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Back-bonding in Organonickel Complexes with Terpyridine Ligands – A Structural Approach

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Abstract. A series of organonickel complexes [(R′terpy)Ni(aryl)]X (R′terpy = derivatives of 2,2′;6′,6″-terpyridine; R′ = 4-H, 4-Cl, 4-Tol and 4,4′,4″-^{t}Bu$_3$; aryl = 2,6-dimethylphenyl = Xyl or 2,4,6-trimethylphenyl = Mes; X = Br or PF_6) have been prepared and characterized. The crystal structures exhibit a number of intermolecular H bond type interactions, but the structure determining force seems to be the packing of the aryl co-ligands. The molecules reveal rather undistorted square planar coordination with a N_3C ligand set, the central Ni–N bond being remarkably short, despite the expected strong *trans* influence of the aryl co-ligands. The long-wavelength absorptions were assigned to charge transfer transitions. No emission is observed at ambient temperature in the solid and in solution and at low temperature in glasses.

Keywords: Terpyridine; Nickel; Crystal structure; Aryl ligands; Absorption spectroscopy

1 Introduction

Organometallic nickel complexes with α-diimine ligands like 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) or diazabutadienes (R-DAB) have gained an enormous interest in the last decade. This is mainly due to their success as effective catalysts in olefin polymerisation or olefin/CO co-polymerisation [1–4], as well as their role in catalytic electrochemically [4, 5] or chemically driven [6] C–C cross-coupling reactions. Associated with this development an increasing interest in the fundamental investigation of structures, spectroscopic and electrochemical properties of such organonickel complexes can be stated [7–13].

The potentially tridentate diimine ligand 2,2′;6′,6″-terpyridine (terpy) combines an orbital pattern with several rather close lying π*-orbitals with a very rigid backbone (when tri-coordinated) and easy chemical variability, mainly of the central pyridine unit [14], which makes terpy a very attractive ligand in coordination chemistry [15]. As a first consequence of the above described properties terpy usually enables corresponding transition metal complexes to exhibit intense and relatively long-wavelength emissions from corresponding $^3\pi$-π^* states [16]. In the field of group 10 organometallic complexes with terpy ligands there are numerous platinum(II) complexes with interesting photophysical properties e.g. long-lived emission [17–19], photocatalysis [20], or photoinduced electron transfer [21]. In contrast to this there are no reports on related photophysical or photochemical properties of corresponding nickel(II) complexes.

The second important property of the terpy ligand, its rigidity, has been frequently used in nickel terpy coordination chemistry e.g. for the build-up of supramolecular assemblies [15a, 22], for crystal engineering [23], and for the preparation of five-coordinated nickel(II) complexes, which are suitable for materials with interesting magnetic properties [22b, 24], to mimic the binuclear nickel/iron sites in [FeNi] or [FeNiSe] hydrogenases [25], or together with MAO as polymerization catalyst in vinyl-type polymerization of norbornene [26].

Very recently *Vicic* et al. have reported the use of methylnickel complexes of terpy in alkyl-alkyl cross-coupling catalysis [6]. Such reactions can be carried out using [(tmeda)Ni(Me)$_2$] and R′terpy ligands as pre-catalysts and the species involved are supposed to be [(R′terpy)Ni(Me)$_2$], [(R′terpy)Ni(Me)] and [(R′terpy)Ni(Me)]$^+$. For the formally reduced complex [(R′terpy)Ni(Me)] the two canonical forms [(R′terpy$^-$)Ni^{II}(Me)] ↔ [(R′terpy)Ni^I(Me)] with either reduced terpy ligand and nickel(II) or neutral terpy and a nickel(I) atom have to be considered. EPR experiments and DFT calculations have proved a markedly higher contribution for the further [6a].

In this paper we want to report on a series of novel organometallic terpy nickel complexes of the type [(R′terpy)-Ni(aryl)]X (R′terpy = terpy, 4′-Cl-terpy (Clterpy), 4′-p-tolyl-terpy (Tolterpy) or 4,4′,4″-^{t}Bu$_3$terpy (Bu$_3$terpy); aryl = 2,6-dimethylphenyl (Xyl) or 2,4,6-trimethylphenyl (Mes); X = Br or PF_6). The use or aryl co-ligand instead of methyl is intended to enhance the stability of such organonickel complexes and thus facilitate thorough investigations of the

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/zaac or from the author molecular and electronic structure. The variation of the terpy ligand will help to shed more light on its role in theses complexes, which seem to have a great potential in organometallic catalysis. We have synthesized and characterized these complexes by NMR and UV/vis absorption spectroscopy and obtained a number of crystal and molecular structures from single crystal XRD experiments, allowing for the first time to probe for these properties in a sizable series of organonickel complexes with terpy ligands.

2 Experimental Part

General Information. Commercially available reagents (solvents and ligands) from Sigma-Aldrich or Acros were used without further purification. Solvents were dried by standard procedures. All reactions involving metal complexes were conducted under argon by standard Schlenk techniques. The complexes *trans*-[$(PPh_3)_2$Ni(aryl)Br] (aryl = Mes or Xyl) were obtained as described for the Mes derivative [10].

