Carbonylnickelates 1. Synthesis and Chemical Characterization of the [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$ Dianions

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Among the carbonylnickelates obtained by reduction of tetracarbonylnickel under a variety of conditions, we have successfully isolated and characterized the [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$ dianions. The yellow [Ni$_5$(CO)$_{12}$]$^{2-}$ dianion has been obtained by reduction of tetracarbonylnickel with alkali metals in THF under carbon monoxide and by reaction of [Ni$_6$(CO)$_{12}$]$^{2-}$ with carbon monoxide. The red [Ni$_6$(CO)$_{12}$]$^{2-}$ dianion has been obtained by reduction of tetracarbonylnickel with alkali metals in boiling diethyl ether or in THF under nitrogen, as well as with alkali hydroxides in methanol. The dodeca-carbonylhexanickelate(2-) dianion is shown to be identical with the previously reported [Ni$_4$(CO)$_9$]$^{2-}$ dianion.

Introduction

Around 1960 there was much interest in the reduction of tetracarbonylnickel, and the polynuclear [Ni$_2$(CO)$_6$]$^{2-}$, [Ni$_3$(CO)$_8$]$^{2-}$, [Ni$_4$(CO)$_9$]$^{2-}$, and [Ni$_5$(CO)$_9$]$^{2-}$ dianions were reported together with their mono- and dihydride derivatives.[1]

In 1967, during the characterization of the polynuclear carbonylplatinate dianions [Pt$_3$(CO)$_6$]$_n$$^{2-}$ (n = 1–6),[2–4] we became interested in comparing the chemical and spectroscopic properties of these dianions with those of the carbonyl-nickelates.[5] We hoped also to be able to contribute to the characterization of the structures of the carbonylnickelates, which were unknown at that time.
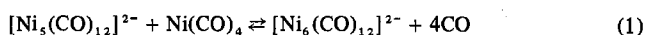
Owing to a number of experimental difficulties and to some unexpected results, we are only now in a position to report our first results in this area.[6]

Results

A. Reduction of Tetracarbonylnickel. The reduction of tetracarbonylnickel to carbonylnickelates has been carried out using a variety of conditions. Small changes in the reaction procedure profoundly affect the results of the reduction.

Tetracarbonylnickel can be reduced, for instance, in THF under nitrogen or carbon monoxide directly with alkali metals (Li, Na, K, and Na–K alloy). However, as found for the direct reduction of Fe(CO)$_5$,[7] at room temperature the reaction is slow and requires several days. It is possible to increase the rate of the reduction in several ways: (a) by increasing the temperature, (b) by use of alkali amalgams,[8] and (c) by addition of anthracene or benzophenone.[9]

At 50–60 °C the reduction of tetracarbonylnickel with alkali metals in THF requires 24–48 h and gives a dark solution, which varies from red to yellow-brown depending on the experimental conditions. The final composition of the reaction mixture does not depend on the particular alkali metal employed but is dependent on the concentration of the unreacted tetracarbonylnickel and on the partial pressure of carbon monoxide. Such behavior is due to the redox condensation[10] equilibrium

$$[Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \rightleftarrows [Ni_6(CO)_{12}]^{2-} + 4CO \qquad (1)$$

which under carbon monoxide (25 °C, 1 atm) is completely shifted to the left.

Although the carbonyl region of the infrared spectrum of these dianions varies with the solvent and cation, the final composition of the reaction mixture can be ascertained by infrared spectroscopy (see Table I).
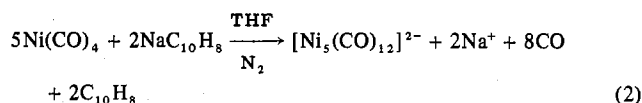
Generally it is convenient to stop the reaction after ca. 90% conversion of Ni(CO)$_4$ in order to avoid formation of nickel metal and other insoluble by-products wich are probably derived from the known[11] reduction and condensation of

carbon monoxide with the alkali metals.

Previously the reduction of the tetracarbonylnickel in THF using sodium, potassium, or magnesium amalgams has been reported to give the red tetranuclear [Ni$_4$(CO)$_9$]$^{2-}$ dianion,[8,12] whereas lithium amalgam, as well as alkali hydroxides in methanol, has been reported to give the red trinuclear [Ni$_3$(CO)$_8$]$^{2-}$ dianion.[8,13]

We find that the use of alkali amalgams, instead of alkali metals, increases the rate of reduction; however, the infrared spectra of the deeply colored solutions obtained by reducing tetracarbonylnickel with lithium or sodium amalgams in THF at room temperature (as well as at 50 °C)[14] show the presence of a variable mixture of [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$. The formation of the former is favored by the CO atmosphere formed when working in small flasks and with a static atmosphere.

