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SYNTHESIS AND CHARACTERIZATION OF A NEW IRON (II)—DINITROGEN COMPOUND WITH PDTA AS LIGAND

M. CARMEN PUERTA,* M. F. GARGALLO and F. GONZALEZ-VILCHEZ
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Cadiz, España

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Abstract—A new dinitrogen complex of formula $Na_2[Fe(PDTA) (N_2)] (H_2O)_2$ has been synthesized in aqueous solution from $[Fe(H\text{-}PDTA) (H_2O)]$, $3/2H_2O$ and NaN_3. The complex has been characterized by chemical analysis, IR and electronic spectra, and magnetic measurements. The thermal decomposition process has been studied by using DTA and TG techniques. The evolution of gases was followed by Gas Chromatography.

Since Allen and Senoff[1] isolated the first dinitrogen complex in 1965, a great interest has been awakened in the clear possibility of carrying out the "fixation" of this molecule by means of coordination compounds.[2–4]

It is a well-known fact that the enzymological fixation of nitrogen requires the presence of Fe and Mo and that the means of the reaction is water. For this reason in chemical nitrogen-fixing systems the synthesis of nitrogen complexes in an aqueous medium is of great interest at the present time.

Numerous works[5–8] have been published on dinitrogen compounds with ligands of a simple aminic type $[M(NH_3)_5(N_2)]^{2+}$, but there are no bibliographical antecedents on dinitrogen compounds which contain complexones as ligands. Only Diamantis[9] showed recently and during the course of our own investigations, the great avidity of the complexone EDTA to act as a pentadentate ligand in dinitrogen complexes, obtaining the species $[Ru(EDTA) (N_2)]^{2+}$ and $[(EDTA)Ru\text{-}N_2\text{-}Ru(EDTA)]^{4+}$ in an aqueous solution.

In our work a general method of synthesis has been used based on the conversion to coordinate N_2 of a ligand which has a nitrogen-nitrogen link,[10] and the compound $Na_2[Fe(PDTA) (N_2)]^2(H_2O)$ from $[Fe(H\text{-}PDTA) (H_2O)]$ $3/2H_2O$ using sodium azide (NaN_3) in an aqueous solution has been synthesised.

EXPERIMENTAL

$Fe(NO_3)_3 \cdot 9H_2O$ and NaN_3 were obtained from Merck, and $PDTA\text{-}H_4$ from Fluka BDH Chem. Ltd. Both of them were used without further purification.

DTA was performed in a Stanton Redcroft 673-4 thermobalance, and TG in a Cahn RG electrobalance. The gases evolved were analysed in a Hewlett-Packard 5700 A chromatograph.

IR spectrum was recorded in the 4000–400 cm^{-1} region using a Perkin-Elmer 577 double beam instrument. The sample was prepared as KBr pellet.

Electronic spectrum was recorded on a Perkin-Elmer 124 spectrophotometer using 2 cm quartz cells, and water as reference.

A Gouy balance was used for magnetic measurements at room temperature. The ESR spectrum at room temperature and 77 K were recorded at the Instituto de Catálisis y petroquímica Rocasolano (C.S.I.C.), Madrid.

C, H, and N analysis were performed at the Departamento de Microanálisis del Instituto de Química Orgánica General del C.S.I.C., Barcelona. Iron was determined by gravimetry and by atomic absorption spectrometry. Sodium was determined by Flame spectrophotometry. The water content was determined in a Karl-Fischer titrator, and confirmed by TG.

Synthesis of $Na_2[Fe(PDTA) (N_2)] \cdot 2H_2O$

0.750 g. of $[Fe(H\text{-}PDTA) (H_2O)]$, $3/2H_2O$,[11] were dissolved in 25 cm^3 of water heated in double saucepan at 40°C. To the resulting green solution, 0.750 g. of solid NaN_3 were added, precipitating then a reddish compound that dissolved almost immediately. The mixture was heated in a double saucepan at 50°C for 3 min, cooled in the refrigerator and when the first microcrystals appeared, 25 cm^3 of absolute ethanol were added. The orange-coloured microcrystalline product was filtered and washed with absolute ethanol, and dried on phosphorous pentoxide. Found: Fe, 11.8; Na, 9.6; C, 28.2; H, 3.2; N, 12.0; H_2O, 7.7. Calc.: Fe, 11.9; Na, 9.7; C, 28.2; H, 3.8; N, 12.0 H_2O, 7.7%.

