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Mössbauer, Far-Infrared and Raman Spectra of Tetrachloro[1,4-Di(*p*-Methoxyphenyl)-2,3-dimethyl-1,4-diazabutadiene] Tin(IV)

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Summary. The dependence of the logarithm of the area under the tin-119 Mössbauer resonance (A at different temperatures are normalized to A_{77}) vs. temperature is measured for tetrachloro[1,4-di(*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadiene] tin(IV). The slope of the plot of $\ln A$ vs. T is $-2.46 \cdot 10^{-2} \mathrm{K}^{-1}$, suggesting a monomeric structure. In the vibrational spectra the significant stretching vibrations agree with a *cis* octahedral configuration of C_{2v} symmetry.

Keywords. Tetrachloro tin(IV); Diazabutadiene; Mössbauer; Far-infrared.

Mössbauer-, Fernes-Infrarot- und Raman-Spektren von Tetrachlor[1,4-di(*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadien]zinn(IV)

Zusammenfassung. Die Abhängigkeit des Logarithmus der Fläche unter der Zinn-119-Mössbauer-Resonanz (A in verschiedenen Temperaturen werden zu A_{77} normalisiert) von der Temperatur wurde für Tetrachlor[1,4-di(*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadien]zinn(IV) gemessen. Der Anstieg $\ln A$ gegen T von $-2.46 \cdot 10^{-2} \mathrm{K}^{-1}$ spricht für eine monomere Struktur. In den Vibrations-Spektren stimmen die wichtigsten Dehnungsschwingungen mit einer *cis*-oktaedrischen Konfiguration von C_{2v}-Symmetrie überein.

Introduction

Molecules containing the 1,4-diaza-1,3-butadiene skeleton proved to be very interesting not only because of their versatile coordination behaviour, but also because of the wide variety of reactivity patterns.

1,4-di(*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadiene have a flat N=C—C=N skeleton in the *E-S-trans-E* conformation [1]. In other α,α′-diimines as 2,2′-bipyridine calculations indicate that the planar *S-trans* conformation is 20–28 KJ mol^{-1} more stable than the *S-cis* form [2] owing mainly to the interaction of the lone pairs.

In this work we studied the complex of tin tetrachloride with 1,4-di(*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadiene, the coordination number and stereometries on basis of IR, Raman and Mössbauer spectra. The structure determination by means of vibrational spectroscopy has been utilized extensively to study these adducts. However, the assignment of stereochemistry by infrared spectroscopy is not always simple and often led to erroneous assignment when infrared and Raman techniques were not used simultaneously. On the other hand, in order to clarify the stereochemistry, the Mössbauer spectroscopy is a useful tool to investigate that question [3–10]. Variable-temperature Mössbauer spectroscopy can help us to solve this problem, and allows in our case, to propose a monomeric structure for this compound.

Experimental

$SnCl_4(C_{18}N_2O_2H_{20})$ was prepared by reacting $SnCl_4$ (Scharlau, distilled under a nitrogen atmosphere in a Vigreux column) in carbon tetrachloride with an equimolecular quantity of ligand in carbon tetrachloride solution. The preparation was carried out in a vacuum line or in a dry-box filled with dry nitrogen. The addition reaction proceeded smothly and the precipitate formed inmediately. The reaction mixture was kept stirring for about 30 min after the first precipitation was observed. Anal. calcd. for $SnCl_4(C_{18}N_2O_2H_{20})$: C 38.6, N 5.0, H 3.6; found: C 38.8, N 5.6, H 3.4.

The Mössbauer spectra were recorded for the polycrystalline samples in transmission standard geometry by using a filtered (Pd 50 μm foil filter) $Ca^{119}SnO_3$ source at room temperature, placed in one of the transducer sides and the other side being used for calibration purposes. Velocity calibration was obtained with α-Fe foil (6.25 μm thick) and isomer shift (δ) reference with respect to the center of a room temperature $BaSnO_3$ spectrum. The maximum statistical error in the experimental point was 0.2%, and the reproducibility of the parameter was $\pm$ 0.02 and $\pm$ 0.03 mm s^{-1} for δ and Γ, respectively. The low temperature instrumentations, control, stability and measurements procedures have been described previously [10]. Data reduction was performed by folding the spectra after determining carefully the folding point. The computation methods and all remaining experimentals details have also been described previously [11].