Synthesis of the complexes [(R′terpy)Ni(aryl)]Br. In a typical reaction 0.35 mmol of arylnickel precursor *trans*-[$(PPh_3)_2$Ni(aryl)Br] and 0.36 mmol of the R′terpy ligand were mixed in 100 mL of toluene and stirred at ambient temperature for at least 8 h, during which the products slowly precipitate. After completion of the reaction the volume of the solvent was reduced to half and the crude products isolated by filtration. After recrystallization from dichlormethane and heptane (3:1) the complexes were obtained as air-stable orange to red microcrystalline materials. Elemental analysis and selected NMR data is summarized in Table 1.

Synthesis of the complexes [(R′terpy)Ni(aryl)]PF_6. In a typical reaction 0.1 mmol of the complex [(R′terpy)Ni(aryl)]Br and 0.1 mmol KPF_6 were mixed in 20 mL of acetone and stirred for three days, during which KBr slowly precipitates. After careful filtration, the filtrate was evacuated to dryness and the residue recrystallized from dichloromethane and heptane (1:1). The complexes were obtained as microcrystalline materials. Elemental analyses are summarized in Table 1. The NMR data is identical to the bromide derivatives.

Instrumentation. Elemental analysis was obtained using a Henatech CHNS EuroEA 3000 analyzer. NMR spectra were recorded on a Bruker AC 200 or Bruker Avance 400 spectrometer (^{1}H: 400,13 MHz, ^{13}C: 100,61 MHz) using a triple resonance ^{1}H,^{19}F,BB inverse probe head. The unambiguous assignment of the ^{1}H was obtained from ^{1}H NOESY and ^{1}H COSY 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/NIR absorption spectra were recorded on Varian Cary 05E or Cary50 Scan spectrophotometers. Luminescence measurements were performed on solid samples (powders) or solution at ambient temperature on a SPEX Fluorolog photospectrometer. For [(terpy)Ni(Mes)Br emission experiments were carried out on samples in glassy frozen MeCN or PrCN at 77 K using an Oxford Instruments cryostat, a Spectra Physics GCR3 Nd:YAG laser as excitation source and an OMA detection system described elsewhere [27].

Crystal structure analysis. The measurement were performed using graphite-monochromatized Mo-K_α radiation (λ = 7.1073 Å) on IPDS I (at 293 K), IPDS II (173 K) (STOE and Cie.), or Bruker P4 (153 K) diffractometers. The structures were solved by direct methods (SHELXS-97) [28] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97) [29]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms were included by using appropriate riding models. Further details are listed in Table 3 and outlined in the text.

Full structural information has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-646981 for [(terpy)Ni(Mes)]Br, -646982 for [(Clterpy)Ni(Mes)]Br, -646983 for [(Clterpy)NiXyl]Br, -646984 for [(terpy)Ni(Xyl)](PF_6) and -646985 for [(Clterpy)Ni(Xyl)](PF_6). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223 336033 or e-mail: **deposit@ccdc.cam.ac.uk**)

3 Results and Discussion

3.1 Preparation

The complexes [(terpy)Ni(aryl)]Br were prepared from the precursor compounds *trans*-[$(PPh_3)_2$Ni(aryl)]Br and the

Table 1 Analytical data of complexes [(R′terpy)Ni(aryl)]X.

			elemental analyses / %		
			found	(calcd.)	
	yield/ %	formula (M_W / g·mol^{-1})	C	H	N
Terpy / Mes / Br	95	$C_{24}H_{22}N_3Ni_1Br_1$ (491.07)	58.73 (58.70)	4.58 (4.52)	8.59 (8.56)
Terpy / Mes / PF_6	98	$C_{24}H_{22}N_3Ni_1P_1F_6$ (560.17)	52.73 (51.83)	3.94 (3.99)	7.59 (7.56)
Tolterpy / Mes / Br	88	$C_{31}H_{28}N_3Ni_1Br_1$ (581.20)	64.03 (64.06)	4.60 (4.86)	7.36 (7.23)
Tolterpy / Mes / PF_6	97	$C_{31}H_{28}N_3Ni_1P_1F_6$ (646.27)	58.73 (58.70)	4.58 (4.52)	8.59 (8.56)
^{t}Bu$_3$terpy / Mes / Br	86	$C_{36}H_{46}N_3Ni_1Br_1$ (659.40)	65.61 (65.57)	7.08 (7.03)	6.38 (6.37)
^{t}Bu$_3$terpy / Mes / PF_6	94	$C_{36}H_{46}N_3Ni_1P_1F_6$ (724.47)	60.16 (59.68)	6.35 (6.40)	5.79 (5.80)
Clterpy / Mes / Br	88	$C_{24}H_{21}N_3Cl_1Ni_1Br_1$ (525.51)	54.82 (54.85)	3.98 (4.03)	8.03 (8.00)
Clterpy / Mes / PF_6	89	$C_{24}H_{21}N_3Cl_1Ni_1P_1F_6$ (724.47)	49.01 (48.81)	3.62 (3.58)	7.08 (7.12)
Terpy /Xyl / Br	83	$C_{23}H_{20}N_3Ni_1Br_1$ (477.04)	57.88 (57.91)	4.31 (4.23)	8.78 (8.81)
Terpy /Xyl / PF_6	92	$C_{23}H_{20}N_3Ni_1P_1F_6$ (542.11)	51.01 (50.96)	3.80 (3.72)	7.73 (7.75)
Tolterpy / Xyl / Br	91	$C_{30}H_{26}N_3Ni_1Br_1$ (567.17)	63.58 (63.53)	4.71 (4.62)	7.43 (7.41)
Tolterpy / Xyl / PF_6	97	$C_{30}H_{26}N_3Ni_1P_1F_6$ (632.24)	56.89 (56.99)	4.10 (4.15)	6.60 (6.65)
^{t}Bu$_3$terpy / Xyl / Br	83	$C_{35}H_{44}N_3Ni_1Br_1$ (645.37)	65.12 (65.14)	6.94 (6.87)	6.66 (6.51)
^{t}Bu$_3$terpy / Xyl / PF_6	95	$C_{35}H_{44}N_3Ni_1P_1F_6$ (710.44)	59.16 (59.17)	6.35 (6.24)	5.83 (5.91)
Clterpy / Xyl / Br	81	$C_{23}H_{19}N_3Cl_1Ni_1Br_1$ (511.49)	54.02 (54.01)	3.78 (3.74)	8.12 (8.22)
Clterpy / Xyl / PF_6	90	$C_{23}H_{19}N_3Cl_1Ni_1P_1F_6$ (567.56)	47.96 (47.91)	3.38 (3.32)	7.30 (7.29)

