



## Article

# Pyridine-2,6-Dicarboxylic Acid Esters (pydicR<sub>2</sub>) as O,N,O-Pincer Ligands in Cu<sup>II</sup> Complexes

Katharina Butsch <sup>1</sup>, Aaron Sandleben <sup>1</sup> , Maryam Heydari Dokoochaki <sup>2</sup>, Amin Reza Zolghadr <sup>2,\*</sup> and Axel Klein <sup>1,2,\*</sup>

<sup>1</sup> Department für Chemie, Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany; Katharinabutsch@web.de (K.B.); a.sandleben@uni-koeln.de (A.S.)

<sup>2</sup> Chemistry Department Faculty of Science, Shiraz University, Shiraz 71454, Iran; maryamhdi5844@gmail.com

\* Correspondence: arzolghadr@shirazu.ac.ir (A.R.Z.); axel.klein@uni-koeln.de (A.K.); Tel.: +49-221-470-4006 (A.K.)

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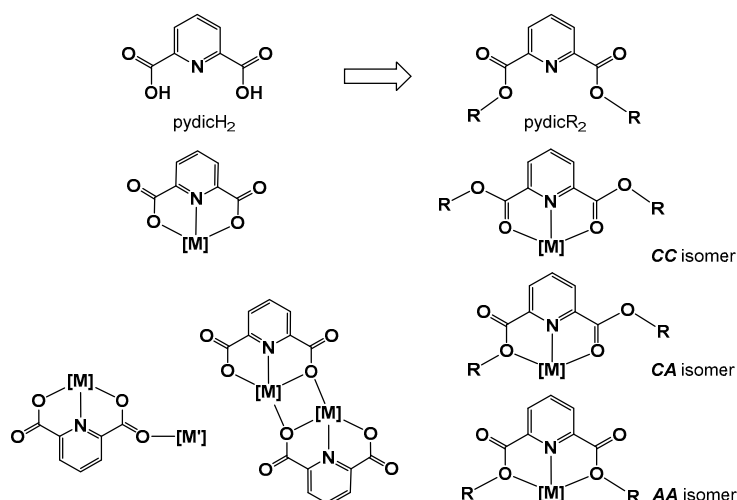


**Abstract:** The pyridine-2,6-carboxylic esters pydicR<sub>2</sub> with R = Me or Ph form the unprecedented mononuclear Cu<sup>II</sup> complexes [Cu(pydicR<sub>2</sub>)Cl<sub>3</sub>]<sup>−</sup> in one-pot reactions starting from pyridine-2,6-carboxychloride pydicCl<sub>2</sub>, Cu<sup>II</sup> chloride, and NEt<sub>3</sub> in MeOH or PhOH solution under non-aqueous conditions. The triethylammonium salts (HNEt<sub>3</sub>)[Cu(pydicR<sub>2</sub>)Cl<sub>3</sub>] were isolated. The methyl derivative could be crystallized to allow a XRD structure determination. Both structures were optimized using DFT calculations in various surroundings ranging from gas phase and the non-coordinating solvent CH<sub>2</sub>Cl<sub>2</sub> to the weakly coordinating acetone and well-coordinating solvents acetonitrile (MeCN) or dimethylformamide (DMF), while detailed calculation showed the charge distribution, dipole moments, and HOMO–LUMO gap energies changing upon solvation. According to these calculations, the ion pairs and the anionic Cu<sup>II</sup> complexes were stable, which shows only Cu–Cl bond elongation and weakening of the charge transfer between the anionic complex and the cation as solvents become polar. Synthesis attempts in the presence of water yielded the Cu<sup>II</sup> complexes [Cu(pydic)(OH<sub>2</sub>)<sub>2</sub>]<sub>n</sub> and [Cu(OH<sub>2</sub>)<sub>6</sub>][{Cu(pydic)}<sub>2</sub>(μ-Cl)<sub>2</sub>], which results from pydicCl<sub>2</sub> hydrolysis. Alternatively, the new pydic(IPh)<sub>2</sub> (IPh = 2-iodo-phenyl) ester ligand was synthesized and reacted with anhydrous CuCl<sub>2</sub>, which yields the new binuclear complex [{Cu(pydic(IPh)<sub>2</sub>)Cl<sub>2</sub>(μ-Cl)<sub>2</sub>}. EPR spectroscopy of the solid compounds reveals typical axial spectra in line with the observed and DFT calculated geometries. Cyclic voltammetry and UV–vis absorption spectroscopy in solution are in line with un-dissociated complex species [Cu(pydicR<sub>2</sub>)Cl<sub>3</sub>]<sup>−</sup>.

**Keywords:** oxido-pincer ligands; Cu<sup>II</sup>; DFT calculations; EPR spectroscopy; electrochemistry

## 1. Introduction

Pyridine-2,6-dicarboxylic esters are interesting oxido pincer ligands with an O,N,O donor set. They are derived from the potentially O,N,O tridentate binding 2,6-dicarboxylic acid (pydicH<sub>2</sub>) (Scheme 1). Pyridine-2,6-dicarboxylate (pydic<sup>2−</sup>) is a frequently used ligand and coordinates are usually in a deprotonated tridentate mode. The coordinates use the N donor atom and the two carboxylate O donor functions, including the possibility of bridging (Scheme 1) [1–14]. In contrast to this, the pydic ester ligands are neutral and have three options of tris-chelate O,N,O binding, which gives rise to three different isomers O<sub>carbonyl</sub>–M–O<sub>carbonyl</sub> (CC isomer), O<sub>carbonyl</sub>–M–O<sub>alkoxy</sub> (CA isomer), and O<sub>alkoxy</sub>–M–O<sub>alkoxy</sub> (AA isomer) (Scheme 1) while a bridging mode observed frequently for pydic<sup>2−</sup> is less probable [15–17].



**Scheme 1.** Binding modes of pydic<sup>2−</sup> compared to pyridine-2,6-dicarboxylic ester ligands (R = alkyl or aryl; [M] = metal ions or metal complex fragments).

Pyridine-2,6-dicarboxylic alkyl- or arylester derivatives pydicR<sub>2</sub> coordinating to metal ions have been reported with R = methyl [15–21], ethyl [18,20,22–26], *iso*-propyl [18], *n*-butyl [26], and benzyl [18], with further complexes containing related non-symmetric or macrocyclic esters RpydicR' [23,24,27–30]. Aryl substituted systems are less frequent [27]. In most of these examples, the ligands coordinate in a tridentate mode. However, bidentate N,O coordination or monodentate N coordination has been observed [15,16,20,21,28]. Recently, Hakimi et al. found in the Cambridge Crystallographic Database that, from the complexes showing tridentate O,N,O coordination, roughly 42% of the submitted structures show O<sub>carbonyl</sub>–M–O<sub>carbonyl</sub> coordination (CC isomers, Scheme 1) [15], while AA (O<sub>alkoxy</sub>–M–O<sub>alkoxy</sub>) and CA (O<sub>carbonyl</sub>–M–O<sub>alkoxy</sub>) isomers make up about 29% each. The CC isomers are expected to be superior to the CA and AA isomers since the carbonyl function provides less steric strain and potentially  $\pi$  back-bonding options in addition to the  $\sigma$  coordination of the O lone pairs. Quite generally, both O<sub>carbonyl</sub> and O<sub>alkoxy</sub> coordination is considered to be relatively weak, e.g., compared to the carboxylate ligand function of pydic<sup>2−</sup>. Ester functions in polydentate ligands have been applied as hemilabile ligand functions in catalysis [31–35].

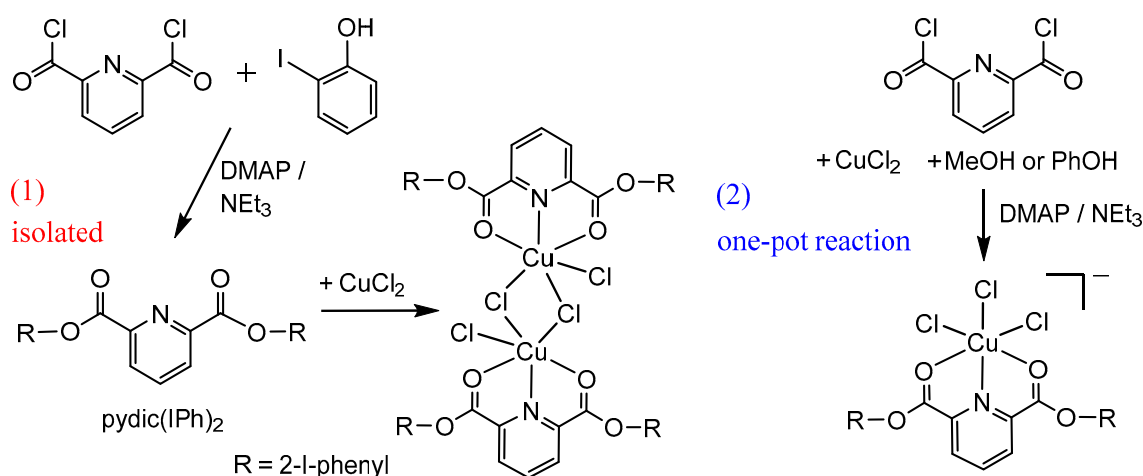
In this contribution, we will report on our investigations about the coordination of Cu<sup>II</sup> toward the pyridine-2,6-dicarboxylic ester pydicR<sub>2</sub> ligands with R = Me, Ph, and 2-iodo-phenyl (IPh). We report their synthesis and compare their molecular structures in the solid using single crystal XRD with the structures under various environments (gas phase, solution) using quantum chemical calculations based on the density functional theory (DFT). In these calculations, we were probing for their structural variability in terms of isomers, ion pair stabilization, or ligand replacement by potentially coordinating solvents such as MeCN and DMF. Detailed DFT calculations also revealed the influence of increasing solvent polarity on the dipole moments and charge distribution in the ion pairs. Since Cu<sup>II</sup> ( $d^9$ ,  $S = \frac{1}{2}$ ) provides very useful spectroscopic (d–d bands, EPR) and electrochemical (Cu<sup>II</sup>/Cu<sup>I</sup> couple) patterns to study geometries and the strength of M–ligand bonds, we added EPR spectroscopy in the solid and solution to this study, together with UV–vis absorption, cyclic voltammetry, and UV–vis spectroelectrochemistry of selected compounds in the solution.

