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ORIGINAL PAPER

Structural Studies of Two Isoelectronic Tetrakis Isocyano Complexes

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Abstract Two isoelectronic tetrakis isocyano compounds, tetra(*p*-isocyanoanisole)nickel(0) and tetra(*p*-isocyanoanisole)copper(I) hexafluorophosphate were synthesized from nickel bis cyclooctadiene and copper (I) tetra acetonitrile hexafluorophosphate and the isonitrile, respectively, and their structures were determined. The nickel complex crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.6709(8)$, $b = 15.2324(13)$, $c = 19.0955(16)$ Å and $Z = 4$. The copper salt forms crystals with a tetragonal setting in P4/n with $a = b = 15.8206(5)$, $c = 6.5848(4)$ Å and $Z = 2$. Both complexes exhibit the approximate tetrahedral coordination environment expected for 18 valence electron complexes with soft σ-donor π-acceptor ligands. Packing in the nickel complex is dominated by weak π–π stacking, C–H···π_{phenyl}, and C–H···π interactions towards the isonitrile carbon and nitrogen atoms, and several slightly stronger C–H···O interactions. In the copper complex the presence of the PF_6 anion allows for the formation of stronger C–H···F interactions, and these in combination with π–π stacking and C–H···O hydrogen bonds dominate the packing.

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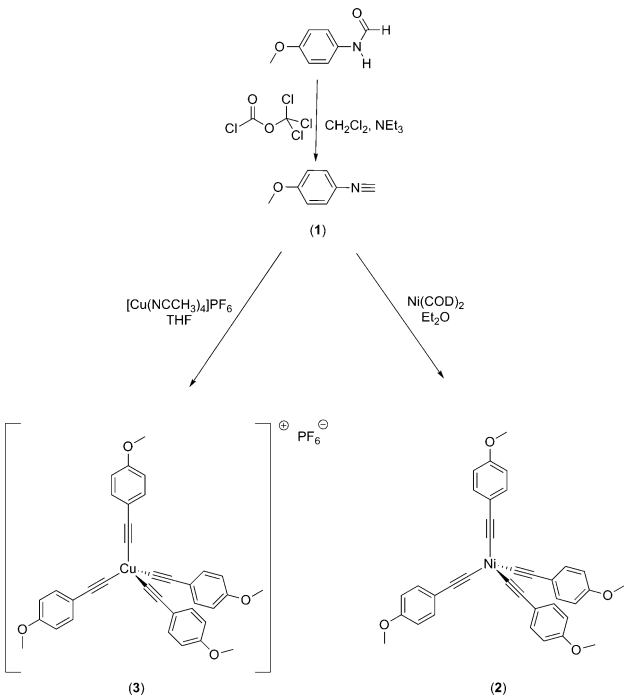
Introduction

Transition metal carbonyl complexes are among the most investigated classes of organometallic complexes and are the textbook examples of σ-donor π-acceptor ligands. They are convenient starting materials in the preparation of a huge number of low valent transition metal compounds, and many of their derivatives are used as homgeneous catalysts in both laboratory as well as industrial settings. The first metal carbonyl complex ever reported, and one of the most famous to this date, is nickel tetracarbonyl, $Ni(CO)_4$. Being a tetrahedral charge neutral complex it is *the* example of an 18 valence electron low valent metal complex with soft σ-donating π-accepting ligands. Because it is a highly volatile and toxic liquid, the verification of its solid state structure by X-ray diffraction was a challenge. High quality data [1, 2] were obtained only about 10 years ago, thus over a century after its original discovery by Ludwig Mond in 1890 [3].

Tetrakis nickel(0) complexes have been investigated for their chemical and electrochemical properties. One of the most intriguing properties of these complexes is their tetrahedral star shape, and with properly chosen coordinating ligands they are expected to have degrees of conjugation down their arms and across their central vertices. Our interest in such highly symmetric tetrahedral low valent compounds prompted us to investigate Ni(0) isonitrile and their isoelectronic Cu(I) complexes as model compounds for more complicated systems, e.g., multifunctional ligands such as 1,4-bisisocyano benzene. In the current contribution



Scheme 1 Synthesis of compounds **1**, **2** and **3**

we would like to present the synthesis and structure of two isoelectronic homoleptic isonitrile complexes, tetrakis (*p*-isocyanoanisole)nickel(0) and tetrakis(*p*-isocyanoanisole)copper(I) hexafluorophosphate (Scheme 1).