Table 2 ^{1}H NMR data of complexes [(R′terpy)Ni(aryl)]X. [a)]

	^{1}H NMR δ/ppm [b)]								
	6,6″	5,5″	4,4″	3,3″	3′,5′	4′	o-CH_3	m-H	p-CH_3
Terpy / Mes	7.48 d	7.61 dd	8.35 dd	8.69 d	8.72 s	8.52 dd	2.96 s	6.72 s	2.29 s
Tolterpy /Mes [c)]	7.48 d	7.64 dd	8.36 dd	8.93 d	9.05 s	–	2.99 s	6.74 s	2.30 s
^{t}Bu$_3$terpy /Mes [d)]	7.34 d	7.57 d	–	8.92 s	8.95 s	–	2.95 s	6.72 s	2.29 s
Clterpy / Mes	7.46 d	7.64 dd	8.34 dd	8.94 d	9.06 s	–	2.93 s	6.70 s	2.27 s
	6,6″	5,5″	4,4″	3,3″	3′,5′;	4′	o-CH_3	m-H	p-H
Terpy / Xyl	7.48 d	7.66 dd	8.40 dd	8.85 d	8.85 s	8.60 dd	3.05 s	6.92 m	6.92 m
Tolterpy /Xyl [e)]	7.47 d	7.63 dd	8.36 dd	8.92 d	9.03 s	–	3.04 s	6.90 m	6.90 m
^{t}Bu$_3$terpy /Xyl [d)]	7.34 d	7.55 dd	–	8.90 d	8.92 s	–	3.01 s	6.88 m	6.88 m
Clterpy / Xyl	7.46 d	7.66 dd	8.37 dd	8.87 d	8.98 s	–	3.00 s	6.87 m	6.87 m

[a)] The nature of X has no impact on the ^{1}H NMR data. [b)] Measured in acetone-d^6. [c)] Further signals at 7.48 (m, 2H, 3,5Tol); 8.20 (d, 2H, 2,6Tol); 2.45 (s, 3H, pTolCH_3) ppm. [d)] Further signal at 1.43 (s, 27H,^{t}Bu) ppm. [e)] Further signals at 7.47 (m, 2H, 3,5Tol); 8.18 (d, 2H, 2,6Tol); 2.45 (s, 3H, pTolCH_3) ppm.

corresponding R′terpy in an alternative way to what has been reported for [(terpy)Ni(Mes)]Br [11]. To enhance the solubility of the cationic complex species [(R′terpy)Ni(aryl)]$^+$ in unpolar solvents the bromide was exchanged by PF_6^- by a typical anion metathesis reaction. Indeed, the solubility of the PF_6-complexes is greatly enhanced in all kind of organic solvents (e.g. up to 100 times in CH_2Cl_2). Analytical data (Table 1) and NMR spectroscopy (Table 2) confirmed the expected constitution of the complexes. The compounds are air-stable and remarkably moisture-stable. It was impossible to determine the melting points of the compounds, since at temperatures above 250-280 °C they decompose.

3.2 Crystal and molecular structures

From five of the complexes single crystals were obtained and submitted to X-ray diffraction experiments. The complexes [(terpy)Ni(Mes)]Br and [(Clterpy)Ni(Xyl)]Br were found to crystallize in the triclinic space group $P\bar{1}$ whereas for [(Clterpy)Ni(Mes)]Br, [(Clterpy)Ni(Mes)](PF_6) and [(Clterpy)Ni(Xyl)](PF_6) the structures were solved and refined in trigonal $R\bar{3}$. Details are listed in Table 3. The overall quality of the two triclinic structures and the structure of [(Clterpy)Ni(Xyl)]Br is rather poor as can be seen from the R values. However, alternative structure solutions have been tried, but failed and the observed residual electron density and holes for the resolved structures are in an acceptable range. Moreover, the molecular structures show a very high degree of conformity (see e.g. Table 4), therefore we are confident that the structure solutions and refinements were carried out correctly and only poor crystal quality has led to the observed deficiencies.