The infrared spectrum was recorded as Nujol and hexachlorobutadiene mulls with CsI plates. A Nicolet 60-SX infrared spectrometer was used for the obtention of the far IR spectrum. As detector a DTGS with polystyrene windows was used. The detector was furnished with MYLAR a beam divider of 6 μ thickness and 2 cm^{-1} resolution. Raman spectra was measured with Jarrell-Ash 25–300 using a Kr laser as a source of excitation.

Results and Discussion

Tin-119 Mössbauer spectra were recorded at temperatures in the range 77–170 K. A representative spectrum is show in Fig. 1. These spectra show a resolved single line according to the Γ measurement through the temperature range. The resulting parameters from a single-line fitting at 77°K are: $\delta = 0.53$ mm s^{-1}, $\Gamma = 0.96$ mm s^{-1} and $\chi^2 = 302$ with 194 degrees of freedom.

Using the thin absorber approximation and the Debye model for the solid, f is linearly dependent to the area under the Mössbauer resonance peak, A, and its temperature variation is defined by the equation:

$$A \alpha f = \exp | -6 E_R T / K \theta^2_D | \qquad \text{for} \qquad T \geqslant \theta_D / 2 E_R$$

and θ_D being the Mössbauer recoil energy and the Debye temperature of the solid respectively. Accordingly, in the high-temperature limit, a plot of $\ln A$ vs. temperature should be linear, and the slope of the straight line may yield information about the intermolecular interactions in the solid [3, 4, 8, 9].

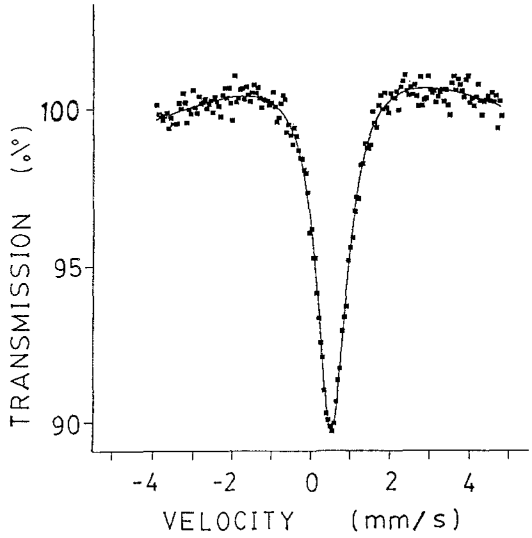

Fig. 1. Mössbauer spectrum of tetrachloro-1,4-di[*p*-methoxyphenyl)-2,3-dimethyl-1,4-diazabutadiene]-tin(IV) at 77°K

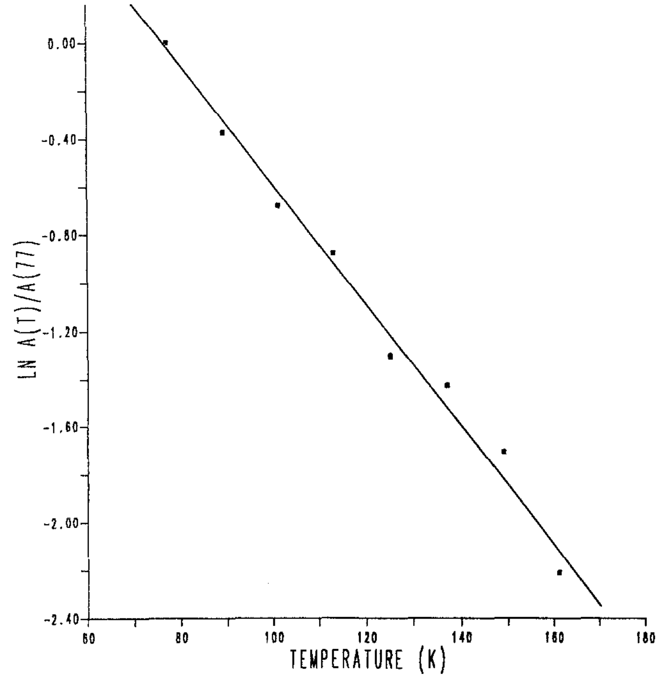

Fig. 2. Temperature dependence of the normalized area under the resonance spectra

A plot of the $\ln A$ (A_T at different temperature are normalized to A_{77}) vs. temperature is displayed in Fig. 2, and a regression straight line ($r = 0.994$) can be obtained with a slope $d(\ln A)/dT = -2.46 \cdot 10^{-2} K^{-1}$.

