Inorg. Chem. 1993, *32,* 5536-5543

Synthesis and Characterization of Novel Types of Adducts of Nickel Carbonyl Clusters with Indium Halides: X-ray Structures of $[\mathrm{NEt_4}]_3[\mathrm{Ni_6}(\mu_3\text{-}\mathrm{InBr_3})(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_5})(\mathrm{CO})_{11}]\cdot\mathrm{Me_2CO}$, $[\mathrm{NEt_4}]_4[\mathrm{Ni_6}(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_5})_2(\mathrm{CO})_{10}]\cdot\mathrm{Me_2CO}$, and $[\mathrm{NEt_4}]_4[\mathrm{Ni_{12}}(\mu_6\text{-}\mathrm{In})(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_4OH})(\mathrm{CO})_{22}]$

Francesco Demartin,[†] **Maria Carmela Iapalucci,**[‡] **and Giuliano Longoni**[*,‡]

Istituto di Chimica Strutturistica Inorganica and Centro del CNR, via G. Venezian 21,
20133 Milano, Italy, and Dipartimento di Chimica Fisica ed Inorganica, viale del Risorgimento 4,
40136 Bologna, Italy

Received April 27, 1993[●]

The reaction in tetrahydrofuran of $\mathrm{InX_3}$ (X = Cl, Br) with $[\mathrm{Ni_6(CO)_{12}}]^{2-}$ up to a 2:1 molar ratio gives rise to several new carbonyl species, which probably consist of adducts of the $\mathrm{InX_3}$ Lewis acid with the $[\mathrm{Ni_6(CO)_{12}}]^{2-}$ Lewis base. IR monitoring of the reaction allows one to distinguish the formation of at least three different compounds, which are respectively obtained with $\mathrm{InX_3}/[\mathrm{Ni_6(CO)_{12}}]^{2-}$ molar ratios of 0.5, 1.0, and 2.0. These suggested adducts could not be isolated and characterized owing to their lability in the miscellaneous organic solvents. However, while for X = Cl the main decomposition products were the parent $[\mathrm{Ni_6(CO)_{12}}]^{2-}$ dianion and $\mathrm{Ni(CO)_4}$, the so far characterized transformation products for X = Br consist of $[\mathrm{NEt_4}]_3[\mathrm{Ni_6}(\mu_3\text{-}\mathrm{InBr_3})(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_5})(\mathrm{CO})_{11}]$, $[\mathrm{NEt_4}]_3[\mathbf{1}]$, and $[\mathrm{NEt_4}]_4[\mathrm{Ni_{12}}(\mu_6\text{-}\mathrm{In})(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_4OH})(\mathrm{CO})_{22}]$, $[\mathrm{NEt_4}]_4[\mathbf{3}]$, salts. The former has been obtained in good yields (70–80% based on indium) from the suggested 2:1 $\mathrm{InBr_3}$:$[\mathrm{Ni_6(CO)_{12}}]^{2-}$ adduct, whereas the latter resulted in low yields (10–20% based on indium) from the disproportionation of the corresponding 1:2 adduct during its working up. A third compound, namely $[\mathrm{NEt_4}]_4[\mathrm{Ni_6}(\eta^2\text{-}\mu_6\text{-}\mathrm{In_2Br_5})_2(\mathrm{CO})_{10}]$, $[\mathrm{NEt_4}]_4[\mathbf{2}]$, has been isolated from the reaction of $[\mathbf{1}]^{3-}$ with $[\mathrm{Ni_5(CO)_{12}}]^{2-}$. All the above compounds have been characterized by elemental analyses and single-crystal X-ray diffraction studies. $[\mathrm{NEt_4}]_3[\mathbf{1}]\cdot\mathrm{Me_2CO}$ is orthorhombic, space group $Pna2_1$, with a = 30.196(8) Å, b = 13.469(7) Å, and c = 16.102(5) Å, $[\mathrm{NEt_4}]_4[\mathbf{2}]\cdot\mathrm{Me_2CO}$ is triclinic, space group $P\bar{1}$, with a = 13.230(11) Å, b = 13.198(7) Å, c = 26.519(6) Å, α = 75.44(3)°, β = 88.69(4)°, and γ = 59.80(5)°, and $[\mathrm{NEt_4}]_4[\mathbf{3}]$ is monoclinic, space group $P2_1/c$, with a = 14.896(2) Å, b = 42.194(8) Å, c = 14.075(3) Å, and β = 110.32°. The $[\mathbf{1}]^{3-}$ trianion displays an octahedral $\mathrm{Ni_6}$ core capped on two adjacent faces by an $\mathrm{In_2Br_5}$ moiety and on a third face, opposite to one of the above, by an $\mathrm{InBr_3}$ molecule. In the related $[\mathbf{2}]^{4-}$ tetraanion there are present two $\mathrm{In_2Br_5}$ moieties capping two opposite pairs of adjacent triangular faces of the $\mathrm{Ni_6}$ octahedron. In both anions, the remaining triangular faces of the octahedron are capped respectively by five and four face-bridging carbonyl groups, whereas each nickel atom binds a terminal carbonyl ligand. The structure of the $[\mathbf{3}]^{4-}$ tetraanion derives from two distinct $\mathrm{Ni_6(CO)_6}(\mu_2\text{-}\mathrm{CO})_5$ moieties sandwiching a unique bare indium atom and bridged by an $\mathrm{In_2Br_4}(\mu_2\text{-}\mathrm{OH})$ moiety. The two $\mathrm{Ni_6(CO)_6}(\mu_2\text{-}\mathrm{CO})_5$ fragments display different geometries. Thus, in one fragment the basic structure of the $[\mathrm{Ni_6(CO)_{12}}]^{2-}$ dianion is retained even though an edge-bridging carbonyl group is replaced by a face-bridging indium atom. In contrast, the second fragment displays a fairly distorted metal framework which can be described as a square pyramid capped on a triangular face by the sixth Ni atom.

Introduction

Several adducts of the transition metal carbonyl clusters with Lewis acids have been reported.[1] The known adducts, however, generally involve Lewis acids such as $\mathrm{H^+}$, $\mathrm{R^+}$, and $\mathrm{AlX_3}$ (X = H, Cl, Br), which may be classified as hard, interacting with an oxygen atom of a bridging carbonyl group, which may be likewise considered as a relatively hard base. In several cases, the resulting dual coordination of carbon monoxide turned out to correspond to an effective activation of the C–O bond preluding to CO splitting and has been exploited for the synthesis of several carbide and ketenylidene clusters,[2-7] as well as for the stoichiometric CO reduction to organic products.[8,9]

To our knowledge, much less work has been addressed to the study of the possible reactions of softer Lewis acids which may be anticipated to preferentially interact with the softer part of a metal carbonyl cluster, that is the metal backbone. Such an interaction appeared of some potential interest, for instance for developing hopefully a new redox condensation method based on the more or less transient presence in solution of such an adduct or in the designed synthesis of intercalated oligomers such as $\{\mathrm{Ag[Rh_6C(CO)_{15}]}\}_n{}^{n-}$.[10] Therefore, we have undertaken an investigation of the reactivity of the $[\mathrm{Ni_3(CO)_6}]_n{}^{2-}$ (n = 2, 3)[11-15] carbonyl clusters with indium trihalides. The compounds so far

---

[*] To whom correspondence should be addressed.

[†] Istituto di Chimica Strutturistica Inorganica and Centro del CNR.

[‡] Dipartimento di Chimica Fisica ed Inorganica.

[●] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

(1) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984,** *23,* 219 and references therein.

(2) Kolis, J. W.; Holt, E. M.; Drezdon, M. A.; Whitmire, K. H.; Shriver, D. F. J. *Am. Chem. Soc.,* **1982,** *104,* 6134.

(3) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983,** *105,* 7307.

(4) Longoni, G.; Ceriotti, A.; Della Pergola, R.; Manassero, M.; Perego, M.; Piro, G.; Sansoni, M. *Phil. Trans. R. Soc. London,* **1982,** *A308,* 47.

(5) Ceriotti, A.; Chini, P.; Longoni, G.; Piro, G. *Gazz. Chim. Ital.* **1982,** *112,* 353.

(6) Sailor, M. J.; Shriver, D. F. *Organometallics* **1985,** *4,* 1476.

(7) Went, M. J.; Sailor, M. J.; Bogdan, P. L.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987,** *109,* 6023.

(8) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981,** *213,* 125.

(9) Drezdon, M. A.; Shriver, D. F. *J. Mol. Catal.* **1983,** *21,* 81.

(10) Heaton, B. T.; Strona, L.; Martinengo, S.; Strumolo, D.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* 1983, 2175.

(11) Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974,** *96,* 2616.

(12) Longoni, G.; Chini, P.; Cavalieri, A. *Inorg. Chem.* **1976,** *15,* 3025.

(13) Ceriotti, A.; Longoni, G.; Marchionna, M. *Inorg. Synth.* **1989,** *26,* 316.

(14) Longoni, G.; Chini, P. *Inorg. Chem.* **1976,** *15,* 3029.

(15) Nagaki, D. A.; Lower, L. D.; Longoni, G.; Chini, P.; Dahl, L. F. *Organometallics* **1986,** *5,* 1764.

0020-1669/93/1332-5536$04.00/0

Table I. Infrared Spectra and Identification Numbers of the Indium Halide Adducts of $[Ni_6(CO)_{12}]^{2-}$

compd	no.	ν_{CO} (cm^{-1})
$[Ni_6(\mu_3\text{-}InBr_3)(\eta^2\text{-}\mu_6\text{-}In_2Br_5)(CO)_{11}]^{3-}$	$[\mathbf{1}]^{3-}$	2050 s, 1830 w, sh, 1810 m^a 2047 s, 1825 w, sh, 1813 m^b
$[Ni_6(\mu_3\text{-}InCl_3)(\eta^2\text{-}\mu_6\text{-}In_2Cl_5)(CO)_{11}]^{3-}$	$[\mathbf{1'}]^{3-}$	2051 s, 1832 w, sh, 1814 m^b
$[Ni_6(\eta^2\text{-}\mu_6\text{-}In_2Br_5)_2(CO)_{10}]^{4-}$	$[\mathbf{2}]^{4-}$	2025 mw, 1976 s, 1784 m^a
$[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Br_4OH)(CO)_{22}]^{4-}$	$[\mathbf{3}]^{4-}$	2017 s, 1830 m^c

^{a} Acetonitrile. ^{b} Acetone. ^{c} THF.

isolated and characterized with their identification numbers adopted in the text and their infrared behavior are reported in Table I.

