

Coordination Chemistry of Polynitriles, I. Syntheses and Crystal Structures of $[\text{Ag}(\text{PCC})(\text{DMF})]$, $[\text{Ni}(\text{DMF})_6](\text{PCC})_2$ and $[\text{Co}(\text{DMF})_6](\text{PCC})_2$ ($\text{PCC} = [\text{C}_5(\text{CN})_5]^-$, $\text{DMF} = N,N\text{-Dimethylformamide}$) [1]

Karlheinz Sünkel and Dietmar Reimann

Ludwig-Maximilians-University Munich, Department of Chemistry, Butenandtstr. 9, 81377 München, Germany

Reprint requests to Prof. Dr. Karlheinz Sünkel. Fax: ++49 89 2180 77774.

E-mail: suenk@cup.uni-muenchen.de

Z. Naturforsch. **2013**, 68b, 546–550 / DOI: 10.5560/ZNB.2013-3077

Received March 1, 2013

Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Recrystallization of silver pentacyanocyclopentadienide $\text{Ag}[\text{C}_5(\text{CN})_5]$ from *N,N*-dimethylformamide (DMF) gives the polymeric 1 : 1 complex $[\text{Ag}\{\text{C}_5(\text{CN})_5\}(\text{DMF})]$ (**1**). The Ag^+ cation is coordinated by three N atoms of three different $[\text{C}_5(\text{CN})_5]^-$ anions and two O atoms of two DMF molecules. Each $[\text{C}_5(\text{CN})_5]^-$ is coordinated *via* three neighboring CN groups to three different Ag^+ ions, while each DMF molecule bridges two Ag^+ ions *via* its O atom. Treatment of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or ZnCl_2 with $\text{Ag}[\text{C}_5(\text{CN})_5]$ in DMF gives the DMF complexes $[\text{M}(\text{DMF})_6][\text{C}_5(\text{CN})_5]_2$ ($\text{M} = \text{Ni}$, **2**; Co , **3**; Zn , **4**). The complexes **2** and **3** were characterized by X-ray diffraction and show octahedral $[\text{M}(\text{DMF})_6]^{2+}$ cations with *O*-coordinated DMF molecules. The $[\text{C}_5(\text{CN})_5]^-$ anions show ideal pentagonal symmetry.

Key words: Silver, Cobalt, Nickel, Zinc, Pentacyanocyclopentadienide, Dimethylformamide Complexes

Introduction

The cyclopentadienide anion $[\text{C}_5\text{H}_5]^-$ and its pentaalkyl-substituted derivatives $[\text{C}_5\text{R}_5]^-$ ($\text{R} = \text{Me}$, Et , *i*-Pr) coordinate usually to most metals *via* their π systems in an η^5 fashion due to the high electron density in the carbon ring [2–5]. When the electron-donating alkyl groups are substituted by electron-withdrawing substituents like halides or ester groups either no coordination occurs at all upon treatment of appropriate metal precursors ($\text{R} = \text{halide}$) [6] or coordination *via* the donor atoms present in the substituent dominates [7]. For the preparation of η^5 -coordinated complexes of these electron-poor cyclopentadienides either the substituents have to be introduced to already η^5 -coordinated ligands or special experimental tricks have to be applied. Thus, it was possible to prepare η^5 complexes of $[\text{C}_5\text{F}_5]^-$, $[\text{C}_5\text{Cl}_5]^-$, $[\text{C}_5\text{Br}_5]^-$, $[\text{C}_5\text{I}_5]^-$ [8], and $[\text{C}_5(\text{COOR})_5]^-$ [9]. However, no example of η^5 coordination of the pentacyanocyclopentadienide ligand $[\text{C}_5(\text{CN})_5]^-$ (PCC) has been proven so far. The

“decacyanoferrrocene” reported over 40 years ago most likely contains Fe^{2+} coordinated to one or more N atoms of the polynitrile ligand. No structural studies have been reported [10, 11]. Recently, some interesting reports on the coordination chemistry of this elusive ligand appeared in the literature, which all showed only coordination *via* one or more nitrile functions [12–16]. This prompts us to publish the results of some of our studies on the coordination behavior of the PCC ligand, which were partially reported by us at the 31st ICCC in 1996 [17].

