

## Thermal and spectral analyses of complexes of zinc(II)tetra-tertbutylphthalocyanine with amines

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**Abstract** Spectral and thermochemical studies of complexes of zinc(II)tetra-tertbutylphthalocyanine ( $\text{Zn}(\text{t-Bu})_4\text{Pc}$ ) with some amines have been carried out. Spectral effects of the complex formation of the metallophthalocyanine with amines have been established. It has been found that an ability of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  to coordinate amines depends on both their nature and conditions of preparation. Similarity of the crystal structures of biligand and monoligand of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  complexes to individual  $\beta$ - and  $\alpha$ -polymorphs of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ , respectively is proved by IR spectroscopy and X-ray diffraction method.

**Keywords** Metallophthalocyanines · Crystallosolvates · Molecular complexes · Thermogravimetry · IR spectra

### Introduction

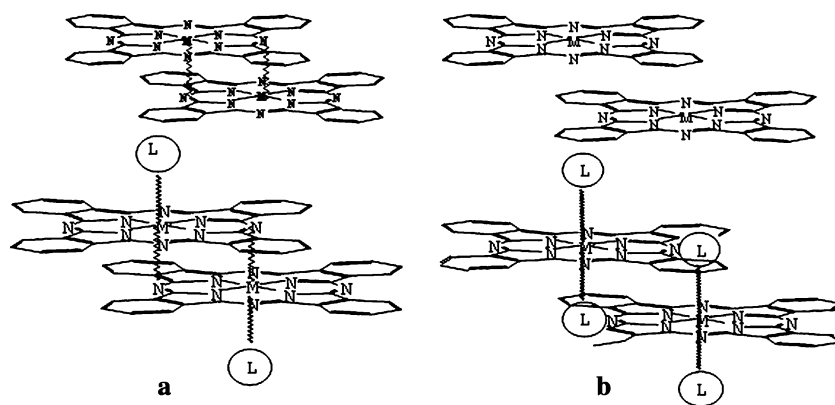
Information on specific intermolecular interactions of metallophthalocyanines (MPc) with solvent molecules is necessary for development of new molecular tests, chemo- and gaseous sensors on the basis of these macrocyclic compounds as well as optimization of their regeneration. In our early work [1] we showed that for crystallosolvates of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pyridine and pipyridine a partial mole stoichiometry is observed. We proposed that the partial mole composition of the

crystallosolvates of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pyridine is due to competition between  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ – $\text{Zn}(\text{t-Bu})_4\text{Pc}$  and  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ –pyridine interactions. At crystallization of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  from organic solvents, a mixture of  $\alpha$ - and  $\beta$ -polymorphs is formed. Due their different structures, the molecules of MPc in the individual polymorphic modification can bind one or two pyridine molecules (according to scheme presented in Fig. 1).

On the other hand, a high aromacity of MPc molecule and a high potential of ionization of some studied ligands as well as rare literature data concerning an effect of conditions of preparation of the complexes on their composition allow proposition about a high energy barrier of formation of biligand MPc complexes. It should be noted that metallophthalocyanine molecules have comparatively big size (about 20 Å). Therefore, the crystal of MPc may contain the solvent molecules filling cavities in the crystal lattice of MPc and non-interacting specifically with the macrocycle. Thermogravimetric analysis of the crystallosolvates allows to estimate intermolecular interactions between MPc and solvent molecules. The enthalpy changes of evaporation ( $\Delta_{\text{evp}}H$ ) of solvent molecules from the crystallosolvate consist of two contributions: (i) the energy losses associated with breaking of macrocycle—solvent bonds and (ii) the work of expansion at transition of the substance to the gaseous phase. The last contribution is negligible (2–3 kJ mol<sup>-1</sup>). Thus, in the first approach,  $\Delta_{\text{evp}}H$  value reflects energetic strength of the macrocycle—solvent bonds. If  $\Delta_{\text{evp}}H$  value is significantly greater than that for pure solvent, it testifies about specific intermolecular interaction between MPc and the solvent (donor–acceptor interaction, hydrogen bonding,  $\pi$ – $\pi$  interaction). Therefore, in the preset work a nature of the interaction between

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**Fig. 1** Scheme of arrangement of MPC molecules in  $\beta$ - (a) and  $\alpha$ - polymorphs (b) and possible pseudo-polymorphs

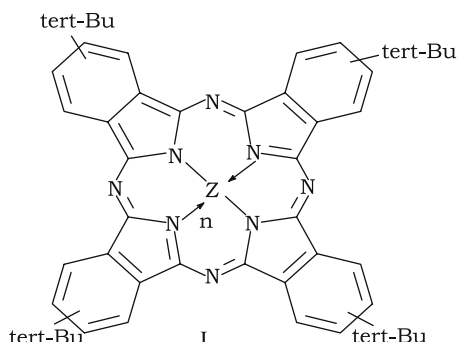


$\text{Zn}(\text{t-Bu})_4\text{Pc}$  and N-containing molecules has been studied by thermogravimetric analysis method and IR spectroscopy.

Besides, the aim of this work is to estimate the dependence of ability of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  to coordinate N-containing ligands on their nature and conditions of preparation of the crystallo-solvates. A comparative analysis of packing of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  molecules and its molecular complexes on the basis of IR spectral data and X-ray diffraction data is an important part of the present work.

