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Uwe Ruschewitz, Alexandra Glees. Three new coordination compounds with push-pull ligand p-aminobenzonitrile (4ABN). Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie, 2009, 635 (12), pp.2046. 10.1002/zaac.200900200 . hal-00512210

HAL Id: hal-00512210 https://hal.science/hal-00512210

Submitted on 28 Aug 2010 $\,$

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Zeitschrift für Anorganische und Allgemeine Chemie

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| Journal: | Zeitschrift für Anorganische und Allgemeine Chemie |
|-------------------------------|--|
| Manuscript ID: | zaac.200900200.R1 |
| Wiley - Manuscript type: | Article |
| Date Submitted by the Author: | 11-May-2009 |
| Complete List of Authors: | Ruschewitz, Uwe; Universität zu Köln, Department für Chemie Glees, Alexandra; Universität zu Köln, Department für Chemie |
| Keywords: | Coordination polymer, Crystal engineering, Crystal structure, Push- pull ligand, Transistion metals |
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Three new coordination compounds with push-pull ligand *p*aminobenzonitrile (4ABN)

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Dedicated to Prof. Martin Jansen on the occasion of his 65th birthday.

Bei der Redaktion eingegangen am

Abstract From ethanolic solutions containing *p*-aminobenzonitrile (4ABN) and the respective metal salt three new coordination compounds were obtained and their crystal structures solved and refined from X-ray single-crystal diffraction data: ${}^{2}_{\infty}$ [Ag(4ABN)_{4/2}]BF₄ (P 2₁/n, Z = 4) (1), ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂](NO₃)₂ · 2 H₂O (P $\overline{1}$, Z = 2) (2) and [Co(4ABN)₂(H₂O)₂Cl₂] (P 2₁/n, Z = 2) (3). **1** is a coordination polymer with a distorted tetrahedral AgN₄ coordination and layered polymeric ${}^{2}_{\infty}$ [Ag(4ABN)_{4/2}⁺] cations, which are held together by van der Waals interactions. It represents the first homoleptic complex of 4ABN. In **2** Jahn-Teller distorted CuN₄O₂ octahedra are connected to polymeric chain-like ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂²⁺] cations, which are interconnected by hydrogen bonds including further water molecules and NO₃⁻ anions. **3** is a complex with an octahedral CoCl₂N₂O₂ coordination. In the solid state structure, they are held together by N-H^{...}Cl hydrogen bonds.

Drei neue Koordinationsverbindungen mit dem Push-Pull-Liganden *p*-Aminobenzonitril (4ABN)

Inhaltsübersicht Aus ethanolischen Lösungen, die p-Aminobenzonitril (4ABN) und ein entsprechendes Metallsalz enthielten, konnten drei neue Koordinationsverbindungen erhalten und ihre Kristallstrukturen anhand von Röntgeneinkristallstrukturanalysen bestimmt werden: $\int_{\infty}^{2} [Ag(4ABN)_{4/2}]BF_4 (P 2_1/n, Z = 4) (1), \int_{\infty}^{1} [Cu(4ABN)_{4/2}(H_2O)_2](NO_3)_2 \cdot 2 H_2O (P \overline{1}, Z = 2)$ (2) und $[Co(4ABN)_2(H_2O)_2Cl_2]$ (P 2₁/n, Z = 2) (3). 1 ist ein Koordinationspolymer mit einer AgN₄-Koordination verzerrten tetraedrischen und schichtartigen polymeren ${}^{2}_{\infty}$ [Ag(4ABN)_{4/2}⁺]-Kationen, die durch van-der-Waals-Wechselwirkungen zusammengehalten werden. Es stellt die erste homoleptische Komplexverbindung mit 4ABN als Liganden dar. In Jahn-Teller 2 verzerrte CuN₄O₂-Oktaeder sind zu polymeren kettenförmigen $\sum_{\infty}^{1} [Cu(4ABN)_{4/2}(H_2O)_2^{2+}]$ -Kationen verknüpft, die wiederum durch Wasserstoffbrückenbindungen über die beiden Kristallwassermoleküle und die NO3-Anionen zusammengehalten werden. 3 ist ein Komplex mit einer oktaedrischen CoCl₂N₂O₂-Koordination. In der Festkörperstruktur werden diese durch N-H^{···}Cl-Wasserstoffbrückenbindungen verknüpft.

Keywords: Coordination Polymer; Crystal Engineering; Crystal Structure; Push-Pull Ligand; Transition Metals

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1 Introduction

In the last years the synthesis and structural characterisation of coordination polymers has been in the focus of many research groups world-wide. This interest is based on the easy synthetic accessibility of these compounds and their potential applications [1]. The latter are mainly concentrated on porous coordination polymers (PCP) or metal-organic frameworks (MOF) [2]. The most prominent members of this class of compounds are MOF-5 [3], MIL-53 [4] and HKUST-1 [5], where metal ions or metal-oxo clusters are linked by anions of polycarboxylic acids. But besides porosity there are also other attractive aspects of non-porous coordination polymers, e.g. magnetic, luminescent or conducting properties [6]. From a more fundamental point of view the rational synthesis of new solid state compounds. But the rational synthesis of acentric coordination polymers is still a great challenge, although several concepts have been suggested.