## 2. Results and Discussion

### 2.1. Synthesis and Molecular Structures of pydicR<sub>2</sub> Ligands and their Cu<sup>II</sup> Complexes

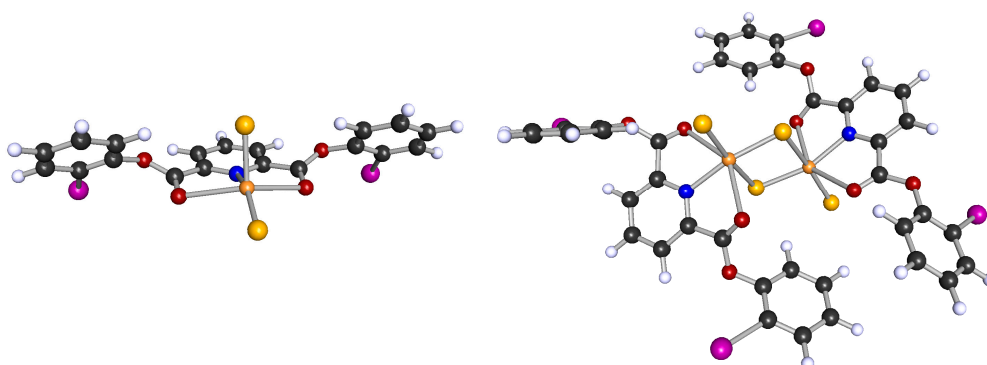
Two different reaction strategies were used to synthesize Cu<sup>II</sup> complexes (Scheme 2). The first route has been previously used, e.g., for the formation of pydic ester complexes [ $\text{Cu}(\text{pydicR}_2)\text{Cl}$ ]<sub>2</sub>( $\mu\text{-Cl}$ )<sub>2</sub>

(R = Me, Et, *i*Pr) [17,22] and consists of two subsequent steps, the synthesis of the pydicR<sub>2</sub> ligand, and its isolation followed by the complex formation reaction (1).



**Scheme 2.** Two reaction strategies to synthesize Cu<sup>II</sup> complexes of pydicR<sub>2</sub> ligands (DMAP = dimethyl 4-aminopyridine).

This method allowed the synthesis of the new ligand pydic(IPh)<sub>2</sub> (IPh = 2-iodo-phenyl) in 82% yield (spectroscopic characterization, see Experimental Section). Single crystals suitable for XRD were obtained from acetone solutions by slow evaporation and the structure was solved in the orthorhombic space group *Pbca* (further details, full data, and Figure S1 in the Supplementary Materials). Reacting pydic(IPh)<sub>2</sub> with anhydrous CuCl<sub>2</sub> gave a new complex as a brown powder in 67% yield with a ligand:Cu ratio of 1:1 from elemental analysis. Similar reactions using pydicMe<sub>2</sub>, pydicEt<sub>2</sub>, or pydic<sup>*i*</sup>Pr<sub>2</sub> have been reported, which yielded binuclear complexes [Cu(pydicR<sub>2</sub>)Cl]<sub>2</sub>(μ-Cl)<sub>2</sub> [17,22,23]. We assume a binuclear structure for [Cu(pydic(IPh)<sub>2</sub>)Cl]<sub>2</sub>(μ-Cl)<sub>2</sub>. DFT-calculated optimized geometries confirmed this with the binuclear structure being more stable by about 75 kJ/mol compared with the mononuclear [Cu(pydic(IPh)<sub>2</sub>)Cl<sub>2</sub>] (Figure 1). Importantly, both the mononuclear and the binuclear complex show the CC isomeric structure (Scheme 1) with the two carbonyl O atoms binding to Cu<sup>II</sup> in the two markedly elongated axial positions of a distorted trigonal pyramidal (mononuclear) or pseudo-octahedral (binuclear) coordination. Comparison of the calculated coordination modes CC, CA, and AA shows that the CC isomer is energetically favored.

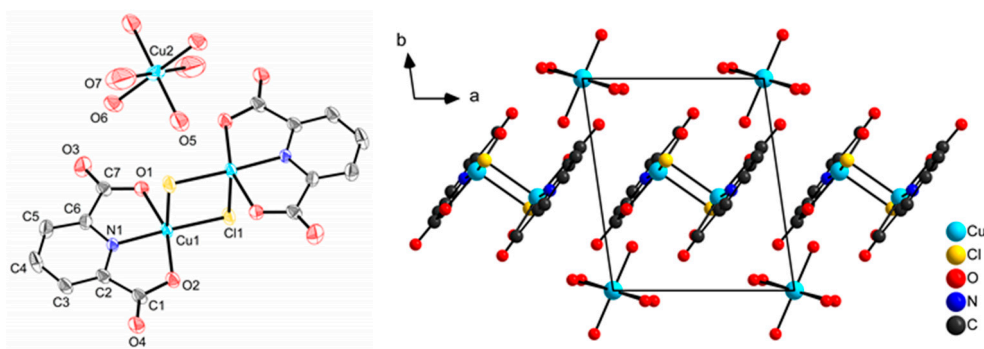


**Figure 1.** DFT-calculated optimized geometry of mononuclear [Cu(pydic(IPh)<sub>2</sub>)Cl<sub>2</sub>] (left) and binuclear [Cu(pydic(IPh)<sub>2</sub>)Cl]<sub>2</sub>(μ-Cl)<sub>2</sub> (right). Calculated at the def-SV(P)/B3LYP level.

In addition to this, we had the idea to set up a one-pot reaction using pyridine-2,6-dicarbonyl dichloride (pydicCl<sub>2</sub>), a Cu<sup>II</sup> source, and the corresponding alcohol (methanol or phenol) to form the ligand in the presence of the coordinating metal ion and a base (2). The base was quite similar to

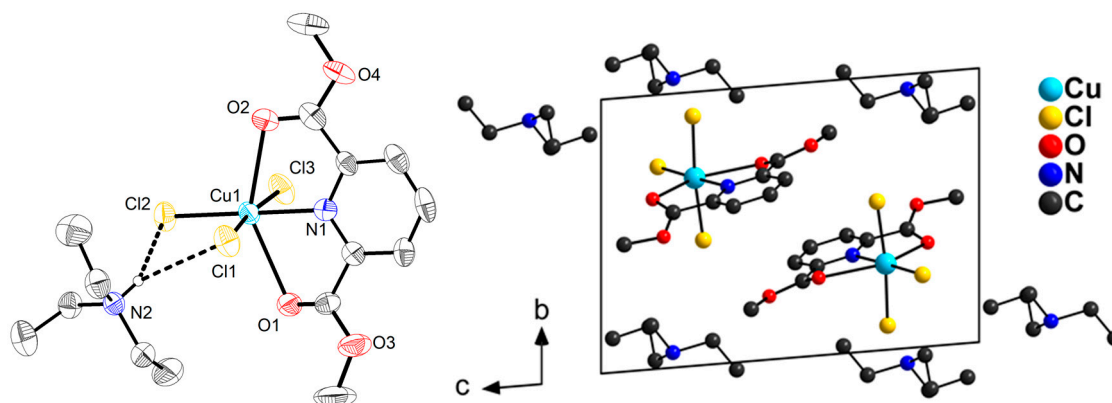
what has been reported recently for the formation of lanthanide coordinated IRMOF-3-PY through a post-synthetic modification [5].