Figure 1 and 2 exhibit the packing of the molecules in two selected samples. The three bromide compounds exhibit a number of intermolecular Br···H interaction (Figure 1), whereas the PF_6 salts show close F···H contacts. Regardless of such X–H interactions, all three trigonal structures exhibit two rosette motifs formed by the aryl co-ligands (Figure 2), whereas the triclinic structures can be characterized by a layer-type packing of the aryl co-ligands.

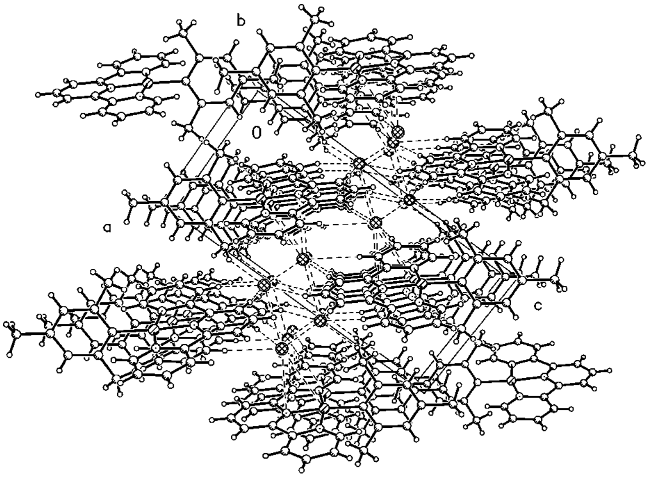


Figure 1 Crystal structure of [(terpy)Ni(Mes)]Br, viewed along the *b* axis.

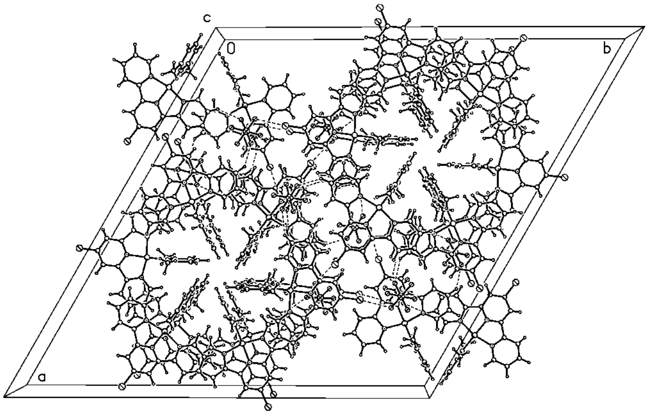


Figure 2 Crystal structure of [(Clterpy)Ni(Xyl)](PF_6), viewed along the *c* axis.

Figure 1 shows the packing of the molecules in the unit cell of [(terpy)Ni(Mes)]Br indicating some of the observed H···Br contacts. For the other complexes similar intermolecular H···Br contacts were found ranging from 2.34 to 3.00 Å. Most of them (values > 2.5 Å) are not significant for effective hydrogen bridges [30], only the short contact of Br···H(4)−C(4) of 2.345(6) in [(terpy)Ni(Mes)Br] lies in the range of significant or strong H bridges. Also the Br···H-C angle of 176(1)° is in line with strong H binding interaction. However, for the isostructural compound [(Clterpy)Ni(Xyl)]Br the analogous contact is far longer (2.926(4) Å) and the aromatic C−H unit is not an ideal H donor function [30]. For the compounds containing PF_6^- anions short contacts were found between F atoms of the anions and H−C(2) units (2.328(3) Å) in [(Clterpy)-Ni(Xyl)](PF_6). In [(terpy)Ni(Xyl)](PF_6) short contacts between F atoms and H−C(2) of 2.552(3) Å, H−C(3) of 2.544(4) Å and H−C(3) units of 2.481(4) Å respectively are observed. Also here the F···H−C angles agree with a strong H bonding interaction (170-180°). In contrast to this, the thermal ellipsoids of the corresponding F atoms do not reveal any sign of orientation towards the H−C unit.

The rosette motif found in the three trigonal structures is formed by two threefold packing of aryl co-ligands in two layers connected by a S_3 axis. In contrast to this, the aryl co-ligands in the triclinic structures are packed in extended layers.

Whether the intermolecular X···H interaction or the co-ligand packing is the dominant force for the formation of the crystal structures cannot be answered unequivocally. In view of the found selectivity $P\bar{1}$ vs. $R\bar{3}$ the packing of the co-ligand being responsible for the crystal structure seems to be more plausible.