To enhance the probability of obtaining acentric compounds metal ions with stereochemically active lone pairs [7] or coordination polymers containing linear and trigonal planar anions [8] were used. Other concepts are based on diamondoid networks [9], helical chains [10] or banana-shaped ligands [11]. The former concept seems to be very versatile, as the diamondoid topology is the topology most frequently found for coordination polymers [12]. In this concept – in simple words – knots (metal ions or clusters), arranged like carbon atoms in the diamond structure, are linked by non-symmetric ligands. If interpenetration is excluded, an acentric compound must result. Several compounds have been prepared, which confirm this concept [9]. Some of them show reasonably high SHG (second harmonic generation) coefficients. These coefficients could be enhanced by the use of so-called push-pull ligands, which contain an acceptor and a donor group connected by a conjugated π -system [13].

In this respect an interesting and simple push-pull ligand is *p*-aminobenzonitrile (4ABN). Surprisingly, only few coordination polymers have been reported with this neutral ligand. In $_{\infty}^{1}$ [Cu(4ABN)_{4/2}(N(CN)₂)₂] [14] and $_{\infty}^{1}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN) [15] 4ABN acts as a linker, which connects octahedral metal centres to a chain-like polymer. In $_{\infty}^{1}$ [Ni(4ABN)₂(SCN)_{4/2}] [15] and $_{\infty}^{1}$ [Cd(4ABN)₂(SCN)_{4/2}] [16] however, 4ABN is not a linking ligand. It is solely coordinating by the amino group in the former and by the cyano group in the latter compound. Here, SCN⁻ acts as a bridging ligand to form chain-like polymers. There are also some other compounds reported in the literature, which contain

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4ABN as ligand, but none of them can be classified as a coordination polymer [14, 17]. In all compounds containing 4ABN as a ligand, the metal centres are coordinated octahedrally and centrosymmetric space groups are found. In the following we will present our first results on the synthesis and structural characterisation of new coordination compounds with *p*-aminobenzonitrile (4ABN).

2 Synthesis

Single crystals of 1 - 3 were obtained from ethanolic solutions containing *p*-aminobenzonitrile (4ABN) and the respective metal salt. Purity was checked by X-ray powder diffraction (Huber G 670, CuK α_1 radiation) and elemental analysis. As the synthesis of new coordination compounds with 4ABN, its coordination behaviour and the crystal chemistry of these new coordination compounds was in the focus of this investigation, it was not attempted to optimise their syntheses with respect to purity and/or yield. Therefore, no yield was determined.

 $_{\infty}^{2}$ [Ag(4ABN)_{4/2}]BF₄ (1): 0.2168 g (1.1 mmol) AgBF₄ were dissolved in 10 mL ethanol and filled in the left leg of a W-shaped tube. The legs were separated by two ceramic filters. The right leg was filled with 0.1978 g (1.7 mmol) 4ABN (*p*-aminobenzonitrile) dissolved in 10 mL ethanol. The remaining leg in the middle was filled up with ethanol so that all legs were filled up to the same level, and finally closed with a plug. After ten days at room temperature yellow, transparent crystals of **1** grew in the middle leg, from which single crystals suitable for a structure analysis were isolated. According to X-ray powder diffraction data the sample is single-phase. This is confirmed by the elemental analysis: calc. for C14 H12 Ag B F4 N4 (430.96): C 39.02 %, N 12.99 %, H 2.81 %; found: C 38.82 %, N 12.89 %, H 2.49 %.

 $_{\infty}^{1}$ [Cu(4ABN)_{4/2}(H₂O)₂](NO₃)₂ · 2 H₂O (**2**): In a beaker 0.2055 g (1 mmol) Cu(NO₃)₂ · H₂O and 0.1181 g (1 mmol) 4ABN (*p*-aminobenzonitrile) were dissolved in 10 mL ethanol. The beaker was sealed with a perforated foil. After evaporation of the solvent at room temperature green crystals precipitated, from which a single crystal of **2** suitable for a structure analysis was isolated. According to X-ray powder diffraction data the sample is not single-phase.

 $[Co(4ABN)_2(H_2O)_2Cl_2]$ (3): In a beaker 0.2378 g (1 mmol) $CoCl_2 \cdot 6 H_2O$ and 0.1181 g (1 mmol) 4ABN (*p*-aminobenzonitrile) were dissolved in 10 mL ethanol. The beaker was sealed

with a perforated foil. After evaporation of the solvent at room temperature red crystals precipitated, from which a single crystal of **3** suitable for a structure analysis was isolated. According to X-ray powder diffraction data the sample contains unreacted $CoCl_2 \cdot 6 H_2O$ next to **3**. This is confirmed by the elemental analysis: calc. for C14 H16 Cl2 Co N4 O2 (402.14): C 41.81 %, N 13.93 %, H 4.01 %; found: C 22.74 %, N 7.48 %, H 2.59 %.