In initial experiments, we reacted  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and not carefully dried  $\text{Cu}(\text{OAc})_2$ , methanol or phenol, and pydic $\text{Cl}_2$  in a 1:1 ratio. In low yields of 12% and 24%, respectively, we could isolate  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$  and  $[\text{Cu}(\text{pydic})(\text{OH}_2)_2]_n$  (pydic $^{2-}$  = pyridine-2,6-dicarboxylate). Both compounds resulted from the hydrolysis of pydic $\text{Cl}_2$  to pydic $^{2-}$  in the presence of water while no ester was formed. The crystal structure (monoclinic  $P2_1/c$ ) of  $[\text{Cu}(\text{pydic})(\text{OH}_2)_2]_n$  was reported before [36,37]. XRD suitable crystals of  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$  were obtained by slow evaporation of a methanol solution. The crystal structure was solved and refined in the triclinic space group  $P\bar{1}$  (Figure 2, further details and full data in the Supplementary Materials). The structure reveals the complex cation  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  and a centrosymmetric binuclear  $\mu$ -chlorido bridged dianionic complex  $[\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]^{2-}$ .  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  can be described as an axially elongated octahedron ( $\text{Cu}2\text{-O}5 = 1.979(9)$  Å,  $\text{Cu}2\text{-O}6 = 1.965(9)$  Å, and  $\text{Cu}2\text{-O}11 = 2.53(2)$  Å), which is in line with previous reports [38,39]. The di-anion  $[\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]^{2-}$  shows a distorted square pyramidal geometry around each copper atom with a short equatorial bond  $\text{Cu-Cl}_{\text{eq}} = 2.212(4)$  Å, long axial bond  $\text{Cu-Cl}_{\text{ax}} = 2.692(3)$  Å, and a rather short equatorial  $\text{Cu-N}$  bond ( $1.93(1)$  Å). Very similar bond parameters have been reported for the dianion  $[\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]^{2-}$  in the compounds  $[\text{Cu}(\text{MeOH})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{pydic})_2(\mu\text{-Cl})_2] \cdot \text{H}_2\text{O}$  [40] and  $[\text{Cu}(\text{Pz})_2(\text{H}_2\text{O})_4][\text{Cu}_2(\text{pydic})_2(\mu\text{-Cl})_2]$  (Pz = pyrazole) [41].



**Figure 2.** Left: ORTEP representation (50% probability level) of the molecular structure of  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$ . H atoms were omitted for clarity. Right: Crystal structure of  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$  along the crystallographic  $c$ -axis.

In further synthesis experiments using freshly distilled starting materials and anhydrous  $\text{CuCl}_2$ , we obtained yellow-green crystalline materials. Repeated re-crystallisation from methanol was necessary but lowered the yields to 32% and 54% of the complexes  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$ . Thus, under water-free conditions, the in situ formation of the corresponding pydic $\text{R}_2$  ligands and coordination to  $\text{Cu}^{\text{II}}$  (one-pot) is possible. Single crystals of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  were obtained from methanol solution and structure solution and refinement were carried out in the triclinic space group  $P\bar{1}$  (data in the Supplementary Materials). The molecular structure is depicted in Figure 3 and shows the Cu ion in a distorted octahedral surrounding the carbonyl oxygen atoms of the O,N,O-ester binding to the copper atom (CC isomer). The three  $\text{Cu-Cl}$  bonds with  $2.306(2)$  Å,  $2.255(2)$  Å, and  $2.306(2)$  Å and the  $\text{Cu-N}1$  bond of  $2.065(4)$  Å define a distorted square plane. The two  $\text{Cu-O}$  bonds  $\text{Cu-O}2 = 2.503(4)$  Å and  $\text{Cu-O}4 = 2.551(3)$  Å are non-equivalent and represent the long bonds of an axially elongated pseudo-octahedron. The real local symmetry at the Cu atom can be idealized as  $\text{C}_{2v}$ . Two strong hydrogen bonds [42] are formed between the triethyl ammonium ion and two chlorido ligands of the complex anion ( $\text{H}22 \cdots \text{Cl}1 = 2.70(4)$  Å and  $\text{H}22 \cdots \text{Cl}2 = 2.48(4)$  Å,  $\text{Cl}1 \cdots \text{H}22 \cdots \text{Cl}2 = 79(1)^\circ$ ).

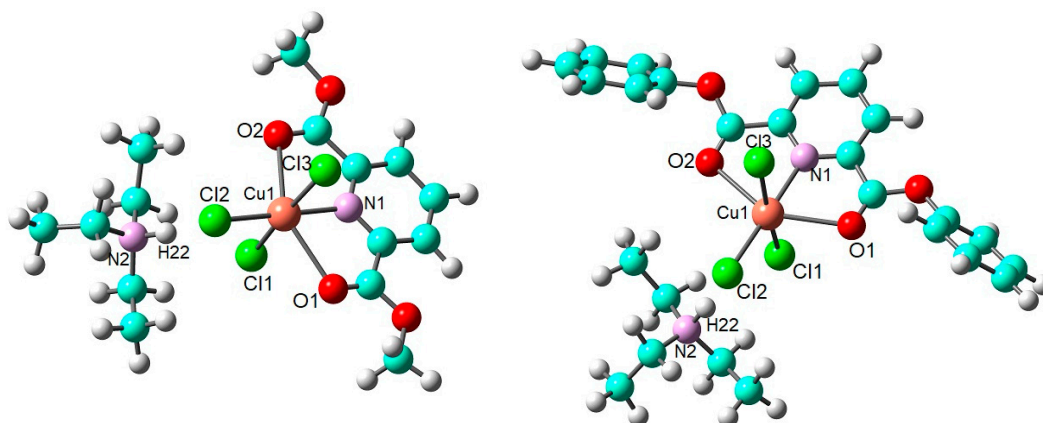


**Figure 3.** ORTEP representation (50% probability level) of the molecular structure of (HNEt<sub>3</sub>)[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>]. H atoms are omitted for clarity. Right: Crystal structure of (HNEt<sub>3</sub>)[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>] along the crystallographic *a*-axis.

Comparison of (HNEt<sub>3</sub>)[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>] with the reported complex [Cu(pydicMe<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> [17] reveals the same bond parameters within the pydicMe<sub>2</sub> ligand, similar Cu–ligand distances in the equatorial plane: Cu–N 1.990(3) Å, Cu–OH<sub>2</sub> 1.992(3), 1.949(3), and 2.000(3) Å, respectively, and long Cu–O<sub>keto</sub> bonds of 2.332(3) and 2.338(3) Å. Thus, both Cl<sup>−</sup> in [Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>] and H<sub>2</sub>O in [Cu(pydicMe<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>] represent stronger ligands than the carbonyl ester O atoms.

## 2.2. DFT Calculations on the Solvation of (HNEt<sub>3</sub>)[Cu(pydicR<sub>2</sub>)Cl<sub>3</sub>] (R = Me or Ph)

To achieve insight into the electronic structure of the compounds, density functional theory (DFT) calculations in the gas phase and various solvent environments are performed (B3LYP/6–31+G(d,p) using Gaussian). The Cu atom was treated using LANL2DZ relativistic pseudo potentials. The final optimized geometry of the compounds in the gas phase is depicted in Figure 4. The calculated *C*<sub>2v</sub>-symmetric structure of the ion pair (HNEt<sub>3</sub>)<sup>+</sup>...[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>]<sup>−</sup> in the gas phase is very similar to the crystal structure, e.g., with two strong hydrogen bonds N2–H22...Cl1 (2.98 Å) and N2–H22...Cl2 (2.01 Å).



**Figure 4.** DFT-calculated geometry-optimized (B3LYP/6–31+G(d,p), Gaussian) structures of (HNEt<sub>3</sub>)[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>] and (HNEt<sub>3</sub>)[Cu(pydicPh<sub>2</sub>)Cl<sub>3</sub>] in the gas phase with numbering.

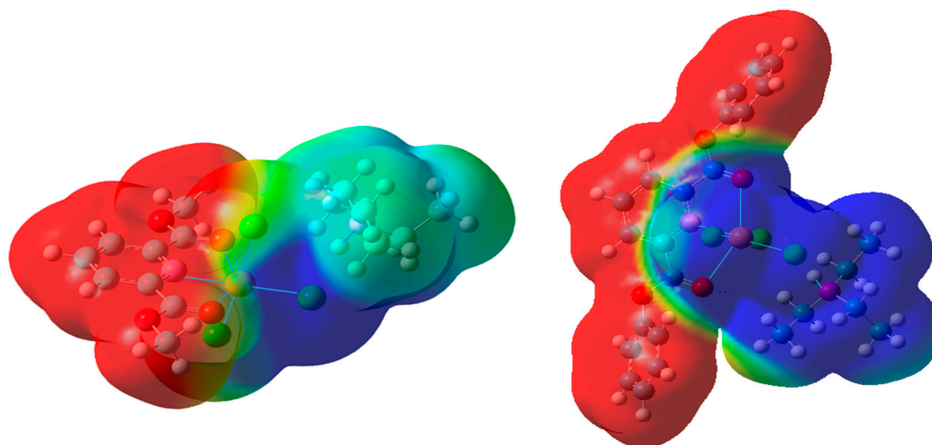
In CH<sub>2</sub>Cl<sub>2</sub>, acetone, DMF, and MeCN solution, the geometry of the complexes remains rather intact. Only the Cu–Cl<sub>3</sub> bond is markedly elongated with a slight tendency of longer bonds for more polar solvents along this series. Even more pronounced is the increasing distance between the ions due to the shielding of electrostatic interactions in these solutions (see Tables S3–S7 in the Supplementary Materials). The computed dipole moments of the complexes are significantly increased in solution

compared with the gas phase (Table 1) and the electric permittivity of the solvents clearly has a very pronounced effect on the dipole moments, even in  $\text{CH}_2\text{Cl}_2$ . In order to investigate the solubility and thermodynamic stability of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  in the surrounding medium, the solvation energies are calculated. The solvation energy of the system is determined by calculating the free energy differences in the solvent and the gas phase (Table 1). The solvation energies vary from about  $-110.88$  to  $-135.12$  kJ/mol and increase together with the dipole moment of the complex when increasing the electric permittivity of the solvents. Negative values of solvation energies denote that solvation of these complexes is spontaneous. To get an idea about the kinetic stability and chemical reactivity of these complexes, we also calculated the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) ( $E_{\text{LUMO}} - E_{\text{HOMO}}$ ) for the complexes in each solvent (Table 1). The spatial distributions of HOMO, SOMO, and LUMO of the complexes are supplied in the Supplementary Materials (Figure S8). In general, molecules with a small energy gap are more polarizable [43] and will have higher chemical activity and lower kinetic stability [44]. Overall, the HOMO–LUMO gap decreases as the electric permittivity of the solvents declines along the series DMF ( $\epsilon = 37.22$ ) > MeCN ( $\epsilon = 35.69$ ) >> acetone ( $\epsilon = 20.49$ ) >>  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 8.93$ ). However, the absolute values are quite similar for all four solvents, which means that a pronounced activation by the polar solvents DMF or MeCN compared with acetone or  $\text{CH}_2\text{Cl}_2$  seems not to be the case.