Furthermore in none of the structures we observe π-stacking interactions of the planar aromatic terpy ligand. Such stacking has been reported for [($^tBu_3$terpy)Ni(Me)] giving rise to dimers in the crystal structure [6b]. Stacking is also very frequent in square planar terpy complexes of palladium(II) [31], platinum(II) [32], or copper(II) [33], the number of examples with no such interaction is marginal. They contain either a sterically highly demanding co-ligand like e.g. [(terpy)Pt(aryl)]$^{3+}$ (aryl = 2,6-di(N-piperidinium-methyl)phenyl) [34], or the terpy ligand is substituted with bulky groups as e.g. in [(tBu$_3$terpy)Pt(C≡CC$_6$H$_4$C≡CH](OTf) [tBu$_3$-terpy = 4,4′4″-tri-$t$butyl(terpyridine)] [35]. It is therefore very likely that the bulky xylyl or mesityl co-ligands prevent effective π-stacking in our complexes.

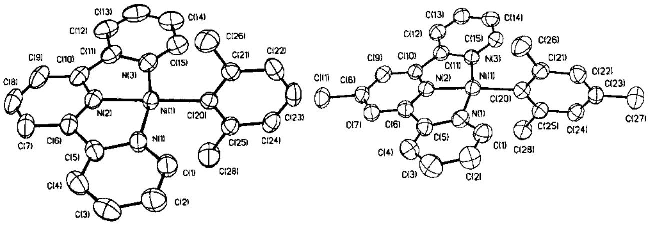


Figure 3 Molecular structures of [(terpy)Ni(Xyl)](PF_6) (left) and [(Clterpy)Ni(Mes)]Br (right) with full numbering. Shown are 30 % thermal ellipsoids, H atoms and Br or PF_6 counter ions are omitted for clarity.

Two examples of the molecular structures are displayed in Figure 3. The coordination around the nickel atom is almost planar. The C(20) atom lies slightly above the plane defined by Ni(1), N(1), N(2) and N(3) with a maximum value of about 0.23 Å found for [(Clterpy)Ni(Mes)]Br (see Figure 3 right). In the same complex also the dihedral angle

Table 3 Crystallographic and structure refinement data of terpy nickel complexes.$^{a)}$

compound	[(terpy)Ni (Mes)]Br	[(Clterpy)Ni (Mes)]Br	[(Clterpy)Ni (Xyl)]Br	[(terpy)Ni (Xyl)](PF_6)	[(Clterpy)Ni (Xyl)](PF_6)
Formula	$C_{24}H_{22}N_3NiBr$	$C_{24}H_{21}ClN_3NiBr$	$C_{23}H_{19}ClN_3NiBr$	$C_{23}H_{20}N_3NiPF_6$	$C_{23}H_{19}ClN_3NiPF_6$
Weight /g·mol^{-1}	491.07	525.51	511.48	542.10	576.54
Crystal system	triclinic	trigonal	triclinic	trigonal	trigonal
Space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$	$R\bar{3}$
Temperature /K	153(2)	293(2)	293(2)	293(2)	173(2)
cell a /Å	8.1620(16)	41.324(6)	7.955(2)	36.991(5)	38.207(5)
b /Å	8.5790(17)	41.324(6)	11.106(3)	36.991(5)	38.207(5)
c /Å	17.136(3)	7.4671(15)	14.907(4)	8.8017(18)	8.5164(17)
α /°	76.81(3)	90	68.16(3)	90	90
β /°	86.28(3)	90	83.46(3)	90	90
γ /°	70.14(3)	120	72.60(3)	120	120
V /Å^3 / Z	1098.7(4) / 2	11043(3) / 18	1166.5(5) / 2	10430(3) Å^3, 18	10766(3) / 18
ρ_{calc} /g cm^{-3}	1.484	1.422	1.456	1.553	1.601
μ /mm^{-1} / $F(000)$	2.716 / 500	2.542 / 4788	2.672 / 516	0.971 / 4968	1.054 / 5256
Limiting indices	$-10 < h < 10$, $-11 < k < 10$, $-22 < l < 22$	$-53 < h < 52$, $-53 < k < 52$, $-8 < l < 9$	$-10 < h < 10$, $-14 < k < 14$, $-19 < l < 19$	$-47 < h < 47$, $-47 < k < 47$, $-10 < l < 11$	$-49 < h < 49$, $-49 < k < 48$, $-10 < l < 10$
Refl. collect. / unique	31507 / 5045	53722 / 5515	14107 / 5261	22171 / 4938	42237 / 5366
R_{int}	0.1195	0.1353	0.2227	0.0718	0.1000
Data / restr. / param.	5045 / 0 / 275	5515 / 0 / 275	5261 / 0 / 274	4938 / 0 / 309	5366 / 0 / 393
Goof. on F^2	1.133	0.882	0.813	0.866	0.911
Final R_1, wR_2 indices [I>2σ(I)]	R1 = 0.0790, wR2 = 0.2171	R1 = 0.0667, wR2 = 0.1739	R1 = 0.1036, wR2 = 0.2170	R1 = 0.0403, wR2 = 0.0940	R1 = 0.0505, wR2 = 0.1274
R_1, wR_2 (all data)	R1 = 0.0993, wR2 = 0.2282	R1 = 0.1488, wR2 = 0.2183	R1 = 0.2839, wR2 = 0.2889	R1 = 0.0862, wR2 = 0.1092	R1 = 0.0808, wR2 = 0.1434
Largest diff. peak and hole /e·Å^{-3}	0.993 and −0.656	0.904 and −0.432	0.975 and −0.737	0.266 and −0.571	0.481 and −0.507

$^{a)}$ Radiation wavelength λ = 0.71073 Å; Refinement method: Full-matrix least-squares on F^2

of the pyridine moieties has its maximum with 10.9(4)°. The values for the whole series range down to 1° but do not correlate with the composition changes along the series. The aryl co-ligands are oriented almost perpendicular to the coordination plane. The corresponding dihedral angles range between 90.40(11) and 99.9(2)°. The ortho-methyl groups effectively shield the nickel atom, the distances (3.10−3.21 Å) lie in the range observed for related complexes [10, 11, 13].