3 Crystal Structures

Single crystals of 1 - 3 were isolated from the precipitates as described above and mounted in sealed glass capillaries on a Stoe IPDS I or Stoe IPDS II single crystal diffractometer (T ≈ 293 K, MoK α radiation). For data collection and reduction the Stoe program package [18] was applied. The structural models were solved using SIR-92 [19] and completed using difference Fourier maps calculated with SHELXL-97 [20], which was also used for final refinement. All programs were run under the WinGX system [21]. All non-hydrogen atoms were refined anisotropically. For 1 and 2 all hydrogen atoms of the 4ABN ligand were calculated and refined "riding" with fixed distances (C-H: 93 pm; N-H: 90 pm). In 2 some positions of hydrogen atoms of water molecules were found in difference Fourier maps, but it was not possible to refine them in a stable way [22]. Therefore they were omitted in the final refinement. The number of observed reflections for 1 and 2 is rather small, which is probably due to the fact that both single crystals were measured on a STOE IPDS I, which occasionally leads low reflection : parameter ratios.

For **3** all hydrogen atoms of the 4ABN ligand were found in difference Fourier maps and refined without constraints. Position of hydrogen atoms of water molecules were also localize in difference Fourier maps and refined with restrained distances (O-H: 82 pm). More details of the structural analysis [23] are given in table 1. Selected interatomic distances and angles are listed in table 2.

< Table 1 > < Table 2 >

1 crystallizes in centrosymmetric space group P $2_1/n$, Z = 4. An ORTEP view of 1 is shown in figure 1 representing the coordination sphere of Ag⁺. Ag is coordinated tetrahedrally by four nitrogen atoms of four different 4ABN ligands, thus representing the first homoleptic complex of 4ABN known up to now. Two of these nitrogen atoms belong to amino groups (N1, N3) and two to cyano groups (N2, N4). The tetrahedron is distorted, the Ag-N distances range

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from 221.0 pm (Ag1-N2) and 231.9 pm (Ag1-N4) to 236.5 pm (Ag1-N1) and 244.8 pm (Ag1-N3). Thus, the Ag-N distances between the Ag⁺ cation and coordinating cyano groups are distinctively shorter. Consistently, the largest N-Ag-N angle is found for N2-Ag1-N4 with 126.4°. The distances and angles within the 4ABN ligand are as expected (table 2) and the BF_4^- anion is heavily disordered as can be seen from the large ellipsoids shown in the ORTEP plot (figure 1).

< Figure 1 >

4ABN ligands connect AgN₄ tetrahedra to a polymeric structure that is sketched in figure 2 in a view along [010]. Each Ag atom is connected to three further Ag atoms by the 4ABN linkers, i.e. two 4ABN linkers connect the same Ag atoms. AgN₄ tetrahedra and linear 4ABN linkers form a corrugated cationic double-layer of composition $\frac{2}{\infty}$ [Ag(4ABN)_{4/2}⁺]. The stacking of two of these double-layers is shown in figure 2.

< Figure 2 >

No short distances between these layers as well as between the cationic layers and BF_4^- anions are found that can be interpreted as strong hydrogen bonds. The shortest F^-H distances are 235.4 pm (F1-H1; F1-N1: 321.4 pm) and 243.9 pm (F3-H3; F3-N3: 324.4 pm), the shortest interlayer contacts are N1⁻⁻N4 = 323.7 pm. The shortest distance between F^- and Ag⁺ is Ag1-F1 = 330.3 pm. Thus it must be assumed that the layers and anions are held together just by van der Waals interactions.

2 crystallizes in centrosymmetric space group P $\overline{1}$, Z = 2. An ORTEP view of **2** is given in figure 3 showing the coordination sphere of Cu1 (above) and Cu2 (below). Both are located on a centre of symmetry and are coordinated octahedrally by four nitrogen atoms of four different 4ABN ligands and two oxygen atoms of two water molecules. The octahedra are distorted due to Jahn-Teller effect as expected for Cu²⁺ (3d⁹). The coordination sphere of Cu1 consists of two short Cu1-O1 (200.0 pm) and two short Cu1-N1 (203.9 pm) contacts. The latter involves the amino group of the 4ABN ligand. A longer bond is formed to the cyano group of the ligand, Cu1-N2 = 246.8 pm. Similarly, the coordination sphere of Cu2 consists of two short Cu2-O2 (195.3 pm), two short Cu2-N3 (208.4 pm) and two longer Cu2-N4 (248.7 pm) contacts. Again, the longer bonds are formed to the cyano groups of the 4ABN ligands. The angles within the CuN4O2 octahedra range from 81.9° to 98.1° (Cu1) and from 82.8° to 97.2° (Cu2). The distances and angles within the 4ABN ligand are as expected (table 2).

