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Deuterated Benzene and Benzene as Guest in the Copper(II)-en Type of Tetracyanonickelates

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Abstract. New host–guest complexes of tetracyanonickelates with deuterated benzene and benzene were prepared having the chemical composition $Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6$ and $Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$. The spectroscopic behaviour in the range 4000–200 cm^{-1}, as well as the thermal properties, were investigated and compared with those of similar clathrate compounds.

Key words. Tetracyanonickelates, host–guest complexes, benzene, deuterated benzene, preparation, properties.

1. Introduction

Compounds of formula $M(en)_2M'(CN)_4 \cdot n\,G$ ($M = Cu$, Zn; $M' = Ni$; $G = C_6H_6$; $n = 0.14$) have been prepared and identified [1] and their properties studied by us earlier [2, 3]. They exhibited very interesting thermal stability. They lost a part of the ethylenediamine (en) between 210–238°C in the case of $Cu(en)_2Ni(CN)_4 \cdot 0.14\,C_6H_6$ and between 167–266°C in the case of $Zn(en)_2Ni(CN)_4 \cdot 0.14\,C_6H_6$ [2]. Only then was the benzene guest component lost ($n = 0$) – near 300°C in both cases. Both were prepared in a microcrystalline form and their nonstoichiometric forms were useful as stationary phases at temperatures higher than in the case of other clathrates [4]. The copper compound was found to allow separation of a mixture of aniline and its derivatives and a very good separation of aromatic hydrocarbons [2, 3]. The zinc complex allowed a good separation of aromatic amines at 160° and 192°C [2, 3]. At that time we could not prepare a fully occupied host structure. When monocrystals of the Cu–Ni compound were prepared no guest benzene could be detected [5]. Therefore, and on the basis of further identified modified types [6] of clathrates (e.g. $Cd(dma)_2Ni(CN)_4 \cdot nG$) or pillared [7] intercalation compounds (as for the smectites [8]) e.g. $Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_{13}OH$, we returned 12 years later to these compounds, changing the conditions of their synthesis, using deuterated benzene as the guest and prolonging the time of crystallization. These compounds of the host–guest type, with copper and nickel present in the host, are the theme of this study.

2. Experimental

2.1. MATERIALS AND INSTRUMENTATION

Chemicals of p.a. grade were used: KCN, $NiSO_4 \cdot 5\,H_2O$, C_6H_6 (Lachema, Brno), ethylenediamine (Milton, Trad Est. Milton), 99.6% C_6D_6 (Radioisotope Prod. Distr. Center). The $K_2Ni(CN)_4$ reagent was prepared starting from KCN and $Ni(CN)_2$.

The elemental analysis of the products was carried out on a Hewlett Packard Model 185 CHN Analyzer. The presence of the individual groups was checked by measuring the IR spectra (Specord IR M-80, Zeiss, Jena), using KBr discs (1 mg/250 mg KBr).

The TG, DTG and DTA analyses were carried out using a derivatograph (MOM OD 102, Hungary) under dynamic conditions in an argon atmosphere, heating rate $9° \mathrm{min}^{-1}$ in Pt crucibles (100 mg sample, sensitivity of derivatographic curves: DTA: 1/10; DTG 1/5).

The analysis of the metals present was carried out by EDS analysis (Electron Microsonda JXA-5A, JEOL) applying Kevex.

The diffractographic measurements were carried out using a Micrometa 2, (Chirana ČSSR): Ni $K_\alpha = 0.165912$ nm, $V = 30$ kV, $I = 12$ mA.

