

STRATEGY FOR THE SYNTHESIS OF SOME BINUCLEAR Co(II) AND Ni(II) COMPLEXES

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Compounds as $[M^{II}(\text{HDEA})(\mu_2\text{-N}_2\text{H}_4)(\text{ONO}_2)]$ where H₂DEA (Diethanolamine), M^{II}: Co^{II} and Ni^{II} were synthesized by a synthesis strategy leading to complex compounds with low number of metallic centers. The IR spectra show that H₂DEA acts as a chelating ligand and N₂H₄ as a bridging one. The AOM analysis of the electronic spectra leads to a distorted octahedral environment for the two metallic ions sustaining the proposed formula as binuclear compounds.

Introduction

The development of synthetic strategies for the design of solid-state structures from soluble components is of intense current interest. The ligand choice is very important from that point of view.

The present report is a part of our aim concerning a strategy of controlled nuclearity complexes. For that purpose two types of coordinating species have been involved:

- 1) ligands with a known ability of assembling a high number of metallic centers, generating polymeric structures (hydrazine);
- 2) chelating ligands showing tendency through the low nuclearity coordination units ("blocking ligands") as amino-alcohols.

Regarding the assembling species, the coordination possibilities of hydrazine as bridging ligand are well known [1÷4].

The coordination chemistry of β-amino-alcohols is of interest because of their ability to form stable complex species at neutral and basic pH values. For a long time were some controversy about the complex abilities of the amino-alcohol moiety that has been considered too weak for chelate formation in aqueous solutions. Actually, alkoxide ion is a strong base in aqueous solution and it is protonated at neutral pH values, preventing complex formation. However, when this group is an appropriate site with respect to another complexing group such as an amino group, the formation of chelat rings of five or six members is not only possible but the favored process in aqueous solution at neutral and basic pH [5].

As the information concerning the "blocking ligands" could be mentioned those referring at amino-alcohols whose structure represents the source for many coordination possibilities as neutral ligand or anionic one, mono- or polydentate, with stable chelating rings formation [6÷13].

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The mentioned strategy has been applied and two compounds of Co^{II} and Ni^{II} were obtained and characterized.

Experimental

The substances Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, NH₄Cl and N₂H₄·H₂O (100%) were all analytical grade reagents (Aldrich). Diethanolamine (H₂DEA) (Merck) were used without further purification.

Syntheses

[Co^{II}(HDEA)(μ₂-N₂H₄)(ONO₂)] (1): Co(NO₃)₂·6H₂O 873mg (3mmol) and NH₄Cl 316mg (6mmol) in 25ml isopropyl alcohol were mixed with H₂DEA 623mg (6mmol) in 20ml isopropyl alcohol. After mixing ten minutes N₂H₄·H₂O 0,143ml (3mmol) (100%) was added. The mixture was refluxed at 90°C for two hours. After filtration a blue precipitate has been obtained which was washed with isopropyl alcohol and dried under vacuum on P₂O₅.

The composition of the complex [Co(HDEA)(μ-N₂H₄)(ONO₂)]₂: composition calculated. Co, 22,9; C, 18,6; N, 21,7; H, 5,4%; found Co, 22,5; C, 18,8; N, 21,5; H, 5,3%.

[Ni^{II}(HDEA)(μ₂-N₂H₄)(ONO₂)] (2). Compound (2) was synthesized in a manner similar to the one described above. Ni(NO₃)₂·6H₂O 889mg (3mmol) and NH₄Cl 327mg (6mmol) in 25ml isopropyl alcohol were mixed with H₂DEA 642mg (6mmol) in 20ml isopropyl alcohol. After mixing ten minutes N₂H₄·H₂O 0,148ml (3mmol) (100%) was added. The mixture was refluxed at 90°C for two hours. After filtration a lilac precipitate has been obtained which was washed with isopropyl alcohol and dried under vacuum on P₂O₅.

The compositions of the complex: [Ni(HDEA)(μ-N₂H₄)(ONO₂)]₂: composition calculated. Ni, 22,8; C, 18,6; N, 21,8; H, 5,0%; found Ni, 22,5; C, 18,2; N, 21,2; H, 5,6%.

The complexes were not soluble in water, being stable in air and can be stored for several months without change.

The metallic ions have been determined by a volumetric method (with EDTA and murexid)[14] and C, N, H% contents by combustion. IR spectra (KBr pellets) were recorded on a BIO-RAD FTS 135 spectrometer.

UV-VIS spectra were measured with a VSU-2P (Carl Zeiss) spectrophotometer (diffuse reflectance technique), using MgO as a standard. Magnetic measurements were performed using Faraday's method, at room temperature. The calibration of the Faraday Balance (susceptibility constant and temperature) was made with Hg[Co(NCS)₄] as a standard. The literature mentions for this standard $\chi_g \cdot 10^6 = 16,44 \text{ cm}^3/\text{g}$ (at 25°C), a Curie-Weiss dependence with temperature, when $C = 2.433$, $\theta = +1,1\text{K}$ and $\chi_{\text{dia}} = -189 \cdot 10^{-6} \text{ cm}^3/\text{mol}$. The conductance measurements have been made on solutions 10⁻³M (DMF) with a conductance bridge Radelkis OK-102/1.

