Inorganica Chimica Acta, 31 (1978) 165–169
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σ-Acetylides of Ni(II), Pd(II), and Pt(II)

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Received February 22, 1978

Several stable alkynyl complexes $K_2[M(C\equiv CR)_4]$ [M = *Ni(II), Pd(II), Pt(II);* $R = -CH_2-C(Ph)_2(CN), -CH_2-C(CH_3)_2(CN)$] *have been obtained. The IR spectra of these complexes have been studied and an attempt to assign* $\nu(M-C)$ *stretching frequencies has been made. Study of the thermal decomposition by thermal analysis (DTA) and other methods has allowed the relative thermal stabilities of these compounds to be established. In some cases thermal decomposition pathways were also investigated.*

Introduction

The first alkynyl Ni(II) complexes of formula $M_2[Ni(C\equiv CR)_4]$ were described by Nast and Vester [1, 2]. These alkynyl complexes are decomposed by water, acids and alkalis with formation of brown products. They are pyrophoric in air, and at room temperature give rise to substances which decompose even under dry nitrogen. On account of these properties it is very difficult to handle these acetylenic derivatives and so information on these compounds is, by and large, limited to the preparative methods. Some IR spectroscopic data is available, but this refers, almost exclusively, to the $\nu(C\equiv C)$ stretching band. No thermal analysis studies have been reported.

The Pd(II) alkynyl complexes are the least studied of the nickel triad. The only compounds referred to in the literature, of the type $M_2[Pd(C\equiv CR)_4]$, are those described by Nast and Hörl [3] (M = Ba, R = H, C_6H_5). Wallenwein [4] described a palladium complex with formula $K_2[Pd(o\text{-DEB})_2]$ (o-DEB = o-phenilenbis-ethinylide).

In contrast to the Pd(II) species, Pt(II) derivatives have been the most studied of this group of metals. Complexes of the type $K_2[Pt(C\equiv CR)_4]$ were first prepared by Nast and Heinz [5]. Both barium tetraalkynylpalladates(II) and potassium tetraalkynylplatinates(II) have a greater thermal stability than the Ni(II) analogues, but are still not sufficiently stable to enable an exhaustive study of them to be made.

Taking account of the unstable character of the Ni(II), Pd(II), and Pt(II) tetraalkynyl compounds, we have attempted to find ligands whose properties are such as to allow sufficiently stable compounds to be obtained. Since bulky ligands can produce steric hindrance, inhibiting nucleophilic attack on the potentially vacant coordination sites of the metal, the ligands 2,2-diphenyl-4-pentyne-nitrile (HDPPN) and 2,2-dimethyl-4-pentyne-nitrile (HDMPN) were chosen. Accordingly, Ni(II), Pd(II), and Pt(II) alkynyls with these ligands have been prepared.

The new compounds have been analysed and characterised by IR spectroscopy. An attempt has been made to assign vibration frequencies of the M–C bonds, of which no data exists in the literature. A comparative study with the different metals and acetylide ligands that form each of the derivatives has been carried out. A study of the differential thermal analysis curves has been undertaken so as to observe the various stages of thermal decomposition of these metallic derivatives.

Experimental

All reactions were carried out in a vacuum apparatus suitable for liquid ammonia syntheses and similar to that described by Nast and Roos [6], allowing reactions to be carried out in complete absence of air and moisture.

To analyse the metal content, the samples were treated with H_2O_2–H_2SO_4 for the Ni(II) complexes, with $HClO_4$–HNO_3 for the Pd(II) complexes, and with HCl–HNO_3 for the Pt(II) species. Nickel was determined by complexometry, while gravimetric analysis was used for palladium and platinum. Potassium was determined by emission photometry using a UNICAM SP90A atomic absorption spectrophotometer. Carbon and hydrogen analyses were carried out with a COLEMAN model 33 semi-micro analyser.