Experimental

Synthesis

All reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were freshly dried before use by distillation from calcium hydride (CH_2Cl_2) or sodium benzophenone (THF, Et_2O).

p-Isocyanoanisole (**1**)

The isocyanide was prepared using a method based on a published procedure by Hanack et al. [4] Para-formamidoanisole [5] (10.0 g, 66.15 mmol), CH_2Cl_2 (200 ml), and triethylamine (45.85 ml, 33.29 g, 0.329 mol) are combined in a nitrogen purged 250 ml three-necked round bottom flask equipped with a nitrogen adapter, reflux condenser, dropping funnel, and magnetic stirring bar. Trichloromethyl chloroformate ("diphosgene") (3.9 ml, 6.54 g, 33.0 mmol) is placed into a dropping funnel containing CH_2Cl_2 (46 ml). The diphosgene solution is added dropwise over a 15 min period and then the solution is heated to reflux of the solvent for an additional 2 h. The solution is allowed to cool to ambient temperature and washed under nitrogen with a 10% solution of Na_2CO_3 (3 × 100 ml) and with H_2O (1 × 100 ml). The organic layer is dried over anhydrous $MgSO_4$. The $MgSO_4$ is filtered off, washed with CH_2Cl_2 (3 × 20 ml), and all volatile materials are removed in vacuo from the combined filtrates (e.g., high vacuum manifold at room temperature). Crystallization of the resulting light brown solid from pentane at 4 °C gave white–yellow needles. The crystals are dissolved in a 2:1 hexane/CH_2Cl_2 mixture (*ca* 40 ml). The solution is filtered through a neutral alumina column (0.5 m) using a 2:1 hexane/CH_2Cl_2 mixture (*ca.* 150 ml) and all volatile materials are removed from the filtrate in vacuo. The solid was again crystallized from pentane at 4 °C to give a 21% yield (1.84 g, 13.8 mmol) of the product as white–yellow needles exhibiting a pronounced isonitrile smell. The crystals start to melt at room temperature and have to be stored under nitrogen at −20 °C to avoid rapid decomposition. No spectroscopic properties were recorded due to the sensitivity of the compound. The identity of the compound was verified by its conversion into the Ni(0) and Cu(1+) tetraisocyanide complexes, see below.

Tetra(*p*-isocyanoanisole)nickel(0) (**2**)

Diethylether (25.0 ml) is added to bis(1,5-cyclooctadiene)nickel(0) (0.580 g, 2.12 mmol, Strem 98+%). The bis(1,5-cyclooctadiene)nickel(0) does not completely dissolve. *p*-Methoxy isocyanobenzene (**1**) (1.41 g, 10.6 mmol) is dissolved in diethylether (40 ml), is added dropwise to the mixture at 0 °C, and the solution is stirred for 2 h at ambient temperature to form a yellow precipitate. The solid is filtered off under nitrogen, and rinsed with hexanes (3 × 10 ml). All the volatile materials are removed in vacuo to obtain an 87% crude yield (0.53 g, 0.896 mmol) of the bright yellow solid. Recrystallization from THF at −20 °C yielded yellow crystals suitable for single-crystal diffraction.

Spectroscopic Properties

^{13}C $\{^1H\}$ NMR (100.565 MHz, $CDCl_3$): 165.373 (d, $^1J(^{13}C, ^{14}N) = 4.73$ Hz, CN), 157.770 (s, Ph-C), 126.653 (s, Ph-C), 123.371 (s, Ph-C), 114.146 (s, Ph-C), 55.473 (s, CH_3-C). ^1H NMR (399.905 MHZ, $CDCl_3$): 6.982 (d, $^3J(^1H,^1H) = 8.40$ Hz, 8H, Ph-H), 6.337 (d, $^3J(^1H,^1H) = 8.40$ Hz, 8H, Ph-H), 3.034 (s, 12H, CH_3). IR (toluene, CaF_2): 2,017 cm^{-1} (s, *v* isonitrile).

