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**ω -Nitroacetophenone as a Chelating Agent. - Part I.
A trimeric nickel complex, and adducts from it with
water, ethanol and pyridine**

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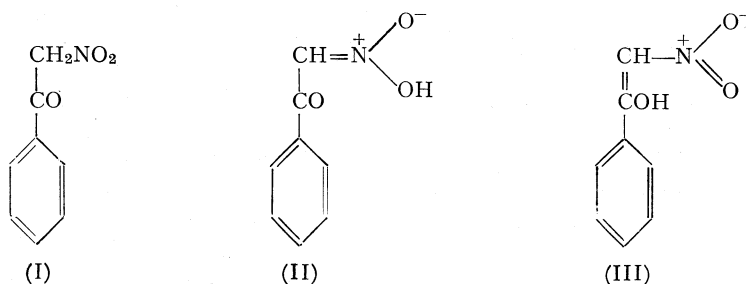
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Chimica. — *ω -Nitroacetophenone as a Chelating Agent.* — Part I. *A trimeric nickel complex, and adducts from it with water, ethanol and pyridine* (*). Nota di CLAUDIO ERCOLANI, INES COLLAMATI, e GUIDO SARTORI, presentata (**) dal Corrisp. G. SARTORI.

RIASSUNTO. — Un nuovo complesso del nichel, il bis-(ω -nitroacetonefenonato- Ni^{II}) ed i suoi addotti con acqua alcool e piridina sono stati preparati usando l' ω -nitroacetofenone come legante. Il complesso desolvato è suscettibile di esistenza soltanto in ambiente secco, all'aria umida dà luogo alla formazione del diidrato stabile. In soluzione di benzolo anidro il suo peso molecolare risulta essere tre volte il teorico calcolato per la forma monomera. Questo risultato lascia supporre che la coordinazione ottaedrica del nichel, evidenziata per questo complesso dalle sue proprietà magnetiche e spettroscopiche si realizzi attraverso un'associazione molecolare, che richiama per molti aspetti quella riscontrata nel bis-(acetilacetionato)- Ni^{II} . Viene fatta un'ipotesi sul tipo di struttura molecolare generata dalla suddetta forma di associazione. Spettri e misure magnetiche dei tre addotti vengono discusse.

ω -Nitroacetophenone (ω -NAP) has been the object of some interest, due to its pseudoacid character. The equilibrium between the nitro- and the isonitro- form ($\text{I} \rightleftharpoons \text{II}$) normally found with nitro-compounds is complicated in the



case of ω -NAP by the presence of a carbonyl group, which introduces the possibility of a keto-enol equilibrium ($\text{I} \rightleftharpoons \text{III}$). From studies undertaken by various workers [1, 2, 3, 4], it seems that both types of equilibrium are possible in solution, and that in non-aqueous solution the keto-enol equilibrium is the more likely one. The sodium, potassium and ammonium salts of ω -NAP are known, but nothing has been reported about its forming complexes with first transition series metals. We have now completed the synthesis and structural investigation of the complex of ω -NAP with nickel, and of the adducts this forms with water, ethanol and pyridine. In the non-solvated molecule, i.e. $\text{Ni}(\omega\text{-NAP})_2$, a nickel atom is joined to two ω -NAP molecules. Here the

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metal-ligand system is of the NiO_4 general type. In the adducts, two molecules of solvent are present in each case, giving formulae: $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ and $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{py}$ ($\text{py} = \text{pyridine}$).

$\text{Ni}(\omega\text{-NAP})_2$ is stable in dry air. In the open it changes to the dihydrate, which can then be reconverted to the anhydrous state by driving off the water by heating in an oven at 100°C for an hour and a half.

It is stable to heat up to about 190°C , at which temperature it decomposes instantly and violently. It is prepared from $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, which in its turn is obtained as needle crystals on mixing hot alcoholic solutions of $\omega\text{-NAP}$ and nickel acetate tetrahydrate. The alcohol is then driven off by heating the complex in an oven at 150°C for one and a half to two hours. The adduct of $\text{Ni}(\omega\text{-NAP})_2$ with pyridine is the most stable to heat of the three described. It retains the solvent up to its decomposition temperature, which is, as for $\text{Ni}(\omega\text{-NAP})_2$, about 190°C .

TABLE I.