**Table 1.** DFT-calculated dipole moments and solvation energies of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$  in the gas phase and solvent media.

Compound		Gas Phase	$\text{CH}_2\text{Cl}_2$	Acetone	MeCN	DMF
$(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$	dipole moment (Debye)	8.27	12.49	13.22	13.49	13.51
	solvation energy (kJ/mol)		$-110.88$	$-128.30$	$-134.74$	$-135.12$
	$E_{\text{LUMO}} - E_{\text{HOMO}}$ (kJ/mol)	323.15	382.64	390.20	392.91	393.06
	charge $[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$	$-0.84006$	$-0.90691$	$-0.91645$	$-0.91969$	$-0.92005$
$(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$	dipole moment (Debye)	7.97	12.29	13.13	13.44	13.46
	solvation energy (kJ/mol)		$-124.86$	$-139.25$	$-146.15$	$-146.55$
	$E_{\text{LUMO}} - E_{\text{HOMO}}$ (kJ/mol)	314.22	369.83	376.68	379.41	379.57
	charge $[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]^-$	$-0.84929$	$-0.90889$	$-0.92116$	$-0.92426$	$-0.92447$

The electron density of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$  in the gas phase can be visualized from the three-dimensional electrostatic potential map (EPM) surfaces (Figure 5). The distribution of negative and positive charges within the EPM surfaces are depicted by red and blue colors, respectively. As a result of change in electron densities in EPM surfaces upon solvation, the charges of the anions and cations both decrease along the series. DMF > MeCN > acetone >  $\text{CH}_2\text{Cl}_2$  >> gas phase (Table 1, Figures S9 and S10 in the Supplementary Materials).



**Figure 5.** Electrostatic potential maps of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  (left) and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$  (right) in the gas phase. Contours are color-coded from red (negative) to blue (positive).

To better understand the inclusion of the solvent effect on the DFT calculations and also the nature of interactions in the  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  compounds, natural bond orbital (NBO) analyses were carried out as implemented in the Gaussian program package. In the NBO analysis, the donor and acceptor interaction energies can be estimated through the second-order perturbation theory, which is described by the equation below.

$$E^{(2)} = q_i \frac{F(i, j)^2}{\varepsilon_i - \varepsilon_j}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$  and  $\varepsilon_i$  are diagonal elements, and  $F(i, j)$  is the off-diagonal NBO Fock matrix element. The most important donor-acceptor interactions with high second-order perturbation energies  $E^{(2)}$  are provided in Table 2 (data for the pydicPh derivative in Table S8 in the Supplementary Materials).

**Table 2.** DFT-calculated second-order perturbation energies  $E^{(2)}$  (kJ/mol) of selected orbital interactions in  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  in the gas phase and solvents <sup>a</sup>.

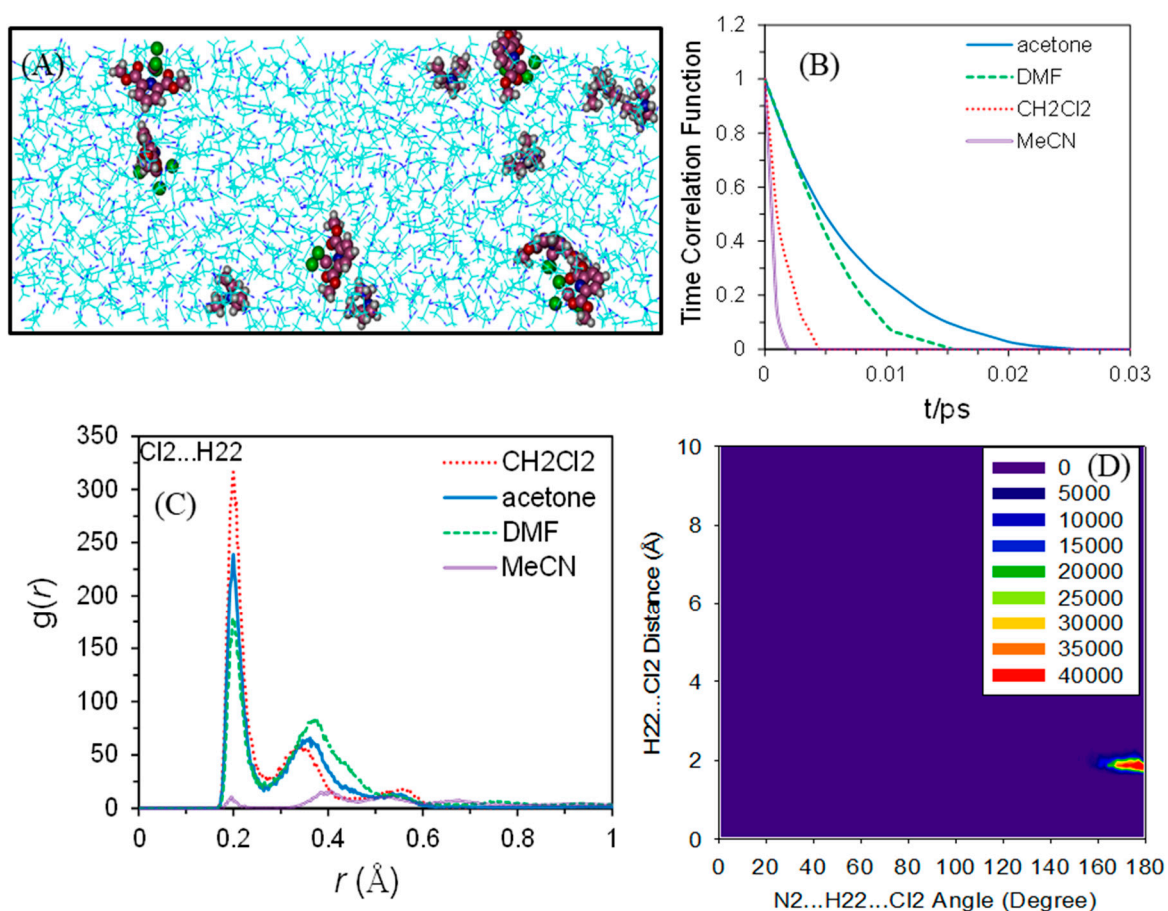
Donor	Acceptor	Gas Phase	$\text{CH}_2\text{Cl}_2$	Acetone	MeCN	DMF
LP*(8) Cu1	BD*(1) N2–H22	18.91	8.24	7.28	6.95	6.90
LP(1) Cl1	LP*(7) Cu1	48.53	50.54	51.21	51.42	51.46
LP(4) Cl1	LP*(6) Cu1	99.62	98.78	99.29	99.54	99.54
LP(4) Cl1	LP*(7) Cu1	167.40	179.53	181.21	181.84	181.88
LP(1) Cl2	LP*(8) Cu1	61.30	57.91	57.74	57.61	57.70
LP(4) Cl2	LP*(6) Cu1	107.15	126.40	128.37	128.99	129.04
LP(4) Cl2	LP*(8) Cu1	153.55	157.32	156.65	156.23	156.27
LP(3) Cl2	BD*(1) N2–H22	66.19	47.49	42.30	40.54	40.30
LP(1) Cl3	LP*(7) Cu1	72.72	64.10	63.26	63.01	63.01
LP(4) Cl3	LP*(6) Cu1	123.85	105.31	102.84	102.00	101.96
LP(4) Cl3	LP*(7) Cu1	206.65	192.67	191.04	190.50	190.50
LP(1) O1	LP*(9) Cu1	31.59	34.64	35.15	35.40	35.40
LP(1) O2	LP*(9) Cu1	36.36	37.24	37.24	37.20	37.20
LP(1) N1	LP*(6) Cu1	63.39	69.83	70.63	70.88	70.88
LP(1) N1	LP*(8) Cu1	64.52	71.55	72.72	73.18	73.22

<sup>a</sup> LP = lone pairs, LP\* = antibonding molecular orbitals of Cu. BD\* = antibonding orbitals.

