Karlheinz Sünkel*, Dietmar Reimann and Patrick Nimax

Synthesis, molecular, and crystal structures of 3d transition metal cyanocyclopentadienides $[M(MeOH)_n(H_2O)_{4-n}\{C_5(CN)_4X\}_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn; X = H, CN, NH_2, NO_2)

https://doi.org/10.1515/znb-2018-0175
Received August 18, 2018; accepted October 31, 2018

Abstract: The reaction of the 3d transition metal dichlorides MCl_2 (M = Mn, Fe, Co, Ni, Cu, Zn) with the silver salts of substituted tetracyanocyclopentadienides Ag^+ $[C_5(CN)_4X]^-$ (X = CN, H, NH_2 NO_2) gives the complexes $[M(MeOH/H_2O)_4\{C_5(CN)_4)X\}_2]$. Nine of these complexes were characterized by X-ray diffraction and it shows that they all are mononuclear with an octahedral $M(N)_2(O)_4$ coordination sphere. In the structures, extensive hydrogen bonding leads to dense three-dimensional network structures.

Keywords: 3d metals; crystal structures; cyanocyclopentadienides.

Dedicated to: Professor Wolfgang Bensch on the occasion of his 65th birthday.

1 Introduction

The coordination chemistry of polynitrile anions with transition metals is studied for quite a while, mainly due to their ability to build coordination polymers with interesting magnetic properties [1–3]. The "small" polynitrile anions like tricyanomethanide $[C(CN)_3]^-$ or dicyanamide $[N(CN)_2]^-$ tend to form three-dimensional networks with MN_6 coordination polyhedra, even when crystallized from water [1], although in some special cases ribbon structures of the formula type "$M(CA)_2(L)_2$" (CA = cyano anion, L = EtOH [4], NH_3 [5]) with MN_4O_2 or $MN_4N'_2$ coordination, could also be obtained. Increasing the size of the polynitrile anions, as in tetracyanidoborate $[B(CN)_4]^-$ or 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide $[C\{C(CN)_2\}_3]^{2-}$ or hexacyanotrimethylenecyclopropanediide $[C_3\{C(CN)_2\}_3]^{2-}$, leads predominantly to ribbon structures (L = H_2O [6–9]), which still allow for electronic communication between the metal centers via the polynitrile bridges. In some cases, however, monomeric complexes of the formula type "$M(CA)_2L_4$" are found [10–14], which still can form network structures through hydrogen bonds. The tetra- and pentacyanocyclopentadienides $[C_5(CN)_4X]^-$ (X = H, CN, NH_2, …) also belong to the "bigger" polynitrile anions. There are some early reports on the synthesis of their (transition) metal salts, e.g. with Mn^{2+}, Fe^{2+}, Al^{3+}, and Bi^{3+}, included in a patent; however, no characterization data were given [15]. One of these salts, termed "decacyanoferrocene" and analyzed as "$[Fe\{C_5(CN)_5\}_2] \cdot H_2O$" was described in two publications and characterized by infrared (IR), conductivity, and magnetic measurements [16, 17]. A polymeric structure with the anion acting as a triply bridging ligand was suggested, but no crystal structure determination was performed. Many years later, two cobalt complexes and one copper (I) complex with the pentacyanocyclopentadienide anion were described, the monomeric $[Co\{C_5(CN)_5\}_2(H_2O)_2(THF)_2]$ and the polymeric $[Co\{C_5(CN)_5\}Cl(THF)_2]_\infty$ and $[Cu\{C_5(CN)_5\}(MeCN)_2]_\infty$, which were all characterized by X-ray diffraction [18]. Soon afterwards, we could show that recrystallization of the pentacyanocyclopentadienides of Co(II), Ni(II), and Zn(II) from dimethylformamide (DMF) yielded the monomeric salts $[M(DMF)_6][C_5(CN)_5]_2$, which contained no coordinated nitrile anions [19]. In this paper we report the preparation of the substituted tetra- and pentacyanocyclopentadienides $[M\{C_5(CN)_4X\}_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn; X = H, CN, NH_2, NO_2) and the crystallographic characterization of the products of recrystallization from methanol.

2 Results and discussion

2.1 Synthesis

When (m)ethanolic solutions of the metal dichlorides MCl_2 (M = Mn, Fe, Co, Ni, Cu, Zn) were treated at room temperature with two equivalents of the silver tetra- and pentacyanocyclopentadienides $Ag[C_5(CN)_4X]$ (X = CN, **1a**; H, **1b**: NH_2, **1c**; NO_2, **1d**), the corresponding bis-tetracyanocyclopentadienides $[M\{C_5(CN)_4X\}_2]$ could be isolated

---

***Corresponding author: Karlheinz Sünkel,** Department of Chemistry, Ludwig-Maximilians University of Munich, Butenandtstraße 9 81377, Munich, Germany, e-mail: suenk@cup.uni-muenchen.de
Dietmar Reimann and Patrick Nimax: Department of Chemistry, Ludwig-Maximilians University of Munich, Butenandtstraße 9 81377, Munich, Germany

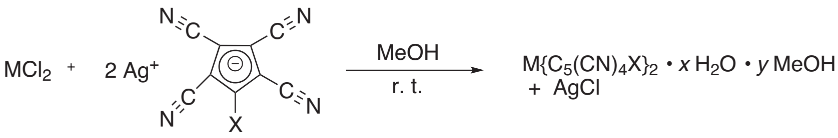


Fig. 1: Preparation of the transition metal bis(tetracyanocyclopentadienides).

after filtering off the precipitated AgCl and evaporation of the filtrates to dryness in vacuo. The IR and mass spectra were obtained for most compounds. Elemental analyses showed that these primary products contained varying amounts of water and methanol (or ethanol, respectively, in case of **2b′** and **3b′**). (Fig. 1, Table 1)

As can be seen from Table 1, in most cases $x+y=4$ which suggests the metal atoms are octahedrally coordinated with a MN_2O_4 chromophor. When the sum is greater than 4, either there might be more solvent molecules enclosed as guest molecules, or the solvents have replaced the cyano ligand from the coordination sphere, or both. In the cases where the sum is smaller than 4, either an oligomeric/polymeric structure, or a complex with a different coordination number might be formed. The IR spectra of the pentacyanocyclopentadienides **2a′**, **4a′**, **5a′** and **6a′** showed two bands in the ν(CN) region, one at ca. 2260–2270 cm^{-1}, which might be assigned to a coordinated nitrile group, and another one at ca. 2220 cm^{-1}, which would correspond to an uncoordinated nitrile group [17]. In the IR spectra of the tetracyanocyclopentadienides **3c′** and **6b′** only a single band at ca. 2220 cm^{-1} could be observed in this region, which might be indicative of the absence of nitrile coordination. However, this might be misleading, as was shown in the case of the polymeric $\{Cu[C_5(CN)_5](MeCN)_2\}$, which contains coordinated and uncoordinated nitrile groups, but shows only one ν(CN) band at ca. 2220 cm^{-1} [18]. As, neither the IR nor the mass spectrometric data allowed for a clear distinction of the different possibilities, attempts to obtain X-ray quality crystals were undertaken by slow recrystallization of the compounds from MeOH or MeCN. Fortunately we were successful in the cases of all $[C_5(CN)_4H]^-$ salts, except for nickel, as well as for the pentacyanocyclopentadienides of Mn(II) and Fe(II), the amino derivative **2c** and the nitro derivative **4d**.

