

# Formation of Novel Copper Nickel Carbonyls: Reactions of Copper Clusters with Ni(CO)<sub>4</sub> in CO Gas

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**Abstract** The gas-phase syntheses of the novel carbonyl compounds  $[\text{Cu}_3(\text{CO})_n(\text{Ni}(\text{CO})_3)_m]^+$ , ( $n = 0 - 3, m = 1, 2$ ) are reported. The experiments are carried out using a secondary ion tandem mass spectrometer, where  $\text{Cu}_3^+$  is exposed to CO that has been in contact with nickel. The abundance of  $[\text{Cu}_3(\text{CO})_n]^+$  ( $n = 1 - 3$ ) is significantly lower than that of  $[\text{Cu}_3(\text{CO})_n\text{Ni}(\text{CO})_3]^+$  ( $n = 0 - 3$ ). For the larger clusters,  $\text{Cu}_n^+$  ( $n = 4 - 7$ ), the formation of  $[\text{Cu}_n(\text{CO})_m]^+$  dominates, and the formation of Ni-containing compounds is barely observed.

Though the first organometallic compound, the “Zeise’s salt”, was reported as early as 1827, [1] organometallic chemistry is still today a highly innovative and rapidly growing field [2, 3]. Up to now organometallic chemistry has mainly been approached by solution chemistry, reporting on the syntheses and characteristics of new, stable organometallic compounds, as well as their applications in the catalyses of stereoselective and nonstereoselective organic syntheses. Recently, a new branch of organometallic chemistry, gas-phase organometallic chemistry, has been attracting increasing interest. This field deals with the provision of quantitative thermochemical data and the study of unstable, coordinately unsaturated organometallic molecules. An additional aspect of gas-phase organometallic chemistry is the coordination compounds of homogeneous and heterogeneous transition metal clusters.

In this paper, we report observations of  $[\text{Cu}_3(\text{CO})_n(\text{Ni}(\text{CO})_3)_m]^+$  with  $n = 0-3$  and  $m = 0-2$ , formed by the interaction of  $\text{Cu}_3^+$  with CO gas that has been in contact with nickel. Contrary to  $\text{Cu}_3^+$ ,  $\text{Cu}_n^+$  with  $n = 4-7$  are not found to form Ni-containing compounds to any extent. In the following

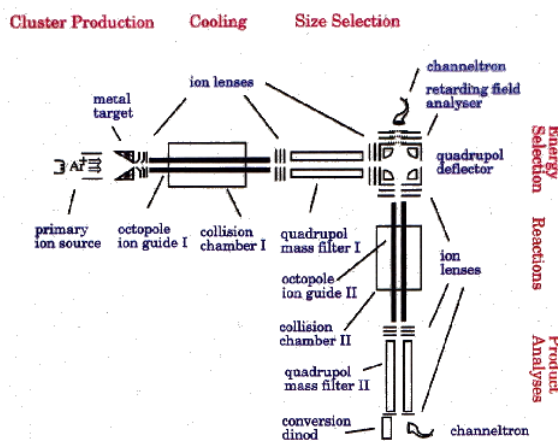


Figure 1. Schematic of the apparatus.

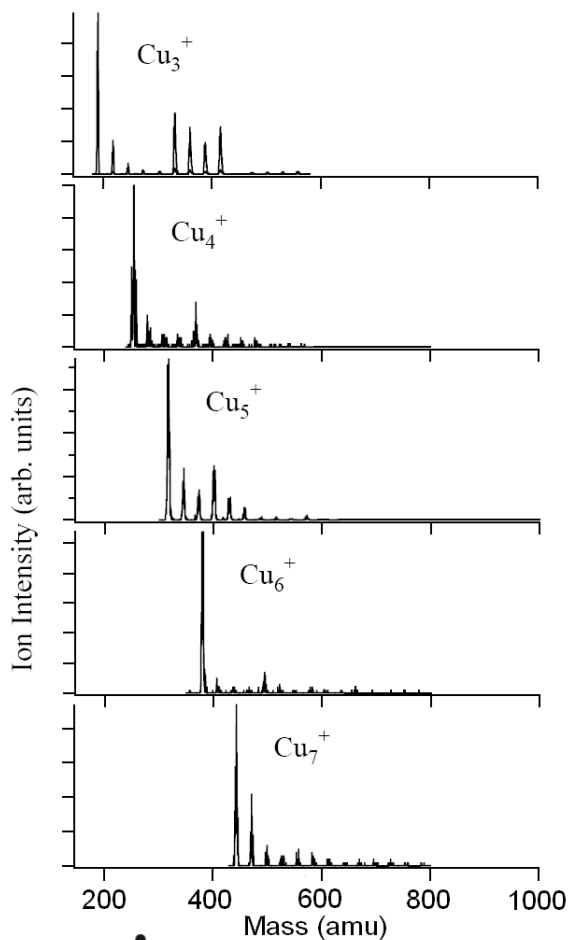
sections, we discuss the formation mechanism of  $[\text{Cu}_3(\text{CO})_n(\text{Ni}(\text{CO})_3)_m]^+$ , with  $n = 0 - 3$  and  $m = 0 - 2$ , as well as the stability of the compounds and their structure.

