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Ni^{II} COMPLEXES WITH 1,8-NAPHTHALENE BIS(DIMETHYLARSINE)*

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A. INTRODUCTION

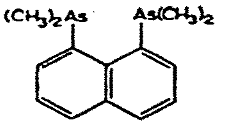
The sector of Inorganic Chemistry concerning pentacoordinated transition metal complexes has been widely investigated in the past few years[1]. Particular attention has been paid to those complexes in which polydentate ligands with low electronegativity donor atoms appear (*e.g.* As, P). In fact such ligands freqeuntly give pentacoordination[2,3].

The most interesting problem in this class of complexes concerns the factors which are responsable for the penta-coordination.

From structural investigations the molecular geometry turns out to be in some cases that of a trigonal bipyramid, in others that of a square pyramid and, finally, in others a distorted form of the previous stereochemistries.

So far it has not been established to which extent the geometry of the complex depends upon the electronic and electrostatic factors and to which extent it depends upon the steric factors, as, for instance, the distance between the donor atoms and their possibility of directing the lone pairs towards the metal.

In order to provide an answer for such a problem we have undertaken a research program involving the preparation and physico-chemical characterization of penta-coordinated complexes, in which we progressively vary the electronic properties and the steric requirements of the ligands. This present paper concerns the complex of Ni^{II} with 1,8-naphthalenebis(dimethylarsine) (I) (*nas*) and its penta-coordinated derivatives.



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The purpose of the research was to establish the steric influence of the two As atoms compared with the corresponding *o*-phenylenebis(dimethylarsine) (*das*) Ni^{II} complexes[3].

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B. EXPERIMENTAL PART

(a) Preparation. The ligand was prepared as described in a previous paper[4] and the compounds as outlined below. From the analyses we could assign the general formula Ni(*nas*)$_2$X$_2$ to the complexes.

Ni(nas)$_2$*(ClO$_4$)$_2$*. $Ni(H_2O)_6(ClO_4)_2$ (0.365 g in 10 ml of hot acetone) and nas (0.672 g in 5 ml of hot acetone) were mixed and refluxed for 10 min.

The intensely coloured solution produced orange crystals upon cooling, which were filtered, washed with cold acetone and ether and finally dried under vacuum (200 °C expl. dec.). The same preparation carried out in nitromethane gave an intense blue compound with an analytical composition exactly equal to that of the orange one. However, the blue compound was unstable in solution and gradually changed into the orange form.

Ni(nas)$_2$*Cl$_2$*. $Ni(H_2O)_6Cl_2$ (0.150 g) in ethanol (3 ml) was added to *nas* (0.212 g) in boiling ethanol (2 ml). After cooling the dark-blue solution, blue crystals precipitated. These crystals were filtered off, washed with cold ethanol and dried under vacuum (dec. 158–160 °C).

Ni(nas)$_2$*Br$_2$*. Hot ethanolic solutions of $Ni(H_2O)_3Br_2$ (0.170 g in 5 ml) and *nas* (0.212 g in 5 ml) were mixed and refluxed for several minutes. The intensely dark-blue solution, when cooled, produced blue crystals which were filtered, washed with cold ethanol and dried under vacuum (dec. 194 °C).

Ni(nas)$_2$*I$_2$*. Hot ethanolic solutions of $Ni(H_2O)_6I_2$ (0.260 g in 5 ml) and *nas* (0.212 g in 4 ml) were mixed and refluxed for several minutes. After cooling dark-blue crystals precipitated. These crystals were filtered, washed with cold ethanol and dried under vacuum (dec. >240 °C).

Ni(nas)$_2$*(SCN)$_2$*. $Ni(H_2O)_6Cl_2$ (0.11 g) in ethanol (10 ml) was treated with NH_4SCN (1 g). The filtered solution was added to *nas* (0.303 g) in boiling ethanol (10 ml). The violet solution, after evaporation, gave violet crystals, which were filtered and recrystallized once from ethanol (m.p. 196–198 °C). Analytical data for these complexes are presented in Table 2.

(b) Conductivity measurements. The conductivity of all prepared complexes was measured in nitromethane by employing a "LKB 3216 B" bridge.