A PERKIN-ELMER 325 spectrophotometer was used to record IR spectra. Samples were prepared in KBr discs or in Nujol using CsI cells. Differential thermal analysis was performed with a DU PONT 990 thermal analyser with a static air atmosphere and a

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dynamic nitrogen atmosphere. The heating rate was 10 °C/min, the sensitivity 0.25 °C/in, and a chromel–alumel thermocouple was employed. The products of thermal decomposition were identified by X-ray diffraction analysis (powder method) using a PHILIPS PW1012 X-ray apparatus, a 114.83 mm diameter powder camera, and CuK$_\alpha$ radiation filtered by nickel. Measurements of magnetic susceptibility were determined by Gouy's [7] method. Because of the very low solubility of the compounds in common organic solvents no NMR spectra could be obtained.

2,2-Dimethyl-4-pentyne-nitrile (HDMPN) was obtained as described by Stevens, Du Pree and Wentland [8]. 2,2-Diphenyl-4-pentyne-nitrile (HDPPN) was prepared by the method described by Salmon-Legagneur and Brunet [9], but some changes were introduced such as the use of propargyl bromide which enabled a higher yield to be obtained. $K_2[Ni(CN)_4]$, $[Pd(CN)_2en]$ and $K_2[Pt(SCN)_4]$ were prepared by literature methods [10–11]. Commercial ammonia was purified by condensation over sodium.

$K_2[Ni(DPPN)_4]\cdot NH_3$

A filtered solution containing 0.31 g (1.29 mmol) of $K_2[Ni(CN)_4]$ was added to a solution of 1.39 g (5.18 mmol) of the potassium salt of HDPPN in liquid ammonia contained in a reaction vessel fitted with a G-4 fritted disc. On mixing the two ammonia solutions, a solid precipitate was formed, which was isolated by filtration, washed several times with liquid ammonia, and pumped on for six hours in a high vacuum to give a yellow powder. The product is diamagnetic, very stable at temperatures below 82 °C. It remains unchanged if left in a N_2 atmosphere for indefinite periods. In the ordinary atmosphere it decomposes very slowly. *Anal.* Found: C, 77.3, H, 4.6; Ni, 5.6; K, 7.5. $K_2NiC_{68}H_{48}N_4\cdot NH_3$ calcd.: C, 77.2; H, 4.5; Ni, 5.6; N, 7.4%.

$K_2[Ni(DMPN)_4]\cdot NH_3$

The method of preparation is analogous to that described above.

The product is a diamagnetic brown solid. On exposure to air it transforms to a substance slippery to the touch, but if kept in a nitrogen atmosphere remains unaltered. It is stable below 55 °C. *Anal.* Found: C, 64.1; H, 6.9; Ni, 11.2; K, 14.8. $K_2NiC_{28}H_{32}N_4\cdot NH_3$ calcd.: C, 64.7; H, 6.7; Ni, 11.3; K, 15.1%.

$K_2[Pd(DPPN)_4]$

A solution containing 0.38 g (1.74 mmol) of $[Pd(CN)_2en]$ in liquid ammonia was added to another solution containing 1.78 g (6.96 mmol) of KDPPN contained a vessel fitted with G-4 fritted disc. The reaction mixture was held at –70 °C for 48 hours, after which, a yellow-orange powdery solid was observed which retained varying amounts of ammonia. The product is diamagnetic, stable in air, and has good thermal stability, not decomposing below 150 °C with complete decomposition not taking place below 495 °C. *Anal.* Found: C, 70.6; H, 4.9; Pd, 9.0; K, 6.5. $K_2PdC_{68}H_{48}N_4$ calcd.: C, 70.8; H, 4.9; Pd, 9.3; K, 6.8%.

$K_2[Pd(DMPN)_4]$

This compound was prepared in the same way as the previous compound.