< Figure 3 >

A simplified packing diagram of the crystal structure of **2** is shown in figure 4. 4ABN ligands connect CuN₄O₂ octahedra to a polymeric cationic chain-like structure of composition $\frac{1}{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂²⁺]. Cu1 and Cu2 are parts of different chains, but both run along [010]. They are arranged similar to a hexagonal rod packing. The chains formed around Cu1 and Cu2 are very similar to each other: CuN₄O₂ octahedra are connected by 4ABN ligands in a way that both amino groups – cyano groups and water molecules as well – are coordinated *trans* to each other. Both *cis* coordinating 4ABN ligands are almost parallel to each other with respect to their phenylene rings, but the coordinating group at one Cu centre is either an amino or a cyano group. The chains formed around Cu1 and Cu2 differ by a different tilting with respect to the c axis (figure 4). This chain-like structural motif in **2** is very similar to the one found in $\frac{1}{\infty}$ [Cu(4ABN)_{4/2}(N(CN)₂)₂] [14] and $\frac{1}{\infty}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN) [15].

< Figure 4 >

The chains are connected with each other to a 3D framework by hydrogen bonds, which involve two crystallographically distinct NO_3^- anions and two additional water molecules. These hydrogen bonds are also shown in figure 4, the distances are listed in table 3. The shortest O^{...}O distances are found between water molecules (O2^{...}O9 = 259.3 pm; O2^{...}O10 = 261.4 pm), the O^{...}O distances between water molecules and the oxygen atoms of the NO₃⁻ anion are slightly longer (shortest distance: O1^{...}O7 = 265.7 pm).

< Table 3 >

3 crystallizes in centrosymmetric space group P $2_1/n$, Z = 2. An ORTEP view of **3** is given in figure 5 showing the coordination sphere of Co1, which is located on a centre of symmetry and coordinated octahedrally by two oxygen atoms of water molecules, two Cl⁻ anions and two nitrogen atoms of the cyano groups stemming from two different 4ABN ligands. Alike ligands are coordinating *trans* to each other. The distances within this octahedron are as expected (table 2) taking the larger size of Cl⁻ into account. The angles within the CoCl₂N₂O₂ octahedron range from 86.96° to 93.04°. The distances and angles within the 4ABN ligand show no unexpected values with the exception of N2-C5 distance, which is slightly shorter than the respective distances in **1** and **2** (table 2). This is due to the fact that in **3** the amino group of 4ABN is non-coordinating. These distances will be discussed in more detail in the following chapter (table 4).

< Figure 5 >

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A packing diagram of the crystal structure of **3** is shown in figure 6. **3** cannot be considered as a coordination polymer, as the amino group of 4ABN is non-coordinating and thus 4ABN is not linking two metal centres. **3** must be described as consisting of isolated complexes. These complexes are connected by hydrogen bonds to form a 3D structure in the solid state. As no $O^{-}O$ and $N^{-}O$ distances shorter than 300 pm are found (shortest $N^{-}O$ distance: $N2^{-}O1 = 300.7$ pm), strong hydrogen bonds between water molecules and nitrogen atoms of the 4ABN ligand can be excluded. Distances in the range discussed for N-H⁻⁻Cl hydrogen bonds [24] are found between N2-H1⁻⁻Cl1 and N2-H2⁻⁻Cl1 (N2⁻⁻Cl1 = 347.9 and 339.5 pm, respectively; table 3). But according to the distances given in the literature (315.9 pm [24a)] – 358.7 pm [24c)]) the N-H⁻⁻Cl hydrogen bonds in **3** must be classified as weak. Still, we consider that these N-H⁻⁻Cl hydrogen bonds connect the complexes to form a 3D structure. These bonds are shown in figure 6 as dashed lines. Also weak O1-H8...Cl1 hydrogen bonds (O1⁻⁻⁻Cl1 = 312.2 pm; table 3) are found. They have been omitted in figure 6.

Conclusion

We have been able to synthesize three new coordination compounds with the 4ABN ligand. Two of them (1, 2) can be classified as coordination polymers. 1 is the first homoleptic complex of 4ABN and the first coordination polymer with 4ABN as linking ligand, in which a non-octahedral coordination is found. In 1 Ag is coordinated tetrahedrally by four linear linking 4ABN ligands. 4ABN connects the central Ag atom with three neighbouring Ag atoms – two 4ABN ligands connect the same Ag atoms - so that not a diamond-like topology results, but a layered structure. 1 as well as 2 and 3, where octahedral coordination spheres of the central metal ions are found, crystallize in centrosymmetric space groups. By varying the ratio of AgBF₄ and 4ABN in the synthesis of 1 from 1:1.5 to 1:1 and 1:2 it was not possible to obtain a new compound. Always 1 was the product of these syntheses. Thus, it was not possible to synthesize a further example of a non-centrosymmetric coordination compound with a diamondoid topology to prove the concept of Evans and Lin [9a)].

