Coordinative flexibility in an acyclic bis(sulfonamide) ligand†

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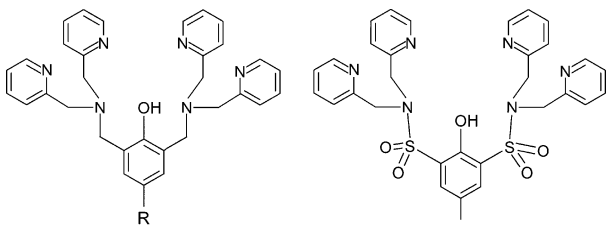
The new acyclic and potentially heptadentate dinucleating ligand, 2,6-bis(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-4-methylphenolato (bpsmp$^-$) contains two tertiary sulfonamide groups. The sulfonamide donors permit a greater degree of control over the accessibility of mono *versus* dinuclear complexes compared to their closely related amine-containing counterparts, on account of their relatively weaker donor properties. A series of air-stable dinuclear complexes of Co^{II}, Mn^{II} and Cu^{II} containing two auxiliary acetate ligands have been prepared. The absence of acetate in reaction mixtures containing Co^{II} and Mn^{II} led to mononuclear complexes, with water ligands completing the coordination spheres of the metal ions, even in the presence of large excess of the metal ions. Thus, bridging acetate ligands appear to stabilise the dinuclear structures for the relatively labile Co^{II} and Mn^{II} ions. A mononuclear complex of V^{IV}=O was isolated even in the presence of acetate, possibly because the oxyl groups on each V^{IV} prevent formation of a bis-acetato-bridged complex. Reaction of one equivalent of $CuCl_2$ with bpsmpH led to isolation of two different mononuclear complexes, dependent on the identity of the solvent. The phenol group is coordinated in only one of these complexes. A dinuclear Cu^{II} complex was isolated when two equivalents of the metal salt were used in the reaction.

Introduction

A major impetus for the preparation of dimetallic complexes lies in the anticipation of cooperativity between metal ions. This cooperativity might reveal itself in altered electronic, magnetic, chemical or catalytic properties which are not additive compared to two equivalents of analogous mononuclear compounds. Biology has taken advantage of this phenomenon for a large range of enzymatic processes including reversible dioxygen binding, catalysis of non-redox hydrolysis, and catalysis of multi-electron redox reactions involving important inorganic substrates like O_2, N_2, H_2 and H_2O. A common approach to construct complexes that can furnish dimetallic "active sites" for coordination of ancillary ligands or substrates is to employ open-ended acyclic dinucleating ligands. In this case, the ligand field strength, stereochemistry and coordinative flexibility of the dinucleating ligand combine to influence the reactivity of the dimetallic active sites towards binding and activation of substrate molecules. In an effort towards discovery of new dimetallic systems that may exhibit enhanced reactivity, we have prepared the new acyclic phenolato-hinged dinucleating ligand 2,6-bis(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-4-methylphenolate, (bpsmp$^-$). This ligand is closely related to 2,6-bis(*N*,*N*-bis(2-pyridylmethyl)aminomethyl)-4-methyl-phenolate (bpmp$^-$)[1] and 2,6-bis(*N*,*N*-bis(2-pyridylmethyl)aminomethyl)-4-*tert*-butylphenolate (bpbp$^-$),[2] except that it contains two tertiary sulfonamide groups *ortho* to the central phenol group, instead of tertiary amine groups (Scheme 1). This paper describes the coordination chemistry of bpsmp$^-$ with copper, manganese, cobalt and vanadium, and compares this to the chemistry that has previously been described for bpmp$^-$ and bpbp$^-$.



bpmpH (R = CH_3)
bpbpH (R = $C(CH_3)_3$)
bpsmpH

Scheme 1 Acyclic dinucleating pro-ligands based on hinging phenolate groups containing two amine or two tertiary sulfonamide groups.

There are few known metal complexes of ligands containing tertiary sulfonamide donors.[3-6] The weaker M–N bond furnished by the sulfonamide N donor relative to comparable amine N donors is clearly demonstrated by comparison of the structures of the matched pair of complexes $[L\mathrm{Ni}(CH_3CN)_3]^{2+}$, where *L* is either bis(1-methylbenzimidazolyl-2-methyl)amine or its 10-camphorsulfonamide derivative:[3] the $Ni–N_{amine}$ bond in the first complex is 2.160(3) Å while the $Ni–N_{sulfonamide}$ bond in the second complex is 2.377(8) or 2.405(10) Å (in two crystallographically independent complexes). The availability of stronger potential auxilary ligands in reactions containing the nickel complexes of bis(1-methylbenzimidazolyl-2-methyl)-10-camphorsulfonamide appears to override the chelate effect so that decoordination of sulfonamide ensues.

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† Electronic supplementary information (ESI) available: S1, Figure and discussion of the structure of 2-hydroxy-3-(*N*,*N*-bis(2-pyridylmethyl)-sulfonamido)-5-methylbenzenesulfonic acid (hpsmsH). CIF files for all structures. S2, A table containing data concerning the geometries around the sulfonamide N atoms. CCDC reference numbers 737969–737978. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912617a

For example, reaction of $[L\mathrm{Ni}(CH_3CN)_3]^{2+}$, where *L* is the tridentate bis(1-methylbenzimidazolyl-2-methyl)-10-camphorsulfonamide, with acetate or chloride results in decoordination of the sulfonamide group so that the ligand becomes bidentate and is bound only through the two N atoms of the benzamidazole units.[3] The coordination sphere of Ni^{2+} is completed by two acetato or two chlorido ligands, resulting in six- or four-coordination in the acetato and chlorido products, respectively. By contrast, decoordination of the amine group does not occur for the Ni^{2+} complexes of the parent bis(1-methylbenzimidazolyl-2-methyl)amine if the acetonitrile complex is treated with acetate or chloride.[3] Nickel(II) complexes of the macrocyclic ligands 1,4,8,11-tetraazacyclotetradecane (cyclam)[7] and its mono-*N*-tosylated counterpart are also known. Decoordination of the sulfonamide does not occur so readily for these complexes,[6] although the $Ni–N_{sulfonamide}$ bond is also at least 0.25 Å longer than the $Ni–N_{amine}$ bonds. The additional stability afforded by a macrocyclic tetradentate *versus* linear tridentate ligand can account for this difference. Metal complexes of secondary sulfonamides, predominantly *N*-coordinated in their basic deprotonated forms, are considerably more common than those of tertiary sulfonamides. For example there are numerous examples of these where the deprotonated sulfonamide is a tosylate group.[8] Deprotonation will compensate for the analogous weak donor properties of the protonated secondary sulfonamides. Clearly, this mechanism for enhancing the ligand field is not possible for a tertiary sulfonamide ligand. The complexes of deprotonated secondary sulfonamides typically have planar conformations around the N atom and short N–S distances consistent with delocalisation of the electrons over the $–NS(O)_2–$ unit.

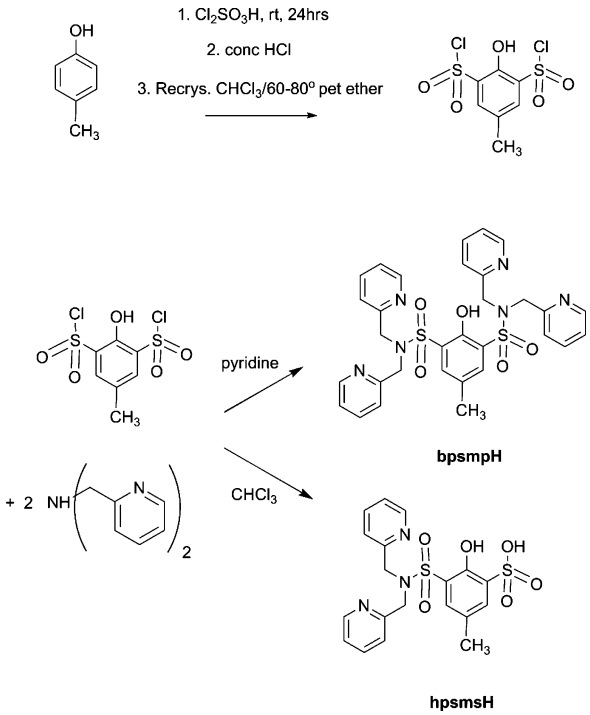
Experimental section

Solvents and starting materials were used as supplied from commercial sources and reactions were carried out in air unless otherwise specified. 2,6-Dichlorosulfone-4-methylphenol[9] was prepared using literature methods, Scheme 2. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Varian Gemini 2000 instrument, using TMS as an internal reference. Electrospray Ionization Mass Spectra (ESI MS) were obtained using a Finnigan TSQ 700 triple quadrapole or Qstar instrument equipped with a Finnigan API source in the nanoelectrospray mode. Acetonitrile was used to dissolve the complexes. IR spectra were measured as KBr discs using a Hitachi 270–30 IR spectrophotometer. UV-visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Elemental analyses were performed at the Chemistry Department II, Copenhagen University, Denmark and Atlantic Microlab, Inc., Norcross, Georgia, USA.