Previously, only the reactions of indium halides with simpler carbonyl metalates had been investigated in some detail.[16,17]

Results and Discussion

1. Synthesis and Spectroscopic Characterization of $[\mathbf{1}]^{3-}$, $[\mathbf{2}]^{4-}$, and $[\mathbf{3}]^{4-}$. The addition of InX_3 (X = Cl, Br) to a tetrahydrofuran (THF) solution of $[NEt_4]_2[Ni_6(CO)_{12}]$ results in the darkening of the originally red solution and in a progressive shift to higher wavenumbers of the infrared absorptions of both the terminal and bridging carbonyl groups up to 2050 and 1860 cm^{-1}, respectively. IR monitoring of the $[Ni_6(CO)_{12}]^{2-}$ solution during the progressive addition of InX_3 allows one to detect at least three distinct steps, which are respectively obtained after addition of *ca.* 0.5, 1.0, and 2.0 mol of InX_3/1 mol of $[Ni_6(CO)_{12}]^{2-}$. The experimental values of the $InX_3/[Ni_6(CO)_{12})]^{2-}$ molar ratios, which are necessary in order to selectively obtain each step, are suggestive of the progressive formation in solution of adducts, and the above species will be tentatively referred to as such in the following text. This suggestion is in keeping with the complete absence in the IR spectra of any other detectable product, suggesting the occurrence of redox reactions. Unfortunately, so far all the attempts to isolate and/or better characterize these adducts have been hampered by their instability. All of them undergo further chemical transformations on standing in most organic solvents.

For instance, on standing overnight in THF solution the presumed $[Ni_6(\mu_3\text{-}InX_3)_2(CO)_{12}]^{2-}$ 2:1 adduct separates out variable amounts of $[NEt_4]_3[\mathbf{1}]$ and $[NEt_4]_3[\mathbf{1'}]$ as orange precipitates. The decomposition of the above adduct is faster and more effective in methanol. For instance, yields of *ca.* 50% (based on indium) in $[NEt_4]_3[\mathbf{1}]$ have been obtained on evaporating under vacuum the dark red THF solution of the 2:1 adduct and by suspending the residue in methanol, as a result of reactions 1 and 2. In keeping with reaction 2, infrared carbonyl absorptions attributable to $Ni(CO)_4$ and $[Ni(CO)_3Br]^-$ were detected in solution. On an increase to 1:3 of the molar ratio between the reagents, the yield of $[NEt_4]_3[\mathbf{1}]$ increases up to ca. 80%. $[NEt_4]_3[\mathbf{1'}]$ has been similarly obtained in ca. 30% yield. This notable yield decrease on changing the halide substituent of indium from bromide to chloride is in keeping with the stability of the resulting $[\mathbf{1}]^{3-}$ and $[\mathbf{1'}]^{3-}$ trianions. Thus, the orange $[\mathbf{1}]^{3-}$ trianion is stable in most organic solvents and has been successfully crystallized as the $[NEt_4]^+$ salt both from acetone and acetonitrile by layering isopropyl alcohol and diisopropyl ether, respectively. Furthermore, it lacks reactivity with several reagents including carbon monoxide at atmospheric pressure and halides, as well as stoichiometric amounts of protic acids such as HX and H_2SO_4 or oxidizing agents such as Ag^+, $Fe(\eta^5\text{-}C_5H_5)_2^+$, and iodine. In contrast, the corresponding $[\mathbf{1'}]^{3-}$ trianion is much less stable and decomposes in a few hours on standing both in acetone or acetonitrile solution.

$$[Ni_6(CO)_{12}]^{2-} + 2InBr_3 \rightleftharpoons [Ni_6(\mu_3\text{-}InBr_3)_2(CO)_{12}]^{2-} \quad (1)$$

$$3[Ni_6(\mu_3\text{-}InBr_3)_2(CO)_{12}]^{2-} + (4CO) \xrightarrow{MeOH} 2[\mathbf{1}]^{3-} + 2[Ni(CO)_3Br]^- + 3Ni(CO)_4 + Ni^{2+} \quad (2)$$

Also all attempts to isolate the suggested 1:2 $InBr_3$:$[Ni_6(CO)_{12})]^{2-}$ adduct, which shows infrared absorptions in THF at 2010 and 1820 cm^{-1}, have so far been fruitless due to its ready transformation into other products. For instance, after precipitation from methanol solution by addition of $[NEt_4]Br$ and water, partial extraction of the resulting red-brown solid material with THF and layering of *n*-hexane affords dark red crystals of $[NEt_4]_4[\mathbf{3}]$ in low yield. $[\mathbf{3}]^{4-}$ has been characterized by combined X-ray and spectroscopic studies. X-ray studies ascertained the presence of an oxygen atom bridging the two In atoms of an $\eta^2\text{-}\mu_6$-coordinated $In_2Br_4(\mu_2\text{-}X)$ moiety. However, EPR investigations of the above crystalline sample failed to show the presence of any signal due to an unpaired electron, both in the solid state and in solution; therefore, an odd-electron $[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Br_4O)(CO)_{22}]^{4-}$ formulation is ruled out. In contrast, an IR spectrum recorded on a powdered crystalline sample showed the presence of a weak and sharp absorption in the region of the OH stretching at 3582 cm^{-1}, consistent with the given formulation.

So far all attempts to isolate a corresponding $[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Cl_4OH)(CO)_{22}]^{4-}$ homologue have been unsuccessful, probably because of different decomposition pathways of the parent 1:2 adduct. Thus, this adduct slowly decomposes on standing in THF or acetone and readily in methanol and water. $Ni(CO)_4$, $[Ni(CO)_3Cl]^-$, the parent $[Ni_6(CO)_{12}]^{2-}$, and $[H_2Ni_{12}(CO)_{21}]^{2-}$ [18,19] have been identified among the decomposition products. It seems conceivable that the above differences in the chemical behavior of the InX_3 adducts with $[Ni_6(CO)_{12}]^{2-}$ could be due to a slight but significant increase in the acceptor strength and the decrease in the In–X bond strength on going from $InCl_3$ to $InBr_3$.

At difference with the orange $[\mathbf{1}]^{3-}$ trianion, the red $[\mathbf{3}]^{4-}$ tetraanion is rapidly degraded by carbon monoxide at atmospheric pressure to a mixture of $Ni(CO)_4$ and a yet uncharacterized yellow derivative showing an infrared spectrum (ν_{CO} at 2020 (w) and 1950 (s) cm^{-1}) reminiscent, but not identical, to that of $[Ni(CO)_3Br]^-$. Besides, $[\mathbf{3}]^{4-}$ reacts with protic acids, HBr included, to give $[H_2Ni_{12}(CO)_{21}]^{2-}$. [18,19]

It appeared possible that $[\mathbf{3}]^{4-}$ could arise from partial hydrolysis of a preformed $[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Br_5)(CO)_{22}]^{4-}$ species. As an attempt to selectively obtain and isolate this suggested intermediate, we have investigated the possible condensation reaction between $[\mathbf{1}]^{3-}$ and $[Ni_5(CO)_{12}]^{2-}$. It was hoped that the latter could both dehalogenate the $\mu_3\text{-}InBr_3$ coordinated to the former and condense on the top of the resulting μ_3-In moiety to give the $[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Br_5)(CO)_{22}]^{4-}$ derivative. In partial agreement with this suggestion, the dehalogenation step occurs as shown by the formation of some $[Ni(CO)_3Br]^-$; however, the reaction of $[\mathbf{1}]^{3-}$ with $[Ni_5(CO)_{12}]^{2-}$ in THF follows the unpredicted course shown in eq 3 and affords $[\mathbf{2}]^{4-}$, rather than $[\mathbf{3}]^{4-}$, as the only indium derivative.

$$4[\mathbf{1}]^{3-} + 3[Ni_5(CO)_{12}]^{2-} \rightarrow 3[\mathbf{2}]^{4-} + 2[Ni_9(CO)_{18}]^{2-} + 2[Ni(CO)_3Br]^- + Ni(CO)_4 + 4CO \quad (3)$$

The tetraethylammonium salt of the red-orange $[\mathbf{2}]^{4-}$ tetraanion slowly separates out as red crystals in 50–60 % yields (based on

---

(16) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95.

(17) Lin, C. C.; Kong, G.; Cho, H.; Whittlesey, B. R. *Inorg. Chem.* **1993**, *32*, 2705.

(18) Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1978**, *No. 167*, 93.

(19) Ceriotti, A.; Chini, P.; Della Pergola, R.; Longoni, G. *Inorg. Chem.* **1983**, *22*, 1595.

Table II. Crystallographic Data for $[NEt_4]_3[\mathbf{1}]\cdot Me_2CO$, $[NEt_4]_4[\mathbf{2}]\cdot Me_2CO$, and $[NEt_4]_4[\mathbf{3}]$

formula	$C_{38}H_{66}N_3O_{12}Br_8In_3Ni_6$	$C_{45}H_{86}N_4O_{11}Br_{10}In_4Ni_6$	$C_{54}H_{81}N_4O_{23}Br_4In_3Ni_{12}$
fw	2092.95	2469.84	2522.88
cryst system	orthorhombic	triclinic	monoclinic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	30.196(8)	13.230(11)	14.896(2)
b (Å)	13.469(7)	13.198(7)	42.194(8)
c (Å)	16.102(5)	26.519(6)	14.075(3)
α (deg)	90	75.44(3)	90
β (deg)	90	88.69(4)	110.32(3)
γ (deg)	90	59.80(5)	90
V (Å^3)	6549(7)	3843(3)	8296(5)
Z	4	2	4
D_{calc} (g cm^{-3})	2.123	2.134	2.020
μ(Mo Kα) (cm^{-1})	76.00	78.00	54.46
min transm coeff	0.46	0.75	0.69
final *R* and R_w indices[a]	0.045, 0.049	0.041, 0.044	0.044, 0.051

[a] $R = [\sum(F_o - k|F_c|)/\sum F_o]$. $R_w = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$.