At room temperature tetracarbonylnickel is reduced rapidly on addition of a THF solution of sodium–naphthalene or –anthracene. The infrared spectrum of the resulting dark yellow solution initially shows formation of the [Ni$_5$(CO)$_{12}$]$^{2-}$ dianion. Generally the conversion is complete after addition of ca. 0.5 mol of sodium–naphthalene/mol of Ni(CO)$_4$

$$5Ni(CO)_4 + 2NaC_{10}H_8 \xrightarrow[N_2]{THF} [Ni_5(CO)_{12}]^{2-} + 2Na^+ + 8CO$$

$$+ 2C_{10}H_8 \qquad (2)$$

Addition of excess reducing agent results in further reduction to a red-orange anionic species which has not yet been isolated and characterized (ν_{CO} in THF at 1945 (s), 1920 (sh), 1870 (mw), 1790 (w), and 1765 (m) cm^{-1}). If this same reduction is carried out under carbon monoxide or the reaction procedure is reversed and tetracarbonylnickel is added dropwise to a suspension of sodium sand in THF in the presence of naphthalene or anthracene, another uncharacterized anionic species, red-violet (ν_{CO} in THF at 1945 (ms) and 1920 (s) cm^{-1}), results.

Reduction in methanol with alkali hydroxides is reasonably rapid (24–48 h) when using saturated solutions of sodium or potassium hydroxides but, unfortunately, it is not possible to monitor the reaction by infrared spectroscopy because of the high absorption of such solutions. However, direct addition of bis(triphenylphosphine)imminium chloride, PPN$^+$Cl$^-$, to the resulting dark red solutions gives a red-orange precipitate which has an infrared spectrum identical with that expected for a mixture of the [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$ dianions. Longer reaction times seem to favor the concurrent formation of a brown anionic species which has been isolated in a crystalline form as tetramethylammonium salt (ν_{CO} in CH$_3$CN at 1965 (s) and 1800 (s) cm^{-1}).

Reduction with alkali hydroxides is very rapid (2–3 h) in solvents such as dimethyl sulfoxide (Me$_2$SO) or dimethyl-

Table I. Infrared Carbonyl Absorption Frequencies of the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ Dianions

| Anion	Cation	Solvent	ν_{CO}, cm^{-1}
$[Ni_5(CO)_{12}]^{2-}$	Li$^+$	THF	1970 s, 1920 m, 1830 w, 1790 w, 1710 mw
	Na$^+$, K$^+$	THF	1970 s, 1920 m, 1822 w, 1795 w, 1760 w, 1740 mw
	NMe$_4$$^+$	THF	1965 s, 1915 m, 1810 w, sh, 1780 m, b, 1760 sh
	PPN$^+$	THF	1965 s, 1915 m, 1810 w, sh, 1780 ms
	Li$^+$, Na$^+$, K$^+$, NMe$_4$$^+$, PPN$^+$	Me$_2$SO^a	1965 s, 1915 m, 1805 w, sh, 1775 ms
$[Ni_6(CO)_{12}]^{2-}$	Li$^+$	THF	1980 s, 1810 m, 1790 m, 1710 w
	Na$^+$, K$^+$	THF	1980 s, 1815 m, 1795 m, 1745 mw
	PPh$_4$$^+$	THF	1975 s, 1810 m, 1780 ms
	Na$^+$, K$^+$, NMe$_4$$^+$, PPh$_4$$^+$	Me$_2$SO^a	1975 s, 1810 m, 1780 ms

^{a} This same spectrum has been observed also in acetonitrile, DMF, and HMPA.
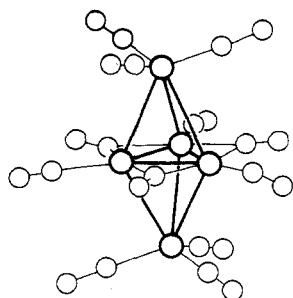
Figure 1. Structure of $[PPN]_2[Ni_5(CO)_{12}]$.

formamide (DMF). The first reduction product detected by ir methods is the uncharacterized red-violet anionic species cited above, which readily reacts with the unreacted Ni(CO)$_4$ to give the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions. However, when most of the Ni(CO)$_4$ has been converted, the hydroxide ions, particularly under carbon monoxide, slowly reduce $[Ni_5(CO)_{12}]^{2-}$ back to the red-violet anion and to another anionic species which has a strong carbonyl absorption in the ir spectrum at 1870 cm^{-1}.

