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Novel aggregation of [Ni(thiolato)$_2$(amine)$_2$]-type square planes assisted by silver(I) ions†

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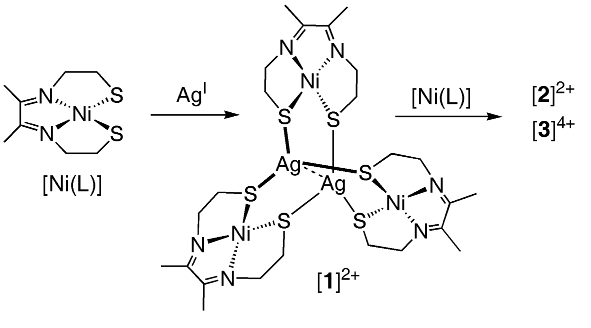
Treatment of [Ni(L)] [L = ($^{-}$SCH$_2$CH$_2$NH=C(CH$_3$)–)$_2$] with Ag$^+$ in water gave a pinwheel-like S-bridged Ni$^{II}_3$Ag$^I_2$ structure in [Ag$_2${Ni(L)}$_3$]$^{2+}$, which further reacted with [Ni(L)] to produce a Ni$^{II}_4$Ag$^I_2$ structure in [Ag$_2${Ni(L)}$_4$]$^{2+}$ and a Ni$^{II}_7$Ag$^I_4$ structure in [Ag$_4${Ni(L)}$_7$]$^{4+}$.

The use of square-planar thiolato Ni^{II} complexes as an S-donating metalloligand is currently of increasing interest, because this is a promising approach to create heterometallic aggregates with unusual structures and properties, which are, in some cases, relevant to structural and catalytic models of nickel-containing metalloenzymes.[1] Since the initial investigations by Jicha and Busch,[2] [Ni(NH$_2$CH$_2$CH$_2$S)$_2$] and its related [Ni(thiolato)$_2$-(amine)$_2$]-type complexes have been shown to act as an effective bidentate-*S,S* metalloligand toward various transition metal ions, such as Fe^{II}, Co^{II}, Zn^{II}, Cu^I and Pd^{II}, giving a variety of S-bridged heterometallic aggregates.[3] However, the ligating ability of these complexes toward Ag^I ion has rarely been investigated, although it has been recognized that Ag^I ion has a great affinity for co-ordinated thiolato groups to form versatile S-bridged polynuclear structures.[4] Thus, as part of our recent project to construct metallo-supramolecules by the aggregation of thiolato metal complexes in combination with Ag^I ions,[5] we investigated the reactions of [Ni(L)] [L = ($^{-}$SCH$_2$CH$_2$NH=C(CH$_3$)–)$_2$][6] with Ag^I. Because Ag^I ion bound by thiolato-type metalloligands tends to adopt a two-coordinate geometry, we expected the formation of an S-bridged tetranuclear [Ag$_2${Ni(L)$_2$}$_2$]$^{2+}$, the structure of which is analogous to that of [Au$_2${Ni(D-penicillaminato-*N,S*)$_2$}$_2$]$^{2-}$.[7] However, the reaction product was found to be an S-bridged Ni$^{II}_3$Ag$^I_2$ pentanuclear complex, which further reacted with [Ni(L)] to construct S-bridged metallo-aggregates with a higher nuclearity (Scheme 1).

Treatment of an aqueous suspension of [Ni(L)] with AgBF$_4$ in a *ca.* 3 : 2 ratio gave an almost black solution, from which black crystals ([**1**](BF$_4$)$_2$·1.5H$_2$O) were isolated in a high yield (77%). A similar reaction in a *ca.* 1 : 1 ratio also afforded [**1**](BF$_4$)$_2$·1.5H$_2$O, but in a low yield (9%). The plasma emission spectral analysis indicated that [**1**](BF$_4$)$_2$·1.5H$_2$O contains Ni and Ag in a 3 : 2 ratio, and its elemental analysis was consistent with the 3 : 2 stoichiometry of [Ni(L)]$_3$(AgBF$_4$)$_2$. The electronic absorption spectrum of [**1**]$^{2+}$ in water is similar to that of the mononuclear [Ni(L)], although the characteristic intense visible band with two components observed for [Ni(L)] (450 nm, 486 nm) is located at the shorter wavelength side for [**1**]$^{2+}$ (440 nm, 465 nm). This is indicative of the existence of square-planar [Ni(L)] units in [**1**]$^{2+}$.