As the interaction between  $(\text{HNEt}_3)^+$  and  $[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]^-$  as the electron acceptor and electron donor increases, the calculated  $E^{(2)}$  value become larger, as expected. Furthermore, the increase in donating tendency from electron donors to electron acceptors is consistent with the enhancement of conjugation of the whole system from  $\text{R} = \text{Me}$  to  $\text{R} = \text{Ph}$ . The results suggest strong orbital interactions between the antibonding molecular orbitals of the Cu atom (LP\*) and the antibonding orbitals of the N2–H22 bond (BD\*) in the gas phase, which leads to a stabilization of 18.91 kJ/mol for  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and 21.30 kJ/mol for  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$ , respectively. In solution with an effect of the solvents, this donor-acceptor behavior between  $(\text{HNEt}_3)^+$  and  $[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$  leads to a reduction of the intermolecular charge transfer with lower values of  $E^{(2)}$  (1.66). The table also reveals that the  $E^{(2)}$  in the LP\*(8) Cu1 and the BD\*(1) N2–H22 and also the LP(3) Cl2 and BD\*(1) N2–H22 are decreasing with an increasing dielectric constant of the solvent. The NBO analysis results illustrate that, in the gas phase, LP(4) Cl2 and LP(4) Cl1 participate as donors and the LP\*(7) Cu1 acts as an acceptor with the strongest intramolecular charge transfer interactions (Table 2). In solvent environments, the  $E^{(2)}$  in the LP(4) Cl2 and LP\*(7) Cu1 and also the  $E^{(2)}$  in the LP(4) Cl1 and LP\*(7) Cu1 are enlarged with increasing dielectric constants of the solvent. However, this trend for the  $E^{(2)}$  in the LP(4) Cl3 and LP\*(7) Cu1 are completely reversed. The trend of charge transfer from LP(1) O1, LP(1) O2, and LP(1) N1 as donors and LP\* Cu1 as an acceptor are increased with a growing dielectric constant of the solvents.

### 2.3. Molecular Dynamics (MD) Simulations of Bulk Solutions

In addition, we also performed molecular dynamic simulations using the GROMACS 4.5.5 package and utilizing the GROMOS force field 53A6. Six ion pairs solvated in 1200 solvent molecules were simulated for each compound. As an example, Figure 6A shows the snapshot of the  $(\text{HNEt}_3)^+ \cdots [\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$  ion pairs solvated in MeCN after 10 ns of simulation. The anion-cation correlation lifetime in various solvents is depicted in Figure 6B. The lifetime of the hydrogen bond between the Cl2 atom of the anion and H22 of the cation for the  $(\text{HNEt}_3)^+ \cdots [\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$  system tends to diminish along the series acetone > DMF >  $\text{CH}_2\text{Cl}_2$  > MeCN, which is not along the general polarity (permittivity) of these solvents. The radial distribution functions ( $g(r)$ ) between the Cl2 atom of the anion and H22 of the cation are calculated and illustrated in Figure 6C for  $(\text{HNEt}_3)^+ \cdots [\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$  ion pairs in various solvents.



**Figure 6.** (A) Snapshots of the DFT calculated dynamic behavior of six ion pairs  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  in MeCN. (B) Time correlation functions, (C) the radial distribution function, and (D) the combined radial/angular distribution function between the Cl2 atom of the anion and H22 of the cation in  $(\text{HNEt}_3)^+ \cdots [\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]^-$ .

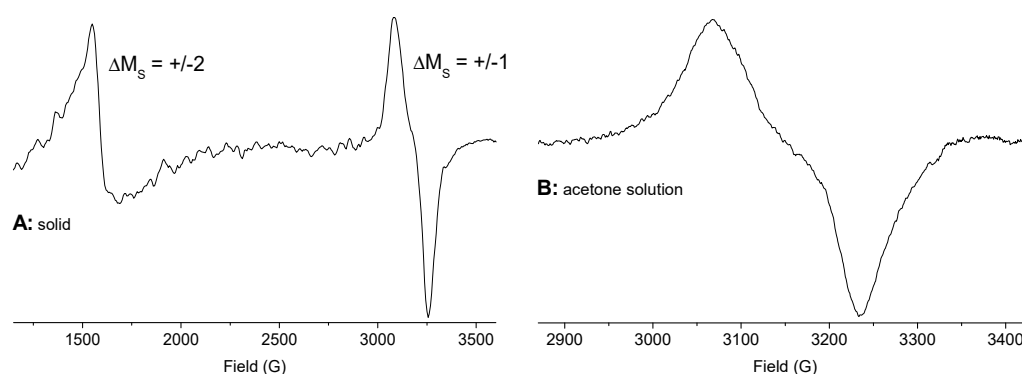
The first peak of the radial distribution function is located at around 1.84 Å, which is an indicator of a strong hydrogen bond. Combined radial/angular distribution function (CDF) is a powerful tool for defining hydrogen bond criteria, since it offers much more information than  $g(r)$  [45]. The combined radial/angular distribution function (see Figure 6D) indicates that this preferred interaction occurs for N2...H22...Cl2 angles ( $\alpha$ ) between 160° and 180°.

All of these calculated data points show a marked difference between the gas phase and solvent surrounding these ion pairs and emphasizing the importance of the proper inclusion of solvents in any DFT calculations. According to our calculations, the electronic structure of the studied solutes is

influenced in a different manner by the non-coordinating  $\text{CH}_2\text{Cl}_2$ , the weakly coordinating acetone, and MeCN and DMF, which are considered suitable ligands for  $\text{Cu}^{\text{II}}$ . With increasing polarity along the series gas phase <  $\text{CH}_2\text{Cl}_2$  < acetone < MeCN < DMF solutions, the  $\text{Cl3-Cu}$  bond is markedly elongated, the distance between the cations and anions are increased, and the dipole moments as well as the extent of charge localization of the cation and anion increases. However, the differences between  $\text{CH}_2\text{Cl}_2$  and MeCN or DMF solutions are not very pronounced. Although more detailed kinetic calculations would be necessary to make a statement on the dissociation of the complexes in MeCN or DMF solution, we assume from the present calculations that the complexes remain stable in solution, which is important in view of the following spectroscopy and electrochemical measurements in the solution.

#### 2.4. EPR Spectroscopy of Solids and Solutions

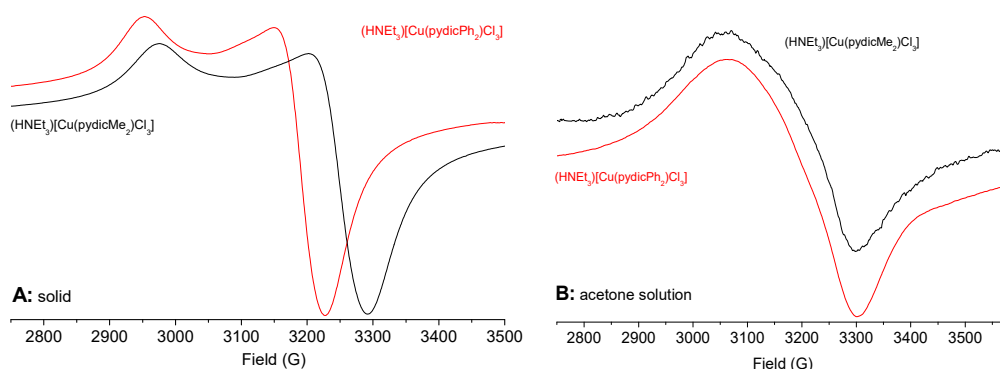
The X-band EPR spectrum of  $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  in the solid shows a very intense signal for the forbidden  $\Delta M_S = \pm 2$  transition and a rhombic  $\Delta M_S = \pm 1$  signal (Figure 7), which is completely in line with the binuclear character of the complex and a triplet ground state. In acetone solution, the spectrum is essentially retained and, thus, the binuclear character remains unchanged. A similar spectrum with very similar  $g$  values has been reported for  $[\{\text{Cu}(\text{pydicEt}_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  [23], while the derivative  $[\{\text{Cu}(\text{pydic}^i\text{Pr}_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  exhibits a markedly different averaged  $g$  value (Table 3) and no  $\Delta M_S = \pm 2$  transition is observed. The difference has been attributed to the different geometries for the central  $\text{Cu}(\mu\text{-Cl})_2\text{Cu}$  unit, which is planar for the  $\text{pydicEt}_2$  complex but bent for the *iso*-propyl derivative [23]. Thus, our results are fully in line with the DFT-calculated structure of  $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$ , which shows a planar  $\text{Cu}(\mu\text{-Cl})_2\text{Cu}$  core (Figure 1). Although the averaged  $g$  value is quite similar for the related binuclear  $\text{Cu}^{\text{II}}$  complex  $[\{\text{Cu}(\text{pydotH}_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  ( $\text{pydotH}_2 = 2,6\text{-bis}(1\text{-hydroxy-1-}o\text{-tolyl-ethyl-}\eta^2\text{-O,O'})\text{pyridine}$ ) [46], the  $g$  anisotropy  $\Delta g$  is markedly increased, while the  $\Delta M_S = \pm 2$  is far less intense. This reflects the different “ligand setting” in this complex containing an ONO pincer ligand based on pyridine-2,6-dimethanol. As deduced from EXAFS data, the O, N, O atoms of the  $\text{pydotH}_2$  ligand and the bridging chlorido ligand form a square plane of the tightly bound ligands. From this bridging  $\text{Cl}^-$ , an elongated  $\text{Cu-Cl}$  bond connects to the second  $\text{Cu}^{\text{II}}$ , while the terminal chloride ligand has a short  $\text{Cu-Cl}$  bond [46]. Thus, while in the binuclear complexes  $[\{\text{Cu}(\text{pydicR}_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  with  $\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$  and  $\text{IPh}$ , the tight binding ligands are N, Cl, and  $2 \times \mu\text{-Cl}$  with the two square planes fused by the bridging  $\mu\text{-Cl}$  atoms. In the  $\text{pydotH}_2$  complex, the two square planes  $\text{O,N,O}, \mu\text{-Cl}$  and the central  $\text{Cu}(\mu\text{-Cl})_2\text{Cu}$  core are perpendicular to each other. The EPR spectra fully reflect this difference.