**B. Isolation and Characterization of the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ Dianions.** Despite the fact that the $[Ni_5(CO)_{12}]^{2-}$ dianion can be readily prepared in solution by direct reduction of tetracarbonylnickel under a variety of conditions, the isolation of its salts in a pure crystalline form has been rather vexing because of its lability. Standard isolation procedures, consisting of the precipitation of its salts by metathesis in water, failed owing to a nearly quantitative transformation into $[Ni_6(CO)_{12}]^{2-}$, tetracarbonylnickel, and some hydrogen. In agreement with these qualitative results the stoichiometry of this reaction could be formulated as

$$3[Ni_5(CO)_{12}]^{2-} + 2H_2O \xrightarrow[H_2O]{N_2} 2[Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4$$

$$+ H_2 + 2OH^- \qquad (3)$$
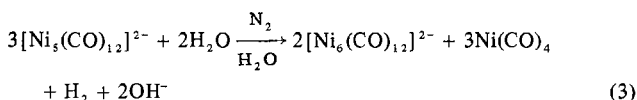
At very high hydroxide concentration, which is the condition during the reduction of Ni(CO)$_4$ with NaOH- or KOH-saturated methanolic solutions, this reaction is probably slowed down considerably while, on the contrary, under neutral conditions it is rapid.

We succeeded in isolating pure crystalline salts of $[Ni_5(CO)_{12}]^{2-}$ by driving equilibrium 1 to the left with carbon monoxide and by subsequent rapid elimination under vacuum of any Ni(CO)$_4$ present; the residual $[Ni_5(CO)_{12}]^{2-}$ salts ([NMe$_4$]$^+$, [NEt$_4$]$^+$, [PPh$_4$]$^+$, [PPN]$^+$) have been directly recrystallized under carbon monoxide using the diffusion technique. The solubility of the $[Ni_5(CO)_{12}]^{2-}$ derivatives with bulky cations follows the usual trend ([NMe$_4$]$^+$ ~ [NEt$_4$]$^+$ > [PPh$_4$]$^+$ ~ [PPN]$^+$); generally these salts are soluble in acetone, acetonitrile, and THF and sparingly soluble or insoluble in 2-propanol or toluene.

The x-ray crystal structure of the anion of [PPN]$_2$[Ni$_5$(CO)$_{12}$] is shown schematically in Figure 1.[15] The
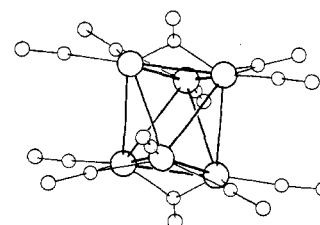
Figure 2. Structure of $[NMe_4]_2[Ni_6(CO)_{12}]$.

five nickel atoms are arranged along an axially distorted trigonal bipyramid analogous to that found in the isoelectronic $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, W) dianions.[16]

Although the $[Ni_6(CO)_{12}]^{2-}$ dianion has been the first and the most frequently isolated carbonylnickelate,[17] owing to equilibrium 1, it is obtained fairly pure by direct reduction of Ni(CO)$_4$ only when the carbon monoxide set free by the reduction is effectively and continuously removed from the reaction atmosphere. A simple method to drive equilibrium 1 to the right is the reduction of tetracarbonylnickel with sodium metal in boiling diethyl ether under nitrogen, which results in the direct separation of Na$_2$[Ni$_6$(CO)$_{12}$]·xEt$_2$O as a crystalline precipitate. Because this reaction is rather slow, it is convenient to add small amounts of a polynuclear hydrocarbon, such as anthracene, in order to dissolve continuously the alkali metal. It is important to stop the reduction when some unreacted tetracarbonylnickel (5–10%) is still present in order to avoid formation of by-products. The solid sodium salt, Na$_2$[Ni$_6$(CO)$_{12}$]·xEt$_2$O, and the unreacted alkali metal are filtered off, and the product is extracted with THF.

More conveniently the potassium salt, K$_2$[Ni$_6$(CO)$_{12}$]·xH$_2$O ($x \approx 4$), can be obtained in about 40–50% yield starting from the mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions which is generally obtained on reduction of tetracarbonylnickel either with alkali metals in THF or with alkali hydroxides in methanol. Thus, evaporation to dryness followed by dissolution in water results in a nearly complete conversion of $[Ni_5(CO)_{12}]^{2-}$ into $[Ni_6(CO)_{12}]^{2-}$, according to reaction 3. The salt K$_2$[Ni$_6$(CO)$_{12}$]·xH$_2$O separates out as a red oil on further addition of solid KBr and crystallizes on removal of the last traces of organic solvents under vacuum.

The potassium salt has been used to prepare other less soluble salts such as the [NMe$_4$]$^+$, [NMe$_3$(CH$_2$Ph)]$^+$, [PPh$_4$]$^+$, and [PPN]$^+$ derivatives. The [PPh$_4$]$^+$ and [PPN]$^+$ salts are sparingly soluble in methanol and the metathesis can be carried out in this solvent, whereas it is necessary to use aqueous solutions in the other cases. All of these salts are soluble in THF, acetone, and acetonitrile, with the exception of the [NMe$_4$]$^+$, [PPh$_4$]$^+$, and [PPN]$^+$ salts which are sparingly soluble in THF. The alkali metal salts are also soluble in alcohols and water; their solubility in water increases in the order Cs$^+$ < K$^+$ < Na$^+$.

