

Spectral Investigations on Bis Monothioacetylacetonate Complexes of Ni(II), Pd(II), Cu(II) and Zn(II)

¹D.T. HAWORTH AND M. DAS, ²L.M. PRONIEWICZ AND ³J. SCIESINSKI

¹Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233 U.S.A.

²Regional Laboratory of Physicochemical Analyses and Structure Research Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

³H. Niewodniczanski Institute of Nuclear Physics, Radzikowskiego 152, 31-342 Krakow, Poland

(Received 14th November, 1994, revised 9th February, 1995)

Summary: Several complexes of some monothioacetylacetonate (TAA) of four-coordinate nickel, copper, zinc and palladium have been prepared in order to examine their low-frequency FT-IR spectra. On the basis of their IR data a relationship between structural changes caused by metal substitution in these complexes is suggested.

Introduction

In recent years metal(II) complexes of tetradentate ligands of $[O_2S_2]^{2-}$ and $[N_2S_2]^{2-}$ types have gained sustained attention since they may serve as model complexes of metalloenzymes active sites. By varying the substituents and chain length in these ligands as well as metal ions one can fine tune their electronic and structural properties to mimic those found in nature. Hundreds of these compounds have been synthesized and their physicochemical properties measured [1,3]. Among them, Ni(II) and Cu(II) complexes have been studied the most since they show extreme sensitivity to the influence of the coordinating ligand as well as they can be substituted into various types of metal-containing enzymes [3-8].

Data obtained from x-ray diffraction, x-ray absorption, electron spin resonance, magnetic circular dichroism and vibrational spectroscopy suggest [1-4, 7-13] that in simple tetradentate complexes, where there is no significant steric interaction, Ni(II) prefers a square-planar, while Cu(II) appears to be in more of a pseudotetrahedral geometry.

Here we report the synthesis and low-frequency FT-IR spectra of $M(TAA)_2$, bis-(monothioacetylacetonato)M complexes, where M = Ni(II), Pd(II), Cu(II) and Zn(II). The main goal of this study is to provide a relationship between structural changes caused by different metal substitution in the complex and their spectral patterns.

Results and Discussion

The FT-IR spectra of $M(TAA)_2$ complexes are presented in Fig. 1. Previously, Siiman *et al.* [12,13] reported IR spectra and band assignment based on normal coordinate analysis of Ni(II) and Pd(II) complexes. Our data agree quite well within the $\pm 5 \text{ cm}^{-1}$ range with those presented earlier. In addition, some weak bands are observed in the spectra presented in this work.

As shown in Figure 1, Ni(II) and Pd(II) complexes exhibit similar patterns in frequency and intensity in the whole range except the bands at 256 (Ni) and 227 cm^{-1} (Pd). As was discussed previously [12,13], $Ni(TAA)_2$ has a cis-planar structure with C_{2v} point symmetry. Thus, two ν (Ni-S) vibrations of A_1 and B_2 symmetry are expected. The ν (Ni-S) of A_1 symmetry appears in IR spectrum as an intense band, while the Ni-S symmetric stretching (B_2) can be missing in IR spectrum due to its low intensity. Thus, the strong band at 256 cm^{-1} is readily assigned to ν (Ni-S), *i.e.* it is up-shifted by 5 cm^{-1} in comparison with this reported earlier. The ν (Ni-S) of B_2 symmetry is not observed in the spectrum. Similar situations are encountered for the $Pd(TAA)_2$ complex which exhibits the ν (Pd-S) mode 227 cm^{-1} , *i.e.* 3 cm^{-1} higher than that reported previously. The ν (Ni-S) and ν (Pd-O) cannot be located easily in the spectra since they strongly mix with the δ (C-CH₃) vibrations. However, these stretchings are expected to appear at around 400 cm^{-1} .

