

Werner Clathrates as Examples of Guest-to-Host Influences

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Abstract. Guest–host and ligand–ligand interactions in solid clathrates of the $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ type have been studied. Using statistical methods it was found that there exists a nearly linear R_a vs. R_e inverse correlation among the metal–ligand distances within the host coordination polyhedra. As the axial distance (R_a) increases the equatorial distance (R_e) decreases and *vice versa*. These data were interrelated with electron transitions and thermal decomposition parameters.

Key words. X-ray data, decomposition temperatures, electron spectra, equatorial–axial interactions, Werner clathrates.

1. Introduction

In trying to understand the reasons for the great number of different shapes of coordination polyhedra of solid complexes, several years ago the authors studied the changes in the central atom–ligand distances in the equatorial plane and those in axial positions and their relationship [1, 2]. For pseudo-octahedral complexes with $[\text{MO}_6]$, $[\text{MN}_6]$ and $[\text{MN}_4\text{O}_2]$ chromophores ($\text{M} = \text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$), it was found that the mean values of the central atom–ligand distances in the equatorial plane (R_e) and of those in axial positions (R_a) correlated along a smooth curve: the values of R_a decrease with increasing R_e and *vice versa*. This correlation indicated a special manifestation of the mutual interactions of ligands, which may be termed the equatorial–axial interactions of ligands [1, 2].

In this paper spectral (especially ${}^3A_{2g} \rightarrow {}^3T_{1g}$ band shifts in visible spectra), structural (R_e and R_a values) and thermal (quasi-equilibrium decomposition temperatures) data were collected with the aim of studying:

- (i) the guest-to-host interactions in Werner clathrates of the $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ type (G being benzene and naphthalene derivatives); and
- (ii) the influence of the guest-to-host interactions on the ligand–metal–ligand (equatorial–axial) interactions in these complexes.

This investigation is untypical in regard to inclusion phenomena in the sense that it is focused not on the influence of the host on the guest but that of the guest on the host.

A wide range of inclusion compounds classified as Werner clathrates are represented by the general formula $[\text{ML}_4\text{X}_2] \cdot n\text{G}$, M being a divalent transition metal, X the anionic ligand and L a neutral substituted pyridine aryl- or alkylamine. The clathrating ability of an $[\text{ML}_4\text{X}_2]$ host complex depends on its molecular structure and, in particular, on the amine ligand (L) coordinated to M. Its clathrating ability is ascribed to the remarkable rotational freedom of the pyridine rings about Ni–N

bonds [5] which enables the complex to adjust its molecular shape according to the size, shape and polarity of an incoming guest molecule. The formation of inclusion compounds is stereo-selective and may be used for the separation of isomer mixtures [6]. The physicochemical behaviour of these clathrates, various crystal structures with different guest molecules and intermolecular host–guest interactions have been reviewed, for example, by Lipkowski [5].

2. Experimental

The clathrate compounds were prepared from solution according to Ref. [3]. The compounds obtained were analysed for Ni, C, H and N content. The electronic absorption spectra were measured on a SPECORD M40 (Carl Zeiss, Jena). To study the quasi-equilibrium decomposition temperatures the Q-Derivatograph was used [4]. This experimental technique facilitates the stabilization of the decomposition temperature, i.e. the experiment proceeds under quasi-isothermal conditions. Using special sample holders it is possible to maintain the pressure of the gaseous products almost constant (for example, a conical crucible provides a pressure of about 90 kPa [7]).

A set of X-ray structure data on Werner clathrates of the type $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2]_n\text{G}$ (G = benzene and naphthalene derivatives) have been collected from the literature. Only the complexes with crystallographic R factors lower than 0.10 have been subjected to analysis.

3. Results and Discussion

We have synthesised the complexes of $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2]_n\text{G}$ type (G = benzene, toluene, *o*-xylene, *p*-xylene and naphthalene derivatives) and characterized their spectral and thermal properties as a first step. In the second part the relationship between spectral, thermal and structural data (taken from the literature) was studied.