Table 1: The prepared penta- and tetracyanocyclopentadienides and their approximate (±0.25) analytical composition.

Compound	M	X	*x*	*y*
2a′	Mn	CN	4	1
2b′	Mn	H	2	2[a]
2c′	Mn	NH_2	4	0.5
3a′	Fe	CN	2	3.5
3b′	Fe	H	2	1.5[a]
3c′	Fe	NH_2	4	0
4a′	Co	CN	5	0
4b′	Co	H	0	2
4c′	Co	NH_2	2.5	1.5
4d′	Co	NO_2	2	3
5a′	Ni	CN	1.2	1.8
5b′	Ni	H	1	3
5c′	Ni	$NH_{2\#}$	2	2
6a′	Cu	CN	4	0
6b′	Cu	H	0.5	2
7a′	Zn	CN	5	2
7b′	Zn	H	1.25	2.25
7c′	Zn	NH_2	4	0.5

[a] EtOH instead of MeOH.

2.2 Molecular and crystal structures

2.2.1 The pentacyanocyclopentadienides of Mn(II) and Fe(II)

The two complexes, **2a** and **3a**, crystallize in the monoclinic space groups $P2_1/c$ and $P2_1/n$, respectively, as mononuclear $[M(PCC)_2(H_2O)_4]$ moieties with the metals being located on an inversion center ($Z=2$). The iron compound contains two additional interstitial water molecules in the crystal structure. Figure 2 shows an ORTEP view of the molecular unit of **2a**.

As a consequence of the inversion center, the nitrile ligands are in mutual *trans* positions. Both the

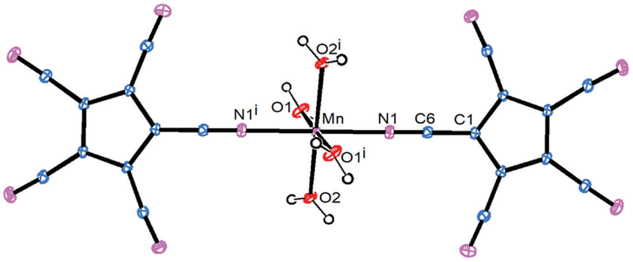


Fig. 2: ORTEP view of compound **2a** in the crystal with displacement ellipsoids at the 30% probability level.

metal-nitrogen and the metal-oxygen bond lengths are substantially shorter in the Fe(II) compound. While the M–N–C angle of **2a** deviates only slightly from linearity (ca. 12°), there is a substantial "kink" in **3a**. The ring carbon –CN bond is linear in both compounds (see Table 2). PLATON analysis shows no space that could be accessible by residual solvent in both structures. As the primary products **1a′** and **3a′** both showed methanol content, it is surprising that after recrystallization from methanol this solvent appears to be no longer present in the crystal structure. A possible explanation might be that the methanol carbon is disordered over the eight hydrogen positions of the "water" molecules, which makes its position indistinguishable from a "full" hydrogen position.

In **2a** all coordinated water molecules act as hydrogen bond donors towards nitrile nitrogen atoms of neighboring molecules, with N4 acting as acceptor of two hydrogen bonds and N5 accepting no hydrogen bond. The donor-acceptor distances vary between 2.80 and 3.00 Å with the O–H…N angles close to linearity (see Table 3). In the iron compound **3a** all water molecules act as hydrogen bond donors, but the coordinating water molecules act also as acceptors. Each coordinated water molecule forms one hydrogen bond towards the nitrile nitrogen atoms N4 and N5 and one hydrogen bond to the guest water oxygen atom O3, which itself forms two hydrogen bonds toward the remaining nitrogen N atoms N2 and N3. The O…O distances are in the range 2.76 ± 0.03 Å, while the O…N distances range from 2.86 to 2.93 Å. The O–H…N angles deviate more from linearity than in the manganese compound (see Table 3 and Fig. 3).

2.2.2 The tetracyanocyclopentadienides $[M\{C_5(CN)_4H\}_2]$ of Mn, Fe, Co, Cu and Zn

The Mn(II), Fe(II), and Zn(II) complexes **2b**, **3b.** and **7b** crystallize in the monoclinic space groups $P2_1/c$ or $P2_1/n$(all with $Z=2$) as tetra(aqua)-bis(nitrile) complexes $[M(TCC)_2(H_2O)_4]$ ("TCC" stands for the $[C_5(CN)_4H]$ anion), with the iron compound containing two more uncoordinating water molecules. As implied by the space group and $Z=2$, in all three compounds the metal atom resides on an inversion center, and it coordinates to one of the nitrile groups next to the CH group of the anion. Figure 4

Table 2: Selected bond lengths (Å) and bond and dihedral angles (deg).

Compound	M–N	M–O	M–N–C	N–C–C_{ring}	∠(Cp^1/Cp^2)
2a	2.2447(12)	2.1487(10)/2.1527(11)	167.96(12)	179.29(15)	0.0
2b	2.1929(15)	2.2158(14)/2.1790(15)	168.69(15)	176.36(18)	0.0
2c	2.186(4), 2.195(4)	2.176(4), 2.148(3), 2.177(4), 2.260(3)	168.9(6), 168.8(4)	177.9(4), 178.0(4)	1.2(3)
3a	2.1774(12)	2.0991(11), 2.0620(11)	152.45(12)	175.79(16)	0.0
3b	2.160(2)	2.098(2), 2.127(2)	162.8(2)	179.3(3)	0.0
4d	2.118(2), 2.118(2)	2.068(2), 2.073(2), 2.062(2), 2.047(2)	171.7(2), 167.9(2)	177.7(3), 175.8(3)	88.22(9)
4b	2.097(3), 2.110(3)	2.098(2), 2.087(2), 2.100(2)	173.1(3), 168.9(3)	175.6(4), 176.7(4)	3.40(8)
	2.088(3), 2.090(3)	2.062(2), 2.086(2), 2.078(2), 2.070(3)	169.3(3), 170.4(3)	178.0(4), 178.2(4)	3.50(5)
36b	2.3751(15)	1.9509(13), 1.9925(13)	163.38(14)	178.63(18)	0.0
7b	2.098(3)	2.100(3), 2.133(2)	169.7(3)	176.5(3)	0.0