Results and Discussions

The molecular formulas (Table 1) are in accord with the molar conductance data showing the (1) and (2) compound as no electrolytes.

Table 1. Molar conductance data for compounds (1) and (2)

| Compounds | Conductance measurements ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) |
|--|--|
| $[\text{Co}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]$ (1) | 22 |
| $[\text{Ni}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]$ (2) | 46 |

The structure proposed for the two compounds is presented in Fig. 1.

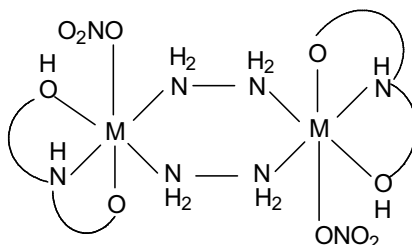


Fig. 1: The proposed structure for compounds (1) and (2).

IR ($4000\div 400\text{cm}^{-1}$), UV-VIS ($8000\div 25000\text{ cm}^{-1}$, reflectance) and magnetic effective moments (measured at room temperature) interpretation sustain the formulation of the complexes.

Infrared Spectra

$[\text{Co}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]$ IR (KBr, cm^{-1}): 3356s, 3290vs, 3226vs, 2962m, 1604s, 1574s, 1383s, 1340m, 1310m, 1260m, 1169vs, 1096s, 1026s, 973m, 803s;

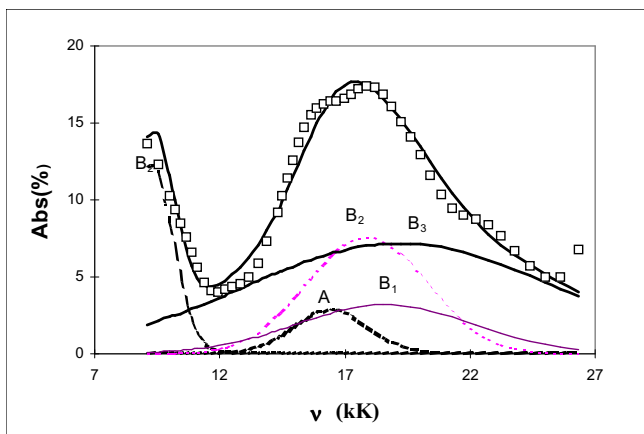
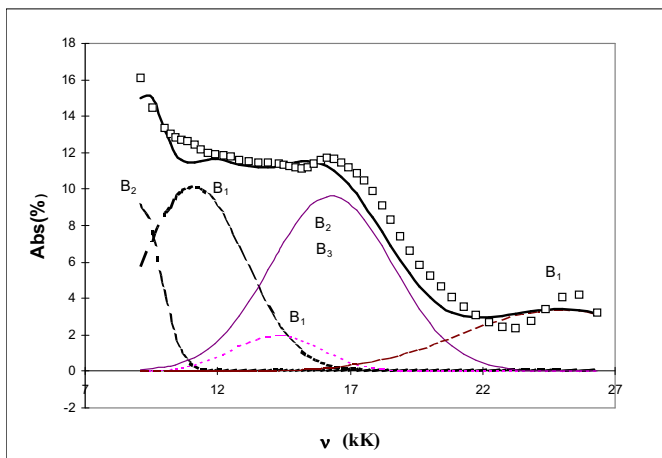
$[\text{Ni}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]$ IR (KBr pellets, cm^{-1}): 3490s, 3291vs, 3228s, 2962m, 1606s, 1575s, 1383s, 1340m, 1314w, 1260m, 1204m, 1171vs, 1096s, 1024s, 978m, 866w, 803s.

N-N stretching frequency 973cm^{-1} for (1) and 974cm^{-1} for (2) suggest a bidentate bridging coordination of N_2H_4 molecules [15,16]. Both compounds show the main CH amino-alcohol vibration modes at 2069 cm^{-1} ; the bands assigned to symmetrical and unsymmetrical vibration for CCN group at 1026 cm^{-1} (1) and 1024cm^{-1} (2) are shifted towards low wave numbers in accord with the amino-alcohol coordination through amino N.

The information given by infrared spectra reveals the presence of the two types of coordination ligands (blocking and assembling ones).

Electronic Spectra

The electronic spectra of compound (1) (Fig. 2) and (2) (Fig. 3) have been analyzed by the Angular Overlap Model-AOM [17÷20].

Fig. 2: Electronic spectra of $[\text{Co}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$ Fig. 3: Electronic spectra of $[\text{Ni}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$

The method consisted in performing the gaussian deconvolution of the spectra simultaneously with the fitting of and the Ligand Field equations. In this way, the maxim of experimental absorption, the experimental transitions for the Ligand Field problem were subject of a fitting.