Tetra(*p*-isocyanoanisole)copper(I) hexafluorophosphate (**3**)

Tetrahydrofuran (25.0 ml) is added to tetrakis(acetonitrile) copper(I) hexafluorophosphate (0.41 g, 1.1 mmol, Strem 98+%). Para-methoxy isocyanobenzene (**1**) (0.62 g,

Table 1 Crystal data and structure refinement of **2** and **3**

	2	**3**
Empirical formula	$C_{32}H_{28}N_4NiO_4$	$C_{32}H_{28}CuF_6N_4O_4P$
Moiety formula	$Ni(C_8H_7NO)_4$	$[Cu(C_8H_7NO)_4]^+[PF_6]^-$
Formula weight	591.29	741.09
Solvent	Diethylether	Tetrahydrofuran/diethylether
Cryst. habit, color	Block, yellow	Block, colourless
Temperature	100(2) K	100(2) K
Crystal system	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$	P4/n
Unit cell dimensions	$a = 9.6709(8)$ Å	$a = b = 15.8206(5)$ Å
	$b = 15.2324(13)$ Å	$c = 6.5848(4)$ Å
	$c = 19.0955(16)$ Å	
Volume	2813.0(4) Å^3	1648.12(12) Å^3
Z	4	2
Density (calculated)	1.396 g cm^{-3}	1.493 g cm^{-3}
Absorption coefficient	0.734 mm^{-1}	0.788 mm^{-1}
$F(000)$	1,232	756
Crystal size	0.4 × 0.4 × 0.2 mm	0.30 × 0.30 × 0.21 mm
θ range for data collection, completeness	1.71–28.28°, 100%	1.82–30.58°, 100%
Index ranges	$-12 \le h \le 12$,	$-22 \le h \le 22$,
	$-20 \le k \le 20$,	$-22 \le k \le 22$,
	$-24 \le l \le 25$	$-9 \le l \le 9$
Reflections collected	28,954	18,867
Independent reflections	6,979 [R(int) = 0.0474]	2,528 [R(int) = 0.0238]
Reflections with $I > 2\ \sigma(I)$	6,048	2,387
Absorption correction	Semiempirical from multi scans	Semiempirical from multi scans
Max. and min. transmission	0.860, 0.740	0.850, 0.633
Data/restraints/parameters	6,979/0/374	2,528/0/119
Goodness-of-fit on F^2	1.050	1.120
Final R indices [$I > 2\sigma\ (I)$]	$R1 = 0.0382$, $wR2 = 0.0787$	$R1 = 0.0392$, $wR2 = 0.0976$
R indices (all data)	$R1 = 0.0488$, $wR2 = 0.0823$	$R1 = 0.0409$, $wR2 = 0.0987$
Absolute Structure Parameter	0.054(10), 3,067 Friedel pairs	–
Largest diff. peak and hole	0.733 and −0.236 e × Å^{-3}	0.565 and −0.214 e × Å^{-3}

4.6 mmol) is dissolved in tetrahydrofuran (40 mL), is added dropwise to the mixture at 0 °C, and the solution is stirred for 5 h at ambient temperature. Reduction in volume and careful addition of diethyl ether induced crystallization. The sample was first cooled to 4 °C, then to −20 °C to yield colourless to slight beige crystals in 86% (0.705 g, 0.95 mmol) yield suitable for single-crystal diffraction.

Spectroscopic Properties

^{13}C {^1H} NMR (100.618 MHz, $CDCl_3$): 160.67 (s, Ph-C), 145.91 (s, broad, CN), 128.60 (s, Ph-C), 177.51 (s, Ph-C), 115.19 (s, Ph-C), 55.79 (s, CH_3-C). ^1H NMR (400.150 MHZ, $CDCl_3$): 7.758 (d, $^3J(^1H,^1H) = 9.03$ Hz, 8H, Ph-H), 7.104 (d, $^3J(^1H,^1H) = 9.03$ Hz, 8H, Ph-H), 3.833 (s, 12H, CH_3). ^{31}P NMR (161.98 MHZ, $CDCl_3$): 144.2 (septet, $^1J(^{19}F,^{31}P) = 711.1$ Hz, 1P).