3.1. SPECTRAL AND THERMAL PROPERTIES

The absorption spectra of $[\text{NiL}_4(\text{NCS})_2]$ complexes have been studied already [8]. The specific complex employed in this work ($\text{L} = 4\text{-Mepy}$), as shown by its crystal structure [9, 10], exhibits a rather small tetragonal distortion. No splitting is observed in the spin-allowed ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition in the absorption spectra of the clathrates, which confirms the nearly O_h symmetry of the chromophore [11]. The observed band shifts are reported as $\Delta\bar{\nu}$, with respect to the reference complex, taking into account only the broad band corresponding to the spin-allowed ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition (Table I). This band shift was taken as a measure of the host–guest interactions in the clathrates [11]. According to $\Delta\bar{\nu}$, the complexes can be ordered (depending on G) in the following sequence

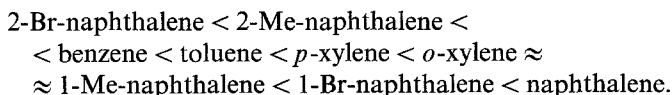
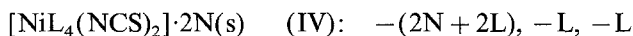
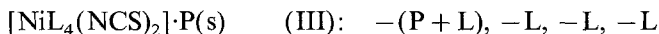
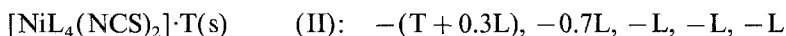
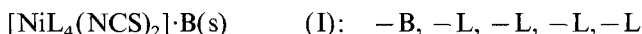


Table I. Spectral and thermal properties of $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates

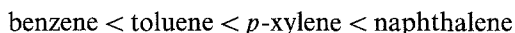
No.	<i>n</i> G	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	T_D ($^\circ\text{C}$)
1.	2(2-Br-naphthalene)	16 950	-350	
2.	2(2-Me-naphthalene)	17 000	-300	
3.	benzene	17 200	-100	122
4.	toluene	17 250	-50	130
5.	none	17 300	0	
6.	<i>p</i> -xylene	17 360	+60	165
7.	<i>o</i> -xylene	17 450	+150	
8.	2(1-Me-naphthalene)	17 450	+150	
9.	2(1-Br-naphthalene)	17 500	+200	
10.	2(naphthalene)	17 730	+430	180

Q-TG curves (measured under the quasi-isothermal and quasi-isobaric conditions) provide comprehensive information about the reaction stoichiometry as well as decomposition temperatures. The thermogravimetric curves show that the stoichiometry (stepwise character) of the thermal decomposition of clathrates is variable in the first steps:



(L = 4-Mepy, B = benzene, T = toluene, P = *p*-xylene, N = naphthalene). The volatile components are released in five (I and II), four (III) or three steps (IV).

The decomposition temperatures derived from quasi-isothermal measurements are suited to the setting up of a qualitative sequence of the thermodynamic stability of the solid compounds [12]. According to quasi-equilibrium decomposition temperatures (Table I) the thermodynamic stability can be ordered in the following sequence:



3.3. RELATIONSHIP BETWEEN STRUCTURAL AND OTHER PARAMETERS

The $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrate with 2-Br naphthalene as a guest component crystallizes with a layer-type molecular packing [13]. Substitution of the guest by a smaller molecule, such as *o*-xylene, leads to a disordered arrangement of the guest in the clathrate [14]. The naphthalene molecule is smaller than the naphthalene derivatives and it is more symmetric. The structure of $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot 2(\text{naphthalene})$ differs significantly from those studied previously. Also the visible spectrum of the crystalline phase is shifted significantly towards higher wavenumbers (Table I).

