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MIXED CLUSTER CARBONYL ANIONS CONTAINING NICKEL AND COBALT

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A INTRODUCTION

In 1968 the formation of the hexanuclear (pentadecacarbonylhexacobaltate)$^{2-}$ anion from cobalt(II) bis(tetracarbonylcobaltate) was explained by assuming that the presence of a weak ligand with high steric requirements, such as isopropanol, on the cobalt(II) cation favours an internal electron redistribution to $Co_6(CO)_{16}$ Further external reduction of this neutral species by excess $[Co(CO)_4]^-$ anion then results in the $[Co_6(CO)_{15}]^{2-}$ species[1] Since then we have been particularly interested in substituting other cations for the cobalt(II) present in the starting (tetracarbonylcobaltate)$^-$, this procedure is expected to produce both new polynuclear species and to afford a test of the proposed mechanism

We chose the nickel(II) cation because the aqueous normal potentials of the two ions are rather similar[2] ($Ni^{2+}/Ni = -0.250$ V, $Co^{2+}/Co = -0.277$ V) Examples of internal reduction of the nickel(II) cation in carbonylmetallates have been reported for the compounds $[Ni(NH_3)_6][Fe(CO)_4H]_2$ (ref 3) and $[Ni(o\text{-phen})_3][Rh(CO)_4]_2$ (ref 4), but in both cases an anion is present which is a stronger reducing agent than the $[Co(CO)_4]^-$ anion In fact the compounds $[Ni(NH_3)_6][Co(CO)_4]_2$ and $[Ni(o\text{-phen})_3][Co(CO)_4]_2$ which have been prepared[5] by Hieber in 1937, are perfectly stable

B RESULTS AND DISCUSSION

(1) Synthesis and characterisation of the $[NiCo_3(CO)_{11}]^-$ anion

As is the case for the cobalt(II) ion, no reaction is observed between aqueous solutions of nickel(II) chloride and sodium tetracarbonylcobaltate On the other hand, by mixing ethanolic solutions of the latter reagents a brown colour appears together with the rapid formation of two characteristic strong infrared absorptions at 2000 and 1740 cm^{-1} and some $Ni(CO)_4$ (2055 cm^{-1})

This reaction system is not stable, and with time (24 – 48 h) the $Ni(CO)_4$ absorption increases while the other bands decrease and eventually disappear Working with different

$Ni^{2+}/Co(CO)_4^-$ ratios (0 5, 1 0, 1 5, 3 0) shows that the formation of both the 2000–1740 cm^{-1} and the 2055 cm^{-1} absorptions is more rapid when the ratio is higher.

The same reaction is obtained by using the more easily accessible $[Co(EtOH)_x][Co(CO)_4]_2$ The reaction is practically complete in half an hour, with disappearance of the $[Co(CO)_4]^-$ absorption at 1890 cm^{-1} At this point addition of an aqueous solution of tetramethyl- or tetraethylammonium chloride gives a mixture, mainly $[NR_4][NiCo_3(CO)_{11}]$ with a minor amount of $[NR_4]_2[Ni_2Co_4(CO)_{14}]$ Pure salts of the tetranuclear anion are obtained by redissolving in methylformate, in which the hexanuclear tetraalkylammonium salts are insoluble, followed by rapid reprecipitation with diisopropyl ether

Analytical data for the brown crystalline tetramethylammonium salt are reported in Table 1 Although these limited analytical data do not allow a precise determination of the number of carbon monoxide groups, it has been possible to confirm the formula $[NiCo_3(CO)_{11}]^-$ by studying the reaction with carbon monoxide In tetrahydrofuran (THF) this reaction is very rapid (1 atm, 25°), and can be carried out in an hypodermic syringe, a procedure which allows both the progressive addition of small amounts of carbon monoxide and the sampling of the solution for infrared spectra The amount of gas absorbed (7–7 5 mole) and the final IR spectrum are consistent with the stoichiometry

$$3[NiCo_3(CO)_{11}]^- + 7CO \xrightarrow[1\ atm,\ 25°]{THF} 3\,Ni(CO)_4 + 2\,Co^{2+} + 7\,[Co(CO)_4]^- \qquad (1)$$

while 10 moles are expected for a $[NiCo_3(CO)_{10}]^-$ anion, and 4 moles for $[NiCo_3(CO)_{12}]^-$