The most striking structural feature is the shortness of the Ni(1)−N(2) bond. The fact that this central Ni−N bond is shorter than the two peripheral ones might be attributed to the relatively rigid ligand geometry allowing only an optimum overlap for the central N(2) atom with the nickel orbitals. E.g. the central Ni−N(2) bond is also shorter compared to the peripheral Ni−N bonds in complexes like [(terpy)Ni(ER)$_2$] (E = Se or S, R = mesityl or xylyl) with a trigonal bipyramidal geometry [25b, 36]. However, the observed values of about 1.86 Å are markedly shorter than those for these non-organometallic derivatives (ca. 1.98 Å), which stands in contrast to the expected strong *trans* influence of the aryl co-ligands. They are also shorter than the Ni−N bonds in the comparable bipyridine complex [(bpy)Ni(Mes)Br] [10a]. In this complex the Ni−N bond *trans* to the mesityl co-ligand was found to be far longer with 1.980(6) or 1.987(6) Å respectively (two independent molecules) and the Ni−N distances *trans* to the weak ligand Br are much the same (1.895(6) or 1.897(6) Å respectively) as the Ni−N(1) and Ni−N(3) distances in the terpy complexes. The Ni−C distances in both systems are also quite similar (1.904(8) or 1.887(8) Å for the bpy complex). Comparison with the recently reported methyl derivative [(^{t}Buterpy)Ni(Me)]I reveals that both Ni−N(2) (1.880(7) Å) and Ni−C bond (1.921(9) Å) are longer in this latter system [6a, b], but still the Ni−N(2) distance is small compared to non-organometallic derivatives (ca. 1.98 Å). Upon reduction of the complex [(^{t}Buterpy)Ni(Me)]$^+$ to [(^{t}Buterpy)Ni(Me)] the distance is reduced from 1.880(7) to 1.845(3) Å, DFT calculation for the terpy derivative [(terpy)Ni(Me)] gave a value of 1.867 Å [6a].

It seems that the strong carbanionic ligand provokes a more effective Ni-terpy back-bonding thus shortening the Ni−N(2) bond. To judge the extend of back-bonding to the terpy ligand, the contraction of the C(5)−C(6) and C(10)−C(11) distances in comparison to the free ligand is a good measure. Going from the analogous methyl complexes [(^{t}Buterpy)Ni(Me)]$^+$ to the reduced species [(^{t}Buterpy)Ni(Me)] the distances decrease from 1.489(11) and 1.465(12) Å to 1.450(4) and 1.455(4) Å, respectively. DFT calculation for the terpy derivative [(terpy)Ni(Me)] gave almost the same values [6a]. The C(5)−C(6) and C(10)−C(11) distances observed for our complexes lie markedly below the values for the free ligand of 1.488(8) and 1.493(8) Å [37] and slightly below the values found for the methyl derivative [(^{t}Buterpy)Ni(Me)]$^+$. This is a strong indication that effective back-bonding takes place in the organometallic complexes, with a slightly higher efficiency for the aryl derivatives. For the chloro substituted derivatives the back-bonding should be enhanced compared to the terpy analogues, due to the electron-withdrawing nature of chlorine, but in our series no such effect was observed.

Interestingly the coordination number of four seems to be restricted to organonickel derivatives, since the numerous so far crystallographically characterized non-organometallic terpy nickel complexes contain two or three co-ligands. The reason for this probably lies in the fact that the terpy

Table 4 Selected structural data of [(terpy)NiMes]Br.