RESULTS

Thermal behaviour

The DTA curve (Fig. 1) obtained in an atmosphere of He, shows the existence of several endothermic effects. The first of these, at 130°C, probably corresponds to the elimination of water of crystallization. The second effect is registered at 220°C and can be attributed to the loss of the coordinated dinitrogen molecule, since decarboxylation in these conditions takes place at higher temperatures, according to what can be remarked in the remaining endothermic effects in the diagram.

The thermogravimetric curve (Fig. 2), shows two not very pronounced jumps between 120 and 240°C to which there corresponds loss of weight of 7.7 and 5.9% respectively, so they can be associated with the elimination of hydration water and coordinated dinitrogen. From 300°C pyrolysis of the compound begins and continues up to 500°C.

These results were corroborated by means of gas chromatography and by volumetric determination of dinitrogen in the complex, following a similar method to that used by Allen,[8] and whose results are included in Table 1. The determinations performed with the recently prepared complex (A) and after three months in a desiccator (B), allow us to deduce that the compound decomposes slowly on contact with air, although long periods of time are necessary for the decomposition to be significant.

IR spectra

In Fig. 3 the IR spectrum of the compound $Na_2[Fe(PDTA) (N_2)] \cdot 2H_2O$ is represented, and in Table 2 the most significant data of the same are shown.

At 3400 cm^{-1} a wide band can be observed which

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*Author to whom correspondence should be addressed.

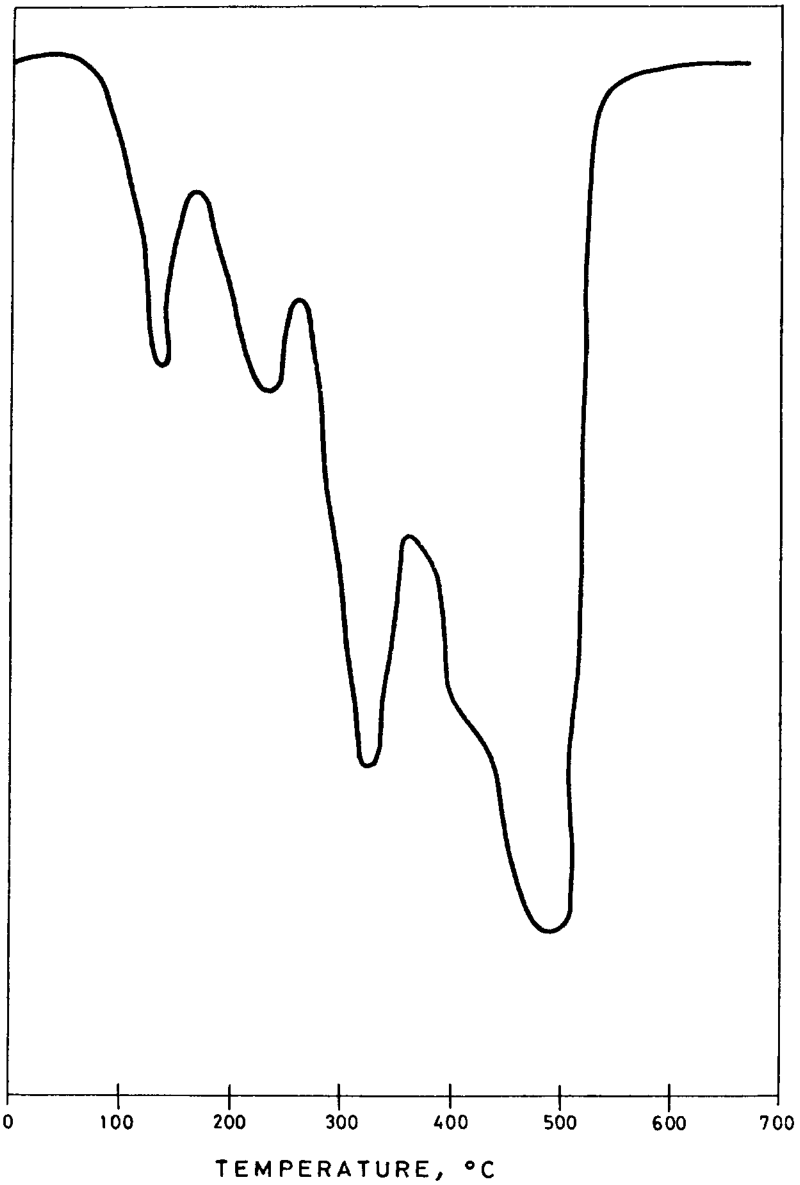

Fig. 1. DTA curve for $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$, obtained under a dynamic helium atmosphere.