The $[NiCo_3(CO)_{11}]^-$ species contains 60 valence electrons, a number which is characteristic of the tetranuclear carbonyl clusters[6]. The infrared spectrum of the brown THF solution is shown in Fig 1, the presence of absorptions at 2000, 1865–1845 and 1740 cm^{-1} is in agreement with terminal, simple bridging and face bridging carbonyl groups. The position of the strong absorption at 2000 cm^{-1} agrees with the presence of a negative charge for the four metal atoms[6]. A tentative structure is similar to that found for the $[Fe_4(CO)_{13}]^{2-}$ anion[7], with the apical $Fe(CO)_3$ group substituted by a Ni(CO) group. In this structure the nickel atom can be considered to be at the centre of a tetrahedron of three nickel–cobalt bonds and one nickel–carbon bond

(ii) Synthesis and characterisation of the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion [8]

When the original brown solution obtained from nickel(II) chloride and cobalt(II) bis(tetracarbonylcobaltate) is warmed under vacuum and then evaporated to dryness instead of being treated with an aqueous tetraalkylammonium halide, new strong infrared bands at 1977, 1958 and 1790 cm^{-1} are observed. This new species can be easily isolated after dissolving it in water, filtering and saturating with potassium bromide The salt $K_2[Ni_2Co_4(CO)_{14}].6\,H_2O$ is obtained as dark red crystals in about 60% yield from the calculated stoichiometry

TABLE 1

Analytical data for $[NiCo_3(CO)_{12}]^-$ and $[Ni_2Co_4(CO)_{14}]^{2-}$ salts

Salt	Cation %		Nickel %		Cobalt %		CO %		Cat/Ni/Co/CO
	Calc	Found	Calc	Found	Calc	Found	Calc	Found	
$[N(CH_3)_4][NiCo_3(CO)_{12}]$	11 98	12 75	9 50	9 9	28 63	28 95	49 87	51	1 0/1 0/2 9/11 3
$K_2[Ni_2Co_4(CO)_{14}]\,6H_2O$	8 41	8 5	12 60	12 5	25 30	24 5	42 08	42 5	1 0/1 0/1 9/7 0
$Cs_2[Ni_2Co_4(CO)_{14}]$	26 29	26 05	11 61	11 2	23 30	22 6	38 78	38 4	1 0/1 0/2 0/7 0
$[N(C_2H_5)_4]_2[Ni_2Co_4(CO)_{14}]$ $2H_2O$	17 43	17 5	7 87	8 15	15 80	15 25			1 0/1 0/1 9
$[N(C_4H_9)_4]_2[Ni_2Co_4(CO)_{14}]$	39 38	38 9	9 55	9 85	19 17	18 95			1 0/1 0/2 0

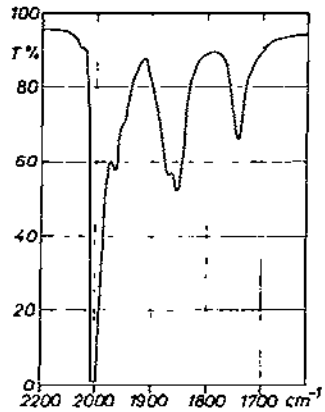

Fig 1 IR spectrum of $NMe_4[NiCo_3(CO)_{14}]$ in THF

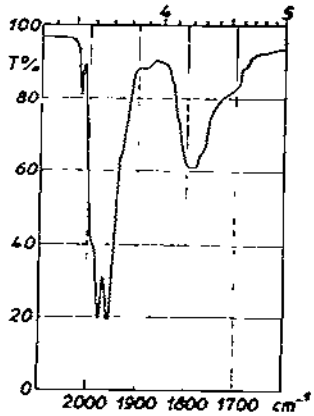

Fig 2 IR spectrum of $K_2[Ni_2Co_4(CO)_{14}]$ in THF

$$11\,NiCl_2 + 14\,[Co(CO)_4]^- \rightarrow 2\,[Ni_2Co_4(CO)_{14}]^{2-} + 7\,Ni(CO)_4 + 6\,CoCl_2 + 10\,Cl^- \quad (2)$$