distances/ Å	[(terpy)Ni (Mes)]Br	[(Clterpy)Ni (Mes)]Br	[(Clterpy)Ni (Xyl)]Br	[(terpy)Ni (Xyl)](PF$_6$)	[(Clterpy)Ni (Xyl)](PF$_6$)
Ni(1)−N(1)	1.906(5)	1.908(6)	1.921(10)	1.899(2)	1.919(3)
Ni(1)−N(2)	1.864(5)	1.865(5)	1.845(11)	1.868(2)	1.860(3)
Ni(1)−N(3)	1.907(5)	1.906(5)	1.917(11)	1.917(3)	1.906(3)
Ni(1)−C(20)	1.899(5)	1.916(6)	1.864(14)	1.898(3)	1.890(3)
C(5)−C(6)	1.478(9)	1.471(9)	1.50(2)	1.464(5)	1.473(5)
C(10)−C(11)	1.472(8)	1.451(9)	1.44(2)	1.478(5)	1.475(5)
Ni(1)−C(26)	3.215(6)	3.210(7)	3.125(10)	3.128(2)	3.153(3)
Ni(1)−C(28)	3.102(6)	3.177(7)	3.132(10)	3.154(2)	3.106(3)
C20 above the terpyNi plane	0.129(6)	0.234(7)	0.014(10)	0.006(3)	0.048(3)
angles / °					
N(2)−Ni(1)−C(20)	175.8(2)	175.6(3)	179.0(6)	178.94(11)	177.79(14)
N(2)−Ni(1)−N(1)	82.9(2)	82.5(2)	81.6(5)	82.87(11)	82.76(12)
N(1)−Ni(1)−N(3)	165.3(2)	164.5(2)	164.6(5)	165.72(10)	165.86(12)
N(2)−Ni(1)−N(3)	82.4(2)	82.6(2)	83.1(6)	82.86(11)	83.12(12)
C(20)−Ni(1)−N(1)	97.7(2)	96.7(3)	97.5(5)	98.20(10)	96.13(13)
C(20)−Ni(1)−N(3)	96.8(2)	98.4(3)	97.9(6)	96.08(11)	97.95(13)
dihedral angles / °					
terpyNi / aryl	93.6(2)	99.9(2)	94.7(5)	90.4(1)	93.6(1)
pyN(1) / pyN(3)	1.0(4)	10.9(4)	4.1(7)	2.2(2)	1.7(2)
pyN(1) / pyN(2)	2.4(4)	5.3(5)	4.6(7)	3.5(2)	6.5(2)
pyN(3) / py N(2)	1.8(5)	6.2(5)	5.3(7)	4.4(2)	6.0(2)

ligand represents three coordinating donor atom but usually cannot cover three fourths of the coordination sphere. The bite angle of the two peripheral pyridine N atoms with the nickel atom [N(1)−Ni−N(3)] lies in most cases about 156° or below. We suppose that strong carbanionic aryl or alkyl co-ligands render the ligand field high enough to shift the preference to four-fold square planar coordination. Furthermore the bite angle in the organometallic systems is increased to about 165° which points to a slight enlargement of the nickel atom resulting from the electron donation by the carbanionic co-ligands. For analogous palladium or platinum complexes the (four-fold) square planar coordination sphere for terpy complexes is the normal case due to the intrinsic higher ligand field and the larger size of the atoms [31, 32, 34, 35].

3.3 Absorption and emission spectroscopy

The absorption spectra of [(terpy)Ni(Mes)]Br have been reported recently in the frame of a number of organonickel complexes [(N^N)Ni(Mes)Br] [11]. The long-wavelengths band systems at around 450 nm (maxima at 487 nm in toluene and 452 nm in MeCN respectively; see Figure 4) are attributed to mixed M(Ni)-L(terpy)/L(Mes)-L(terpy) charge transfer transitions (MLCT/L′LCT), on the basis of their similarity to the complexes [(N^N)Ni(Mes)Br], for which the assignment is supported by a combination of spectroscopy (absorption, resonance Raman) and quantum chemical calculations [11]. The more intense structured bands at around 340 nm (maximum at 341 in toluene and 337 nm in MeCN) are assigned to intraligand(terpy) (π-π^*) transitions. The variation of the R′ substituent does not lead to marked shifts of the absorption energy. There is a slight red-shift for the intra-ligand band around 340 nm along the series ^{t}Bu > Cl > H > Tol, however, for the charge transfer band at around 450 nm the sequence is ^{t}Bu > H > Cl > Tol. In the free ligand the a_2 LUMO exhibits only marginal electron density at the 4, 4′ and 4″ positions (Scheme 1) [38]. Calculation for the reduced complex [(terpy)Ni(Me)] by *Vicic* et al. revealed that the SOMO has b_1 character with a small but appreciable contribution from the 4, 4′ and 4″ positions [6a]. This explains well our finding that the ^{t}Bu group exhibits the highest and the Tol group the lowest absorption energies in the series, since the first destabilizes the b_1 LUMO, whereas the latter extends the π-systems thus stabilizing the LUMO. The strong electron-donating power of the co-ligands, destabilizing the HOMO, is manifested in the relatively low-lying charge transfer absorptions. Variation of the co-ligand has almost no impact on the absorption energy, as expected for the very similar groups Mes vs. Xyl. Table 5 lists the observed absorption maxima for the complexes of this study.

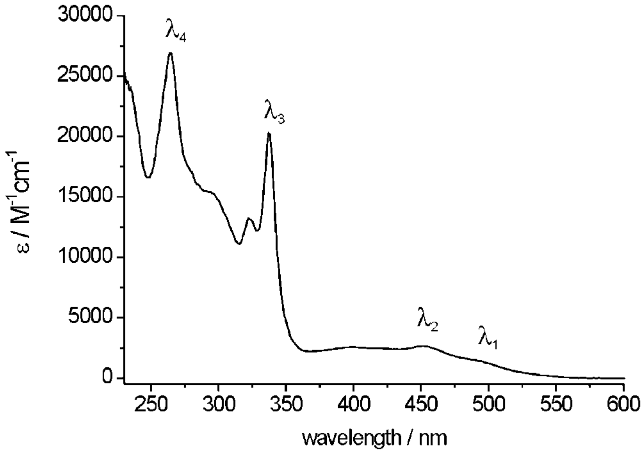
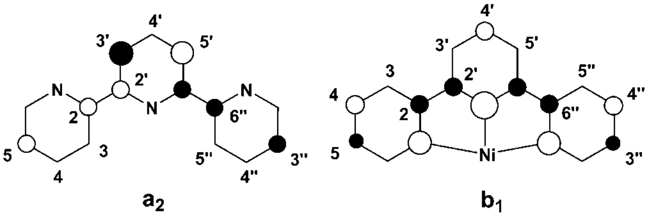


Figure 4 Absorption spectrum of [(terpy)Ni(Mes)]Br in MeCN solution.