The analytical data obtained for these salts (see Experimental Section) have been fully confirmed by an x-ray structural determination of the [NMe$_4$]$^+$ derivative.[17] The
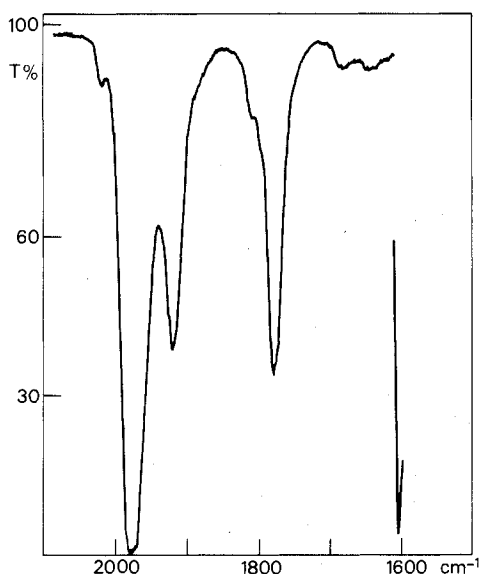
Figure 3. Infrared spectrum of [PPN]$_2$[Ni$_5$(CO)$_{12}$] in THF solution.
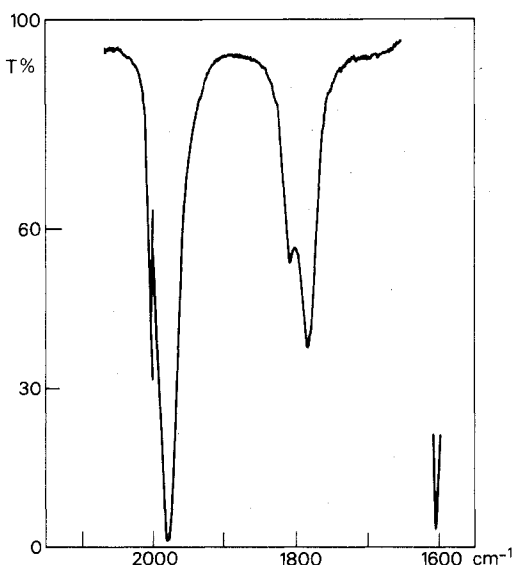
Figure 4. Infrared spectrum of [NEt$_4$]$_2$[Ni$_6$(CO)$_{12}$] in THF solution.

six nickel atoms of the [Ni$_6$(CO)$_{12}$]$^{2-}$ dianion (see Figure 2) are arranged in a trigonal-antiprismatic geometry generated by two staggered M$_3$(CO)$_3$(μ-CO)$_3$ triangular units, which is analogous to the geometry found in the [Ni$_5$(CO)$_{12}$]$^{2-}$ dianion[15] and in the platinum clusters with general formula [Pt$_3$(CO)$_6$]$_n$$^{2-}$.[3]

In agreement with the presence in the crystal structure of terminal and edge-bridging carbonyl groups, the infrared spectra of the [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$ dianions show both types of absorptions (Figures 3 and 4). However the corresponding alkali salts in THF give slightly more complex spectra. This is probably due to formation of ion pairs as shown by the fact that the infrared spectra of the same salts in solvents with higher dielectric constants, such as acetonitrile, Me$_2$SO, DMF, or hexamethylphosphoramide (HMPA), are identical with those of the corresponding tetrasubstituted ammonium or phosphonium derivatives (see Table I).

C. Chemical Behavior. The salts of the [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$ dianions are air sensitive both in solution and in the solid state; air oxidation results in the formation of some tetracarbonylnickel and, therefore, they must be handled with care.

Because of the easy interconversion between [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$, as illustrated by equilibrium 1 and by reaction 3, the chemical behaviors in solution of these two dianions are often interdependent. Thus both compounds react with water under carbon monoxide to give a colorless solution which shows infrared absorptions at 2005 (ms) and 1950 (s) cm^{-1} and a ^{1}H NMR signal at ca. τ 18. This new derivative has not yet been completely characterized owing to its reactivity. However, both the similarity of its ir spectrum to those of the [Ni(CO)$_3$X]$^-$ (X = Cl, Br, I) anions[18] and the position of the ^{1}H NMR signal indicate the related species [Ni(CO)$_3$H]$^-$. Addition of acids, in the attempt to improve the yield, results in complete decomposition.