The data obtained show that Ni(*nas*)$_2$(ClO$_4$)$_2$ is markedly different from the other compounds (Table 1). In fact from studies carried out on a large number of compounds it is known that the molecular conductivity of a 10^{-3} M solution of a uni-univalent electrolyte in nitromethane is 70–80 mho., whereas for a uni-bivalent electrolyte it is close to 160 mho[3]. From the data obtained it is evident that Ni(*nas*)$_2$(ClO$_4$)$_2$ is a bi-univalent electrolyte and that the other compounds Ni(*nas*)$_2$X$_2$ ($X = Cl^-, Br^-, I^-, SCN^-$) are uni-univalent. This means that one of the X atoms is bound to the Ni atom.

In order to find support for this fact, conductimetric titrations of Ni(*nas*)$_2$-

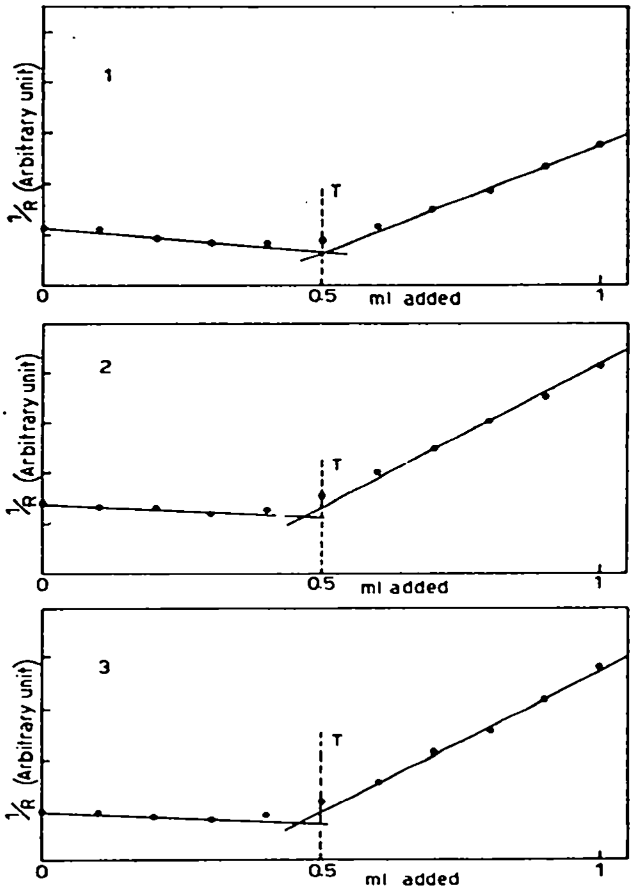

Fig. 1. Conductimetric titration of 40 ml of $2.5 \cdot 10^{-4}$ *M* [Ni(*nas*)$_2$] [ClO$_4$]$_2$ with $2 \cdot 10^{-3}$ *M*. 1, [Ph$_4$As]Cl; 2, [(n-bu)$_4$N]Br; 3, [(n-bu)$_4$N]I in nitromethane at 25 °C. T = calc. end-point.

$(ClO_4)_2$ were carried out with tetraphenylarsonium chloride, tetra-n-butylammonium bromide and iodide. As we expected, all the titration curves showed a sharp end point when only one equivalent of halide was added (Fig. 1).

Thus, it is clear that the Ni atom in Ni(*nas*)$_2$(ClO$_4$)$_2$ is tetracoordinated, [Ni(*nas*)$_2$](ClO$_4$)$_2$, and that in Ni(*nas*)$_2$X$_2$ (X = Cl^-, Br^-, I^-, SCN^-) it is pentacoordinated [Ni(*nas*)$_2$X]X.

This conclusion was further supported by the observed spectra.

(c) The electronic spectra. The spectra were determined in nitromethane solution ($5 \cdot 10^{-4}$ *M*) by an "Optica CF 4" recording spectrophotometer (Table 1 and Figs. 2 and 3).

Likewise in these measurements Ni(*nas*)$_2$(ClO$_4$)$_2$ showed a quite different behaviour.