Table III. Fractional Atomic Coordinates with Esd's in Parentheses of the Non-Hydrogen Atoms of $[NEt_4]_3[\mathbf{1}]\cdot Me_2CO$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
In(1)	0.80039(7)	0.2070(2)	0.310	C(31)	0.980(1)	0.086(3)	0.174(2)
In(2)	0.80886(8)	−0.0500(2)	0.3499(1)	C(41)	0.818(1)	0.049(2)	0.162(2)
In(3)	0.97981(8)	0.2688(2)	0.3107(2)	C(51)	0.821(1)	0.117(2)	0.488(2)
Br(1)	0.7695(2)	0.2709(3)	0.1727(3)	C(61)	0.909(1)	−0.178(3)	0.352(2)
Br(2)	0.7680(2)	0.3423(3)	0.4051(3)	N(1)	0.3492(8)	0.430(2)	0.821(2)
Br(3)	0.7871(1)	−0.1297(3)	0.4878(2)	N(2)	0.6386(9)	0.068(2)	0.099(1)
Br(4)	0.7875(2)	−0.1915(3)	0.2512(3)	N(3)	0.360(1)	−0.096(2)	0.063(2)
Br(5)	0.7341(1)	0.0653(3)	0.3350(2)	C(111)	0.358(1)	0.491(3)	0.897(2)
Br(6)	0.9832(1)	0.3765(3)	0.1780(3)	C(112)	0.391(1)	0.459(2)	0.960(2)
Br(7)	0.9876(2)	0.4059(3)	0.4210(3)	C(113)	0.317(1)	0.479(3)	0.762(2)
Br(8)	1.0603(1)	0.2059(3)	0.3147(3)	C(114)	0.335(2)	0.559(3)	0.723(3)
Ni(1)	0.8906(1)	0.2281(3)	0.3117(3)	C(115)	0.329(1)	0.337(3)	0.852(2)
Ni(2)	0.9394(1)	0.1224(3)	0.4020(3)	C(116)	0.293(2)	0.363(4)	0.911(3)
Ni(3)	0.9397(1)	0.0955(3)	0.2524(3)	C(117)	0.396(1)	0.416(3)	0.773(2)
Ni(4)	0.8564(1)	0.0708(3)	0.2489(2)	C(118)	0.391(1)	0.363(3)	0.696(2)
Ni(5)	0.8558(1)	0.1034(3)	0.4094(2)	C(211)	0.644(1)	0.181(3)	0.121(3)
Ni(6)	0.8996(1)	−0.0324(3)	0.3459(3)	C(212)	0.597(1)	0.230(3)	0.080(2)
OT(1)	0.9018(7)	−0.026(1)	0.528(1)	C(213)	0.684(1)	0.017(3)	0.131(2)
OT(2)	0.8909(7)	0.219(1)	0.129(1)	C(214)	0.681(1)	−0.086(3)	0.126(2)
OT(3)	0.8909(7)	0.286(1)	0.488(1)	C(215)	0.629(2)	0.046(3)	0.003(3)
OT(4)	1.0010(8)	−0.028(1)	0.344(1)	C(216)	0.670(1)	0.098(3)	−0.049(2)
OT(5)	0.9041(8)	−0.092(2)	0.173(1)	C(217)	0.598(2)	0.005(4)	0.136(4)
O(11)	0.8756(8)	0.438(2)	0.294(1)	C(218)	0.603(2)	0.019(3)	0.232(3)
O(21)	0.9946(9)	0.149(2)	0.545(2)	C(311)	0.374(1)	0.007(3)	0.056(3)
O(31)	0.999(1)	0.082(2)	0.113(2)	C(312)	0.346(1)	0.074(3)	−0.006(3)
O(41)	0.7996(8)	0.033(2)	0.106(1)	C(313)	0.362(2)	−0.140(4)	−0.025(4)
O(51)	0.7980(8)	0.137(2)	0.548(1)	C(314)	0.353(1)	−0.255(3)	−0.016(2)
O(61)	0.913(1)	−0.249(2)	0.360(2)	C(315)	0.311(1)	−0.100(3)	0.079(2)
CT(1)	0.894(1)	0.014(2)	0.463(2)	C(316)	0.298(1)	−0.043(3)	0.164(3)
CT(2)	0.893(1)	0.177(2)	0.194(2)	C(317)	0.383(2)	−0.147(3)	0.130(3)
CT(3)	0.894(1)	0.223(2)	0.434(2)	C(318)	0.434(2)	−0.159(3)	0.114(3)
CT(4)	0.970(1)	0.030(2)	0.338(2)	O(900)	0.425(1)	0.181(2)	0.856(2)
CT(5)	0.895(1)	−0.021(3)	0.225(3)	C(900)	0.474(2)	0.209(3)	0.953(3)
C(11)	0.882(1)	0.362(2)	0.298(2)	C(901)	0.469(2)	0.183(4)	0.866(3)
C(21)	0.978(1)	0.135(2)	0.481(2)	C(902)	0.494(2)	0.163(3)	0.788(3)

indium) on standing of the reaction solution, owing to its low solubility in acetone . The observation in its infrared spectrum (see Table I) of two well-separated absorptions in the region of the terminal carbonyl groups is in keeping with the presence in the solid-state structure of terminal ligands bound to unequivalent nickel atoms.

2. X-ray Structures of $[NEt_4]_3[\mathbf{1}]\cdot Me_2CO$, $[NEt_4]_4[\mathbf{2}]\cdot Me_2CO$, and $[NEt_4]_4[\mathbf{3}]$. The crystallographic data of $[NEt_4]_3[\mathbf{1}]\cdot Me_2CO$, $[NEt_4]_4[\mathbf{2}]\cdot Me_2CO$, and $[NEt_4]_4[\mathbf{3}]$ are collected in Table II, whereas their fractional atomic coordinates are reported in Tables III–V, respectively. Selected interatomic distances within the $[\mathbf{1}]^{3-}$ trianion and the $[\mathbf{2}]^{4-}$ and $[\mathbf{3}]^{4-}$ tetraanions are collected in Tables VI–VIII. ORTEP[20] drawings of the structure of the three anions, with the adopted labeling scheme, are shown in Figures 1–3.

As shown in Figure 1, the $[\mathbf{1}]^{3-}$ trianion displays an octahedral Ni_6 core capped on two adjacent faces by an In_2Br_5 moiety and on a third face, opposite to one of the above, by an $InBr_3$ molecule. The remaining five triangular faces of the octahedron are capped by five face-bridging carbonyl groups, whereas each nickel atom binds a terminal carbonyl ligand. The idealized symmetry of the whole anion is C_s, with the mirror plane containing the Ni(1), Ni(6), In(1), In(2), In(3), Br(5), and Br(8) atoms, the terminal CO groups bonded to Ni(1) and Ni(6), and the face-bridging carbonyl group labeled as COT(4). The Ni–Ni bond lengths are found in the 2.437(5)–2.620(4)-Å range and show an average value of 2.529 Å; the longest bond distance is the edge common to the two adjacent faces capped by the In_2Br_5 moiety. As a result of the capping of all the triangular faces, either with carbon monoxide groups or indium atoms, the Ni_6 kernel conforms to an octahedral geometry more closely than the parent $[Ni_6(CO)_{12}]^{2-}$ dianion, whose structure has been described as deriving from an antiprismatic stacking of two $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties.[11]

---

[20] Johnson, K. C. ORTEP, A FORTRAN thermal ellipsoids plot program for crystal structure illustration. Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