Contrary to the behavior of [Ni$_5$(CO)$_{12}$]$^{2-}$, the [Ni$_6$(CO)$_{12}$]$^{2-}$ dianion is stable in neutral aqueous solution under nitrogen and can be recovered unchanged after several days. This increasing hydrolytic stability is in keeping with the decreasing negative charge formally present on each nickel atom. However, longer times (about 2 weeks) give a greenish brown anionic derivative (ν_{CO} in THF at 1990 (s), 1830 (s) cm^{-1}; ^{1}H NMR signal in acetone at ca. τ 34; analytical ratios [PPh$_4$]$^+$:Ni:CO:H = 1:3.98:7.08:0.4). This same compound has been more conveniently obtained by hydrolysis of [Ni$_6$(CO)$_{12}$]$^{2-}$ in slightly acidic conditions (pH ∼6). At lower pH (ca. 4) a different silky red-violet species precipitates out from the solution (ν_{CO} in THF at 2020 (s), 1860 (s) cm^{-1}; ^{1}H NMR signal in acetone at ca. τ 28; analytical ratios [PPh$_3$(CH$_2$Ph)]$^+$:Ni:CO:H = 1:5.48:9.97:1). Both of these species have been isolated as pure crystalline salts. Their analytical data do not agree with the formula [Ni$_6$(CO)$_{12}$H]$^-$, and in both cases indicate clusters of higher nuclearity; their x-ray characterization is currently in progress.[19]

[NMe$_4$]$_2$[Ni$_5$(CO)$_{12}$] starts to decompose on heating at about 75 °C, whereas the corresponding [NMe$_4$]$_2$[Ni$_6$(CO)$_{12}$] decomposes to nickel metal over the temperature range 190–230 °C. In both cases thermogravimetric analysis produces no evidence for the formation of intermediate products.

Discussion

We have been unable to reproduce the reported preparations of the red [Ni$_3$(CO)$_8$]$^{2-}$ and [Ni$_4$(CO)$_9$]$^{2-}$ dianions;[8,13] the most reduced species present using the experimental conditions previously reported in the literature is the pentanuclear dianion [Ni$_5$(CO)$_{12}$]$^{2-}$. However, work still in progress indicates that other more reduced anionic species are formed under different conditions: for instance, by reduction of tetracarbonylnickel under carbon monoxide with alkali hydroxides in Me$_2$SO or DMF, with alkali metals in HMPA, or with alkali metals in THF in the presence of anthracene.

The nature of the reported trinuclear species is still obscure. However, there can be no doubt that the reported [Ni$_4$(CO)$_9$]$^{2-}$ dianion has to be reformulated as [Ni$_6$(CO)$_{12}$]$^{2-}$ since their ir spectra in THF solution are coincident.[8] Furthermore, the [Ni$_6$(CO)$_{12}$]$^{2-}$ dianion, as stated in the literature for [Ni$_4$(CO)$_9$]$^{2-}$,[8,12,20,22] is always the most frequently isolated product on reduction of tetracarbonylnickel using a variety of conditions. Even the previously reported preparation of [Ni$_4$(CO)$_9$]$^{2-}$ by disproportionation of tetracarbonylnickel in a mixture of pyridine and ethylenediamine gives, in our hands, a mixture of [Ni$_5$(CO)$_{12}$]$^{2-}$ and [Ni$_6$(CO)$_{12}$]$^{2-}$.

Nevertheless, one puzzling observation remains: the fact that "[Ni$_4$(CO)$_9$]$^{2-}$" has been reported to undergo ready hydrolysis to give the monohydride derivative [Ni$_4$(CO)$_9$H]$^-$, whereas we find that [Ni$_6$(CO)$_{12}$]$^{2-}$ only hydrolyzes in acidic conditions. However, it is worthwhile noting that these hydrolysis products have analytical data not far from the empirical formulas [Ni$_4$(CO)$_9$H]$^-$ and [Ni$_5$(CO)$_9$H]$^-$ which were previously supposed to correspond to the products formed by

hydrolysis of the $[Ni_4(CO)_9]^{2-}$ and $[Ni_5(CO)_9]^{2-}$ dianions.

Related to $[Ni_5(CO)_{12}]^{2-}$ seems to be the pentanuclear brown dianion $[Ni_5(CO)_9]^{2-}$, which has been reported to result on disproportionation of tetracarbonylnickel in the presence of pyridine under vacuum.[20] Unfortunately the lack of any infrared data for $[Ni_5(CO)_9]^{2-}$ prevents a direct comparison between these two pentanuclear species.

It has also been reported that $[Ni_5(CO)_9]^{2-}$ reacts readily with separation of nickel metal according to the reaction[20]

$$[Ni_5(CO)_9]^{2-} \rightarrow [Ni_4(CO)_9]^{2-} + Ni \qquad (4)$$

We do not have evidence for a similar formation of nickel metal from $[Ni_5(CO)_{12}]^{2-}$ and, furthermore, because $[Ni_4(CO)_9]^{2-}$ has to be reformulated as $[Ni_6(CO)_{12}]^{2-}$, reaction 4 would be clearly inconsistent with the formation of nickel metal.