2.2. SYNTHESIS

The clathrates $Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ (**1**) and $Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6$ (**2**) were prepared as follows:

$$K_2Ni(CN)_4 + CuSO_4 \rightarrow Cu\,Ni(CN)_4 + K_2SO_4$$

$$Cu\,Ni(CN)_4 + x\,en \rightarrow Cu(en)_mNi(CN)_4 + (x - m)en$$

$$Cu(en)_mNi(CN)_4 + y\,C_6H_6 \rightarrow Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6 + \\ + (y - 2)C_6H_6 + (m - 2)en$$

or

$$Cu(en)_mNi(CN)_4 + z\,C_6D_6 \rightarrow Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6 + \\ + (z - 1)C_6D_6 + (m - 2)en$$

The blue precipitate formed according to the reaction of the saturated solution of 0.1 M $K_2Ni(CN)_4$ (2.4 g) and of 0.1 M $CuSO_4 \cdot 5\,H_2O$ (2.49 g) in 50 mL H_2O was filtered and washed (S-3 fritted glass).

The ethylenediamine (1.2 g) was added with intensive mixing in order to solubilise the precipitate. The benzene, or deuterated benzene (200 mL) was added (forming a layer) to the filtered solution of $Cu(en)_mNi(CN)_4$ after the acidification of the medium by CH_3COOH, and the solution was left to crystallize for 2–3 months.

Small crystals were formed in both cases and they were filtered off, washed with ethyl alcohol and dried over silicagel in a desiccator.

For the preparation of compound **2** containing C_6D_6 we also used other methods. One synthesis used solid $CuNi(CN)_4$ (300 mg) as the starting material. It was dissolved in deuterated water (20 mL^2) and then in ethylenediamine (5 mL^2) also using ethanol as an auxiliary solvent (20 mL). Only after mixing and then filtering off the mixture was deuterated benzene (25 mL) added. The mixture was left to crystallize for different periods of time.

The compounds studied here were prepared by the latter method. The products **1** and **2** were left to crystallize for 3 months.

Many products were prepared as single crystals, but only one was suitable for an X-ray diffraction study [9]. It was prepared by the first method (without D_2O) and was left to crystallize for 12 months. This crystal turned out to be the empty host lattice containing no C_6D_6.

The diffractographic patterns of the microcrystalline powders of samples **1** and **2** were very different.

Anal. found/calc: C 46.89/47.80; H 5.54/5.61 and N 22.31/22.30; Cu 12.57/12.63; Ni 11.62/11.67% for compound **1**.

C 38.42/39.07; H 3.56/3.74 and N 26.12/26.03; Cu 14.45/14.75; Ni 13.27/13.64% for compound **2**.

The solubility of compounds (**1**) and (**2**) in ethylenediamine is good, but they are insoluble in other solvents, such as $CHCl_3$, CCl_4, dimethyl ether, dimethyl formamide and dimethyl sulfoxide. Compound (**1**) is insoluble in ethyl alcohol, but soluble in warm water. Compound (**2**) is well soluble in water, ethyl and methyl alcohol.

3. Results and Discussion

The results of the chemical analyses and TG measurements (Table I, Figures 1, 2) confirmed that the products formed are different from those prepared previously [1]. Previously, we could achieve only a partial occupancy of the cavities ($n = 0.14$); now the synthesis conditions helped us to produce compounds of the host–guest complex type with $n = 2$ in the case of (**1**) and with $n = 1$ in the case of (**2**).

Table I. Characteristics of the thermal decomposition of $Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ and its deuterated form.

Compound	Temperature of the decomposition (max. DTA) (°C)	Weight loss found Δm (g/mol)	Released component (mol/mol)	Weight loss theor. Δm (g/mol)	Note about the course of DTA curve
$Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ dark	90	45.20	0.75 en	(45)	weak *endo*
red violet	160	80.36	1.33 en	(79.80)	
crystals	340	165.74	2 C_6H_6	(156)	sharp *endo*
(1)	480	55.24	1$(CN)_2$	(52)	strong *exo*
$Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6$	80	40.67			weak *endo*
blue violet	220	86.42	2 en	(120)	sharp *endo*
crystals	300	71.17	1 C_6D_6	(84)	strong *endo*
(2)	400	106.72	2$(CN)_2$	(104)	strong *exo*