CAUTION! Although we encountered no problems during preparation of the perchlorate salts, care should be exercised when handling these potentially explosive compounds.

2,6-Bis(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-4-methylphenol, (bpsmpH)

The reaction was carried out under dinitrogen. 2,6-Dichlorosulfone-4-methylphenol (0.766 g, 2.51 mmol) was added over a period of fifteen minutes to a mixture of bis-2-methylpyridylamine (1.00 mL, 5.56 mmol) and pyridine (2.00 mL, 24.8 mmol). The solution turned dark red and was allowed to stand one day with stirring. Methanol (10 mL) was then added and the mixture was cooled to −18 °C causing precipitation of a yellow-white product. The product was filtered off, washed with ice-cold methanol and recrystallized from methanol. Yield 0.979 g (62%). M.p. 141 °C. Anal. calcd. for $C_{31}H_{30}N_6O_5S_2$: C, 59.03; H, 4.79; N, 13.32; S, 10.17. Found: C, 59.20; H, 4.49; N, 13.17; S, 10.09%. ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, CH_3C), 4.68 (s, 8 H, NCH_2C), 7.13 (m, 4 H, J = 1.2 Hz, J = 1.5 Hz, J = 2.7, pyridine NCHCHCH), 7.36 (dd, 4 H, J = 1.2 Hz, J = 0.9 Hz, pyridine CHCHC), 7.61 (multiplet, 4 H, J = 1.8 Hz, J = 3 Hz, J = 1.5 Hz, pyridine CHCHCH), 7.92 (s, 2 H, CCHC), 8.46 (multiplet, 4 H, J = 0.9 Hz, J = 2.1 Hz, pyridine NCHCH). ^{13}C NMR ($CDCl_3$): δ = 20.41 (CH_3C), 52.66 (NCH_2C), 122.86 (pyridine NCHCHCH), 122.90 (pyridine CHCHC), 128.57 (CHCSC), 131.08 ($(CH)_2CCH_3$), 136.21 (pyridine CHCHCHC), 137.43 (CCHC), 148.87 (pyridine NCHCH), 153.06 (C_2COH), 155.91 (pyridine CHCN). MS (MALDI): *m*/*z* (%, assignment): 675 (72, [2Na(bpsmp − H)]$^+$), 631 (2, [bpsmpH]$^+$), 438 (42), 220 (100). IR (KBr): ν/cm^{-1} = 1592(m), 1572(m), 1476(m), 1438(m), 1328(vs), 1143(vs), 1091(w), 1056(w), 929(m), 816(s), 769(s), 712(w), 617(m), 571(s).



Scheme 2 Preparation of the protonated bpsmpH and hpsmsH from commercial starting materials.

2-Hydroxy-3-(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-5-methylbenzenesulfonic acid (hpsmsH)

The reaction and crystallisation was carried out under dinitrogen. 2,6-Dichlorosulfone-4-methylphenol (0.21 g, 0675 mmol) was added to bis-2-methylpyridylamine (0.25 mL, 1.39 mmol) dissolved in chloroform (4 mL) over a period of 20 min under N_2. The mixture turned red and crystals of the product deposited after about 2 days. The crystals decompose rapidly when removed

from the mother liquor, and no yield has been recorded. For X-ray crystallographic work (see ESI†), the crystals were transferred directly from their mother liquor to polyfluoroether oil then moved rapidly into the N_2 stream of the cryostat, operating at 180 K. Once mounted in the N_2 stream, the crystals were stable for the duration of the data collection.

[VO(bpsmpH)](ClO$_4$)$_2$·1.7CH$_3$OH·1.6H$_2$O (1)[10]

Solutions of bpsmpH (0.0507 g, 0.0809 mmol) in methanol (2 mL) and $VO(ClO_4)_2$ (0.2 mL, 0.8 M) in a 0.5 M aqueous $HClO_4$ were mixed. The solution turned blue, then purple, and crystals of the product formed within a few hours. Yield 45 mg (75%). Anal. calcd. for $C_{32}H_{36}Cl_2N_6O_{16}S_2V$ ([VO(bpsmpH)](ClO$_4$)$_2$·CH$_3$OH·H$_2$O): C, 40.60; H, 3.83; N, 8.88. Found: C, 40.42; H, 3.43; N, 9.01%. ESIMS, *m/z* (%, assignment): 736.1 (23, [NaVO(bpsmp)(OH)]$^+$), 714.2 (11, [VO(bpsmp)(H$_2$O)]$^+$), 696.1 (100, [VO(bpsmp)]$^+$). IR (KBr) ν/cm^{-1}: 1612 (m), 1465 (s), 1341 (m) (asym. SO), 1150 (vs) (sym. SO).

[Mn(bpsmp)(H$_2$O)$_2$]ClO$_4$·1$\frac{1}{2}$CH$_3$CN·$\frac{1}{2}$H$_2$O (2)

BpsmpH (0.0577 g, 0.0918 mmol) and $Mn(ClO_4)_2·6H_2O$ (0.1625 g, 0.6403 mmol) were mixed in methanol (5 mL) to give a slightly yellow solution. Reduction of the solution volume on standing in an open vessel overnight resulted in the formation of white crystals. Yield 71.0 mg (95%). Anal. calcd. for $C_{31}H_{33}ClMnN_6O_{11}S_2$ ([Mn(bpsmp)(H$_2$O)$_2$]ClO$_4$): C, 45,40; H, 4,06; N, 10,25. Found: C, 44.57; H, 3.86; N, 9.96%. ESIMS, *m/z* (%, assignment): 784.1 (3, [Mn(bpsmpH)ClO$_4$]$^+$); 720.1 (63, [Mn(bpsmp)(H$_2$O)]$^+$); 684.1 (100, [Mn(bpsmp)]$^+$); 653.2 (4, [Na(bpsmpH)]$^+$); 631.2 (89, [bpsmpH$_2$]$^+$). IR (KBr): ν/cm^{-1}: 1606 (s), 1417 (s), 1336 (m) (asym. SO), 1150 (vs) (sym. SO).

[Co(bpsmpH)(H$_2$O)$_2$](ClO$_4$)$_2$·CH$_3$CH$_2$OH·H$_2$O (3)

A solution of bpsmpH (0.0790 g, 0.1252 mmol) in methanol (3.5 mL) was added to a solution of $Co(ClO_4)_2·6H_2O$ (0.2410 g, 0.6586 mmol) in water (2mL) to give a pink solution which yielded red needles of the product after approx. two hours. Yield 103 mg (83%). Anal. calcd. for $C_{31}H_{36}Cl_2CoN_6S_2O_{16}$ ([Co(bpsmpH)(H$_2$O)$_2$](ClO$_4$)$_2$·H$_2$O): C, 39.49; H, 3.85; N, 8.92. Found: 39.59 H, 3.72; N, 8.80%. ESIMS, *m/z* (%, assignment): 788.0 (44, [Co(bpsmpH)ClO$_4$]$^+$); 724.1 (14, [Co(bpsmp)(H$_2$O)$_2$]$^+$); 688.1 (73, [Co(bpsmp)]$^+$); 631.2 (55, [(bpsmpH)]$^+$); 491.0 (100); 344.6 (43, [Co(bpsmpH)]$^{2+}$). IR (KBr) ν/cm^{-1}: 1610 (m), 1472 (s), 1333 (m) (asym. SO), 1145 (vs) (sym. SO).