In fact, Ni(*nas*)$_2$(ClO$_4$)$_2$ has only one, not very intense, band at 22,200 cm^{-1}

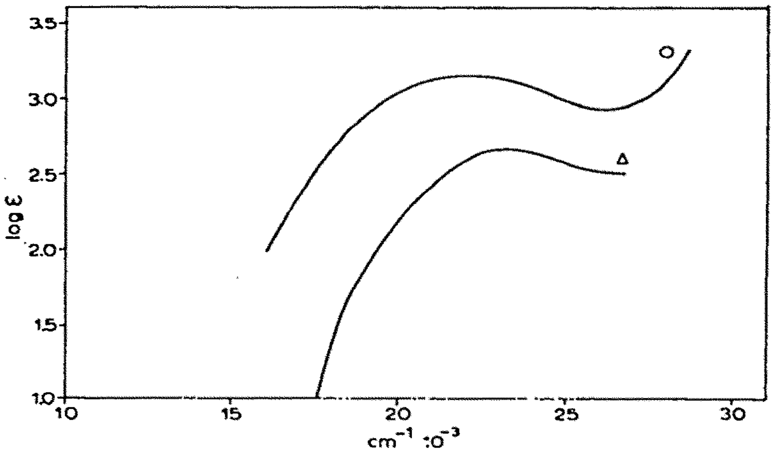

Fig. 2. Absorption spectra of nitromethane solutions of: △, $[Ni(das)_2][ClO_4]_2$; ○, $Ni(nas)_2]$-$[ClO_4]_2$. (△ taken from reference 3).

and the other compounds have similar spectra with three maxima in the range 13,000–29,000 cm^{-1}.

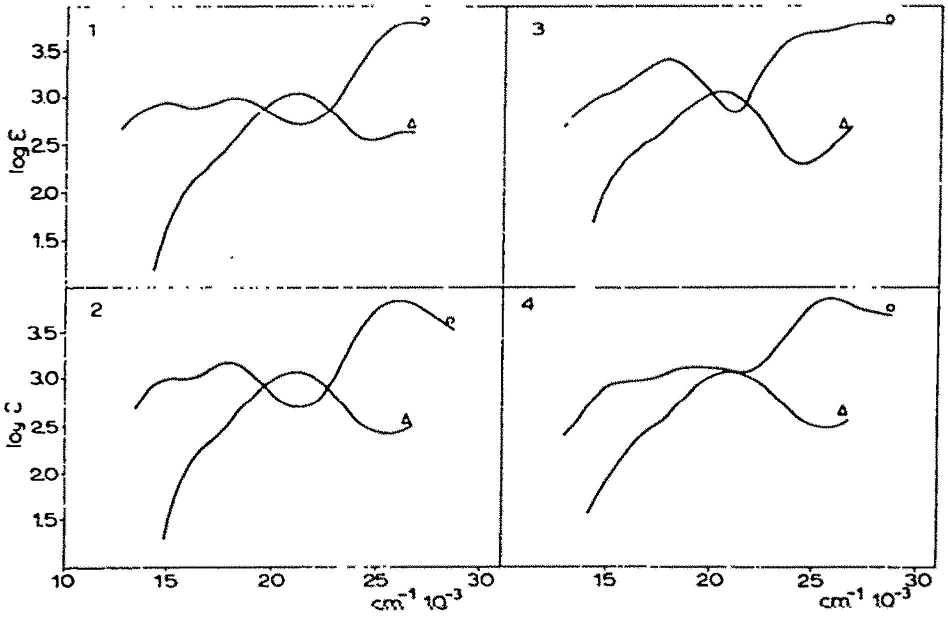

Fig. 3. Absorption spectra of nitromethane solutions of: △, $[Ni(das)_2X]X$; ○, $[Ni(nas)_2X]X$. (1, X = Cl; 2, X = Br; 3, X = I; 4, X = SCN) (△ taken from reference 3).

(d) Magnetic susceptibility. The measurements were carried out by the Gouy method at 25 °C. The values are not given since all compounds are diamagnetic.

A compilation of the physico-chemical properties is found in Table 1.