**Figure 7.** X-band EPR spectra of  $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  at 298 K. (A) in the solid. (B) in acetone solution.

The mononuclear compounds  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$  reveal EPR spectra of axial symmetry with  $g_{\parallel} > g_{\perp}$  in the solid (Figure 8), which is typical for elongated octahedral or square pyramidal  $\text{Cu}^{\text{II}}$  complexes [23,47–52]. The Cu hyperfine structure (coupling

to the  $^{63}\text{Cu}$  (69.17%) and  $^{65}\text{Cu}$  (30.83%) nuclei with  $I = 3/2$  [53]) was not observed in line with observations for similar mononuclear complexes [46,52]. A rhombic EPR spectrum was reported for the complex  $[\text{Cu}(\text{pydotH}_2)(\text{DMF})\text{Cl}_2]$  [46], which has an axially elongated distorted pseudo-octahedral geometry with the O,N,O ligand located in the square plane of tight Cu–ligand bonds. Yet, in  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$ , the N,Cl<sub>3</sub> coordination represents the short = strong bonds and the O<sub>carbonyl</sub> functions are in the elongated positions. Nevertheless, the averaged  $g$  values and  $g$  anisotropy ( $\Delta g$ ) are very similar. Far smaller averaged  $g$  values were reported for the square pyramid or trigonal bipyramidal complexes listed in Table 3. Thus, the observed spectra represent the overall geometry around  $\text{Cu}^{\text{II}}$  than the ligand strength of  $\text{Cl}^-$ , DMF, and O atoms in the O, N, O ligands.



**Figure 8.** X-band EPR spectra of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$ . (A) in the solid, (B) in acetone solution measured at 298 K.

**Table 3.** X-band EPR data of the reported and comparable  $\text{Cu}^{\text{II}}$  complexes <sup>a</sup>.

Compounds	$g_{av}$	$g_{\parallel}$ or $g_1$	$g_{\perp}$ or $g_2$	$g_3$	$\Delta g$	State
reported compounds						
$[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}_2(\mu\text{-Cl})_2]$	2.157	2.260	2.115	2.095	0.165	solid
$[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}_2(\mu\text{-Cl})_2]$	2.130	2.197	2.102	2.091	0.106	acetone
$(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$	2.182	2.351	2.098		0.253	solid
$(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$	2.131	2.211	2.091		0.120	acetone
$(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$	2.196	2.362	2.113		0.249	solid
$(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2)\text{Cl}_3]$	2.126	2.201	2.089		0.112	acetone
related mononuclear complexes						
$[\text{Cu}(\text{pydic})(\text{H}_2\text{O})_2] (\text{sq})^b$	2.156	2.324	2.102	2.043	0.281	solid
$[\text{Cu}(\text{pydimH}_2)\text{Cl}_2] (\text{sq})^c$	2.158	2.311	2.094	2.068	0.243	solid
$[\text{Cu}(\text{pydipH}_2)\text{Cl}_2] (\text{tbp})^c$	2.138	2.220	2.220	1.973 <sup>e</sup>	0.223	solid
$[\text{Cu}(\text{pydotH}_2)(\text{DMF})\text{Cl}_2] (\text{aeo})^c$	2.194	2.353	2.120	2.108	0.245	solid
related binuclear complexes						
$[\{\text{Cu}(\text{pydicEt}_2)\text{Cl}_2(\mu\text{-Cl})_2]^d$	2.147	2.21	2.12	2.11	0.100	solid
$[\{\text{Cu}(\text{pydic}^i\text{Pr}_2)\text{Cl}_2(\mu\text{-Cl})_2]^d$	2.130	2.17	2.16	2.06	0.110	solid
$[\{\text{Cu}(\text{pydotH}_2)\text{Cl}_2(\mu\text{-Cl})_2]^c$	2.148	2.418	2.081	1.946	0.472	solid

<sup>a</sup> measured at 298 K;  $g_{av}$  = averaged  $g$  value =  $(g_{\parallel} + 2g_{\perp})/3$  or  $(g_1 + g_2 + g_3)/3$ ;  $\Delta g = g_{\parallel} - g_{\perp}$  or  $g_1 - g_3$ . <sup>b</sup> From Reference [52]. <sup>c</sup> From Reference [46]. sq = square pyramidal, tbp = trigonal bipyramidal, aeo = axially elongated pseudo-octahedral. <sup>d</sup> From Reference [23].

Samples dissolved in acetone or MeCN (at ambient temperatures) exhibit axial signal symmetry even though the averaged  $g$  values and the  $g$  anisotropy ( $\Delta g$ ) are markedly decreased. We conclude that the ion pairs and the anionic complexes in  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  are basically retained in acetone or MeCN solution with minor alterations in complex geometry. This is completely in line with our DFT calculations showing changes in the geometry and charge transfer of the ion pairs upon solvation and likely shows no dissociation.

### 2.5. UV–Vis Absorption Spectroscopy

The binuclear complex  $[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$  and the mononuclear compounds  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2\text{Cl}_3)]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2\text{Cl}_3)]$  dissolved in MeCN show intense UV bands around 290 or 260, respectively, which is assignable to ligand-centered  $\pi\text{-}\pi^*$  transitions (Table 4, spectra in the Supplementary Materials). The three complexes all show a characteristic absorption band at around 460 nm, which is assignable to a ligand(Cl)-to-metal(Cu) charge transfer LMCT transition. In the visible range, broad bands assigned to d–d transitions ( $a_2, b_1, b_2 \rightarrow a_1$  in  $C_{2v}$  symmetry) were observed. Their exact energies are difficult to determine but lie around 820 nm for  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2\text{Cl}_3)]$ , 890 nm for  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2\text{Cl}_3)]$ , and 830 nm for  $[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$ . These are in line with values recently reported for related  $\text{Cu}^{\text{II}}$  complexes with O,N,O ligands of the pyridine-2,6-dimethanol type [46,54]. In the spectrum of  $\text{K}_2[\text{CuCl}_4]$  in MeCN, the long wavelength d-d band is observed at 1074 nm, which is in line with a markedly stronger ligand field for the  $[\text{Cu}(\text{pydicR}_2\text{Cl}_3)]^-$  and  $[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$  complexes.

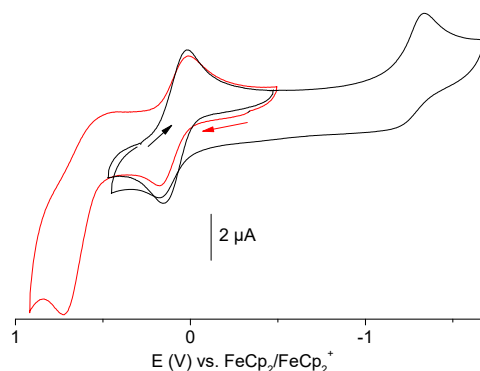
**Table 4.** Absorption maxima for  $\text{Cu}^{\text{II}}$  complexes <sup>a</sup>.

Compounds	$\lambda/\text{nm}$ ( $\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) <sup>c</sup>
$(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2\text{Cl}_3)]$	261 (48400), 462 (3290), 822 (160)
$(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2\text{Cl}_3)]$	261 (44400), 307 (14400) <sup>b</sup> , 462 (4580), 890 (310)
$[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$	289 (27100), 464 (3740), 830 (200)
$\text{K}_2[\text{CuCl}_4]$	312, 346sh, 462, 1074

<sup>a</sup> Measured in MeCN. <sup>b</sup> Absorption assigned to  $\pi(\text{Ph})\text{-}\pi(\text{Py})$  transitions. <sup>c</sup> extinction coefficient.