Table 1. N_2 contents determined for samples A and B in $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$

	Initial weight of compound(mg)	Silicon oil pressure(mm)	(N_2) in compound	$\%(N_2)$ over the theoretical value
A)	20.5	160.5	4.23×10^{-5}	97.5
B)	24.0	29.0	0.76×10^{-5}	17.3

A) Sample recently synthesised.

B) Sample three months after its synthesis.

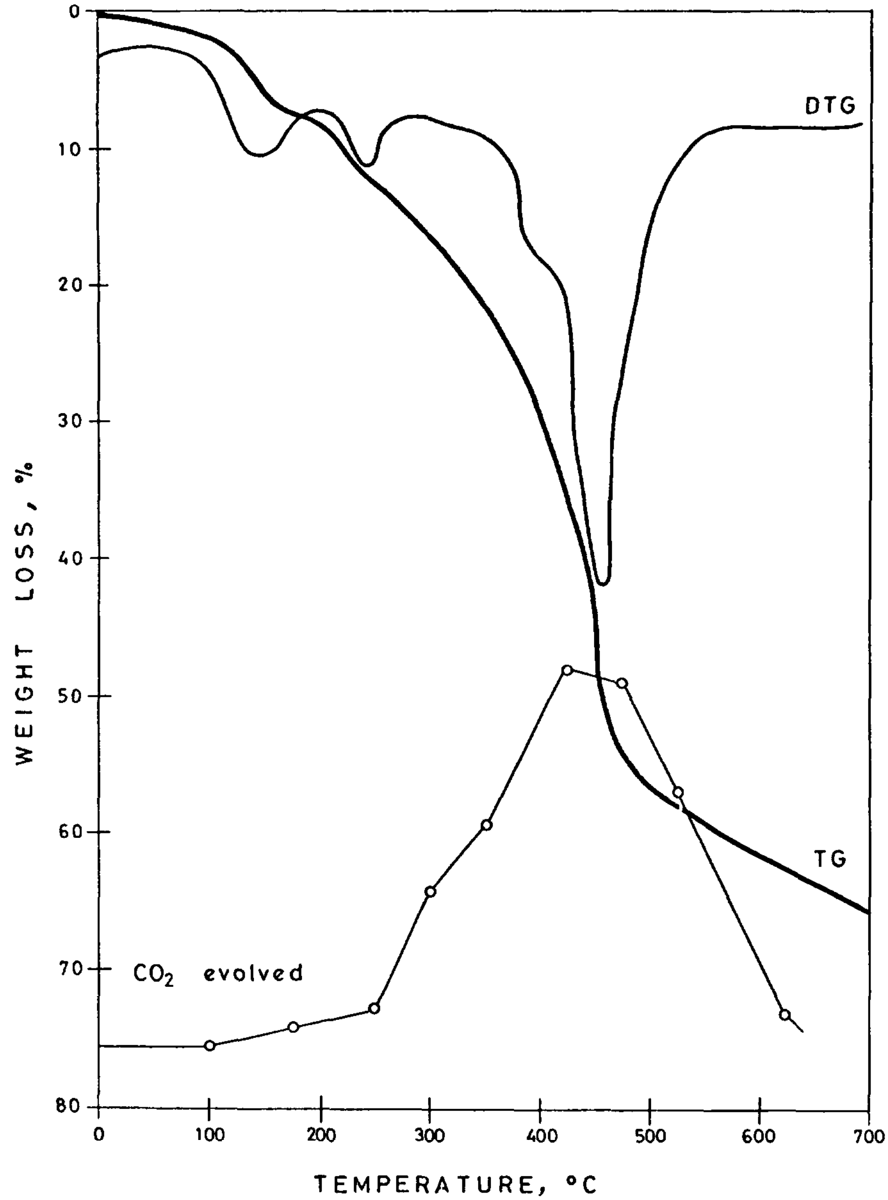

Fig. 2. TG and DTG curves for $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$, obtained under a synamic helium atmosphere.

