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NOTE

DINITROGEN COMPLEXES OF IRON(II) WITH CHELATING AGENTS AS LIGANDS

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Abstract—Two new dinitrogen compounds of formulae $Na_2[Fe(EDTA)N_2].2H_2O$ and $Na_2[Fe(CDTA)N_2].2H_2O$ have been synthesized from $[Fe(H–EDTA)H_2O]$ and $[Fe(H–CDTA)–H_2O]$, respectively, and NaN_3. Both complexes have been characterized by IR and electronic spectra. The thermal behaviour has been studied by TG and DTA techniques.

Since the first report of a dinitrogen complex by Allen and Senoff in 1965,[1] many papers have been published dealing with the study of dinitrogen complexes with a simple amine ligand, $[M(NH_3)_5(N_2)]^{+2}$. However, the interest for analogous compounds with chelating agents of the EDTA family has been much less. In a recent paper, Diamantis[2] synthesized the species $[Ru(EDTA)N_2]^{+2}$ and $[(EDTA)–Ru–N_2–Ru(EDTA)]^{+4}$ showing the ability of EDTA to act as a pentadentate ligand in dinitrogen complexes.

In previous papers, we described a general method of synthesis for these compounds based on the conversion to coordinated dinitrogen of a ligand with a N–N bond. This method has been successfully applied to the syntheses of $Na_2[Fe(PDTA)N_2].H_2O$,[3] $Na_2[Ru(PDTA)N_2].H_2O$,[4] and $Na[Cr(PDTA)N_2].2H_2O$.[5] In this paper, we report the synthesis in aqueous solution and using sodium azide of $Na_2[Fe(EDTA)N_2].2H_2O$ and $Na_2[Fe(CDTA)N_2].2H_2O$ from $[Fe(H–EDTA)H_2O]$ and $[Fe(H–CDTA)H_2O]$.

EXPERIMENTAL

$Fe(NO_3)_3.9H_2O$, NaN_3, $EDTA–H_4$, and $CDTA–H_4$ were obtained from Merck. All compounds were used without further purification.

C, H and N analyses were performed at the Departamento de Microanalisis of the Instituto de Química Orgánica General, C.S.I.C., Madrid. The water content of the samples was determined from the TG curves.

IR spectra were recorded in the 4000–200 cm^{-1} region using a Pye-Unicam, SP3-300 spectrophotometer. The samples were prepared as KBr pellets. TG and DTA curves were obtained with a Mettler TA–HE–20 system.

Synthesis of $Na_2[Fe(EDTA)N_2].2H_2O$

0.500 g of $[Fe(H–EDTA)H_2O]$[6] were dissolved in 75 cm^3 of water at 70°C. 0.500 g of NaN_3 were added to the resulting solution, precipitating then a reddish compound that dissolved almost immediately. The mixture was heated at 70°C for 60 min, and was cooled in the refrigerator. When the precipitation began to occur, 50 cm^3 of absolute ethanol were added to the solution, producing an orange–brown product that was filtered and washed with absolute ethanol and dried over P_2O_5. Found: C, 26.6; H, 3.6; N, 11.4; H_2O, 8.0. Calc: C, 26.5; H, 3.6; N, 12.3; H_2O, 7.9%.

Synthesis of $Na_2[Fe(CDTA)N_2].2H_2O$

This product was obtained from 0.500 g of $[Fe(H–CDTA)H_2O]$[7] using the same procedure as described above for the analogous compound with EDTA. The conditions were the same except the time of heating at 70°C (120 min). The solid product obtained was also orange–brown coloured. Found: C, 33.2; H, 4.6; N, 8.5; H_2O, 9.0. Calc: C, 33.1; H, 4.4; N, 11.0; H_2O, 7.1%.

RESULTS

UV and visible spectra

The ion Fe(II) in these compounds is a low-spin d^6 system with fundamental term $^1A_{1g}$. The formation of this type of complex is favoured by

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ligands causing an intense field, in conjunction with the reduction of the electronic density on the metal by means of the back-bonding from the "*d*" orbitals of the metal to the empty π^* orbitals of the dinitrogen ligand.

