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Na₂(smbipy) – A Bipyridine-Derived Ligand with Chelating Sulfonate Tags and Its 3d Metal Complexes

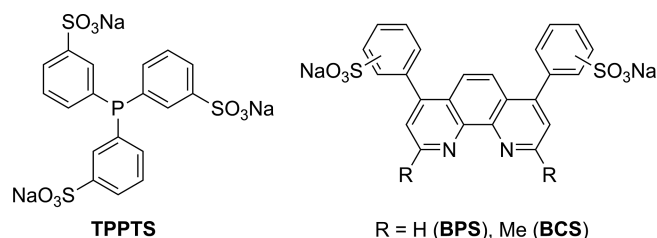
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The sulfonated bipyridine derivative disodium 6,6'-bis-(sulfonatomethyl)-2,2'-bipyridine [Na₂(smbipy)] was synthesized, and its complexation behaviour towards divalent 3d metals in aqueous solution was explored. The complexes of late 3d metals [M(smbipy)(H₂O)₂·H₂O (M = Co, Ni, Zn) and [Cu(smbipy)(H₂O)] are sparingly soluble in water, and their crystal structures show fourfold equatorial coordination (κ^4N,N',O,O') of the smbipy ligand. Ammonia-rich solutions of the Ni^{II} and Cu^{II} aqua complexes yield the decomplexation

products [Ni(NH₃)₆](smbipy), [Ni(NH₃)₅(H₂O)](smbipy) and [Cu(NH₃)₄](smbipy)·2H₂O. Buffered solutions with a reduced ammonia content lead to [Ni(smbipy)(NH₃)₂] and [Cu(smbipy)(NH₃)₃·2H₂O], and the latter shows twofold coordination of the smbipy ligand through the nitrogen atoms only (κ^2N,N'). When nearly quantitative amounts of ammonia are applied, two closely related complexes with the core motif [(smbipy)Cu(μ-OH)₂Cu] form. Crystal structures of all complexes were obtained, and their features are discussed.

Introduction

Highly polar tags are well-known and widely used to solubilize and immobilize homogeneous catalysts in polar phases, especially in bi- or multiphase systems.^[1] The most prominent example of such a tag is the sulfonate group, which has been extensively employed because of its high chemical stability and excellent solubilization properties with respect to aqueous phases. Furthermore, the sulfonate group is usually thought not to strongly interfere with coordination at the metal centre owing to a combination of its relatively poor complexation behaviour towards soft metal ions and the positioning of the tags, which are usually in the ligand backbone far away from the binding sites.^[2] Two typical examples of such sulfonated ligands are shown in Scheme 1. Tris(*m*-sulfonatophenyl)phosphane (TPPTS)^[3] is the parent compound of a wide variety of arylsulfonate-substituted phosphanes^[4] and is used in industrial-scale Rh-catalyzed hydroformylation reactions.^[5] On the other hand, bathophenanthroline disulfonate (BPS) and bathocuproine disulfonate (BCS) were studied as water-soluble ligands in olefin and alcohol oxidations.^[6] In general, the metal complexes of these ligands with “innocent tags” behave in a roughly similar way as their non-sulfonated parent compounds and, thus, facilitate the realization of catalytic transformations in polar environments.



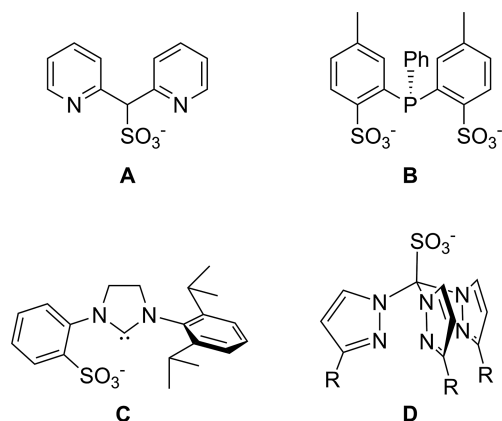
Scheme 1. Examples of sulfonated ligands that do not show significant sulfonate binding towards metal centres.

In addition to the use of “inert” sulfonate tags, which has been very successful and is vitally important for several catalytic reactions in water and other polar phases, it appears potentially attractive to use (weakly) metal-binding sulfonate tags. Thus, it could be possible to design catalysts with intramolecular leaving groups that would help to stabilize coordinatively unsaturated species in the catalytic cycle. This use of sulfonate-bearing ligands as semilabile ligands has not been investigated in great detail; some compounds featuring this structural motif are shown in Scheme 2.

Di(2-pyridyl)methanesulfonates (**A**) were used to stabilize dimethyl platinum(IV) hydrides through the reversible coordination of the sulfonate group.^[7] Reducing the solvent polarity from water to dichloromethane led to a strengthening of the Pt···O₃S contact and, thus, increased the stability of the hydrides. In palladium-based polymerization catalysts with *ortho*-phosphinoarenesulfonate ligands with one sulfonate group, the ligand usually binds to the palladium centre in a κ^2P,O -chelating fashion throughout the catalytic cycle.^[10] However, when two sulfonate groups are applied (**B**), one or both can coordinate to the metal centre depending on the solvation of the cation and the accessibility

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Scheme 2. Examples of sulfonated ligands that feature reversible sulfonate binding towards the metal.^[7–9]

of additional donors.^[8] In a related study, palladium complexes of sulfonated N-heterocyclic carbenes (**C**) showed pronounced association–dissociation processes, which led to *cis*–*trans* isomerization and different insertion behaviour of monomethyl complexes.^[9] Sulfonated tris(pyrazolyl)methanes (**D**) exhibit unusual coordination behaviour as they tend to adopt a κ^3N,N',O coordination mode despite the strong tendency of tris(pyrazolyl)methanes to symmetrically ligate metals in a κ^3N,N',N'' fashion.^[11] Furthermore, exchange equilibria between these two modes were reported for some examples.^[12]

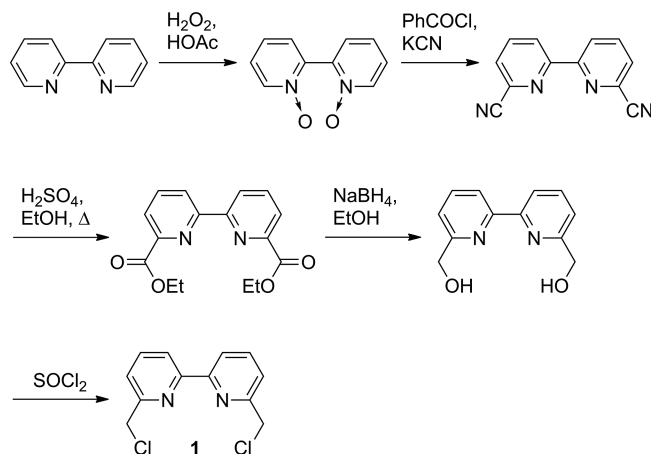
We identified 6,6'-bis(sulfonatomethyl)-2,2'-bipyridine (smbipy²⁻) as a candidate for a bipyridine-based semilabile ligand. This initial study is concerned with the question of whether this ligand is able (and likely) to coordinate to divalent metal ions in a κ^4N,N',O,O' fashion. Heavier metals of the first transition row (Co to Zn) were chosen for these experiments because of their importance in various catalytic transformations as well as their labile complexes, which seemed suitable for the study of potential ligand exchange equilibria.

Results and Discussion

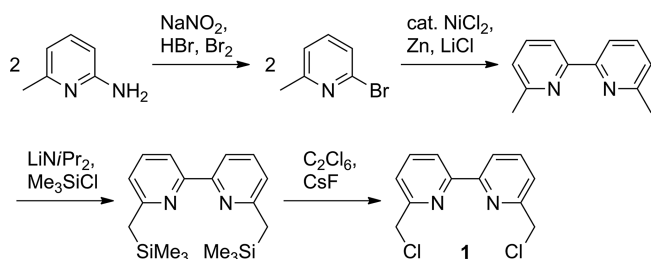
Ligand Synthesis

For the coordination of sulfonate tags to be sterically preferable, substitution at the 6,6'-positions of bipyridine seems adequate. The usual starting material for such ligands is 6,6'-bis(chloromethyl)-2,2'-bipyridine (**1**). Two literature-known syntheses of this compound were tested: the first starts from 2,2'-bipyridine (Scheme 3), and the second starts from 2-amino-6-methylpyridine (Scheme 4).