Results and Discussion

Recrystallization of $\text{Ag}[\text{C}_5(\text{CN})_5]$ from dimethylformamide gives brownish-yellow needles of the mono-solvato complex $[\text{Ag}\{\text{C}_5(\text{CN})_5\}(\text{HCONMe}_2)]$, ($[\text{Ag}(\text{PCC})(\text{DMF})]$), **1**, which slowly become opaque when taken out of the solvent. However, when left in contact with a drop of solvent, they can be examined by X-ray diffraction. Fig. 1 shows an ORTEP-3 view of

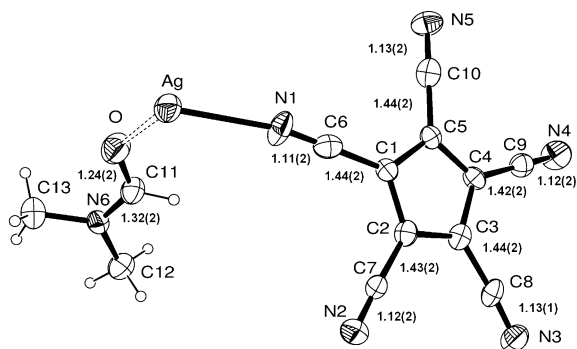


Fig. 1. ORTEP-3 view of the asymmetric unit of **1** (30 % probability ellipsoids) with important distances.

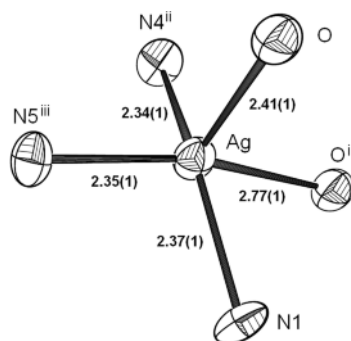


Fig. 2. Coordination sphere of the Ag^+ ion in crystals of **1** (distances in Å). Symmetry operators: (i) $x - 1, y, z$; (ii) $x, y + 1, z$; (iii) $1 - x, -y, 1 - z$.

the asymmetric unit of **1**, which contains one formula unit of $[\text{Ag}(\text{PCC})(\text{DMF})]$.

However, the Ag^+ ion is coordinated additionally to two symmetry-related PCC anions as well as one symmetry-related DMF molecule, thus producing a distorted square-pyramidal coordination sphere of the metal atom (Fig. 2).

As a consequence of this, the PCC anion acts as a bridging ligand. First, *via* N1 and N5 two inversion-

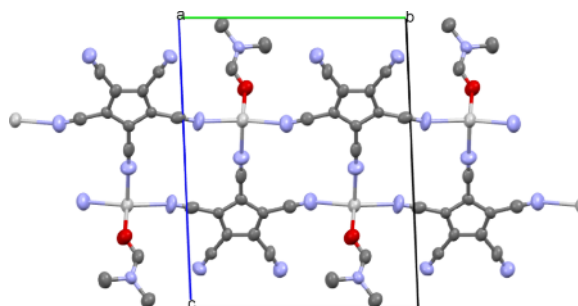


Fig. 4 (color online). Ribbon structure of **1** as viewed along the crystallographic b direction.

related molecules form a 14-membered ring, which is, however, not planar (Figs. 3a and 3b).

The intra-ring distance of the two AgI ions is $7.571(1)$ Å, the distance between the two PCC ring planes is 0.921 Å. Second, these rings are bridged along the b direction *via* N1 and N4 to give a ribbon-like structure (Fig. 4).

This ribbon structure corresponds to the reported powder diffraction structure of AgPCC , obtained by crystallization from acetonitrile [16]. Finally these ribbons are connected *via* the DMF ligands along the a direction to give a three-dimensional network (Fig. 5).