In conclusion, we should stress that our present knowledge of the carbonylnickelates is still unsatisfactory and very unhomogeneous. In only a few cases have complete structural characterizations yet been carried out; more often these formulations are based on analytical data or even only on infrared spectra. At this stage it is therefore difficult to present a comprehensive and reliable picture of the field and to compare all of our findings with what has been reported in the literature.[1] Our present data can be tentatively summarized in the following series of anions:[21] $[Ni(CO)_3H]^-$ (?), colorless, 1950 cm^{-1}; $[Ni_2]^{2-}$ (?), orange, 1870 cm^{-1}; $[Ni_3]^{2-}$ (?), violet, 1920 cm^{-1}; $[Ni_4]^{2-}$ (?), orange, 1945 cm^{-1}; $[Ni_5(CO)_{12}]^{2-}$, yellow, 1970 cm^{-1}; $[Ni_6(CO)_{12}]^{2-}$, red, 1980 cm^{-1}; $[Ni_{13}H]^{3-}$ (?), brown, 1990 cm^{-1}; $[Ni_9(CO)_{18}]^{2-}$, cherry red, 2005 cm^{-1};[6] $[Ni_{13}H_2]^{2-}$ (?), red-violet, 2020 cm^{-1}. Clearly the chemistry of the carbonylnickelates is extremely complicated, and its elucidation would require much future work.

Experimental Section

Owing to the well-known toxicity of $Ni(CO)_4$, all of the operations were carried out under a hood in a well-ventilated room. All reactions were performed under pure and dry nitrogen or carbon monoxide in carefully purified and dried solvents. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using calcium fluoride cells. The analytical data were obtained following the procedure given here. A first sample was decomposed by bubbling a slow stream of chlorine through its stirred suspension in methanol at -80 °C. The resulting clear solution was warmed slowly to room temperature, diluted with water, and boiled a few minutes to eliminate the methanol. Potassium, tetraalkylammonium, and tetraphenylphosphonium ions were then determined as tetraphenylborates. Nickel was determined on the same solution by atomic absorption using a AA-5 Varian Techtron instrument. A second sample was decomposed under vacuum with excess iodine in pyridine at 80 °C. The evolved gas was transferred to a calibrated flask with a Toepler pump and measured. In all cases it was found by gas chromatography to be pure carbon monoxide.

1. Synthesis of $[PPN]_2[Ni_5(CO)_{12}]$ from $[PPN]_2[Ni_6(CO)_{12}]$. $[PPN]_2[Ni_6(CO)_{12}]$ (1.32 g) was suspended in anhydrous THF (20 ml). During stirring under carbon monoxide most of the red precipitate dissolved to give a yellow-brown solution containing $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$. The solution was filtered and evaporated to dryness. The residue was dissolved in THF (15 ml) under carbon monoxide, the mixture was filtered, and precipitation was effected by slow diffusion of toluene (30 ml) saturated with CO. In 2 days the solution separated out well-shaped dark prisms of $[PPN]_2[Ni_5(CO)_{12}]$. The product is soluble in acetone, acetonitrile, and THF, less soluble in methanol, and insoluble in nonpolar solvents. Anal. Calcd: PPN, 63.08; Ni, 17.21; PPN:Ni = 1:2.5. Found: PPN, 63.41; Ni, 17.0; PPN:Ni = 1:2.45.

2. Synthesis of $[NMe_4]_2[Ni_5(CO)_{12}]$ from $[NMe_4]_2[Ni_6(CO)_{12}]$. $[NMe_4]_2[Ni_6(CO)_{12}]$ (2.12 g) was suspended in anhydrous methanol (20 ml). During stirring under carbon monoxide the red solid slowly dissolved to give a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $Ni(CO)_4$, as shown by ir methods. While some red precipitate of $[NMe_4]_2[Ni_6(CO)_{12}]$ was still present, $[NMe_4]_2[Ni_5(CO)_{12}]$ began to precipitate out as

brown microcrystals. In 4 h the transformation was completed. The brown crystals were filtered off under CO, washed with methanol (5 ml), and dried under vacuum; yield 1.37 g. The product is soluble in acetone, acetonitrile, and THF.

3. Synthesis of $[NEt_4]_2[Ni_5(CO)_{12}]$ from $Ni(CO)_4$. $Ni(CO)_4$ (3 ml), sodium metal (2 g), and anhydrous THF (30 ml) were placed in a 100-ml, two-necked, round-bottomed flask equipped with an efficient condenser. During 24–48 h of stirring at 50–60 °C the solution became red-brown, owing to the presence of a mixture of the $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$ dianions. The suspension was filtered, and the resulting solution was stirred under carbon monoxide for 1 h and, then, evaporated to dryness under vacuum. The residue was dissolved in anhydrous methanol under carbon monoxide and solid tetraethylammonium chloride was added in large excess. The resulting brown precipitate was filtered, washed with methanol (5 ml), and dried. The product is soluble in acetone, acetonitrile, and THF. Anal. Calcd: NEt$_4^+$, 29.23; Ni, 33.0; NEt$_4^+$:Ni = 1:2.5. Found: NEt$_4^+$, 29.87; Ni, 32.5; NEt$_4^+$:Ni = 1:2.4.