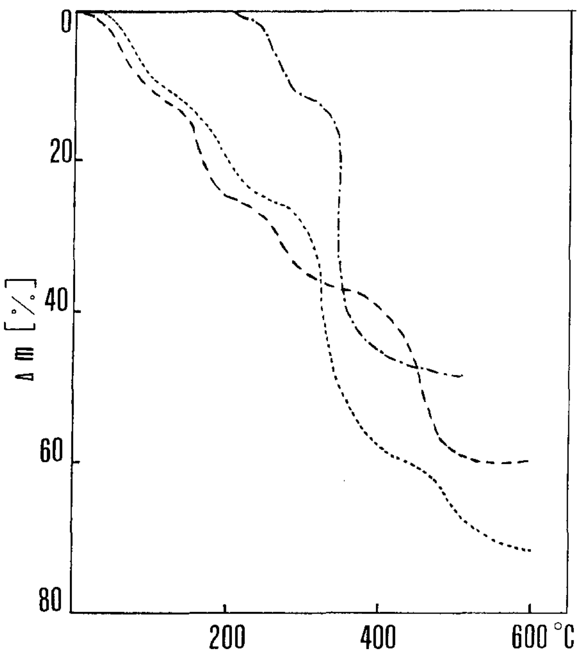

Fig. 1. TG curves of clathrates containing full or non-stoichiometric amount of the guest component. .... $Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ (**1**); ---- $Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6$ (**2**); —·— $Cu(en)_2Ni(CN)_4 \cdot 0.14\,C_6H_6$.

3.1. THERMAL ANALYSIS

$Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ (**1**)

The thermal decomposition starts with an endothermic process (40–120°C) with a maximum on the DTA curve at 90°C, where 3/8 of the total amount of ethylenediamine (0.75 mol) is lost. The remaining portion is lost (120–185°C) with a maximum on the DTA curve at 160°C.

The guest component is lost in an argon atmosphere in a different way from that in air in a further but well-differentiated endothermic process (between 185–420°C), with a maximum on the DTA curve at 340°C. The exothermic degradation of the cyano groups only then proceeds between 420–560°C. As final products we obtained metallic copper and nickel.

$Cu(en)_2Ni(CN)_4 \cdot 1\,C_6D_6$ (**2**)

This compound, containing deuterated benzene, is a little less stable to thermal degradation than compound **1**. Both ethylenediamine ligands are lost in two endothermic processes (between 35–105 and 110–240°C) with maxima on the DTA curve at 80°C and 220°C. The second endothermic process is stronger than the first. The deuterated benzene (one mol) as the guest component is lost again in a strong endothermic process at 240–395°C (with the maximum on the DTA curve at 300°C). The exothermic degradation of the cyanocomplexes proceeds between