The reaction of $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ with $\text{Na}[\text{C}_5(\text{CN})_5]$ in THF was reported to give $[\{\text{C}_5(\text{CN})_5\}_2\text{Co}(\text{H}_2\text{O})_2(\text{THF})_2]$ and $[\{\text{C}_5(\text{CN})_5\}\text{CoCl}(\text{THF})_2]_\infty$, which contain coordinated solvent and have the PCC ligand acting as a monodentate or 1,2-(CN)₂ bridging ligand and [13]. When the halide salts $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 are treated with $\text{Ag}[\text{C}_5(\text{CN})_5]$ in DMF and the formed AgCl precipitate is removed by filtration, slow evaporation of the solvent gives crystals of **2**, **3** and **4** that all become opaque on standing. When left in contact with DMF, however, they can be examined by X-ray diffraction. All three compounds have triclinic unit cells with one formula unit of

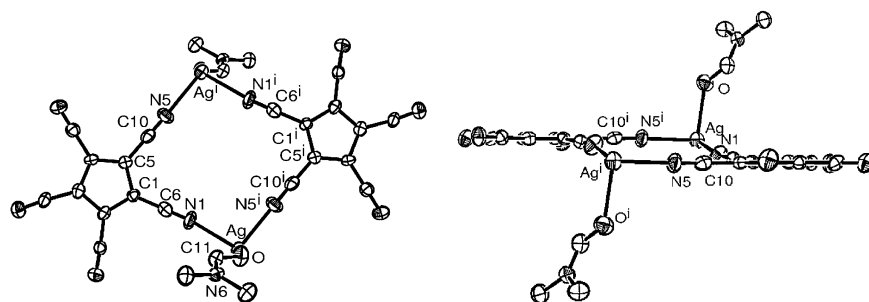


Fig. 3. Top view of the 14-membered ring formed by two inversion-related molecules in **1** (left); side view of the 14-membered ring in **1** (right).

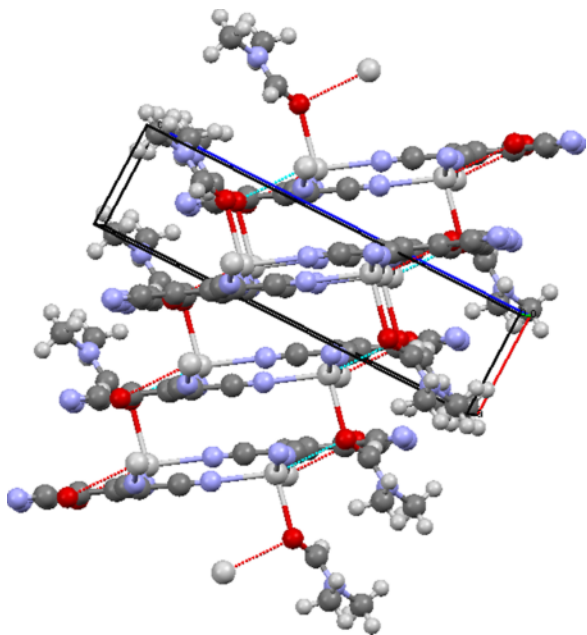


Fig. 5 (color online). Three-dimensional network structure of **1**.

$[M(\text{DMF})_6](\text{PCC})_2$ in them. The asymmetric unit contains the metal atom on an inversion center, three *O*-coordinated DMF molecules and one free $[\text{C}_5(\text{CN})_5]$ anion. Because the Ni and Zn compounds **2** and **4** have nearly identical cell parameters, the structure of **4** was not fully refined. A view of the $[\text{Co}(\text{DMF})_6]^{2+}$ cation of **3** together with the uncoordinated PCC anion is shown in Fig. 6. Some important bond parameters of **2** and **3** are collected in Table 1.