## Experimental

The synthesized zinc(II)tetra-tertbutylphthalocyanine (I) was purified by chromatography on  $\text{Al}_2\text{O}_3$  (activity II) and then sublimated under vacuum ( $0.8\text{--}0.9\text{ kgf cm}^{-1}$ ) at 473 K. Morpholine, piperidine, pyridine, 3-dimethylaminopropionitrile, diethylamine, *n*-propylamine, quinoline, diethylaniline were purified according to known procedures before use: the reagents were treated by NaOH and 4 Å molecular sieves and then distilled. Content of water in the reagents was determined by chromatography. It was not greater than 0.01% for all solvents under study.



## Preparation of the samples

The samples of the crystallo-solvates were prepared by two methods. “Cool” preparation: the sample of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  was dissolved in the corresponding solvent at room temperature. The solution was filtered. Excess of the solvent was removed by evaporation of the filtrate by flow of cool air. The saturated solution of MPC was kept for slow crystallization. “Hot” preparation: the sample of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  was dissolved in the corresponding solvent. The obtained solution was refluxed for 6–8 h and then the solution was filtered and kept for slow crystallization.

Individual  $\alpha$ - and  $\beta$ -polymorphs of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  were prepared in accordance with recommendations [2, 3]. Solution of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  in concentrated  $\text{H}_2\text{SO}_4$  was slowly flowed out on ice. The obtained crystals of the  $\alpha$ -polymorph of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  were washed by distilled water up to pH = 7 and dried at room temperature. To obtain the crystals of  $\beta$ -polymorph, the sample of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  was kept at 453–473 K for 5–6 h.

The molecular complexes  $\text{Zn}(\text{t-Bu})_4\text{Pc}\cdot n\text{L}$  for IR spectral and X-ray diffraction analysis were prepared by heating of the corresponding crystallo-solvates up to a temperature that is lower by 5–10 °C than the temperature of destruction of the molecular complexes (Table 1).

For IR spectral measurements the molecular complexes  $\text{Zn}(\text{t-Bu})_4\text{Pc}\cdot n\text{L}$  were mixed with KBr in 1:300 ratio.

## Methods

### Infrared spectroscopy

IR spectra of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  complexes were registered using Perkin Elmer “SpectrumBX” and Avatar 360 FT $\nu$  IR ESP spectrophotometers in 4000–400  $\text{cm}^{-1}$  region.

**Table 1** Physical chemical characteristics of molecular complexes of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with ligands

| Ligand                        | Method of preparation | Zn(t-Bu) <sub>4</sub> Pc:L | T <sub>destr</sub> (K) | Δ <sub>evp</sub> H (kJ mol <sup>-1</sup> ) |
|-------------------------------|-----------------------|----------------------------|------------------------|--------------------------------------------|
| Pyridine                      | “Hot”                 | 1:2                        | 380                    | 95.4                                       |
|                               | “Cool”                | 1:1                        | 408                    | 116.7                                      |
| Piperidine                    | “Hot”                 | 1:6                        | 366                    | 47.7                                       |
|                               |                       | 1:2                        | 399                    | 86                                         |
|                               | “Cool”                | 1:5                        | 366                    | 47.7                                       |
| Diethylamine                  | 1:6                   | 1:1                        | 407                    | 120.1                                      |
|                               |                       | 1:2                        | 338                    | 49.5                                       |
|                               | 1:2                   | 352                        | 93.5                   |                                            |
| <i>n</i> -Propylamine         | 1:6                   | 1:6                        | 353                    | 64.2                                       |
|                               |                       | 1:2                        | 373                    | 70                                         |
|                               | 1:2                   | 401                        | 57.7                   |                                            |
| Quinoline                     | 1:2                   | 401                        | 57.7                   |                                            |
| 3-Dimethylamino propionitrile | 1:2                   | 432                        | 80.1                   |                                            |
| Morpholine                    | 1:2                   | 360                        | 154.7                  |                                            |
| Diethylaniline                | 1:2                   | 401                        | 76                     |                                            |

### Thermogravimetric analysis

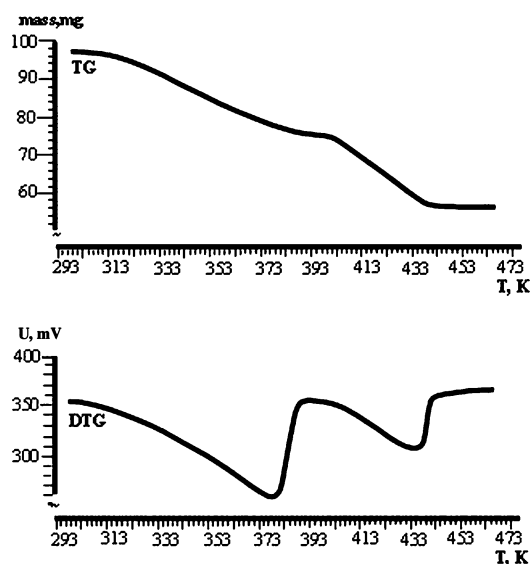
Thermogravimetric measurements were made with 1000D (MOM, Hungary) Derivatograph at a heating rate of  $0.6\text{ }^\circ\text{C min}^{-1}$ . Crystallosolvates that are in equilibrium with saturated solution were placed in platinum crucible. Samples of 100–200 mg were heated to  $500\text{ }^\circ\text{C}$  at the following sensitivities: DTG 1 mV, DTA 250  $\mu\text{V}$ , TG 200 mg/200 mm of the instrument scale. Accuracy of measurement of temperature of the sample was checked by characteristic temperatures of test substances [4]. Procedure of calculation of  $\Delta_{\text{evp}}H$  values and their errors was described in [5].