Table IV. Fractional Atomic Coordinates with Esd's in Parentheses of the Non-Hydrogen Atoms of $[NEt_4]_4[\mathbf{2}]\cdot Me_2CO$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
In(1)	0.37356(9)	0.17642(8)	0.57757(4)	N(1)	0.3607(9)	0.9357(9)	0.8100(4)
In(2)	0.34906(8)	−0.08178(8)	0.58258(4)	N(2)	0.1404(9)	0.6051(8)	0.6892(4)
In(3)	0.87360(8)	0.37241(8)	0.07771(4)	N(3)	0.205(1)	0.7040(9)	0.4011(5)
In(4)	0.84899(8)	0.65019(8)	0.08261(4)	N(4)	0.297(1)	0.8092(8)	0.0997(5)
Br(1)	0.2083(2)	0.4006(1)	0.54990(7)	C(111)	0.233(1)	0.995(1)	0.8251(6)
Br(2)	0.2404(1)	0.0901(1)	0.64007(6)	C(112)	0.138(1)	1.063(1)	0.7781(7)
Br(3)	0.4765(1)	0.1923(1)	0.65517(6)	C(121)	0.377(1)	0.846(1)	0.7785(6)
Br(4)	0.1550(1)	−0.0726(1)	0.56074(7)	C(122)	0.359(1)	0.742(1)	0.8093(7)
Br(5)	0.4429(1)	−0.2782(1)	0.66014(7)	C(131)	0.440(2)	0.874(1)	0.8602(7)
Br(6)	0.7082(1)	0.3412(1)	0.04995(7)	C(132)	0.570(2)	0.805(2)	0.8556(8)
Br(7)	0.7401(1)	0.5299(1)	0.13992(6)	C(141)	0.384(1)	1.029(1)	0.7736(6)
Br(8)	0.9766(2)	0.1757(1)	0.15514(7)	C(142)	0.373(1)	1.126(1)	0.7983(7)
Br(9)	0.9431(1)	0.6746(1)	0.16034(6)	C(211)	0.265(1)	0.555(1)	0.6761(6)
Br(10)	0.6553(2)	0.8565(1)	0.06087(7)	C(212)	0.361(1)	0.477(1)	0.7227(7)
Ni(1)	0.3441(1)	0.0870(1)	0.50125(6)	C(221)	0.119(1)	0.687(1)	0.7247(6)
Ni(2)	0.5100(1)	0.1323(1)	0.49630(6)	C(222)	0.126(1)	0.799(1)	0.7026(7)
Ni(3)	0.5321(1)	−0.0449(1)	0.57092(6)	C(231)	0.061(2)	0.675(1)	0.6390(7)
Ni(4)	1.0099(1)	0.3614(1)	−0.00359(7)	C(232)	−0.067(2)	0.730(2)	0.6445(8)
Ni(5)	0.8438(1)	0.5675(1)	0.00123(6)	C(241)	0.123(1)	0.502(1)	0.7198(6)
Ni(6)	1.0323(1)	0.4420(1)	0.07070(6)	C(242)	0.141(1)	0.408(1)	0.6919(7)
OT(1)	0.2995(8)	0.3065(7)	0.4181(4)	C(311)	0.151(2)	0.784(2)	0.348(1)
OT(2)	0.2771(7)	−0.0141(7)	0.4277(4)	C(312)	0.166(2)	0.891(2)	0.327(1)
OT(3)	0.8012(7)	0.4759(6)	−0.0817(3)	C(321)	0.194(1)	0.595(1)	0.4094(7)
OT(4)	1.2215(8)	0.1914(7)	0.0723(4)	C(322)	0.071(1)	0.615(1)	0.4092(7)
O(1)	0.0887(8)	0.2453(9)	0.4906(5)	C(331)	0.335(1)	0.667(1)	0.4066(8)
O(2)	0.5119(9)	0.3558(7)	0.4868(4)	C(332)	0.408(1)	0.597(1)	0.3712(8)
O(3)	0.6106(9)	−0.1362(8)	0.6826(4)	C(341)	0.145(2)	0.777(1)	0.4399(8)
O(4)	1.0124(9)	0.1446(7)	−0.0126(5)	C(342)	0.177(2)	0.710(2)	0.4947(8)
O(5)	0.5882(8)	0.6762(9)	−0.0090(4)	C(411)	0.311(1)	0.697(1)	0.0905(8)
O(6)	1.1134(9)	0.3403(8)	0.1828(4)	C(412)	0.431(2)	0.594(1)	0.0917(7)
CT(1)	0.360(1)	0.213(1)	0.4435(5)	C(421)	0.168(2)	0.906(1)	0.0924(7)
CT(2)	0.351(1)	−0.012(1)	0.4510(5)	C(422)	0.092(1)	0.874(1)	0.1287(8)
CT(3)	0.868(1)	0.479(1)	−0.0542(5)	C(431)	0.352(2)	0.782(2)	0.1546(9)
CT(4)	1.152(1)	0.288(1)	0.0484(6)	C(432)	0.334(2)	0.883(2)	0.1751(9)
C(1)	0.185(1)	0.183(1)	0.4973(6)	C(441)	0.355(1)	0.862(1)	0.0602(9)
C(2)	0.510(1)	0.268(1)	0.4903(5)	C(442)	0.315(2)	0.886(2)	0.0029(9)
C(3)	0.575(1)	−0.0965(9)	0.6393(5)	O(900)	0.251(1)	0.618(1)	0.2505(6)
C(4)	1.013(1)	0.227(1)	−0.0083(5)	C(900)	0.248(2)	0.527(1)	0.2504(8)
C(5)	0.688(1)	0.637(1)	−0.0041(6)	C(901)	0.323(2)	0.453(1)	0.2141(7)
C(6)	1.075(1)	0.382(1)	0.1391(6)	C(902)	0.181(2)	0.490(1)	0.2847(8)

The average Ni–In and $In–Br_{term}$ distances are respectively 2.729 and 2.567 Å; the latter is only slightly longer than that reported for the $[InBr_4]^-$ anion (average 2.498 Å).[21] The unique bridging bromine atom shows slightly different In–Br contacts of 2.796(4) and 2.751(4) Å; however, the average of these two value (2.774 Å) compares well with that found in $[\{Re(CO)_5\}_2In(\mu_2\text{-}Br)]_2$ (2.764 Å).[22] The Br–In–Br angles are found in the 95.42(14)–99.68(15)° range, whereas the In(1)–Br(5)–In(2) angle, involving the unique bridging bromine atom, is 79.07(9)°. This is significantly more acute than the corresponding angle previously ascertained in the above bromine-bridged Re–In compound (ca. 95°) and slightly wider than the average In–Br–In angle found in $In_3Br_3Co_4(CO)_{15}$ (ca. 75°).[23] The poor quality of the crystal investigated affected some individual bond lengths of the carbonyl ligands, which are slightly anomalous even though an anisotropic thermal parameter could not be refined for these atoms. In spite of that, the average values computed over homogeneous sets of distances are in line with those reported for other nickel carbonyl clusters.

The asymmetric unit in the triclinic cell of $[NEt_4]_4[\mathbf{2}]\cdot Me_2CO$ consists of two "half" $[Ni_6(\eta^2\text{-}\mu_6\text{-}In_2Br_5)_2(CO)_6(\mu_3\text{-}CO)_4]^{4-}$ anions located about two different crystallographic inversion centers and four $[NEt_4]^+$ cations in a general position of the space group. As shown in Figure 2, the structure of the tetraanion is very similar to that of the parent $[\mathbf{1}]^{3-}$ trianion, the only difference arising from the replacement of a bridging carbonyl and the μ_3-$InBr_3$ moiety with a bidentate $[In_2Br_5]^+$ ligand. The resulting idealized symmetry of the whole anion is D_{2h} (*mmm*). The average Ni–Ni distance (computed over the two anions) is 2.545 Å, to be compared with an average distance of 2.529 Å in the trianion. The average Ni–In distance (2.706 Å) is slightly shorter than that found in the related trianion, whereas a small lengthening is observed for both the $In–Br_{term}$ and $In–Br_{bridg}$ distances (average 2.582 and 2.826 Å, respectively). The latter small variations may arise from a greater transfer of electron density on the indium atoms with respect to the parent $[\mathbf{1}]^{3-}$ trianion.

In order to assign 86 cluster valence electrons (CVE) to the Ni_6 core of both $[\mathbf{1}]^{3-}$ and $[\mathbf{2}]^{4-}$, it may be useful to envisage that $InBr_3$ and $[In_2Br_4(\mu_2\text{-}Br)]^+$ moieties, respectively, acting as mono- and a bidentate Lewis acids, are interacting with a $[Ni_6(CO)_6(\mu_3\text{-}CO)_5]^{4-}$ and $[Ni_6(CO)_6(\mu_3\text{-}CO)_4]^{6-}$ base, respectively. Alternately, neutral $In_2Br_4(\mu_2\text{-}Br)$ moieties may be considered to contribute a single electron through one of the two indium atoms to a $[Ni_6(\mu_3\text{-}InBr_3)(CO)_6(\mu_3\text{-}CO)_5]^{3-}$ and $[Ni_6(CO)_6(\mu_3\text{-}CO)_4]^{4-}$ moiety, respectively.

A closely related $In_2Br_4(\mu_2\text{-}OH)$ moiety is also present in the $[\mathbf{3}]^{4-}$ tetraanion, which is shown in Figure 3; the structure of the anion derives from two distinct $Ni_6(CO)_6(\mu_2\text{-}CO)_5$ moieties condensed on a unique bare indium atom and bridged by the above $In_2Br_4(\mu_2\text{-}OH)$ moiety. Interestingly, the two $Ni_6(CO)_6(\mu_2\text{-}CO)_5$ fragments display different geometries. Thus, in one fragment the basic structure of the $[Ni_6(CO)_{12}]^{2-}$ dianion is retained even though an edge-bridging carbonyl group is replaced by a face-bridging indium atom. In contrast, the second fragment displays a fairly distorted metal framework. This can be envisioned to derive from the conversion of the trigonal antiprism into a prism followed by a sliding of one interlayer edge so to give rise to a square pyramid (the basal square face is individuated

---

[21] Staffel, T.; Meyer, G. *Z. Anorg. Allg. Chem.* **1989**, *574*, 107.

[22] Haupt, H. J.; Preut, H.; Wolfes, W. *Z. Anorg. Allg. Chem.* **1979**, *448*, 93.

[23] Cradwick, P. D.; Hall, D. J. Organomet. Chem. **1970**, *22*, 203.

