

FT IR STUDY OF A MANGANESE(II) ACETATE COMPLEX WITH IMIDAZOLE – A POTENTIAL MODEL FOR THE MANGANESE CONTAINING ENZYMES

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Abstract: An imidazole adduct of Mn(II) acetate was synthesized and the regions of the OH/OD, NH/ND and COO stretchings in the low temperature FT IR spectra of its protiated and partially deuterated forms were studied. On the basis of the comparison with the spectra of other imidazole complexes, certain structural inferences about the prepared adduct were made.

The spectrum of the compound was substantially different from that of the Mn(II) compound obtained from EtOH as well as from the spectra of other bis(imidazole)M(II) diacetates (M = Co, Ni, Cu). The presence of two $\nu(\text{ND})$ bands indicates that there are at least two non-equivalent imidazole ligands in the compound. The appearance of the $\nu(\text{COO})$ spectral region implies that there is only a single type of monodentate acetate anions in its structure.

Key words: FT IR spectra, imidazole adduct, Mn(II) acetate

1. Introduction

Complexes of manganese(II) carboxylates with various ligands have received appreciable attention as models for the active sites of the Mn(II)-containing enzymes [1]. Recently, the scope in this research field was focused on the preparation of dimanganese complexes that feature similar coordination geometry around the metal ions with the active centers of some enzymes (e.g., arginase, ribonuclease H domain of HIV-1 transcriptase, etc.) [2].

As a part of our spectroscopic and structural studies of model compounds for metal-biomolecule interactions, we have synthesized an adduct of Mn(II) acetate with imidazole, a compound which could mimic the Mn(II) sites contacted by imidazole-containing biomolecules. The FT IR spectrum of this compound recorded at the boiling temperature of liquid nitrogen (LNT) is briefly reported here and compared with those of several other M(II) imidazole acetates.

2. Experimental

The imidazole adduct of manganese(II) acetate (MnIMAC) was synthesized from *n*-PrOH solutions of the corresponding acetate and imidazole (in molar ratio 1 : 4). Well-shaped, large pale tan crystals crystallized out, at room temperature, after a week. Some other imidazole acetates were prepared from the corresponding metal(II) acetates and imidazole, but using H₂O or EtOH as solvents.

The FT infrared spectra in the 4000–400 cm^{-1} frequency range were recorded with a System 2000 interferometer (Perkin–Elmer), using a P/N 21525 (Graseby Specac) variable-temperature cell, 32 background and 64 sample spectra being averaged (resolution was 4 cm^{-1}). Since, in the preliminary examination no differences were found between the sample spectra recorded in Nujol and KBr, all spectra were recorded from KBr pellets.

3. Results and Discussion

As can be seen from Fig. 1, the spectrum of MnIMAC differs from that of the imidazole adduct of manganese acetate obtained from EtOH. It is beyond any doubt, then, that although both Mn compounds comprise acetate ions and imidazole molecules, their structures are substantially different. The spectrum of the studied adduct is clearly different from those of the series of M(II)bis(imidazole) diacetates (M = Co, Ni, Cu; Fig. 1) as well, as it would be expected from the fact that MnIMAC is a solid *hydrate*, while the rest are anhydrous, as the determination of the structure of the Cu compound showed [3].

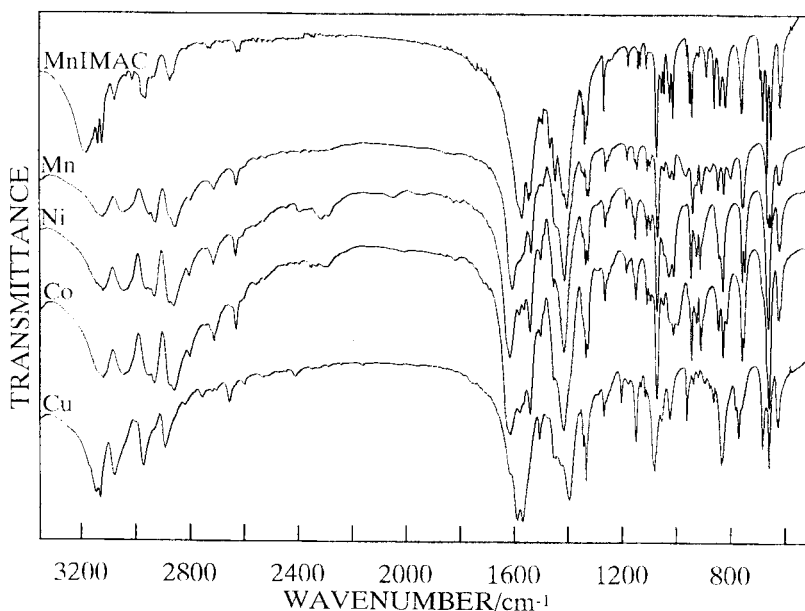


Fig. 1. The LNT FT IR spectra of MnIMAC and the bis(imidazole) diacetates of Mn, Co, Ni and Cu

3.1. XY (X = O, N; Y = H, D) Stretching Region

A single, strong, complex and relatively broad $\nu(\text{OH})$ band (3179 cm^{-1}) appears in the LNT spectrum of MnIMAC (Fig. 1). A doublet of sharp and almost equally intense $\nu(\text{NH})$ bands (3135 and 3120 cm^{-1}) as well as several lower-frequency bands (around 2965 and 2870 cm^{-1}) that probably also involve a large contribution from the $\nu(\text{NH})$ modes, are present as well. The spectral picture is much simpler in the $\nu(\text{OD/ND})$ region of the nearly 40% deuterated MnIMAC (Fig. 2).