Table 3: Hydrogen bond parameters (Å, deg) of **2a** and **3a.**

Compound	D–H	H…A	D…A	<(DHA)	D–H…A	Symm. op. (A)
2a	0.87(3)	1.95(3)	2.7996(17)	166(3)	O1–H12…N2	$-x+2, -y+1, -z+1$
	0.88(2)	1.99(2)	2.8384(17)	163(2)	O2–H22…N3	$x-1, -y+3/2, z+1/2$
	0.83(3)	2.18(3)	2.9949(17)	165(2)	O1–H11…N4	$x, -y+3/2, z+1/2$
	0.80(3)	2.14(3)	2.9419(17)	177(3)	O2–H21…N4	$-x+1, y-1/2, -z+3/2$
3a	0.76(2)	2.20(2)	2.9359(18)	166(2)	O3–H31…N2	$x, y+1, z$
	0.85(2)	1.90(2)	2.7353(16)	168(2)	O2–H21…O3	$x+, 1, y, z$
	0.80(2)	1.99(2)	2.7898(17)	175(2)	O1–H11…O3	$x+1, y-1, z$
	0.79(2)	2.15(2)	2.9309(18)	173(2)	O1–H12…N5	$x, y-1, z$
	0.74(2)	2.16(2)	2.8766(18)	164(2)	O2–H22…N4	$-x+3/2, y-1/2, -z+1/2$
	0.83(3)	2.12(3)	2.862(2)	149(2)	O3–H32…N3	$-x+1/2, y+1/2, -z+1/2$

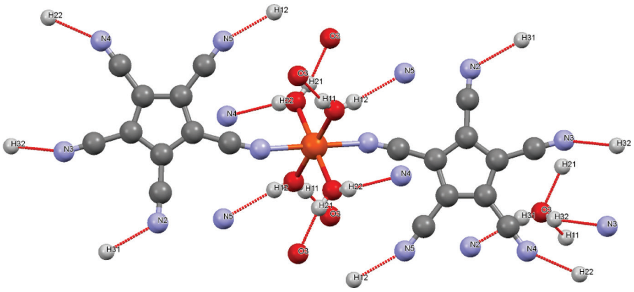


Fig. 3: The hydrogen bond system in the crystal structure of **3a.**

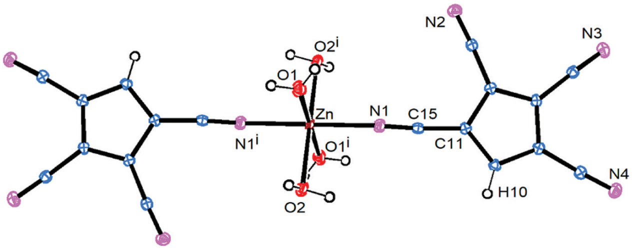


Fig. 4: Ortep view of compound **7b** in the crystal with displacement ellipsoids at the 30% probability level.

shows an Ortep view of the molecular unit of the zinc complex **7b**.

The metal-nitrogen bond lengths decrease from Mn to Zn, while the metal-oxygen bond lengths for Fe and Zn are approximately the same and both shorter than the Mn–O bond lengths. The M–N–C bond angles in **2b** and **7b** show only minor deviations from linearity, while similar to **3a** the iron compound **3b** is significantly "kinked" (see Table 2). In **2b** and in **7b,** both coordinated water molecules act as hydrogen bond donors, O1 towards the nitrile atoms N2 and N3 and O2 to the nitrile atom N4, and the water oxygen O1 of a neighboring molecule. In the iron compound **3b** both the uncoordinated and guest water molecules each donates one hydrogen bond towards one nitrile nitrogen atom and one towards a water oxygen atom. Thus, the guest water molecule accepts two hydrogen bonds and the coordinated water molecules each accept one hydrogen bond. The O…N distances vary from 2.82 to 2.90 Å in **2b** and **7b** and from 2.78 to 2.89 Å in **3b**, while the O…O distances are rather long in **2b** and **7b** (2.97 and 3.02 Å, respectively). In **3b** these distances involving the guest water molecule acting as acceptor are rather short (2.74 Å), whereas for cases where it is acting as donor they are long (3.09 and 3.21 Å). The O–H…N and O–H…O angles range from 142° to 176° (Table 4). In all cases, a three-dimensional network is built. Figure 5 shows a view of the molecular packing in **2b**.

The copper complex **6b** differs from the complexes described above by the fact that it contains two coordinated MeOH and two coordinated water molecules together with two unidentate TCC ligands. It still crystallizes in the monoclinic space group $P2_1/c$ with the Cu atom residing on an inversion center ($Z=2$). Complex **6b** shows substantial Jahn-Teller distortion with the Cu–N bonds being approximately 0.40 Å longer than the Cu–O bonds, a situation different from the compounds described so far, where the two bond lengths were within ± 0.10 Å. The Cu–N–C bond is slightly "kinked" (Table 2). Each coordinated water molecule donates two hydrogen bonds to the nitrile nitrogen atoms N103 and N104, while the methanol donates one hydrogen bond to the remaining uncoordinated nitrile N 102. The O…N distances are within 2.81 ± 0.01 Å with OHN angles at 162 ± 2° (Table 4, Fig. 6).

The cobalt complex **4b′**, which apparently contained no water and only two MeOH molecules, was recrystallized from (moist) acetonitrile. The resulting structure of **4b** contains two different complexes (together with two interstitial water molecules) in the noncentrosymmetric-monoclinic space group $P2_1$. One of them is the "usual" $[Co(TCC)_2(H_2O)_4]$ complex, and the other one has the formula $[Co(TCC)_2(H_2O)_3(MeCN)]$ (Fig. 7). This rather unexpected result hints at a polymeric structure of the primary product, most likely of the "ribbon" type mentioned in the introduction, which was then broken up into monomeric units by the water present in the solvent.

In the Co1-centered molecule, the Co–N bond lengths are slightly longer than in the Co2-centered molecule; the same is true for the Co–O bond lengths. All Co–N–C angles deviate only slightly from linearity, and the deviation is even less for the ring carbon-CN bonds. The cyclopentadienyl ring planes are only slightly twisted against each other (Table 2). All water molecules and all nitrile nitrogen atoms except of N112 are involved in a complicated hydrogen bond system (Fig. 8).

Some water molecules donate two (O21 and O23) or even three (O12) hydrogen bonds to nitrile N atoms, others (O11, O13, O22, O24, and O1) donate one hydrogen bond to another water molecule and a nitrile N atom, and one guest water molecule (O2) two hydrogen bonds to nitrile nitrogen atoms and one to a coordinated water molecule. Five water oxygen atoms accept one (O1, O11, O13, O23), or two (O2) hydrogen bonds, and there are three nitrile N atoms which accept two hydrogen bonds (N104, N114, and N204). The O…O distances range from 2.62 to 2.93 Å, while the O…N distances span the range from 2.81 to 3.18 Å, with the O–H…N and O–H…O angles ranging from 117° to 175° (Table 4).