When Zn(II) binds to the TAA ligands this metal complex adopts a tetrahedral structure,

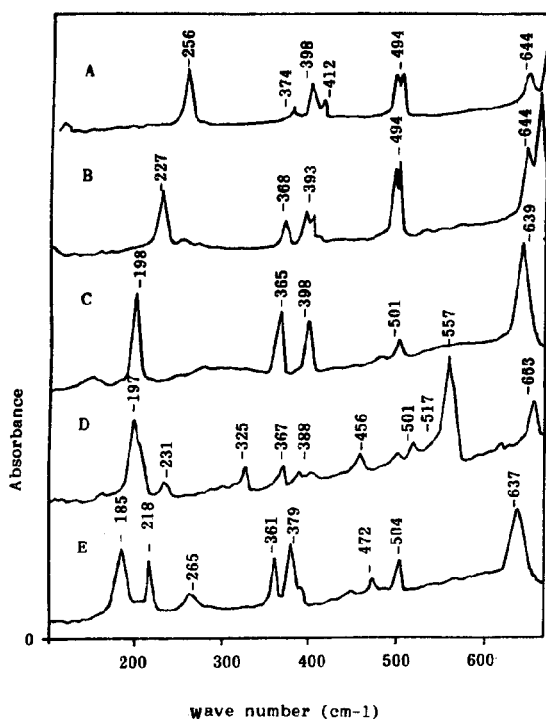


Fig. 1: FT-IR spectra of $M(\text{TAA})_2$ complexes A - $\text{Ni}(\text{TAA})_2$, B - $\text{Pd}(\text{TAA})_2$, C - $\text{Zn}(\text{TAA})_2$, D - $\text{Zn}(2'\text{-thienylCSCHCOCF}_3)_2$, E - $\text{Cu}(\text{TAA})_2$.

where the C_2 axis bisects the SZnS and OZnO angles [17]. Therefore, the symmetric displacement of the sulfur atoms is along the same C_2 axis as in the previously discussed *cis*-planar structure. Consequently, the Zn-S symmetric stretching is expected to appear in the IR spectrum as an intense band, while the Zn-S asymmetric stretching will be either very weak or absent in this spectrum. Examination of Figure 1 allows us to assign the band at 198 cm^{-1} to the $\nu(\text{Zn-S})$ vibration since this is the only single, intense band in the 200 cm^{-1} range. Also, when both methyl groups in TAA are substituted by thienyl and $-\text{CF}_3$ groups, the IR spectrum changes. However, the band at 197 cm^{-1} stays showing that this band has to be assigned to $\nu(\text{Zn-S})$. Similar to $\text{Ni}(\text{II})$ and $\text{Pd}(\text{II})$ complexes, the Zn-S asymmetric stretching and $\nu(\text{Zn-O})$ are not observed in the spectra.

The Cu 1:2 metal to ligand complexes of monothioacetylacetonates have been reported from dipole moment data to assume a distortion

from square planar toward a tetrahedral configuration (1). The IR spectra of $\text{Cu}(\text{TAA})_2$ differs from those spectra discussed above. The most puzzling features in the $\text{Cu}(\text{TAA})_2$ spectrum are two strong bands at 185 and 218 cm^{-1} . It is less likely that the distortion of the symmetry from *cis*-planar geometry can cause the appearance of these two bands, *i.e.* TAA has to form two different Cu-S bands. Taking in account our discussion about $\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$ and $\text{Zn}(\text{II})$ complexes, as well as a mass effect on a metal-sulfur vibration and a half-band width of those bands, we assign the 218 cm^{-1} band to $\nu(\text{Cu-S})$, while the assignment of the 185 cm^{-1} band cannot be certain at this moment.

A further analysis of the spectra in Fig. 1 shows features for the $\text{Cu}(\text{TAA})_2$ complex which are quite similar to the $\text{Zn}(\text{TAA})_2$ complex but different from the $\text{Ni}(\text{TAA})_2$ and $\text{Pd}(\text{TAA})_2$ complexes. For example, the one band at 637 cm^{-1} (out of plane, C-H) in the $\text{Cu}(\text{TAA})_2$ complex is comparable to the 639 cm^{-1} band in $\text{Zn}(\text{TAA})_2$, whereas, the Ni and Pd complexes show two bands in this region. Similarly, one band at *ca.* 500 cm^{-1} [$\delta(\text{C-CH}_3) + \delta(\text{CCS}) + \delta(\text{CCO}) + \delta(\text{CCC})$] in the $\text{Cu}(\text{TAA})_2$ and $\text{Pd}(\text{TAA})_2$ complexes [12,13]. Evidence for a distortion of $\text{Cu}(\text{TAA})_2$ towards a tetrahedral geometry is also shown in the IR spectrum of the Zn complex (Fig. 1) where the methyl groups have been substituted by thienyl and $-\text{CF}_3$ groups.