[Cu(bpsmp)Cl]·4H$_2$O (4)

A solution of bpsmpH (0.080 g, 0.1269 mmol) in methanol (6 mL) was mixed with $CuCl_2·2H_2O$ (0.0206 g, 0.1208 mmol) dissolved in methanol (1 mL). The solution first turned brown, then finally became dark green. The solution was evaporated to dryness then redissolved in a mixture of methanol (1 mL) and water (2 mL). Dark green crystals of the product were deposited on standing. Yield 43 mg (49%). Anal. calcd. For $C_{31}H_{35}ClCuN_6O_8S_2$ ([Cu(bpsmp)Cl]·3H$_2$O): C, 47.57; H: 4.51; N, 10.74. Found: C, 47.60; H, 4.28; N, 10.55%. ESIMS, *m/z* (%, assignment): 750.1 (10, [Cu(bpsmp)(Cl)Na]$^+$); 692.1 (100, [Cu(bpsmp)]$^+$). IR (KBr): ν/cm^{-1} = 1610 (m), 1475 (vs), 1330 (m) (asym. SO), 1141 (vs) (sym. SO).

[Cu(Hbpsmp)Cl$_2$]·2CH$_3$CN (5)

A solution of Hbpsmp (0.0246 g, 0.039 mmol) in methanol (4 mL) was mixed with $CuCl_2·2H_2O$ (0.0067 g, 0.039 mmol) in methanol (0.5 mL) to give a dark green solution. The solution was evaporated to dryness and the residue redissolved in acetonitrile. After approximately two hours, the solution had turned dark red, and red crystals precipitated overnight. Yield 10.7 mg (36%). Anal calcd. for $C_{31}H_{30}Cl_2CuN_6O_5S_2$ ([Cu(bpsmpH)Cl$_2$]): C, 48.66; H: 3.95; N, 10.98. Found: C, 48.02; H, 4.00; N, 10.58%. ESIMS, *m/z* (%, assignment): 728.1 (18, [Cu(Hbpsmp)Cl]$^+$); 692.1 (100, [Cu(bpsmp)]$^+$); 631.2 (4, H$_2$bpsmp$^+$); 431.0 (75); 346.6 (25, [Cu(Hbpsmp)]$^{2+}$).

[Cu$_2$(bpsmp)Cl$_2$]$_2$CuCl$_4$ (6)

A solution of bpsmpH (0.0619 g, 0.0982 mmol) in methanol (4 mL) was mixed with $CuCl_2·2H_2O$ (0.0519 g, 0.3045 mmol) dissolved in methanol (2 mL). The resultant grass green precipitate was filtered off and washed with methanol (3 × 1.5 mL). Yield 67 mg (72%). Anal. calcd. for $C_{62}H_{58}Cl_8\ Cu_5N_{12}O_{12}S_4$ ([Cu$_2$(bpsmp)Cl$_2$]$_2$CuCl$_4$): C, 39.34; H, 3.09; N, 8.88. Found: C, 38.99, 38.90; H, 3.04, 3.17; N, 8.51, 8.55%. ESIMS, *m/z* (%, assignment): 825.0 (100, [Cu$_2$(bpsmp)Cl$_2$]$^+$); 395.0 (75, [Cu$_2$(bpsmp)Cl]$^{2+}$). IR (KBr): ν/cm^{-1} = 1611(m), 1485 (s), 1341 (m) (asym. SO), 1149(vs) (sym. SO).

[Mn$_2$(bpsmp)(CH$_3$CO$_2$)$_2$]ClO$_4$·CH$_3$CN (7)

A solution of bpsmpH (0.0686 g, 0.1088 mmol) in acetonitrile (4 mL), $Mn(ClO_4)_2·6H_2O$ (0.0608 g, 0.2395 mmol) in water (1 mL) and sodium acetate (0.0268 g, 0.3265 mmol) in water (1 mL) were mixed. This was followed by addition of $NaClO_4·H_2O$ (15.3 mg, 0.1088 mmol) in acetonitrile (0.5 mL). Slow evaporation afforded colourless crystals after 1 day. The crystals were separated, and washed with water. Yield 57 mg (54%). Anal. calcd. for $C_{37}H_{38}N_7S_2O_{13}Mn_2Cl$ ([Mn$_2$(bpsmp)-(CH$_3$CO$_2$)$_2$]ClO$_4$.CH$_3$CN): C, 44.52; H, 3.84; N, 9.82. Found: C, 46.02; H, 3.79; N, 9.96%. ESIMS, *m/z* (%, assignment): 857.0 (70, [Mn$_2$(bpsmp)(OOCCH$_3$)$_2$]$^+$); 684.1 (100, [Mn(bpsmp)]$^+$). IR (KBr): ν/cm^{-1}: 1594(vs) (asym. CO_2), 1471 (s), 1438 (vs) (sym. CO_2), 1338 (m) (asym. SO), 1151 (vs) (sym. SO).

[Co$_2$(bpsmp)(CH$_3$CO$_2$)$_2$]ClO$_4$·CH$_3$OH·2H$_2$O (8)

BpsmpH (0.050 g, 0.0798 mmol) and $Co(CH_3CO_2)_2·4H_2O$ (0.0397 g, 0.1596 mmol) were mixed in methanol (15 mL). The solution was heated for a few minutes during which time the colour changed from pink to purple. $NaClO_4·H_2O$ (0.022 g, 0.16 mmol) was added and the solution was cooled. Pink crystals were deposited overnight. Yield 60 mg (78%). Anal. calcd. for $C_{35}H_{39}ClCo_2N_6O_{15}S_2$. ([Co$_2$(bpsmp)(CH$_3CO_2$)$_2$]ClO$_4$·2H$_2$O): C, 42,00; H, 3,93; N, 8,40. Found: C, 41.96. H, 3.71; N, 8.29%. ESIMS, *m/z* (%, assignment): 865.4 (100, [Co$_2$(bpsmp)(CH$_3$CO$_2$)$_2$]$^+$); 837.3 (22, [Co$_2$(bpsmp)(HCO$_2$)$_2$]$^+$). IR (KBr) ν/cm^{-1}: 1608 (vs)

(asym. CO_2), 1435 (s) (sym. CO_2), 1341 (m) (asym. SO), 1154 (vs) (sym. SO).

$[Cu_2(bpsmp)(CH_3CO_2)_2](ClO_4)$ (9)

Hbpsmp (0.1066 g, 0.1692 mmol) and $NaCH_3CO_2{\cdot}3H_2O$ (0.0921 g, 0.6766 mmol) were dissolved in methanol (4 mL). $Cu(ClO_4)_2{\cdot}6H_2O$ (0.1379 g, 0.3722 mmol) in methanol (2 mL) was added, turning the solution dark green. After few hours of standing, a light-green solid formed, which was isolated and washed with small amounts of methanol. Yield: 104.6 mg (65%). Anal. calcd. for $C_{35}H_{35}ClCu_2N_6O_{13}S_2$: C: 43.14; H: 3.62; N: 8.63. Found C: 43.00; H: 33.67; N: 8.87. ESIMS, *m*/*z* (%, assignment): 913.03 (10; $[Cu^{II}_2(bpsmp)(CH_3CO_2)ClO_4]^+$), 889.0 (7; $[Cu^{II}_2(bpsmp)(H_2O)(OH)ClO_4]^+$); 873.06 (32; $[Cu^{II}_2(bpsmp)(CH_3CO_2)_2]^+$); 859.1 (17; $[Cu^{II}_2(bpsmp)(CH_3CO_2)(HCO_2)]^+$); 814.1 (7; $[Cu^{II}Cu^{I}(bpsmp)(CH_3CO_2)^+$); 774.2 (31, $[Cu^{II}(bpsmp)(CH_3CO_2)Na]^+$,); 755.1 (100; $[Cu^{I}_2(bpsmp)]^+$); 692.13 (74; $[Cu(bpsmp)]^+$). IR (KBr): ν/cm^{-1} 1611 (s), 1574 (m), 1466 (m), 1438 (s), 1331 (m), 1151(s), 1121 (s), 1108 (s).