Table 4: Hydrogen bond parameters (Å, deg) of **2b–7b.**

Compound	D–H	H...A	D...A	<(DHA)	D–H...A	Symm. op. (A)
2b	0.91(3)	2.07(3)	2.967(2)	172(3)	O2–H21...O1	−x+1, −y+1, −z+1
	0.97(4)	1.89(4)	2.823(2)	159(4)	O1–H11...N4	x, −y+1/2, z–1/2
	0.78(4)	2.08(4)	2.833(2)	160(3)	O1–H12...N3	x+1, y+1/2, −z+1/2
	0.77(4)	2.15(4)	2.902(2)	167(3)	O2–H22...N2	−x+1, −y+1, −z+1
3b	0.84(5)	2.08(5)	2.888(3)	159(4)	O1–H11...N3	−x+1/2, y−1/2, −z+1/2
	0.85(4)	1.89(4)	2.737(3)	173(4)	O1–H12...O3	
	0.90(5)	1.99(5)	2.843(3)	159(4)	O2–H21...N2	−x, −y+1, −z
	0.78(4)	1.96(4)	2.736(3)	170(4)	O2–H22...O3	x–1, y, z–1
	0.84(4)	1.94(4)	2.783(3)	174(4)	O3–H31...N4	x+1/2, −y+3/2, z+1/2
	0.76(5)	2.55(5)	3.205(3)	145(4)	O3–H32...O1	x+1, −y+1, −z+1
	0.76(5)	2.45(5)	3.088(4)	143(4)	O3–H32...O2	−x+1, −y+1, −z+1
4b	0.83(3)	1.99(3)	2.811(4)	170(5)	O1–H1A...O2	
	0.86(3)	2.29(3)	3.063(5)	149(4)	O2–H2A...N112	
	0.86(3)	2.58(5)	3.062(4)	117(4)	O2–H2A...O23	x, y, z+1
	0.91(3)	2.11(3)	2.972(4)	159(4)	O11–H11A...N203	−x+1, y+1/2, −z−1
	0.82(3)	1.82(3)	2.621(4)	163(5)	O11–H11B...O1	x, y, z−1
	0.93(3)	2.09(3)	2.946(4)	151(4)	O12–H12E...N104	−x+1, y+1/2, −z
	0.86(3)	1.79(3)	2.649(4)	174(5)	O13–H13A...O2	
	0.87(3)	1.98(3)	2.828(4)	165(5)	O21–H21A...N204	−x+2, y+1/2, −z−1
	0.93(3)	1.95(3)	2.880(4)	176(5)	O13–H13B...N113	x+1, y−1/2, −z+1
	0.83(3)	2.11(3)	2.930(3)	170(5)	O22–H22A...O11	x+1, y, z
	0.91(3)	1.95(3)	2.853(4)	171(5)	O22–H22B...N213	x+2, y−1/2, −z
	0.96(5)	2.03(5)	2.891(4)	149(4)	O23–H23B...N104	−x+1, y+1/2, −z
	0.85(5)	2.01(5)	2.854(4)	173(5)	O24–H24A...N103	−x+1, y+1/2, −z−1
	0.85(3)	2.09(3)	2.890(3)	155(4)	O24–H24B...O13	x, y, z−1
	0.90(3)	1.93(3)	2.818(4)	169(4)	O21–H21B...N214	−x+2, y−1/2, −z−1
	0.94(3)	2.00(3)	2.895(4)	159(4)	O2–H2B...N204	−x+1, y+1/2, −z
	0.96(5)	2.58(5)	3.184(4)	121(3)	O12–H12D...N114	−x+1, y−1/2, −z
	0.96(5)	2.25(5)	3.113(4)	149(4)	O12–H12D...N202	x, y, z+1
	0.92(3)	2.23(4)	3.007(5)	142(4)	O1–H1B...N102	x, y, z+1
	0.90(3)	1.93(3)	2.832(4)	175(4)	O23–H23A...N114	−x+1, y−1/2, −z
6b	0.76(3)	2.10(3)	2.818(2)	160(3)	O1W–H1W...N104	−x+1, y−1/2, −z+3/2
	0.78(3)	2.04(3)	2.799(2)	164(3)	O1W–H2W...N103	X–1, −y+1/2, z+1/2
	0.72(3)	2.10(3)	2.793(2)	161(3)	O1M–H1M...N102	x–1, y, z
7b	0.86(4)	2.04(4)	2.837(4)	154(4)	O2–H22...N3	x–1, −y+1/2, z+1/2
	0.81(5)	2.07(5)	2.829(4)	158(4)	O2–H21...N4	x+1, y+1/2, −z+3/2
	0.78(5)	2.25(5)	3.022(4)	170(5)	O1–H11...O2	x+1, y, z
	0.82(5)	2.09(5)	2.895(4)	167(5)	O1–H12...N2	x+2, −y+1, −z+1

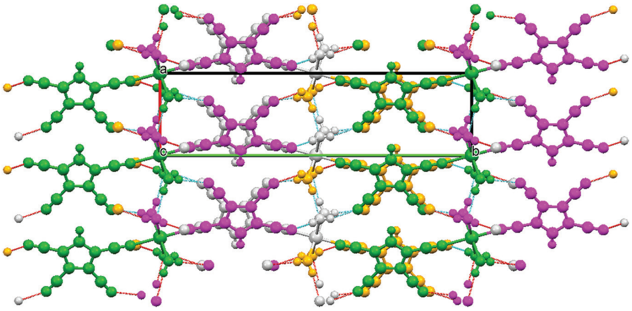


Fig. 5: Packing diagram of **2b** in the crystal.

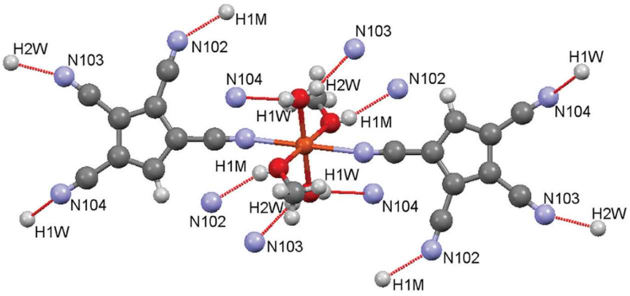


Fig. 6: The hydrogen bond system in the crystal structure of **6b.**

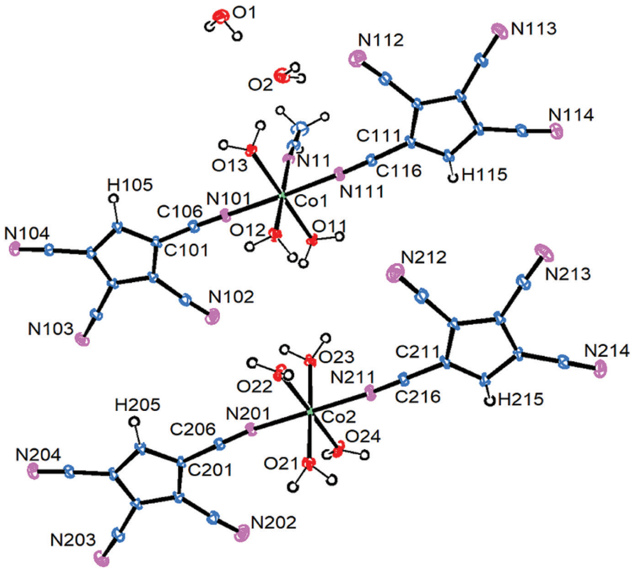


Fig. 7: The two different cobalt complexes in the crystal structure of **4b** (displacement ellipsoids at the 30% probability level).