COMPOUND	SUSCEPTIBILITY $\chi \cdot 10^6$				$\bar{\mu}$
	$\bar{\chi}_g$	$\bar{\chi}_M$	λ	$\bar{\chi}'_M$	
$\text{Ni}(\omega\text{-NAP})_2$ (light yellow)	10.27	3970	170	4140	3.13 ± 0.06
$\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{H}_2\text{O}$ (green yellow)	9.70	4100	200	4300	3.19 ± 0.02
$\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ (light green)	8.64	4140	240	4380	3.22 ± 0.03
$\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{py}$ (light green)	7.30	3970	270	4240	3.17 ± 0.04

The magnetic susceptibility data given in Table I show that all the complexes are paramagnetic. This paramagnetism, corresponding to two unpaired electrons, shows that in each case the fundamental state is a triplet. The magnetic moment of $\text{Ni}(\omega\text{-NAP})_2$ does not definitely exclude its having a planar structure, for, on purely theoretical grounds, a triplet fundamental state is indeed possible for such a structure in a sufficiently weak field [5, 6]. When the value of this magnetic moment (3.13 B.M.) is considered, a tetrahedral structure for $\text{Ni}(\omega\text{-NAP})_2$ does not appear very probable, for values higher than $3.3 - 3.4 \text{ B.M.}$ are normally observed for nickel complexes with this type of structure. Rather, the magnetic datum leads one to think that, despite the stoichiometry of the complex, the metal atom in the $\text{Ni}(\omega\text{-NAP})_2$ molecular arrangement has an environment of octahedral symmetry. The ease with

which adducts are formed, and the stability to heat, reveal a pronounced tendency for nickel in this type of complex to be six-coordinated.

In fig. 1 are given the reflectance spectrum and the spectrum in anhydrous benzene solution of $\text{Ni}(\omega\text{-NAP})_2$ from 7000 to 23000 cm^{-1} (other data are given further on in Table II). The values of the molar extinction coefficients for the benzene solution are given on the left-hand ordinate, and the optical density for the solid on the right-hand ordinate. As will be seen from

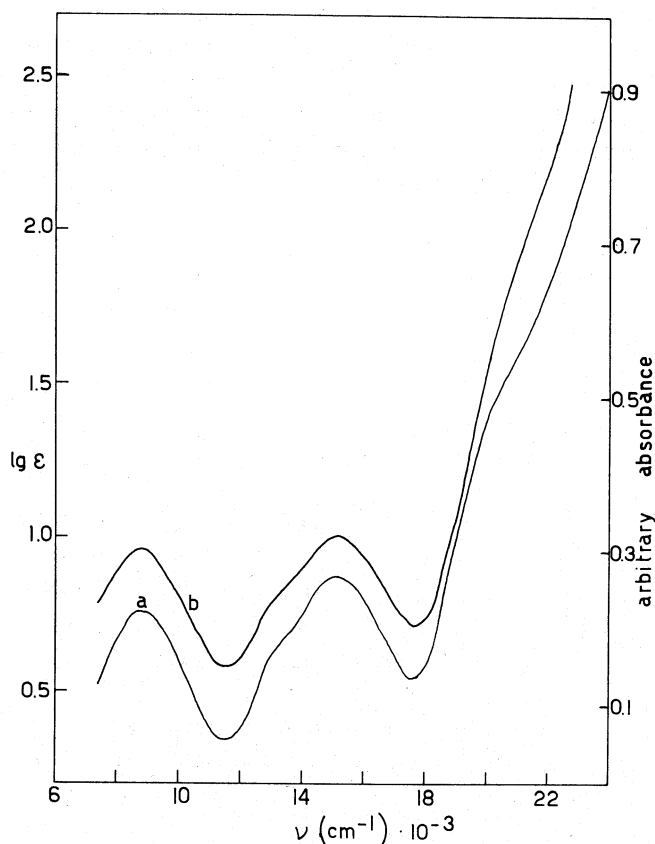


Fig. 1. – $\text{Ni}(\omega\text{-NAP})_2$.

a) reflectance spectrum; b) spectrum of dry benzene solution ($c=1.8 \cdot 10^{-2}$ M, P.M. 387).