The absorption spectra of both compounds in aqueous solution (Fig. 1) shows an intense charge-transfer band at 196 nm and a band at 470 nm (EDTA complex) or 460 nm (CDTA complex) which can be assigned to the $^1T_{1g} \leftarrow {}_1A_{1g}$ transition. Other bands appear in both spectra at 250 or 270 nm (EDTA and CDTA complexes, respectively) and can be assigned to the $^1T_{2g} \leftarrow {}_1A_{1g}$ transition.

IR spectra

Figures 2 and 3 shows the IR spectra of both compounds and the numerical values for the positions of the most significant bands are listed in Table 1.

Both compounds show a band in the characteristic region for dinitrogen complexes, i.e. 2100–1900 cm^{-1}. This band corresponds to the N–N stretching vibration and appears at 2040 and 2060 cm^{-1} for the EDTA and CDTA complexes, respectively. The position and intensity of this band is normally used as a measure of the covalent character of the metal–dinitrogen bond. For these complexes, the medium intensity can be considered indicative of a moderate covalent character of the bond.

The broad band observed in both spectra at *ca.* 3400 cm^{-1} corresponds to the stretching of O–H bonds of the water of crystallization. Two bands appear in the C–H stretching region for both compounds. The intensity of these bands is

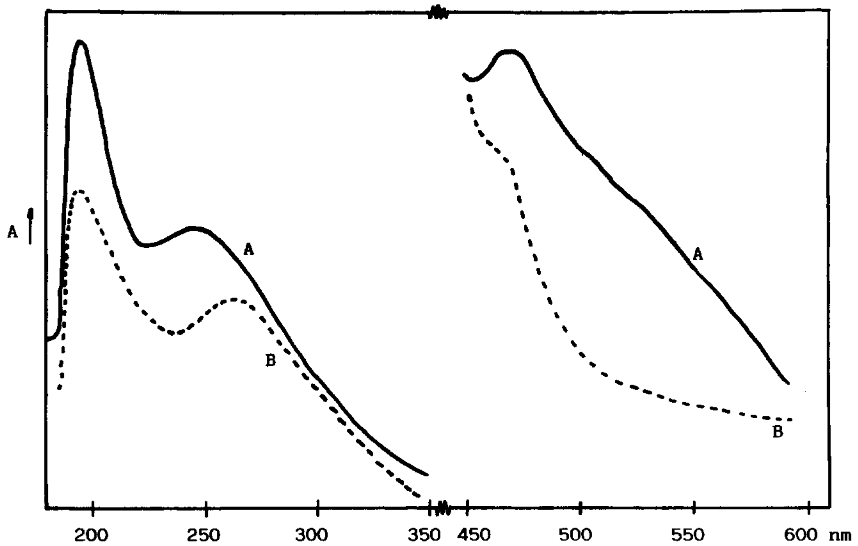

Fig. 1. UV and visible spectra of $Na_2[Fe(EDTA)N_2].2H_2O$ (A) and $Na_2[Fe(CDTA)N_2].2H_2O$ (B).