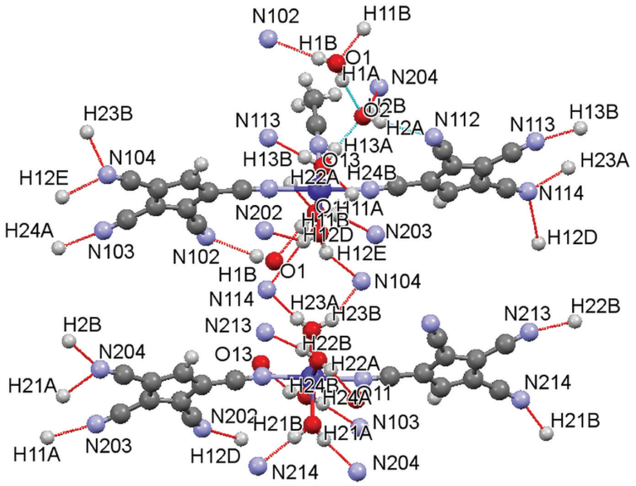


Fig. 8: The hydrogen bond system in the crystal structure of **4b**.

2.2.3 The aminotetracyanocyclopentadienyl complex 2c

The compound 2c crystallizes as a twin in the monoclinic space group $P2_1/n$ with $Z=2$ as a monomeric octahedral complex of formula $[Mn\{C_5(CN)_4NH_2\}_2(H_2O)_4]$. Quite unexpected, the anion coordinates via the nitrile group next to the amino substituent, with no interaction of the amino group with the metal atom (Fig. 9).

The manganese atom resides on a general position and the asymmetric unit consists of the complete molecule. The metal atoms thus reside on noncrystallographic inversion centers. The Mn–N bond lengths are identical within 2*σ*, and this is also true for the O1/O3 water molecules. Surprisingly, the Mn–O2 bond is significantly shorter (by 0.11 Å, corresponding to 36σ) than the Mn–O4 bond. The Mn–N–C bonds deviate only slightly from linearity, as was observed in nearly all other structures described here, and both cyclopentadienyl rings are close to coplanar (Table 2). All water molecules act as hydrogen bond donors: atom O1 donates one hydrogen bond each to another water molecule (O4) of a neighboring complex and to a nitrile nitrogen atom (N2); all the other water molecules donate two hydrogen bonds to nitrile N atoms. The amino nitrogen atoms donate one (N5) or two (N15) hydrogen bonds to nitrile N atoms. All nitrile N atoms act as acceptors, with some of them (N2, N12, and N13) accepting even two hydrogen bonds. Only one oxygen atom (O4) acts as an acceptor, which might be the reason for the longer Mn–O4 bond length (Table 5). All these hydrogen bonds lead to a complicated three-dimensional network, which is shown in Figs. 10 and 11.

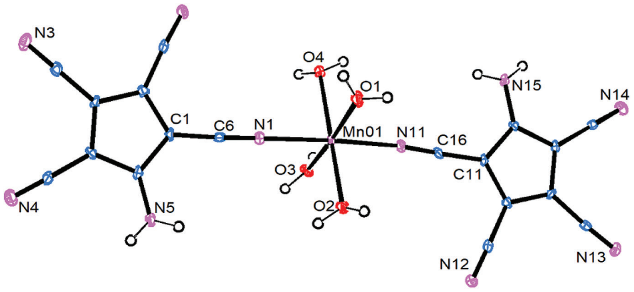


Fig. 9: View of the molecular unit of **2c** in the crystal (displacement ellipsoids at the 30% probability level).

Besides extensive hydrogen bonding, the cyclopentadienyl rings show also π stacking along *a* with a stacking distance of 3.79 Å, which corresponds to a rather weak interaction.

2.2.4 The nitrotetracyanocyclopentadienyl complex 4d

4d is the only compound in this study that crystallizes with methanol only as an auxiliary ligand $[Co\{C_5(CN)_4NO_2\}_2(MeOH)_4]$ (triclinic, space group $P\bar{1}$). There is no coordination of the nitro groups, which are positionally disordered (approximately 3:1) with cyano groups, one with that in the *α*'-position relative to the Co-coordinated nitrile function, and the other with that in the *ß*-position. **4d** is also the only compound where the cyclopentadienyl planes are nearly perpendicular to each other (Table 2, Fig. 12).

Both Co–N–C bonds deviate only slightly from linearity, and so do the ring-carbon-CN bonds. If one looks at the hydrogen bonds (Table 5), all methanol O atoms donate one hydrogen bond each to four nitrile N atoms (N13, N14,

Table 5: Hydrogen bond parameters (Å, deg) of **2c** and **4d**.

Compound	D–H	H...A	D...A	<(DHA)	D–H...A	Symm. op. (A)
2c	0.82(3)	2.49(3)	3.206(5)	146(4)	N15–H11...N12	$x+1/2, -y+3/2, z-1/2$
	0.82(3)	2.64(3)	3.425(5)	159(4)	N15–H12...N13	$x+1/2, -y+3/2, z-1/2$
	0.84(3)	2.12(3)	2.947(5)	173(7)	O1–H101...O4	$-x+1, -y+1, -z+1$
	0.84(3)	2.05(3)	2.857(5)	161(7)	O1–H102...N2	$-x+1, -y+1, -z+1$
	0.84(3)	2.14(3)	2.956(5)	164(7)	O2–H111...N4	$-x+1/2, y+1/2, -z+3/2$
	0.84(3)	2.07(3)	2.885(5)	166(7)	O2–H112...N3	$x-1/2, -y+1/2, z+1/2$
	0.84(3)	2.23(3)	3.051(5)	163(6)	O3–H121...N4	$-x+3/2, y+1/2, -z+3/2$
	0.84(3)	2.07(3)	2.886(5)	163(7)	O3–H122...N12	$-x+1, -y+1, -z+2$
	0.85(3)	2.01(3)	2.828(5)	162(6)	O4–H131...N14	$-x+3/2, y-1/2, -z+3/2$
	0.84(3)	2.04(3)	2.868(5)	168(7)	O4–H132...N13	$x+1/2, -y+3/2, z-1/2$
	0.83(3)	2.28(3)	3.038(6)	153(4)	N5–H1...N2	$x-1/2, -y+1/2, z+1/2$
4d	0.88(4)	1.94(4)	2.786(3)	163(4)	O1M–H1M...N23	$-x+1, -y, -z$
	0.72(3)	2.11(4)	2.806(3)	165(4)	O2M–H2M...N14	$-x+2, -y+2, -z+1$
	0.70(4)	2.15(4)	2.833(3)	166(4)	O3M–H3M...N22	$-x+1, -y+1, -z$
	0.76(4)	2.02(4)	2.788(3)	177(4)	O4M–H4M...N13	$-x+1, -y+2, -z+1$

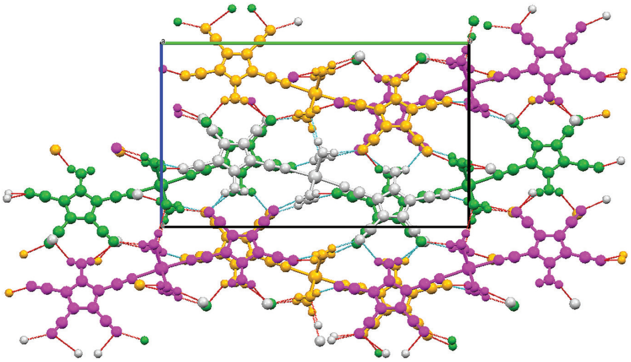


Fig. 10: Packing diagram of **2c**, looking down the *a* axis.