The experiments were carried out with a secondary ion tandem mass spectrometer. Figure 1 shows a schematic diagram of the apparatus that has been described in detail elsewhere [4], but is briefly

outlined here. Copper clusters are produced by the fast ion bombardment of a conic copper target. The resulting metal cluster ions are extracted with a skimmer lens and focused into an octopole ion guide. The octopole ion guide channels the cluster ions through a He filled cooling chamber where collisional cooling takes place. Upon exit of the cooling chamber, the clusters are focused into a quadrupole mass filter and one cluster size is selected. The size selected cluster beam is then injected into a quadrupole deflector and deflected  $90^\circ$ . Following the deflection, the cluster beam is focused into a second octopole ion guide that guides the size selected reactant cluster ions through a reaction chamber, containing a neutral CO gas at  $2 \times 10^{-3}$  Torr. The reaction products are analyzed by a second quadrupole mass filter and detected with a channeltron in combination with a conversion dynode.

Figure 2 shows the mass spectra of a single isotope composition of compounds from reaction of  $\text{Cu}_3^+$ ,  $\text{Cu}_4^+$ ,  $\text{Cu}_5^+$ ,  $\text{Cu}_6^+$  and  $\text{Cu}_7^+$ , with CO at a pressure of  $2 \times 10^{-3}$  Torr. For  $\text{Cu}_n^+$  with  $n = 4-7$ , the formation of  $\text{Cu}_n(\text{CO})_m^+$  is found to dominate, with the product intensity peaking at  $n = m$  for  $\text{Cu}_4(\text{CO})_m^+$  and at  $m = n - 2$  for  $\text{Cu}_5(\text{CO})_m^+$  and  $\text{Cu}_6(\text{CO})_m^+$ . For  $\text{Cu}_3(\text{CO})_m^+$ , on the other hand, three progressions are clearly observed. The second and third shifted by two and four amu, respectively, with respect to the first progression. This clearly shows that the second and third progression can not be attributed to further CO addition to the trimer. This is surprising, as the second progression is found to exceed the first one in intensity.

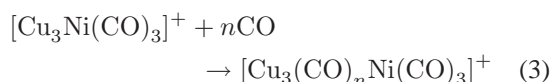
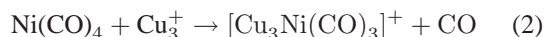
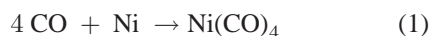
Figure 3 shows a mass spectrum of the products derived from  $^{63}\text{Cu}_3^+$  after interaction with the CO gas, with individual peaks recorded using a high mass resolution. The shift of the second and third progression in the product spectra is found to be concordant with the addition of one and two  $\text{Ni}(\text{CO})_3$  units to  $\text{Cu}_3(\text{CO})_n$  ( $n = 0-3$ ). Furthermore, the isotope ratio of the mass peaks from the second and third progression, marked b and c in Figure 3, unambiguously documents the addition of one and two Ni atoms, respectively. The only rational explanation for the formation of those Ni-containing compounds is that CO reacts with the nickel-containing stainless steel of the gas inlet system, which consists of an on/off-valve in combination with a high precision variable leak valve.



**Figure 2.** Mass spectra of a single isotope composition of compounds derived from reactions of  $\text{Cu}_n^+$  ( $n = 3 - 7, 9$ ) with CO at a pressure of  $2 \times 10^{-3}$  Torr.

To unambiguously identify the origin of the  $\text{Ni}(\text{CO})_3$  units in the product compounds it would be advantageous to introduce  $\text{Ni}(\text{CO})_4$  directly into the reaction chamber. However, as the instrumentation used in this experiment is not available for such an experiment we have to build our case on the hypotheses that  $\text{Ni}(\text{CO})_4$  is being formed through the reaction of CO with nickel from the valves of the inlet system. This is not unreasonable, as CO is known to react with Ni at room temperature under ambient pressure to form  $\text{Ni}(\text{CO})_4$ , and interestingly, the discovery of  $\text{Ni}(\text{CO})_4$  was originally initiated through a chance observation by the ammonia-soda process, where a CO-containing gas was passed through nickel valves [5]. As  $\text{Ni}(\text{CO})_4$

is known to readily undergo ligand exchange, we suggest the following formation mechanism leading to the observation of  $[\text{Cu}_3(\text{CO})_n\text{Ni}(\text{CO})_3]^+$  with  $n = 0 - 3$ :

