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Polynuclear Nickel(II) Complexes with Nitrito Bridge and 1,3-Diaminopropane as Ligand

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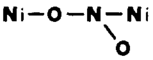
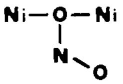
In the literature [1] there is great interest in polynuclear transition metal nitrite complexes, with the nitrite group acting as bridging ligand. Focusing our attention on these complexes with amine ligands, the majority are with ethylenediamine (en) [2–4] or its derivatives [3, 5, 6]. The interest of these compounds lies in the possibility of magnetostructural studies, taking into account the three possibilities of the nitrite group to act as a bridging ligand [2–4, 7, 8]:



I



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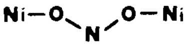

III

From Goodgame and co-workers [5] it is known that the steric factors play a very important role in the possibility to obtain mononuclear or polynuclear species (in which the NO_2^- always acts like **I** or **II** but never like **III**). For instance, with ethylenediamine ligand (en), under certain experimental conditions the following complexes can be obtained: $[Ni(en)_2(NO_2)_2]$ (nitro-monodentate); $[Ni(en)_2(NO_2)]X$ (nitro-quelate; X = Cl^-, Br^-, I^-); $[Ni(en)_2(NO_2)]X$ (nitrite bridge; X = ClO_4^-, PF_6^-, BF_4^-, I_3^-; polynuclear 1D complexes); $[Ni(en)_2(NO_2)](BPh_4)$ (nitrite bridge; dinuclear complex) and, finally, $[Ni_5(en)_4(OH)_2(NO_2)_8]$ (pentamer with nitrite and OH^- bridging) [1]. With larger NN-ethylenediamine derivatives only mononuclear or pentameric species are described, not dinuclear or 1D polynuclear.

Our aim is to study systematically the stabilizing conditions to obtain dinuclear or polynuclear complexes rather than mononuclear with amine ligands greater than ethylenediamine, but lower than its NN-derivatives. We present here the preliminary study and results with 1,3-diaminopropane (tn) ligand, very similar to en ligand but with more voluminous 6-ring chelate. We were able to obtain mononuclear, polymeric 1D and pentameric complexes with nitrite ligand, all of these analogous to the ethylenediamine compounds.

Experimental

$[Ni(tn)_2(NO_2)]ClO_4$

The $[Ni(tn)_2(NO_2)_2]$, previously prepared [9, 10], was dissolved in methanol, giving a blue solution. To this filtered solution, $NaClO_4$ in excess was added and then was left to stand at room temperature. Red crystals appeared after a few days. *Anal.* Calcd.: C, 20.45; N, 5.72; H, 19.87. Found: C, 20.60; N, 5.63; H, 20.22%.

$[Ni_5(tn)_4(NO_2)_8(OH)_2]\cdot 2H_2O$

This complex can prepared by three different methods:

a) The $[Ni(tn)_2(NO_2)_2]$ [9, 10] was dissolved in the minimum amount of water, giving a blue solution due to $[Ni(tn)_2(H_2O)_2]^{2+}$ cation. When an excess (3 or 4 times) of $NaNO_2$ was added a red precipitate of pentameric complex slowly formed.

b) A Nickel(II) hydrated salt was dissolved in water and the stoichiometric quantity of tn and a large excess of $NaNO_2$ were added. The pentameric complex was formed slowly. Without the large excess of $NaNO_2$ the monomeric $[Ni(tn)_2(NO_2)_2]$ was formed rapidly.

c) From $Ni(NO_2)_2aq$ dissolved in methanol, with addition of tn ligand with molar ratio 0.95:1. A red precipitate was formed rapidly. This method is similar to that described by Finney *et al.* [6] to prepare the ethylenediamine analogue. *Anal.* Calcd.: C, 14.02; H, 4.51; N, 21.80. Found: C, 14.20; H, 4.42; N, 22.00%.

Results and Discussion

The two new compounds were characterized by IR and electronic spectroscopy and magnetic measurements, and in all cases compared with the ethylenediamine analogue.

With regard to $[Ni(tn)_2(NO_2)]ClO_4$, the IR spectrum shows the two characteristic bands of nitrite bridging coordinated simultaneously via nitrogen and oxygen atoms (I), ν_{as} at *ca.* 1360 cm^{-1}(s) and ν_s at 1265 cm^{-1} (vs) [1]. The strong band near 1400 cm^{-1} is the most typical feature of this kind of nitrite bridge, as it is found in the ethylenediamine analogue [1]. The visible spectrum also agrees with

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TABLE I. Variation of Molar Susceptibility ($\times 10^{-6}$, c.g.s.u.) and Effective Magnetic Moment with Temperature (K).