In the synthesis of 1 - 3 three different anions (BF₄⁻, NO₃⁻, Cl⁻) were used. Best results were obtained with BF₄⁻ in **1**. As BF₄⁻ is only weakly coordinating it is neither involved in the coordination of Ag nor does it form strong hydrogen bonds. Although ethanol was not dried prior to the synthesis, no inclusion of water was observed. The coordination sphere of Ag in **1** is only formed by 4ABN ligands. In **2** NO₃⁻ is part of a complex hydrogen bonding network, which involves coordinating and crystal water molecules. These water molecules probably

stem from Cu(NO₃)₂ · H₂O, which was used as starting material, and the solvent, which was again non-dried ethanol. In **3** water molecules as well as Cl⁻ anions are part of the coordination sphere of Co. Again, the starting material CoCl₂ · 6 H₂O and the solvent (non-dried ethanol) must be assumed as the source of the water molecules. From these results further experiments with weakly coordinating anions (BF₄⁻, PF₆⁻ etc.) and metal ions, which prefer a tetrahedral coordination sphere (e.g. Zn²⁺), are most promising to obtain a coordination polymer with 4ABN and a diamondoid topology.

In table 4 we have summarized some structural data of coordination compounds containing 4ABN. The atom-numbering scheme is given in scheme 1:

< Scheme 1 >

Up to now four compounds are known, in which 4ABN acts as a linking ligand. In 1 and $\int_{\infty}^{1} [Ni(4ABN)_{4/2}(SCN)_2](4ABN)$ the M-N(cyano) bond is distinctively shorter than the M-N(amino) bond. This is the expected behaviour, as the cyano group is a better σ -donor and a better π -acceptor ligand compared with the amino group. Especially for electron rich metals like Ag and Ni a strong backbonding is expected for M^{...}N=C coordination. Surprisingly, in both copper compounds the axial coordination of the Jahn-Teller distorted Cu octahedron is formed by cyano groups with distinctively longer Cu-N(cyano) bonds compared to Cu-N(amino) bonds, which are formed in the equatorial plane. Usually, stronger ligands prefer the equatorial positions. It is possible that specific steric reasons are responsible for this behaviour.

2, ${}_{\infty}^{1}$ [Cu(4ABN)_{4/2}(N(CN)₂)₂] and ${}_{\infty}^{1}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN) form chain-like polymers, in **1** a layered polymeric cation is formed. Thus, a 3D coordination polymer is still unknown for compounds with the 4ABN ligand. In the introduction it was already mentioned that 4ABN is an interesting push-pull ligand, in which electrons can easily transferred between its functional groups. This should have an influence on the bond distances within the ligand if coordinating to metal ions. As can be seen in table 4 only the C₄-N₄ distances show a significant influence in this respect. For a coordinating amino group the C₄-N₄ bond is several pm longer (140.6 – 143.0 pm; d_{mean} = 142.0 pm) than for 4ABN with a non-coordinating amino group (136.2 – 138.8 pm; d_{mean} = 137.1 pm). ${}_{\infty}^{1}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN) contains a non-coordinated 4ABN molecule. Here C₄-N₄ is 135.4 pm. This behaviour can easily be explained by two mesomeric forms of 4ABN shown in scheme 1. For non-coordinating 4ABN an aromatic and an iminoquinone form can be formulated. The latter is the explanation

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for a shorter C₄-N₄ bond as found for free 4ABN in $_{\infty}^{-1}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN). A similar behaviour is found, if the cyano group of 4ABN is coordinating. But in case of a coordinating amino group the iminoquinone form is no longer relevant and C₄-N₄ distances as expected for a C-N single bond are found.

The distances within the cyano group do not show such a correlation. For free 4ABN in $\frac{1}{\infty}$ [Ni(4ABN)_{4/2}(SCN)₂](4ABN) no elongation of the C₇-N₇ bond is found (114.7 pm), as expected from the influence of the mesomeric iminoquinone form. For a coordinating cyano group C₇-N₇ distances between 112.5 and 114.8 pm are observed (d_{mean} = 113.9 pm) and for 4ABN with a non-coordinating cyano group bonds range from 113.4 to 114.8 pm (d_{mean} = 114.2 pm). This is not significant as well as the trend of the distances between C₁ and C₇. Thus, only d(C₄-N₄) can be used as a structural indicator for a donor-acceptor behaviour of 4ABN in coordination compounds. But it should be mentioned that frequencies of the CN stretching vibrations are probably a much better indicator for donor-acceptor behaviour of 4ABN than C-N distances. Unfortunately – to our knowledge – no such data are given for the compounds reported in the literature up to now [14-17]. We obtained the following data (IR, KBr) for 1 (v(CN)/cm⁻¹: 2215 s, 2231 sh, 2246 w) and 3 (v(CN)/cm⁻¹: 2243 s, 2263 w). The smaller frequencies in **1** are a good indicator for the stronger backbonding of electron rich Ag⁺ compared to Co²⁺ in **3**.