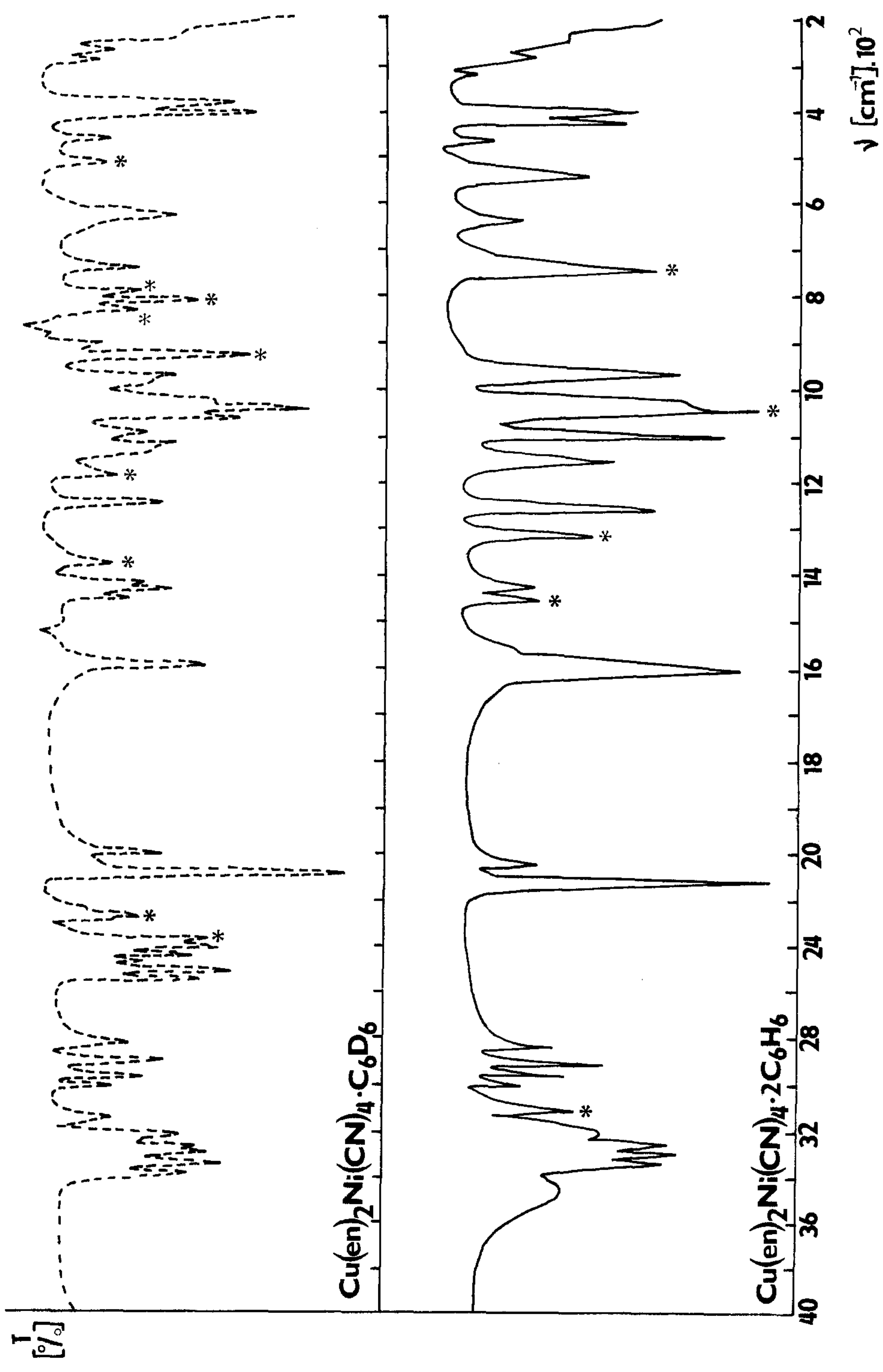

Fig. 2. IR spectra of Cu(en)$_2$Ni(CN)$_4$ · 2 C_6H_6 (1)—and Cu(en)$_2$Ni(CN)$_4$ · 1 C_6D_6 (2) - - - - Guest bands marked with asterisks.

395–545°C. These results (Table I) show that benzene is more strongly held in the cyanocomplex than the deuterated species in compound (**2**).

Both compounds however, are less stable than the non-stoichiometric compound Cu $(en)_2Ni(CN)_4 \cdot 0.14\,C_6H_6$, prepared twelve years ago [1, 2], which starts its thermal decomposition only at higher temperatures (210°C). This fact agrees with a general comparison of the thermal stabilities of the tetracyanocomplex clathrates, where the less occupied area in the host component contributes to the greater stability of the compound.

There are two causes, the first being the energetic conditions depending upon the amount of the guest component present and the second is the number of the en ligands present in the host.