the figure, the spectrum of $\text{Ni}(\omega\text{-NAP})_2$ in the power form is practically the same as that of its benzene solution. This means that the complex retains in solution in a non-coordinating solvent such as benzene the same symmetry that it has in the solid state. The energy and extinction coefficient values of the bands of the complex in solution in benzene enable one to exclude the possibility that the complex might have a tetrahedral structure, in agreement with the predictions from the magnetic data. Rather, the spectrum is that of an octahedral complex. As regards this, the two bands of roughly the same inten-

sity at 1130 and 650 $m\mu$ may be assigned to triplet-triplet transitions. The less intense shoulder at 775 $m\mu$ is most probably a triplet-singlet band. Also the shoulder at about 480 $m\mu$, lying on the tail of a band of much greater intensity at higher frequency is certainly a $d-d$ band of the metal, even though it is not easy to assign it.

Molecular weight measurements support the hypothesis that the nickel atom in $Ni(\omega-NAP)_2$ may be octahedrally coordinated, in agreement with the indications from spectral and magnetic measurements. In solution in benzene, in the same range of concentration as used for the spectral runs, $Ni(\omega-NAP)_2$ gave a mean molecular weight of 1160, corresponding to an association factor of three (Mol. Wt. calculated for the monomer is 387). The experimental values give a deviation of ± 0.3 on this association factor, which may be considered not excessive considering the limitations imposed by the low solubility and hygroscopic nature of the compound. In view of the narrow range of the concentrations examined, both for the spectral runs and the molecular weight determinations, it is not legitimate to draw any conclusions as to a dependence of the degree of association on the concentration. However, the concentrations used were really quite low, which works in favour of a stable trimeric form. Hence $Ni(\omega-NAP)_2$ is present in benzene solution in associated form, and it is possible to imagine that in this form, the octahedral coordination of the metal suggested by the spectrum is attained. Measurements of the magnetic moment in solution would have been useful to establish whether paramagnetism was present or not, but it was not possible to execute them, again because of the low solubility of the complex. A form of intermolecular association of the type found in solution could just as well account for the paramagnetism and the spectra, observed for the solid state.

Before putting forward some hypothesis as to the way the $Ni(\omega-NAP)_2$ molecule is built up, both in solution and in the solid state, it would be as well to touch briefly on what has been reported in the literature in the last few years about complexes having local symmetry around the nickel atom, of the type NiO_4 . In many cases, especially in the β -diketonate series, this type of complex shows peculiar magnetic and spectral behaviour. A typical example is bis-(acetylacetonate)- $Ni^{II}((Ni(acac)_2))$, whose structure was elucidated by physical chemical studies conducted by Cotton and Fackler [7, 8, 9], followed by a structural determination by Bullen et al. [10]. The molecule of the complex turned out to be composed of three $Ni(acac)_2$ units (see fig. 2), with the three nickel atoms arranged on the same axis, held together by some of the acetylacetonate groups by means of oxygen atoms acting as bridges between the metal atoms. The pseudo-octahedral character assumed by the metal in order to build up this quite characteristic type of intermolecular association clearly explains the magnetic and spectral properties of $Ni(acac)_2$, both in the solid state and in solution. It has been established that also in solution it maintains its trimeric nature [8]. Resorting to the same type of intermolecular association enables the experimental results for many other complexes belonging essentially to the β -diketonate series, to be explained [11].

A detailed comparison, still from an experimental point of view, between results for $\text{Ni}(\omega\text{-NAP})_2$ and those for $\text{Ni}(\text{acac})_2$ and the other β -diketonates reveals a notable correspondence. This correspondence is not limited merely to the magnetic and spectral properties, but applies also to molecular association and the extent of this association. This observation invites one to enquire into the factors determining the similarity in behaviour between the two

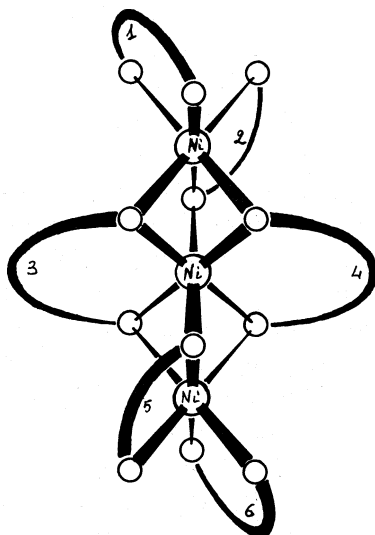
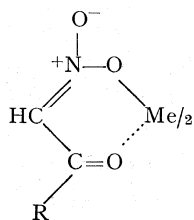