Although both strategies were serviceable, the second one was preferably used because of the smaller number of synthetic steps. Additionally, the quantitative use of cyanide can be avoided in this way. There are a variety of known coupling reactions that (directly or indirectly) form 6,6'-dimethyl-2,2'-bipyridine from 2-bromo-6-methylpyridine, including Stille coupling,^[18] electrocatalysis^[21] and reductive couplings based on Ni^[19,22] and Pd catalysts.^[21,23] We de-

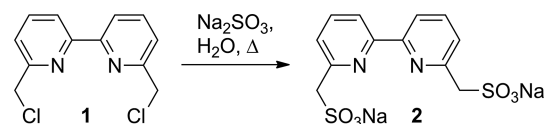


Scheme 3. Synthesis of **1** from 2,2'-bipyridine.^[13–17]



Scheme 4. Synthesis of **1** from 2-amino-6-methylpyridine.^[18–20]

cidated to employ the method described by Liao et al.^[19] because of its simple handling and ligand-free reaction conditions. It should also be mentioned that the chlorination of 6,6'-dimethyl-2,2'-bipyridine is traditionally effected by radical chlorination with *N*-chlorosuccinimide in carbon tetrachloride.^[24] The sequence shown (deprotonation followed by chlorination with C₂Cl₆) uses less-harmful solvents and, thus, presents a considerable improvement from a practical point of view.^[20] The subsequent reaction of **1** with sodium sulfite yielded the desired ligand as a disodium salt (Scheme 5).

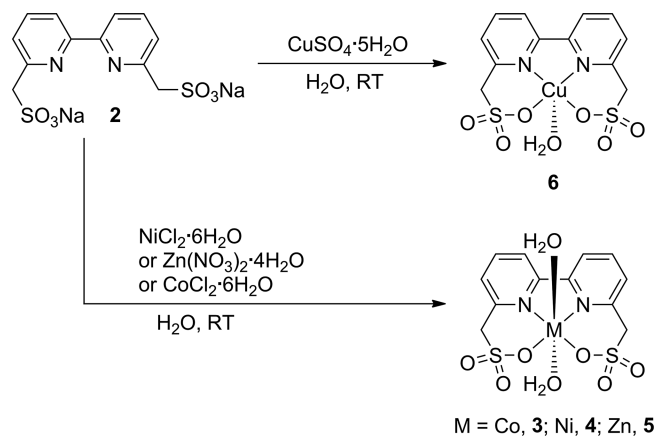


Scheme 5. Synthesis of disodium 6,6'-bis(sulfonatomethyl)-2,2'-bipyridine [Na₂(smbipy), **2**] from **1**.

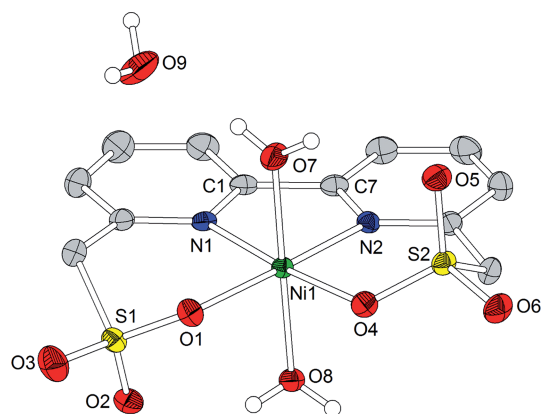
As three disodium salts potentially occur in the crude product (**2**, Na₂SO₃ and Na₂SO₄ as an oxidation side product) and the byproduct NaCl also shows similar solubility, careful extraction was necessary to ensure an effective purification of the ligand (see Exp. Sect. for details). Compound **2** is highly soluble in water, moderately soluble in dimethyl sulfoxide (DMSO), hardly soluble in alcohols and acetonitrile, and insoluble in less-polar organic solvents.

Aqua Complexes – Synthesis and Structures

To get insight into the coordination chemistry of the new hydrophilic ligand, the complexation of divalent 3d metal ions in water was studied. Upon mixing aqueous solutions containing $[M(\text{H}_2\text{O})_6]^{2+}$ ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and smbipy^{2-} , microcrystalline precipitates of $[M(\text{smbipy})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ($M = \text{Co}, \mathbf{3}; \text{Ni}, \mathbf{4}; \text{Zn}, \mathbf{5}$) and $[\text{Cu}(\text{smbipy})(\text{H}_2\text{O})] (\mathbf{6})$ were obtained almost instantly in good yields (Scheme 6). In contrast, no precipitates were obtained with $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

Scheme 6. Formation of aqua complexes with smbipy^{2-} .

Single crystals of **3–6** were obtained by slow evaporation of the respective mother liquors. X-ray diffraction (XRD) studies showed the complexes of cobalt, nickel and zinc to be isostructural (Figure 1). Selected bond lengths and angles are given in Table 1, and the crystallographic details for all compounds discussed herein are provided in the Supporting Information (Table S1). For improved clarity, no hydrogen bonds are shown in the structural depictions.

Figure 1. Molecular structure of **4**. The cobalt complex **3** and the zinc complex **5** are isostructural.

The complexes crystallize as monohydrates in the monoclinic space group $P2_1/c$ with $Z = 4$. The metal centre is coordinated in an octahedral fashion; the dianionic ligand binds to all four equatorial coordination sites in a κ^4N,N',O,O' mode, and two water molecules occupy the axial positions. As the sulfonate groups are located below

Table 1. Selected bond lengths and angles of aqua complexes **3**, **4**, **5** and **6**.

Bond length [pm]	$[M(\text{smbipy})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$			$[M(\text{smbipy})(\text{H}_2\text{O})]$
	M = Co, 3	M = Ni, 4	M = Zn, 5	M = Cu, 6
M–N1	211.7(2)	206.95(19)	213.6(2)	198.32(14)
M–N2	211.57(19)	206.45(19)	213.2(2)	202.01(14)
M–O1	209.15(17)	207.10(16)	207.21(19)	199.65(13)
M–O4	208.19(18)	205.01(16)	205.26(18)	195.12(13)
M–O7	205.6(2)	204.33(18)	210.2(2)	214.90(15)
M–O8	209.52(19)	208.14(16)	213.09(19)	–
Bond angle [°]				
N1–M–N2	80.38(8)	81.77(7)	79.38(8)	81.47(6)
N1–M–O1	93.13(7)	94.15(7)	92.89(8)	93.38(6)
N2–M–O4	94.84(7)	95.64(7)	94.66(8)	95.57(6)
O1–M–O4	91.86(7)	88.52(7)	93.29(7)	86.15(6)
N1–M–O7	86.35(8)	86.57(8)	85.52(8)	96.23(6)
N2–M–O7	90.93(8)	90.53(8)	91.37(9)	108.79(6)
N1–M–O8	94.14(8)	93.12(7)	94.35(8)	–
N2–M–O8	88.19(8)	88.59(7)	87.92(8)	–
Torsion angle [°]				
N1–C1–C7–N2	0.5(3)	0.5(3)	0.1(3)	3.5(2)
C1–N1–M–O1	177.92(16)	179.75(15)	178.28(17)	145.82(12)
C7–N2–M–O4	174.14(16)	175.36(14)	173.00(16)	163.39(12)

(S1) and above (S2) the equatorial plane, the molecular symmetry is approximated by C_2 (Figure 1). The main deviation from an ideal octahedral coordination is caused by the bipyridine N–M–N bite angle, which ranges from 79.4 to 81.8° (for Zn and Ni, respectively). This is slightly less acute than the typical values in related 2,2'-bipyridine (bipy) complexes such as $[\text{Co}(\text{bipy})(\text{OAc})_2(\text{H}_2\text{O})_2]$ (76.6°),^[25] $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4](\text{SO}_4)$ (79.4°),^[26] and $[\text{Zn}(\text{bipy})(\text{H}_2\text{O})_4](\text{C}_6\text{H}_4-1,4-\text{CO}_2)$ (76.1°).^[27] The M–N bond lengths fall in the expected ranges. Likewise, the sulfonate–metal bonds of 205.3 to 209.2 pm are at the lower end of typical chelating sulfonate bonds towards these metal centres; for example, these bonds are 210.3 pm in $[\text{Co}(\text{3-mpSO}_3)_2(\text{H}_2\text{O})_2]$ (3-mpSO₃H = 3-methylpyridine-2-sulfonic acid),^[28] 207.2 and 210.3 pm in $[\text{Ni}(\text{phen})(\text{H}_2\text{O})_2\{\text{CH}_2(\text{SO}_3)_2\}]$ (phen = 1,10-phenanthroline)^[29] and 209.8 pm in $[\text{Zn}\{\text{O}_3\text{S}(\text{CH}_2)_2\text{N}(\text{Me})(\text{CH}_2)_2\text{N}(\text{Me})(\text{CH}_2)_2\text{SO}_3\}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.^[30]