The corresponding caesium and tetraalkylammonium salts are obtained from the potassium salt by a double exchange reaction in water The analytical data are reported in Table 1, and they establish the formula $\{[Cat]\,[NiCo_2(CO)_7]\}_n$ which corresponds to 14 33 valence electrons for each metal atom or 86 electrons for six metal atoms

All the hexanuclear carbonyl clusters known at the present moment (see Table 2) share 86 electrons in the valence shell, and there is a close relationship between this electronic structure and the octahedral geometry Therefore the anion can be formulated as octahedral $[Ni_2Co_4(CO)_{14}]^{2-}$ This assignment is reinforced by the similar solubilities of the alkali salts of the doubly charged $[Co_6(CO)_{15}]^{2-}$ anion [1] both potassium salts are soluble in water but they can be precipitated by saturation with potassium bromide, and both caesium salts are much less water-soluble

In solution the anion $[Ni_2Co_4(CO)_{14}]^{2-}$ is reddish-brown and the infrared spectra of the different salts present only minor differences in the carbonyl stretching region, the spectrum of the potassium salt in THF is presented in Fig 2 The terminal carbonyl group absorption at 1977 and 1958 cm^{-1} is consistent with the presence of a negative charge for three metal atoms [6], while the absorption at 1790 and 1740 cm^{-1} is in agreement with the presence of bridging carbonyl groups The anion is probably isostructural with one of the isomeric forms of the $[Co_6(CO)_{14}]^{4-}$ anion [18] but a close comparison of the infrared spectra is not possible due to the differing negative charges and the related differing association in solution

In THF solution the hexanuclear $[Ni_2Co_4(CO)_{14}]^{2-}$ anion reacts easily with carbon monoxide (1 atm, 25°) After addition of 7–8 moles of carbon monoxide only absorptions due to $Ni(CO)_4$ and $[Co(CO)_4]^-$ are observed, viz

TABLE 2

Hexanuclear carbonyl clusters

Cluster	References		
	Preparation	IR	X-ray
$[Fe_6(CO)_{16}C]^{2-}$	9	9	9
$Ru_6(CO)_{17}C$	10	10	11
$Ru_6(CO)_{14}(arene)C$	10	10	12
$Ru_6(CO)_{18}H_2$	13	13	13
$Co_6(CO)_{16}$	14	15	16
$[Co_6(CO)_{15}]^{2-}$	1	1	17
$[Co_6(CO)_{14}]^{4-}$	18	18	19
$Co_2Rh_4(CO)_{16}$	20 21	20 21	
$Rh_6(CO)_{16}$	22 23	15 24	25
$Rh_6(CO)_{16-n}(PR_3)_n$	26,27	26 27	
$[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, SCN, COOR, CONHR)	28	28	34
$[Rh_6(CO)_{15}]^{2-}$	21	21 29	
$[Rh_6(CO)_{14}]^{4-}$	30	30	
$[Rh_{12}(CO)_{30}]^{2-}$ [a]	31	31	32
$[Rh_7(CO)_{16}]^{3-}$ [b]	30	30	33
$Ir_6(CO)_{16}$	29	29	
$[Ir_6(CO)_{15}]^{2-}$	29	29	

[a] 85 electrons and one metal–metal bond for 6 metal atoms
[b] 84 electrons for 6 metal atoms, heptanuclear

$$3\,[Ni_2Co_4(CO)_{14}]^{2-} + 22\,CO \rightarrow 6\,Ni(CO)_4 + 10[Co(CO)_4]^- + 2\,Co^{2+} \qquad (3)$$

Other reactions confirm that the most important characteristic of this hexanuclear anion is its ease of breaking into simpler products. For example, the reaction with triphenylphosphine in THF requires about 6 moles of ligand and gives a complex mixture from which $Co_2(CO)_6(PPh_3)_2$, $Ni(CO)_2(PPh_3)_2$ and the $[Co(CO)_3(PPh_3)]^-$ anion have been isolated and identified by comparison of the infrared spectra[35–37].