### Power X-ray diffraction

The powder X-ray diffractograms were performed with the DRON3 diffractometer ( $\text{CuK}\alpha$ ,  $\lambda = 1.54\text{ \AA}$ ). The irradiation was filtered by Ni filter. The size of split was 0.25 mm. The X-ray measurements were carried out at 298.15 K,  $2\theta = 3.2\text{--}50^\circ$  (the uncertainty was  $\pm 0.2^\circ$ ). The diffractograms was calculated using Ito method.

## Results and discussion

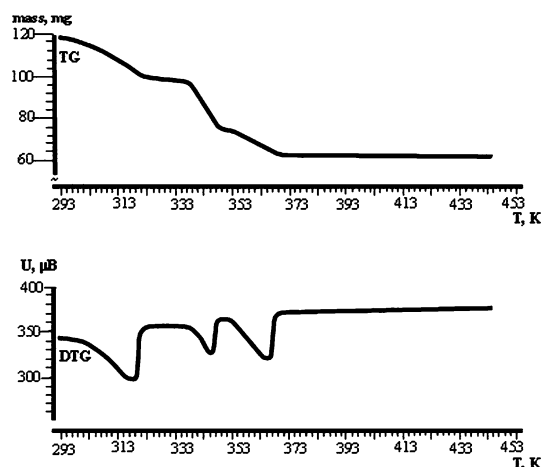
The obtained thermograms of the crystallosolvates of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pyridine, quinoline 3-dimethylaminopropionitrile, morpholine, diethylaniline are typical and exhibit two steps (Fig. 2). At the first step the  $\Delta_{\text{evp}}H$  values are very close to those for pure solvent (Table 1). This may be attributed to breakdown of the solvate structures formed due to universal interactions  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with the solvent molecules. The second

**Fig. 2** Thermogram of the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with diethylaniline.

peak on the DTG curve at higher temperatures corresponds to  $\text{Zn}(\text{t-Bu})_4\text{Pc:nL}$  ( $n = 1$  or  $2$ ) stoichiometric composition and reflects destruction of the axial complexes.

The thermograms of the crystallosolvates of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with the primary and the secondary amines studied (except morpholine) differ from the considered above (Fig. 3). The processes of removing of the solvent molecules exhibit three steps.

As an example, let us consider a typical thermogram of removing of diethylamine from the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  (Fig. 3). The first step (293–323 K) is associated with the losses of diethylamine molecules that interact due to universal forces with  $\text{Zn}(\text{t-Bu})_4\text{Pc}$

**Fig. 3** Thermogram of the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with diethylamine.

(the obtained  $\Delta_{\text{evp}}H$  value within the uncertainty is equal to  $\Delta_{\text{evp}}H$  for the pure solvent).

At the second step at 338 K the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with diethylamine of a stoichiometry 1–6 is destructed. Four energetically equivalent molecules of the solvent are simultaneously removed. The enthalpy change of solvation ( $\Delta_{\text{solv}}H$ ) of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  by four molecules of diethylamine was estimated according to Eq. 1 [5]

$$\Delta_{\text{solv}}H = -n \cdot (\Delta_{\text{evp}}H - \Delta_{\text{evp}}H^0), \quad (1)$$

where  $n$  is the number of solvent molecules that interact specifically with  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ ;  $\Delta_{\text{evp}}H$  is the enthalpy change of evaporation of solvent molecules from crystallosolvate;  $\Delta_{\text{evp}}H^0$  is the enthalpy change for pure solvent.

It is to be  $72.92 \text{ kJ mol}^{-1}$ . The composition of the crystallosolvate, energetically equivalence of four diethylamine molecules and the  $\Delta_{\text{evp}}H$  value corresponding to the energy of four hydrogen bonds ( $72.92:4 = 18.23 \text{ kJ mol}^{-1}$ ) suggests the removal of diethylamine molecules solvating *meso*-nitrogen atoms of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  at this step. At higher temperature of 352 K two latter molecules of diethylamine are simultaneously removed from the crystallosolvate.

Thus, for the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pipyridine, diethylamine, propylamine at the first step the amine molecules that interact due to universal forces with the metallophthalocyanine are removed. Then at higher temperatures the crystallosolvate  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot n(\text{amine})$  is destructed ( $n = 6$  for pipyridine (“hot” preparation), diethylamine, propylamine;  $n = 5$  for pipyridine (“cool” preparation)). At this step four molecules of the solvent solvating *meso*-nitrogen atoms of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  are removed simultaneously. Then at more higher temperature two axially coordinated molecules of the solvent are removed (one

molecule for the crystallosolvates with pipyridine (“cool” preparation)). The specific solvation of *meso*-nitrogen atoms of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  by morpholine has not been found because film is formed on the surface of the sample of the crystallosolvate with morpholine with a stoichiometry  $>1:4$  (see Fig 4).