The copper complex **6** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ (Figure 2). The metal shows fivefold coordination, which results in a distorted square pyramid with a water molecule in the apical position and the bipyridine derivative in the basal positions. As both sulfonate groups are located below the basal plane, the molecular symmetry is approximated by C_s . The Cu–N bond lengths (198.3 and 202.0 pm) are significantly shorter than those in **3–5**, as are the equatorial Cu–O bond lengths (195.1 and 199.7 pm). As expected, the axial Cu–O bond length is subsequently lengthened (214.9 pm) owing to the d^9 electron configuration. However, the apical water molecule is still at a quite short distance from the metal centre in comparison to the distances in related complexes such as $[\text{Cu}(\text{bipy})(\text{PhCO}_2)_2(\text{H}_2\text{O})]$ ^[31] (222.7 pm) and $[\text{Cu}(\text{bipy})(4\text{-Me-C}_6\text{H}_4\text{CO}_2)_2(\text{H}_2\text{O})]$ (235.9 pm).^[32] Interestingly and in contrast to the octahedral complexes **3–5**, the planes de-

finer by the heteroaromatic rings and the basal plane do not coincide, as demonstrated by the C1–N1–Cu1–O1 (145.8°) and C7–N2–Cu1–O4 torsion angles (163.4°). This effect appears to be partly caused by the overall distortion of the coordination polyhedron (see below).

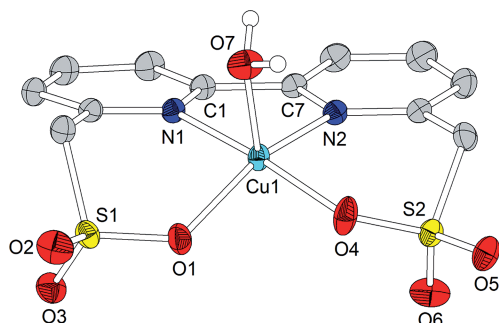


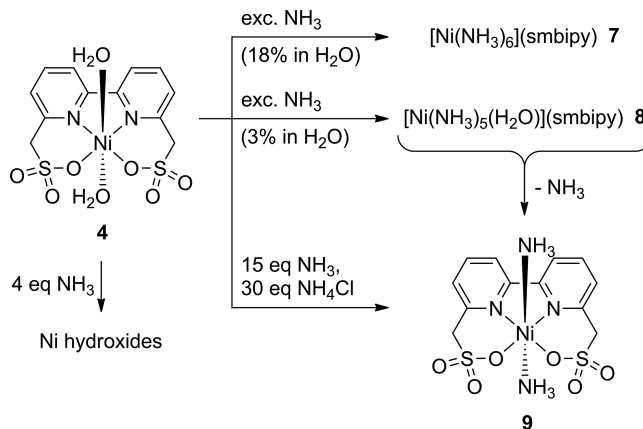
Figure 2. Molecular structure of **6**.

Aqueous solutions of **3**, **4** and **6** show absorption maxima in the visible region that are shifted hypsochromically in comparison to those of the respective hexaqua complexes {493 nm for **3** compared with 515 nm for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$; 622 nm for **4** compared with 658 and 720 nm for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$; 715 nm for **6** compared with 794 nm for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ }. Furthermore, the related nickel complexes $[\text{Ni}(\text{bipy})\text{L}_4]^{2+}$, generated in situ from $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ and the respective ligand L, feature absorption bands similar to that of **4** (622 nm) for the oxygen-bound ligands dimethyl sulfoxide (622 nm) and *N,N*-dimethylformamide (605 nm).^[33] It can be concluded that no decomplexation of smbipy^{2-} occurs in aqueous solution, and this is likely to be the main reason for the rather limited solubility of the complexes in water.

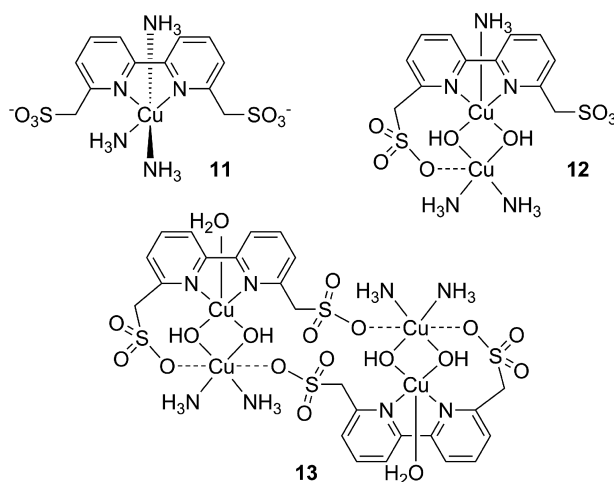
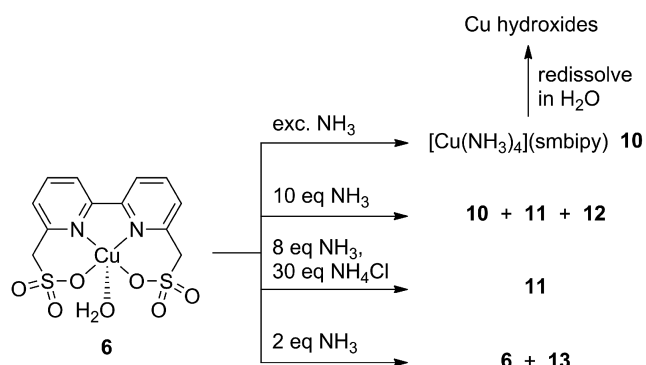
Reactions with Ammonia – Synthesis and Structures of (Partially) Decomplexed Products

As the synthesis of 3d metal complexes with smbipy^{2-} was straightforward in aqueous solutions, ligand exchange reactions in this medium seemed to be a natural next step towards a detailed understanding of the properties of the ligand. To this end, the divalent nickel (**4**) and copper (**6**) aqua complexes were treated with aqueous ammonia, which resulted in several (partly unexpected) products (Schemes 7 and 8). All of the described products were obtained in crystalline forms upon layering the aqueous solutions with ethanol.

The pale blue nickel complex **4** reacts with an excess of ammonia to form the highly water-soluble light violet salt $[\text{Ni}(\text{NH}_3)_6](\text{smbipy})$ (**7**). However, this compound readily exchanges ammonia ligands when subjected to reduced NH_3 concentrations; as a result, the violet-blue mono aqua substitution product $[\text{Ni}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{smbipy})$ (**8**) could additionally be isolated. Furthermore, additional degradation slowly occurs to afford the violet-green diammine complex $[\text{Ni}(\text{smbipy})(\text{NH}_3)_2]$ (**9**) when the solid compound is dried under vacuum or left to stand with little mother



Scheme 7. Reactions of **4** with ammonia.



Scheme 8. Reactions of **6** with ammonia (top) and isolated partial decomplexation products (bottom).

liquor. Attempts to directly access this compound by using only a small excess of ammonia resulted in the precipitation of nickel hydroxide. On the other hand, a solution buffered by ammonium chloride was successfully used to directly obtain **9**.

The reaction of copper complex **6** with an excess of ammonia yields the highly soluble violet complex $[\text{Cu}(\text{NH}_3)_4](\text{smbipy})$ (**10**). Although this reaction is rather similar to the decomplexation of the analogous nickel complex **4**, the

product appears to be relatively stable in the solid state at room temperature, and no decomposition products were identified. However, upon the dissolution of **10** in water, copper hydroxide is formed. When **6** was treated with lower concentrations of ammonia, various products were observed. With only a small excess of ammonia, a deep green solution was obtained, from which the starting material **6** and small amounts of the dark blue-green tetranuclear complex $[\text{Cu}_2(\text{smbipy})(\mu\text{-OH})_2(\text{H}_2\text{O})(\text{NH}_3)_2]_2$ (**13**) were isolated. An attempt to selectively synthesize the latter by increasing the amount of ammonia to 10 equiv. surprisingly led to the closely related dinuclear complex $[\text{Cu}_2(\text{smbipy})(\mu\text{-OH})_2(\text{NH}_3)_3]$ (**12**) as well as smaller amounts of **10**. The third product isolated from this reaction was the blue complex $[\text{Cu}(\text{smbipy})(\text{NH}_3)_3]\cdot 2\text{H}_2\text{O}$ (**11**), which could also be selectively obtained by buffering the reaction mixture with NH_4Cl .