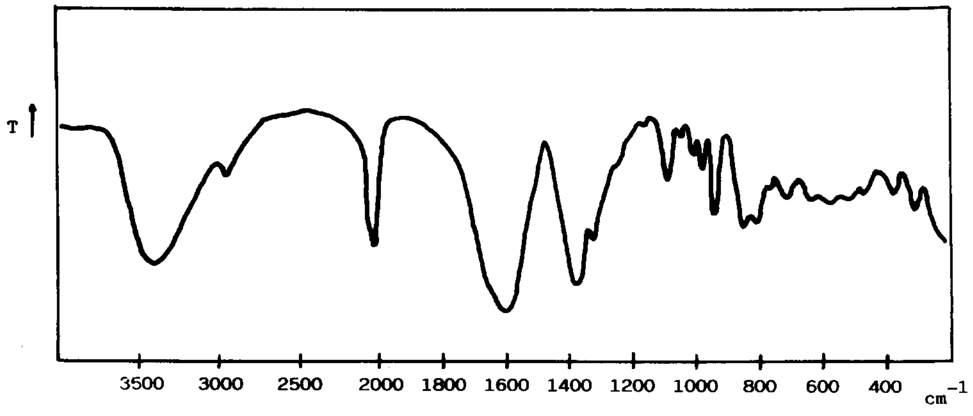

Fig. 2. IR spectrum of $Na_2[Fe(EDTA)N_2].2H_2O$.

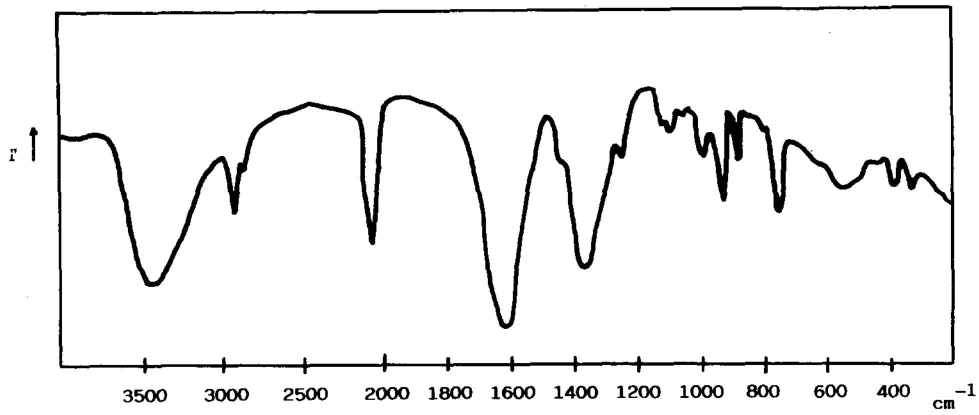

Fig. 3. IR spectrum of $Na_2[Fe(CDTA)N_2].2H_2O$.

Table 1. Main IR absorption bands of dinitrogen complexes

	ν_{O-H}	ν_{-CH_2}	$\nu_{(N\equiv N)}$	$\nu_{(COO^-)}$ assym.	$\nu_{(COO^-)}$ sym.	$\nu_{(C-N)}$
$Na_2[Fe(EDTA)N_2].2H_2O$	3400	2970 2930 (sh)	2040	1600	1380	1090
$Na_2[Fe(CDTA)N_2].2H_2O$	3400	2940 2860	2060	1620	1390	1095

different in each case as a consequence of the different central backbone of both ligands, although a contribution of minor differences between the CH_2 groups of the glycinate rings cannot be ignored.

The symmetrical stretching vibration of carboxylate groups appears at 1380 cm^{-1} for both compounds, but the position of the asymmetrical one is somewhat different, 1600 and 1620 cm^{-1} for the EDTA and CDTA complexes, respectively. However, for both compounds, the separation between the asymmetrical and symmetrical bands suggests a moderately covalent character of the metal–carboxylate bonds.[8]

Thermal behaviour

The DTA and TG curves obtained in air atmosphere of static air for both compounds are given in Figs. 4 and 5.

Between 50 and 200°C, there is an initial weight loss associated with an endothermic effect, both corresponding to the elimination of the water of crystallization. The theoretical values for the elimination of two water molecules are in accordance with the experimental values.