Acknowledgements

We would like to thank Dr. Ingo Pantenburg, Dr. Irena Stein and Mrs. Ingrid Müller for their help with X-ray single crystal data collection and analysis as well Prof. Dr. Axel Klein for helpful discussions.

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| [23] | Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-724675 ($_{\infty}^{2}$ [Ag(4ABN) _{4/2}]BF ₄ (1)), CCDC- 724676 ([Co(4ABN) ₂ (H ₂ O) ₂ Cl ₂] (3)), and CCDC-724677 ($_{\infty}^{1}$ [Cu(4ABN) _{4/2} (H ₂ O) ₂](NO ₃) ₂ · 2 H ₂ O (2)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]. |
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Table 1Details of single crystal structural analysis of ${}^{2}_{\infty}$ [Ag(4ABN)_{4/2}]BF₄ (1), ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H_2O)_2](NO_3)_2 · 2 H_2O (2) and [Co(4ABN)_2(H_2O)_2Cl_2] (3) (4ABN: *p*-aminobenzonitrile).

| | $_{\infty}^{2}$ [Ag(4ABN) _{4/2}]BF ₄ (1) | $_{\infty}^{1}$ [Cu(4ABN) _{4/2} (H ₂ O) ₂](NO ₃) ₂ · 2 H ₂ O (2) | $[Co(4ABN)_2(H_2O)_2Cl_2]$ (3) |
|---------------------------|---|--|---------------------------------|
| Formula | C14 H12 Ag B F4 N4 | C14 H20 Cu N6 O10 | C14 H16 Cl2 Co N4 O2 |
| Crystal size/mm | 0.2 x 0.2 x 0.2 | 0.8 x 0.3 x 0.1 | 0.2 x 0.2 x 0.05 |
| Crystal color | yellow | green | red |
| Diffractometer, λ | Stoe IPDS I; 71.073 pm | Stoe IPDS I; 71.073 pm | Stoe IPDS II; 71.073 pm |
| Temperature/K | 293(2) | 293(2) | 293(2) |
| Space group; Z | P 2 ₁ /n (no. 14); 4 | P 1 (no. 2); 2 | P 2 ₁ /n (no. 14); 2 |
| Unit cell | a = 933.1(13) pm | a = 751.6(3) pm | a = 893.8(2) pm |
| | b = 973.80(11) pm | b = 966.5(2) pm | b = 576.25(6) pm |
| | c = 1826.3(3) pm | c = 1464.5(3) pm | c = 1646.8(3) pm |
| | $\alpha = 90^{\circ}$ | $\alpha = 81.01(3)^{\circ}$ | $\alpha = 90^{\circ}$ |
| | $\beta = 91.47(2)^{\circ}$ | $\beta = 80.51(4)^{\circ}$ | $\beta = 104.92(1)^{\circ}$ |
| | $\gamma = 90^{\circ}$ | $\gamma = 80.52(4)^{\circ}$ | $\gamma = 90^{\circ}$ |
| Volume | $1.659(2) \text{ nm}^3$ | $1.0258(5) \text{ nm}^3$ | $0.8196(2) \text{ nm}^3$ |
| Density calculated | 1.726 kg/dm^3 | 1.579 kg/dm^3 | 1.630 kg/dm^3 |
| $2\theta_{max}$ | 56.4° | 56.2° | 54.6° |
| Number of reflections: | | | |
| independent | 4048 | 4581 | 1832 |
| | | | |

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| $F^2 > 2\sigma(F^2)$ | 1389 | 1459 | 1374 |
|--|--|--|--|
| µ/mm ⁻¹ | 1.26 | 1.13 | 1.39 |
| R1 (F ² > $2\sigma(F^2)$) | 0.0442 | 0.0341 | 0.0322 |
| wR2 (all data) | 0.1054 | 0.0800 | 0.0879 |
| GooF | 0.748 | 0.568 | 1.055 |
| Number of refined | | | |
| parameters | 220 | 284 | 139 |
| $\Delta ho_{min/max}$ /pm ⁻³ | -0.75·10 ⁻⁶ / 0.69·10 ⁻⁶ | -0.31·10 ⁻⁶ / 0.34·10 ⁻⁶ | -0.45.10 ⁻⁶ / 0.31.10 ⁻⁶ |

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Table 2 Selected interatomic distances (pm) and angles (°) in ${}^{2}_{\infty}$ [Ag(4ABN)_{4/2}]BF₄ (1), ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂](NO₃)₂ · 2 H₂O (2) and [Co(4ABN)₂(H₂O)₂Cl₂] (3) (4ABN: *p*-aminobenzonitrile).