Table II. Structural data of $[\text{Ni}(\text{4-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates

No.	<i>n</i> G	R_a (pm)	R_e (pm)	Ref.
1.	2(2-Br-naphthalene)	202.9	216.1	15
2.	2(2-Me-naphthalene)	204.6	216.2	15
3.	<i>p</i> -xylene	205.5	213.7	16
4.	<i>o</i> -xylene	206.1	213.4	14
5.	none (β)	206.4	212.8	9
6.	none (α)	206.8	212.8	10
7.	<i>p</i> -cymene	206.8	214.7	18
8.	<i>m</i> -xylene	206.8	214.5	16
9.	CH ₃ OH	207.0	212.5	16
10.	2(1-Me-naphthalene)	207.4	213.6	17
11.	2(naphthalene)	207.6	212.4	13

A set of X-ray structural data on $[\text{Ni}(\text{4-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ compounds has been collected in Table II. Of interest are the R_a ($2 \times$) and R_e ($4 \times$) metal–ligand distances and the tetragonality parameter $\tau = R_e/R_a$ or its inverse value τ^{-1} of the host complex. The R_a values have been plotted vs. R_e and the corresponding dependences are shown in Figure 1. The linear relationship arises from the least-squares fitting. On the basis of the above data the following conclusions can be drawn.

(i) The coordination polyhedra of the host complex $[\text{Ni}(\text{4-Mepy})_4(\text{NCS})_2]$ with different guest components prefer an axially distorted octahedral configuration, namely the slightly compressed tetragonal bipyramid.

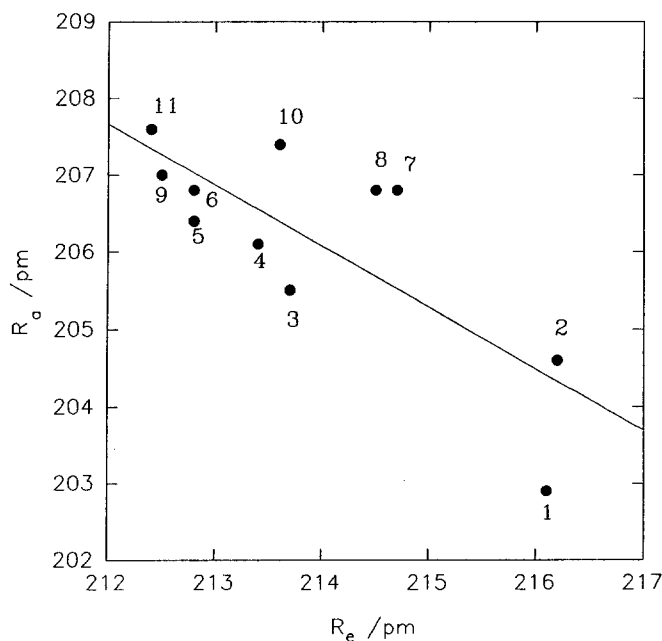


Fig. 1. R_a vs. R_e dependence for the title compounds. See Table II for identification of the compounds.

(ii) A test of the correlation coefficients at the level of significance 0.01 with $\nu = n - 2$ degrees of freedom (n representing the number of experimental data in the respective set) allows us to reject the null hypothesis on mutual independence of the R_a and R_e parameters in the cases under study (correlation coefficient $r = -0.8038$, $r_{\text{crit}} = 0.0797$). The nearly linear correlation can be considered significant ($|r| > r_{\text{crit}}$) at the level of significance 0.01.

Thus, the Ni—N(NCS) distances depend on the Ni—N(L) distances in the host complex. An increase in the central atom—ligand distances in the equatorial plane results in strengthening of axial bonds. The equatorial—axial interactions within the set of $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates are thus demonstrated as an integral redistribution of the bond strengths along three axes of the host complex: weakening of the bonds on one axis causes strengthening of the bonds on the remaining two axes.

(iii) It is evident from Table II that the properties of the guest components play an important role in the tetragonal distortion of coordination polyhedra of the host complex. Namely, a comparison of the mean values of R_e and R_a distances shows a smaller tetragonal distortion for naphthalene compared to that for 2-Br- and 2-Me-naphthalene clathrates. These data allow us to conclude that the change of properties of guest components may alter the shape and the metal—ligand distances in the host complex.

(iv) An increase of the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ band shift ($\Delta\tilde{\nu}$) in the visible spectra with the increase of the inverse tetragonality parameter $\tau^{-1} = R_a/R_e$ is observed (Figure 2).