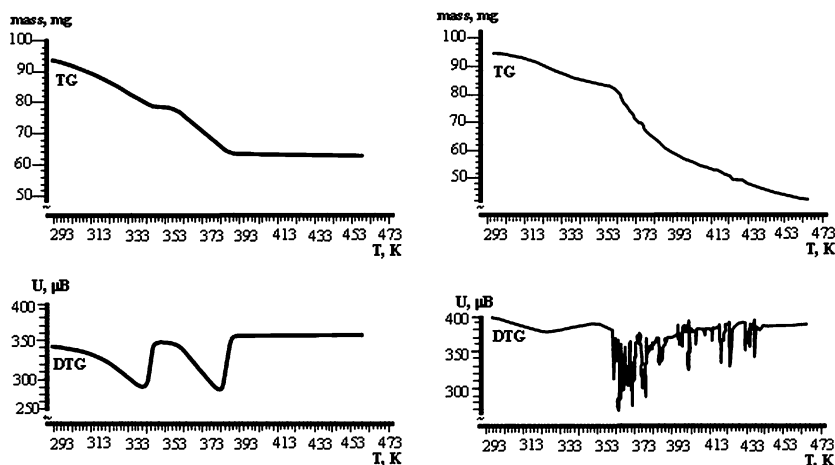
Obviously, the ability of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  to coordinate pyridine and pipyridine (Table 2) depends significantly on the conditions of preparation of the crystallosolvates. “Hot” preparation promotes formation of bilingand complexes while at “cool” preparation monoligand complexes are formed.

It should be noted that other studied solvents (diethylamine, *n*-propylamine, quinoline, 3-dimethylaminopropyronitrile, morpholine, diethylamine) form biligand axial complexes at any conditions of preparation of their crystallosolvates.

These two groups of the solvents differ from each other by values of potential of ionization (PI) of electron donating atoms that are responsible for complex formation. The solvent molecules forming 1:2 molecular complexes with  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  are characterized by low potential of ionization (Table 2). On the contrary, the PI values for pyridine and pipyridine are higher than 9.2 eV. This testifies about high energetic barrier of the process of axial coordination of electron donating ligands on  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ .

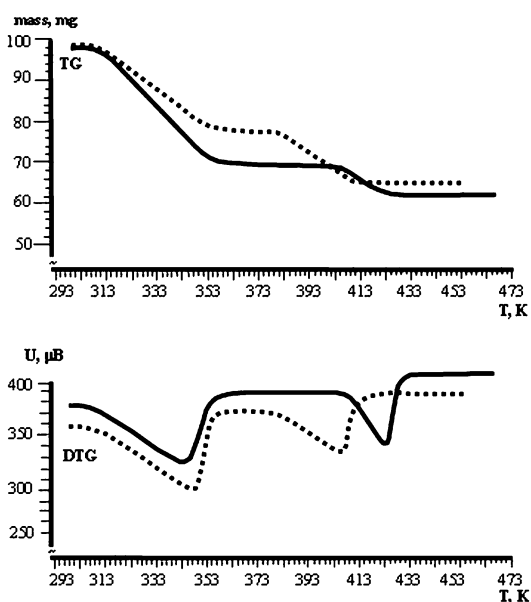
As an example, let us consider the thermograms of the crystallosolvates of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pyridine obtained by “hot” and “cool” preparations (Fig. 5). The process removal of the solvent from the crystallosolvates has two steps. At the first step (293–353 K) the  $\Delta_{\text{evp}}H$  value was found to be  $38 \text{ kJ mol}^{-1}$ . Within the uncertainty ( $\sim 7\%$ ), this value is equal to that for pure pyridine ( $40.4 \text{ kJ mol}^{-1}$  at 298 K,  $35.5 \text{ kJ mol}^{-1}$  at 388 K [10]). It may be concluded that the solvate structures formed due to universal interactions are destructed.

**Fig. 4** Thermogram of the crystallosolvate of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with morpholine: (a) initial stoichiometry of the crystallosolvate is 1:4; (b) initial stoichiometry of the crystallosolvate is 1:10



**Table 2** Physical chemical characteristics of solvents

| Solvent                      | T <sub>boil</sub> (K) | Ref | PI   | Ref    | $\Delta_{\text{evp}}H^0$ (kJ mol <sup>-1</sup> ) | Ref |
|------------------------------|-----------------------|-----|------|--------|--------------------------------------------------|-----|
| Pyridine                     | 388                   | [6] | 9.76 | [7]    | 40.21 <sup>a</sup><br>35.09 <sup>b</sup>         | [6] |
| Pipridine                    | 379                   | [6] | 9.20 | [7]    | 39.29 <sup>b</sup>                               | [8] |
| Diethylamine                 | 329                   | [6] | 8.44 | [7]    | 31.31 <sup>a</sup><br>29.06 <sup>b</sup>         | [6] |
| <i>n</i> -Propylamine        | 320                   | [6] | 8.78 | [8]    | 31.27 <sup>a</sup><br>29.55 <sup>b</sup>         | [8] |
| Quinoline                    | 510                   | [6] | 8.30 | [7]    | 59.30 <sup>a</sup><br>49.70 <sup>b</sup>         | [6] |
| 3-Dimethylaminopropionitrile | 448                   | [6] | 8.72 | [7]    | 40.23 <sup>a,c</sup>                             | [8] |
| Morpholine                   | 402                   | [6] |      |        | 37.10 <sup>b</sup>                               | [8] |
| Diethylaniline               | 489                   | [6] | 7.15 | [7, 9] | 53.44 <sup>a,c</sup>                             | [8] |
|                              |                       |     | 7.51 |        |                                                  |     |

<sup>a</sup> T=298.15 K; <sup>b</sup> T=T<sub>boil</sub> K;<sup>c</sup> Our data**Fig. 5** Thermograms of crystallosolvates Zn(t-Bu)<sub>4</sub>Pc with pyridine; ... biligand complex; — monoligand complex

The temperatures of beginning of the second steps of destruction of the crystallosolvates obtained by “hot” and “cool” preparations are different. The crystallosolvate obtained by “hot” preparation is destructed at a temperature of 380 K. Two energetically equivalent molecules of pyridine ( $\Delta_{\text{evp}}H = 95.4$  kJ mol<sup>-1</sup>) are removed. The crystallosolvate prepared by “cool” procedure has a 1:1 stoichiometry and a temperature of destruction of 408 K. The corresponding to this process  $\Delta_{\text{evp}}H$  value is 116.7 kJ mol<sup>-1</sup>. These data also testify about high energetic barrier of formation of biligand complex. The energetic stability of biligand complex are higher than those for monoligand complex. The mentioned above  $\Delta_{\text{evp}}H$  values indicate that the interactions Zn(t-Bu)<sub>4</sub>Pc with pyridine are specific.