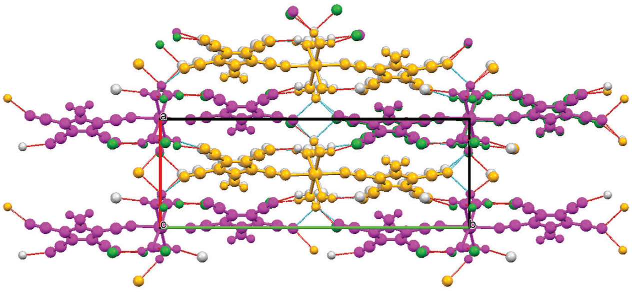


Fig. 11: Packing diagram of **2c**, looking down the *c* axis.

N22, and N23). All O...N distances are within a narrow range from 2.79 to 2.83 Å, and all O–H...N angles are close to linearity. Due to the disorder problem, no comment can be offered about the involvement in hydrogen bonds of the nitro and the remaining cyano groups. The fact that there is positional disorder makes this participation in hydrogen bonds rather improbable.

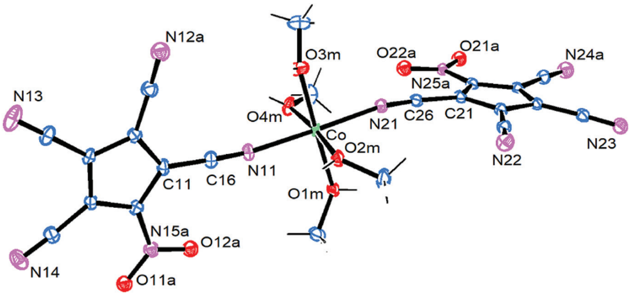


Fig. 12: View of the molecular unit of compound **4d.** Only the major occupied of the disordered positions is shown. Displacement ellipsoids at the 30% probability level.

3 Experimental part

3.1 General remarks

All reactions were performed under nitrogen, using standard Schlenk techniques; work-up procedures including chromatography were performed in air. The solvents used were of analytical grade and used as supplied. The starting materials **1a–d** were obtained as described by us earlier [20]. The metal chlorides were obtained as hydrates from Sigma-Aldrich Chemie, Munich, Germany, in “analytical grade.” Anhydrous metal chlorides were prepared from the corresponding hydrates by heating in the presence of $SOCl_2$. Mass spectra were recorded with a Jeol Mstation JMS 700 (Jeol, Tokyo, Japan). Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument (Bitterfeld-Wolfen, Germany).

3.2 Syntheses

3.2.1 General procedure for the synthesis of 2–7

A solution of the metal dichloride (0.25 mmol) in methanol (20 mL) was treated with a solution of Ag{$C_5(CN)_4X$} (0.50 mmol) in methanol (20 mL) at room temperature. Stirring was continued for 16 h. After filtering off the precipitated AgCl, the product was precipitated by addition of dichloromethane, isolated by filtration, and dried in vacuo.

3.2.2 Yields and characterization

2a′: From 49 mg $MnCl_2 \cdot 4H_2O$ a yield of 411 mg (81%) was obtained (light brown powder). –MS((–)–FAB): *m/z* = 625.6 $[Mn(PCC)_3]^-$; 696.6 $[Mn(PCC)_3(H_2O)_4]^-$. –IR (KBr, cm^{-1}): ν(CN) = 2245m, 2222s. –$C_{21}H_{12}MnN_{10}O_5$ (539.3): calcd. C 46.77, H 2.24, N25.97; found C 47.02, H 2.25, N25.81. Recrystallization from MeOH gave single crystals of **2a** suitable for X-ray diffraction (see below).

2b′: From 49 mg $MnCl_2 \cdot 4H_2O$, using a mixed MeOH/EtOH solvent, a yield of 388 mg (85%) was obtained (light brown powder). –MS((–)–FAB): *m/z* = 549.7 $[Mn(TCC)_3]^-$. –$C_{22}H_{18}MnN_8O_4$ (513.38): calcd. C 51.47, H 3.53, N 21.83; found C 51.56, H 2.90, N 21.54. Recrystallization from MeOH gave single crystals of **2b** suitable for X-ray diffraction (see below).

2c′: From 49 mg $MnCl_2 \cdot 4H_2O$, a yield of 405 mg (83%) was obtained (red powder). –$C_{18.5}H_{14}MnN_{10}O_{4.5}$ (503.24): calcd. C 44.15, H 2.80, N 27.83; found C 44.52, H 2.70, N 27.78. Recrystallization from MeOH gave single crystals of **2c** suitable for X-ray diffraction (see below).

3a′: From 31 mg $FeCl_2$ a yield of 213 mg (42%) was obtained (yellow powder). –MS((–)–FAB): *m/z* = 626.6 $[Fe(PCC)_3]^-$. –$C_{23.5}H_{18}FeN_{10}O_{5.5}$(584.2): calcd. C 48.31, H 3.11, N 22.96; found C 48.72, H 3.19, N 24.04. Recrystallization from MeOH gave single crystals of **3a** suitable for X-ray diffraction (see below).

3b′: From 31 mg $FeCl_2$ in mixed MeOH/EtOH solvent a yield of 179 mg (39%) was obtained (yellow powder). –MS((–)–FAB): *m/z* = 550.5 $[Fe(TCC)_3]^-$. –$C_{21}H_{15}FeN_8O_{3.5}$ (491.2): calcd. C 51.35, H 3.08, N 22.80; found C 51.46, H 2.60, N 22.48. Recrystallization from MeOH gave single crystals of **3a** suitable for X-ray diffraction (see below).

3c′: From 31 mg $FeCl_2$ a yield of 70 mg (69%) was obtained (red powder). –IR (ATR, cm^{-1}): ν(CN) = 2212m. –$C_{18}H_{12}FeN_{10}O_4$ (488.2): calcd. C 44.28, H 2.48, N 28.69; found C 44.49, H 2.64, N 28.15.

4a′: From 51 mg $CoCl_2 \cdot 6H_2O$ a yield of 65 mg (49%) was obtained (yellow-green powder). –IR (KBr, cm^{-1}): ν(CN) = 2269s, 2220s. –MS(FAB^+): m/z = 285.3 $[Co(PCC)(H_2O)_2]^+$. –$C_{20}H_{10}N_{10}CoO_5$ (529.3) calcd. C 45.38, H 1.90, N 26.46; found C 45.37, H 1.87, N 26.19.

4b′: From 32 mg $CoCl_2$ a yield of 378 mg (82%) was obtained (red powder). –$C_{20}H_{10}N_8CoO_2$ (453.3) calcd. C 52.99, H 2.22, N 24.72; found C 52.06, H 2.27, N 24.22. Recrystallization from MeCN gave single crystals of **4b**.

4c′: From 32 mg $CoCl_2$ a yield of 80 mg (77%) was obtained (yellow powder). –$C_{19.5}H_{15}N_{10}CoO_4$ (512.2) calcd. C 45.70, H 2.95, N 27.33; found C 45.11, H 3.03, N 26.79.