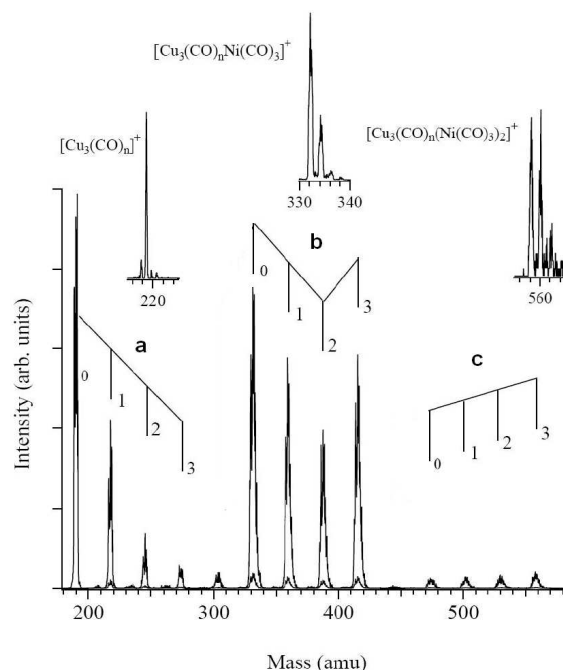


Though we are confident with the assignment of the mass spectra to the compounds  $[\text{Cu}_3(\text{CO})_n(\text{Ni}(\text{CO})_3)_m]^+$  with  $n = 0 - 3$  and  $m = 0 - 2$ , no definite conclusion can be drawn as to whether the copper trimer ion picks up CO

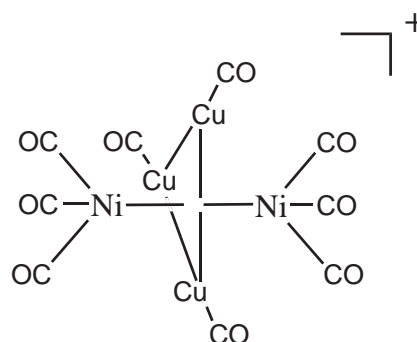
prior to reacting with  $\text{Ni}(\text{CO})_4$  or if the formation of  $\text{Cu}_3\text{Ni}(\text{CO})_3^+$  and  $[\text{Cu}_3(\text{Ni}(\text{CO})_3)_2]^+$  are the initial steps. Nevertheless, the intensity ratios, and the existence of  $[\text{Cu}_3(\text{CO})_n\text{Ni}(\text{CO})_3]^+$  ( $n = 0 - 2$ ) suggest that the formation of  $[\text{Cu}_3\text{Ni}(\text{CO})_3]^+$  is predominantly the first step.

It is interesting to note that, according to the electronic shell model,  $\text{Cu}_3^+$  has a closed shell structure with two electrons in an *s*-shell. Therefore,  $\text{Cu}_3^+$  should be able to act as a "lone pair" donor, and hence overtake the function of CO. The intense signals of  $[\text{Cu}_3(\text{CO})_n\text{Ni}(\text{CO})_3]^+$  (see Figs. 2 and 3) indicate high stability of these species, which is consistent with the 18-electron rule. Under these circumstances, a reasonable structure would contain the equilateral triangular  $\text{Cu}_3^+$  as a central unit, and the Ni atom from  $\text{Ni}(\text{CO})_3$  would interact with  $\text{Cu}_3^+$  as one unit. Furthermore, based on steric considerations, one would expect the tetrahedral symmetry of  $\text{Ni}(\text{CO})_4$  to be distorted, thus narrowing the angle between the remaining three CO's. A possible structure for  $[\text{Cu}_3(\text{CO})_n(\text{Ni}(\text{CO})_3)_m]^+$  with  $n = 0$  and 3 and  $m = 1$  would then possess a  $C_3$  symmetry and a possible structure for  $n = 0$  and 3 and  $m = 2$  would possess a  $D_3$  symmetry as shown in Figure 4 for  $[\text{Cu}_3(\text{CO})_3(\text{Ni}(\text{CO})_3)_2]^+$ .

In light of the large cross section for the formation of these compounds in the gas phase, it would be an interesting task in the vast field of organometallic chemistry to synthesize the corresponding salts, and to unambiguously determine their structure and characterize their properties.



**Figure 3.** Mass spectrum of compounds derived from reactions of  $^{63}\text{Cu}_3^+$  with CO at a pressure of  $2 \times 10^{-3}$  Torr. The insets show the highest intensity peak for each progression recorded with a high mass resolution. The shift of the second and third progression (marked a and b) is found to be concordant with the addition of one and two  $\text{Ni}(\text{CO})_3$  units to  $[\text{Cu}_3(\text{CO})_n]^+$  ( $n = 0 - 3$ ). Further, the isotope ratio of the mass peaks from the second and third progression unambiguously documents the addition of one and two Ni-atoms, respectively.



**Figure 4.** A possible structure for  $[\text{Cu}_3(\text{CO})_3(\text{Ni}(\text{CO})_3)_2]^+$ .

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