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Preliminary communication

DIRECT SYNTHESIS USING COPPER VAPOUR: A ROUTE TO NOVEL BINARY ETHYLENE COMPLEXES OF ZEROVALENT COPPER, $(C_2H_4)_nCu$ (WHERE $n = 1, 2$ OR 3)

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Summary

The cocondensation reaction of Cu atoms with pure C_2H_4 and C_2H_4/Ar mixtures at 10 K is shown by matrix infrared spectroscopy to lead to the first well-characterized examples of binary zerovalent copper—ethylene complexes, $(C_2H_4)_nCu$ (where $n = 1, 2$ or 3).

Not long after the reported synthesis of $(C_2H_4)_3Ni$ by conventional chemical techniques [1], it was demonstrated that the same compound could be directly obtained by cocondensing Ni atoms with C_2H_4 at —200°C [2]. Since this report, triethylene and tris(bicyclo[2.2.1]heptene) complexes of Ni, Pd, Pt and Co have been obtained by the metal atom route and their thermal stabilities established [2,3]. More recently we have managed to synthesize monoethylenesilver(0) [4] by cocondensing Ag atoms with either pure C_2H_4 or C_2H_4/Ar mixtures at 10 K.

In this brief report we wish to communicate that the corresponding reaction between Cu atoms and ethylene at 10 K leads not only to monoethylenecopper, $(C_2H_4)Cu$, but also to $(C_2H_4)_2Cu$, the first example of a binary diethylene—transition metal complex, and $(C_2H_4)_3Cu$, which can be considered to be the next highest member of the series $(C_2H_4)_3Co$ and $(C_2H_4)_3Ni$. Experimental techniques and apparatus were similar to those described previously [5].

For example, when Cu atoms are cocondensed with $C_2H_4/Ar \cong 1/100$ at 10 K (using very low concentrations of Cu to eliminate complications due to cluster formation, $Cu/Ar \cong 10^{-4}$ [6], aside from infrared absorptions belonging to free ethylene isolated in the Ar matrix (labelled e), new absorptions were observed at 3120, 1475, 1164, 1155, 840 cm^{-1} (Fig. 1A and 1B). On warming the matrix to 35—40 K, this new set of lines gradually diminishes in intensity but maintains the same relative intensity pattern throughout the annealing process, suggesting that they are probably associated with a single species I. At 45 K, the absorptions ascribed to species I have essentially disappeared. Meanwhile, during this warming process, a new set of absorptions is observed to grow in at 1508, 1230, 1216, 862 cm^{-1} (Fig. 1C—1E), these too maintaining the same relative intensities, and are assigned to species II.

In matrices which are more heavily doped with ethylene, $C_2H_4/Ar \cong 1/10$, the group of lines associated with species I and II both appear on deposition (Fig. 2B) with comparable intensities, together with some slight indication of new lines at 1517, 1252 and 810 cm^{-1}, possibly belonging to a third species III. On warming the 1/10 matrices in the range 10—40 K, the lines belonging to species I gradually diminish in intensity (i.e., paralleling the behaviour observed in 1/100 matrices), leaving behind species II as the major absorbing species in the infrared spectrum.

That a third species III exists in the Cu/C_2H_4 system is best seen from experiments in which Cu atoms are cocondensed with pure C_2H_4 at 10 K (Fig. 2A). The infrared spectrum on deposition shows trace amounts of species I and comparable quantities of species II and III, the latter being associated with absorptions at 1517, 1252 and 810 cm^{-1}. On warming these matrices to 40 K one finds that species II and III dominate, and at 70 K only