As can be seen, the metals are centers of slightly elongated octahedra with bond lengths and angles as usually observed in complexes with these cations [18–21]. The only unusual feature is the rather widespread distribution of the M–O–C angles in the cobalt compound, for which we have no explanation. As might be expected for a free uncoordinated pentacyanocyclopentadienide [22], the geometry of the an-

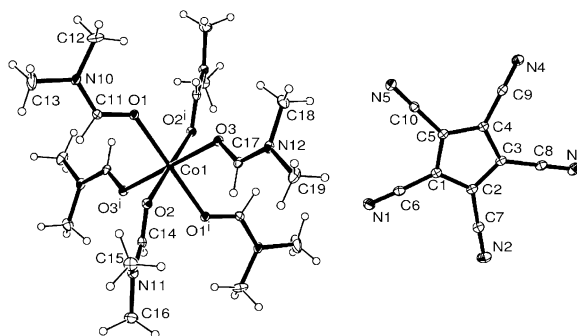


Fig. 6. ORTEP-3 view (30% probability ellipsoids) of the cation and anion of **3**.

ion is highly symmetrical in both compounds. In the low-temperature structure of **3** the bond lengths are identical within one standard deviation, while in the room-temperature structure of **2** the spread is within 2σ .

Experimental Section

All reactions were performed in air. $\text{Ag}[\text{C}_5(\text{CN})_5]$ was prepared according to the literature [16]. *N,N*-Dimethylformamide was obtained in analytical grade from Aldrich and used as received.

(*Pentacyanocyclopentadienido*)(*N,N*-dimethylformamide)-silver(I), $[\text{Ag}(\text{PCC})(\text{DMF})]$, **1**

100 mg of $\text{Ag}[\text{C}_5(\text{CN})_5]$ were dissolved in *ca.* 5 mL DMF with slight warming. Standing of this solution in an open crystallization vessel for several days produced brownish-yellow needles that were transferred with a drop of solvent to a capillary which was sealed afterwards and measured on a Syntex Nicolet R3 diffractometer. When left in air or put under vacuum the crystals became opaque; no meaningful elemental analyses could be obtained.

Hexakis(dimethylformamide)nickel(II) bis(pentacyanocyclopentadienide), $[\text{Ni}(\text{DMF})_6](\text{PCC})_2$, **2**

A solution of $\text{Ag}[\text{C}_5(\text{CN})_5]$ (153 mg, 0.51 mmol) in DMF (4 mL) was added to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (52 mg,

	2	3
M–OC	2.034(2); 2.036(2); 2.057(2)	2.074(1); 2.076(1); 2.109(1)
MO=C	1.230(4); 1.240(4); 1.240(5)	1.233(2); 1.249(2); 1.250(2)
O–M–O _{cis}	87.7(1)–92.3(1)	86.74(5)–93.26(5)
M–O–C	120.5(3); 122.2(2); 122.8(2)	116.7(1); 121.3(1); 127.4(1)
(C–C) _{ring}	1.390(5)–1.409(4)	1.404(3)–1.409(3)
C–CN	1.416(5)–1.434(5)	1.421(3)–1.427(3)
C≡N	1.126(4)–1.148(5)	1.144(3)–1.150(3)

Table 1. Some important bond parameters (Å, deg) of **2** and **3**.

Table 2. Crystal structure data of 1–3.