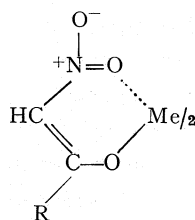
Fig. 2. - Schematic diagram of the structure of $\text{Ni}(\text{acac})_2$.

types of complex. Substantial help is given by an analysis of the chelating system. If we consider for the moment just the stoichiometric unit $\text{Ni}(\omega\text{-NAP})_2$, it can be formulated in two ways (IV) and (V) corresponding to the two forms (II) and (III) written initially for $\omega\text{-NAP}$. In both cases the nitrogen atom has sp^2 hybridization, so the nitrogen atom and the three atoms joined to it (one carbon and two oxygens) must all lie in a plane. The same reasoning can be applied to the two carbon atoms nearby. From this one can deduce



R=phenyl

(IV)



(V)

that the whole chelating system must be planar. (The oxygen atom left out of the chelating system, and the first carbon atom of the benzene ring, will lie in the same plane). In forms (IV) and (V) it is seen that the nitrogen

atom is isoelectronic and isosteric with a carbon atom. This fact, taken together with the planarity of the chelating system, could well account for the similarities in behaviour found between $\text{Ni}(\text{acac})_2$ and $\text{Ni}(\omega\text{-NAP})_2$. In conclusion, it may be supposed that the molecules are built in the same way. Evidently the presence in $\omega\text{-NAP}$ of a phenyl group in an asymmetric position does not give rise to sufficient steric hindrance to impede association. The same happens in bis-(benzoylacetate)- Ni^{II} , which, in spite of having a phenyl in an asymmetric position, is none the less trimeric, at least at room temperature [11].

TABLE II.

$\text{Ni}(\omega\text{-NAP})_2$ (a)		$\text{Ni}(\omega\text{-NAP})_2$ (b)			$\text{Ni}(\omega\text{-NAP})_2 \cdot 2 \text{H}_2\text{O}$ (a)		$\text{Ni}(\omega\text{-NAP}) \cdot 2 \text{C}_2\text{H}_5\text{OH}$ (a)		$\text{Ni}(\omega\text{-NAP})_2 \cdot 2 \text{py}$ (a)	
$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$	ϵ	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$
1130	8850	1125	8900	5.7	1100	9100	1025	9750	990	10100
775	12900	775	12900	4.0	770	13000			775	12900
655	15250	660	15150	7.5	640	15600	610	16400	590	17000

(a) Reflectance spectra; (b) spectrum of dry benzene solution; $c = 2 \cdot 10^{-2} \text{M}$, 1 cm cell).

The reflectance spectra of the three solvated complexes are shown in fig. 3. They have an aspect typical of octahedral nickel complexes (see also Table II). In each of them there are two bands of roughly the same intensity (ν_2 and ν_3). These too may be assigned, as in the case of $\text{Ni}(\omega\text{-NAP})_2$, to triplet-triplet transition. A less intense band (ν_2) at 775 $\text{m}\mu$, not easily discernible in the case of $\text{Ni}(\omega\text{-NAP})_2 \cdot \text{C}_2\text{H}_5\text{OH}$, is probably in each case a triplet-singlet band. The band appearing as a shoulder at 480 $\text{m}\mu$, lying on the tail of a much more intense band at higher frequency, is probably also a $d-d$ band. On going from the non-solvated complex to its adducts with water, ethanol and pyridine successively, there is a progressive shift of the ν_1 and ν_3 bands towards higher frequencies, which may be attributed to an increasing perturbation acting on $\text{Ni}(\omega\text{-NAP})_2$ by the solvents in the order given, in agreement with their position in the spectrochemical series. Comparison with the spectra of the analogous adducts of $\text{Ni}(\text{acac})_2$ is particularly revealing [12]. Apart from the qualitative similarity of the spectra, also for these complexes there is a continued shift of the two principal bands arising from spin permitted transitions whilst the bands of lesser intensity lying between them stay at fixed frequency. Calculations by G. Maki [12] on $\text{Ni}(\text{acac})_2 \cdot 2 \text{py}$ regarded as a sixacoordinated complex of tetragonal symmetry have led to the assign-

ments given in Table III for the three bands observed. The close resemblance between the spectra of $\text{Ni}(\text{acac})_2 \cdot 2\text{py}$ and $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{py}$, both in the position and the relative intensity of the bands, clearly suggests assigning the observed transitions in the same way.