| ${}^{2}_{\infty}$ [Ag(4ABN) _{4/2}]BF ₄ (1) | $_{\infty}^{1}$ [Cu(4ABN) _{4/2} (H ₂ O) ₂](NO ₃) ₂ · 2 H ₂ O (2) | $[Co(4ABN)_2(H_2O)_2Cl_2]$ (3) | | |
|--|--|--------------------------------|--|--|
| Ag1 - N2 221.0(4) | Cul - Ol 200.0(3) 2x | Col - Ol 211.3(2) 2x | | |
| - N4 231.9(5) | - N1 203.9(4) 2x | - N1 216.2(2) 2x | | |
| - N1 236.5(5) | - N2 246.8(5) 2x | - Cl1 241.84(7) 2x | | |
| - N3 244.8(6) | Cu2 - O2 195.3(3) 2x | | | |
| | - N3 208.4(4) 2x | | | |
| | - N4 248.7(6) 2x | | | |
| N1 - C1 141.7(7) | N1 - C1 142.1(6) | N1 - C1 114.0(3) | | |
| N2 - C7 113.9(6) | N2 - C7 113.1(6) | N2 - C5 138.9(3) | | |
| N3 - C8 140.6(7) | N3 - C8 143.0(6) | | | |
| N4 - C14 113.9(7) | N4 - C14 114.3(6) | | | |
| N2 - Ag1 - N4 126.4(2) | Ol - Cul - Nl 87.8(2) 2x | O1 - Co1 - N1 87.71(8) 2x | | |
| N2 - Ag1 - N1 119.2(2) | O1 - Cu1 - N2 88.2(1) 2x | O1 - Co1 - Cl1 88.48(6) 2x | | |
| N4 - Ag1 - N1 96.4(2) | N1 - Cu1 - N2 81.9(2) 2x | N1 - Co1 - Cl1 86.96(7) 2x | | |
| N2 - Ag1 - N3 99.9(2) | 02 - Cu2 - N3 88.7(2) 2x | | | |
| N4 - Ag1 - N3 96.1(2) | O2 - Cu2 - N4 89.3(2) 2x | | | |
| N1 - Ag1 - N3 118.1(2) | N3 - Cu2 - N4 82.8(2) 2x | | | |
| C1 - N1 - Ag1 115.1(4) | C1 - N1 - Cu1 118.4(3) | C1 - N1 - Co1 170.2(2) | | |
| C7 - N2 - Ag1 172.1(6) | C7 - N2 - Cu1 154.0(5) | | | |
| C8 - N3 - Ag1 113.4(4) | C8 - N3 - Cu2 117.9(3) | | | |

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| C14 - N4 - Ag1 | 146.5(6) | C14 - N4 - Cu2 | 152.7(5) | | |
|----------------|----------|----------------|----------|--------------|----------|
| C4 - C7 - N2 | 178.5(7) | C4 - C7 - N2 | 177.3(6) | C2 - C1 - N1 | 179.5(3) |
| C11 - C14 - N4 | 178.7(7) | C11 - C14 - N4 | 176.7(6) | | |

| Table 3 | Hydrogen bonds (pm) and selected interatomic angles (°) in ${}^{1}_{\infty}$ [Cu(4ABN) _{4/2} (H ₂ O) ₂](NO ₃) ₂ · 2 H ₂ O (2) and [Co(4ABN) ₂ (H ₂ O) ₂ Cl ₂] |
|---------------------|---|
| (3) (4ABN: | <i>p</i> -aminobenzonitrile). |

| $_{\infty}^{1}$ [Cu(4ABN) _{4/2} (H ₂ O) ₂](NO ₃) ₂ · 2 H ₂ O (2) | | $[Co(4ABN)_2(H_2O)_2Cl_2]$ (3) | | | | | |
|--|----------|--------------------------------|-------|--------|----------|---------|--|
| | DA | | D-H | НА | DA | D-H···A | |
| 01 04 | 269.2(7) | N2 - H1 ··· Cl1 | 88(3) | 262(3) | 347.9(3) | 166(3) | |
| 01 07 | 265.7(5) | N2 - H2 ··· Cl1 | 89(4) | 267(4) | 339.5(3) | 140(3) | |
| 02 09 | 259.3(5) | 01 - H8 ··· Cl1 | 83(2) | 233(3) | 312.2(3) | 162(3) | |
| 02 010 | 261.4(7) | 01 – H9 ··· N2 | 82(3) | 219(3) | 300.7(4) | 174(3) | |
| 03 09 | 277.5(5) | | | | | | |
| 05 … 010 | 286.4(6) | | | | | | |
| 07 09 | 269.2(6) | | | | | | |
| 08 010 | 281.9(6) | | | | | | |