Scheme 1

The divalent S-bridged structure in [**1**]$^{2+}$, which consists of three square-planar [Ni(L)] units and two Ag^I atoms, was determined by X-ray analysis.‡ The bond distances and angles about each [Ni(L)] unit (av. Ni–S = 2.149(2) Å, S–Ni–S = 97.42(9)°) are essentially the same as those found in the mononuclear [Ni(L)] (av. Ni–S = 2.147(3) Å, S–Ni–S = 97.1(1)°).[8] As shown in Fig. 1, each of the two Ag^I atoms has a trigonal-planar geometry (av. Ag–S = 2.549(2) Å, S–Ag–S = 119.88(8)°) co-ordinated by three thiolato S atoms from three different [Ni(L)] units. The two AgS$_3$ trigonal planes face to each other joined by three perpendicular NiN$_2$S$_2$ square planes, forming a pinwheel-like S-bridged pentanuclear structure with an averaged C_{3h} symmetry. The two Ag^I atoms lie 0.07 Å (Ag1) and 0.11 Å (Ag2) out of the S$_3$ trigonal planes toward the center of the structure with a Ag···Ag distance of 3.039(1) Å. This is suggestive of the presence of an appreciable bonding interaction between the two trigonal-planar Ag^I atoms in [**1**]$^{2+}$.[9] It should be noted that in [**1**](BF$_4$)$_2$·1.5H$_2$O a BF$_4^-$ anion and a water molecule contact with the apical positions of Ag2 and Ag1 with Ag···F and Ag···O distances of 3.02(1) Å and 3.16(1) Å, respectively. The ^{1}H NMR spectrum of [**1**](BF$_4$)$_2$· 1.5H$_2$O in d_6-DMSO exhibits only one methyl signal and furthermore, its ^{13}C NMR spectrum gives only one set of four signals due to four kinds of carbon atoms of the ligand L. This result suggests that the C_{3h} symmetrical structure in [**1**]$^{2+}$ is retained in solution. Consistent with this, the electrospray mass (ES-MS) spectrum of [**1**](BF$_4$)$_2$ in H$_2$O gave a main signal at *m*/*z* = 499, the calculated molecular mass and the isotopic distribution of which match well with those for [Ag$_2${Ni(L)}$_3$]$^{2+}$.

The apical interaction of Ag^I atoms with a BF$_4^-$ anion or a water molecule found in [**1**](BF$_4$)$_2$·1.5H$_2$O prompted us to investigate the reactions of this complex with additional [Ni(L)], which may produce some adducts of [**1**]$^{2+}$ with [Ni(L)]. Indeed,

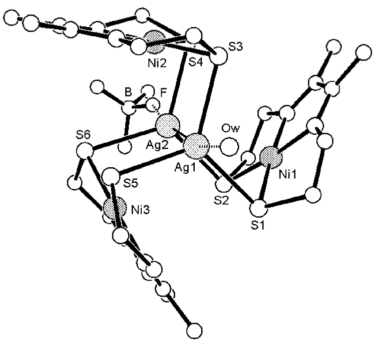


Fig. 1 A perspective view of complex cation [**1**]$^{2+}$.

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† Electronic supplementary information (ESI) available: detailed experimental data for complexes **1**–**3**. See http://www.rsc.org/suppdata/cc/b4/b404512b/

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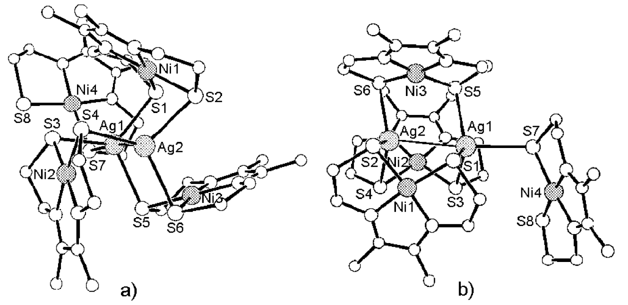

Fig. 2 a) Top and b) side perspective views of complex cation [**2**]$^{2+}$.

when [**1**]$(BF_4)_2\cdot 1.5H_2O$ was treated with ca. 2 molar equiv of [Ni(L)] in water, black crystals of [**2**]$(BF_4)_2$, which contains [Ni(L)] and Ag^I in a 2 : 1 ratio, were isolated. X-Ray analysis demonstrated that [**2**]$^{2+}$ is a novel S-bridged $Ni^{II}{}_4Ag^I{}_2$ hexanuclear complex, in which one square-planar [Ni(L)] unit is bound to a pinwheel-like $[Ag_2\{Ni(L)\}_3]^{2+}$ unit through the weak Ag1–S7 bond (2.771(2) Å), as illustrated in Fig. 2.‡ The overall structure of the $[Ag_2\{Ni(L)\}_3]^{2+}$ unit in [**2**]$^{2+}$ (av. Ag–S = 2.574(2) Å, S–Ag–S = 116.85(7)°) is similar to that of [**1**]$^{2+}$. However, in [**2**]$^{2+}$ Ag1 is considerably deviated from the S1–S3–S5 plane by 0.46 Å toward S7 of the pendant [Ni(L)] unit, while the Ag···Ag distance in [**2**]$^{2+}$ (3.1933(8) Å) is only 0.15 Å longer than that in [**1**]$^{2+}$ owing to the large deviation of Ag2 from the S2–S4–S6 plane (0.46 Å) in the same direction. Thus, it is considered that the pinwheel-like $[Ag_2\{Ni(L)\}_3]^{2+}$ structure inherently involves a bonding interaction between two trigonal-planar Ag^I atoms. In the ES-MS spectrum in water, [**2**]$^{2+}$ gives the signal for $[Ag_2\{Ni(L)\}_3]^{2+}$ (m/z = 499), besides a signal at m/z = 629, which is assignable to $[Ag\{Ni(L)\}_2]^+$ rather than to $[Ag_2\{Ni(L)\}_4]^{2+}$ based on the isotopic distribution. This suggests that the pinwheel-like $[Ag_2\{Ni(L)\}_3]^{2+}$ unit in [**2**]$^{2+}$ is, at least in part, retained in solution. Despite the presence of the pendant [Ni(L)] unit in [**2**]$^{2+}$, its NMR spectral behaviour is essentially the same as that for [**1**]$^{2+}$, showing one methyl signal in the^{1}H NMR spectrum and one set of four signals in the ^{13}C NMR spectrum. Thus, the exchange of the four [Ni(L)] units in [**2**]$^{2+}$, which is fast on the NMR time scale, seems to occur in solution.