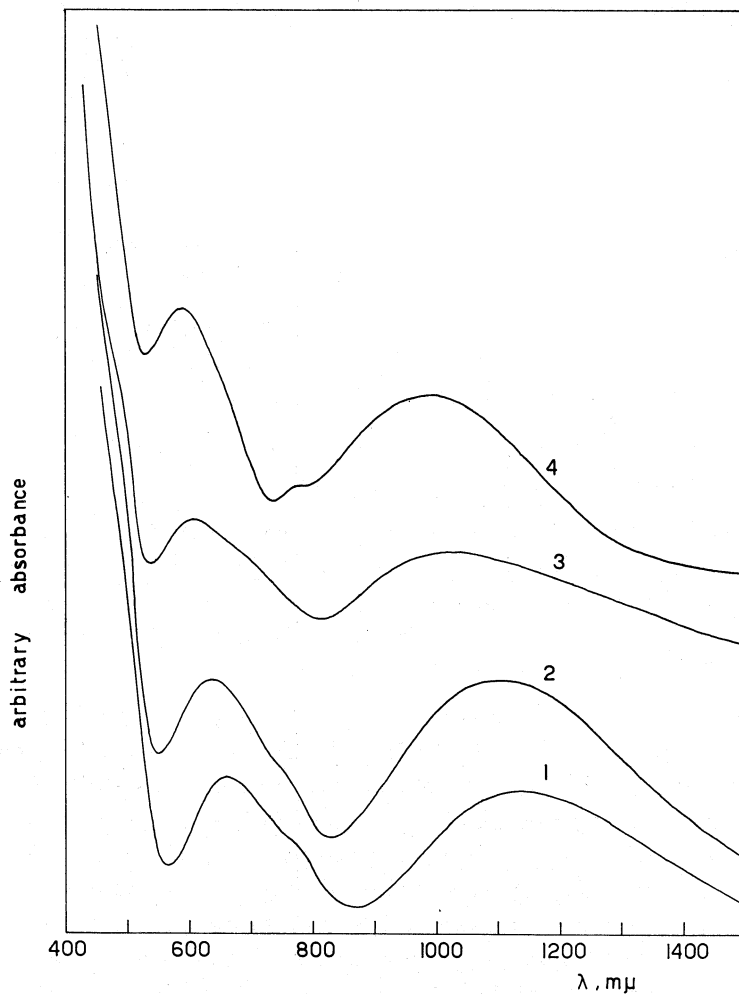


Fig. 3. - Reflectance spectra.

1) $\text{Ni}(\omega\text{-NAP})_2$; 2) $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{H}_2\text{O}$; 3) $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$; 4) $\text{Ni}(\omega\text{-NAP})_2 \cdot 2\text{py}$.

The study of other complexes formed by $\omega\text{-NAP}$ with first transition series metals is under way in this laboratory. Their similarity to the corresponding acetylacetonate complexes will obviously be of particular interest. Such a resemblance will serve to obtain indirectly information on the structure of the $\omega\text{-NAP}$ complexes. But still more, it is proposed to establish how much influence the analogies previously discussed between the two chelating systems have in determining the analogous properties and structure of the complexes

they form. Other lines of investigation (spectrophotometric in the IR and UV, and X-ray) have been started to obtain information more specifically about the chelating system, so as to establish whether one or the other of the two formulae proposed for the nickel complex (IV) and (V) is the only valid one, or whether, as seems more likely, the ring formed by metal atom and chelating group is rather the site of a benzene-type resonance such as is generally found in β -diketonates.

TABLE III.

TRANSITION	ΔE CALCULATED	EXPTL ΔE
$^3B_2g \rightarrow ^1A_1g$	10500	
$^3B_2g \rightarrow ^3B_1g$	10500	10030
$^3B_2g \rightarrow ^3A_2g$	11400	
$^3B_2g \rightarrow ^1B_2g$	14400	13100
$^3B_2g \rightarrow ^3Eg$	16400	16800

EXPERIMENTAL.