The weight loss between 180 and 250°C is also an endothermic process and can be associated with

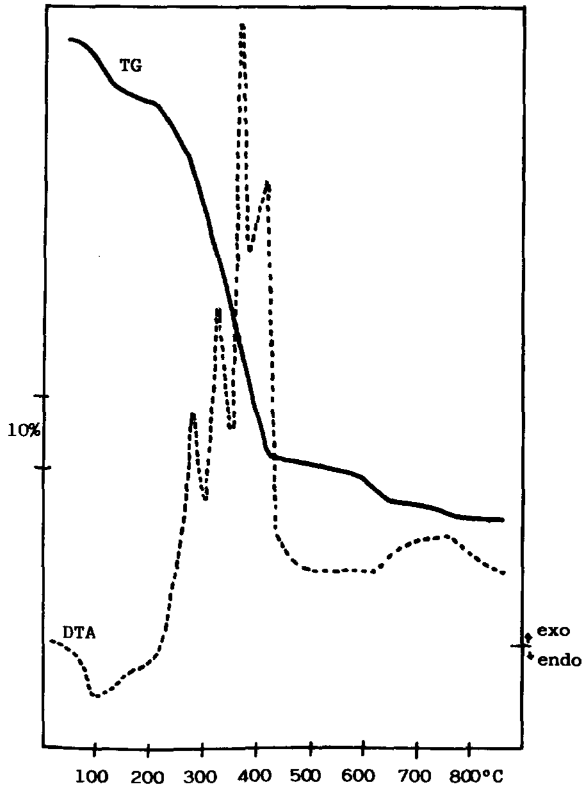

Fig. 4. TG (———) and DTA (-----) curves for $Na_2[Fe(EDTA)N_2].2H_2O$.

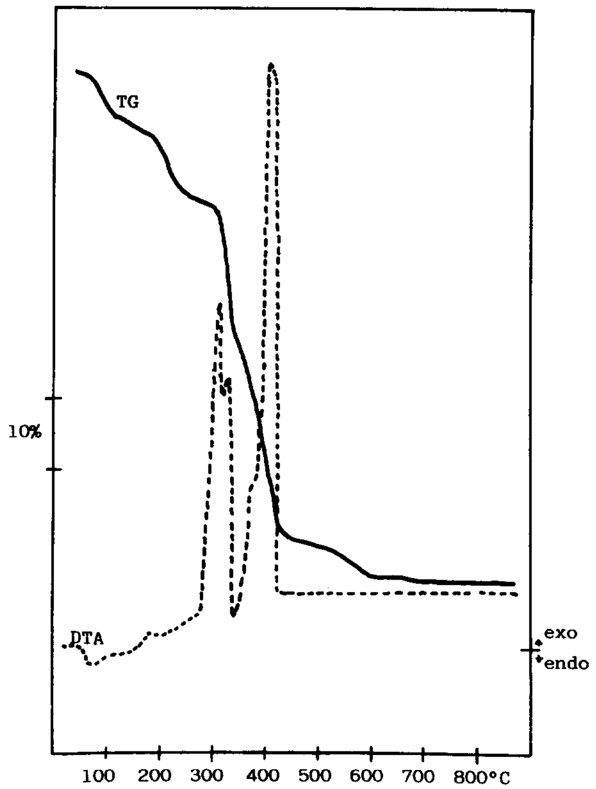

Fig. 5. (———) and DTA (-----) curves for $Na_2[Fe(CDTA)N_2].2H_2O$.

the loss of the coordinated dinitrogen molecule, although the theoretical values (6.77 and 5.54% for the EDTA and CDTA complexes) are somewhat lower than the experimental one (7% for both cases). This fact can be explained having in mind that the elimination of coordinated dinitrogen overlaps with the following stages in the thermal decomposition of the compounds.

The exothermic effects between 280 and 500°C in the DTA curves are similar to those found for analogous complexes[9] except in the temperature range, and correspond to the decarboxylation and further decomposition of the complexes with formation of Na_2CO_3 and FeO. This results in a great weight loss in the TG curves, corresponding in the total values for the anhydrous compounds of 52.3 (EDTA complex) and 56.5% (CDTA complex). The theoretical values for the formation of Na_2CO_3 and FeO are 52.97 and 57.87% for the EDTA and CDTA complexes, respectively. At higher temperatures, decomposition of Na_2CO_3 causes the formation of Na_2O_3 and FeO as final products at 900°C.

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