Single-crystal X-ray diffraction

Diffraction data were collected at 180(2) K on a Bruker–Nonius X8 APEX-II instrument (MoKα radiation). Structure solution and refinement was carried out using SHELXTL.[11] Selected crystallographic data are presented in Table 1. Complex **1** exhibits disorder between coordinated H_2O and MeOH molecules: in the refined model, MeOH is considered to be present in 70% of the complexes while H_2O is present in the other 30%. Where H_2O is present, an associated H-bonded lattice H_2O molecule is also present. Thus, the structure is most clearly represented as 70% $[VO(bpsmpH)(MeOH)](ClO_4)_2{\cdot}2MeOH{\cdot}H_2O$ and 30% $[VO(bpsmpH)(H_2O)](ClO_4)_2{\cdot}2MeOH{\cdot}2H_2O$. In most cases, H

Table 1 Selected crystallographic details for bpsmpH, hpsmsH and complexes **1–8**

	bpsmpH	hpsmsH	**1**	**2**	**3**
Empirical formula	$C_{31}H_{30}N_6O_5S_2$	$C_{20}H_{20}Cl_3N_3O_6S_2$	$C_{33.7}H_{44}Cl_2N_6O_{18.3}S_2V$	$C_{68}H_{77}Cl_2Mn_2N_{15}O_{23}S_4$	$C_{33}H_{42}Cl_2CoN_6O_{17}S_2$
Formula weight	630.73	568.86	1011.93	1781.47	988.68
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$	P-1	$P2_1/c$
a/Å	8.8121(2)	8.1135(9)	13.9275(11)	13.1117(7)	12.8054(10)
b/Å	99.746(2)	11.9046(17)	25.6124(17)	16.4295(7)	21.2676(14)
c/Å	33.1686(7)	13.1532(19)	14.0430(10)	19.0495(12)	15.8384(11)
α/°	90	72.956(5)	90	77.147(2)	90
β/°	94.344(1)	87.292(6)	119.576(3)	86.282(2)	96.797(3)
γ/°	90	89.602(4)	90	80.932(1)	90
V/Å^3	2907.05(11)	1213.3(3)	4356.7(6)	3948.9(4)	4283.1(5)
Z	4	2	4	2	4
D_{calc}/g cm^{-3}	1.441	1.557	1.543	1.498	1.533
μ(Mo Kα)	0.237	0.593	0.528	0.577	0.701
Total data	32567	8967	86785	91586	67973
Unique data	5903	4856	8891	16090	8080
R_{int}	0.036	0.045	0.068	0.039	0.054
Observed data [$I > 2\sigma(I)$]	4384	2748	6006	12128	5569
$R1$ [$I > 2\sigma(I)$]	0.037	0.094	0.050	0.045	0.088
$wR2$ (all data)	0.096	0.286	0.144	0.129	0.279
Goodness of fit, S	1.05	1.05	1.07	1.07	1.02
ρ_{min}, ρ_{max}/e Å^{-3}	–0.34, 0.30	–0.90, 0.99	–0.50, 0.89	–1.37, 1.40	–0.90, 2.32

	4	**5**	**6**	**7**	**8**
Empirical formula	$C_{31}H_{37}ClCuN_6O_9S_2$	$C_{35}H_{36}Cl_2CuN_8O_5S_2$	$C_{62}H_{58}Cl_8Cu_5N_{12}O_{10}S_4$	$C_{37}H_{38}ClMn_2N_7O_{13}S_2$	$C_{36}H_{43}ClCo_2N_6O_{16}S_2$
Formula weight	800.78	847.28	1860.74	998.19	1033.19
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$Pbcn$	$P2_1/c$	$C2/c$
a/Å	12.3780(9)	17.2665(16)	28.033(2)	10.3700(4)	32.4899(9)
b/Å	12.6820(9)	23.398(3)	15.1201(11)	13.7747(6)	17.0596(5)
c/Å	12.7179(7)	9.6361(11)	17.8190(13)	28.8164(12)	18.0011(5)
α/°	114.347(2)	90	90	90	90
β/°	104.098(2)	106.029(4)	90	92.712(2)	119.150(1)
γ/°	92.327(2)	90	90	90	90
V/Å^3	1741.5(2)	3741.6(7)	7552.8(9)	4111.6(3)	8713.7(4)
Z	2	4	4	4	8
D_{calc}/g cm^{-3}	1.527	1.504	1.636	1.613	1.575
μ(Mo Kα)	0.886	0.892	1.841	0.855	0.995
Total data	27383	59920	58312	29239	79861
Unique data	6012	6629	6692	7244	8879
R_{int}	0.063	0.087	0.096	0.043	0.043
Observed data [$I > 2\sigma(I)$]	3657	4884	4948	5470	7092
$R1$ [$I > 2\sigma(I)$]	0.052	0.041	0.124	0.043	0.047
$wR2$ (all data)	0.134	0.091	0.305	0.122	0.137
Goodness of fit, S	1.02	1.02	1.12	1.01	1.04
ρ_{min}, ρ_{max}/e Å^{-3}	–0.59, 0.40	–0.56, 0.29	–1.73, 2.56	–0.51, 0.73	–1.45, 1.08

atoms associated with N and O atoms could be located in difference Fourier maps, but were included as riding on their parent atoms for subsequent refinement. Where the H atoms could not be located, they were included so as to form a reasonable H-bond network (see CIFs in the ESI for complete details†). The monoclinic lattice of **5** approximates orthorhombic-*C* and the crystal was *pseudo*-merohedrally twinned according to the twin law [1 0 1/0–1 0/0 0–1] (refined batch scale factor 0.1453(6)). The structure of **6** is of relatively low quality, but was the best that could be obtained from several batches. Modelling of the disordered $CuCl_4^{2-}$ counter anion seems to be only a moderate source of difficulty. Although the largest peaks in the difference density lie in this area, application of a continuous solvent-area model (using SQUEEZE in PLATON[12]) to account for this anion improves *wR*2 to only about 25%. Solvent-accessible voids of *ca* 80 Å^3 remain in the final refined structure, but no further atomic sites could be resolved and application of SQUEEZE to the final model again gave no significant improvement. In all structures containing perchlorate anions, the geometry of ClO_4^- was restrained to be tetrahedral, by restraining all Cl–O distances to a single refined value and all O···O distances to be 1.633 times that value. In cases with apparent rotational disorder, the ClO_4^- anions are modelled either in two orientations and/or with distorted anisotropic displacement ellipsoids.

Results and discussion

Ligand synthesis and X-ray crystal structures

Reaction of 2,6-dichlorosulfone-4-methylphenol with two equivalents of bis-(2-methylpyridyl)amine gives 2,6-bis(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-4-methylphenol, (bpsmpH) in good yield when the reaction is carried out in pyridine, Scheme 2. Initial attempts to carry out the reaction in chloroform resulted only in mono-substitution of the dichlorosulfonic acid by bis-2-methylpyridylamine, while the second chlorosulfonic acid group was hydrolysed to give 2-hydroxy-3-(*N*,*N*-bis-(2-pyridylmethyl)-sulfonamido)-5-methylbenzenesulfonic acid (see ESI for crystallographic details†).

The X-ray crystal structure of bpsmpH (Fig. 1) suggests that its deprotonated form is appropriate for the provision of two metal binding cavities. All four sulfone O atoms are located on one side of the plane defined by the phenol group so that the potential metal binding cavities are located on the opposite side of the plane. One of the pyridine groups forms an H-bond to the phenol group (N···O distance 2.4819(19) Å), with the H atom apparently disordered between N···H–O and N^+–H···O^- arrangements. Each sulfonamide N atom is located approximately 0.3 Å from the plane formed by the two C atoms and one S atom to which it is connected, and the N–S distance is shorter by around 0.1 Å compared to the corresponding distance in the metal complexes (*vide infra*). Thus, there must be significant electron delocalisation in the sulfonamide unit with the N atoms close to sp^2 hybridised, similar to that observed in complexes of deprotonated secondary sulfonamides. Inspection of the X-ray structures of the metal complexes of bpsmp$^-$ (*vide infra*) indicates that the electron density is redistributed on coordination, and a more pyramidal geometry is approached around the sulfonamide N atoms.