Table 5 Absorption spectra of complexes [(R′terpy)Ni(aryl)]Br in MeCN solution. [a)]

Compound	λ_4 (ε)	λ_3 (ε)	λ_2 (ε)	λ_1 (ε)
[(terpy)Ni(Xyl)]Br	264 (22.8)	337 (16.8)	451 (2.1)	491sh (1.1)
[(Clterpy)Ni(Xyl)]Br	262 (28.3)	336 (19.4)	454 (2.8)	487sh (1.5)
[(Tolterpy)Ni(Xyl)]Br	269 (29.0)	339 (22.0)	454 (2.3)	497sh (1.0)
[(^{t}Bu$_3$terpy)Ni(Xyl)]Br	263 (25.1)	334 (20.2)	443 (2.9)	484sh (1.5)
[(terpy)Ni(Mes)]Br	264 (26.9)	337 (20.3)	452 (2.6)	481sh (1.6)
[(Clterpy)Ni(Mes)]Br	262 (28.9)	336 (20.5)	455 (3.0)	487sh (1.5)
[(Tolterpy)Ni(Mes)]Br	268 (21.9)	339 (15.8)	455 (2.5)	497sh (0.9)
[(^{t}Bu$_3$terpy)Ni(Mes)]Br	262 (24.7)	334 (19.7)	444 (2.8)	481sh (1.5)

[a)] Wavelengths λ in nm (extinction coefficients ε in 1000 $M^{-1}cm^{-1}$).



Scheme 1 Schematic representation of the a_2 LUMO in the free ligand terpy [38] and of the b_1 SOMO in [(terpy)Ni(Me)] [6a].

The extinction coefficients ε for the charge transfer bands lie in the range of 2000 to 3000 $M^{-1}cm^{-1}$. They are comparable to those observed for the diimine complexes [(N^N)Ni(Mes)Br] (N^N = α-diimine ligands such as bpy) [11], but are considerably lower than the values obtained for iron(II) complexes; e.g. for $[Fe(terpy)_2]^{2+}$ the charge transfer band at 550 nm (in MeOH) has an ε of about 10000 $M^{-1}cm^{-1}$ [39]. From this side, the assumption of very effective back-bonding strengthening the Ni-terpy bonds is not supported, however, the intensity of absorption bands is ruled by many factors [16]. Quantum chemical calculations might provide a better insight in these systems and are thus sought for in the future.

For the recently investigated complexes [(N^N)Ni(Mes)Br] (N^N = α-diimine ligands such as bpy) no luminescence was observed and we assume rapid radiationless deactivation to be responsible for this [11]. Since the rigidity of the terpy ligands should hamper some of the deactivation pathways (vibrations) we anticipated luminescence for the present complexes, at least at low temperatures. All the compounds were examined in the solid (microcrystalline powders) and in MeCN solution at ambient temperature, additionally the compound [(terpy)Ni(Mes)]Br was measured at in at 110 K in glassy frozen MeCN solution). However, no luminescence was observed.

4 Summary and Outlook

The present series of arylnickel complexes with various R′terpy ligands has allowed for the first time an extended investigation of the molecular structures and their absorption spectroscopy. The most striking feature in the molecular structures is the extremely short central Ni–N(2) distance compared to the distances to the peripheral N(1) and N(3) atoms, but also compared to Ni–N(2) distances found in non-organometallic nickel complexes of terpy. The shortening of the Ni–N(2) bond compared to Ni–N(1) and Ni–N(3) is primarily due to the ligand geometry. The shortening of the Ni–N(2) bond in comparison with non-organometallic derivatives can be explained by an enhanced back-donation from nickel to the terpy π* orbital. Whether arylnickel derivatives are advantageous over methyl derivatives due to additional co-ligand-nickel interactions (potentially π-accepting) can only be assumed from the obtained data. Since the R′ substituent on the terpy has a marked impact on the corresponding π* LUMO and the only so far structurally characterized methyl derivative [(^{t}Buterpy)Ni(Me)]I contains the ^{t}Buterpy ligand, which is missing in our series, an unambiguous conclusion in that respect is not feasible. The results from optical spectroscopy agree qualitatively well with the assumptions derived from the molecular structures. Future investigation will seek to close three gaps. First, the crystal and molecular structures of ^{t}Buterpy derivatives need to be studied, secondly, electrochemical and spectroelectrochemical measurement might provide even better insight into the electronic structure. And finally quantum chemical calculation will probably amend the understanding of the optical spectra of such complexes.

Supporting Information. 25 tables containing full structural information and 7 supplementary figures illustrating the crystal and molecular structures are provided.

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