ω -Nitroacetophenone ω -NAP.—This compound was prepared essentially according to the method of Long and Troutman [13]. The following modifications were made: *a*) the nitroalcohol was oxidized without previous distillation *b*) during the oxidation of the nitroalcohol, after its addition to the reaction vessel, the temperature was immediately taken to 60–65°. After about thirty minutes, heating was stopped, and the solution filtered. Starting from 31.4 g of nitromethane and 52.3 g of benzaldehyde, the reaction gave altogether 32 g of ω -nitroacetophenone, which was then purified by crystallization from ethanol.

Bis-(ω -nitroacetophenone)bis-(ethanol)-Ni^{II} $Ni(\omega\text{-NAP})_2 \cdot 2C_2H_5OH$.—Calculated quantities of ω -nitroacetophenone and nickel acetate tetrahydrate (in molar ratio 2 : 1) were dissolved in hot ethanol in separate vessels. The ω -nitroacetophenone solution was added over thirty minutes to the acetate solution, which was kept at a temperature of 50°, with stirring. The solution became turbid right from the beginning through formation of the complex. After the two solutions had been completely mixed, they were kept stirred for a further thirty minutes. After allowing to cool, the solution was filtered, and the solid obtained was crystallized from 95% ethanol. The complex was obtained as needle shaped light-green crystals (yield 80–90%) (Found: C, 49, 79; H, 5, 00; N, 5, 67; $C_{20}H_{24}N_2O_2Ni$ requires: C, 50, 14; H, 5, 05; N, 5, 85%).

Bis-(ω -nitroacetophenone)-Ni^{II}Ni(ω -NAP)₂.—This complex was prepared by heating the bis-ethanolate in an oven at 150° for 1 1/2 to 2 hours. The same time and the same temperature were needed for desolvation under vacuum (10⁻¹ mm Hg). Ni(ω -NAP)₂ does not melt up to about 190°, at which temperature it decomposes violently. It is a light yellow colour, darkening in air due to formation of the dihydrate. (Found: C, 50,75; H, 3,12; N, 7,20; C₁₆H₁₂N₂O₆Ni requires: C, 50,64; N, 3,10; N, 7,23%).

Bis-(ω -nitroacetophenone)(bis-(aquo)-Ni^{II} Ni(ω -NAP)₂ · 2 H₂O.—This complex was prepared by simply exposing Ni(ω -NAP)₂ to air for 15–20 hours. Heating in an oven at 100° for 1 1/2 hours gave the anhydrous compound again. (Found: C, 45,46; H, 3,78; N, 6,62; C₁₆H₁₆N₂O₈Ni requires: C, 45,30; H, 3,78; N, 6,61%).

Bis-(ω -nitroacetophenone)bis-(pyridine)-Ni^{II} Ni(ω -NAP)₂ · 2 py.—The bis-(pyridine) complex can be obtained in quantitative yield by dissolving the bis-(ethanolate) in hot pyridine. On cooling, the complex precipitates (though not completion) in crystalline form. The solvent was evaporated off, and the green solid obtained was dried to constant weight by heating at 80° under vacuum (10⁻¹ mm Hg). The dipyridinate is stable up to a temperature of about 190°, at which temperature it decomposes violently. (Found: C, 57,42; H, 3,97; N, 10,20; C₂₆H₂₂N₄O₆Ni requires: C, 57,20; H, 4,05; N, 10,49%).

Magnetic, spectroscopic and molecular weight measurements.—The magnetic susceptibility measurements were carried out at room temperature with a Gouy balance, using HgCo(CNS)₄ as calibrant. By using four different magnetic field intensities, it was possible to exclude the presence of ferromagnetism in any of the samples. The corrections for the diamagnetism of the organic part were evaluated using Pascal constants. The value of μ_{eff} was obtained from the formula $\mu_{\text{eff}} = 2.83 \sqrt{\chi_{\text{M}}^{\text{corr}} \cdot T}$.

A Beckmann DK2 spectrophotometer was used to run the spectra in the visible region. For the reflectance measurements, the spectrometer was adapted with an accessory supplied by the makers. Magnesium oxide was used as a reference. The absorption spectra were run on solutions in anhydrous benzene. All operations were carried out in an atmosphere of dry nitrogen. The molecular weight measurements for Ni(ω -NAP)₂ were carried out with a Mechrolab Inc. Model 301A vapor pressure osmometer at 25°. The non-solvated compound was prepared by heating the bis-ethanolate either in an oven or under vacuum. Anhydrous benzene was used as the solvent.

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