cm}^{-1}$ ) for aluminium dicarbonyl in a krypton matrix*

Observed <sup>a</sup>	Calculated <sup>b</sup>	Assignment
1988	1987.5	$\text{Al}_x(\text{C}^{16}\text{O})_2$
1969	1968.9	$\text{Al}_x(\text{C}^{16}\text{O})(\text{C}^{18}\text{O})$
1941	1939.6	$\text{Al}_x(\text{C}^{18}\text{O})_2$
1890	1889.1	$\text{Al}_x(\text{C}^{16}\text{O})_2$
1861	1861.0	$\text{Al}_x(\text{C}^{16}\text{O})(\text{C}^{18}\text{O})$
1844	1843.6	$\text{Al}_x(\text{C}^{18}\text{O})_2$

<sup>a</sup> frequency accuracy  $\pm 1 \text{ cm}^{-1}$ ; <sup>b</sup> assuming  $K(\text{CO}) = 15.18 \text{ mdyn/\AA}$ ,  $K(\text{CO}, \text{CO}) = 0.77 \text{ mdyn/\AA}^\dagger$

$= 0.77 \text{ mdyn/\AA}$ . The Table compares the six frequencies observed in the  $\text{C}^{16}\text{O}/\text{C}^{18}\text{O}$  experiments with those calculated using these two Cotton-Kraihanzel force constants, and the satisfactory agreement suggests that the band assignments given are correct.

The significance of these results lies in the fact that at the present time, the theories<sup>5</sup> put forward to account for the

stability of metal carbonyls involve a mechanism of "back-bonding" from filled or partly filled metal  $d$ -orbitals to the  $\pi^*$  antibonding orbitals on CO. This picture could conceivably still be used to account for the existence of tin carbonyls,<sup>2</sup> but would predict that pre-transition metal carbonyls should be unstable at normal temperatures.

It is interesting to note that previous matrix isolation studies<sup>6,7</sup> on the vaporisation of  $\text{Al}-\text{Al}_2\text{O}_3$  mixtures have yielded i.r. bands in the frequency range  $1750\text{--}2000 \text{ cm}^{-1}$ , notably<sup>7</sup> at  $1995$ ,  $1907.4$ , and  $1867 \text{ cm}^{-1}$ . These bands have previously been assigned as overtone or combination bands of the molecule  $\text{Al}_2\text{O}$ . However, in our experience, traces of carbon monoxide are frequently produced in matrix isolation studies on high temperature systems, and we suggest that these bands are due to aluminium carbonyls. This view is supported by a series of experiments<sup>8</sup> on the  $\text{Al}-\text{Al}_2\text{O}_3$  system in which we have observed a direct correlation between the intensities of these "overtone" features and the proportion of carbon monoxide present in the matrix.

Financial support from the Science Research Council and the Central Electricity Generating Board is gratefully acknowledged.

(Received, 10th January 1972; Com. 033.)

$^\dagger 1 \text{ mydn/\AA} = 100 \text{ N m}^{-1}$ .

<sup>1</sup> J. L. Slater, R. K. Sheline, K. C. Lin, and W. Weltner, jun., *J. Chem. Phys.*, 1971, **55**, 5129.

<sup>2</sup> A. Bos, *Chem. Comm.*, in the press.

<sup>3</sup> J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189.

<sup>4</sup> F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

<sup>5</sup> See, for example, E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1969, **23**, 325.

<sup>6</sup> M. J. Linevsky, D. White, and D. E. Mann, *J. Chem. Phys.*, 1964, **41**, 542.

<sup>7</sup> D. M. Makowiecki, D. A. Lynch, jun., and K. D. Carlson, *J. Phys. Chem.*, 1971, **75**, 1963.

<sup>8</sup> A. J. Hinchcliffe, D.Phil. Thesis, Oxford, 1972.