These values correspond to an arrangement of noninteracting monomeric molecules in the solid [3].

In the vibrational spectra the wave numbers of the significant stretching vibrations agree with a *cis* octahedral configuration of C_{2v} symmetry. With respect to the free ligand, the strong band corresponding to the C = N stretching frequency is shifted to lower wave numbers for about 15 cm^{-1} upon coordination. The apparent

Table 1. SnCl and SnN infrared and Raman vibrational frequencies (cm^{-1}) for $SnCl_4(C_{18}N_2O_2H_{20})$

IR	R	
329 (sh, s)	330 (s)	ν_{Sn-Cl}
320 (vs)	—	
304 (w)	305 (m)	
292 (w)	292 (m)	
183 (vw)	190 (m)	ν_{Sn-N}
166 (m)	167 (m)	

lack of splitting of the $\nu(C=N)$ in a *cis* adduct is explicable in terms of the mass of the tin atom.

Four Sn—Cl stretching frequencies have been observed between 340 and 280 cm^{-1}, corresponding to $2A_1 + B_1 + B_2$ modes. The Sn—Cl stretching region (usually 350–300 cm^{-1}) [12–14] is often obscured by other vibrations such as Sn-*L* stretching and ligand bands, but the free ligand show only a weak absorption at 328 cm^{-1}. The Sn—N stretching bands often are difficult to assign. Two bands at 183 and 166 cm^{-1} are observed, corresponding to $A_1 + B_2$ modes, in concordance with [13–15], where the Sn—N stretching vibrations of the *bipy* and *phen* complexes at 183–160 cm^{-1} have been assigned based on metal isotope data. The main peaks observed in the infrared spectrum coincide with lines found in the Raman spectrum, indicating the lack of a center of symmetry. Two bands between 150–142 cm^{-1} may be assigned to the skeletal bending modes. Table 1 shows the far infrared and Raman frequencies in cm^{-1} for ν(Sn—Cl) and ν(Sn—N).

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References

[1] Navarro-Ranninger M. C., Hoyos M. A., Martínez-Carrera S. (to be published)

[2] Benedix R., Birner P., Birnstock F., Hennig H., Hoffman H. J. (1979) J. Mol. Struct. **51**: 99

[3] Molloy K. C., Bigwood M. P., Herber R. H., Zuckerman J. J. (1982) Inorg. Chem. **21**: 3709

[4] Cunningham D., Firtear P., Molloy K. C., Zuckerman J. J. (1983) J. Chem. Soc. Dalton Trans.: 1523

[5] Lefferts J. L., Molloy K. C., Zuckerman J. J., Haiduc I., Curtui M., Guta C., Ruse D. (1980) Inorg. Chem. **19**: 2861

[6] Harrison P. G., Phillips R. C., Thornton E. W. (1977) J. Chem. Soc. Chem. Comm.: 603

[7] Harrison P. G., Sharpe N. N., Pelizzi C., Pelizzi G., Tarasconi P. (1983) J. Chem. Soc. Dalton Trans.: 921

[8] Harrison P. G., Lambert K., King T. J., Majee B. (1983) J. Chem. Soc. Dalton Trans.: 363

[9] Harrison P. G., Sharpe N. N., Pelizzi C., Pelizzi G., Tarasconi P. (1983) J. Chem. Soc. Dalton Trans.: 1687

[10] Tudela D., Fernández V., Tornero J. D. (1985) Inorg. Chem. **24**: 3892
[11] Tudela D., Fernández V., Tornero J. D. (1984) Z. anorg. allg. Chem. **509**: 174
[12] Ohkaku N., Nakamoto K. (1973) Inorg. Chem. **12**: 2440
[13] Fowles G. W. A., Rice D. A., Walton R. A. (1976) Spectrochim. Acta, Part A **25**: 1035
[14] Clark R. J. H., Davies A. G., Ruddephatt R. J. (1968) J. Chem. Soc. A: 1828
[15] Kawano Y., Hase Y., Sala O. (1976) J. Mol. Struct. **30**: 45

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