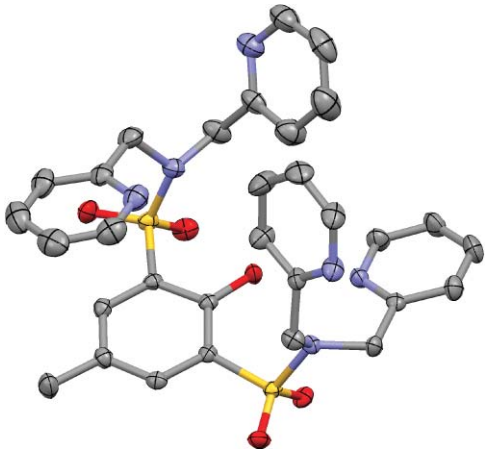


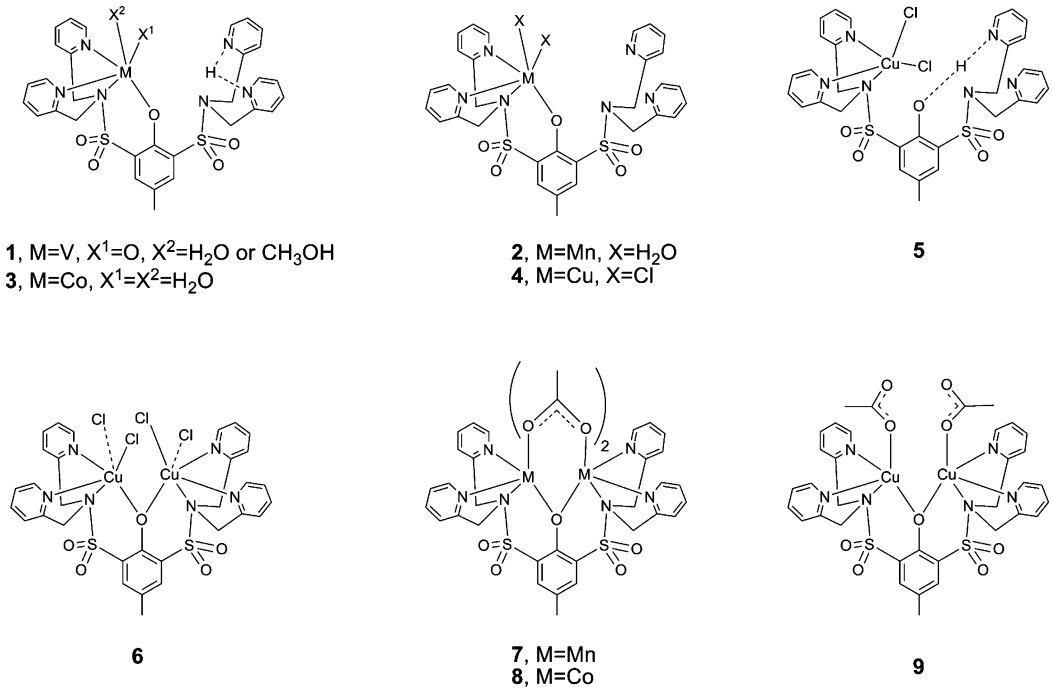
Fig. 1 X-ray crystal structure of bpsmpH with displacement ellipsoids drawn at 50% probability (H atoms omitted).

Synthesis and X-ray crystal structures of the metal complexes

Mononuclear $V^{IV}O$, Mn^{II}, Co^{II}, Cu^{II}, and dinuclear Mn^{II}_2, Co^{II}_2 and Cu^{II}_2 complexes of bpsmpH have been prepared (Scheme 3). In contrast to our experience with the phenolate-hinged dinucleating ligands, bpmp$^-$ and bpbp$^-$, it is apparent that a much greater degree of control is possible over the formation of mono *versus* dinuclear complexes using bpsmp$^-$. This is not controlled by reaction stoichiometry, rather it is by the nature of the potential ancillary ligands and the specific metal ions provided in reactions. For example, reaction of more than two equivalents of the perchorate salts of M^{II} (M = Mn or Co) with one equivalent of bpsmpH leads to isolation of the mononuclear aqua M^{II} complexes in high yields. By contrast, reaction under similar conditions of bpbpH with more than two equivalents of the perchorate salts of M^{II} (M = Mn, Co or Cu) gives dinuclear Co^{III}_2, Mn^{II}_2, $Mn^{III}Mn^{II}$ and Cu^{II}_2 complexes containing combinations of water- or methanol-derived ligands and/or perchlorate auxiliary ligands.[13-17] Given similarities of these ligand systems and product complexes with respect to charge and topology this observation is thus not likely to be due to solubility effects, rather it attests to the relatively weaker ligand field provided by the second binding site once the first is occupied by a metal ion in cases where relatively weakly coordinating auxiliary ligands are provided. When the geometrically suitable bridging, negatively charged acetate ligand is introduced to reaction mixtures, high yields of the dinuclear complexes are attained, even in the presence of stoichiometric amounts of the metal ions.

Mononuclear complexes

Reaction of bpsmpH with vanadyl(IV), manganese(II) and cobalt(II) perchlorate gave the mononuclear complexes, **1**, **2** and **3** (Scheme 3), while reaction of bpsmpH with copper(II) chloride led to three different compounds depending on the solvent and reaction stoichiometry. Mononuclear complexes **4** and **5** were formed with one equivalent of $CuCl_2$. Complex **4** was isolated from methanol/water, while **5** was isolated from acetonitrile. The dinuclear complex **6** was obtained by adding more than two equivalents of $CuCl_2$ to the reaction.



Scheme 3 Structurally-characterised complexes **1–8** (charges are not depicted).

The X-ray crystal structures of **1–5** are shown in Figs. 2–6. In complexes **1–3**, the metal ions show an octahedral geometry coordinated by the phenolate O atom and one bis-(2-methylpyridyl)sulfonamide group in a *fac* coordination mode. Two water ligands complete the coordination sphere in the Mn^{II} and Co^{II} complexes, while the $V^{IV}O$ complex has an oxido ligand and either a methanol or water ligand (disordered in the crystal structure). In this case, the oxido group lies *trans* to the sulfonamide N-donor (Fig. 2). In **1**, the two pyridine rings in the non-coordinated bis-(2-methylpyridyl)sulfonamide group adopt an approximately coplanar arrangement (akin to the *mer* coordination mode in complexes **4–6**), and the proton associated with the bpsmpH ligand links the two rings through an N^+–H···N hydrogen bond (N···N distance 2.740(4) Å). Complex **2** contains two complexes in its crystallographic asymmetric unit, with closely comparable geometries (rms deviation 0.18 Å for least-squares overlay of 47 non-H atoms). Both pyridine rings of the non-coordinated bis-(2-methylpyridyl)sulfonamide group accept H-bonds from coordinated water molecules in an adjacent complex, and phenolate and sulfonate O atoms also accept H-bonds from one of these water molecules. In this way, the crystallographically distinct complexes are associated into H-bonded pairs having approximate (non-crystallographic) C_2 symmetry (Fig. 3(b)). In the structure of **3**, the non-coordinated pyridine rings adopt an approximately coplanar arrangement similar to that in **1**, forming an N^+–H···N hydrogen bond (N···N distance 2.705(8) Å).

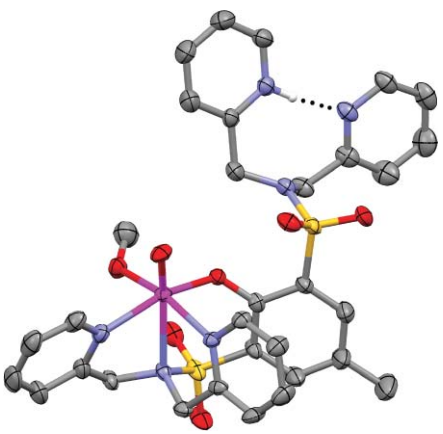


Fig. 2 Cation in **1** with displacement ellipsoids drawn at 50% probability. H atoms are omitted, except for that involved in the intra-complex N^+–H···N hydrogen bond (dotted line). The coordinated methanol molecule is disordered; alternatively, a water molecule occupies this coordination site.

In **4**, the Cu^{2+} ion adopts 5+1 octahedral coordination, bound by the phenolate O atom and the bis-(2-methylpyridyl)sulfonamide group in a *mer* coordination mode. One chloride ligand with a Cu–Cl distance of 2.2485(12) Å lies approximately in the same plane as the three N donors of the bis-(2-methylpyridyl)sulfonamide group, while a second chloride from an adjacent complex is associated with the copper ion *trans* to the phenolate group, with Cu–Cl = 3.410(2) Å. Thus, the [Cu(bpsmp)Cl] complexes are associated into centrosymmetric dimeric units through typical rhomboid-type Cu(μ-Cl)$_2$Cu bridges. The non-coordinated bis-(2-methylpyridyl)sulfonamide group forms a "pincer" type conformation in which the two pyridine rings come into approximate face-to-face contact, and the N atoms of both rings are involved in an H-bonded network through the lattice water molecules. One pyridine ring is apparently disordered and is modelled in two orientations. In one orientation, the N atom accepts an H-bond from a lattice water molecule, while in the other orientation it is involved in a C–H···N contact with an adjacent pyridine ring (H···N = 2.49 Å).