Table V. Fractional Atomic Coordinates with Esd's in Parentheses of the Non-Hydrogen Atoms of $[NEt_4]_4[\mathbf{3}]$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
In(1)	0.13496(7)	0.10618(3)	0.70153(8)	C(5)	0.488(1)	0.1244(4)	0.607(1)
In(2)	0.31277(7)	0.15485(3)	0.90205(8)	C(6)	0.495(1)	0.0304(5)	0.866(1)
In(3)	0.03000(8)	0.14769(3)	0.84527(8)	C(7)	0.003(2)	0.1319(6)	0.393(2)
Br(1)	0.3636(2)	0.15357(5)	1.1024(1)	C(8)	−0.262(1)	0.0886(5)	0.552(2)
Br(2)	0.3660(1)	0.21512(4)	0.9073(1)	C(9)	0.061(1)	0.0288(4)	0.616(1)
Br(4)	0.0454(2)	0.12866(5)	1.0249(2)	C(10)	0.046(1)	0.0606(4)	0.827(1)
Br(5)	−0.0456(1)	0.20351(5)	0.8570(2)	C(11)	−0.234(1)	0.1395(5)	0.756(2)
Ni(1)	0.3002(1)	0.13449(4)	0.7180(1)	C(1,2)	0.288(1)	0.1152(4)	0.595(1)
Ni(2)	0.2969(1)	0.07920(5)	0.6816(1)	C(12)	0.026(1)	0.1690(4)	0.604(1)
Ni(3)	0.3030(1)	0.09406(5)	0.8482(1)	C(2,3)	0.297(1)	0.0541(4)	0.793(1)
Ni(4)	0.4690(1)	0.12548(5)	0.8812(2)	C(4,5)	0.497(1)	0.1499(4)	0.783(1)
Ni(5)	0.4663(1)	0.11124(5)	0.7127(2)	C(4,6)	0.492(1)	0.0882(4)	0.961(1)
Ni(6)	0.4670(2)	0.07005(5)	0.8323(2)	C(5,6)	0.510(1)	0.0706(4)	0.721(1)
Ni(7)	−0.0320(2)	0.10930(6)	0.4776(2)	C(7,8)	−0.162(1)	0.1180(4)	0.443(1)
Ni(8)	−0.1463(2)	0.09130(5)	0.5527(2)	C(7,9)	0.042(1)	0.0746(4)	0.473(1)
Ni(9)	0.0026(2)	0.06351(5)	0.5812(2)	C(8,9)	−0.116(1)	0.0496(5)	0.588(1)
Ni(10)	−0.0132(1)	0.09055(5)	0.7516(2)	C(10,11)	−0.123(1)	0.0861(4)	0.781(1)
Ni(11)	−0.1475(1)	0.12531(6)	0.7142(2)	C(11,12)	−0.142(1)	0.1572(4)	0.626(1)
Ni(12)	−0.0245(1)	0.13834(5)	0.6482(1)	C(111)	0.440(1)	0.0768(4)	0.245(1)
OH	0.1702(7)	0.1687(2)	0.8902(7)	C(112)	0.511(1)	0.1030(4)	0.302(1)
O(1)	0.2753(8)	0.1970(3)	0.6339(9)	C(121)	0.465(1)	0.0485(4)	0.413(1)
O(2)	0.2798(9)	0.0275(3)	0.5442(9)	C(122)	0.542(1)	0.0256(5)	0.399(1)
O(3)	0.2548(8)	0.0748(3)	1.0207(9)	C(131)	0.326(1)	0.0833(4)	0.342(1)
O(4)	0.584(1)	0.1647(4)	1.043(1)	C(132)	0.242(1)	0.0964(4)	0.257(1)
O(5)	0.4989(9)	0.1363(3)	0.539(1)	C(141)	0.336(1)	0.0314(4)	0.250(1)
O(6)	0.510(1)	0.0041(4)	0.885(1)	C(142)	−0.280(1)	−0.0116(4)	0.696(1)
O(7)	0.007(1)	0.1435(4)	0.322(1)	C(211)	0.187(1)	0.2609(4)	0.676(1)
O(8)	−0.340(1)	0.0875(4)	0.551(1)	C(212)	0.201(1)	0.2756(4)	0.585(1)
O(9)	0.1000(9)	0.0043(3)	0.634(1)	C(221)	0.036(1)	0.2940(4)	0.655(1)
O(10)	0.0815(9)	0.0393(3)	0.8817(9)	C(222)	−0.037(1)	0.2668(5)	0.617(1)
O(11)	−0.280(1)	0.1501(4)	0.800(1)	C(231)	0.129(1)	0.2636(4)	0.821(1)
O(1,2)	0.2686(8)	0.1209(3)	0.5080(8)	C(232)	0.086(1)	0.2827(4)	0.889(1)
O(12)	0.0548(9)	0.1907(3)	0.5771(9)	C(241)	0.195(1)	0.3143(4)	0.765(1)
O(2,3)	0.2765(8)	0.0274(3)	0.8092(8)	C(242)	0.299(1)	0.3083(5)	0.838(1)
O(4,5)	0.5213(8)	0.1756(3)	0.7714(9)	C(311)	−0.328(2)	0.2646(6)	0.282(3)
O(4,6)	0.5142(8)	0.0802(3)	1.0475(9)	C(312)	−0.314(2)	0.2693(7)	0.174(2)
O(5,6)	0.5458(9)	0.0522(3)	0.681(1)	C(321)	−0.460(2)	0.2240(7)	0.184(2)
O(7,8)	−0.226(1)	0.1310(3)	0.380(1)	C(322)	−0.540(1)	0.2473(5)	0.190(2)
O(7,9)	0.0823(9)	0.0623(3)	0.4225(9)	C(331)	−0.390(2)	0.2303(9)	0.366(2)
O(8,9)	−0.147(1)	0.0252(3)	0.605(1)	C(332)	0.581(2)	0.3106(7)	0.874(2)
O(10,11)	−0.1643(9)	0.0676(3)	0.818(1)	C(341)	−0.292(3)	0.2054(7)	0.271(3)
O(11,12)	−0.1887(9)	0.1789(3)	0.5800(9)	C(342)	0.811(2)	0.2878(6)	0.853(2)
N(1)	−0.3932(8)	−0.0600(3)	0.6847(9)	C(411)	0.922(2)	0.0647(7)	1.097(2)
N(2)	0.1369(9)	0.2834(3)	0.7289(9)	C(412)	0.007(2)	−0.0403(5)	0.848(2)
N(3)	0.637(1)	0.2700(4)	0.778(1)	C(421)	0.221(2)	−0.0295(7)	0.927(3)
N(4)	0.8222(9)	0.0614(3)	1.111(1)	C(422)	0.227(2)	−0.0191(6)	1.034(1)
C(1)	0.285(1)	0.1732(4)	0.672(1)	C(431)	0.763(2)	0.0857(8)	1.046(2)
C(2)	0.283(1)	0.0481(4)	0.597(1)	C(432)	0.207(2)	−0.1207(5)	0.924(3)
C(3)	0.275(1)	0.0840(4)	0.954(1)	C(441)	−0.166(2)	0.0650(8)	0.213(2)
C(4)	0.532(1)	0.1488(5)	0.980(1)	C(442)	0.737(1)	0.0588(5)	1.240(2)

by Ni(7), Ni(9), Ni(10), and Ni(12), whereas Ni(8) represents the apex) capped on a triangular face by the sixth Ni(11) atom. The octahedral and the capped square pyramidal geometries are known to require the same number of CVE, and it has already been shown than the metal frames are sufficiently soft to be affected by the stereochemical requirements of the ligands (compare for instance the structures of $[HOs_6(CO)_{18}]^-$ and $H_2Os_6(CO)_{18}$).[24] However, to our knowledge, the molecular structure of the $[\mathbf{3}]^{4-}$ tetraanion represents the first example of metal cluster fragments with identical stoichiometry which display different geometries; besides the different architectures of the two $Ni_6(CO)_{11}$ fragments are comprised in a single molecule.

The unique indium atom sandwiched between the two $Ni_6(CO)_{11}$ units is six- rather than seven-coordinated and displays a distorted trigonal prismatic coordination, being at a bond distance from only three nickel atoms (In–Ni$_{av}$ = 2.668 Å) of the square face of the capped square-pyramidal $Ni_6(CO)_{11}$ moiety. The fourth Ni atom of the above square face shows an In–Ni interatomic separation of 3.270(2) Å, which is clearly nonbonding. It seems conceivable that this unusual stereochemistry of the semi-encapsulated In atom, as well as the conversion in a capped square pyramid of one of the two $Ni_6(CO)_{11}$ moieties, could be necessary in order to provide a suitable settlement for the $In_2Br_4(\mu_2\text{-OH})$ bridging moiety (vide infra).

The interfragment η^2-μ_6-coordinated $In_2Br_4(\mu_2\text{-OH})$ unit deserves some comments. First of all the In–O–In angle (137.9(4)°) is much wider than that displayed by the bromine of the corresponding intrafragment η^2-μ_6-coordinated $In_2Br_4(\mu_2\text{-Br})$ moieties in both the $[\mathbf{1}]^{3-}$ and $[\mathbf{2}]^{4-}$ anions (77.8–79.1°), as well as the oxygen in the $(t\text{-}Bu_2InOEt)_2$ (104.8(2)°) four-membered ring.[25] However, wide In–O–In angles are not anomalous in octahedral In compounds, when they are not constrained by belonging to a ring, and have previously been found both in the μ-hydroxo $[L_4In_4(\mu\text{-OH})_6]^{6+}$ (130.8° average of six) and μ-oxo $[L_2In_2(MeCOO)_4(\mu\text{-O})]$ (142.5°; L = 1,4,7-triazacyclononane) complexes.[26] The average In–O bond distance (2.152 Å) compares well with those of other μ-hydroxo In derivatives, e.g. $[L_4In_4$-

---

[24] McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* 1976, 883.

[25] Bradley, D. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *Organometallics* **1988**, *7*, 1112.

[26] Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1654.

Table VI. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses within the $[\mathbf{1}]^{3-}$ Anion