Finally, the dipole moments of the Ni and Pd complexes of the ligand, $\text{CH}_3\text{CSCH}_2\text{COCH}_3$, are 2.26 D and 2.21 D , respectively, whereas the Zn and Cu complexes have similar dipole moments of 2.89 D and 2.90 D , respectively [18]. These data also support a distortion towards a tetrahedral configuration for $\text{Cu}(\text{TAA})_2$.

Experimental

The monothioacetylacetonate used in this work was prepared by the method of Dius and Anthonsen [14]. The crude ligand was used to prepare the complexes.

To 4.0 g of $\text{CH}_3\text{CSCH}_2\text{COCH}_3$ was added a boiling solution of zinc acetate dihydrate (2.0 g) in 60 mL of absolute ethanol. The solution was immediately filtered and cooled in an ice bath for 30 min . The $\text{Zn}(\text{CH}_3\text{CSCHCOCH}_3)_2$ was filtered

and recrystallized from 60 mL of absolute ethanol. The other metal complexes of TAA were prepared by our previously reported receipts [15].

Anal. Calc for $C_{10}H_{14}S_2O_2Zn$; C, 40.62; H, 4.77; S, 21.68. Found: C, 40.54; H, 4.99; S, 21.4.

The $Zn(2\text{-thienylCSCHCOF}_3)_2$ was accomplished by previously reported method [16].

Depending on a sample 3.5-5.5 mg of complex was suspended in Apiezon L vacuum grease and placed between polyethylene windows to measure solid-state IR spectra at room temperature. These spectra were recorded on a Digilab (Bio-Rad) FT-IR 14 Model interfaced to an IBM 486 computer. To obtain a good quality spectrum, usually 200 - 300 scans were taken at a 2 cm^{-1} resolution. Spectra were then imported into SpectraCalc software (Galactic Instruments, Nashua, NH) for further data analysis.

References

1. S.E. Livingstone, *J. Organometal. Chem.*, **239**, 163 (1982).
2. R.C. Mehrotra, B. Bohra and D.P. Gaur, in "Metal β -Diketonates and Allied Derivatives", Academic Press, New York (1978).
3. J. Lancaster, ed. "The Bioinorganic Chemistry of Nickel", VCH Publishers, Inc., New York (1988).
4. R. Cammack, *Adv. Inorg. Chem.*, **32**, 297 (1988).
5. S.K. Mondal, P. Paul, R. Roy and K. Nag. *Transition Met. Chem., (Weinheim Ger.)*, **9**, 247 (1984).
6. J.A. Blaszak, E.L. Ulrich, J.L. Markley and D.R. McMillin, *Biochemistry*, **21**, 6253 (1982).
7. R.D. Bereman, J.R. Dorfman, J. Border, D.P. Rillema, P. McCarthy and G.D. Shields, *J. Inorg. Biochem.*, **16**, 47 (1982).
8. E.M. Martin, R.D. Bereman and P. Singh, *Inorg. Chem.*, **30**, 957 (1991).
9. S.P.J. Albracht, A. Kroger, J.W. Wan der Zwaan, G. Uden, R. Bocher, H. Mell and R.D. Fontijn, *Biophys. Acta*, **874**, 116 (1986).
10. P.A. Lindhal, N. Kojima, R.P. Hausinger, J.A. Fox, B.K. Teo, C.T. Walsh and W.H. Orme-John, *J. Am. Chem.Soc.*, **106**, 3062 (1984).
11. R.A. Scott, S.A. Wallin, M. Czechowski, D.V. Der Vartanian, J. LeGall, H.D. Peck and I. Moura, *J. Am. Chem. Soc.*, **106**, 6864 (1984).
12. O. Siiman, D.T. Titus, C.D. Cowman, J. Fresco and H.B. Gray, *J. Am. Chem. Soc.*, **96**, 2353 (1974).
13. O. Siiman, J. Fresco and H.B. Gray, *J. Am. Chem. Soc.*, **96**, 2347 (1974).
14. F. Duus and J.W. Anthonsen, *Acta Chem. Scand.*, **B31**, 40 (1977).
15. M. Das, *Inorg. Chim. Acta.*, **36**, 79 (1979).
16. M. Das, *Transition Met. Chem.*, **5**, 17 (1980).
17. U. Thewalt, private communication.
18. M. Das and D.T. Haworth, *Synth. React. Inorg. Met-Org. Chem.*, **13**, 449 (1983).