### 2.6. Electrochemical Measurements

The electrochemical properties of the new complexes and the new ligand  $\text{pydic}(\text{IPh})_2$  were studied by cyclic voltammetry in  $\text{MeCN}/^m\text{Bu}_4\text{NPF}_6$  solution. The complex  $[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$  shows a reversible redox wave around 0 V vs. ferrocene/ferrocenium, which can be assigned to the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple (Figure 9). Additionally, an irreversible oxidation wave at 0.73 V and an irreversible reduction wave at  $-1.33$  V were observed. They both occurred for the uncoordinated ligand at similar potentials (Table 5) and were, thus, assigned to ligand-centered processes. Assuming two electrons for the reversible  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  wave of the binuclear complex, the oxidation wave is markedly larger and more than two electrons might be involved in this process. The redox features of the mononuclear compounds  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2\text{Cl}_3)]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicPh}_2\text{Cl}_3)]$  are very similar, with a reversible  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  wave at around 0.1 V, irreversible oxidations at around 1 V, and reductions at around  $-1.3$  V (Figure S4 in the Supplementary Materials). For the phenyl derivative  $[\text{Cu}(\text{pydicPh}_2\text{Cl}_3)]^-$ , the second reduction wave is partially reversible, while the methyl derivative shows a broad irreversible wave. The bulky phenyl groups seem to stabilize the reduced complex, which is in line with the idea that the reduction is ligand-centered.



**Figure 9.** Cyclic voltammograms of  $[\text{Cu}(\text{pydic}(\text{IPh})_2\text{Cl})_2(\mu\text{-Cl})_2]$  in  $\text{MeCN}/^m\text{Bu}_4\text{NPF}_6$ .

**Table 5.** Selected electrochemical data <sup>a</sup>.

Compounds	$E_{pa}$ ox	$E_{\frac{1}{2}}$ Cu <sup>I</sup> /Cu <sup>II</sup>	$E_{pc}$ red
pydic(IPh) <sub>2</sub>	0.72	-	-1.52
pydicPh <sub>2</sub>	0.91	-	-1.63
pydicMe <sub>2</sub>	0.86	-	-1.60
[{Cu(pydic(IPh) <sub>2</sub> )Cl} <sub>2</sub> (μ-Cl) <sub>2</sub> ]	0.73	0.08	-1.33
(HNEt <sub>3</sub> )[Cu(pydicPh <sub>2</sub> )Cl <sub>3</sub> ]	1.11	0.09	-1.32
(HNEt <sub>3</sub> )[Cu(pydicMe <sub>2</sub> )Cl <sub>3</sub> ]	0.84	0.14	-1.33
K <sub>2</sub> [CuCl <sub>4</sub> ]	1.12	0.08	-1.48

<sup>a</sup> From cyclic voltammetry in MeCN/<sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> solutions. Half-wave potentials  $E_{\frac{1}{2}}$  for reversible waves, cathodic peak potentials  $E_{pc}$  for irreversible reduction, and anodic peak potentials  $E_{pa}$  for irreversible oxidation. All potentials in V vs. FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>.

Spectro-electrochemical (SEC), in situ UV–vis absorption spectra during cathodic or anodic electrolysis measurements of (HNEt<sub>3</sub>)[Cu(pydicPh<sub>2</sub>)Cl<sub>3</sub>] and [{Cu(pydic(IPh)<sub>2</sub>)Cl}<sub>2</sub>(μ-Cl)<sub>2</sub>] confirm the full reversibility of the Cu<sup>II</sup>/Cu<sup>I</sup> waves. However, no conclusive spectra were obtained for the reduced species at around -1.3 or the oxidized complexes at around +1 V (for figures, see Supplementary Materials). Importantly, the reduction wave at -1.3 V for (HNEt<sub>3</sub>)[Cu(pydicPh<sub>2</sub>)Cl<sub>3</sub>], which appears reversible in the relatively fast cyclic voltammetry experiment with a timescale of a few seconds turns out to be completely irreversible in the much slower SEC experiments, which are run on a minute timescale.

### 3. Experimental Section

#### 3.1. Methods and Instrumentation

NMR spectra were recorded on a Bruker Avance II 300 MHz spectrometer (Bruker, Rheinhausen, Germany), using a triple resonance <sup>1</sup>H, <sup>n</sup>BB inverse probe head. The unambiguous assignment of the <sup>1</sup>H and <sup>13</sup>C resonances was obtained from <sup>1</sup>H NOESY, <sup>1</sup>H COSY, gradient selected <sup>1</sup>H, <sup>13</sup>C HSQC, and HMBC experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts were relative to TMS. UV–vis absorption spectra were measured on a Shimadzu UV-3600 photo spectrometer (Shimadzu Europe, Duisburg, Germany). Elemental analyses were carried out using a HEKATECH CHNS EuroEA 3000 Analyzer (Hekatech, Wegberg, Germany). EPR spectra were recorded in the X-band on a Bruker System ELEXSYS 500E equipped with a Bruker Variable Temperature Unit ER 4131VT (500 to 100 K) (Bruker, Rheinhausen, Germany). The *g* values were calibrated using a dp<sup>pp</sup> sample. Electrochemical experiments were carried out in 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> solutions using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl pseudo reference), an Autolab PGSTAT30 potentiostat (Metrohm, Filderstadt, Germany), and a function generator. Experiments were run at a scan rate of 100 mV/s at ambient temperature. The ferrocene/ferrocenium couple (FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>) served as the internal reference. UV–vis spectro-electrochemical measurements were performed with an optical transparent thin-layer electrochemical (OTTLE) cell [55,56].

#### 3.2. Crystal Structure Determination

The measurements were performed at 293(2) K using graphite mono-chromatized Mo Kα radiation (λ = 0.71073 Å) on IPDS II (STOE and Cie., Darmstadt, Germany). The structures were solved by direct methods using SHELX-97 and WinGX (SHELXS-97) [57–59] and refined by full-matrix least-squares techniques against *F*<sup>2</sup> (SHELXL-2017/1) [60,61]. The numerical absorption corrections (X-RED V1.22; Stoe & Cie, 2001) were performed after optimizing the crystal shapes using the X-SHAPE V1.06 (Stoe & Cie, 1999) [62,63]. The non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included by using appropriate riding models. CCDC 1878796 ([Cu(OH<sub>2</sub>)<sub>6</sub>][{Cu(pydic)<sub>2</sub>(μ-Cl)<sub>2</sub>}], 1878795 ((HNEt<sub>3</sub>)[Cu(pydicMe<sub>2</sub>)Cl<sub>3</sub>]), and 1878792 (pydic(IPh)<sub>2</sub>)

contain the full crystallographic data. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ UK. Fax: +44-1223-336-033; Email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

### 3.3. Quantumchemical and Molecular Dynamics Calculations

DFT-calculations on the structures of mononuclear  $[\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}_2]$  vs. binuclear  $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$  were carried out on a def-SV(P)[64]/B3LYP [65–67] level using the TURBOMOLE [68] program package and TmoleX user interface [69].

$(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) structures were optimized using DFT calculations at the B3LYP/6–31+G(d,p) level in different environments (gas phase, various solvents) using the Gaussian 09 program [70]. The Cu atom was treated using LANL2DZ relativistic pseudo potentials. The solvent effect was introduced by applying the polarized continuum model (PCM) embedded in the Gaussian 09 package. In the natural bond, the orbital (NBO) analysis and the donor and acceptor interaction energies can be estimated through the second-order perturbation theory, described using the equation below.

$$E^{(2)} = q_i \frac{F(i, j)^2}{\varepsilon_i - \varepsilon_j}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$  and  $\varepsilon_i$  are diagonal elements, and  $F(i, j)$  is the off-diagonal NBO Fock matrix element.

Molecular dynamics (MD) simulations on  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) were carried out using the GROMACS package [71] and utilizing the GROMOS force field 53A6 [72]. Six-ion pairs solvated in 1200 solvent molecules were simulated for each compound. The equations of motion have been solved by the leapfrog integrator with a time step of 2 fs. After initial energy minimizations and preliminary simulations adjustments in NVT and NPT ensembles, MD simulations were extended for an additional time of 10 ns collecting statistical data under the NPT condition at  $T = 298$  K with periodic boundary conditions in all directions. The temperature was maintained at 298 K using the Berendsen thermostat [73] and the pressure was kept at 1 bar by coupling semi-isotropically to a barostat with a coupling constant of 1 ps. Both the electrostatic and van der Waals interactions used a short-range cutoff of 1.2 nm and the long-range electrostatics were evaluated using the particle mesh Ewald (PME) method [74].

### 3.4. Syntheses

#### 3.4.1. General

Water-free reactions were carried out under inert gas conditions and performed using Schlenk techniques. Solvents were dried using a MBRAUN MB SPS-800 solvent purification system. Pyridine-2,6-dicarbonyl dichloride [51] was synthesized according to a literature procedure.

Data *pyridine-2,6-dicarbonyl dichloride*: Elemental analysis calcd. for  $\text{C}_7\text{H}_3\text{NO}_2\text{Cl}_2$  (204.01): C 41.21, H 1.48, N 6.87; found: C 41.13, H 1.30, N 6.83%.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ):  $\delta = 8.55\text{--}8.41$  (m, 3H, 3,4,5Py).  $^{13}\text{C}$  NMR (75.47 MHz, acetone- $d_6$ ):  $\delta = 170$  (2C, C=O), 150 (2C, 2,6Py), 142 (1C, 4Py), 131 (2C, 3,5Py) ppm.