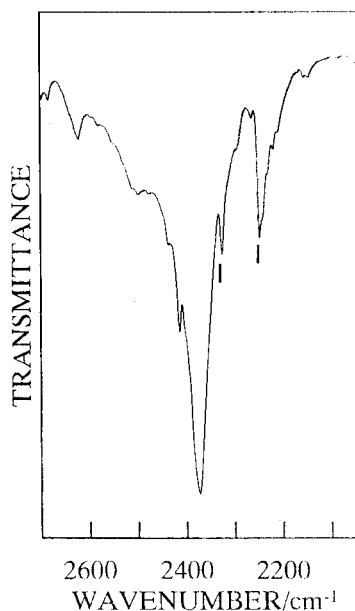


Fig. 2. The $\nu(\text{OD/ND})$ region in the LNT spectrum of deuterated ($\approx 40\%$ D) MnIMAC

The presence of the two $\nu(\text{ND})$ bands (2324 and 2246 cm^{-1} , Fig. 2) indicates that there are at least two non-equivalent imidazole ligands in the structure of the compound, one of the imino groups participating in rather weak hydrogen bonds and the other in hydrogen bonds of appreciable strength.

3.2. COO Stretching Region

The presence of additional bands (e.g., from the imidazole ring or the crystal water) in the $\nu(\text{COO})$ region (Fig. 1) complicates the assignment of the $\nu(\text{COO})$ modes in the spectrum of MnIMAC. Namely, according to the inelastic neutron scattering results and several *ab initio* calculations on imidazole [4], at least *three* imidazole ring stretching modes, two of which being largely mixed with NH bending modes, are expected for each structural type of imidazole ligands in the $1660\text{--}1360\text{ cm}^{-1}$ region.

On the basis of their appearance, thermal behavior and the deuteration effects, however, a single pair of bands (1571 and 1403 cm^{-1} at LNT, Fig. 1) could be assigned to the stretching mode of the acetate groups in the spectrum of MnIMAC. This could be an indication that either all acetate groups in the structure of the studied compound are structurally equal or that they have very similar geometries.

Several attempts have been made previously to correlate the positions of the antisymmetric and the symmetric acetate carbonyl stretching bands or the frequency difference between them on the one hand, with the type of the bonding of the acetate ions on the other [5–7]. All these criteria, however, should be taken with caution [8]. What was generally concluded from these studies was that the value of the difference between the two carbonyl stretching modes in the case of *ionic* acetate groups is expected to lie within the $164\text{--}171\text{ cm}^{-1}$ interval, while larger values are expected in the case of monodentate, and lower for the biden-

tate helating acetate groups. From the value of the frequency difference in the case of MnIMAC (168 cm^{-1}), therefore, it can be predicted that the acetate groups in its structure are either ionic or, probably, *monodentate*. The confirmation of these predictions, however, needs further structural investigations.

4. Conclusions

The structure of the imidazole adduct of Mn(II) acetate synthesized from *n*-propanol is different from those of the bis(imidazole) diacetates of Co(II), Ni(II), Cu(II) and Mn(II) (the last synthesized from EtOH). It is probable that there are at least two structural types of imidazole molecules and a single type of monodentate acetate groups in its structure.

5. References

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ИЗУЧУВАЊЕ НА ФУРИЕ ТРАНСФОРМНИТЕ ИНФРАЦРВЕНИ СПЕКТРИ НА МАНГАН(II) АЦЕТАТЕН КОМПЛЕКС СО ИМИДАЗОЛ – ПОТЕНЦИЈАЛЕН МОДЕЛ ЗА ЕНЗИМИТЕ ШТО СОДРЖАТ МАНГАН

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Апстракт: Синтетизиран е адукт на Mn(II) ацетат со имидазол и проучени се областите на OH/OD, NH/ND и COO валентните вибрации во Фурие трансформните инфрацрвени спектри на неговите протирани и парцијално деутерирани аналози, снимени на ниска температура. Врз основа на споредбата со спектрите на други имидазолни комплекси, направени се определени претпоставки во врска со структурата на синтетизираното соединение.

Најдено е дека спектарот на испитуваниот комплекс значително се разликува од тој на Mn(II) имидазол ацетатот синтетизиран од EtOH, како и од спектрите на други бис(имидазол)M(II) диацетати (M = Co, Ni, Cu). Присуството на две $\nu(\text{ND})$ ленти укажува на тоа дека постојат најмалку два структурни типа на имидазолни лиганди. Од изгледот на $\nu(\text{COO})$ областа може да се претпостави дека сите ацетатни групи во испитуваното соединение се монодентатни и структурно еквивалентни.