A similar fragmentation of the cluster is observed on reaction both with mild oxidising and strong reducing agents, two types of reaction in which we were particularly interested, because they have been used [14,18] to transform the analogous anion $[Co_6(CO)_{15}]^{2-}$ into the related hexanuclear clusters $Co_6(CO)_{16}$ and $[Co_6(CO)_{14}]^{4-}$. By cautious reaction with iron(III) chloride in aqueous conditions we were able to isolate only $Co_4(CO)_{12}$, while the reaction with iodine in THF gave first an unidentified product which had carbonyl

stretching absorptions at about 1995 and 1955 cm^{-1}, and which therefore could not be the desired uncharged species After addition of about only 1/3 of the amount of iodine necessary for the complete oxidation of all the metal atoms present in the cluster the infrared spectrum agreed with the reaction

$$2\,K_2[Ni_2Co_4(CO)_{14}] + 5\,I_2 \rightarrow 3\,Ni(CO)_4 + 4\,K[Co(CO)_4] + Ni\,I_2 + 4\,Co\,I_2 \qquad (4)$$

In ethanolic solution nickel(II) chloride also behaved as an oxidant, with formation of $Ni(CO)_4$ and of a black unidentified solid

Sodium in THF reacted slowly giving rise to the $[Co(CO)_4]^-$ anion and $Ni(CO)_4$, while in ethanol there was no reaction with sodium tetracarbonylcobaltate The addition of hydrochloric acid in methanol failed to give any new species, we were only able to observe some formation of the $[NiCo_3(CO)_{11}]^-$ anion (see later)

(iii) Study of the formation and interconversion of the cluster anions

The formation of the $[NiCo_3(CO)_{11}]^-$ anion can be reasonably assumed to take place through the steps

$$[Ni(EtOH)_6][Co(CO)_4]_2 + [Co(CO)_4]^- \rightleftharpoons \{Ni(EtOH)_3[Co(CO)_4]_3\}^- + (x-y)\,EtOH$$

$$\downarrow$$

$$[NiCo_3(CO)_{11}]^- + CO + y\,EtOH \qquad (5)$$

The intermediate addition product would be analogous to the well known addition product which has been independently isolated by several authors [38-40] in the reaction between $Hg[Co(CO)_4]_2$ and $[Co(CO)_4]^-$ anion viz

$$Hg[Co(CO)_4]_2 + [Co(CO)_4]^- \rightleftharpoons \{Hg[Co(CO)_4]_3\}^- \qquad (6)$$

In fact we have confirmed that this is a reaction which can be reversed by simple solvent effects e g water will decompose the addition product and will leave insoluble $Hg[Co(CO)_4]_2$ while toluene will also bring about a similar decomposition leaving insoluble $Na[Co(CO)_4]$ The formation of the mixed tetranuclear anion is similarly inhibited by water, and in this case it seems probable that the first addition step is hindered The strong effect of the $Ni^{2+}/Co(CO)_4^-$ ratio on the synthesis of the $[NiCo_3(CO)_{11}]^-$ anion is in agreement with scheme (5) if competition between the different cations present in solution toward the $[Co(CO)_4]^-$ anion is assumed

When a solution of the tetramethyl- or tetraethylammonium salt of the $[NiCo_3(CO)_{11}]^-$ anion in EtOH is left standing, a slow precipitation of the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion, together with formation of the characteristic infrared absorption bands of the $[Co(CO)_4]^-$ anion and of $Ni(CO)_4$ (minor amounts), is observed The reaction is represented by the equilibria

$$2\,[NiCo_3(CO)_{11}]^- \rightleftharpoons [Ni_2Co_4(CO)_{14}]^{2-} + Co_2(CO)_8 \quad (7)$$

$$3\,Co_2(CO)_8 + x\,B \rightleftharpoons 2\,[CoB_x]\,[Co(CO)_4]_2 + 8\,CO \quad (8)$$