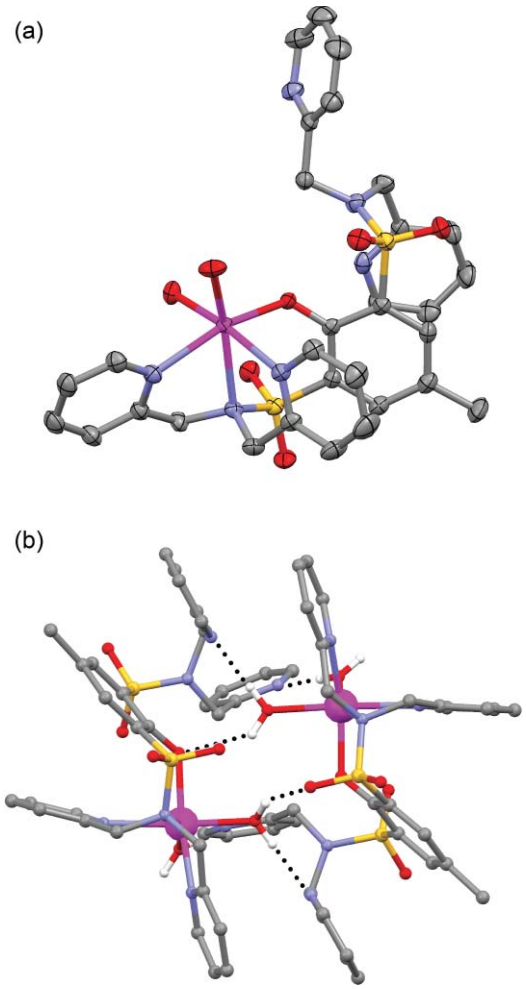


Fig. 3 (a) One of the two crystallographically distinct cations in **2** with displacement ellipsoids drawn at 50% probability (H atoms omitted). (b) Pair of complexes in **2** associated through O–H···N and O–H···O hydrogen bonds, projected along the approximate C_2 symmetry axis.

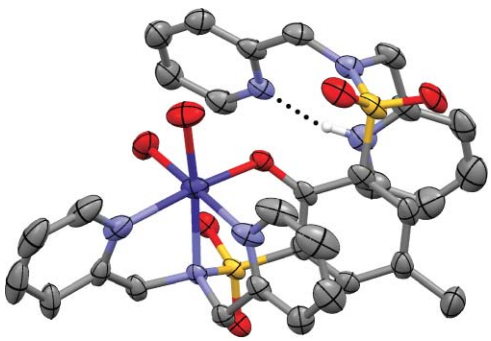


Fig. 4 Cation in **3** with displacement ellipsoids drawn at 50% probability. H atoms are omitted, except for that involved in the intra-complex N^+–H···N hydrogen bond (dotted line).

In the structure of **5**, the Cu^{2+} ion is bound by one bis-(2-methylpyridyl)sulfonamide group in a *mer* coordination mode and by two chlorides, giving a geometry between square-pyramidal and trigonal-bipyramidal (Addison parameter, $\tau = 0.27$).[18] The complex is unique amongst those described herein in that the phenolate O atom is not involved in metal coordination. Instead, the O atom

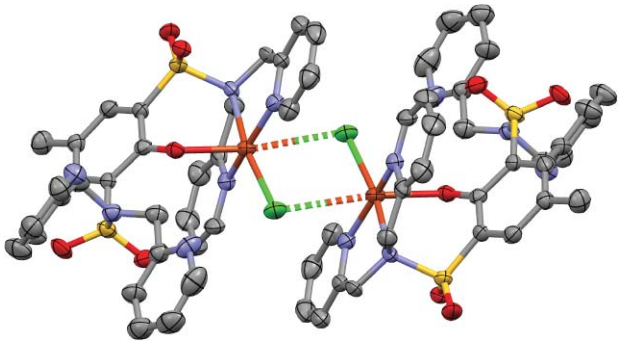


Fig. 5 Two complexes in **4** with displacement ellipsoids drawn at 50% probability (H atoms omitted). The dimeric unit is formed across a crystallographic centre of inversion.

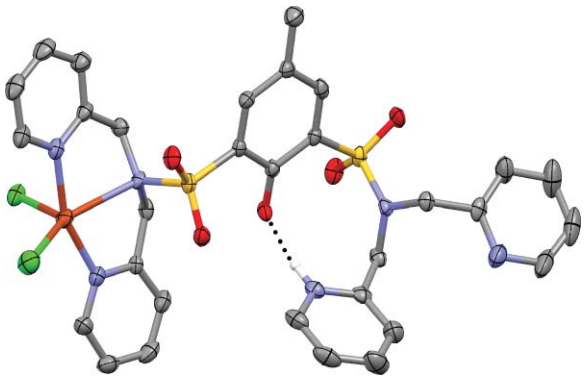


Fig. 6 Complex **5** with displacement ellipsoids drawn at 50% probability. H atoms are omitted, except for that involved in the intra-complex N^+–H···O hydrogen bond (dotted line).

accepts an intra-complex H-bond from one protonated pyridine ring in the non-coordinated bis-(2-methylpyridyl)sulfonamide group (N···O distance 2.529(4) Å). The N atom of the other non-coordinated pyridine ring does not form any H-bond interaction or any other obviously significant intermolecular interaction in the crystal structure.

In all of the mononuclear complexes **1**–**5**, most of the non-coordinated N-donors are either protonated or involved in H-bonding interactions (the exceptions being one N-donor in **5** and the N atom in one component of the disordered pyridine ring in **4**). Thus, after complexation of the first metal ion, the second potential metal binding does not appear to out-compete protonation and/or H-bonding interactions with polar protic solvents. Attempts to prepare dinuclear complexes simply by increasing the pH were unsuccessful, showing that protonation state alone is not sufficient to control formation of mononuclear *versus* dinuclear complexes.

Dinuclear complexes

The X-ray crystal structure of the dinuclear Cu^{2+} complex **6** is shown in Fig. 7. Both Cu^{2+} ions are coordinated by a bis-(2-methylpyridyl)sulfonamide group and the bridging phenolato O atom. The *mer* coordination mode of the bis-(2-methylpyridyl)sulfonamide group is consistent with that observed in the mononuclear Cu^{2+} complexes (**4** and **5**). The sulfonamide N atoms lie on opposite sides of the plane of the phenol ring, in

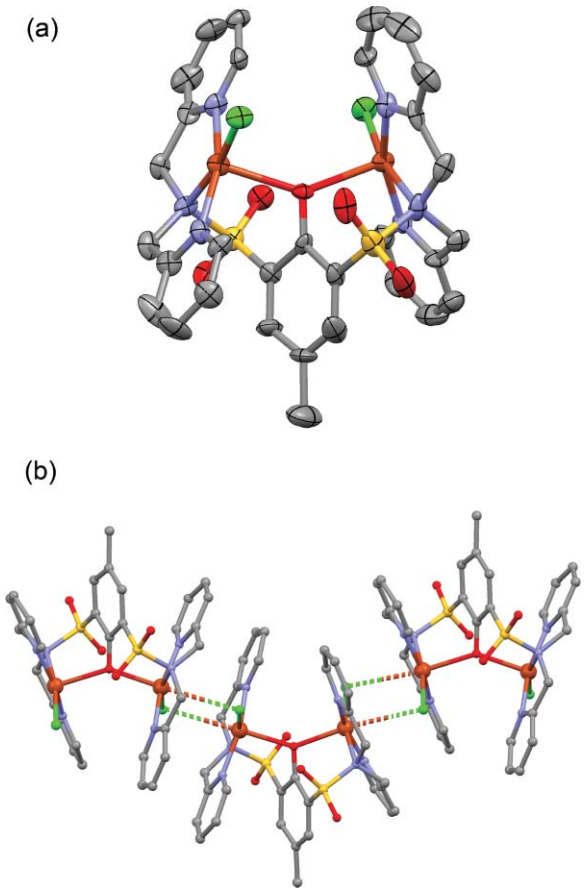


Fig. 7 (a) Complex **7** with displacement ellipsoids drawn at 50% probability (H atoms are omitted). (b) Coordination polymer formed through $Cu(\mu\text{-}Cl)_2Cu$ bridges.

contrast to the conformation observed in the crystal structure of the free bpsmpH ligand. The geometry around the Cu^{2+} ions is 5+1 octahedral. In addition to the donor O and N atoms derived from $bpsmp^-$, two chlorides complete the Cu^{2+} coordination sphere, with one short (Cu–Cl av. 2.25 Å) and one long (Cu···Cl av. 3.32 Å) distance. The longer Cu···Cl contacts associate the complexes into dimeric units through $Cu(\mu\text{-}Cl)_2Cu$ bridges comparable to those in **4**, thereby constructing a 1D coordination polymer (Fig. 7(b)). The stoichiometry of the reaction that produced **6** was approximately 1:3 bpsmpH:$CuCl_2$ and the excess $CuCl_2$ is found in the $CuCl_4^{2-}$ counter anion.