The molecular complexes of Zn(t-Bu)<sub>4</sub>Pc with the studied amines of a 1:1 or 1:2 stoichiometry were obtained by heating of the crystallosolvates up to corresponding temperatures (Table 1). The composition of the complexes was checked additionally by element analysis method.

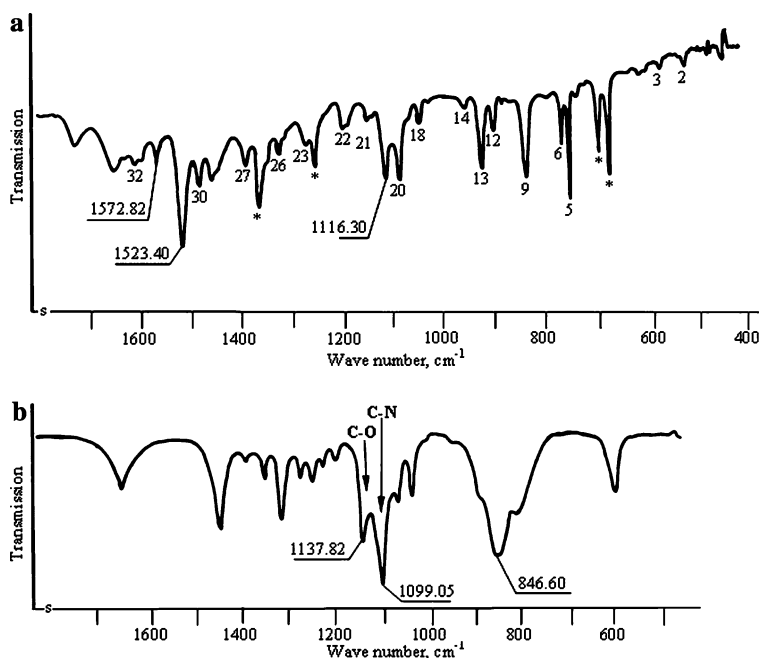
Donor–acceptor interaction between metallophthalocyanine and electron donating ligand can lead to the following spectral effects: (i) the change of frequencies of vibrations of donor and acceptor molecules due to change of bond character at complex formation; (ii) the appearance of the forbidden by selection rules of vibrations due to change of symmetry of molecules; (iii) the appearance of new bands due to new vibrations of atoms or atom groups in relation to the formed donor–acceptor bond; (iiii) the change of intensity of some bands of initial reagents.

Let us consider the results of IR study of the molecular complexes of Zn(t-Bu)<sub>4</sub>Pc with the electron donating ligands.

#### IR spectral characteristics of the Zn(t-Bu)<sub>4</sub>Pc · 2morpholine complex

Morpholine molecule has a few centers which are able to axial coordination on Zn(t-Bu)<sub>4</sub>Pc. However, from IR data it is impossible to identify the heteroatom of morpholine molecule donating electron pair to form the Zn(t-Bu)<sub>4</sub>Pc·2 morpholine complex (Fig. 6a). It is due to close positions of the bands assigned to the C–O (1138 cm<sup>-1</sup>) and C–N (1099 cm<sup>-1</sup>) valent vibrations [11, 12], which change their positions at the formation of O–Zn or N–Zn bonds (Fig. 6a, b). In the IR spectrum of the Zn(t-Bu)<sub>4</sub>Pc · 2morpholine complex a new band appears at 1116 cm<sup>-1</sup> in comparison with initial reagents (Fig. 6a). The identification of the center of binding of morpholine according to change of position of bands of neighboring atom groups is also

**Fig. 6** (a) IR spectrum of  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{morpholine}$  complex (b) IR spectrum of morpholine



problematic because the band assigned to N–H vibrations and a wide band at  $3100\text{--}3300\text{ cm}^{-1}$  is overlapped. This band is associated with water molecules in KBr. The wagging vibrations of N–H bond is also covered by the intensive and wide band at  $847\text{ cm}^{-1}$  (Fig. 6b) [11].

Analysis of the bands assigned to polymorphic modifications, indicated that the packing of  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{morpholine}$  molecules should be similar to that for  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  in  $\beta$ -polymorphic modification.