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| Table 4 | Selected interatomic | distances in | n coordination | compounds | containing | <i>p</i> -aminobenzonitrile | (4ABN) | as ligand | (atom-numbering |
|----------------|----------------------|--------------|----------------|-----------|------------|-----------------------------|--------|-----------|-----------------|
| according to s | cheme 1). | | | | | | | | |

| Compound | M-N ₇ | C ₇ -N ₇ | C ₁ -C ₇ | M-N ₄ | C ₄ -N ₄ | Ref. | | | | |
|---|------------------|--------------------------------|--------------------------------|------------------|--------------------------------|-----------|--|--|--|--|
| Amino and cyano group of 4ABN coordinating | | | | | | | | | | |
| 1 | 221.0 | 113.9 | 142.5 | 236.5 | 140.6 | this work | | | | |
| | 231.9 | 113.9 | 141.6 | 244.8 | 141.7 | | | | | |
| 2 | 246.8 | 113.1 | 144.1 | 203.9 | 142.1 | this work | | | | |
| | 248.7 | 114.3 | 143.1 | 208.4 | 143.0 | | | | | |
| ${}^{1}_{\infty}$ [Cu(4ABN) _{4/2} (N(CN) ₂) ₂] | 249.7 | 114.8 | 144.5 | 205.5 | 142.8 | [14] | | | | |
| $^{1}_{\infty}$ [Ni(4ABN) _{4/2} (SCN) ₂](4ABN) | 207.7 | 114.0 | 144.0 | 217.7 | 141.8 | [15] | | | | |
| | 208.5 | 114.4 | 143.8 | 218.1 | 142.2 | | | | | |
| | | 114.7 ^a | 143.4 | | 135.4 | | | | | |
| | | Only amino grou | p of 4ABN coord | inating | I | | | | | |
| $^{1}_{\infty}$ [Ni(4ABN) ₂ (SCN) _{4/2}] | | 113.4 | 144.8 | 214.4 | 142.4 | [15] | | | | |
| | | 113.9 | 143.3 | 215.0 | 142.5 | | | | | |
| $[Ni(4ABN)_2(N(CN)_2)_2(H_2O)_2]$ | | 114.8 | 144.0 | 215.1 | 141.7 | [14] | | | | |
| $[Cu(4ABN)_2(N(CN)_2)_2(H_2O)_2]$ | | 114.7 | 144.2 | 214.8 | 141.7 | [14] | | | | |
| | | Only cyano grou | p of 4ABN coord | inating | 1 | | | | | |
| $^{1}_{\infty}$ [Cd(4ABN) ₂ (SCN) _{4/2}] | 234.1 | 113.7 | 142.8 | | 136.2 | [16] | | | | |
| 3 | 216.1 | 114.2 | 143.7 | | 138.8 | this work | | | | |

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| [Ni(4ABN)(PPh ₃)(Cp)]PF ₆ | 185.4 | 112.5 | 142.2 | | 136.2 | [17] |
|--|----------------|------------------|-------------|-----|-------|------|
| ^a The crystal structure contains one | 4ABN molecule, | which is non-coo | ordinating. | 1 1 | | |
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Figure captions

Fig. 1 ${}_{\infty}^{2}$ [Ag(4ABN)_{4/2}]BF₄ (1): ORTEP diagram of the coordination sphere around Ag1 showing 50% probability thermal ellipsoids and the atom-numbering scheme.

Fig. 2 ${}_{\infty}^{2}$ [Ag(4ABN)_{4/2}]BF₄ (1): Sketch of the crystal structure in a projection along [010]; Ag: large spheres, N: small spheres. The 4ABN ligand is sketched by a rod with terminating nitrogen atoms. Atoms of different layers are drawn in dark grey and light grey, respectively. BF₄⁻ anions have been omitted for clarity.

Fig. 3 ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂](NO₃)₂ · 2 H₂O (**2**): ORTEP diagram of the coordination sphere around Cu1 (above) and Cu2 (below) showing 50% probability thermal ellipsoids and the atom-numbering scheme.

Fig. 4 ${}^{1}_{\infty}$ [Cu(4ABN)_{4/2}(H₂O)₂](NO₃)₂ · 2 H₂O (**2**): Packing diagram in a projection along [100]; the 4ABN ligand is sketched by a rod with terminating nitrogen atoms. Hydrogen bonds between oxygen atoms are drawn as dashed lines.

Fig. 5 [Co(4ABN)₂(H₂O)₂Cl₂] (**3**): ORTEP diagram of the coordination sphere around Co1 showing 50% probability thermal ellipsoids and the atom-numbering scheme.

Fig. 6 $[Co(4ABN)_2(H_2O)_2Cl_2]$ (3): Packing diagram in a projection along [010]; hydrogen bonds between chlorine and hydrogen atoms are drawn as dashed lines.

Scheme 1 Mesomeric forms and atom-numbering scheme of *p*-aminobenzonitrile (4ABN) as used in table 4.