Tetracarbonylcobaltate anion is the product expected from the decomposition of $Co_2(CO)_8$ in the presence of Lewis basic solvents, while the small amount of $Ni(CO)_4$ can be accounted for by the reaction between the carbon monoxide set free in reaction (8) and the mixed clusters. Equilibria (7) and (8) also allow rationalisation of the synthesis, because it seems reasonable that during the warming and evaporation of the original $[NiCo_3(CO)_{11}]^-$ solution the $Co_2(CO)_8$ in equilibrium is continously removed through decomposition due to reaction (8).

Reaction (7) can be easily reversed, for instance, by addition at 0° in isopropanol–toluene of one mole of $Co_2(CO)_8$ to one mole of $K_2[Ni_2Co_4(CO)_{14}]$ immediate transformation into the $[NiCo_3(CO)_{11}]^-$ anion is observed, as shown in Fig. 3(a). The simultaneous formation of minor amounts of $Ni(CO)_4$ and $[Co(CO)_4]^-$ anion are probably due to carbon monoxide from the decomposition of $Co_2(CO)_8$, although this reaction is slow at 0°. That the main reaction is not due to the carbon monoxide set free in the decomposition of $Co_2(CO)_8$ is shown by comparison with Fig. 3(b), in which the infrared spectrum is given for the reaction between the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion and carbon monoxide at the point where the hexanuclear species disappears. In fact, at this point the complete disappearance of the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion requires 5 moles of carbon monoxide and corresponds to the stoichiometry

$$[Ni_2Co_4(CO)_{14}]^{2-} + 5\,CO \rightarrow Ni(CO)_4 + [Co(CO)_4]^- + [NiCo_3(CO)_{11}]^- \quad (9)$$

Reactions between a carbonylmetallate and a metal carbonyl in which there is redistribution of the negative charge on a larger number of metal atoms such as the reverse of reaction (7), are fairly common. Examples of such reactions from the work of Ruff [41] are

$$Fe_2(CO)_9 + [Mn(CO)_5]^- \rightarrow [Fe_2Mn(CO)_{12}]^- + 2\,CO \quad (10)$$

$$Mn_2(CO)_{10} + [Cr_2(CO)_{10}]^{2-} \rightarrow 2\,[MnCr(CO)_{10}]^- \quad (11)$$

In all these cases the driving force is probably the tendency to increase the average energy of the metal carbon bonds through a more uniform distribution of the negative charges and greater back-donation.

It is clear that the synthesis of the hexanuclear $[Ni_2Co_4(CO)_{14}]^{2-}$ cluster takes place through the intermediate tetranuclear $[NiCo_3(CO)_{11}]^-$ anion. This synthesis can be summarised as

$$2\,M_3 + 2\,M^- \rightarrow 2\,M_4^- \rightleftharpoons M_6^{2-} + M_2 \quad (12)$$

The initial hypothesis of a process analogous to that postulated for the synthesis of the $[Co_6(CO)_{15}]^{2-}$ anion, e.g.

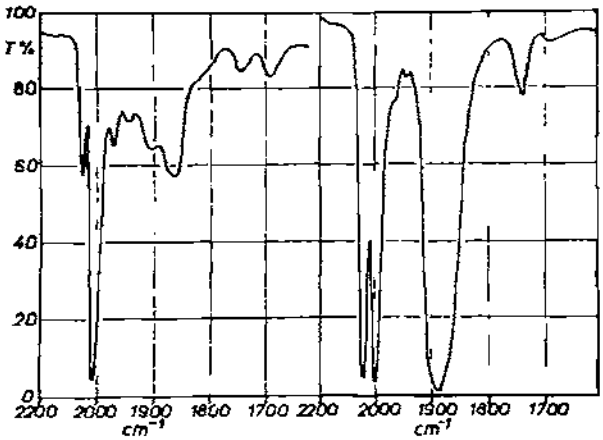

Fig 3 IR spectra of the solutions obtained from (a) $K_2[Ni_2Co_4(CO)_{14}]$ and $Co_2(CO)_8$ in isopropanol-toluene at 0° C, and (b) $Cs_2[Ni_2Co_4(CO)_{14}]$ and CO (5 mole) in THF