In our case, during the first synthesis [1], two en ligands closed the host structure area before the complete sorption of the guest and therefore the first product started its decomposition only at higher temperature. This fact agrees with previously compared thermal stabilities of the fully or partially occupied host structures [10] and we compare this situation concerning the TG curves in Fig. 1.

3.2. IR SPECTRA

The ν (C≡N), $\nu_{s,as}$ Ni—C values are equally affected by the presence of C_6H_6 and C_6D_6 (Figure 2) in comparison with the simple tetracyanocomplexes $Ni(CN)_4^{2-}$ and equally with the compound containing NH_3 as ligands and deuterated H_2O as guest studied in [11]. Two en ligands being present (the mode of linking not yet stated) in the host structure are weakening the Ni–CN bonds in the host. The characteristics of the guest C_6H_6 and C_6D_6 are also shifted to lower values than in other clathrates with deuterated water [11–16].

The bands characteristic of the ethylenediamine are similar in both compounds, indicating very similar interactions between the host and the guest. In other cases [6] the composition and the thermal analysis data suggest that some cavitites may exist and may be occupied by the second en ligand.

4. Conclusions

Deuterated benzene is more efficiently sorbed by the $Cu(en)_2Ni(CN)_4$ host. The quantity sorbed is higher than the amount of the benzene sorbed in the same host in our first experiments 12 years ago. Further the mode of preparation of $Cu(en)_2Ni(CN)_4 \cdot 1C_6D_6$ was used to synthesize the compound $Cu(en)_2Ni(CN)_4 \cdot 2\,C_6H_6$ containing the stoichiometric amount of benzene. Naturally both compounds are thermally less stable than the original non-stoichiometric form, $Cu(en)_2Ni(CN)_4 \cdot 0.14\,C_6H_6$, but their IR spectra and thermal analysis properties indicate both to be new products. Therefore it is anticipated that both compounds may show sorptive properties in organic mixtures and may possess the capacity to exchange the original guest G for further convenient compounds, although at relatively lower temperatures.

References

1. A. Sopková, J. Chomič and E. Matejčíková: *Monatsh Chem.* **102**, 961 (1971).
2. A. Sopková and M. Šingliar: in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.): *Inclusion Compounds*, Vol. 3., p. 245 (1984), Academic Press, London.
3. A. Sopková, M. Šingliar, J. Chomič, J. Skoršepa and E. Matejčíková: *Czech. Patent* 186492, 6 July (1978).
4. D. Sybilska and E. Smolková – Keulemansová in: J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.): *Inclusion Compounds* Vol. 3., p. 173 (1984), Academic Press, London.
5. M. Dunaj-Jurčo, J. Garaj, J. Chomič, P. Valach and V. Haluška: *Acta Crystallogr.* **31A**, Part S 3, 64 (1975).
6. T. Iwamoto in: J. L. Atwood, J. E. D. Davies and D. D. Mac Nicol (eds.): *Inclusion Compounds* Vol. 1., p. 29 (1984), Academic Press, London.
7. T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **6**, 549 (1988).
8. R. Burch: *Catalysis Today*, **2**, 185 (1988).
9. J. Lokaj, K. Györyová and A. Sopková: *Coll. Czech Chem. Commun.* in press.
10. A. Sopková: *Proc. Termanal* '73, Vysoké Tatry 1973, A 77 (1973).
11. A. Sopková, K. Györyová and M. Šingliar: *J. Incl. Phenom.* **4**, 369 (1986).
12. L. S. Suzuki, W. J. Orville-Thomas, A. Sopková and J. Skoršepa: *J. Mol. Struct.* **54**, 1 (1981).
13. E. F. H. Brittain: *Introduction to Molecular Spectroscopy*, Academic Press London, p. 198 (1970).
14. K. Nakamoto: *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley, London (1962).
15. L. Gabalica: *Spectrochim. Acta* **32A**, 377 (1976).
16. J. R. Ferraro: *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York (1971).