Table 2. Main IR absorption bands of $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$ (cm^{-1})

ν_{O-H}	ν_{-CH_2}	$\nu_{(N\equiv N)}$	$\nu_{(COO^-)}$ assym	$\nu_{(COO^-)}$ sym.	$\nu_{(C-N)}$
3400	2960 2940	2030	1620	1390	1100

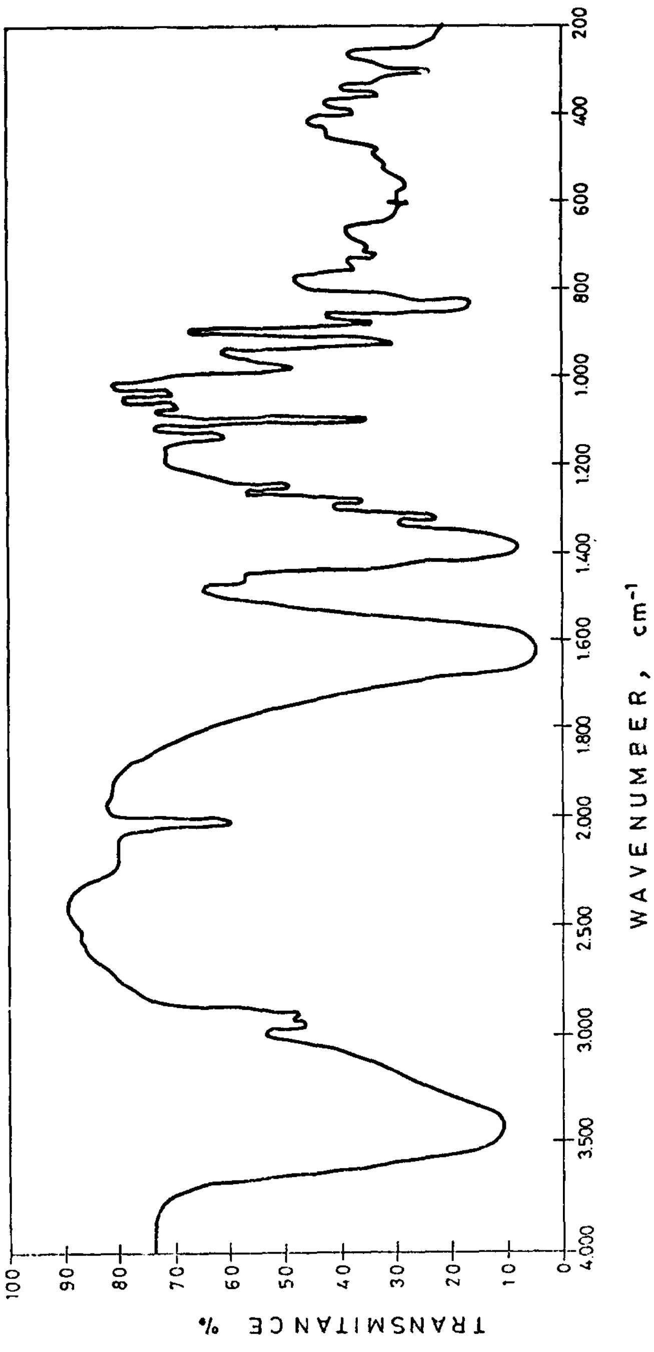

Fig. 3. IR spectrum of $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$.