TABLE 1

Compound	*Colour*	*Mol. cond. (mho) at 25 °C in* $\mathrm{MeNO_2}$ ($c = M/1000$)	*Spectrum*	
			$\nu_{\max}$ *($cm^{-1} \cdot 10^{-3}$)*	$\varepsilon \cdot 10^{-3}$
$[\mathrm{Ni}(nas)_2](\mathrm{ClO_4})_2$	orange	180	22.2	1.42
$[\mathrm{Ni}(nas)_2\mathrm{Cl}]\mathrm{Cl}$	blue	78	14.9	0.88
			18.3	1.02
			26.6	6.90
$[\mathrm{Ni}(nas)_2\mathrm{Br}]\mathrm{Br}$	blue	83	15.8	1.02
			18.0	1.50
			26.1	7.30
$[\mathrm{Ni}(nas)_2\mathrm{I}]\mathrm{I}$	dark-blue	85	15.4	1.28
			18.1	2.63
			24.4[a]	4.90[a]
			27.3	6.50
$[\mathrm{Ni}(nas)_2\mathrm{SCN}]\mathrm{SCN}$	violet	88	16.5	0.99
			19.4	1.42
			25.9	8.20

[a] shoulder.

C. DISCUSSION

The behaviour of *nas* with $\mathrm{Ni^{II}}$ is similar to that of *das*. Therefore, before discussing the results and making any comparison, it is convenient to examine the different steric situations.

Throughout this examination we shall assume that the four As atoms coordinated to the Ni atom are coplanar.

(a) The steric requirements of das and nas. The steric requirements of the bidentate ligands *das* and *nas* are as follows:

(1) The distance between the two As donor atoms is fixed (approximately 3.21 Å for *das* and 2.49 Å for *nas*). Therefore, in the planar complexes we are necessarily dealing with a rectangular structure, except in the very particular case

TABLE 2

ANALYSES(%) OF NICKEL(II) COMPLEXES WITH THE LIGAND *nas*(I)

Compound		*Ni*		*C*		*H*		*Halogen*		*S*		*N*	
		Found	*Reqd.*	*Found*	*Reqd.*	*Found*	*Reqd.*	*Found*	*Reqd.*	*Found*	*Reqd.*	*Found*	*Reqd.*
$[\mathrm{Ni}(nas)_2](\mathrm{ClO_4})_2$	orange	6.5	6.31	35.9	36.17	3.9	3.90						
	blue	6.4	6.31	35.5	36.17	4.0	3.90						
$[\mathrm{Ni}(nas)_2\mathrm{Cl}]\mathrm{Cl}$		7.3	7.32	41.1	41.94	4.6	4.53	8.6	8.84				
$[\mathrm{Ni}(nas)_2\mathrm{Br}]\mathrm{Br}$		6.4	6.59	37.7	37.75	4.1	4.07	17.8	17.94				
$[\mathrm{Ni}(nas)_2\mathrm{I}]\mathrm{I}$		6.1	5.96	34.7	34.15	3.7	3.69	26.3	25.78				
$[\mathrm{Ni}(nas)_2\mathrm{SCN}]\mathrm{SCN}$		6.8	6.93	42.4	42.54	4.1	4.28			7.7	7.57	3.3	3.31

in which the ratio between the metal–As bond length and the As–As distance is exactly $1/\sqrt{2}$. Now the latter situation is almost true in in Ni^{II} complexes with *das*[5] but not in those with *nas* where the ratio is close to 1.

(2) The hybrid orbitals of the As lone pairs tend to point as much as possible towards the Ni atom in such a way as to have the greatest degree of overlap.

By assuming for simplicity an sp^3 hybridization state, one can readily see that in the case of *das* complexes the above requirement is verified when the benzene ring of *das* is almost coplanar with the As atoms and Ni plane (the hybrid orbitals pointing towards the Ni atom form an angle close to 90°).

In the case of *nas* complexes, because of the shorter As–As distance, the hybrid orbitals can be directed towards the Ni atom only when the naphthalene plane forms a dihedral angle of about 112° with the plane of Ni and As atoms. Thus, in this case we must expect two isomers (Fig. 4) with a different arrangement of the *nas* molecules.

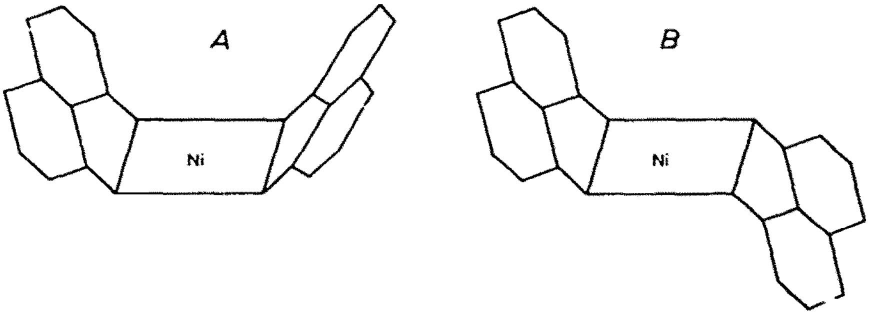

Fig. 4. The Ni(*nas*)$_2^{++}$ isomers.

