Infrared Spectroscopic Evidence for Copper and Silver Carbonyls

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Summary Co-condensation of copper or silver atoms with carbon monoxide at 20 K leads to the formation of copper or silver carbonyls; these are detected by i.r. spectroscopy.

PURE carbonyls are known for a wide range of transition metals, but apart from a number of chemisorption studies,[1] there seems to be little evidence for the formation of copper or silver carbonyls. Here we present i.r. evidence for the formation of molecular carbonyls when copper or silver atoms are condensed at low temperatures with a large excess of carbon monoxide.

The technique of condensing metal atoms with a potentially reactive ligand at low temperatures has been used for some time as a preparative method[2] although until very recently[3] there has been no spectroscopic detection of metal carbonyls produced in this way. In this work, metal atoms are produced in a resistively heated Knudsen cell and condensed with a large excess (*ca.* 1000-fold) of carbon monoxide on a caesium iodide window cooled to 20 K. The carbon monoxide behaves both as a reactant and,

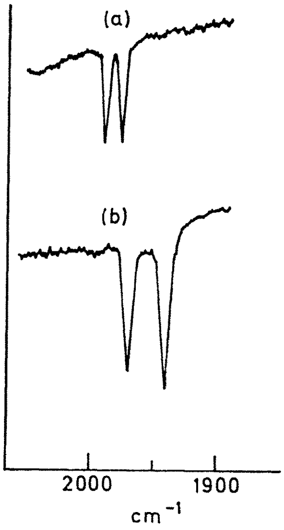

FIGURE. *I.r. spectrum in solid* CO *at* 20 K *of (a) copper carbonyl (b) silver carbonyl.*

when frozen at 20 K, as a solid matrix which can isolate any reaction product. By deposition on an optically transparent window, it is possible to characterise any new species by i.r. spectroscopy, and the experiment thus resembles very closely the more conventional matrix isolation studies which have been carried out on high temperature chemical species.[4]

Figure (a) shows part of the i.r. spectrum obtained when a low flux of copper atoms, produced by heating metallic copper to *ca.* 1150 °C, is condensed with a large excess of carbon monoxide ($C^{16}O$) at 20 K. Two sharp peaks are observed at 1989 and 1975 cm^{-1} in addition to the bands expected for solid carbon monoxide.[5] Figure (b) shows the corresponding spectrum obtained from metallic silver at *ca.* 1000 °C in which a similar doublet is observed at 1968 and 1939 cm^{-1}. These frequencies are accurate to ± 1 cm^{-1}. Grade "X" (B.O.C.) carbon monoxide was used, and the metals had a stated purity of 99·99%. When isotopically enriched carbon monoxide ($C^{18}O$) is used (90 atom %), these bands are all shifted down in frequency by *ca.* 45 cm^{-1} confirming that they arise from carbonyl vibrations. Irradiation of the deposits using either a medium-pressure mercury lamp or, in the case of the Ag–CO system, simply with the i.r. beam, produced a steady decrease in the intensity of the bands. It is well known that metal carbonyls rapidly undergo photolysis when trapped in matrices[6] and the fact that in either system both bands fall in intensity together suggests that they arise from the same species.

These bands are assigned to terminal carbonyl groups by comparison with the spectra of other pure metal carbonyls.[7] The sharpness of the absorptions (*ca.* 5 cm^{-1} wide) indicates that isolated discrete molecules are present, and the similarity between the two spectra suggests that the trapped copper and silver carbonyls may be isostructural.

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