4. Reduction of $Ni(CO)_4$ with Sodium–Naphthalene. $Ni(CO)_4$ (1.1 ml) in anhydrous THF (30 ml) was reacted dropwise with a 0.615 M THF solution of sodium–naphthalene under nitrogen. On addition of the reducing solution, the reaction mixture turned yellow-brown and the conversion of $Ni(CO)_4$ into $[Ni_5(CO)_{12}]^{2-}$ was complete after addition of 6.8 ml (ca. 0.5 mol of sodium–naphthalene/mol of $Ni(CO)_4$). On further addition of the sodium–naphthalene solution, the formation of a more reduced anionic species was indicated by ir analysis, but attempts to isolate this species in a pure crystalline state have been so far unsuccessful.

5. Synthesis of $[NMe_4]_2[Ni_6(CO)_{12}]$ from $Ni(CO)_4$ and Sodium Metal in Diethyl Ether. $Ni(CO)_4$ (2 ml) was added under nitrogen to a stirred suspension of sodium wires (1.58 g) in refluxing anhydrous diethyl ether (30 ml) in the presence of anthracene (0.3 g). A vigorous reaction took place with carbon monoxide evolution and separation of a red microcrystalline precipitate of $Na_2[Ni_6(CO)_{12}]\cdot xEt_2O$. After 2 h of stirring, the suspension was filtered. The solid residue was washed two times with diethyl ether (20 ml), extracted with THF (50 ml), and evaporated to dryness under vacuum. The residue was dissolved in water (50 ml), the solution was filtered, and precipitation was accomplished by addition of an excess of tetramethylammonium chloride. The resulting red precipitate of $[NMe_4]_2[Ni_6(CO)_{12}]$ was separated out and crystallized from acetone–2-propanol; yield 20–40%. Anal. Calcd: NMe$_4^+$, 17.7; Ni, 42.1; CO, 40.2; NMe$_4^+$:Ni:CO = 1:3:6. Found: NMe$_4^+$, 17.8; Ni, 44.3; CO, 37.0; NMe$_4^+$:Ni:CO = 1:3.1:5.7.

6. Synthesis of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ from $Ni(CO)_4$ and Sodium Metal in THF. $Ni(CO)_4$ (4 ml), sodium metal (2 g), and anhydrous THF (30 ml) were placed in a 100-ml, two-necked, round-bottomed flask equipped with an efficient condenser. After 24–48 h of stirring at 50–60 °C the solution became red-brown and its ir spectrum showed the presence of a mixture of $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_5(CO)_{12}]^{2-}$. The suspension was filtered under nitrogen and the resulting solution was evaporated to dryness under vacuum. The residue was dissolved in water (50 ml) and treated with solid potassium bromide (25 g). The resulting microcrystalline red precipitate was filtered, washed with a saturated aqueous solution of potassium bromide (10 ml), and dried under vacuum. $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ was purified and crystallized by extraction in THF (50 ml) and concentration under vacuum; yield 1.7 g. Anal. Calcd for $x = 4$: K$^+$, 9.32; Ni, 42.01; K$^+$:Ni = 1:3. Found: K$^+$, 9.01; Ni, 41.5; K$^+$:Ni = 1:3.08.

7. Synthesis of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ from $Ni(CO)_4$ and Potassium Hydroxide in Methanol. $Ni(CO)_4$ (5 ml) and KOH (13 g) in methanol (50 ml) were stirred 24 h under nitrogen. The resulting deep red suspension was evaporated under vacuum and the residue was dissolved in water (50 ml). Upon addition of solid potassium bromide (20 g) and further evaporation under vacuum to eliminate the last traces of methanol, red microcrystals of $K_2[Ni_6(CO)_{12}]\cdot xH_2O$ separated out. The product was worked up as in section 6; yield 2.2 g.

The corresponding cesium and tetrasubstituted ammonium, phosphonium, or arsonium salts were directly obtained by one of the methods described above or by double-exchange reactions in water from preformed $K_2[Ni_6(CO)_{12}]\cdot xH_2O$. They have been crystallized from acetone–2-propanol or THF–toluene.

8. Synthesis of $[PPh_4]_2[Ni_6(CO)_{12}]$ from $Ni(CO)_4$ and Sodium Hydroxide in Dimethylformamide. $Ni(CO)_4$ (3 ml) was added under nitrogen to a stirred suspension of sodium hydroxide in pellets (0.7 g) in dimethylformamide (20 ml). After 6 h of stirring the resulting

yellow-brown suspension was quenched with water (50 ml). After standing for 24 h the solution turned red. Addition to the filtered solution of solid tetraphenylphosphonium bromide (1 g) gave a red precipitate. This was filtered, washed with water (30 ml), and dried under vacuum. Crystallization by dissolution in acetone (30 ml) and precipitation with 2-propanol (30 ml) afforded 2.5 g of dark red prisms of [PPh4]2[Ni6(CO)12]. Anal. Calcd: PPh4+, 49.62; Ni, 25.78; CO, 24.59. Found: PPh4+, 49.26; Ni, 25.67; CO, 24.61; PPh4+:Ni:CO = 1:3.01:6.05.