Compounds **7** and **8** both crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$ (Figures 3 and 4). Selected bond lengths and angles are given in Table 2.

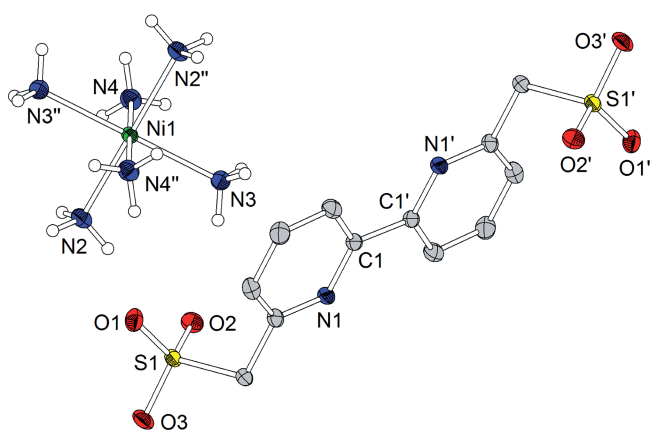


Figure 3. Molecular structure of **7**. Symmetry-related atoms are generated by (') $1 - x, -y, 2 - z$; (')' $1 - x, -y, 1 - z$.

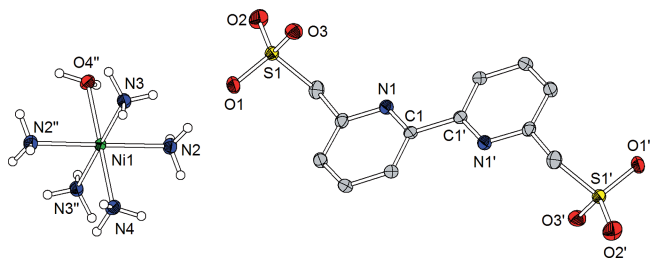


Figure 4. Molecular structure of **8**. Symmetry-related atoms are generated by (') $1 - x, 2 - y, 1 - z$; (')' $1 - x, -y, -z$. Only one occupation of the disordered N4/O4 site is shown (for details see Supporting Information).

The structure of **7** comprises a hexaaquanickel(II) dication and the ligand dianion, both of which are situated on an inversion centre. All bond lengths and angles within the only slightly distorted octahedral cation lie in the expected ranges. The nitrogen atoms of the smbipy^{2-} anion are arranged in a *trans* conformation, as is frequently found for

Table 2. Selected bond lengths and angles of **7**, **8** and **10**.

Bond length [pm]	$[\text{M}(\text{NH}_3)_x(\text{H}_2\text{O})_y](\text{smbipy})$		
	M = Ni 7	M = Ni 8	M = Cu 10 ^[a]
M–N _{min}	210.57(14)	212.32(14)	200.42(13)
M–N _{max}	214.83(16)	212.88(14)	202.05(13)
M–O	–	212.32(14) ^[b]	271.51(12) ^[c]
Bond angle [°]			
N–M–N _{min}	86.92(7)	88.18(6)	89.40(6)
N–M–N _{max}	93.08(7)	91.82(6)	90.60(6)
N–M–O _{min}	–	88.18(6) ^[b]	88.72(5) ^[c]
N–M–O _{max}	–	91.82(6) ^[b]	91.28(5) ^[c]
Torsion angle [°]			
N1–C1–C1'–N1'	180.00(13)	180.00(14)	179.98(14)

[a] Crystallizes as a dihydrate. [b] Involving water ligand. [c] Involving sulfonate group.

2,2'-bipyridine and its derivatives in the absence of (transition) metal atoms.^[34]

The structure of **8** is similar to that of **7** as both the cation and the anion are on an inversion centre. This results in a substitutional disorder of N4 and O4 with equal occupancies of 50%. All intramolecular geometric characteristics are comparable to those in **7**. A detailed discussion of the structural differences between **7** and **8** is provided as Supporting Information.

The diammine complex **9** crystallizes in the monoclinic space group $I2/a$ with $Z = 4$ (Figure 5). All bond lengths and angles are comparable to those of the diaqua analogue **4**. Owing to the crystal symmetry, the complex molecule adopts strict C_2 symmetry in this case. The most notable difference between the solid-state structures of **4** and **9** appears to be the twist of the pyridyl rings, which is significantly larger in the latter (9.7° compared with 0.5°) and also exceeds the respective value for all other smbipy complexes described herein.

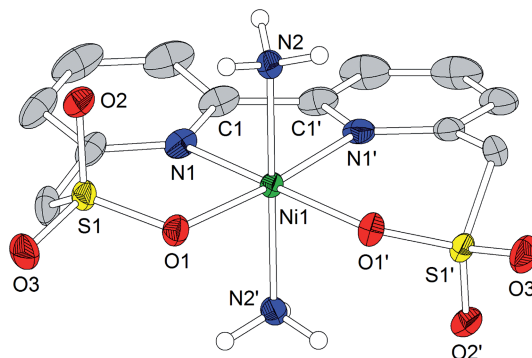


Figure 5. Molecular structure of **9**. Symmetry-related atoms are generated by (') $1/2 - x, y, -z$. Selected bond lengths [pm] and angles [°]: Ni1–N1 207.9(2), Ni1–N2 207.2(2), Ni1–O1 209.77(17); N1–Ni1–N1' 80.66(12), N1–Ni1–O1 95.24(8), O1–Ni1–O1' 88.99(2), N1–Ni1–N2 93.77(8), N1'–Ni1–N2 89.92(8); N1–C1–C1'–N1' 9.7(3), C1–N1–Ni1–O1 174.54(17).

Compound **10** crystallizes as a dihydrate in the triclinic space group $P\bar{1}$ with $Z = 1$ (Figure 6). Selected bond

lengths and angles are given in Table 2. The structure of the copper compound **10** bears some resemblance to the corresponding nickel salts **7** and **8** as it also features both the anion and the cation on inversion centres. However, the copper atom is coordinated in a tetragonal-bipyramidal manner not only by four ammonia ligands (equatorial positions) but also by two oxygen atoms from the sulfonate groups of neighbouring anions (axial positions). A comparison of the respective bond lengths [200.4 and 202.1 pm (NH_3) vs. 271.5 pm (RSO_3^-)] shows that there is a strong Jahn–Teller effect. Although the Cu–N bond lengths fall in the expected range, the sulfonate contacts are unusually long in comparison with those of related structures such as $[\text{Cu}(\text{H}_2\text{O})_4(\text{MeSO}_3)_2]^{[35]}$ (238.7 pm) and $[\text{Cu}(\text{NH}_3)_4(\text{EtOCH}_2\text{CO}_2)_2]^{[36]}$ (251.5 pm). An example of a complex with a similarly weak axial sulfonate coordination is $[\text{Cu}(4\text{-MeC}_5\text{H}_4\text{N})_4(\text{OTs})_2]\cdot 2\text{H}_2\text{O}$ (272.1 pm; OTs = tosylate).^[37] In **10**, the dianionic nature of smbipy^{2-} leads to the formation of infinite strands through sulfonate coordination. As the compound is readily soluble in ammonia-containing solutions, it appears likely that these contacts are lost upon dissolution.

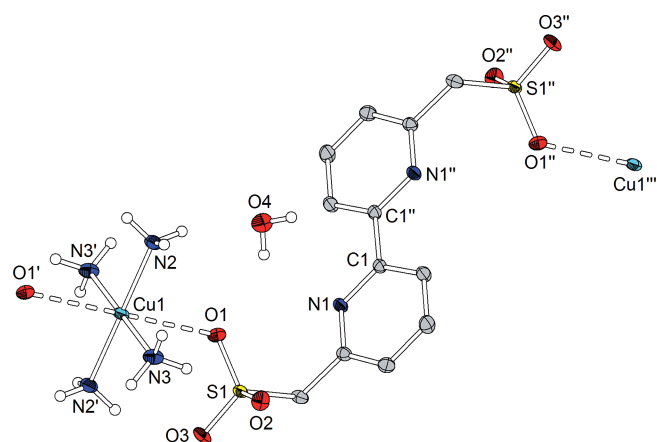


Figure 6. Molecular structure of **10**. Symmetry-related atoms are generated by (') $-x, 1-y, 1-z$; (') $1-x, 1-y, -z$; (') $1+x, y, -1+z$.