Diffraction data were collected using a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo K_α radiation with the omega scan technique. The unit cells were determined using SMART and SAINT+ and the data were corrected for absorption using SADABS [6–8]. The structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL [6–8]. Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions with C–H distances of 0.95 and 0.98 Å for aromatic and methyl H atoms respectively. H atoms were refined with $U_{iso}(H) = 1.2\ Ueq(C_{arom})$ or 1.5 $U_{eq}(C_{methyl})$ of the adjacent carbon atom. Methyl hydrogen

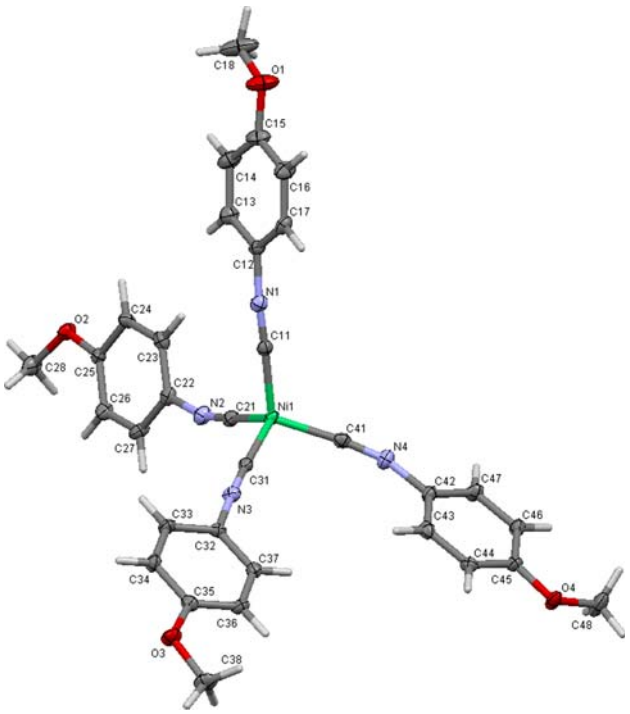


Fig. 1 ORTEP style representation of **2**, ellipsoids at 50% probability. Hydrogen labels are omitted for clarity

atoms were allowed to rotate around the C–C bond at a fixed angle to best fit the experimental electron density. Crystal data and experimental details are listed in Table 1.

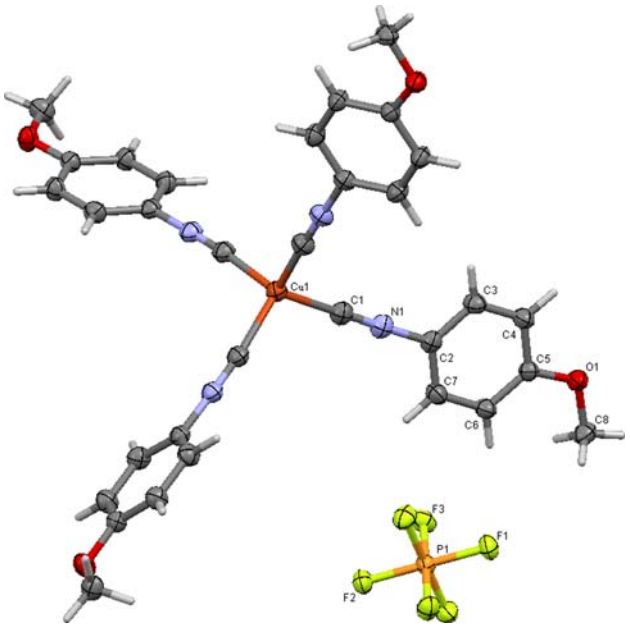


Fig. 2 ORTEP style representation of **3**, ellipsoids at 50% probability. Hydrogen labels and labels of symmetry dependent atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°)