Registry No. [PPN]2[Ni5(CO)12], 57108-14-2; [NMe4]2[Ni5-(CO)12], 60464-16-6; [NEt4]2[Ni5(CO)12], 60464-15-5; K2[Ni6(CO)12], 60464-09-7; [PPh4]2[Ni6(CO)12], 60464-17-7; [PPN]2[Ni6(CO)12], 60464-20-2; [NMe4]2[Ni6(CO)12], 60464-19-9; [NEt4]2[Ni6(CO)12], 60464-18-8; [Ni6(CO)12]2-, 52261-68-4; [Ni5(CO)12]2-, 56938-71-7; Ni(CO)4, 13463-39-3.

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Carbonylnickelates. 2. Synthesis and Chemical Characterization of the Dianion [Ni9(CO)18]2-

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The cherry red [Ni9(CO)18]2- dianion has been obtained both by redox condensation between Ni(CO)4 and [Ni6(CO)12]2- and by oxidation of [Ni6(CO)12]2- with nickel(II) chloride. It has been isolated as [NMe3(CH2Ph)]+, [PPh4]+, [PPh3Me]+, [AsPh4]+, and [PPN]+ salts. The octadecacarbonylenneanickelate(2–) dianion is rapidly degraded by carbon monoxide (25 °C, 1 atm) to [Ni5(CO)12]2- and tetracarbonylnickel.
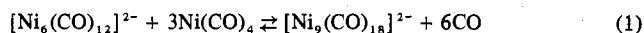
Introduction

We have recently reported the synthesis and the structural characterization of a series of carbonylplatinates having the general formula [Pt3(CO)6]n2- (n = 1–6)[1,2] and of the dianion [Ni6(CO)12]2-.[3] The structure of all of these dianions is based on triangular [M3(CO)3(μ-CO)3] units stacked along the ternary axes. Although the stackings of these triangular units in [Ni6(CO)12]2- and [Pt6(CO)12]2- are different and give rise to approximately trigonal-antiprismatic and trigonal-prismatic geometries, respectively, it seemed possible that an enneanuclear carbonylnickelate dianion analogous to that of platinum might exist.

We now report the synthesis and the chemical characterization of the [Ni9(CO)18]2- dianion.

Results

The [Ni9(CO)18]2- dianion can be prepared in THF solution by a redox condensation reaction[4] between tetracarbonylnickel and the preformed [Ni6(CO)12]2- dianion. The reaction takes place according to the equilibrium

$$[Ni_6(CO)_{12}]^{2-} + 3Ni(CO)_4 \rightleftarrows [Ni_9(CO)_{18}]^{2-} + 6CO \qquad (1)$$

However this type of synthesis presents some difficulties due both to the unfavorable position of equilibrium 1 under carbon monoxide at 25 °C and to the high volatility of the tetracarbonylnickel. In practice it is necessary to carry out the

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reaction under vacuum using an efficient condenser at about −20 °C in order to recycle the solvent and the tetracarbonylnickel and to remove the evolved carbon monoxide. After a few hours at these conditions the transformation into [Ni9(CO)18]2- is practically complete.

The redox condensation equilibrium (1) is also significant during the initial step of the reduction of tetracarbonylnickel with alkali metals in THF,[5] when Ni(CO)4 is still present in large excess. Thus formation of the enneanuclear dianion has been monitored by infrared spectroscopy during the first hours of reaction, although it then disappears probably due to the progressive lowering of the Ni(CO)4 concentration. The decrease in Ni(CO)4 concentration not only has a negative effect on equilibrium 1 but also makes easier further reduction of the [Ni9(CO)18]2- dianion itself.

The synthesis of the [Ni9(CO)18]2- dianion is more conveniently carried out by reaction of the preformed [Ni6-(CO)12]2- dianion with oxidizing agents such as nickel(II) chloride. Progressive addition, from a microburet, of an ethanolic solution of NiCl2 and monitoring the reaction by ir spectroscopy give the stoichiometry

$$3[Ni_6(CO)_{12}]^{2-} + NiCl_2 \xrightarrow{\text{EtOH}} 2[Ni_9(CO)_{18}]^{2-} + Ni + 2Cl \qquad (2)$$
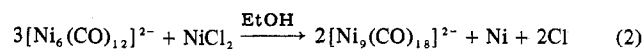
Although the formation of nickel metal has only been verified in a qualitative way, addition of a large excess of nickel(II) chloride results in complete decomposition to nickel metal and tetracarbonylnickel. With proper use of this oxidizing agent the [Ni9(CO)18]2- dianion is obtained in nearly quantitative