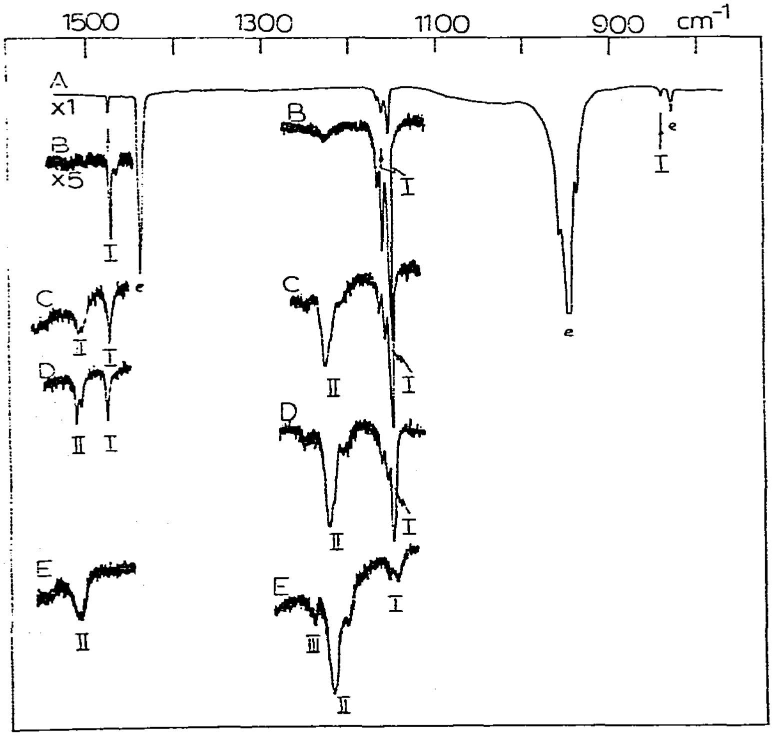

Fig.1. The matrix infrared spectrum observed (A) on depositing Cu atoms with a $C_2H_4/Ar \sim 1/100$ mixture at 10 K, (B) the same as A but with 5 X scale expansion, and (C)—(E) after warm-up to 35, 40, 45 K, respectively (absorptions associated with free C_2H_4 in the matrix are labelled e), showing $(C_2H_4)Cu$ and $(C_2H_4)_2Cu$, labelled I and II, respectively.

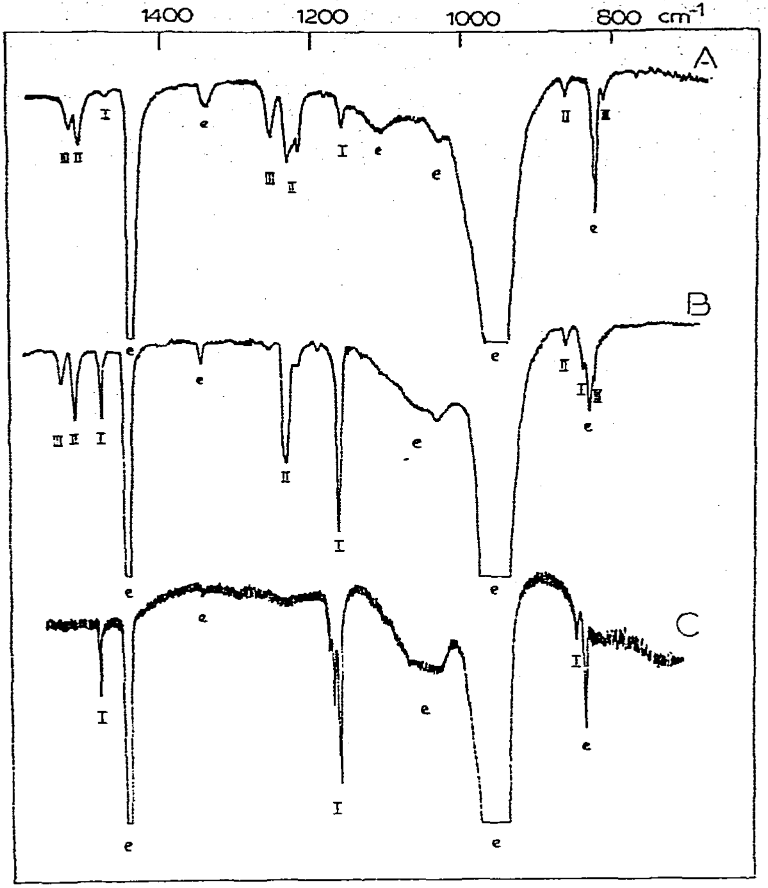

Fig.2. The matrix infrared spectrum observed on depositing Cu atoms with (A) pure C_2H_4, (B) $C_2H_4/Ar \sim 1/10$, and (C) $C_2H_4/Ar \sim 1/100$ at 10 K (absorptions associated with free C_2H_4 in the matrix are labelled e), showing $(C_2H_4)Cu$, $(C_2H_4)_2Cu$ and $(C_2H_4)_3Cu$, labelled I, II and III, respectively.

species III remains (at which temperature ethylene is slowly subliming from the optical window).

Unlike the Ag/C_2H_4 system [4] which yields only a monoethylene complex no matter whether pure C_2H_4 or dilute C_2H_4/Ar matrices are used, the corresponding Cu/C_2H_4 system is found to yield three distinct, mononuclear binary ethylene complexes, $(C_2H_4)_nCu$.

An a priori assignment of these species from the warm-up and ethylene concentration studies is shown below, the monoethylene complex being I = $(C_2H_4)Cu$, II = $(C_2H_4)_2Cu$ and III = $(C_2H_4)_3Cu$, favoured in dilute C_2H_4/Ar matrices (cf. CuCO [7]), whereas the triethylene complex forms readily only in pure C_2H_4 matrices (cf. $Cu(CO)_3$ [7]).