For **2**			
Ni1-C41	1.840(2)	C11-Ni1-C21	103.26(10)
Ni1-C31	1.846(2)	C31-Ni1-C11	109.66(9)
Ni1-C11	1.847(2)	C31-Ni1-C21	112.24(10)
Ni1-C21	1.852(2)	C41-Ni1-C11	114.37(10)
C11-N1	1.169(3)	C41-Ni1-C21	114.25(10)
C21-N2	1.173(3)	C41-Ni1-C31	103.28(10)
C31-N3	1.171(3)	N1-C11-Ni1	177.7(2)
C41-N4	1.181(3)	N2-C21-Ni1	174.3(2)
N1-C12	1.392(3)	N3-C31-Ni1	176.41(19)
N2-C22	1.395(3)	N4-C41-Ni1	173.6(2)
N3-C32	1.392(3)	C11-N1-C12	170.0(2)
N4-C42	1.398(3)	C21-N2-C22	163.4(2)
		C31-N3-C32	176.9(2)
		C41-N4-C42	160.0(2)
For **3**			
P1-F2	1.6043(19)	F2-P1-F1	180.000(1)
P1-F1	1.6046(19)	F2-P1-F3	90.04(4)
P1-F3	1.6051(9)	F1-P1-F3	89.96(4)
Cu1-C1	1.9521(15)	F3-P1-F3	179.92(8)
N1-C1	1.152(2)	F3-P1-F3^{i}	90.003(1)
N1-C2	1.3988(18)	F3-P1-F3^{i}	90.0
C1^{iii}-Cu1-C1	106.70(9)	F2-P1-F3^{ii}	90.04(4)
C1^{iv}-Cu1-C1	110.88(5)	F3-P1-F3^{ii}	90.000(1)
C1-Cu1-C1^{v}	110.87(5)		
C1-N1-C2	178.87(16)		
N1-C1-Cu1	175.48(13)		

Symmetry codes: (i) $-y + 3/2, x, z$; (ii) $y, -x + 3/2, z$; (iii) $-x + 3/2, -y + 1/2, z$; (iv) $y + 1/2, -x + 1, -z$; (v) $-y + 1, x - 1/2, -z$

Table 3 Intermolecular interactions for **2** ([Å] and angles (°))

Donor-H···acceptor	D-H	H···A	D···A	D-H···A
C17-H17···O2^{i}	0.95	2.55	3.480(3)	166
C33-H33···O4^{ii}	0.95	2.53	3.471(3)	170
C48-H48A···C11^{iii}	0.98	2.89	3.797(4)	154
C48-H48A···N1^{iii}	0.98	2.71	3.601(3)	152
C27-H27···C18^{iv}	0.95	2.87	3.790(4)	163
C24-H24···C11^{v}	0.95	2.86	3.806(3)	173
C28-H28B···C44^{vi}	0.98	2.86	3.810(3)	164
C13-H13···C31^{v}	0.95	2.82	3.523(3)	132
C44-H44···C31^{iv}	0.95	2.86	3.805(3)	171
C37-H37···C11^{iv}	0.95	2.76	3.556(3)	142
C16-H16···Cg3^{vii}	0.95	2.77	3.451(3)	129
C34-H34···Cg2^{viii}	0.95	2.74	3.674(2)	167

Symmetry codes: (i) $-x, 1/2 + y, 3/2 - z$; (ii) $-x, -1/2 + y, 3/2 - z$; (iii) $-1 - x, -1/2 + y, 3/2 - z$; (iv) $-x, -1/2 + y, 3/2 - z$; (v) $-x, 1/2 + y, 3/2 - z$; (vi) $1/2 + x, 3/2 - y, 2 - z$, (vii) $-1/2 + x, 3/2 - y, 1 - z$; (viii) $1 - x, -1/2 + y, 3/2 - z$