#### IR spectral characteristics of the $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2(3\text{-dimethylaminopropyronitrile})$ complex

3-Dimethylaminopropyronitrile contains two heteroatoms which are possible reactive centers for axial coordination on  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ . Unfortunately, from the IR data it is also impossible to identify the heteroatom responsible for the complex formation with the metallophthalocyanine because the bands assigned to valent N–C vibrations of tertiary amines at  $1220\text{--}1020\text{ cm}^{-1}$  and the band assigned to  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  are overlapped (Table 3). The bands assigned to CN-group vibrations are in low frequency region ( $2773$ ,  $2861$ ,  $2946\text{ cm}^{-1}$ ). At the complex formation of 3-dimethylaminopropyronitrile with  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  these bands are shifted to  $2955$ ,  $2895$ ,  $2859\text{ cm}^{-1}$ , respectively (Table 3). It is known from literature data [13] that a decrease of frequencies of vibration of CN-group is mainly associated with  $\pi\text{--}\pi$  or donor–acceptor interaction. In the case of the formation of  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2(3\text{-dimethylaminopropyronitrile})$  com-

plex an opposite tendency is observed: the frequencies of vibration of CN-group increase. It may be proposed that 3-dimethylaminopropyronitrile interacts with  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  due to accepting of electron pair of N-atom of the amine by  $\text{Zn}^{2+}$  ion but not due to  $\pi\text{--}\pi$  interaction of aromatic system of the macrocycle with  $\pi$ -electrons of CN-group of 3-dimethylaminopropyronitrile.

#### IR spectral characteristics and X-ray diffraction data of the $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$ complex

Typical spectra of the  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$  complex and diethylamine are presented in Fig. 7a, b. The complex formation between  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  and diethylamine leads to appearance of new bands at  $800$ ,  $1522$ ,  $1571\text{ cm}^{-1}$  which are absent in the spectra of the initial reagents (Table 3). The bands at  $1453$ ,  $1378$ ,  $1138$  and  $730\text{ cm}^{-1}$  are the most intensive. The latter is characteristic band for wagging N–H vibrations in the molecules of secondary and tertiary amines [11, 12]. It is interesting to note that the band at  $1453$ ,  $1378\text{ cm}^{-1}$  are present in the spectrum of the molecular complex but a shift of  $2\text{--}10\text{ cm}^{-1}$  is observed. However, the band at  $731\text{ cm}^{-1}$  disappears practically. This may be attributed to strong donor–acceptor interaction between  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  and diethylamine (Fig. 7a, b).

It should be emphasized that the position and intensities of the bands which are sensitive to crystal packing in the IR spectra of  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$  coincide with the analogous data for  $\beta$ -polymorph of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  (Table 3). This conclu-

**Table 3** IR spectral characteristics of molecular complexes of Zn(t-Bu)<sub>4</sub>Pc with ligands at the 1780–450 cm<sup>-1</sup> range

| No | nL                             |                                |              |                  |                       |                                  |
|----|--------------------------------|--------------------------------|--------------|------------------|-----------------------|----------------------------------|
|    | 2 Diethylamine                 | 1 Pipyrindine “cool”           | 2 Morpholine | 2 Pyridine “hot” | 1 Pyridine “cool”     | 2(3 Dimethylamino propionitrile) |
| 2  | 526 w                          | 526 w                          | 517 w        | 520              | 519 w                 | 526                              |
| 3  |                                |                                | 567 w        |                  | 567 w                 | 568 w                            |
| 4  | 603 w<br>673 s<br>690<br>731 w | 605 w<br>674<br>691 s<br>736 w | 676 s<br>693 | 675 s<br>695 w   | 603 w<br>673<br>695 s | 603 w<br>671 s<br>693            |
| 5  | 749 vs                         | 750 s                          | 750 vs       | 748 vs           | 750 s                 | 747 vs                           |
| 6  | 763<br>801                     | 762                            | 769          | 763              | 762                   | 764                              |
| 8  |                                | 831 sn                         |              |                  | 831 m                 |                                  |
| 9  | 829 s                          |                                | 831 s        | 831 s            |                       | 829 s                            |
| 10 | 862 w                          |                                |              |                  | 861                   |                                  |
| 11 |                                | 895 w                          |              |                  | 896 w                 |                                  |
| 12 | 893 m                          |                                | 898 m        | 899 m            |                       | 895 m                            |
| 13 | 921 s                          | 921 s                          | 921 s        | 921 s            | 919 s                 | 922 s                            |
| 14 | 957 w                          | 961 w                          | 959 w        | 959              | 961 w                 | 958 w                            |
| 17 | sh No 18                       |                                |              |                  |                       |                                  |
| 18 | 1047 s                         | 1047                           | 1047         | 1047             | 1047                  | 1048                             |
| 20 | 1088 s                         | 1089 s                         | 1088 s       | 1083 s           | 1087 s                | 1089 s                           |
|    |                                |                                | 1116         |                  |                       |                                  |
| 21 | 1153                           | 1151                           | 1148         |                  | 1151                  | 1151                             |
| 22 | 1200 mn                        | 11200 vw                       | 1202 mn      | 1206 mn          | 1200 vw               | 11200 nm                         |
|    | 1259                           | 1257                           | 1257         | 1257             | 1257                  | 1256                             |
| 23 | 1284                           | 1281 w                         | 1280 vw      | 1281             | 1280                  | 1280                             |
| 26 | 1329                           | 1330                           | 1329         | 1326             | 1330                  | 1331                             |
|    | 1368                           | 1369                           | 1369         | 1367             | 1368                  | 1363                             |
| 27 | 1394 w                         | 1394                           | 1394         | 1394             | 1394                  | 1392                             |
|    | 1457                           | 1463                           | 1463         | 1463             | 1464                  | sh No 30                         |
| 30 | 1490                           | 1490                           | 1490         | 1484             | 1489                  | 1489                             |
|    | 1522                           | 1524                           | 1523         | 1524             | 1523                  |                                  |
|    | 1571                           | 1572                           | 1573         | 1572             | 1572                  |                                  |
| 32 | 1613                           | 1613                           | 1619         | 1603             | 1619                  | 1613<br>1716<br>1776             |

sion is in agreement with the results of X-ray analysis (Table 4, Fig. 8). The results demonstrate that position of the neighboring phthalocyanine molecules within  $\pi$ -stacking and in  $\beta$ -polymorph is the same [14].