$$2\,M_3 \rightleftharpoons M_6 \xrightarrow{\text{reduction}} M_6^{2-} \qquad (13)$$

is therefore incorrect Moreover the present results show that mechanism (12) should also be considered for the synthesis of the $[Co_6(CO)_{15}]^{2-}$ anion itself In fact in this case we have reported [18] the isolation of an unstable tetranuclear species $[Co_4(CO)_{11-12}]_n^{n-}$ which may be a possible intermediate analogous to $[NiCo_3(CO)_{11}]$ Further study of this problem is in progress

EXPERIMENTAL

All the solvents were carefully purified and saturated with nitrogen before use Infrared spectra were recorded on a Perkin–Elmer 457 instrument using calcium fluoride cells Analyses were carried out as previously [1,18], nickel and cobalt were separated using dimethylglyoxime in the presence of ammonium salts

(1) Preparation of [NMe$_4$][NiCo$_3$(CO)$_{11}$]

$Co_2(CO)_8$ (6 7 g) and anhydrous ethanol (25 ml) were reacted under vacuum in a 2 litre flask at 30–50° for about 2 h, until the infrared spectrum showed the complete disappearance of $Co_2(CO)_8$ The resulting dark red solution was treated with a 0 646 *M* solution of $NiCl_2$ in anhydrous ethanol (40 ml, $Ni^{2+}/Co(CO)_4^- = 1$), previously prepared from ethanol and $NiCl_2 \cdot 6H_2O$ by azeotropic distillation in the presence of benzene. After half an hour a solution of $[N(CH_3)_4]Cl$ (4 5 g) in water (250 ml) was slowly added and the brown precipitate was separated by filtration, washed with water and vacuum dried

Extraction of this precipitate with methyl formate (35 ml) and addition of diisopropyl ether (60 ml) to the resulting solution gave the pure product as fine brown crystals (about 2 g) The residual original solid was soluble in acetonitrile and the IR spectrum showed it to consist of $[NMe_4]_2[Ni_2Co_4(CO)_{14}]$

The corresponding tetraethylammonium salt has been obtained similarly Both the tetramethyl and tetraethylammonium salts are soluble in THF and ethanol

(ii) Preparation of $K_2[Ni_2Co_4(CO)_{14}]\ 6H_2O$

An ethanolic solution of $[Co(EtOH)_x][Co(CO)_4]_2$ prepared from $Co_2(CO)_8$ (14 9 g) as in (*i*) was reacted with a 0 646 *M* solution of $NiCl_2$ in ethanol (90 5 ml, $Ni^{2+}/Co(CO)_4^- = 1$). The mixture was warmed in a static vacuum for 12 h and then evaporated to dryness The residual black solid was dissolved in water (60 ml) and the solution was separated by filtration and then saturated with solid KBr (40 g) After 2 h the dark red crystalline precipitate was separated by filtration washed with an aqueous saturated solution of KBr, and vacuum dried The pure product was separated from the KBr by dissolving it in THF, filtering and evaporating (yield 5 g, 64%) It was soluble in acetone and ethanol, and on heating it decomposed at about 165–190°

(iii) Preparation of the caesium and tetraalkylammonium salts of the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion

These salts were all obtained by double exchange reactions in aqueous solution. The caesium salt could be recrystallised from acetone–water, and the tetrabutylammonium salt from acetone–isopropanol

The caesium salt was soluble in THF, ethanol, acetone and CH_3CN, on heating it decomposed at about 165–190°