Complex **11** crystallizes as a dihydrate in the monoclinic space group $P2_1/n$ with $Z = 4$ (Figure 7). Selected bond lengths and angles are given in Table 3.

The coordination sphere around the copper atom is distorted square-pyramidal with three molecules of ammonia and one pyridyl nitrogen atom (N2) in the basal plane, and the second pyridyl nitrogen atom (N1) fills the apical position. Thus, the Cu–N bond lengths differ significantly (208.4 and 220.9 pm for Cu2–N2 and Cu2–N1, respectively). Comparable geometries have been reported for some related complexes, for example, $[\text{Cu}(\text{bipy})(\text{PMDETA})](\text{ClO}_4)_2$ (202.1 and 223.2 pm; PMDETA = N,N,N',N',N' -pentamethyldiethylenetriamine),^[38] but this geometry can be regarded as relatively uncommon in comparison to the usual symmetric 2,2'-bipyridine coordination. As there are no contacts between the sulfonate groups and the metal

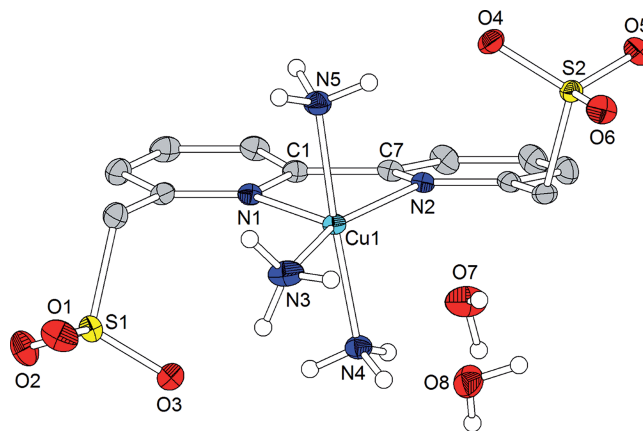


Figure 7. Molecular structure of **11**.

centre (κ^2N,N' coordination mode), **11** can be seen as an example of the selective partial decomplexation of smbipy .

Dinuclear complex **12** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Figure 8). Selected bond lengths and angles are given in Table 3.

The structure features two copper atoms with distorted square-pyramidal coordination. The coordination sphere of Cu2 consists of one ammonia molecule, two bridging hydroxide ligands, one of the two pyridyl nitrogen atoms (N2) in the basal plane and the second pyridyl nitrogen atom (N1) in the apical position. In comparison with that of **11**, the difference between the two bond lengths Cu–N1 and Cu–N2 is almost twice as large (23.2 compared with 12.5 pm). The second copper atom features two hydroxide ligands as well as two ammine ligands in the basal plane, and the apical coordination site is occupied by one of the sulfonate groups of smbipy with an elongated Cu–O distance of 251.7 pm. The Cu_2O_2 core is characterized by a Cu...Cu distance of 293.5 pm, which is within the usual range for hydroxido-bridged copper dimers.^[39] The basal planes of Cu2 and Cu1 roughly coincide. Interestingly, although a plethora of similarly bridged Cu complexes has been reported, only a limited number of unsymmetrical dimers have been structurally characterized.^[40]

The tetranuclear complex **13** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ (Figure 9).

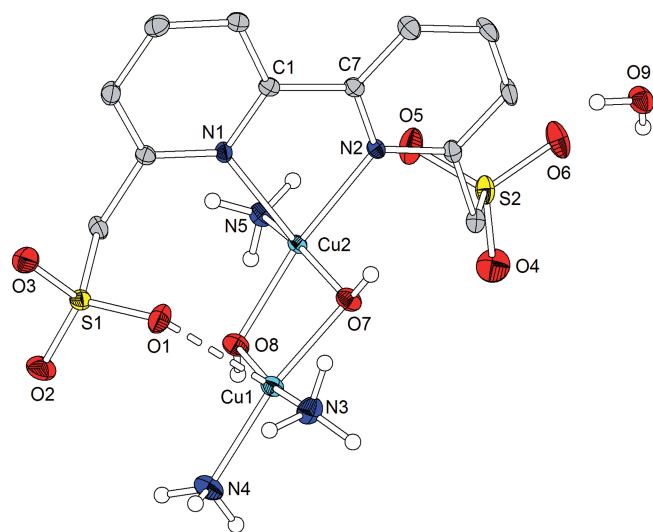
The complex is centrosymmetric and consists of two subunits that are structurally closely related to **12**. In the coordination sphere of Cu2, the ammine ligand in **12** is formally replaced by a water molecule, and the remaining geometric characteristics around this metal atom are roughly similar in both structures. The second copper atom (Cu1) is coordinated in a tetragonally elongated octahedral fashion. In contrast to the situation in **12**, there is an additional copper–sulfonate contact that originates from the second sulfonate group of another complex moiety. Thus, a dimeric overall structure arises with Cu–O bond lengths of 251.7 and 270.3 pm, which demonstrate the high variability of these rather weak contacts. Again, the basal plane of Cu2 and the equatorial plane of Cu1 roughly coincide.

In all pentacoordinate copper complexes (**6**, **11**, **12** and **13**), more or less distorted square-pyramidal geometries

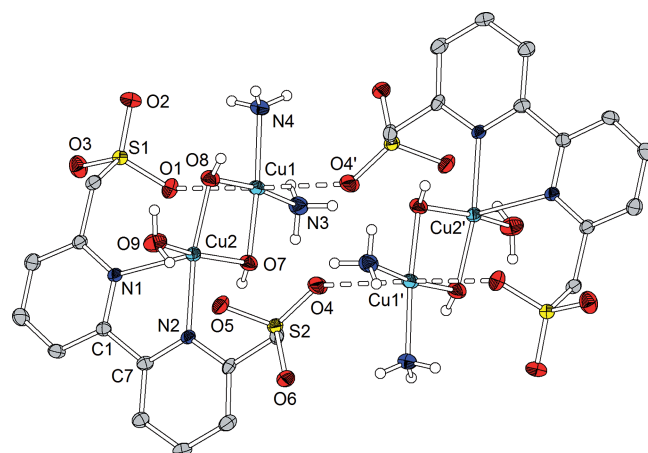
Table 3. Selected bond lengths and angles of **11**, **12** and **13**.

Bond length [pm]	[(smbipy)CuL ₃]		[(smbipy)CuL(μ-OH) ₂ Cu(NH ₃) ₂] _x	
	L = NH ₃ , 11 ^[a]	Bond length [pm]	L = NH ₃ , x = 1, 12 ^[b]	L = H ₂ O, x = 2, 13
Cu1–N1	220.92(13)	Cu2–N1	228.5(3)	227.1(2)
Cu1–N2	208.39(12)	Cu2–N2	205.3(3)	204.0(2)
Cu1–N3	200.24(15)	Cu2–O7	193.5(3)	192.65(19)
Cu1–N4	202.14(14)	Cu2–O8	193.9(3)	192.6(2)
Cu1–N5	201.94(14)	Cu2–L ^[c]	201.2(4)	200.9(2)
		Cu1–O7	191.9(3)	192.62(19)
		Cu1–O8	195.5(3)	196.6(2)
		Cu1–N3	199.5(4)	199.5(3)
		Cu1–N4	197.6(4)	198.8(2)
		Cu1–O1	251.7(4)	270.3(2)
		Cu1–O4'	329.6 ^[d]	251.7(2)
		Cu1...Cu2	293.49(7)	293.15(5)
Bond angle [°]				
N1–Cu1–N2	78.04(5)	N1–Cu2–N2	76.46(13)	77.11(8)
N1–Cu1–N4	94.77(5)	N1–Cu2–O7	98.01(13)	102.94(8)
N1–Cu1–N3	121.21(6)	N1–Cu2–O8	106.72(13)	109.08(8)
N1–Cu1–N5	90.48(6)	N1–Cu2–L ^[c]	99.77(14)	93.82(9)
N2–Cu1–N4	88.40(5)	N2–Cu2–O7	89.42(13)	90.44(8)
N2–Cu1–N3	160.57(7)	N2–Cu2–O8	169.37(13)	170.60(9)
N2–Cu1–N5	92.44(5)	N2–Cu2–L ^[c]	96.33(14)	91.17(9)
N3–Cu1–N4	87.32(6)	O7–Cu2–O8	80.11(13)	81.35(8)
N3–Cu1–N5	90.18(6)	Cu1–O7–Cu2	99.18(14)	99.09(9)
N4–Cu1–N5	174.74(6)	Cu1–O8–Cu2	97.84(14)	97.72(9)
		O7–Cu1–O8	80.13(13)	80.34(8)
		O1–Cu1–O4'	150.0 ^[d]	166.78(7)
Torsion angle [°]				
N1–C1–C7–N2	8.0(2)	N1–C1–C7–N2	6.0(5)	3.5(3)
		N2–Cu2–O7–Cu1	169.19(16)	175.15(9)
		L–Cu2–O8–Cu1 ^[c]	175.79(15)	172.49(9)
		Cu2–O7–Cu1–N3	160.91(16)	166.36(10)
		Cu2–O8–Cu1–N4	177.76(17)	171.46(10)

[a] Crystallizes as a dihydrate. [b] Crystallizes as a hydrate. [c] L equals N5 and O9 for **12** and **13**, respectively. [d] Nonbonded interatomic distance/angle.