Electronic spectra of $[\text{Co}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$ (**1**) could be analyzed by a simplified way, assuming the same value of the parameter e_σ (and $e_\pi = 0$) for all N donors, whatever is the ligand, hydrazine or diethanolamine, and also, only a pair of parameters e_σ , e_π , for all the oxygen atoms, both diethanolamine and coordinated nitrate. The obtained results are presented in Tables 2 and 3.

Table 2. AOM parameters for $[\text{M}^{\text{II}}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$

| Compound | e_σ^{N} | e_π^{N} | e_σ^{O} | e_π^{O} | B |
|---|-----------------------|--------------------|-----------------------|--------------------|------|
| $[\text{Co}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$ (3) | 3.69 | 0 | 2.73 | 0.474 | 0.74 |
| $[\text{Ni}(\text{HDEA})(\mu\text{-N}_2\text{H}_4)(\text{ONO}_2)_2]_2$ (4) | 4.70 | 0 | 2.41 | 0.480 | 0.82 |

Table 3. Electronic absorption maxims (gaussian deconvolution and calculated) for [Co^{II}(HDEA)(μ -N₂H₄)(ONO₂)₂]₂ (1)

| Experimental Spectra | | | | Calculated transitions (kK) |
|----------------------|-----------|-------|----------------|-----------------------------|
| Transitions | Intensity | Width | Assignment | |
| - | - | - | b ₁ | 6.91 |
| - | - | - | b ₃ | 8.06 |
| 9.30 | 12.38 | 0.87 | b ₂ | 9.30 |
| 16.50 | 2.80 | 1.46 | a | 16.81 |
| 17.90 | 7.61 | 2.37 | b ₂ | 18.09 |
| 18.60 | 3.20 | 3.50 | b ₃ | 18.40 |
| 19.20 | 7.19 | 6.19 | b ₁ | 18.62 |

One may observe a relatively high difference between the nitrogen and oxygen donor parameters, the latter corresponding to a weak intensity of a ligand field, as it is expected for the alcohol and for the nitrate as ligands. The higher values of the nitrogen average parameter, as compared to those obtained for hydrazine itself can be attributed to the contribution of the amino group from the amino-alcohol.

The spectral analysis of [Ni(HDEA)(μ -N₂H₄)(ONO₂)₂]₂ (2) compound is similar from the point of view of working hypothesis. The spectrum shows that the ν_1 as the ν_2 bands are highly splitted, so that the neighboring components of the two groups of transitions are overlapping. The donor distribution determines an ideal D_{2h} symmetry with and then a triple split of each octahedral band. Thus, considering the position of donors on the orthogonal axis, the x-axis will be assigned to the nitrogen atoms, the y-axis to the median nitrogen of the multibrige ligand and oxygen donors and z axis dedicated to the oxygen donors. The AOM parameter values obtained by the mentioned hypothesis indicate a high difference between the actions of nitrogen donors (strong σ donor) and oxygen atom (weak σ donor), determining the observed high splitting of bands. The simultaneous analysis of Ligand Field and of spectral deconvolution in gaussian components led to a good correlation between the experimental and simulated spectrum (Tables 2, 4).

Table 4. Electronic absorption maxims (gaussian deconvolution and calculated) for [Ni^{II}(HDEA)(μ -N₂H₄)(ONO₂)₂]₂

| Experimental spectra | | | | Calculated transitions (kK) |
|----------------------|-----------|-------|----------------|-----------------------------|
| Transition | Intensity | Width | Assignment | |
| | | | b ₃ | 7.42 |
| 9.07 | 5.50 | 1.69 | b ₂ | 9.23 |
| 11.14 | 8.80 | 2.79 | b ₁ | 11.66 |
| 14.27 | 3.50 | 1.99 | b ₁ | 14.85 |
| 16.30 | 7.93 | 2.20 | b ₂ | 15.98 |
| | | | b ₃ | 16.60 |
| 24.90 | 3.42 | 3.76 | b ₁ | 24.79 |
| | | | b ₂ | 25.61 |
| | | | b ₃ | 26.31 |

One may remark a high difference between e_{σ}^N and e_{σ}^O , the former corresponding to a high donor action while the latter a weak one.

Since the straight of the donors as resulted from the spectral analysis is in line with the expect ability of chemical intuition one may advocate for the validity of the assumed stereochemistry on the basis of which the given results were attained.

The information given by electronic spectra analysis is in good accordance with the magnetic moments values 5.18BM (1) and 3.9BM (2), calculated from the room temperature magnetic susceptibilities measurements.

The fact that the compounds were obtained as amorphous powders and not as single crystals means that no complete structure determination could be carried out. However, magnetic, conductance, spectroscopic data enable us to suggest the environment of the metal in complexes. As we expect the complexes are binuclear, the hydrazine double-bridging the two metallic centers, H₂DEA representing in the dimmer structures the chelating terminal ligands, showing the maximum coordination capacity.

Conclusion

Using the knowing coordination modalities and capacities of different ligands and the metallic ions, two complex compounds with predictable low nuclearity were obtained and characterized. Hydrazine acts as bridging ligand as expected and the amino-alcohol as chelating one. IR and AOM analysis of spectra sustain the formulation as binuclear compounds

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