Compound	1	2	3
Empirical formula	C ₁₃ H ₇ AgN ₆ O	C ₃₈ H ₄₂ N ₁₆ NiO ₆	C ₃₈ H ₄₂ CoN ₁₆ O ₆
Formula weight	371.12	877.59	877.81
Crystal size, mm ³	0.68 × 0.20 × 0.13	0.78 × 0.60 × 0.55	0.158 × 0.148 × 0.095
Temperature, K	298(2)	298(2)	100(2)
Radiation; λ, Å		Mo K _α ; 0.71073	
Crystal system		triclinic	
Space group		<i>P</i> $\bar{1}$ (no. 2)	
Unit cell dimensions			
<i>a</i> , Å	4.0100(10)	7.992(3)	8.6513(3)
<i>b</i> , Å	11.640(2)	11.875(2)	9.4255(3)
<i>c</i> , Å	14.924(3)	13.212(2)	14.2367(5)
α, deg	87.570(10)	92.070(10)	78.478(2)
β, deg	88.91(2)	92.96(2)	78.4470(10)
γ, deg	88.44(2)	108.17(2)	89.600(2)
Volume, Å ³	695.6(3)	1188.0(5)	1113.80(7)
<i>Z</i>	2	1	1
<i>D</i> _{calcd.} , g cm ^{−3}	1.77	1.23	1.31
μ (Mo K _α), mm ^{−1}	1.5	0.5	0.5
<i>F</i> (000), e	364	458	457
θ range data coll., deg	2.18–22.55	2.31–20.06	2.40–27.53
<i>hkl</i> index ranges	−4, ±12, ±16	±7, ±11, ±12	±11, ±12, ±18
Refl. collected / unique / <i>R</i> _{int}	2232 / 1838 / 0.0418	4561 / 2234 / 0.0864	21898 / 5139 / 0.0345
Completeness to θ _{max} , %	99.5	99.6	99.7
Absorption correction		semi-empirical from equivalents	
Transmission max. / min.	0.8333 / 0.4376	0.7834 / 0.7124	0.746 / 0.681
Data / ref. parameters	1838 / 190	2234 / 294	5139 / 295
Final <i>R</i> 1 / <i>wR</i> 2 [<i>I</i> > 2 σ(<i>I</i>)]	0.0615 / 0.1641	0.0362 / 0.0825	0.0334 / 0.0808
Final <i>R</i> 1 / <i>wR</i> 2 (all data)	0.0836 / 0.1996	0.0445 / 0.0866	0.0471 / 0.1075
Goodness-of-fit on <i>F</i> ²	1.097	1.103	1.412
Extinction coefficient	–	0.067(3)	–
Largest diff. peak / hole, e Å ^{−3}	2.057 / −1.222	0.235 / −0.241	0.455 / −0.555

0.25 mmol) in DMF (3 mL). The immediately formed precipitate of AgCl was removed by filtration, and the filtrate was allowed to evaporate on air for several days. Green crystalline blocks formed which were transferred with a drop of solvent to a capillary that was sealed afterwards and measured on a SYNTEX Nicolet R3 diffractometer. When left in air or put under vacuum the crystals became opaque; no meaningful elemental analyses could be obtained. – IR (KBr, cm^{−1}): ν = 2941w, 2775w, 2267m, 2246sh, 2218s, 1656vs, 1469m, 1422w, 1379m, 1256w, 1117m, 690m.

Hexakis(dimethylformamide)cobalt(II)

bis(pentacyanocyclopentadienide), [Co(DMF)₆](PCC)₂, **3**

A solution of Ag[C₅(CN)₅] (153 mg, 0.51 mmol) in DMF (3 mL) was added to a solution of CoCl₂ · 6H₂O (52 mg, 0.25 mmol) in DMF (3 mL). The immediately formed precipitate of AgCl was removed by filtration, and the reddish solution was evaporated *in vacuo*. The residue was taken up in *ca.* 2 mL DMF, and the solution was filtered and left to stand in air. After a few days beige needles and some

brown blocks had formed. One of the brown blocks was transferred with a drop of oil on top of a glass fiber and measured at 100 K with a Bruker D8 venture diffractometer. When left in air or put under vacuum the crystals became opaque; no meaningful elemental analyses could be obtained.

Hexakis(dimethylformamide)zinc(II)

bis(pentacyanocyclopentadienide), [Zn(DMF)₆](PCC)₂, **4**

A solution of ZnCl₂ (74 mg, 0.54 mmol) in DMF (3 mL) was added to a solution of Ag[C₅(CN)₅] (161 mg, 0.54 mmol) in DMF (5 mL). The immediately formed precipitate of AgCl was removed by filtration, and the solution was evaporated *in vacuo*. The colorless residue was taken up in *ca.* 2 mL DMF, and the solution was filtered and left to stand in air. Colorless thin needles formed. When left in air or put under vacuum the crystals became opaque; no meaningful elemental analyses could be obtained. – IR (KBr, cm^{−1}): ν = 2940m, 2775w, 2221vs, 2211s, 1650m, 1494m, 1469m, 1438m, 1421s, 1376vs, 1252m, 1114m, 686s, 666m.