#### IR spectral characteristics of the Zn(t-Bu)<sub>4</sub>Pc · pipyrindine molecular complex

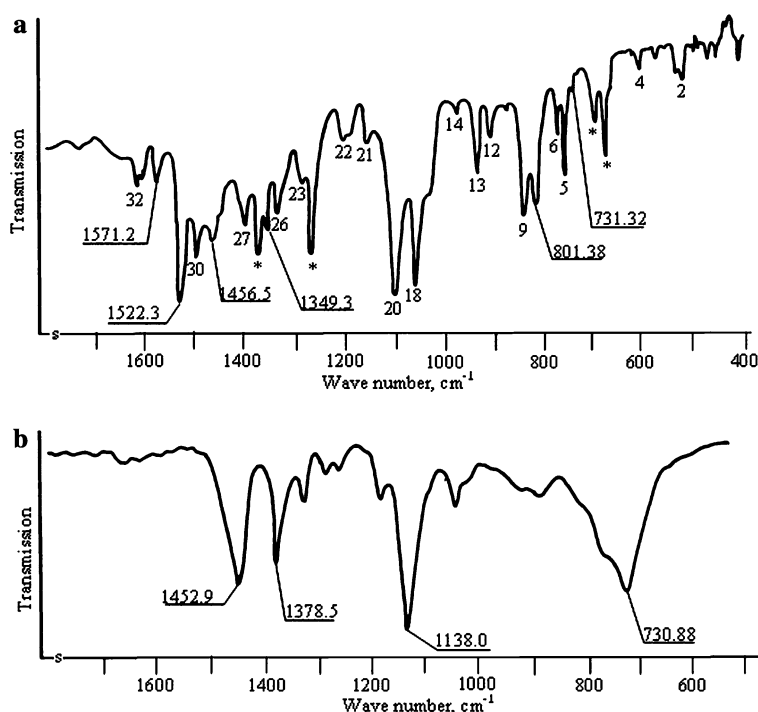
In the IR spectrum of Zn(t-Bu)<sub>4</sub>Pc with pipyrindine (Table 4) an decrease of the intensity of the band assigned to N–H wagging vibrations (736 cm<sup>-1</sup>) and its shift in comparison with pure pipyrindine (747 cm<sup>-1</sup>) is observed. Unfortunately, a shift of the band assigned to the N–H valent vibrations [11, 12] cannot be analyzed because of its screening by the intensive band assigned to O–H vibrations of water molecules containing in KBr. The positions of the bands and ratio of their intensities in the IR spectrum for the Zn(t-Bu)<sub>4</sub>Pc · pipyrindine complex are similar to those

for  $\alpha$ -polymorph of Zn(t-Bu)<sub>4</sub>Pc, except the intensity of the band No 8. It may be due to overlapping of intensities of this band and the band assigned to pipyrindine.

#### IR spectral characteristics of molecular complex of Zn(t-Bu)<sub>4</sub>Pc with pyridine

Substitution of alkyl N-containing ligand by aromatic amine (pyridine) affects significantly physical chemical properties of the molecular complexes (Tables 2, 3). Let us consider some peculiarities of mono- and bilingand complexes of Zn(t-Bu)<sub>4</sub>Pc with pyridine. In the IR spectrum of Zn(t-Bu)<sub>4</sub>Pc · 2pyridine, the intensive bands at 1572, 1524 and 1463 cm<sup>-1</sup> were registered (Fig. 9a) which are absent in the spectrum of Zn(t-Bu)<sub>4</sub>Pc · pyridine. Analogous bands at 1633, 1580 and 1482 cm<sup>-1</sup> are presented in the initial spectrum of pyridine. It should be noted that according to recommendations [11], the bands at 1580 and 1482 cm<sup>-1</sup> are

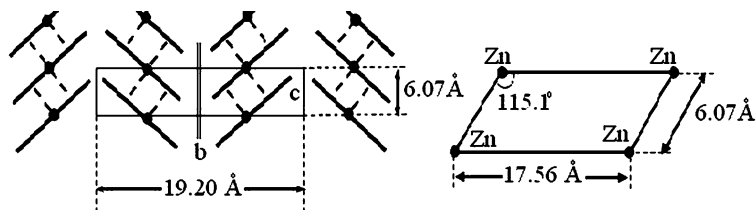
**Fig. 7** IR spectrum of the  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$  complex (a) and diethylamine (b)



**Table 4** The experimental, in Å, and theoretical, in Å, values of distance between planes of reflection, indexes and lattice parameters of molecular complexes  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$

| N | HKL                     | $d_{\text{exp}}$ (Å) | $d_{\text{calc}}$ (Å) |                                                                                                                                                                        |
|---|-------------------------|----------------------|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | 100                     | 15.76                | 15.90                 | Monoclinic: $a = 17.56 \text{ \AA}$ , $b = 19.20 \text{ \AA}$ , $c = 6.07 \text{ \AA}$ , $\beta = 115.1^\circ$ space group Pm $V_{\text{latt}} = 1843.9 \text{ \AA}^3$ |
| 2 | 001                     | 6.12                 | 6.12                  |                                                                                                                                                                        |
| 3 | $22\bar{1} \ 31\bar{1}$ | 6.04                 | 6.04                  |                                                                                                                                                                        |
| 4 | 021 320                 | 5.46                 | 5.50                  |                                                                                                                                                                        |
| 5 | 041                     | 5.29                 | 5.29                  |                                                                                                                                                                        |
| 6 | 141                     | 4.44                 | 4.45 4.40             |                                                                                                                                                                        |
| 7 | 311                     | 3.30                 | 3.28                  |                                                                                                                                                                        |
| 8 | $12\bar{2}$             | 2.80                 | 2.80                  |                                                                                                                                                                        |
| 9 | 122                     | 2.43                 | 2.45                  |                                                                                                                                                                        |