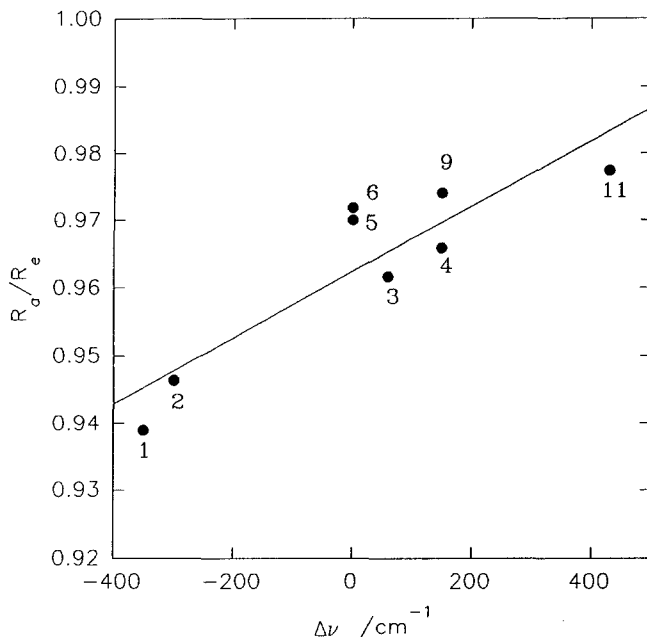


Fig. 2. Inverse tetragonality parameter $\tau^{-1} = (R_a/R_e)$ vs. band shift $\Delta\tilde{\nu}$. See Table II for identification of the compounds.

Thus, the larger the parameter τ^{-1} , the larger is the positive band shift and also the larger is the quasi-equilibrium decomposition temperature. In other words, the more compressed the tetragonal bipyramid, the lower in energy the $d-d$ transition and *vice versa*. As the R_e value increases, the Ni—L (metal—volatile ligand) bond is weakened and the decomposition temperature decreases.

3.3. THEORETICAL QUESTIONS

The equatorial–axial interactions have been subjected to a theoretical analysis [1]. It was found that the tetragonal distortion mode (of e_g symmetry) of octahedra may be considered as a soft mode relative to the symmetric stretching (of a_{1g} symmetry). This deduction was also proved by extensive quantum-chemical calculations [19] according to which the adiabatic potential (the total energy function) $E_T(R_a, R_e)$ exhibits a valley along the R_a vs. R_e reaction coordinate ξ so that the tetragonal distortion is facilitated as a minimum energy path. The solid state acts on the particular coordination polyhedron via an additional lattice potential V_L which alters the E_T function and its extremum points (Figure 3). In our particular case, however, the lattice potential V_L , is almost constant, with the exception of the guest electric properties, such as permittivity, polarizability or dipole moment. Surprisingly, these effects are considerable, as the alteration of R_a and R_e parameters within the host coordination polyhedra is not negligible. The above findings have stimulated a subsequent, more detailed investigation of particular factors influencing the solid-state stereochemistry [20].

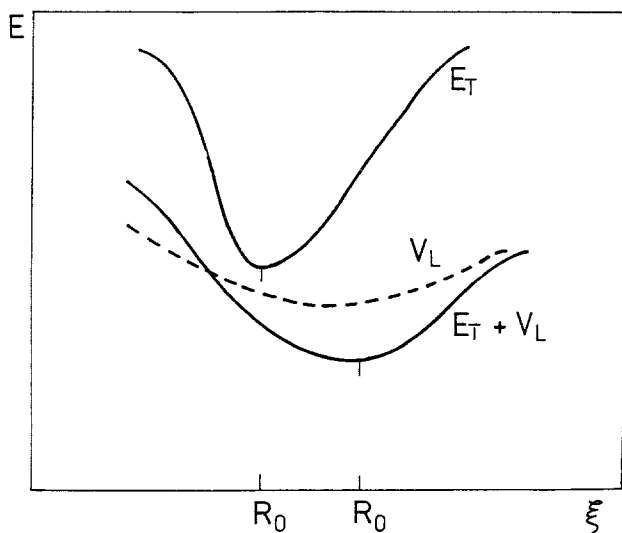


Fig. 3. Schematic representation of integral lattice potential V_L to the extremum of the adiabatic potential surface E_T .

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