Crystal structure determinations of **1**–**3**

The structures of **1** and **2** were solved with SHELX-86, the structure of **3** with SIR97 [23]. All structures were refined with SHELXL-97 [24], all contained in the WINGX program package [25].

Details of the crystal structure determinations are collected in Table 2.

CCDC 926774–926776 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- [1] Taken in part from the dissertation of Dietmar Reimann, *Untersuchungen zur Komplexchemie von 1,2,3,4,5-Pentacyanocyclopentadienid und 2,3,5,6-Tetracyano-1,4-dithiin*, Herbert Utz Verlag, München, **1996**; ISBN 3-931327-43-4.
- [2] C. Janiak, H. Schumann, *Adv. Organomet. Chem.* **1991**, *33*, 291.
- [3] P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969.
- [4] N. J. Coville, K. E. Du Plooy, W. Pickl, *Coord. Chem. Rev.* **1992**, *116*, 1.
- [5] D. Weismann, D. Saurenz, R. Boese, D. Bläser, G. Wolmershäuser, Y. Sun, H. Sitzmann, *Organometallics* **2011**, *30*, 6351.
- [6] G. Paprott, S. Lehmann, K. Seppelt, *Chem. Ber.* **1988**, *121*, 727.
- [7] M. I. Bruce, P. A. Humphrey, M. L. Williams, *Austr. J. Chem.* **1997**, *50*, 113, and refs. cited therein.
- [8] For a review see: K. Sünkel, *Chem. Ber./ Recueil* **1997**, *130*, 1721.
- [9] L. S. Micallef, B. T. Loughrey, P. C. Healy, P. G. Parsons, M. L. Williams, *Organometallics* **2010**, *29*, 6237.
- [10] O. W. Webster, *J. Am. Chem. Soc.* **1966**, *88*, 3046.
- [11] R. E. Christopher, L. M. Venanzi, *Inorg. Chim. Acta* **1973**, *7*, 489.
- [12] R. J. Less, B. Guan, N. M. Muresan, M. McPartlin, E. Reisner, T. C. Wilson, D. S. Wright, *Dalton Trans.* **2012**, *41*, 5919.
- [13] R. J. Less, T. C. Wilson, M. McPartlin, P. T. Wood, D. S. Wright, *Chem. Commun.* **2011**, *47*, 10007.
- [14] J. Bacsá, R. J. Less, H. E. Skelton, Z. Soracevic, A. Steiner, T. C. Wilson, P. T. Wood, D. S. Wright, *Angew. Chem. Int. Ed.* **2011**, *50*, 8279.
- [15] R. J. Less, M. McPartlin, J. M. Rawson, P. T. Wood, D. S. Wright, *Chem. Eur. J.* **2010**, *16*, 13723.
- [16] C. daSilva, M. Bergamo, R. Cerny, A. F. Williams, *Helv. Chim. Acta* **2009**, *92*, 2480.
- [17] K. Sünkel, *31st Int. Conf. Coord. Chem.*, Vancouver (Canada) **1996**, poster 5P1.
- [18] W.-S. Li, A. J. Blake, N. R. Champness, M. Schröder, D. W. Bruce, *Acta Crystallogr.* **1998**, *C54*, 349.
- [19] V. McKee, T. Metcalfe, J. Wikaira, *Acta Crystallogr.* **1996**, *C52*, 1139.
- [20] F. Eissmann, T. Böhle, F. O. R. L. Mertens, E. Weber, *Acta Crystallogr.* **2010**, *E66*, m66.
- [21] D. F. Back, G. N. M. de Oliveira, R. A. Burrow, E. E. Castellano, U. Abram, E. S. Lang, *Inorg. Chem.* **2007**, *46*, 2356.
- [22] R. L. Lord, S. E. Wheeler, H. F. Schaefer III, *J. Phys. Chem. A* **2005**, *109*, 10084.
- [23] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
- [24] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
- [25] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.