Ni(1)–Ni(2)	2.513(5)	Ni(1)–Ni(3)	2.510(5)
Ni(1)–Ni(4)	2.565(5)	Ni(1)–Ni(5)	2.529(5)
Ni(2)–Ni(3)	2.437(5)	Ni(2)–Ni(5)	2.540(6)
Ni(2)–Ni(6)	2.569(6)	Ni(3)–Ni(4)	2.536(6)
Ni(3)–Ni(6)	2.587(6)	Ni(4)–Ni(5)	2.620(4)
Ni(4)–Ni(6)	2.463(5)	Ni(5)–Ni(6)	2.478(5)
In(1)–Ni(1)	2.739(4)	In(1)–Ni(4)	2.681(4)
In(1)–Ni(5)	2.705(4)	In(2)–Ni(4)	2.712(4)
In(2)–Ni(5)	2.683(4)	In(2)–Ni(6)	2.752(4)
In(3)–Ni(1)	2.749(4)	In(3)–Ni(2)	2.747(5)
In(3)–Ni(3)	2.793(5)	In(1)···In(2)	3.531(3)
In(1)–Br(1)	2.546(4)	In(2)–Br(3)	2.553(4)
In(1)–Br(2)	2.575(4)	In(2)–Br(4)	2.564(4)
In(1)–Br(5)	2.796(4)	In(2)–Br(5)	2.751(4)
In(3)–Br(6)	2.584(4)	In(3)–Br(7)	2.573(5)
In(3)–Br(8)	2.574(4)		
Ni(1)–C(11)	1.831(34)	Ni(2)–C(21)	1.732(35)
Ni(3)–C(31)	1.768(45)	Ni(4)–C(41)	1.846(31)
Ni(5)–C(51)	1.667(28)	Ni(6)–C(61)	1.987(46)
Ni(2)–CT(1)	2.222(35)	Ni(1)–CT(2)	2.025(32)
Ni(5)–CT(1)	1.885(35)	Ni(3)–CT(2)	2.017(34)
Ni(6)–CT(1)	2.002(33)	Ni(4)–CT(2)	2.013(34)
Ni(1)–CT(3)	1.973(28)	Ni(2)–CT(4)	1.869(30)
Ni(2)–CT(3)	1.984(30)	Ni(3)–CT(4)	1.876(30)
Ni(5)–CT(3)	2.022(31)	Ni(6)–CT(4)	2.300(28)
Ni(3)–CT(5)	2.126(43)	Ni(4)–CT(5)	1.739(46)
Ni(6)–CT(5)	1.963(41)		
CT(1)–OT(1)	1.194(31)	CT(2)–OT(2)	1.189(32)
CT(3)–OT(3)	1.225(29)	CT(4)–OT(4)	1.219(29)
CT(5)–OT(5)	1.289(43)	C(11)–O(11)	1.042(31)
C(21)–O(21)	1.165(34)	C(31)–O(31)	1.127(42)
C(41)–O(41)	1.083(29)	C(51)–O(51)	1.214(28)
C(61)–O(61)	0.974(43)		
Br(1)–In(1)–Br(2)	97.97(15)	Br(3)–In(2)–Br(4)	99.33(14)
Br(1)–In(1)–Br(5)	95.42(14)	Br(3)–In(2)–Br(5)	95.85(13)
Br(2)–In(1)–Br(5)	97.17(14)	Br(4)–In(2)–Br(5)	99.11(14)
Br(6)–In(3)–Br(7)	99.46(15)	Br(6)–In(3)–Br(8)	99.68(15)
Br(7)–In(3)–Br(8)	97.59(17)	In(1)–Br(5)–In(2)	79.07(9)
Ni(1)–C(11)–O(11)	175.9(32)	Ni(2)–CT(1)–Ni(5)	75.9(12)
Ni(2)–C(21)–O(21)	163.7(33)	Ni(2)–CT(1)–Ni(6)	74.7(12)
Ni(3)–C(31)–O(31)	165.0(41)	Ni(5)–CT(1)–Ni(6)	79.2(13)
Ni(4)–C(41)–O(41)	171.7(29)	Ni(2)–CT(1)–OT(1)	124.7(26)
Ni(5)–C(51)–O(51)	171.6(25)	Ni(5)–CT(1)–OT(1)	143.8(28)
Ni(6)–C(61)–O(61)	175.3(49)	Ni(6)–CT(1)–OT(1)	131.9(25)
Ni(1)–CT(2)–Ni(3)	76.8(12)	Ni(1)–CT(3)–Ni(2)	78.8(11)
Ni(1)–CT(2)–Ni(4)	78.9(12)	Ni(1)–CT(3)–Ni(5)	78.6(11)
Ni(3)–CT(2)–Ni(4)	78.0(12)	Ni(2)–CT(3)–Ni(5)	78.7(11)
Ni(1)–CT(2)–OT(2)	131.0(25)	Ni(1)–CT(3)–OT(3)	132.8(23)
Ni(3)–CT(2)–OT(2)	135.1(28)	Ni(2)–CT(3)–OT(3)	135.8(25)
Ni(4)–CT(2)–OT(2)	134.2(27)	Ni(5)–CT(3)–OT(3)	130.1(23)
Ni(2)–CT(4)–Ni(3)	81.2(13)	Ni(3)–CT(5)–Ni(4)	81.3(18)
Ni(2)–CT(4)–Ni(6)	75.3(10)	Ni(3)–CT(5)–Ni(6)	78.4(15)
Ni(3)–CT(4)–Ni(6)	75.8(10)	Ni(4)–CT(5)–Ni(6)	83.2(19)
Ni(2)–CT(4)–OT(4)	139.5(25)	Ni(3)–CT(5)–OT(5)	122.5(30)
Ni(3)–CT(4)–OT(4)	137.9(26)	Ni(4)–CT(5)–OT(5)	144.6(32)
Ni(6)–CT(4)–OT(4)	117.7(20)	Ni(6)–CT(5)–OT(5)	124.3(31)

Table VII. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses within the $[\mathbf{2}]^{4-}$ Anion[a]

Ni(1)–Ni(2)	2.542(2)	Ni(4)–Ni(5)	2.528(2)
Ni(1)–Ni(2)′	2.529(2)	Ni(4)–Ni(5)″	2.547(2)
Ni(1)–Ni(3)	2.620(2)	Ni(4)–Ni(6)	2.550(2)
Ni(1)–Ni(3)′	2.477(2)	Ni(4)–Ni(6)″	2.544(2)
Ni(2)–Ni(3)	2.546(2)	Ni(5)–Ni(6)	2.622(2)
Ni(2)–Ni(3)′	2.559(2)	Ni(5)–Ni(6)″	2.472(2)
In(1)···In(2)	3.552(1)	In(3)···In(4)	3.550(1)
In(1)–Br(1)	2.558(2)	In(3)–Br(6)	2.575(2)
In(1)–Br(2)	2.844(2)	In(3)–Br(7)	2.839(2)
In(1)–Br(3)	2.601(2)	In(3)–Br(8)	2.589(2)
In(1)–Ni(1)	2.710(2)	In(3)–Ni(4)	2.763(2)
In(1)–Ni(2)	2.764(2)	In(3)–Ni(5)	2.700(2)
In(1)–Ni(3)	2.653(2)	In(3)–Ni(6)	2.669(2)
In(2)–Br(2)	2.809(2)	In(4)–Br(7)	2.810(2)
In(2)–Br(4)	2.581(2)	In(4)–Br(9)	2.600(2)
In(2)–Br(5)	2.586(2)	In(4)–Br(10)	2.564(2)
In(2)–Ni(1)	2.657(2)	In(4)–Ni(4)″	2.756(2)
In(2)–Ni(2)′	2.752(2)	In(4)–Ni(5)	2.668(2)
In(2)–Ni(3)	2.696(2)	In(4)–Ni(6)	2.688(2)
Ni(1)–CT(1)	2.051(15)	Ni(1)–CT(2)	2.064(15)
Ni(2)–CT(1)	2.068(17)	Ni(2)′–CT(2)	1.980(17)
Ni(3)′–CT(1)	2.076(13)	Ni(3)′–CT(2)	2.054(15)
Ni(4)–CT(3)	1.969(15)	Ni(4)–CT(4)	1.995(16)
Ni(5)–CT(3)	2.026(14)	Ni(5)″–CT(4)	2.057(14)
Ni(6)″–CT(3)	2.042(14)	Ni(6)–CT(4)	2.080(14)
Ni(1)–C(1)	1.820(17)	Ni(2)–C(2)	1.761(15)
Ni(3)–C(3)	1.763(14)	Ni(4)–C(4)	1.788(14)
Ni(5)–C(5)	1.772(16)	Ni(6)–C(6)	1.763(18)
CT(1)–OT(1)	1.113(15)	CT(2)–OT(2)	1.180(16)
CT(3)–OT(3)	1.176(14)	CT(4)–OT(4)	1.143(14)
C(1)–O(1)	1.100(16)	C(3)–O(3)	1.135(13)
C(2)–O(2)	1.147(14)	C(5)–O(5)	1.151(15)
C(4)–O(4)	1.126(13)		
C(6)–O(6)	1.154(15)		
Br(1)–In(1)–Br(2)	95.65(6)	Br(6)–In(3)–Br(7)	95.77(6)
Br(1)–In(1)–Br(3)	96.07(6)	Br(6)–In(3)–Br(8)	96.08(7)
Br(2)–In(1)–Br(3)	95.66(6)	Br(7)–In(3)–Br(8)	95.60(6)
Br(2)–In(2)–Br(4)	92.26(6)	Br(7)–In(4)–Br(9)	98.86(6)
Br(2)–In(2)–Br(5)	98.57(6)	Br(7)–In(4)–Br(10)	91.87(6)
Br(4)–In(2)–Br(5)	98.33(6)	Br(9)–In(4)–Br(10)	98.47(6)
In(1)–Br(2)–In(2)	77.84(4)	In(3)–Br(7)–In(4)	77.86(4)
Ni(1)–CT(1)–Ni(2)	76.2(6)	Ni(4)–CT(3)–Ni(5)	78.5(6)
Ni(1)–CT(1)–Ni(3)′	73.7(5)	Ni(4)–CT(3)–Ni(6)″	78.7(6)
Ni(2)–CT(1)–Ni(3)′	76.3(6)	Ni(5)–CT(3)–Ni(6)″	74.8(5)
Ni(1)–CT(1)–OT(1)	136.1(12)	Ni(4)–CT(3)–OT(3)	137.7(11)
Ni(2)–CT(1)–OT(1)	135.0(12)	Ni(5)–CT(3)–OT(3)	132.3(11)
Ni(3)′–CT(1)–OT(1)	134.0(12)	Ni(6)″–CT(3)–OT(3)	130.9(11)
Ni(1)–CT(2)–Ni(2)′	77.4(6)	Ni(4)–CT(4)–Ni(5)″	77.9(6)
Ni(1)–CT(2)–Ni(3)′	73.9(5)	Ni(4)–CT(4)–Ni(6)	77.4(6)
Ni(2)′–CT(2)–Ni(3)′	78.3(6)	Ni(5)″–CT(4)–Ni(6)	73.4(5)
Ni(1)–CT(2)–OT(2)	132.5(11)	Ni(4)–CT(4)–OT(4)	136.4(12)
Ni(2)′–CT(2)–OT(2)	136.3(11)	Ni(5)″–CT(4)–OT(4)	134.9(12)
Ni(3)′–CT(2)–OT(2)	134.0(12)	Ni(6)–CT(4)–OT(4)	131.9(12)
Ni(1)–C(1)–O(1)	174.0(15)	Ni(4)–C(4)–O(4)	178.0(14)
Ni(2)–C(2)–O(2)	178.8(12)	Ni(5)–C(5)–O(5)	175.6(13)
Ni(3)–C(3)–O(3)	174.7(12)	Ni(6)–C(6)–O(6)	173.6(14)

[a] Symmetry codes: ′ = $1 - x, -y, 1 - z$; ″ = $2 - x, 1 - y, -z$.

$(\mu\text{-OH})_6]^{6+}$ (2.144 Å)[26] and $In(OH)_3$ (2.171 Å),[27] and is significantly longer than that of μ-oxo bridged species, e.g. $[L_2In_2(MeCOO)_4(\mu\text{-O})]$ (2.114 Å).[26]

In all the three above reported Ni–In compounds the distances between the indium atoms are very long in comparison to typical In–In bonds, e.g. 2.7 Å in $[In_2Br_6]^{2-}$,[28] and are clearly nonbonding.