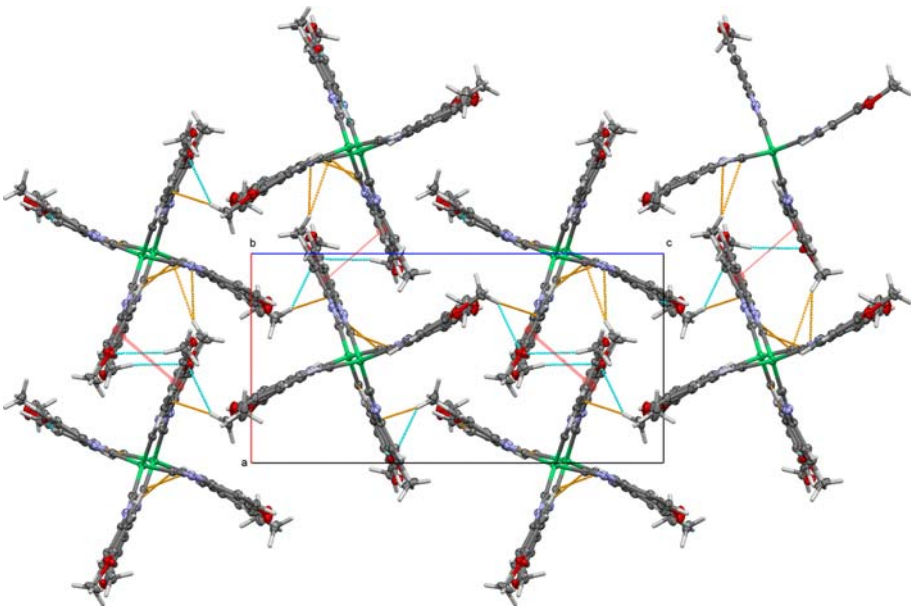


Fig. 3 Packing view of **2**, view down the b-axis. Ellipsoids are at 50% probability. *Orange dashed lines* symbolize C–H···π interactions towards isonitrile groups and phenyl π systems. *Blue dashed lines* are C–H···O hydrogen bonds, and *red dashed lines* represent π···π interactions between phenyl rings (*red spheres* are centroids of aromatic rings C32–C37 and C42–C47; centroid to centroid distance is 3.4955(9) Å, symmetry operator for C42–C47: (ix) 1 + x, y, z). (color figure online)

Table 4 Intermolecular interactions for **3** ([Å] and angles [deg])

Donor-H···acceptor	D-H	H···A	D···A	D-H···A
C4-H4···O1^{v}	0.95	2.54	3.4455(18)	160
C6-H6···F3	0.95	2.47	3.1686(17)	131
C3-H3···C1^{vi}	0.95	2.85	3.756(2)	160

Symmetry codes: (v) 1 − x, 1 − y, 2 − z, (vi) 1 − y, −1/2 + x, 1 − z

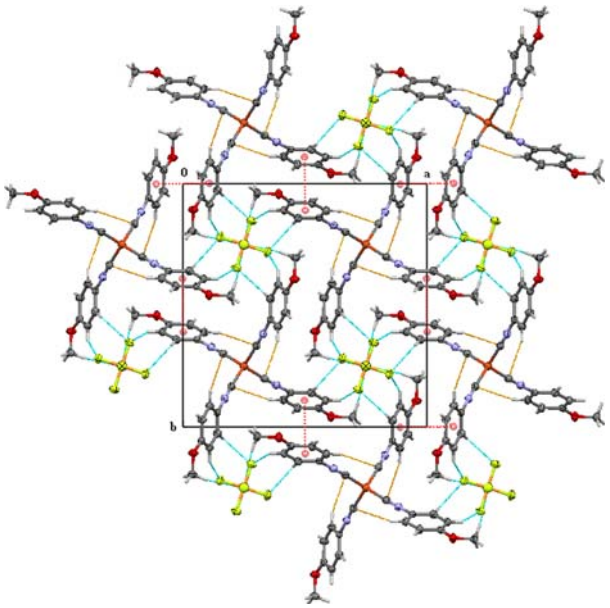


Fig. 4 Packing view of **3**, view down the c-axis. Ellipsoids are at 50% probability. Color coding similar to Fig. 3: *Orange dashed lines*: C–H···π interactions; *blue dashed lines* are C–H···O/F hydrogen bonds, and *red dashed lines* represent π···π interactions between phenyl rings (red spheres are centroids of aromatic rings C2–C7; centroid to centroid distance is 3.5910(9) Å, symmetry operator for the second phenyl ring: (vii) 1 − x, 1 − y, 1 − z). (Color figure online)

Results and Discussion

Ni(0) complexes were often prepared using nickel tetracarbonyl as the starting material. Its high toxicity has a, however, led to its substitution by other Ni(0) complexes with weakly coordinated ligands. In recent years bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) has established itself as a common starting material for Ni(0) compounds and a variety of complexes were synthesized this way such as NiL_4, NiL_2, and $NiL_2(UN)$ (e.g., L = phosphine, arsine, stibine, nitrogen base, or isocyanide, and UN = olefin, acetylene, or azide). [9] $Ni(COD)_2$ has been found to be an exceptionally good starting material for homoleptic isocyanide nickel(0) complexes. [10, 11] Treatment of bis(1,5-cyclooctadiene)nickel(0) with para-methoxy isocyanobenzene (**1**) gave the homoleptic isocyano complex (**2**) in excellent yield. The equivalent reaction of tetrakis(acetonitrile) copper(I) hexafluorophosphate provided the isoelectronic copper hexafluorophosphate complex (**3**). Both complexes were characterized by multinuclear NMR and IR spectroscopy, and single crystals suitable for X-ray crystallographic analysis were obtained from THF-diethyl ether mixtures.