4d′: From 32 mg $CoCl_2$ a yield of 44.5 mg (81%) was obtained (brown powder). –MS((–)–FAB): *m/z* = 689.5 $[Co(NTCC)_3]^-$. –$C_{21}H_{16}N_{10}CoO_9$ (611.35) calcd. C 41.26, H 2.64, N 22.91; found C 40.94, H 2.52, N 23.15. Recrystallization from MeOH gave single crystals of **4d** suitable for X-ray diffraction (see below).

5a′: From 32.4 mg $NiCl_2$ a yield of 53 mg (24%) was obtained (blue powder). –IR (ATR, cm^{-1}): ν(CN) = 2269s, 2214s. –MS((–)–FAB): *m/z* = 627.9 $[Ni(PCC)_3]^-$. –$C_{21.8}H_{9.6}N_{10}NiO_3$ (518.20) calcd. C 50.52, H 1.87, N 27.01; found C 50.47, H 1.62, N 26.94.

5b′: From 32.4 mg $NiCl_2$ a yield of 30 mg (31%) was obtained (white powder). –$C_{21}H_{16}N_8NiO_4$ (503.10) calcd. C 50.13, H 3.21, N 22.27; found C 50.40, H 3.04, N 23.05.

5c′: From 32.4 mg $NiCl_2$ a yield of 27 mg (26%) was obtained (yellow powder). –$C_{20}H_{16}N_{10}NiO_4$ (519.10) calcd. C 46.85, H 2.48, N 28.76; found C 46.99, H 2.45, N 29.26.

6a′: From 43 mg $CuCl_2 \cdot 2H_2O$ a yield of 90 mg (70%) was obtained (yellow-green powder). –IR (KBr, cm^{-1}): ν(CN) = 2261m, 2246m, 2222s. –MS((–)–FAB): *m/z* = 443.1 $[Cu(PCC)_2]^-$. –$C_{20}H_8N_{10}CuO_4$ (515.9): calcd. C 46.56, H 1.56, N 27.13; found C 46.88, H 1.87, N 27.03.

6b′: From 33 mg $CuCl_2$ a yield of 68 mg (69%) was obtained (yellow powder). –IR (ATR, cm^{-1}): ν(CN) = 2221s. –MS((–)–FAB): *m/z* = 393.1 $[Cu(TCC)_2]^-$, 620.7 $[Cu(TCC)_3]^-$. –$C_{20}H_{11}N_8CuO_{2.5}$(466.9): calcd. C 51.44, H 2.37, N 23.99; found C 51.23, H 2.26, N 23.72. Recrystallization from MeOH gave single crystals of **6b** suitable for X-ray diffraction (see below).

7a′: From 34 mg $ZnCl_2$ a yield of 97 mg (88%) was obtained (white powder). –MS((–)–FAB): *m/z* = 634.5 $[Zn(PCC)_3]^-$. –$C_{22}H_{18}N_{10}ZnO_7$ (599.8): calcd. C 44.04, H 3.02, N 23.33; found C 44.05, H 2.26, N 23.42.

7b′: From 34 mg $ZnCl_2$ a yield of 100 mg (86%) was obtained (white powder). –$C_{20.25}H_{13.5}N_8ZnO_{3.5}$ (490.2): calcd. C 49.61, H 2.78, N 22.85; found C 49.45, H 2.41, N 22.76. Recrystallization from MeOH gave single crystals of **7b** suitable for X-ray diffraction (see below).

Table 6: Experimental details of the crystal structure determinations.

Compound	**2a**	**2b**	**2c**	**3a**	**3b**	**4d**	**4b**	**6b**	**7b**
Formula	$C_{20}H_8MnN_{10}O_4$	$C_{18}H_{10}MnN_8O_4$	$C_{18}H_{12}MnN_{10}O_4$	$C_{20}H_{12}FeN_{10}O_6$	$C_{18}H_{14}FeN_8O_6$	$C_{22}H_{16}CoN_{10}O_8$	$C_{38}H_{25}Co_2N_{17}O_9$	$C_{20}H_{14}CuN_8O_4$	$C_{18}H_{10}N_8O_4Zn$
Formula weight	253.65	228.64	487.32	544.25	494.22	607.38	981.61	246.97	233.85
Temperature	293(2) K	100(2) K	100(2) K	173(2) K	153(2) K	108(2) K	153(2) K	103(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/c$
Unit cell dimensions									
a, Å	7.5964(3)	5.8342(3)	7.6691(5)	10.5785(5)	7.0650(5)	9.2241(18)	9.9204(11)	6.6994(3)	5.8073(3)
b, Å	20.9665(7)	22.1005(11)	21.6776(16)	6.7919(3)	23.5461(17)	11.701(3)	22.534(2)	21.9401(10)	21.8668(10)
c, Å	7.4990(3)	7.7782(4)	13.0060(9)	17.8819(8)	7.3384(5)	13.475(3)	9.9920(11)	7.2585(3)	7.7462(4)
α, deg	90	90	90	90	90	101.382(7)	90	90	90
β, deg	98.257(2)	93.790(2)	96.290(2)	105.1340(10)	115.601(3)	107.166(7)	105.861(4)	92.6360(10)	93.852(2)
γ, deg	90	90	90	90	90	99.621(8)	90	90	90
Volume, Å^3	1181.98(8)	1000.72(9)	2149.2(3)	1240.22(10)	1100.92(14)	1322.3(5)	2148.7(4)	1065.77(8)	981.44(8)
Z	2	2	2	2	2	2	2	2	2
D_{calcd}, g cm^{-3}	1.43	1.52	1.51	1.46	1.49	1.53	1.52	1.54	1.58
μ, mm^{-1}	0.6	0.7	0.7	0.7	0.7	0.7	0.8	1.1	1.3
$F(000)$, e	510	462	988	552	504	618	996	502	472
Crystal size, mm^3	0.09 × 0.07 × 0.05	0.09 × 0.07 × 0.04	0.03 × 0.02 × 0.01	0.1 × 0.09 × 0.07	0.04 × 0.03 × 0.02	0.05 × 0.04 × 0.03	0.1 × 0.06 × 0.04	0.07 × 0.05 × 0.03	0.1 × 0.07 × 0.04
Crystal color	Colorless	Yellow	Colorless	Pale yellow	Yellow	Yellow	Yellow	Colorless	Colorless
θ range, deg	3.335 to 28.300°	1.843 to 27.541°	2.452 to 25.361°	2.360 to 26.381°	1.730 to 30.506°	1.639 to 27.529°	1.807 to 28.335°	2.959 to 27.537°	1.863 to 28.309°
Index ranges	$-8 \le h \le 10$ $-27 \le k \le 27$ $-9 \le l \le 9$	$-7 \le h \le 7$ $-28 \le k \le 28$ $-10 \le l \le 10$	$-9 \le h \le 9$ $0 \le k \le 26$ $0 \le l \le 15$	$-13 \le h \le 13$ $-8 \le k \le 8$ $-19 \le l \le 22$	$-10 \le h \le 9$ $-33 \le k \le 33$ $-10 \le l \le 10$	$-11 \le h \le 11$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-13 \le h \le 13$ $-30 \le k \le 30$ $-13 \le l \le 13$	$-8 \le h \le 8$ $-28 \le k \le 28$ $-9 \le l \le 9$	$-7 \le h \le 7$ $-29 \le k \le 26$ $-10 \le l \le 10$
Refl. total	12739	14832	4010	19471	13018	32966	37174	20906	17739
Refl. unique/R_{int}	2916/0.0243	2312/0.0372	4010	2551/0.0383	3349/0.0470	5990/0.0600	10665/0.0325	2461/0.0427	2447/0.0369
Abs. Correction	Semi-empirical from equivalents								
T_{max}/T_{min}	0.746/0.684	0.746/0.682	0.745/0.619	0.745/0.696	0.746/0.657	0.746/0.698	0.746/0.691	0.746/0.702	0.746/0.675
Data/restraints/ parameters	2916/0/176	2312/0/162	4010/34/337	2551/0/188	3349/0/179	5990/41/379	10665/17/663	2461/0/168	2447/0/162
S	1.053	1.328	0.927	1.054	1.166	0.990	1.085	1.019	1.218
$R1/wR2$ [$I > 2\sigma(I)$]	0.0280/0.0954	0.0309/0.1052	0.0492/0.1132	0.0273/0.0658	0.0614/0.1181	0.0483/0.1059	0.0300/0.0811	0.0276/0.0720	0.0505/0.1236
$R1/wR2$ (all data)	0.0325/0.0994	0.0361/0.1192	0.0736/0.1253	0.0369/0.0701	0.0847/0.1270	0.0644/0.1144	0.0355/0.0950	0.0351/0.0772	0.0557/0.1260
Flack Parameter x	–	–	–	–	–	–	0.038(6)	–	–
Largest diff. peak/ hole, e Å^{-3}	0.37/−0.28	0.55/−0.47	0.70/−0.51	0.22/−0.24	0.84/−0.52	0.52/−0.61	0.32/−0.40	0.62/−0.41	0.87/−0.47
CCDC number	1862594	1862595	1862597	1862602	1862596	1862598	1862600	1862599	1862601