When [**1**]$(BF_4)_2\cdot 1.5H_2O$ was treated with *ca.* 1 molar equiv of [Ni(L)] in water, another S-bridged polynuclear complex ([**3**]$(BF_4)_4\cdot H_2O$) consisting of two $[Ag_2\{Ni(L)\}_3]^{2+}$ pentanuclear units and a [Ni(L)] mononuclear unit was produced. The assignment of [**3**]$^{4+}$ was made by the elemental and plasma emission spectral analyses, together with the electronic absorption and NMR spectroscopies. Furthermore, X-ray analysis for [**3**]$(BF_4)_2(PF_6)_2$ established a unique S-bridged $Ni^{II}{}_7Ag^I{}_4$ structure,‡ in which two pinwheel-like $[Ag_2\{Ni(L)\}_3]^{2+}$ units are spanned by one [Ni(L)] unit through two Ag–S bonds (Fig. 3), although a detailed structure discussion is precluded because of the poor crystal quality.[10]

In summary, the present study first shows the aggregation of [Ni(L)] square planes assisted by Ag^I ions, which generates the pinwheel-like S-bridged $Ni^{II}{}_3Ag^I{}_2$ pentanuclear structure in [**1**]$^{2+}$ having a Ag···Ag bonding interaction between two trigonal-planar Ag^I atoms. Interestingly, [**1**]$^{2+}$ showed reactivity toward additional [Ni(L)] to produce S-bridged $Ni^{II}{}_4Ag^I{}_2$ and $Ni^{II}{}_7Ag^I{}_4$ aggregates, retaining the pinwheel-like $Ni^{II}{}_3Ag^I{}_2$ structure. Thus, [**1**]$^{2+}$ and its related $M_3Ag^I{}_2$-type complexes could be available as a new class of heterometallic building blocks for creating a variety of metallo-supramolecules through a combination of other building blocks that contain donor groups toward Ag^I ion.

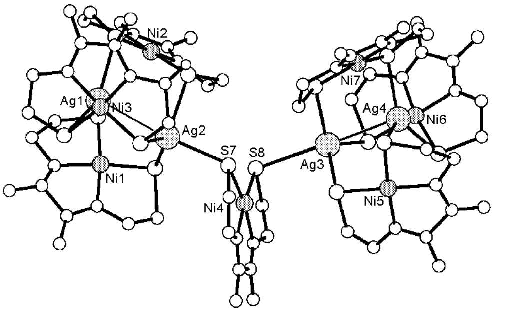

Fig. 3 A perspective view of complex cation [**3**]$^{4+}$.

Notes and references

‡ Crystal data for [**1**]$(BF_4)_2\cdot 1.5H_2O$: M = 1199.5, monoclinic, space group $P2_1/n$, a = 12.050(2), b = 21.185(3), c = 16.590(2) Å, β = 98.30(1)°, V = 4190(1) Å^3, Z = 4, μ(Mo–Kα) = 2.605 mm^{-1}, T = 293 K, 9636 unique reflections, 4702 reflections with $I > 2.0\sigma(I)$, R = 0.051 ($I > 2.0\sigma(I)$), wR = 0.135 (all data). CCDC 234576. Crystal data for [**2**]$(BF_4)_2$: M = 1433.5, monoclinic, space group $P2_1/c$, a = 13.438(2), b = 20.621(5), c = 18.811(3) Å, β = 93.03(1)°, V = 5205(1) Å^3, Z = 4, μ (Mo–Kα) = 2.537 mm^{-1}, T = 296 K, 11923 unique reflections, 8762 reflections with $I > 2.0\sigma(I)$, R = 0.045 ($I > 2.0\sigma(I)$), wR = 0.143 (all data). CCDC 234577. Crystal data for [**3**]$(BF_4)_2(PF_6)_2$: a = 29.913(8), b = 23.007(6), c = 13.787(4) Å, β = 98.74(2)°, V = 9378(4) Å^3, Z = 4. See http://www.rsc.org/suppdata/cc/b4/b404512b/ for crystallographic data in .cif format.

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10 The NMR and ES-MS spectral features of [**3**]$^{4+}$ are very similar to those of [**2**]$^{2+}$, suggestive of the existence of the pinwheel-like $[Ag_2\{Ni(L)\}_3]^{2+}$ units and of the facile exchange of the [Ni(L)] units in solution.