Support for the monoethylene copper formulation I stems from the remarkably close similarity of its infrared spectrum to that of $(C_2H_4)Ag$ [4] (Table 1A).

TABLE 1

INFRARED SPECTRA FOR BINARY TRANSITION METAL ETHYLENE COMPLEXES[a,e]

A	$(C_2H_4)Cu$ (this study)		$(C_2H_4)Ag$ (ref. 4)	Approximate description of mode[b]
	3120		3105	$\nu(CH)$
	1475		1476	$\nu(C=C)$
	1164 1155		1152 1132	$\delta(CH_2)$
	840		794	$\rho_w(CH_2)$
B	$(C_2H_4)_3Co$ [2b]	$(C_2H_4)_3Ni$ [2a,b]	$(C_2H_4)_3Cu$ (this study)	
	—	3065 [d]	3054	$\nu(CH)$
	1499	1510	1517	$\nu(C=C)$
	1225	1244	1252	$\delta(CH_2)$
	—	—	810	$\rho_w(CH_2)$
C	$(C_2H_4Cu$	$(C_2H_4)_2Cu$ (this study)		
	3120	[c]	3054	$\nu(CH)$
	1475	1508	1517	$\nu(C=C)$
	1164 1155	1230 1216	1252	$\delta(CH_2)$
	840	862	810	$\rho_w(CH_2)$

[a] Frequencies in cm^{-1}. [b] ν = stretch, δ = deformation, ρ_w = wag. [c] Overlap with the $\nu(CH)$ stretching modes of free C_2H_4 in the matrix. [d] The $\nu(CH)$ stretching mode was observed in pure $(C_2H_4)_3Ni$ [1]. [e] The infrared frequencies observed for free ethylene isolated in an argon matrix (1/10) occur at 3095s, 3070m, 3012w, 3004w, 2980s, 2042w, 1890w, 1437ms, 1035 w(br), 949vs, 937ms and 824w cm^{-1}. Note that the C=C stretching and CH_2 bending modes of free ethylene occur at 1623 cm^{-1} (Raman) and 1437 cm^{-1} (IR) and shift to 1475—1517 and 1155—1252 cm^{-1}, respectively, upon complexation to zerovalent copper. The shifts for $(C_2H_4)_nCu$ shown above are consistent with increasing C=C and C—H bond strengths with increasing *n*.

The triethylenecopper formulation for species III is reinforced by the close correspondence with the infrared absorptions of the 15- and 16-electron triethylene complexes $(C_2H_4)_3Co$ and $(C_2H_4)_3Ni$, respectively [2], as seen in Table 1B. The 17-electron $(C_2H_4)_3Cu$ complex can be considered to be the next highest member of this series, which is in keeping with the observed trend of increasing C=C bond strength (as measured by $\nu(C=C)$ in Table 1B) on passing from $(C_2H_4)_3Co$ to $(C_2H_4)_3Cu$. This is consistent with the idea of decreasing $M(d\pi)\rightarrow C_2H_4(\pi^\star)$ charge transfer (or back-bonding in the original Dewar—Chatt—Duncanston terminology [8,9]) on moving from the elements on the left of the first transition series to those on the right.

The close resemblance of the infrared spectra of $(C_2H_4)_3M$ (where M = Co, Ni or Cu) would also tend to indicate that the complexes are isostructural, probably with a planar D_{3h} geometry by analogy with the theoretically predicted D_{3h} planar, minimum energy configuration for $(C_2H_4)_3Ni$ [10] and the crystallographically established planar geometry for $(C_2H_4)_2$-$(C_2F_4)Pt$ [11].

From the experimental results, species II in the Cu/C_2H_4 system would appear to be best formulated as $(C_2H_4)_2Cu$, which would represent the first case of a binary diethylene complex (Table 1C). The frequency of its ν(C=C) stretching mode, intermediate between those of $(C_2H_4)Cu$ and $(C_2H_4)_3Cu$, is certainly consistent with this view.

A final point worth mentioning is the observation of increasing C=C bond strength (as measured by the ν(C=C) stretching frequency) on passing from $(C_2H_4)Cu$ to $(C_2H_4)_2Cu$ to $(C_2H_4)_3Cu$ (Table 1C), which would be consistent with the view that $C_2H_4(\pi) \rightarrow Cu(\sigma)$ and $Cu(d\pi) \rightarrow C_2H_4(\pi^\star)$ acceptor—donor interactions [8,9] decrease as the ethylene coordination number increases. An exactly similar trend has been observed in the k(CO) bond stretching force constants of binary carbonyl complexes, $M(CO)_n$ (where M = Ni [12], Pd [13], Pt [14], Co [15]).

Matrix infrared, laser Raman, UV-visible, ESR, and molecular orbital investigations of Group IB binary ethylene complexes are currently underway in our laboratories and full details will be reported soon.

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