When reactions of bpsmpH with two equivalents of copper(II) manganese(II) or cobalt(II) perchlorate are carried out in the presence of acetate ions, the products are the dinuclear complexes **7–9** (Scheme 3). A similar reaction using $VO(ClO_4)_2$ resulted only in isolation of the mononuclear complex **1**; apparently, the possibility for $V^{IV}O$ to coordinate only one bridging acetato ligand is not sufficient to yield dinuclear vanadyl complexes. The dinuclear complexes of $bpsmp^-$ are isolated in lower oxidation states under aerobic conditions compared to their $bpmp^-$ and $bpbp^-$ counterparts, for which $Co^{II}Co^{III}$, $Co^{III}Co^{III}$, and $Mn^{II}Mn^{III}$ dominate.[14,16,19] This resistance to aerobic oxidation is consistent with the presence of electron-withdrawing sulfonamide groups. ESI mass spectra show all of the relevant cations as the dominant species, but daughter ions assignable to mononuclear species such as $[M(bpsmp]^+$ are also present. This is not the case for the ESI mass spectra of analogous $[M_2(bpbp)(CH_3CO_2)_2]^{+/2+}$ complexes.[14] Thus, it is apparent again that the affinity of $bpsmp^-$ for binding a second metal ion is less than that for binding the first.

In the crystalline state, the structures of complexes **7** and **8** are closely comparable (rms deviation 0.44 Å for least-squares overlay of 54 non-H atoms). The structure of **8** is shown in Fig. 8. The complexes exhibit approximate (non-crystallographic) C_2 symmetry, with the *pseudo*-rotation axis lying along the $C–O_{phenolate}$ bond. The bis-(2-methylpyridyl)sulfonamide groups adopt a *fac* coordination mode and the M^{2+} ions adopt distorted octahedral coordination geometries. In both complexes, the $M–N_{sulfonamide}$ bonds are significantly longer than the $M–N_{pyridine}$ bonds: 2.443(3) and 2.481(3) Å in **7** *cf* $Mn–N_{pyridine}$ ave 2.276 Å; 2.263(3) and 2.312(3) Å in **8** *cf* $Co–N_{pyridine}$ ave 2.123 Å. The $M–O_{acetato}$ distances are slightly more asymmetric in **7** compared to **8**, with the $Mn–O_{acetato}$ bond *trans* to the sulfonamide N donor being slightly longer than the $Mn–O_{acetato}$ bond *trans* to the pyridine N donor (2.122(2) and 2.103(2) *cf* 2.054(2) and 2.068(2) Å).

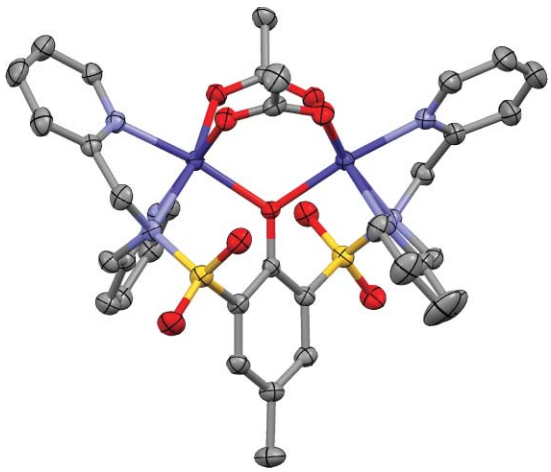


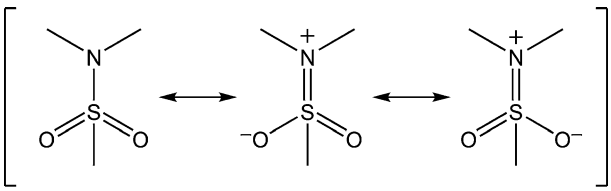
Fig. 8 Complex **8** with displacement ellipsoids drawn at 50% probability (H atoms are omitted).

To date, crystals of the dinuclear Cu^{II} complex **9** suitable for structural analysis have not been obtained. Two possibilities are conceivable for its structure: both acetato ligands could bridge the Cu^{2+} ions in a conformation comparable to **7** and **8**, or each acetato ligand could be coordinated to only one Cu^{2+} ion in a monodentate manner to give a structure more similar to that of **6** (Scheme 3) The first proposal gives six-coordinated Cu^{2+} with a *fac* coordination mode for the bis-(2-methylpyridyl)sulfonamide groups, while five-coordinated Cu^{2+} and a *mer* coordination mode are most commonly seen in Cu^{II}_2 complexes of $bpbp^-$ and $bpmp^-$.[17,20] Furthermore the ESI mass spectra of the **9** shows a different pattern of ions compared to **7** and **8**. Ions containing two metal ions and either one or two acetates along with ions containing one metal ion and an acetate. By contrast the Co and Mn systems gave ESIMS spectra showing either the molecular cation containing two metal ions and two acetates or mononuclear ions with no acetate. Taken together these results point to **9** containing non-bridging auxiliary acetato ligands. The most probable structure of **9** is therefore given by the second proposal. Mono-coordinated acetate has previously been observed

in the mono- and di-nuclear pentacoordinated Cu^{II} complexes of bis(2-pyridylmethyl)aniline.[21,22]

Discussion of the structural chemistry

Comparison of the N–S bond distances and angles around the sulfonamide N atoms of coordinated *versus* non-coordinated groups (in bpsmpH and its mono-substituted analogue†) reveals that the N–S distances in the non-coordinated groups are shorter by about 0.1 Å and that there is a near planar conformation around the N atom of an uncoordinated tertiary sulfonamide (for full details, see Table in ESI†). This confirms significant contribution from the canonical forms containing an N=S double bond in the resonance structures shown in Scheme 4. Although involvement of the N lone pair in coordination bonding should reduce the contribution of the N=S forms, inductive effects are still expected to decrease significantly the strength of the M–N bond. Thus, a tertiary sulfonamide N atom is a poorer electron donor than the N atom of a tertiary amine.



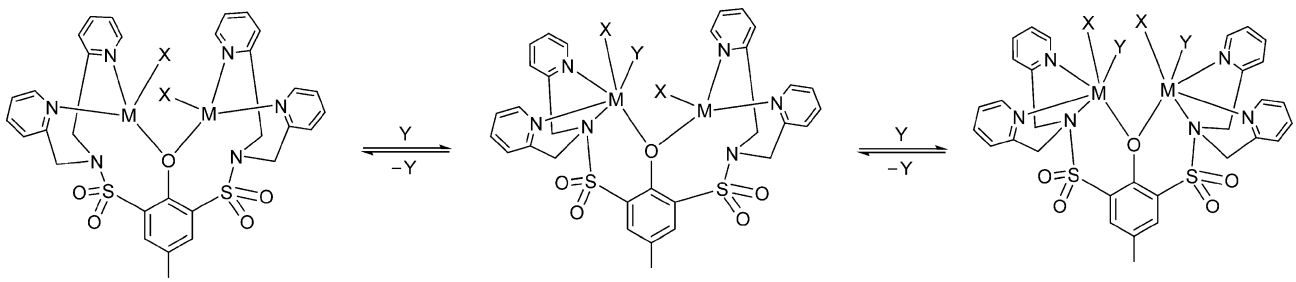
Scheme 4 Resonance structures for the tertiary sulfonamide group.

The two halves of the $bpsmp^-$ ligand are chemically equivalent until the first metal ion is bound. After coordination of the first metal ion, the donor strength of the bridging phenolate group is apparently reduced to such an extent that a second metal ion cannot be coordinated without the stabilising effect of auxiliary ligands, at least in polar and hydroxylic solvents. This effect is clearly not as strong for the $bpbp^-$ system. Apparently, two bridging acetate ligands are required to form dinuclear complexes for Mn^{2+} and Co^{2+}. For the vanadyl complexes, the presence of V=O prohibits more than one bridging acetate ligand and dinuclear complexes with $bpsmp^-$ have not been observed. For Cu^{2+}, the propensity for 5 or 5+1 coordination means that the dinuclear complex **6** could be synthesised without supporting acetate bridges, although some stabilisation must also be provided by formation of the coordination polymer in the solid state.