The product is a diamagnetic brown solid, which on losing ammonia becomes paler until it adopts an ochre colour. It is stable in air, no change taking place below 75 °C. *Anal.* Found: C, 49.2; H, 6.2; Pd, 18.6; K, 13.4. $K_2PdC_{28}H_{32}N_4$ calcd.: C, 49.1; H, 6.1: Pd, 18.7; K, 13.7%.

$K_2[Pt(DPPN)_4]$

A filtered solution containing 0.46 g (0.92 mmol) of $K_2[Pt(SCN)_4]$ was added to a solution of KDPPN [0.84 g (3.68 mmol)] in liquid ammonia in a reaction vessel fitted with a G-4 fritted disc. After maintaining the reaction mixture at –74 °C for 24 hours a yellow precipitate was observed, which was filtered and washed five times with liquid ammonia. Filtration was carried out at a low temperature so as to prevent the product dissolving.

The product is a diamagnetic yellow solid, stable in air. It does not change below 185 °C and complete decomposition does not take place below 540 °C. *Anal.* Found: C, 68.6; H, 4.0; Pt, 16.1; K, 6.2. $K_2PtC_{68}H_{48}N_4$ calcd.: C, 68.4; H, 4.0; Pt, 16.4; K, 6.6%.

$K_2[Pt(DMPN)_4]$

The preparation is similar to that of the previous compound.

The product is a diamagnetic solid, stable in air below 75 °C. *Anal.* Found: C, 48.1; H, 4.5; Pt, 27.2; K. 11.3. $K_2PtC_{28}H_{32}N_4$ calcd.: C, 48.2; H, 4.6; Pt, 27.3; K, 11.2%.

Results and Discussion

All the new Ni(II), Pd(II), and Pt(II) complexes are four coordinate and their diamagnetic behaviour confirms a square-planar configuration around the metal atom.

The tetracoordinated Ni(II) complexes tend to bond other molecules such as water or ammonia. In the first case, the breaking of the M–C bond by reaction with water begins by coordination of the water molecule to the metal atom and the complex decomposes [12]. However, both the $K_2[Ni(DPPN)_4]$ and the $K_2[Ni(DMPN)_4]$ complexes are hydrophobic although the latter, once evacuated, hydrolyzes slowly. The high stability to hydrolysis exhibited by $K_2[Ni(DPPN)_4]$ may be caused by the large size of

TABLE I. Stretching Frequencies of Ni(II), Pd(II) and Pt(II) Compounds.

Compound	ν(C≡C) (cm^{-1})	ν(C≡N) (cm^{-1})	ν(M–C) (cm^{-1})
$K_2[Ni(DPPN)_4]$	2036 m	2238 m	564 m
$K_2[Ni(DMPN)_4]$	2020 w	2238 w 2165 m	510 w
$K_2[Pd(DPPN)_4]$	2037 w	2238 m	576 m 580 m 583 m
$K_2[Pd(DMPN)_4]$	2020 w	2224 m	590 m
$K_2[Pt(DPPN)_4]$	2038 w	2238 m	582 w
$K_2[Pt(DMPN)_4]$	2022 vw	2224 m	600 w

TABLE II. Initial and Final Temperatures of Thermal Decomposition.

Compound	$T_{initial}$ (°C) and type		T_{final} (°C)
	Air	Nitrogen	
$K_2[Ni(DPPN)_4]$	80 exo	80 endo	480
$K_2[Pd(DPPN)_4]$	150 exo	150 endo	495
$K_2[Pt(DPPN)_4]$	185 endo	185 endo	540
$K_2[Ni(DMPN)_4]$	55 endo	55 endo	410
$K_2[Pd(DMPN)_4]$	75 exo	75 endo	440
$K_2[Pt(DMPN)_4]$	75 exo	75 exo weak	445

the organic moieties which prevents attack by external agents. The DMPN ligand has a smaller size and thus the $K_2[Ni(DMPN)_4]$ complex will tend to surround itself by ammonia molecules, but the partial loss of these by evacuation would render the metal more vulnerable to the action of water.