7c′: From 34 mg $ZnCl_2$ a yield of 90 mg (85%) was obtained (yellow powder). –$C_{18.5}H_{14}N_{10}ZnO_{4.5}$(513.7): calcd. C 43.25, H 2.75, N 27.25; found C 43.73, H 2.72, N 27.42.

3.3 Crystal structure determination

Most details of the crystallographic studies are collected and shown in Table 6. All crystals except for **3a** (Bruker D8 Quest) were measured using a Bruker D8 Venture instrument (Bruker AXS, Karlsruhe, Germany). Cell determination and refinement, data processing, and absorption correction were performed with the respective diffractometer software. The program package WINGX was used for structure solution and refinement as well as for structure evaluation, production of the CIFs, and crystallographic tables [21–25]. Nearly all structures were solved using SHELXT; the structures of **3a** (SIR97) and **6b** (SIR2014) were solved by different programs. All structures were refined with SHELXL (version2014/7). The crystals of **2c** turned out to be twinned and were, therefore, refined with the HKLF5 dataset (BASF = 0.458; twin matrix: –1.001 –0.001 –0.005; 0.012 –1.000 0.008; 0.361 –0.002 1.001).

The Cambridge Crystallographic Data Center (CCDC) 1862594–1862602 (see Table 6) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] D. R. Turner, A. S. R. Chesman, K. S. Murray, G. B. Deacon, S. R. Batten, *Chem. Commun*. **2011**, *47*, 10189.

[2] S. Benmansour, C. Atmani, F. Setifi, S. Triki, M. Marchivie, C. J. Gómez-García, *Coord. Chem. Rev*. **2010**, *254*, 1468.

[3] S. R. Batten, K. S. Murray. *Coord. Chem. Rev*. **2003**, *246*, 103.

[4] S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, R. Robson, *J. Chem. Soc. Dalton Trans*. **1999**, 2977.

[5] O. Reckeweg, A. Schulz, F. J. DiSalvo, *Z. Naturforsch*. **2015**, *70b*, 177.

[6] C. Nitschke, M. Köckerling, *Z. Anorg. Allg. Chem*. **2009**, *635*, 503.

[7] C. Nitschke, M. Köckerling, *Inorg. Chem*. **2011**, *50*, 4313.

[8] S. Triki, J. S. Pala, M. Decoster, P. Molinié, L. Toupet, *Angew. Chem. Int. Ed*. **1999**, *38*, 113.

[9] A. M. Kutasi, D. R. Turner, P. Jensen, B. Moubaraki, S. R. Batten, K. S. Murray, *Inorg. Chem*. **2011**, *50*, 6673.

[10] J. A. Schlueter, U. Geiser, J. L. Manson, *Acta Crystallogr*. **2003**, *C59*, m1.

[11] E. Lefebvre, F. Conan, N. Cosquer, J.-M. Kerbaol, M. Marchivie, J. Sala-Pala, M. M. Kubicki, E. Vigier, C. J. Gómez-García, *New J. Chem*. **2006**, *30*, 1197.

[12] Q. Li, Y. Wang, P. Yan, G. Hou, G. Li, *Inorg. Chim. Acta* **2014**, *413*, 32.

[13] S. I. Gurskiy, V. A. Tafeenko, *CrystEngComm* **2012**, *14*, 2721.

[14] J. C. Bullinger, D. M. Eichhorn, *Inorg. Chim. Acta* **2009**, *362*, 4510.

[15] O. W. Webster, United States Patent 3,835,943, **1974**.

[16] O. W. Webster, *J. Am. Chem. Soc*. **1966**, *88*, 4055.

[17] R. E. Christopher, L. M. Venanzi, *Inorg. Chim. Acta* **1973**, *7*, 489.

[18] R. J. Less, T. C. Wilson, M. McPartlin, P. T. Wood, D. S. Wright, *Chem. Commun*. **2011**, *47*, 10007.

[19] K. Sünkel, D. Reimann, *Z. Naturforsch*. **2013**, *68b*, 546.

[20] P. R. Nimax, K. Sünkel, *ChemistrySelect* **2018**, *3*, 3330.

[21] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[22] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van derStreek, *J. Appl. Crystallogr*. **2006**, *39*, 453.

[23] A. L. Spek, *J. Appl. Crystallogr*. **2003**, *36*, 7.

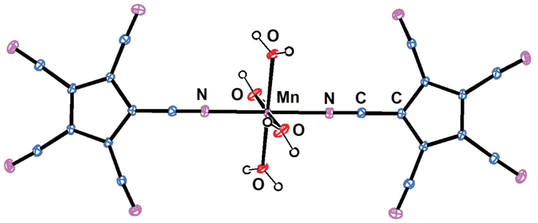
[24] G. M. Sheldrick, *ActaCrystallogr*. **2008**, *A64*, 112.

[25] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. J. Spagna, *J. Appl. Crystallogr*. **1999**, *32*, 115.

Graphical synopsis

Karlheinz Sünkel, Dietmar Reimann and Patrick Nimax

Synthesis, molecular, and crystal structures of 3d transition metal cyanocyclopentadienides [M(MeOH)$_n$ (H$_2$O)$_{4-n}${C$_5$(CN)$_4$X}$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn; X = H, CN, NH$_2$, NO$_2$)



https://doi.org/10.1515/znb-2018-0175
Z. Naturforsch. 2018; x(x)b: xxx–xxx