Figure 8. Molecular structure of **12**.

have been found. This deviation from ideal tetragonal symmetry can be described in terms of the τ index as introduced by Addison et al.,^[41] and the relevant data is compiled in Table 4. It becomes evident that the coordination is indeed

Figure 9. Molecular structure of **13**. Symmetry-related atoms are generated by (') $-x, 1-y, 1-z$.

more adequately described as distorted square-pyramidal than as distorted trigonal-bipyramidal (all $\tau \ll 0.5$). However, the distortions observed for **6** and **11** are relatively large for pentacoordinate bipy complexes of copper as exemplified by the τ indices of **6** (0.27) and [Cu(bipy)(4-Me-

$C_6H_4CO_2)_2(H_2O)]$ (0.16). For **6** in particular, this suggests that the sulfonate tags of the ligand have a considerable structural flexibility.

Table 4. τ Indices of pentacoordinate copper complexes discussed herein.^[a]

Complex	α [°]	β [°]	τ
6	171.71(6)	155.76(6)	0.27
11	174.74(6)	160.57(7)	0.24
12	169.37(13) ^[b]	162.14(15) ^[b]	0.12 ^[b]
	171.15(15) ^[c]	163.23(15) ^[c]	0.13 ^[c]
13	170.60(9) ^[b]	163.10(9) ^[b]	0.13 ^[b]
[Cu(bipy)(4-Me-C ₆ H ₄ CO ₂) ₂ (H ₂ O)] ^[32]	172.5(2)	163.1(2)	0.16
[Cu(bipy)(PMDETA)](ClO ₄) ₂ ^[38]	167.89(10)	159.28(13)	0.14

[a] $\tau = (\alpha - \beta)/60^\circ$; α and β are the two largest ligand–metal–ligand angles. Thus, $\tau = 0$ for a perfect square-pyramidal coordination, and $\tau = 1$ for an ideal trigonal bipyramid.^[41] [b] Values for the κ^2N,N' -coordinated copper atom (Cu2). [c] Values for the copper atom not chelated by smbipy²⁻ (Cu1).

Conclusions

6,6'-Bis(sulfonatomethyl)-2,2'-bipyridine (smbipy²⁻) is a suitable candidate for a semilabile bipyridine-based ligand. Its sulfonate tags act as chelates towards heavier first-row transition metals in aqueous solutions, whereas complete decomplexation is observed in the presence of large amounts of ammonia. Partial decomplexation, that is, the detachment of only the sulfonate groups from the metal centre, has also been demonstrated by copper complexes.

These results encourage further studies with smbipy²⁻ and noble metals such as palladium and platinum, as it is to be expected that these softer metal ions will show a stronger discrimination between the bipyridine and sulfonate binding sites. Furthermore, variations of the linker are likely to change the complexation behaviour significantly, as the formation of larger chelate rings is not as thermodynamically favourable. Such studies are underway. Finally, catalytic studies on a model reaction will be utilized to determine whether semilabile bipyridine ligands with metal-chelating sulfonates can serve as a useful tool in homogeneous catalysis in polar phases.

Experimental Section

General Remarks: Starting material **1** was prepared by published procedures^[13–20] or by minor modifications thereof. Metal salts were obtained from commercial sources (Sigma–Aldrich, Merck) and used as received. All complexes were synthesized without an inert atmosphere.

NMR spectra were recorded at ambient temperature with a Bruker Avance 3 (400 MHz) spectrometer with D₂O or [D₆]DMSO as solvent. Chemical shifts are given with respect to tetramethylsilane (¹H and ¹³C); calibration of the spectra was accomplished with the solvent signals. IR spectra of neat samples were recorded with a Perkin–Elmer Spectrum 100 FTIR spectrometer with an attenuated total reflectance (ATR) measurement setup at room temperature. Elemental analysis (CHNS) was performed with an Elementar Vario MICROcube analyzer; values are given in weight percent. UV/

Vis spectra were recorded with a Hewlett–Packard HP8453 diode-array FT spectrometer at ambient temperature with quartz cuvettes and saturated aqueous solutions. Owing to the limited solubilities, the molar absorption coefficients were not calculated. Details of the single-crystal XRD studies are given as Supporting Information.

Disodium 6,6'-Bis(sulfonatomethyl)-2,2'-bipyridine [Na₂(smbipy), **2**]:

A mixture of 6,6'-bis(chloromethyl)-2,2'-bipyridine (2.05 g, 8.23 mmol) and disodium sulfite (2.11 g, 16.74 mmol) was suspended in water (50 mL) and heated to reflux for 4 h. The remaining residue was removed by filtration, and the resulting pale yellow solution was evaporated to dryness. The crude product was digested once with tetrahydrofuran (THF) and twice with methanol (80 mL each). The dried colourless powder was tested with AgNO₃(aq.)/HNO₃ and BaCl₂(aq.) and showed no significant halide content but some sulfate/sulfite impurities. Thus, it was dissolved in water (80 mL), and ethanol (ca. 150 mL) was added to the hot solution until it stayed turbid. The mixture was cooled to room temperature overnight, and the precipitate was collected by filtration and dried in vacuo. A second crop was obtained by treating the mother liquor with additional ethanol (200 mL). Both fractions showed no significant halide or sulfate/sulfite content. Yield: 2.01 g (63%), colourless powder. An analytically pure sample was obtained as follows: An aqueous solution of **2** was passed over an acidic ion exchange resin, concentrated to dryness and washed with methanol and ether. The obtained free acid was dissolved in water, and **2** was regenerated by the addition of aqueous sodium hydroxide to pH 7. The solution was concentrated, and ethanol was added until the solution became turbid, whereupon it was cooled to 4 °C; the resulting precipitate was dried to afford the product. C₁₂H₁₀N₂Na₂O₆S₂ (388.33): calcd. C 37.12, H 2.60, N 7.21, S 16.51; found C 36.81, H 2.73, N 7.07, S 16.25. ¹H NMR (400 MHz, D₂O): δ = 4.43 (s, 4 H, CH₂), 7.60–7.65 (m, 2 H, 5-H), 7.97–8.00 (m, 4 H, 3-H and 4-H) ppm. ¹³C NMR (101 MHz, D₂O): δ = 58.4 (CH₂), 122.1, 125.6, 138.8, 151.7, 155.6 ppm. ¹H NMR (400 MHz, [D₆]DMSO): δ = 4.20 (s, 4 H, CH₂), 7.68 (d, ³J_{H,H} = 7.6 Hz, 2 H, 5-H), 8.10 (t, ³J_{H,H} = 7.8 Hz, 2 H, 4-H), 8.27 (d, ³J_{H,H} = 7.4 Hz, 2 H, 3-H) ppm. ¹³C NMR (101 MHz, [D₆]DMSO): δ = 58.2 (CH₂), 120.6, 126.5, 139.7, 151.2, 154.7 ppm. IR (neat): $\tilde{\nu}$ = 1739 (m), 1568 (m), 1444 (m), 1406 (w), 1366 (w), 1278 (w), 1264 (w), 1228 (vs), 1188 (vs), 1139 (s), 1083 (m), 1058 (vs), 990 (m), 894 (w), 840 (w), 813 (s), 778 (m), 742 (m) cm⁻¹.

Synthesis of Aqua Complexes (General Procedure): An aqueous solution of the respective metal salt (ca. 0.5 mmol in 5 mL) was added to an aqueous solution of Na₂(smbipy) (ca. 0.5 mmol in 10 mL) at room temperature while stirring. Stirring was continued for at least 1 h, usually overnight, to ensure complete reaction. The resulting precipitate was allowed to settle, and then the mother liquor was decanted. The crude product was washed with ethanol and dried in vacuo.