Conclusion

The products of the reaction of InX_3 (X = Cl, Br) with $[Ni_6(CO)_{12}]^{2-}$ so far characterized are a variance of their direct Lewis acid–base adducts. However, the presence of a μ_3-$InBr_3$ moiety in the structure of $[\mathbf{1}]^{3-}$ and the infrared observations reported in the text suggest the intermediate existence of such adducts as probable. It may be possible that their lability arises from the too low negative charge of the $[Ni_6(CO)_{12}]^{2-}$ dianion. On the other hand, the formation of $[X_2In(\mu_2\text{-}X)InX_2]^+$ moieties and the flexibility of their In–X–In angle on changing X provides the opportunity to stabilize unprecedented compounds containing either intra- or interfragment $[In_2X_5]^+$ moieties. For instance, the wide In–O–In angle present in $[\mathbf{3}]^{4-}$ seems at the origin of its existence. Indeed, the dihedral angles between the facing triangular faces of two stacked $Ni_6(CO)_{11}$ moieties sandwiching an In atom with a trigonal prismatic stereogeometry (such as documented by the above compound, as well as in the alternate possible case consisting of two octahedral $Ni_6(CO)_{11}$ fragments) imply an In–X–In angle of the interfragment η^2-μ_6-coordinated $In_2X_4(\mu_2\text{-}X)$ moiety much wider than provided by formal sp^3 or sp^2 hybridization. In contrast, E–X–E angles not constrained by belonging to a ring often only slightly exceed 90° when X is a

---

(27) Christensen, A. N.; Brock, N. C.; Heidenstam, O. V.; Nilsson, A. *Acta Chem. Scand.* **1967**, *21*, 1046.

(28) Staffel, T.; Meyer, G. *Z. Anorg. Allg. Chem.* **1988**, *563*, 27.

Table VIII. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses within the $[3]^{4-}$ Anion

In(1)–Ni(1)	2.673(2)	In(1)–Ni(9)	2.771(2)
In(1)–Ni(2)	2.769(2)	In(1)–Ni(10)	2.624(2)
In(1)–Ni(3)	2.684(2)	In(1)–Ni(12)	2.609(2)
In(1)···Ni(7)	3.270(2)		
In(2)–Br(1)	2.654(2)	In(3)–Br(4)	2.586(2)
In(2)–Br(2)	2.657(2)	In(3)–Br(5)	2.640(2)
In(2)–Ni(1)	2.673(2)	In(3)–Ni(10)	2.715(2)
In(2)–Ni(3)	2.664(2)	In(3)–Ni(11)	2.810(2)
In(2)–Ni(4)	2.741(2)	In(3)–Ni(12)	2.635(2)
In(2)–OH	2.153(9)	In(3)–OH	2.151(9)
Ni(1)–Ni(2)	2.386(2)	Ni(1)–Ni(3)	2.494(2)
Ni(1)–Ni(4)	2.780(2)	Ni(1)–Ni(5)	2.687(2)
Ni(2)–Ni(3)	2.399(2)	Ni(2)–Ni(5)	2.761(2)
Ni(2)–Ni(6)	2.708(3)	Ni(3)–Ni(4)	2.700(2)
Ni(4)–Ni(5)	2.432(3)	Ni(3)–Ni(6)	2.724(2)
Ni(4)–Ni(6)	2.435(2)	Ni(5)–Ni(6)	2.417(3)
Ni(7)–Ni(8)	2.417(3)	Ni(8)–Ni(9)	2.416(3)
Ni(7)–Ni(9)	2.367(3)	Ni(8)–Ni(10)	2.814(3)
Ni(7)–Ni(12)	2.663(3)	Ni(8)–Ni(11)	2.693(3)
Ni(8)–Ni(12)	2.710(2)	Ni(9)–Ni(10)	2.740(3)
Ni(10)–Ni(11)	2.386(3)	Ni(11)–Ni(12)	2.388(2)
Ni(10)–Ni(12)	2.458(2)		
Ni(1)–C(1)	1.741(15)	Ni(1)–C(1,2)	1.866(14)
Ni(2)–C(2)	1.738(15)	Ni(2)–C(1,2)	1.926(13)
Ni(3)–C(3)	1.737(16)	Ni(2)–C(2,3)	1.890(14)
Ni(4)–C(4)	1.694(19)	Ni(3)–C(2,3)	1.847(14)
Ni(5)–C(5)	1.720(17)	Ni(4)–C(4,5)	1.885(15)
Ni(6)–C(6)	1.750(19)	Ni(4)–C(4,6)	1.897(15)
Ni(7)–C(7)	1.743(23)	Ni(5)–C(4,5)	1.877(15)
Ni(8)–C(8)	1.726(20)	Ni(5)–C(5,6)	1.822(15)
Ni(9)–C(9)	1.687(18)	Ni(6)–C(4,6)	1.884(16)
Ni(10)–C(10)	1.687(16)	Ni(6)–C(5,6)	1.887(16)
Ni(11)–C(11)	1.707(22)	Ni(7)–C(7,8)	1.862(18)
Ni(12)–C(12)	1.715(16)	Ni(7)–C(7,9)	1.843(17)
Ni(8)–C(7,8)	1.860(18)	Ni(8)–C(8,9)	1.844(17)
Ni(9)–C(7,9)	1.864(17)	Ni(9)–C(8,9)	1.895(17)
Ni(10)–C(10,11)	1.837(16)	Ni(11)–C(10,11)	1.878(16)
Ni(11)–C(11,12)	1.853(16)	Ni(12)–C(11,12)	1.844(16)
C(1)–O(1)	1.128(14)	C(1,2)–O(1,2)	1.178(14)
C(2)–O(2)	1.130(14)	C(2,3)–O(2,3)	1.210(14)
C(3)–O(3)	1.144(15)	C(4,5)–O(4,5)	1.174(15)
C(4)–O(4)	1.167(18)	C(4,6)–O(4,6)	1.191(16)
C(5)–O(5)	1.145(16)	C(5,6)–O(5,6)	1.191(16)
C(6)–O(6)	1.144(18)	C(7,8)–O(7,8)	1.190(17)
C(7)–O(7)	1.128(23)	C(7,9)–O(7,9)	1.202(16)
C(8)–O(8)	1.149(19)	C(8,9)–O(8,9)	1.181(17)
C(9)–O(9)	1.169(17)	C(10,11)–O(10,11)	1.209(16)
C(10)–O(10)	1.183(15)	C(11,12)–O(11,12)	1.198(15)
C(11)–O(11)	1.151(21)	C(12)–O(12)	1.132(15)
Ni(1)–C(1)–O(1)	173(1)	Ni(7)–C(7)–O(7)	163(2)
Ni(2)–C(2)–O(2)	175(1)	Ni(8)–C(8)–O(8)	179(2)
Ni(3)–C(3)–O(3)	174(1)	Ni(9)–C(9)–O(9)	176(2)
Ni(4)–C(4)–O(4)	172(2)	Ni(10)–C(10)–O(10)	176(1)
Ni(5)–C(5)–O(5)	172(2)	Ni(11)–C(11)–O(11)	168(2)
Ni(6)–C(6)–O(6)	178(2)	Ni(12)–C(12)–O(12)	175(1)
Ni(1)–C(1,2)–Ni(2)	78(1)	Ni(2)–C(2,3)–Ni(3)	80(1)
Ni(1)–C(1,2)–O(1,2)	142(1)	Ni(2)–C(2,3)–O(2,3)	139(1)
Ni(2)–C(1,2)–O(1,2)	139(1)	Ni(3)–C(2,3)–O(2,3)	138(1)
Ni(4)–C(4,5)–Ni(5)	81(1)	Ni(4)–C(4,6)–Ni(6)	80(1)
Ni(4)–C(4,5)–O(4,5)	140(1)	Ni(4)–C(4,6)–O(4,6)	140(1)
Ni(5)–C(4,5)–O(4,5)	140(1)	Ni(6)–C(4,6)–O(4,6)	139(1)
Ni(5)–C(5,6)–Ni(6)	81(1)	Ni(7)–C(7,8)–Ni(8)	81(1)
Ni(5)–C(5,6)–O(5,6)	143(1)	Ni(7)–C(7,8)–O(7,8)	141(1)
Ni(6)–C(5,6)–O(5,6)	136(1)	Ni(8)–C(7,8)–O(7,8)	137(1)
Ni(7)–C(7,9)–Ni(9)	79(1)	Ni(8)–C(8,9)–Ni(9)	81(1)
Ni(7)–C(7,9)–O(7,9)	142(1)	Ni(8)–C(8,9)–O(8,9)	144(1)
Ni(9)–C(7,9)–O(7,9)	138(1)	Ni(9)–C(8,9)–O(8,9)	136(1)
Ni(10)–C(10,11)–Ni(11)	80(1)	Ni(11)–C(11,12)–Ni(12)	80(1)
Ni(10)–C(10,11)–O(10,11)	142(1)	Ni(11)–C(11,12)–O(11,12)	140(1)
Ni(11)–C(10,11)–O(10,11)	138(1)	Ni(12)–C(11,12)–O(11,12)	140(1)
Br(1)–In(2)–Br(2)	91.00(6)	Br(4)–In(3)–Br(5)	96.35(7)
Br(1)–In(2)–OH	89.9(2)	Br(4)–In(3)–OH	95.3(2)
Br(2)–In(2)–OH	91.1(2)	Br(5)–In(3)–OH	90.3(2)
In(2)–OH–In(3)	137.9(4)		

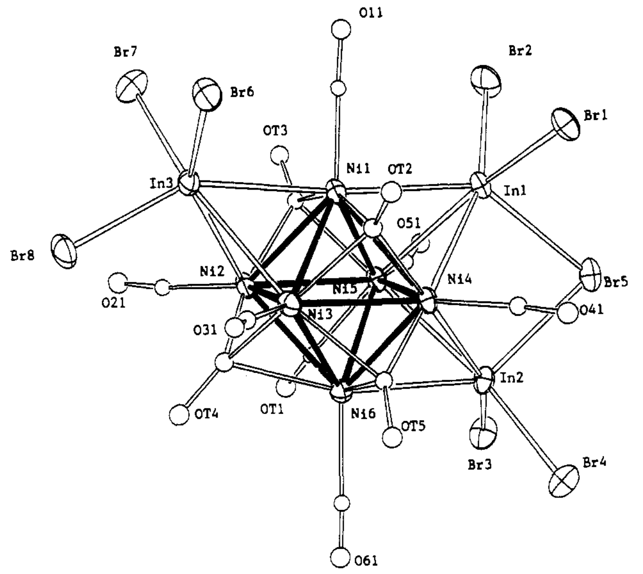

Figure 1. ORTEP drawing of the $[Ni_6(\mu_3\text{-}InBr_3)(\eta^2\text{-}\mu_6\text{-}In_2Br_5)(CO)_{11}]^{3-}$, $[1]^{3-}$, trianion.