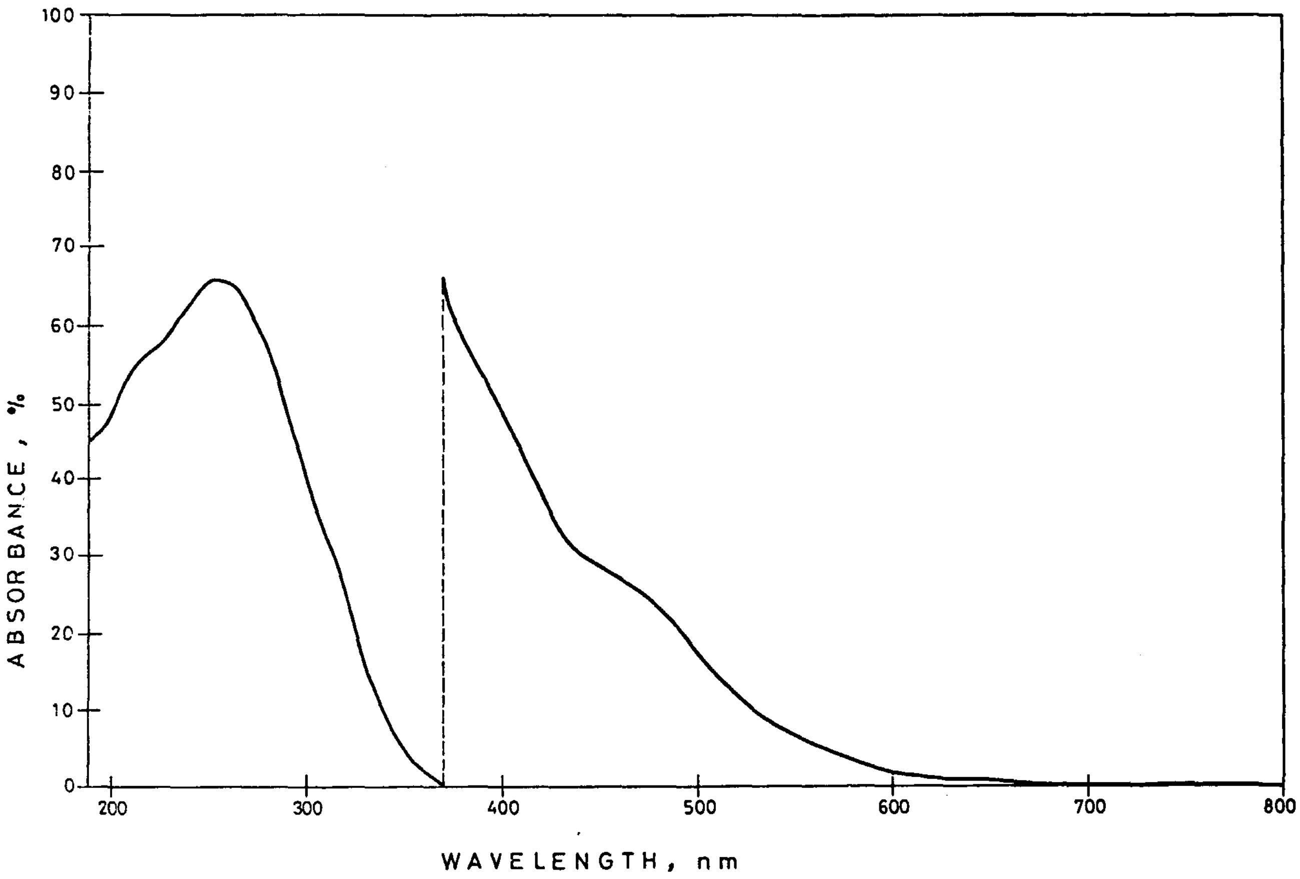

Fig. 4. Electronic spectrum of $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$ in aqueous solution.

corresponds to the vibrations of symmetrical and asymmetrical stretching of the O-H link of the crystallization water.

The bands which correspond to the stretching vibrations of the methylene groups have a similar intensity, which suggests an analogous character among all the methylene groups of the ligand.

The characteristic absorption of the dinitrogen complexes which appears between 2100 and 1900 cm^{-1}, corresponds to the stretching vibration of $N \equiv N$. The intensity and frequency of this band indicate the degree of covalency of the metal–nitrogen link.[12,13] The said band is registered in this compound at 2030 cm^{-1} with medium intensity, which seems to suggest a moderate overlapping of the metal "*d*" orbitals with the π^* of the N_2 and as a result of this a not very pronounced degree of covalency for the metal–dinitrogen link.

At 1620 cm^{-1} a band appears which can be attributed to the assymetrical stretching vibration of the carboxylate groups. The difference between the latter and the most intense peak which corresponds to the symmetrical vibration of the $-COO^-$ groups which is recorded at 1390 cm^{-1}, (225 cm^{-1}), suggests a moderately covalent link in the carboxylate–metal combinations.

UV and visible spectra

The Fe(II) in the $Na_2[Fe(PDTA)(N_2)]\cdot 2H_2O$ complex, is a d^6 system of low spin and fundamental term $^1A_{1g}$. The formation of this type of compound (t_{2g}) of low spin is favoured by ligands with an intense field, which facilitate besides the reduction of the electronic density on the metal, that is to say the electronic back-bonding from the "*d*" orbitals of the metal to the empty (π^*) orbitals of the ligand.

The absorption spectrum in an aqueous solution (Fig. 4) shows a not very intense band at 460 nm (21700 cm^{-1}), $\epsilon = 71$, due probably to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$. In the UV region there appears a band at 38500 cm^{-1} and another in the form of a shoulder, at 221 nm (45400 cm^{-1}) which through their energy and intensity can be considered as charge-transfer bands.

Study of the magnetic properties

In the Fe(II) compound of low spin, there exists no Zeeman effect of the first order ($J = S = 0$) and the magnetic susceptibility is due therefore the Zeeman effect of the second order.

The corrected magnetic molar susceptibility of the diamagnetism of the ligand, of the ion Na^+ and of the water molecules, has a value of 78.3 X_M to which there corresponds an effective magnetic momentum of 0.38 B.M.

The diamagnetism of this compound has been checked in addition by spectroscopy of ESR, which only registers a very weak signal due perhaps to the impurities of Fe^{3+}.

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