**Fig. 8** Arrangement of  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{diethylamine}$  molecules in elementary cell (*tert*-butyl substitutes and axially coordinated diethylamine molecules are not shown)



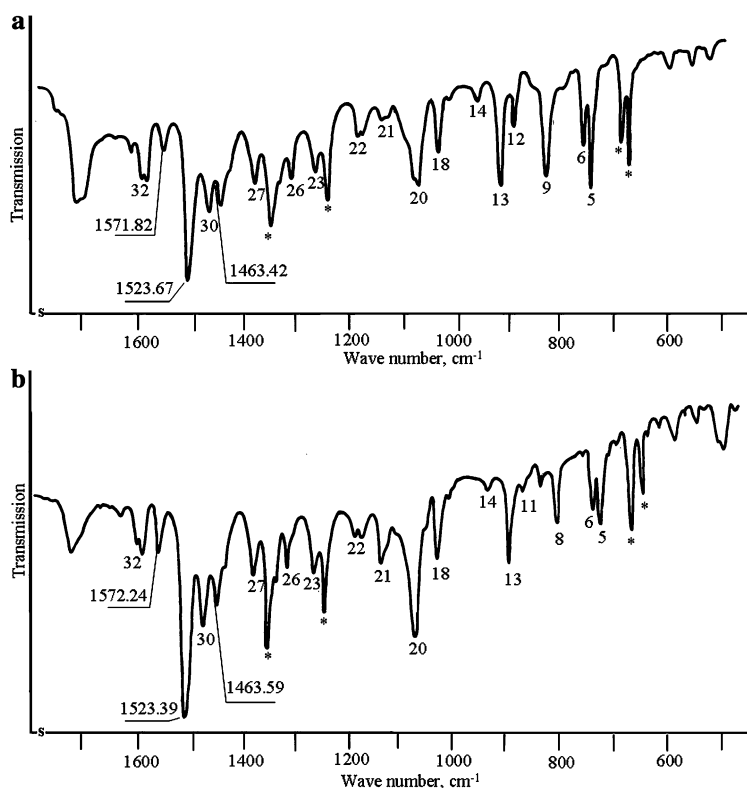
assigned to pyridine. It is likely that at the coordination of pyridine on  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  the indicated bands of vibrations are shifted to low-frequency region. This may be due to formation of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  donor–acceptor bond between pyridine and  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ .

It is interesting to note that similar changes in IR spectra were registered for the monoligand complex of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with pyridine. The bands mentioned above are observed at 1523 and  $1,464 \text{ cm}^{-1}$  (Fig. 9).

The band No 13 ( $922 \text{ cm}^{-1}$ ) assigned to a state of central metal ion in the metallophthalocyanine [15] exhibits a shift of  $2\text{--}4 \text{ cm}^{-1}$  ( $918\text{--}919 \text{ cm}^{-1}$ ) to low-frequency region upon the coordination of one pyridine molecule. The formation of biligand complex leads to a shift of  $1\text{--}2 \text{ cm}^{-1}$  ( $920\text{--}921 \text{ cm}^{-1}$ ). It is likely that the greater shift to low-frequency region of the bands for  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot \text{pyridine}$  in comparison with  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{pyridine}$  results from a different



**Fig. 9** IR spectrum of the  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 2\text{pyridine}$  complex (a) and  $\text{Zn}(\text{t-Bu})_4\text{Pc} \cdot 1\text{pyridine}$  complex (b)



influence of the coordinated ligand on geometry of the complex. It is known that binding of the first axial ligand to coordination position 5 of central metal ion leads to its displacement out of plane of phthalocyanine macrocycle. The binding of the second axial ligand leads to drawing of the central metal ion into plane of the macrocycle. This explains the observed value of the shift of the band No 13. Positions of the bands No 5, 8, 9, 11, 12, 14, 22 and a ratio of the intensities of the bands at 675 and 695  $\text{cm}^{-1}$  indicate that packing of molecules of the biligand complex is similar to that for the  $\beta$ -polymorphous modification of the metallophthalocyanine. The monoligand complex exhibits the similarity to the  $\alpha$ -modification. These results are in agreement with those obtained from X-ray studies [16–19].

## Conclusions

The spectral and thermochemical studies showed that the molecular complexes of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  with the studied amines are formed due to donor–acceptor interactions but not due to inclusion of solvent molecules into crystal lattice of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ . The coordination properties of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  in relation to the

amines depend on potential ionization of the solvents. At a high potential of ionization ( $>9.2$  eV) and usual condition, biligand complexes of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  are not formed. The monoligand and biligand complexes of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$  are pseudopolymorphs of  $\beta$ - and  $\alpha$ -polymorphic modifications of  $\text{Zn}(\text{t-Bu})_4\text{Pc}$ , respectively.

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