Ortep style plots of the two compounds are given in Figs. 1 and 2, the most important crystallographic data are summarized in Tables 1, 2, and 3. The compounds are both

approximately tetrahedral as expected for 18 valence electron low valent metal complexes, but the shape of the *p*-anisole isocyanide ligand—it is neither linear nor does it have threefold rotational symmetry—does not allow for the formation of exactly tetrahedral complexes in a crystallographic or symmetry sense. Tetra(*p*-isocyanoanisole) nickel(0) (**2**) crystallized in a chiral orthorhombic setting in $P2_12_12_1$ with one crystallographically independent molecule located on a general position. The molecule is approximately tetrahedral, but the C–Ni–C angles do differ somewhat from the ideal value of 109.5°. The smallest value found is 103.26(10)°, with the largest at 114.37(10)°. The Ni–C≡N–C units are slightly bent, especially at the nitrogen atoms: the Ni–C≡N angles are with 173.6(2)–177.7(2)° relatively close to the ideal 180°, the C≡N–C angles are on average 167.6°, and the smallest angle has a value of only 160.0(2)° (Table 2). This is, however, still within the usual range found for the three previously reported structures of Ni(0) isonitrile complexes. [11] The Ni–C distances in (**2**) range from 1.840(2) to 1.852(2) Å, which is slightly larger but comparable to those found for other Ni tetraisonitrile complexes (1.828–1.841 Å for the three previously reported structures of Ni(0) complexes [11], 1.831–1.839 Å for the single structurally described square planar Ni(II) tetraisonitrile salt) [12].

Tetra(*p*-isocyanoanisole)copper(I) hexafluorophosphate (**3**), while also not perfectly tetrahedral, has higher crystallographic symmetry. It crystallizes in the tetragonal setting P4/n with the PF_6 anion located on the fourfold axis at ¼, ¼, z with four of the six fluoride anions being crystallographically related by this axis. The cationic copper complex is located on the fourfold inversion axis with the Cu(I) center at ¾, ¼, 0, thus leading to the presence of only one crystallographically independent isonitrile ligand. The angles at the metal center for **3** are closer to the ideal 109.5° than in **2** with values between 106.70(9)° and 110.87(5)° (Table 3). The same is observed for the Ni–C≡N and C≡N–C angles, which are much closer to the ideal 180° than in nickel complex **2** (178.87(16) and 175.48(13)°, respectively). The Cu–C distance is 1.9521(15) Å which agrees very well with values reported for other homoleptic Cu(I) isocyanide complexes which cluster around 1.96 Å [13–18].

C≡N and N–C bond lengths vary not significantly for the four *p*-isocyanoanisole ligands in **2** and that in **3** and are in the expected ranges (Tables 2, 3). C≡N distances in **2** range between 1.169(3) and 1.181(3) Å, in **3** the value is 1.152(2) Å. N–C bond lengths are 1.392(3)–1.398(3) Å and 1.3988(18) Å in **2** and **3**. These values are in the same range as observed for all other structurally described homoleptic Ni(0) and Cu(I) tetraisocyano complexes.

Intermolecular interactions in **2** and **3** are somewhat similar, but still distinctively different. Packing in **2** is dominated by rather weak interactions such as π–π stacking interactions between phenyl rings, C–H···π interactions towards aromatic π-systems, C–H···π interactions towards isonitrile carbon and nitrogen atoms, and several slightly stronger C–H···O interactions (Table 3; Fig. 3). In **3** the presence of the hexafluoro phosphate anion allows for the formation of stronger C–H···F interactions in addition to the interactions also found in **2**.. There is still one C–H···C interaction towards the carbon atoms of the isonitrile functional group, but this rather weak interaction is probably simply a result of the directional forces of the much stronger C–H···F interactions, and it is these in combination with C–H···O hydrogen bonds and strong π–π stacking interactions that dominate the packing of the copper complex salt **3** (Table 4; Fig. 4).

Supplementary Material

CCDC-736014 & 736015 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

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