The tetraethylammonium salt was insoluble in ethanol and THF, but dissolved in acetone and CH_3CN

The tetrabutylammonium salt was soluble in THF and acetone

(iv) Reaction between $K_2[Ni_2Co_4(CO)_{14}]$ and PPh_3

A solution of $K_2[Ni_2Co_4(CO)_{14}]\ 6H_2O$ (285 6 mg) in THF (10 ml) was reacted with increasing amounts of PPh_3 (910 mg) in THF (4 ml) using a microburette After addition of about 6 mole PPh_3 per mole, the IR spectrum did not show any further change, and showed absorption bands at 1998, 1938, 1925, 1885, 1840 and 1815 cm^{-1} The orange precipitate was separated by filtration, and had IR absorption bands at 1966w, 1950sh, 1942s, 1985w and 1880w cm^{-1} (Nujol mull) identical with those of an authentic sample of $Co_2(CO)_6(PPh_3)_2$ (ref. 35) Solid $[NEt_4]Br$ was added to the solution, and the THF was evaporated Benzene extraction gave a product which had strong IR absorption at 1998 and 1940 cm^{-1}, identical with that of an authentic sample of $Ni(CO)_2(PPh_3)_2$ (ref 36)

Acetonitrile extraction gave a solution which had strong IR absorption bands at 1922 and 1835 cm^{-1}, identical with those observed on reduction of $Co_2(CO)_6(PPh_3)_2$ with sodium metal [37]

(v) Reaction between $K_2[Ni_2Co_4(CO)_{14}]$ and iodine

The reaction was carried out in a way similar to that described in (iv) Carbon monoxide was liberated only after addition of about 2 5 mole I_2 per mole At this point the brown solution became brilliant green and the IR spectrum showed the presence of only $Ni(CO)_4$ and the $[Co(CO)_4]^-$ anion

(vi) Reaction between $Cs_2[Ni_2Co_4(CO)_{14}]$ and carbon monoxide

A solution of $Cs_2[Ni_2Co_4(CO)_{14}]$ (81 mg) in THF (5 ml) was prepared in a hypodermic syringe, and carbon monoxide (2 ± 0 1 ml, about 1 0 mole per mole salt) was added After each addition the IR spectrum of the solution was recorded The spectrum obtained after addition of 10 ml of carbon monoxide is shown in Fig 3(b).

(vii) Reaction between $[NMe_4][NiCo_3(CO)_{11}]$ and carbon monoxide

The reaction was carried out as reported in (vi) starting from a THF solution (15 ml) of salt (139 mg) It required 2 3–2 5 mole gas per mole

(viii) Reaction between $K_2[Ni_2Co_4(CO)_{14}]$ and $Co_2(CO)_8$

A solution of $K_2[Ni_2Co_4(CO)_{14}].6H_2O$ (218 mg, $2\ 3 \times 10^{-5}$ mole) in isopropanol (15 ml) was reacted at 0° with a solution of resublimed $Co_2(CO)_8$ (80 mg, $2\ 3 \times 10^{-5}$ mole) in toluene (2 75 ml) and the IR spectrum was recorded after 5 min (Fig 3(a))

SUMMARY

Reaction between nickel(II) chloride and sodium or cobalt(II) tetracarbonylcobaltate (−I) in anhydrous ethanol gives the tetranuclear anion $[NiCo_3(CO)_{11}]^-$, which has been characterised as the tetramethylammonium salt. In solution this tetranuclear anion transforms slowly into the hexanuclear anion $[Ni_2Co_4(CO)_{14}]^{2-}$ and $Co_2(CO)_8$, this is a reversible reaction The hexanuclear anion has been characterised as alkali (K, Cs) and tetraalkylammonium (NEt_4, NBu_4) salts Both these cluster anions react rapidly with carbon monoxide giving $Ni(CO)_4$ and the $[Co(CO)_4]^-$ anion. The reactions of the hexanuclear anion with PPh_3 and iodine have also been investigated.

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