Diaqua-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinecobalt(II) Hydrate {[Co(smbipy)(H₂O)₂]·H₂O, **3**}: Prepared from Na₂(smbipy) (200 mg, 0.52 mmol) and CoCl₂·6H₂O (128 mg, 0.54 mmol). Yield: 194 mg (83%), light pink powder. C₁₂H₁₆CoN₂O₉S₂ (455.33): calcd. C 31.65, H 3.54, N 6.15, S 14.08; found C 31.56, H 3.52, N 6.11, S 13.97. IR (neat): $\tilde{\nu}$ = 3477 (m), 3386 (br, m), 3101 (w), 2985 (w), 2922 (w), 1740 (w), 1632 (w), 1597 (m), 1575 (m), 1475 (w), 1467 (w), 1435 (m), 1403 (w), 1337 (w), 1323 (w), 1298 (w), 1241 (s), 1196 (vs), 1140 (vs), 1122 (sh), 1043 (vs), 944 (w), 931 (w), 891 (w), 827 (w), 805 (s), 782 (s), 738 (w), 674 (m) cm⁻¹. UV/Vis (H₂O): λ = 493 nm.

Diaqua-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinenickel(II) Hydrate {[Ni(smbipy)(H₂O)₂]·H₂O, **4**}: Prepared from Na₂(smbipy) (207 mg,

0.53 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (132 mg, 0.56 mmol). Yield: 209 mg (86%), pale blue powder. $\text{C}_{12}\text{H}_{16}\text{N}_2\text{NiO}_6\text{S}_2$ (455.10): calcd. C 31.67, H 3.54, N 6.16, S 14.09; found C 31.66, H 3.53, N 6.15, S 14.81. IR (neat): $\tilde{\nu} = 3456$ (m), 3391 (br, m), 3101 (w), 2982 (w), 2922 (w), 1632 (w), 1599 (m), 1575 (m), 1477 (m), 1469 (m), 1435 (m), 1402 (w), 1340 (w), 1324 (w), 1302 (m), 1241 (s), 1195 (vs), 1139 (vs), 1123 (sh), 1045 (s), 1033 (vs), 1018 (sh), 946 (w), 926 (w), 891 (w), 827 (m), 806 (s), 783 (s), 737 (w), 666 (s) cm^{-1} . UV/Vis (H_2O): $\lambda = 622, 914$ nm.

Diaqua-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinezinc(II) Hydrate $\{\{\text{Zn}(\text{smbipy})(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O}, \mathbf{5}\}$: Prepared from $\text{Na}_2(\text{smbipy})$ (215 mg, 0.55 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (145 mg, 0.55 mmol). Yield: 196 mg (77%), colourless powder. $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_9\text{S}_2\text{Zn}$ (461.79): calcd. C 31.21, H 3.49, N 6.07, S 13.89; found C 30.52, H 3.40, N 6.07, S 13.67. ^1H NMR (400 MHz, D_2O): $\delta = 4.66$ (4 H, CH_2), 7.75 (2 H), 8.25 (2 H), 8.47 (2 H) ppm. IR (neat): $\tilde{\nu} = 3487$ (m), 3392 (br, m), 3102 (w), 2986 (w), 2923 (w), 1739 (w), 1634 (w), 1597 (m), 1576 (m), 1467 (w), 1437 (m), 1403 (w), 1337 (w), 1323 (w), 1299 (w), 1243 (s), 1195 (vs), 1139 (vs), 1123 (s), 1044 (s), 1029 (vs), 946 (w), 931 (w), 891 (w), 827 (w), 806 (s), 783 (s), 753 (w), 738 (w), 675 (m) cm^{-1} .

Aqua-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinecopper(II) $\{\{\text{Cu}(\text{smbipy})(\text{H}_2\text{O})\}, \mathbf{6}\}$: Prepared from $\text{Na}_2(\text{smbipy})$ (201 mg, 0.52 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (134 mg, 0.54 mmol). Yield: 173 mg (79%), green powder. $\text{C}_{12}\text{H}_{12}\text{CuN}_2\text{O}_7\text{S}_2$ (423.92): calcd. C 34.00, H 2.85, N 6.61, S 15.13; found C 33.87, H 2.89, N 6.54, S 15.09. IR (neat): $\tilde{\nu} = 3344$ (br, m), 3085 (w), 3059 (w), 3019 (w), 2997 (w), 1653 (w), 1600 (m), 1573 (m), 1485 (m), 1472 (m), 1433 (m), 1394 (w), 1342 (w), 1315 (sh), 1302 (m), 1274 (s), 1251 (s), 1221 (s), 1209 (s), 1194 (s), 1167 (s), 1135 (vs), 1119 (s), 1031 (sh), 1022 (s), 1006 (vs), 918 (w), 888 (m), 854 (w), 827 (m), 810 (s), 789 (s), 749 (s), 717 (w), 655 (s) cm^{-1} . UV/Vis (H_2O): $\lambda = 715$ nm.

Hexaaminenickel(II) 6,6'-Bis(sulfonatomethyl)-2,2'-bipyridine $\{\{\text{Ni}(\text{NH}_3)_6(\text{smbipy})\}, \mathbf{7}\}$: To a suspension of **4** (46 mg, 0.10 mmol) in water (5 mL) was added aqueous ammonia (15 mL, 25% in water). The resulting pale violet solution was layered with ethanol and allowed to stand for several days to afford light violet crystals. The mother liquor was decanted, and the product was briefly dried in vacuo. Yield: 41 mg (80%), light violet crystalline powder. $\text{C}_{12}\text{H}_{28}\text{N}_8\text{NiO}_6\text{S}_2$ (503.22): calcd. C 28.64, H 5.61, N 22.27, S 12.74; found C 28.59, H 5.49, N 21.97, S 12.46. IR (neat): $\tilde{\nu} = 3356$ (m), 3285 (br, w), 3077 (w), 2932 (w), 1637 (m), 1619 (m), 1594 (w), 1565 (m), 1434 (m), 1403 (w), 1393 (w), 1272 (m), 1245 (m), 1224 (m), 1195 (s), 1175 (vs), 1128 (s), 1079 (m), 1035 (vs), 991 (m), 892 (w), 840 (w), 813 (s), 769 (w), 743 (s) cm^{-1} .

Pentaaminemonoaquanickel(II) 6,6'-Bis(sulfonatomethyl)-2,2'-bipyridine $\{\{\text{Ni}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{smbipy})\}, \mathbf{8}\}$: Prepared from **4** (50 mg, 0.11 mmol) in water (20 mL) and ammonia (3 mL, 25% in water) according to the abovementioned procedure. Yield: 11 mg (20%), light blue crystals. $\text{C}_{12}\text{H}_{27}\text{N}_7\text{NiO}_7\text{S}_2$ (504.21): calcd. C 28.59, H 5.40, N 19.45, S 12.72; found C 28.59, H 5.33, N 19.25, S 12.90. IR (neat): $\tilde{\nu} = 3346$ (s), 3282 (m), 3208 (m), 3069 (w), 2938 (w), 1625 (m), 1610 (m), 1576 (m), 1562 (m), 1440 (m), 1403 (w), 1395 (w), 1228 (s), 1195 (s), 1181 (vs), 1158 (s), 1128 (s), 1081 (m), 1036 (vs), 991 (m), 889 (w), 818 (s), 773 (m), 743 (s) cm^{-1} .

Both **7** and **8** are unstable in the solid state at room temperature and slowly lose ammonia.

Diammine-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinenickel(II) $\{\{\text{Ni}(\text{smbipy})(\text{NH}_3)_2\}, \mathbf{9}\}$: Method A: A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (69 mg, 0.29 mmol) in water (5 mL) was added to a solution of **1** (109 mg, 0.28 mmol) in water (10 mL) at room temperature. After 15 min of

stirring, aqueous ammonia (5 mL, 25% in water) was added, and stirring was continued overnight. The resulting light blue-violet solution was layered with ethanol to yield a precipitate of **7/8** after several days. The mother liquor was almost completely decanted, and the precipitate was allowed to stand without drying overnight, after which time the primary precipitate had redissolved to allow the crystallization of **9**. The resulting product was dried in vacuo. Yield: 65 mg (53%), blue-green solid.