$[Ni(tn)_2(NO_2)](ClO_4)$			$[Ni_5(tn)_4(NO_2)_8(OH)]\cdot 2H_2O$			$[Ni_5(en)_4(NO_2)_8(OH)_2]\cdot 2H_2O$		
T	χ_M	$\mu_{ef.}$	T	χ_M	$\mu_{ef.}$	T	χ_M	$\mu_{ef.}$
294.0	3297.87	2.79	295.0	20482.71	3.12	296.0	20774.46	3.14
243.0	3799.50	2.73	243.0	25071.92	3.13	246.0	25087.09	3.15
196.0	4475.65	2.64	194.0	30699.77	3.10	194.0	31258.60	3.13
135.0	5548.77	2.46	137.0	43347.76	3.10	134.0	45014.45	3.12
77.0	6776.99	2.07	77.0	72298.85	3.00	77.0	74608.01	3.04
(diam. corr. = -267.92×10^{-6})			(diam. corr. = -624.4×10^{-6})			(diam. corr. = -602.8×10^{-6})		

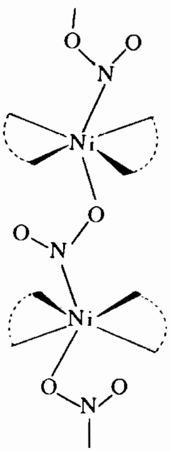

Fig. 1. Schematic diagram of polymeric $[Ni(tn)_2(NO_2)]^+$ cation.

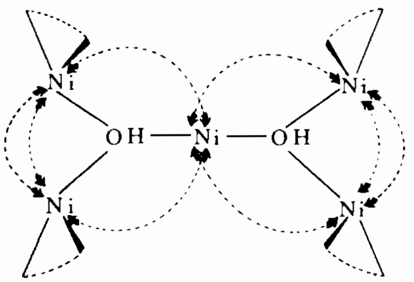

Fig. 2. Schematic diagram of the $[Ni_5(tn)_4(NO_2)_8(OH)_2]$ complex. The nitrite bridges are indicated by arrow curves; the others are the chelating tn.

the corresponding ethylenediamine compound [1, 2], with two defined bands at *ca.* 750 and 500 nm (in solid state or Nujol mull, due to its decomposition in solution). These bands can be assigned to $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ in an octahedral coordination. The most important characteristic of the new complex is its magnetic behaviour studied down to 77 K. The susceptibility measurements and effective moments are given in Table I. These values are in agreement with those obtained by $[Ni(en)_2(NO_2)]ClO_4$ [2, 7], the structure of which is known [7]. We find the same slight deviation of the last point (77 K) with regard to the Curie-Weiss law indicating that at 77 K we are near the maximum curve χ *vs.* T.

Effectively, taking into account all the calculated values, the regression coefficient r is 0.997 with $\theta = -118.9$ K. With elimination of the 77 K value, the r is 0.9998 and $\theta = -95.40$ K. The ethylenediamine analogue exhibits a maximum at around 62 K [7]. We are trying to obtain a single crystal for X-ray structural determination and to study the magnetic susceptibility at 4 K. By comparing our results with the ethylenediamine analogue we can assume that the structure corresponds with that of the en compound shown in Fig. 1.

With regard to the pentamer $[Ni_5(tn)_4(NO_2)_8(OH)_2]\cdot 2H_2O$, the IR spectrum is very similar to the en analogue (which has been recently characterized by X-ray diffraction [6]). In the regions of nitrite vibrations we find three strong and defined bands: ν_{as} at 1425 cm^{-1}, 1390 cm^{-1} (vs); ν_s at 1250 cm^{-1}, 1235 cm^{-1} (vs) and δ(ONO) at 850 cm^{-1}, 840 cm^{-1} (w). The en analogue exhibits these bands at 1420 cm^{-1} (vs), 1245 cm^{-1} (vs) and 825–835 cm^{-1} (w). The en and tn compounds also show a sharp peak between 3510–3600 cm^{-1} due to the bridging OH group.

The visible spectra are also in agreement: they present bands at 810–815 nm (with shoulders at 840 nm and 760 nm) ($^3T_{2g} \leftarrow {}^3A_{2g}$) and 498–500 nm (the more intense and defined) due to $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ in an octahedral geometry [6].

The magnetic measurements (Table I) are difficult to interpret, lacking in the literature the results of the en analogue. The effective moment is almost constant until 77 K and the linear regression for $1/\chi$ *vs.* T is very high (0.9998) with a small value of θ (-8.3 K). This slight deviation of the Curie law can indicate systems with low positive exchange coupling constant (J), being necessary to study this interaction until 4 K. This fact is found with other polynuclear compounds of nickel(II) with several bridging ligands, as NCS^- [11], X^- [12, 13] or in polymeric structures like $[Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4]$ [14]. To compare, we have measured the susceptibility data for the en analogue, until 77 K. The results are identical (Table I).

We are working with this and other similar compounds. The results described here permit us to assign a structure similar to that determined for the en analogue [6] (Fig. 2).

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