(b) The tetra-coordinated complexes. From the above considerations it is clear that the structures of [Ni(*das*)$_2$]$^{2+}$ and [Ni(*nas*)$_2$]$^{2+}$ belong, respectively, to the symmetry point groups D_{2h} and C_{2v} (isomer A) or C_{2h} (isomer B). However, by considering the influence of the benzene or naphthalene rings on the electronic distribution around the Ni atom as a first approximation to be small, such molecules can be considered to have D_{4h} and D_{2h} symmetries with slight distortion.

The order of molecular energy levels in the d^8 square planar complexes is not definitely known and is still subject to much discussion. However, it is generally accepted that all the antibonding molecular orbitals (MO) are filled except the one derived from the $d_{x^2-y^2}$ atomic orbital (AO). Therefore, the lowest transitions must occur from the filled MO's to the empty $d_{x^2-y^2}$ MO. In the case of D_{4h} and D_{2h} symmetries such transitions are forbidden, while some of them become allowed in lower symmetries (*e.g.* C_{4v} and C_{2v}).

The observed spectra of [Ni(*das*)$_2$]$^{2+}$ and [Ni(*nas*)$_2$]$^{2+}$ (Fig. 2) are rather similar; both show a rather weak ($\varepsilon = 470$ and $\varepsilon = 1420$) and very broad band with maxima at 23,100 cm^{-1} and 22,200 cm^{-1}, respectively. Owing to the low intensity it is evident that such a band must be assigned to a d–d transition. However, for the present it is not possible to give a precise assignment.

With regard to $[Ni(nas)_2]^{2+}$, as previously pointed out, we found different characteristics depending upon the reaction conditions. Thus we obtained two forms: one orange and stable and the other blue and unstable. So far the spectrum of the latter has not been studied, however, qualitatively, it is different from that of the orange form, it changes with time to the orange form and it shows a definite isosbestic point.

We think that the orange and blue forms are those that we would expect from the steric requirements previously examined.

(c) Pentacoordinated complexes. It has been reasonably assumed that in solution $[Ni(das)_2X]^+$ complexes have a square pyramid structure[3]. According to this assumption the molecular symmetry (C_{2v}), as a first approximation, can be considered C_{4v} and, hence, only one transition is allowed from the $e(d_{xz}, d_{yz})$ MO's to the $b_1(d_{x^2-y^2})$ MO. The observed spectra show a band at 21,000 cm^{-1}, more intense and at a lower wave number than that of $[Ni(das)_2]^{2+}$.

With regard to $[Ni(nas)_2X]^+$ we would expect two pentacoordinated isomers: experimentally, only one form was found. Thus, we think that only one form is possible because of steric hindrance. On the basis of very simple considerations carried out using the Stuart–Briegleb models, by taking into account that the As atoms are not strictly in an sp^3 hybridization state[5] and that probably in a pentacoordinated complex the Ni atom is no longer coplanar with the As but slightly shifted towards X. We feel that the most stable form is that derived from the A isomer (Fig. 4) and, hence, the symmetry of the $[Ni(nas)_2X]^+$ complex is C_{2v}. According to this symmetry group, the following three transitions are allowed:

$a_1(d_{z^2}) \rightarrow a_1(d_{x^2-y^2})$
$b_1(d_{xz}) \rightarrow a_1(d_{x^2-y^2})$
$b_2(d_{yz}) \rightarrow a_1(d_{x^2-y^2})$

In the observed spectra two d–d bands and a charge transfer band appear (Fig. 3). Probably, one of the three d–d allowed transitions is less intense than the others and is hidden.

At any rate it is evident from the steric considerations that the rectangular arrangement of the As atoms around Ni is the factor which determines the appearance of several distinct d–d bands in the $[Ni(nas)_2X]^+$ spectrum.

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