#### 3.4.2. Synthesis of bis(2-iodophenyl)pyridine-2,6-dicarboxylic ester pydic(IPh) $_2$ and $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$

*Synthesis of pydic(IPh) $_2$* . A total of 1.0 g (5 mmol) pyridine-2,6-dicarbonyl dichloride was dissolved in 20 mL dry diethyl ether. In addition, 2.3 g (10 mmol) of 2-iodo-phenol were dissolved in 30 mL dry diethyl ether. Furthermore, 10 mg 4-dimethylaminopyridine (5% $_{\text{mol}}$ ) and 0.7 mL  $\text{NEt}_3$  were added to the alcohol mixture, which was then cooled using an ice bath. The acid chloride solution was dropped slowly into the alcohol mixture and precipitation of the product started immediately. After stirring for 1 h at 0 °C, 0.7 mL  $\text{NEt}_3$  were added at an ambient temperature and the mixture was stirred for 16 h.

The formed colorless precipitate was filtered off and washed with 5 mL diethyl ether. The remaining powder was dried yielding 2.35 g (82%) of a colorless solid. Elemental analysis calcd. for  $C_{19}H_{11}NO_4I_2$  (571.10): C 39.96, H 1.94, N 2.45; found: C 39.89, H 1.93, N 2.43%.  $^1H$  NMR (300 MHz,  $dmf-d_7$ ):  $\delta$  = 8.64 (d, 2H, 3,4Py), 8.47 (t, 1H, 5Py), 7.94 (d, 2H, 3Ph), 7.51 (t, 2H, 5Ph), 7.47 (d, 2H, 6Ph), 7.11 (t, 2H, 4Ph) ppm.

*Synthesis of  $[Cu(pydic(IPh)_2)Cl]_2(\mu-Cl)_2$ .* 100 mg (0.18 mmol)  $pydic(IPh)_2$  were dissolved in 15 mL MeOH. 24 mg (0.18 mmol) anhydrous  $CuCl_2$  were dissolved in 10 mL MeOH and both solutions were mixed and stirred at an ambient temperature for 16 h. The solvent was evaporated to yield a brown powder. Recrystallization from MeOH gave 85 mg (67%) of brown microcrystalline material. Elemental analysis calcd. for  $C_{19}H_{11}CuCl_2NO_4I_2$  (705.56): C 32.34, H 1.57, N 1.99; found: C 32.33, H 1.62, N 2.02.

### 3.4.3. One Pot Reactions

*Synthesis of  $(HNEt_3)[Cu(pydicMe_2)Cl_3]$ .* 100 mg (0.5 mmol) pyridine-2,6-dicarbonyl dichloride were dissolved in 15 mL dried MeOH while 67 mg (0.5 mmol) anhydrous  $CuCl_2$  were added, which was followed by 1 mL (excess) anhydrous  $NEt_3$ . The reaction mixture was stirred at ambient temperature for 16 h. The resulting green solution was evaporated to dryness and the residue was recrystallized from MeOH solution to yield 175 mg (0.37 mmol, 75%) green-brown crystals.  $C_{15}H_{25}CuCl_3N_2O_4$  (467.27) calcd.: C 38.56, H 5.39, N 6.00; found: C 38.63, H 5.39, N 6.02%.

*Synthesis of  $(HNEt_3)[Cu(pydicPh_2)Cl_3]$ .* A total of 200 mg (1 mmol) pyridine-2,6-dicarbonyl dichloride were mixed with 15 g phenol and 132 mg (1 mmol) anhydrous  $CuCl_2$  followed by the addition of 1 mL  $NEt_3$ . The mixture was warmed up to 50 °C to get a clear homogenous mixture (melting point of phenol = 40.5 °C) and stirred for 96 h. During that time, the excess phenol solidified in the upper part of the flask and the product complex remained as brown oil. The oil was transferred to a new flask and cooled down to 20 °C, upon which the oil solidified as a brownish powder. The crude product was suspended in acetone and carefully filtered. Slow evaporation yielded 350 mg (0.6 mmol, 60%) of a green-yellow microcrystalline powder.  $C_{25}H_{29}CuCl_3N_2O_4$  (591.41) calcd.: C 50.77, H 4.94, N 4.74; found: C 50.72, H 4.98, N 4.76%.

### 3.4.4. Complexes from $pydicCl_2$ Hydrolysis

In a typical reaction, 100 mg (0.5 mmol) pyridine-2,6-dicarbonyl dichloride were dissolved in 15 mL moist MeOH. 85 mg (0.5 mmol)  $CuCl_2 \cdot 2H_2O$  and 1 mL (excess)  $NEt_3$  were added and the whole mixture was stirred at an ambient temperature for 16–24 h. The resulting green solutions were slowly evaporated and individual crystals were collected. Thus, 33 mg (24%) turquoise crystals of  $[Cu(pydic)(OH_2)_2]_n$  were obtained. Elemental analysis calcd. for  $C_7H_7CuNO_6$  (264.68): C 31.76, H 2.67, N 5.29; found: C 31.79, H 2.72, N 5.24%, see also the XRD Section. In the same way, 21 mg (12%) blue-green crystals of  $[Cu(OH_2)_6][Cu(pydic)_2(\mu-Cl)_2]$  were obtained. Elemental analysis calcd. for  $C_{14}H_{18}Cu_3Cl_2N_2O_{14}$  (699.84): C 21.74, H 1.82, N 3.62; found: C 21.80, H 1.79, N 3.58%, see also XRD section.

## 4. Conclusions

New  $Cu^{II}$  complexes of the pyridine-2,6-dicarboxylic ester ligands ( $pydicR_2$ ; with R = Me, Ph and IPh) were synthesized and characterized. The pyridine-2,6-carboxylic esters  $pydicR_2$  with R = Me or Ph form the unprecedented mononuclear  $Cu^{II}$  complexes  $[Cu(pydicR_2)Cl_3]^-$  in one-pot reactions starting from pyridine-2,6-carboxychloride  $pydicCl_2$ , anhydrous  $Cu^{II}$  chloride, and  $NEt_3$  in MeOH or PhOH solution under non-aqueous conditions. The triethyl ammonium salts  $(HNEt_3)[Cu(pydicR_2)Cl_3]$  were isolated. The methyl derivative was crystallized to allow an XRD structure determination. Synthesis attempts in the presence of water yielded the  $Cu^{II}$  complexes  $[Cu(pydic)(OH_2)_2]_n$  and  $[Cu(OH_2)_6][Cu(pydic)_2(\mu-Cl)_2]$  resulting from  $pydicCl_2$  hydrolysis. The new  $pydic(IPh)_2$  (IPh = 2-iodo-phenyl) ester ligand was synthesized and reacted with anhydrous  $CuCl_2$  yielding the

new binuclear complex  $[\{\text{Cu}(\text{pydic}(\text{IPh})_2)\text{Cl}\}_2(\mu\text{-Cl})_2]$ . EPR, UV–vis absorption spectroscopic and electrochemical investigations confirm similarities between copper complexes of pydic ester ligands and corresponding Cu complexes of pyridine-2,6-dialcohols. HOMO–LUMO gap, dipole moments, and electrostatic potential maps for the ion pairs  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  are calculated using DFT methods. These quantities were decreasing along the series  $\text{DMF} > \text{MeCN} > \text{acetone} > \text{CH}_2\text{Cl}_2 > \text{gas phase}$ . The second order delocalization energies obtained from the NBO analysis confirm the occurrence of the intramolecular charge transfer between the  $(\text{HNEt}_3)^+$  and  $[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]^-$  ions. However, increasing the dielectric constant of the solvent environment leads to a reduction of charge transfers between cations and anions. Furthermore, time correlation functions as well as radial and combined distribution functions between cations and anions were calculated by MD simulations. All of these data show a marked difference between the gas phase and a different solvent media ranging from the non-coordinating  $\text{CH}_2\text{Cl}_2$  and the weakly coordinating acetone to the MeCN and DMF, which are both frequently used as ligands in  $\text{Cu}^{\text{II}}$  complexes. We assume that the spectroscopy and electrochemistry in such solutions represent the complexes under study and not dissociated  $\text{Cu}^{\text{II}}$  species.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2304-6740/7/4/53/s1>. (A) Figures S1–S10 showing crystal and molecular structures, CVs, UV–vis absorption spectra and electrostatic potential maps of  $(\text{HNEt}_3)[\text{Cu}(\text{pydicR}_2)\text{Cl}_3]$  in solvents. (B) Tables S1–S8 presenting full crystal structure and refinement data alongside with calculated structure parameters and second-order perturbation energies. (C) Experimental details on structure solution and description of structural details of  $\text{pydic}(\text{IPh})_2$  and  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$ . (D) Cif and Checkcif files of the ligand  $\text{pydic}(\text{IPh})_2$  and the compounds  $[\text{Cu}(\text{OH}_2)_6][\{\text{Cu}(\text{pydic})_2(\mu\text{-Cl})_2\}]$  and  $(\text{HNEt}_3)[\text{Cu}(\text{pydicMe}_2)\text{Cl}_3]$ .

**Author Contributions:** K.B. carried out synthesis, analysis, and spectroscopic and electrochemical analysis of the compounds. K.B. and A.S. collected data and solved and refined XRD datasets. A.S., M.H.D., and A.R.Z. performed the quantum chemical calculations. A.R.Z. coordinated these calculations. A.K. designed the project and wrote the manuscript. All authors have given approval to the final version of the manuscript.

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