Method B: A mixture of **4** (49 mg, 0.11 mmol) and NH_4Cl (168 mg, 3.14 mmol) was treated with water (5 mL). Aqueous ammonia (0.8 mL, 1.6 mmol, 2 mol L^{-1}) was added to afford a pale violet solution, which was layered with ethanol to afford blue-green crystals after a couple of days. The mother liquor was decanted, and the product was washed with ethanol and dried in vacuo. Yield: 36 mg (77%), blue-green crystalline powder. $\text{C}_{12}\text{H}_{16}\text{N}_4\text{NiO}_6\text{S}_2$ (435.10): calcd. C 33.13, H 3.71, N 12.88, S 14.74; found C 32.88, H 3.77, N 12.76, S 14.61. IR (neat): $\tilde{\nu} = 3364$ (m), 3349 (m), 3284 (w), 3206 (w), 3078 (w), 2969 (w), 2924 (w), 1596 (m), 1574 (m), 1476 (w), 1468 (w), 1432 (m), 1406 (w), 1335 (w), 1317 (w), 1296 (m), 1235 (s), 1195 (vs), 1143 (vs), 1126 (s), 1036 (vs), 1019 (s), 947 (w), 927 (w), 889 (m), 829 (w), 812 (s), 797 (s), 784 (m), 749 (w), 740 (w), 676 (s), 656 (s) cm^{-1} .

Tetraamminecopper(II) 6,6'-Bis(sulfonatomethyl)-2,2'-bipyridine Dihydrate $\{\{\text{Cu}(\text{NH}_3)_4(\text{smbipy}) \cdot 2\text{H}_2\text{O}\}, \mathbf{10}\}$: Complex **6** (43 mg, 0.10 mmol) was suspended in a mixture of aqueous ammonia (5 mL, 25% in water) and water (15 mL). The mixture was heated briefly to ca. 80 °C until all of the solid dissolved. The mixture was cooled to room temperature, and the resulting blue solution was treated with ethanol (20 mL). To isolate the precipitated product, the mother liquor was decanted, and the solid was dried in vacuo. Yield: 26 mg (50%), violet powder. $\text{C}_{12}\text{H}_{26}\text{CuN}_6\text{O}_8\text{S}_2$ (510.07): calcd. C 28.26, H 5.14, N 16.48, S 12.57; found C 28.52, H 4.93, N 16.34, S 12.86. IR (neat): $\tilde{\nu} = 3564$ (w), 3335 (m), 3267 (w), 3187 (w), 1611 (w), 1576 (m), 1563 (m), 1439 (m), 1413 (w), 1394 (w), 1259 (s), 1225 (w), 1180 (vs), 1138 (s), 1094 (w), 1077 (w), 1035 (vs), 993 (m), 822 (s), 770 (w), 741 (s), 723 (s) cm^{-1} .

Triammine-6,6'-bis(sulfonatomethyl)-2,2'-bipyridinecopper(II) Dihydrate $\{\{\text{Cu}(\text{smbipy})(\text{NH}_3)_3 \cdot 2\text{H}_2\text{O}\}, \mathbf{11}\}$: A mixture of **6** (43 mg, 0.10 mmol) and NH_4Cl (162 mg, 3.03 mmol) was treated with water (5 mL). Aqueous ammonia (0.4 mL, 0.8 mmol, 2 mol L^{-1}) was added to afford a blue-green solution, which was layered with ethanol to afford blue needles after a couple of days. The mother liquor was decanted, and the product was washed with ethanol and dried in vacuo. Yield: 25 mg (50%), blue crystalline powder. $\text{C}_{12}\text{H}_{23}\text{CuN}_5\text{O}_8\text{S}_2$ (493.02): calcd. C 29.23, H 4.70, N 14.21, S 13.01; found C 29.18, H 4.44, N 14.03, S 12.92. IR (neat): $\tilde{\nu} = 3465$ (br, w), 3316 (m), 3248 (w), 3180 (w), 3084 (w), 2975 (w), 2936 (w), 1601 (m), 1574 (m), 1476 (w), 1462 (m), 1436 (m), 1305 (sh), 1274 (s), 1260 (s), 1235 (s), 1182 (vs), 1137 (vs), 1113 (s), 1092 (m), 1031 (vs), 1008 (s), 927 (w), 889 (w), 814 (vs), 765 (m), 751 (sh), 736 (s) cm^{-1} .

Triammine-6,6'-bis(sulfonatomethyl)-2,2'-bipyridine(dihydroxido)copper(II) Hydrate $\{\{\text{Cu}_2(\text{smbipy})(\mu\text{-OH})_2(\text{NH}_3)_3 \cdot \text{H}_2\text{O}\}, \mathbf{12}\}$: Complex **6** (45 mg, 0.11 mmol) was suspended in water (5 mL). The addition of ammonia (0.5 mL, 1.0 mmol, 2 mol L^{-1}) led to a blue-green solution, which was layered with ethanol. After several days, the resulting crystalline product was dried in vacuo and manually separated into three fractions according to crystal colour. Combined yield: ca. 20 mg blue-green plates (**12**), blue needles (**11**) and violet blocks (**10**; ratio **12/11/10** \approx 3:1:2). $\text{C}_{12}\text{H}_{23}\text{Cu}_2\text{N}_5\text{O}_9\text{S}_2$ (572.56): calcd. C 25.17, H 4.05, N 12.23, S 11.20; found C 25.23, H 4.09, N 12.29, S 11.19. IR (neat): $\tilde{\nu} = 3552$ (sh), 3494 (w), 3445

(sh), 3360 (w), 3314 (m), 3113 (w), 2997 (w), 1662 (w), 1600 (m), 1576 (m), 1481 (w), 1467 (m), 1435 (w), 1278 (m), 1262 (m), 1229 (sh), 1209 (sh), 1189 (vs), 1180 (vs), 1141 (s), 1117 (s), 1105 (sh), 1093 (m), 1034 (vs), 1006 (m), 902 (w), 814 (s), 774 (m), 762 (m), 741 (s), 695 (br, m) cm^{-1} .

Diammineaqua-6,6'-bis(sulfonatomethyl)-2,2'-bipyridine(dihydroxido)dicopper(II) Dimer, $\{[\text{Cu}_2(\text{sm}(\text{bipy})(\mu\text{-OH})_2(\text{H}_2\text{O})(\text{NH}_3)_2)_2, \mathbf{13}]:$ Aqueous ammonia (0.1 mL, 0.2 mmol, 2 mol L^{-1}) was added to a suspension of **6** (43 mg, 0.10 mmol) in water (5 mL). The resulting green solution was layered with ethanol and allowed to stand for several days. After this time, green crystals of the starting material **6** had formed together with a few greenish-blue prisms of **13**. The low yield of **13** and its mixture with the starting material rendered analyses requiring bulk material such as elemental analysis and IR spectroscopy unfeasible. Attempts to synthesize **12** and **13** without the accompanying side-products were unsuccessful under a variety of conditions.

CCDC-1015530 (for **3**), -1015531 (for **4**), -1015532 (for **5**), -1015533 (for **6**), -1015534 (for **7**), -1015535 (for **8**), -1015536 (for **9**), -1015537 (for **10**), -1015538 (for **11**), -1015539 (for **12**) and -1015540 (for **13**) 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.

Supporting Information (see footnote on the first page of this article): Details on XRD studies, structural comparison of **7** and **8**, UV/Vis spectra.

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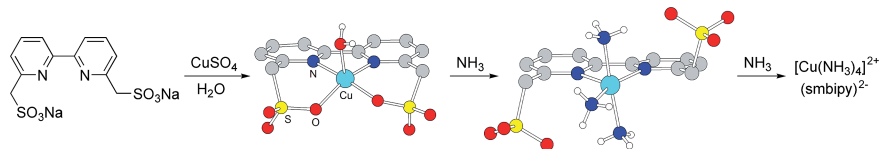
Sulfonated Ligands

B. Oelkers* 1–12



Na₂(smbipy) – A Bipyridine-Derived Ligand with Chelating Sulfonate Tags and Its 3d Metal Complexes

Keywords: N,O ligands / Coordination modes / Water chemistry / Nickel / Copper



The sulfonated bipyridine ligand disodium 6,6'-bis(sulfonatomethyl)-2,2'-bipyridine [Na₂(smbipy)] shows pronounced chelating behaviour of the sulfonate tags towards Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions in aqueous

solution. In the presence of ammonia, sequential decomplexation enables the isolation of a nitrogen-only-ligated smbipy–copper complex.