The $M–N_{sulfonamide}$ distances in the eight crystal structures described herein show a relatively large range, from 2.114(11) in **6** to 2.481(3) Å in **7**. The latter distance is more than 0.4 Å greater than the sum of the standard covalent radii for the Mn and N atoms concerned (1.35 + 0.68 = 2.03 Å)[23] and might therefore be regarded as a non-bonding contact. Thus, the structures of complexes **1–8** demonstrate a significant degree of topological and coordinative flexibility for the $bpsmp^-$ ligand. Although the tertiary sulfonamide N atom may be ostensibly non-bonded, it is unable to move too far from the metal ion since it connects three donor atoms in three chelating rings. This contrasts to the situation in the Ni^{2+} complexes of bis(1-methylbenzimidazolyl-2-methyl)-10-camphorsulfonamide (*L*),[3] where only two donor atoms in two chelating rings are connected by the sulfonamide. On decoordination in those cases, the sulfonamide can move away from the metal centre, resulting in $M \cdots N_{sulfonamide}$ distances greater than 3.65 Å in the octahedral $[LNi(CH_3CO_2)_2]^{2+}$ and tetrahedral $LNiCl_2$ complexes, and a loss of integrity in the overall structure of the complex through coordination of additional compensating ligands. In $bpsmp^-$, the sulfonamide group cannot be lost to the complex on decoordination, but rather is forced to remain in close proximity to the metal ions so that the integrity of the dinuclear complexes is retained. This feature permits speculation about feasible processes of *pseudo*-decoordination of the tertiary sulfonamide group(s) in $bpsmp^-$ complexes, for the purpose of stabilising various metal geometries needed for electrochemical or catalytic events involving coordination expansion or reduction (Scheme 5).

Conclusions

The ability to control the outcome of reactions of $bpsmp^-$ with metal ions, in terms of whether mononuclear or dinuclear complexes are isolated, stands in sharp contrast to the coordination chemistry observed for the counterpart acyclic dinucleating ligands containing tertiary amine groups in the same position ($bpmp^-$ and $bpbp^-$). One determining factor favouring the formation of dinuclear complexes is the availability of bridging acetate ligands. For example, reactions using Mn^{2+} or Co^{2+} carried out in the absence of acetate yielded only mononuclear complexes, even in the presence of excess metal ions (greater than 2 equivalents per $bpsmp^-$). The addition of acetate yielded dinuclear complexes from similar reaction mixtures, even without the presence of excess metal ions. The propensity for 5 or 5+1 coordination means that Cu^{2+} complexes behave differently from the other metal ions described here, and dinuclear complexes could be synthesised without supporting acetate bridges. By contrast, under similar reaction conditions dinuclear copper,[17] manganese,[13] cobalt[17] and vanadium[24] complexes containing exclusively dioxygen-,



Scheme 5 Proposal for coordination flexibility of the tertiary sulfonamide groups $bpsmp^-$ in accordance with metal geometry changes during addition and elimination reactions involving both metal centres.

water- or methanol-derived auxiliary ligands have been isolated using bpbp$^-$. The formation of mononuclear complexes of bpsmp$^-$ can be ascribed to the fact that the sulfonamide groups of bpsmp$^-$ are weaker donors compared to, for example, the corresponding amine groups of bpmp$^-$ and bpbp$^-$. The controllable accessibility in high yield of a range of mononuclear bpsmp$^-$ complexes might find use in stepwise preparations of mixed-metal complexes.

In addition to the control over metal nucleation a comparatively extensive range of structural types were observed *via* the coordination/decoordination of the pyridine, sulfonamide and phenol donors of bpsmp$^-$ compared to the structural topologies of the metal complexes of related heptadentate phenolato-hinged dinucleating ligands. The coordinative flexibility of bpsmp$^-$ evidenced here suggests potential for bpsmp$^-$ to be used for construction of complexes which might furnish a coordinatively flexible dimetallic active site for addition and elimination reactions, with the concurrent assistance of M–$N_{sulfonamide}$ coordination/decoordination. Thus, the ditopic site could potentially support two metal ions in various and different geometries. Future work will focus on a search for reactions which might be promoted or catalysed by such a geometrically and redox-flexible dimetallic site.

Notes and references

1 M. Suzuki, H. Kanatomi and I. Murase, *Chem. Lett.*, 1981, 1745–1748.
2 M. Ghiladi, C. J. McKenzie, A. Meier, A. K. Powell, J. Ulstrup and S. Wocadlo, *J. Chem. Soc., Dalton Trans.*, 1997, 4011–4018.
3 M. Calligaris, O. Carugo, G. Crippa, G. De Santis, M. Di Casa, L. Fabbrizzi, A. Poggi and B. Seghi, *Inorg. Chem.*, 1990, **29**, 2964–2970.
4 C.-H. Sun, T. J. Chow and L.-K. Liu, *Organometallics*, 1990, **9**, 560–565.
5 M. H. Klingele, B. Moubaraki, K. S. Murray and S. Brooker, *Chem.–Eur. J.*, 2005, **11**, 6962–6973.
6 W.-Z. Lee, H.-S. Tseng and T.-S. Kuo, *Dalton Trans.*, 2007, 2563–2570.
7 E. K. Barefield, A. Bianchi, E. J. Billo, P. J. Connolly, P. Paoletti, J. S. Summers and D. G. Van Derveer, *Inorg. Chem.*, 1986, **25**, 4197–4202.
8 See for example several complexes containing the bidentate chelate (*p*-toluenesulfonylamidomethyl)pyridine which can be related to a tridentate N_2O chelate of bpsmp$^-$(where bpsmp$^-$has a N_3O chelate because of the tertiary rather than secondary sulfonamide): L. Gutierrez, G. Alzuet, J. A. Real, J. Cano, J. Borras and A. Castineiras, *Inorg. Chem.*, 2000, **39**, 3608–3614; L. Gutierrez, G. Alzuet, J. Borras, M. Liu-Gonzalez, F. Sanz and A. Castineiras, *Polyhedron*, 2001, **20**, 703–709; A. Congreve, R. Kataky, M. Knell, D. Parker, H. Puschmann, K. Senanayake and L. Wylie, *New J. Chem.*, 2003, **27**, 98–106; M. L. Duran, J. A. Garcia-Vazquez, C. Gomez, A. Sousa-Pedrares, J. Romero and A. Sousa, *Eur. J. Inorg. Chem.*, 2002, 2348–2354.
9 J. Pollak, E. Gebauer-Füllneg and E. Riesz, *Monatsh. Chem.*, 1925, **46**, 383–397.
10 For simplicity of formulation the total solvent content of the crystal is written outside of the square brackets. The complex exhibits disorder in its crystal structure, with either MeOH or H_2O occupying the sixth coordination site on V. See the discussion in the text.
11 G. M. Sheldrick, *SHELXTL*, Bruker, AXS, Madison, WI, USA, 2000.
12 P. Vandersluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194–201; implemented as the SQUEEZE procedure in A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.
13 A. Boisen, A. Hazell and C. J. McKenzie, *Chem. Commun.*, 2001, 2136–2137.
14 K. B. Jensen, E. Johansen, F. B. Larsen and C. J. McKenzie, *Inorg. Chem.*, 2004, **43**, 3801–3803.
15 F. B. Larsen, A. Boisen, K. J. Berry, B. Moubaraki, K. S. Murray, V. McKee, R. C. Scarrow and C. J. McKenzie, *Eur. J. Inorg. Chem.*, 2006, 3841–3852.
16 M. Ghiladi, J. T. Gomez, A. Hazell, P. Kofod, J. Lumtscher and C. J. McKenzie, *Dalton Trans.*, 2003, 1320–1325.
17 P. Dalgaard, A. Hazell, C. J. McKenzie, B. Moubaraki and K. S. Murray, *Polyhedron*, 2000, **19**, 1909–1915.
18 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
19 H. Diril, H. R. Chang, X. H. Zhang, S. K. Larsen, J. A. Potenza, C. G. Pierpont, H. J. Schugar, S. S. Isied and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 6207–6208.
20 S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. Le Pape and D. Luneau, *Inorg. Chem.*, 2000, **39**, 3526–3536.
21 A. Nielsen, A. D. Bond and C. J. McKenzie, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, 478–480.
22 A. Nielsen, S. Veltze, A. D. Bond and C. J. McKenzie, *Polyhedron*, 2007, **26**, 1649–1657.
23 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19.
24 R. K. Egdal, A. D. Bond and C. J. McKenzie, *Dalton Trans.*, 2009, 3833–3839.