Infrared Spectra

The IR spectra of these complexes both in the HDMPN and HDPPN derivatives show C≡C stretching frequencies at lower values than in the starting acetylenic compounds. In the Ni(II), Pd(II), and Pt(II) complexes with HDPPN, the shift of this frequency towards lower values is approximately equal for all of them (84 cm^{-1}). The same occurs for the HDMPN derivatives (100 cm^{-1}). In the latter the ν(C≡C) frequency is lower than in the HDPPN derivatives. From the essentially constant value of the stretching frequency ν(C≡C) for the complexes of the three metals a strengthening of the σ bond and a growing participation of π bonding on going from Ni(II) to Pt(II) can be inferred.

There is no reported information on the vibration modes associated with the M–C≡ [M = Ni(II), Pd(II), Pt(II)] bonds. Data on only the corresponding tetracyano complexes can be found, and even for these there are inconsistencies in some assignments [13, 14]. In general it is considered that δ(M–C) < ν(M–C) and that the ν(M–C) stretching frequency is found in the 500–600 cm^{-1} region. In the compounds studied this frequency is found in this range and varies in the order

$$\nu(\text{Ni–C}) < \nu(\text{Pd–C}) < \nu(\text{Pt–C})$$

In the absence of a π contribution to the M–C bond, this variation would seem to indicate a growing strength of the σ M–C bond from Ni(II) to Pt(II). On the other hand, a π component to the bond is also expected to increase on going from Ni(II) to Pt(II).

All the IR data are given in Table I.

Thermal Decomposition

The DTA curves of the compounds were performed by heating in a static air atmosphere and also in a dynamic nitrogen atmosphere.

Table II shows the temperatures at which the first signs of decomposition of the substances were observed. The temperature at which the complete decomposition takes place is also given. The single appreciable difference in the DTA curves of several of these compounds heated in a dynamic nitrogen atmosphere with respect to the results obtained by heating in a static air atmosphere was the endo-

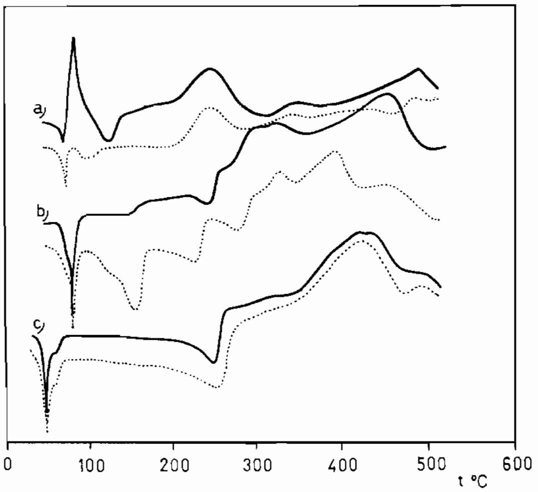

Figure 1. DTA thermograms: a) $K_2[Ni(DPPN)_4]$, b) $K_2[Pd(DPPN)_4]$, c) $K_2[Pt(DPPN)_4]$ (solid line: air atmosphere; broken line: N_2 atmosphere).

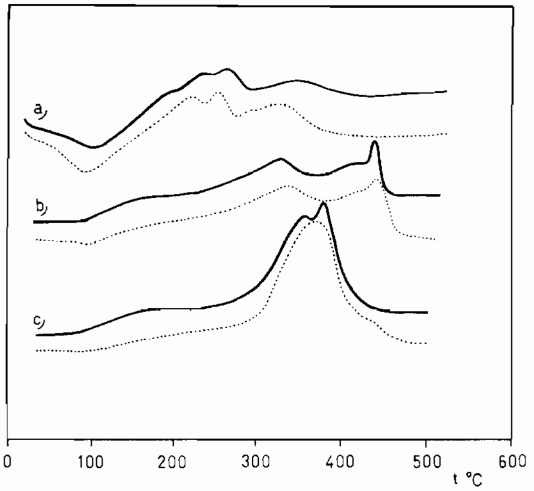

Figure 2. DTA thermograms: a) $K_2[Ni(DMPN)_4]$, b) $K_2[Pd(DMPN)_4]$, c) $K_2[Pt(DMPN)_4]$ (solid line: air atmosphere; broken line: N_2 atmosphere).