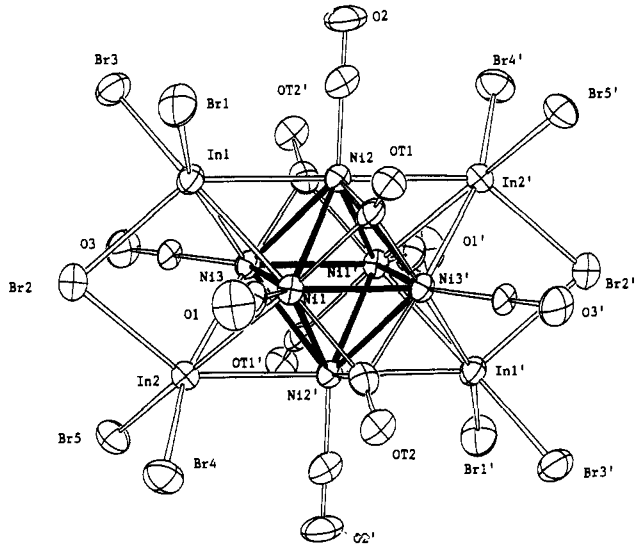

Figure 2. ORTEP drawing of one of the two independent $[Ni_6(\eta^2\text{-}\mu_6\text{-}In_2Br_5)_2(CO)_{10}]^{4-}$, $[2]^{4-}$, tetraanions.

main group element belonging to the third or a subsequent row,[29] such as bromine. This may explain the failure in obtaining a related $[Ni_{12}(\mu_6\text{-}In)(\eta^2\text{-}\mu_6\text{-}In_2Br_5)(CO)_{22}]^{4-}$ compound and suggests the alternate use of indium alkoxides and dialkylamides as potential precursors of such interfragment η^2-μ_6-coordinated $In_2X_4(\mu_2\text{-}X)$ moieties.

Experimental Section

All reactions including sample manipulations were carried out with standard Schlenk techniques under nitrogen in dried solvents. The $[Ni_6(CO)_{12}]^{2-}$ and $[Ni_5(CO)_{12}]^{2-}$ salts were prepared according to literature methods,[12,13,30] and analyses have been performed as follows. The nickel content has been measured by atomic absorption, bromine has been measured by potentiometry, and NEt_4^+ has been gravimetrically determined as the BPh_4^- salt. Infrared spectra were recorded on a Perkin-Elmer 1605 interferometer using CaF_2 cells. Proton NMR spectra were recorded on a Bruker WP-200 spectrometer, and EPR spectral measurements have been carried out on a Varian E-104 spectrometer.

1. Synthesis of $[NEt_4]_3[1]$ and $[NEt_4]_3[1']$. A crystalline sample of $[NEt_4]_2[Ni_6(CO)_{12}]$ (2.45 g) was suspended in THF (30 mL) and treated

---

(29) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984.

(30) Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 5034.

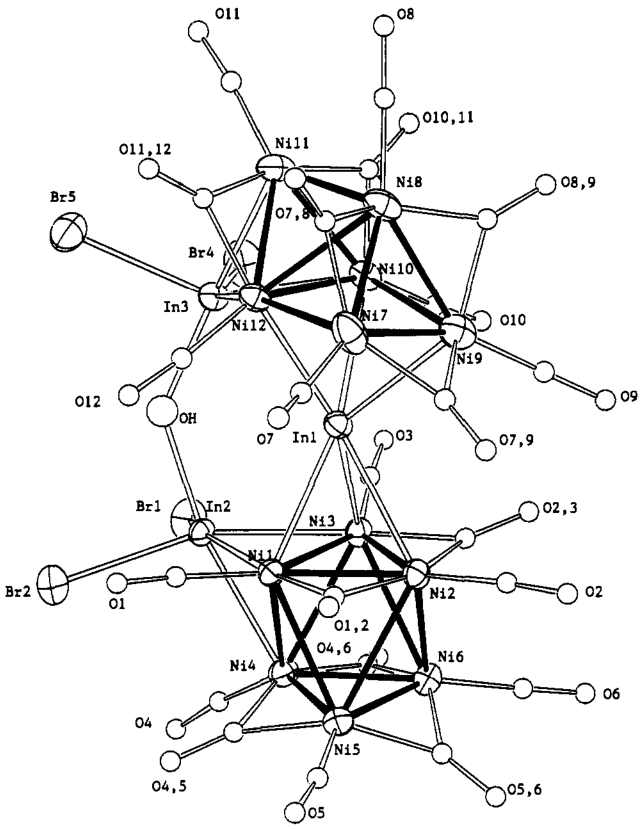

Figure 3. ORTEP drawing of the $[Ni_{12}(\mu_6\text{-In})(\eta^2\text{-}\mu_6\text{-In}_2Br_4OH)(CO)_{22}]^{4-}$, $[3]^{4-}$, tetraanion.

under stirring with 2.74 g of $InBr_3$ in small portions. The resulting suspension was dried in vacuum, and the residue was suspended in methanol (50 mL) and filtered. The precipitate was dissolved in acetone (30 mL) and crystallized by slow diffusion of isopropyl alcohol (80 mL) to give well-shaped orange crystals of $[NEt_4]_3[1]\cdot Me_2CO$. Yield: 4.02 g. [Anal. Found: NEt_4^+,18.5; Ni,16.3; Br, 29.8. Calcd for $[NEt_4]_3[1]\cdot Me_2CO$: NEt_4^+,18.65; Ni,16.83; Br,30.55.]

$[NEt_4]_3[1']$ has been analogously obtained on using $InCl_3$, rather than $InBr_3$.

2. Synthesis of $[NEt_4]_4[2]$. A crystalline sample of $[NEt_4]_3[1]\cdot Me_2CO$ (0.84 g) was dissolved in anhydrous acetone (20 mL), and the solution was treated under stirring with a solution of $[NEt_4]_2[Ni_5(CO)_{12}]$ (0.56 g in 20 mL of acetone). The resulting red solution was filtered. On standing of the solution, well-shaped dark-red crystals of $[NEt_4]_4[2]$ separated out. After 5 days the solvent was siphoned out and the crystals were washed with THF (20 mL) and dried. Yield: 0.37 g. $[NEt_4][2]$ is soluble in acetonitrile, sparingly soluble in THF and acetone, and insoluble in nonpolar solvents. [Anal. Found: NEt_4^+, 20.3; Ni, 13.9; Br, 32.7. Calcd for $[NEt_4]_4[2]\cdot Me_2CO$: NEt_4^+, 21.08; Ni, 14.27; Br, 32.36.]

3. Synthesis of $[NEt_4]_4[3]$. A crystalline sample of $[NEt_4]_2[Ni_6(CO)_{12}]$ (1.51 g) was dissolved in anhydrous THF (20 mL), and the solution was treated with $InBr_3$ in portions up to a 2:1 molar ratio (0.29 g). The resulting red solution was evaporated to dryness. The residue was suspended in methanol, and precipitation was completed by addition of $[NEt_4]Br$ and water. The solid was extracted in the minimum amount of acetone (*ca.* 20 mL) and precipitated by slow diffusion of hexane (30 mL) to give 0.17 g of well-shaped dark-red crystals of $[NEt_4]_4[3]$. These are soluble in acetone and acetonitrile and sparingly soluble or insoluble in THF and nonpolar solvents. [Anal. Found: NEt_4^+, 20.1; Ni, 28.3; Br, 11.8. Calcd for $[NEt_4]_4[3]$: NEt_4^+, 20.63; Ni, 27.93; Br, 12.67.]

4. X-ray Data Collections and Structure Determinations. The crystal data and other experimental details are summarized in Table VII. The diffraction experiments were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The diffracted intensities were corrected for Lorentz, polarization, decay, and absorption (empirical correction)[31] but not for extinction. Scattering factors for all the atomic species and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from ref 32. All structures were solved by direct methods (MULTAN)[33] and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Only for $[NEt_4]_4[2]\cdot Me_2CO$ the hydrogen atoms of the cations were introduced at calculated positions (C–H = 0.95 Å); for the other two structures their contribution to the structure factor calculation was not taken into account. For the noncentrosymmetric $[NEt_4]_3[1]\cdot Me_2CO$ the handedness of the crystal was tested by refining the coordinates of the two enantiomorphs. The refinement yielded significantly different results, the R and R_w factors respectively being 0.047 and 0.051 for the rejected enantiomer and 0.044 and 0.051 for the enantiomer shown in Figure 1.

In $[NEt_4]_4[3]$ some of the ethyl moieties of the cations display carbon atoms bound to nitrogen affected by disorder; a successful model of disorder could not be refined, because the positions occupied by the disordered atoms are too close. As a consequence, the thermal parameters of these atoms are high with respect to those of the subsequent carbon atom of the ethyl group.

The calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[34]

Acknowledgment. We wish to thank Mrs. Petra Kohler and acknowledge the EEC and the MURST for financial assistance.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all non-hydrogen atoms, and bond distances and angles for $[NEt_4]_3[1]\cdot Me_2CO$, $[NEt_4]_4[2]\cdot Me_2CO$, and $[NEt_4]_4[3]$ (60 pages). Ordering information is given on any current masthead page.

---

(31) North, A. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(32) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(33) Germain, G.; Main, P.; Woolfson, M. N. *Acta Crystallogr.* **1971**, *A27*, 368.

(34) B. A. Frenz and Associates, SDP Plus Version 1.0, Enraf-Nonius, Delft, The Netherlands, 1980.