thermic or exothermic character, respectively, of the peak that appears at the lowest temperature. As can be seen, the HDPPN derivatives have a higher thermal stability than the HDMPN ones. On taking into account the different metals, the thermal stability is observed to increase on going from the Ni(II) derivatives to the Pt(II) species although the stability of the latter and that of the Pd(II) derivatives is very similar (Figs. 1, 2).

However, the thermal stability of the Ni(II) derivatives is very high and different from that of all the tetraalkynylniccolate(II) salts described in the literature which decompose at room temperatures or, in some cases, below room temperature, even under dry nitrogen atmosphere.

Table III gives the most important transformation observed during the heating of the different substances in a static air atmosphere together with the temperatures at which these transformations take place. All the HDPPN derivatives melt before decomposing.

The substances, after heating at different temperatures, were studied by IR spectroscopy. In all cases, decomposition started with a change in the acetylenic band.

In the IR spectrum of $K_2[Pd(DPPN)_4]$, heated at 250 °C, a band at 2045 cm^{-1} appears which is different in shape and intensity from that assigned to the stretching frequency $\nu(C{\equiv}C)$. Owing to the great ease with which palladium forms hydrides and from

TABLE III. Transformation in the Thermal Decomposition of the Ni(II), Pd(II) and Pt(II) Compounds.

Compound	T (°C)	Transformation[a]
$K_2[Ni(DPPN)_4]$	70	Melting
	82	$\nu C{\equiv}C$ band changes
$K_2[Pd(DPPN)_4]$	80	Melting
	250	Partial transformation into Pd hydride and Pd amide
	320	Complete transformation into Pd hydride and Pd amide
$K_2[Pt(DPPN)_4]$	55	Melting
	330	$\nu C{\equiv}C$ and $\nu Pt{-}C$ bands disappear
$K_2[Ni(DMPN)_4]$	98	NH_3 lost
	150–250	$\nu C{\equiv}C$ and $\nu C{\equiv}N$ bands change
	370	Complete transformation into carbonate
$K_2[Pd(DMPN)_4]$	375	Complete transformation into carbonate and isocyanate
$K_2[Pt(DMPN)_4]$	350	$\nu C{\equiv}C$ and $\nu C{\equiv}N$ bands disappear
		$\nu C{=}C$ band appear
	395	Complete transformation into isocyanate

[a] The products of heating at the indicated temperatures were identified by their IR spectra.

the IR data found in the literature for palladium hydrides [15], this band is assigned to a ν(Pd–H) stretching frequency. At 468 cm^{-1} a new band appears which is assigned to a ν(Pd–N) stretching frequency. This, together with the presence of stretching and bending frequencies of the N–H group, suggests that the decomposition of $K_2[Pd(DPPN)_4]$ takes place with formation of palladium hydride and amide.

The thermal decomposition of the $K_2[Ni(DMPN)_4]$, $K_2[Pd(DMPN)_4]$ and $K_2[Pt(DMPN)_4]$ complexes occurs for the Ni(II) compound with carbonate formation, and for the Pd(II) and Pt(II) complexes with isocyanate and carbonate formation. The presence of isocyanate and carbonate species during the thermal decomposition was verified by IR spectroscopy. All these decomposition pathways involve a reaction with oxygen, even in the case of heating in a dynamic nitrogen atmosphere. This fact can be due to the impossibility of eliminating the last traces of oxygen in the DTA apparatus.

The results lead us to conclude that the relative stability of Ni(II), Pd(II) and Pt(II) tetraalkynyl complexes seems to be related to the size of the acetylenic group bonded to the metal atom.

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