Encapsulation of a trinuclear silver(I) cluster by two imido-nitrido metalloligands [{Ti(η⁵-C₅Me₅)(μ-NH)}₃(μ₃-N)]

Avelino Martín, Noelia Martínez-Espada, Miguel Mena and Carlos Yélamos*

Departamento de Química Inorgánica, Universidad de Alcalá. 28871 Alcalá de Henares-Madrid (Spain). E-mail: carlos.yelamos@uah.es

Abstract:

Treatment of the metalloligand [{Ti(η⁵-C₅Me₅)(μ-NH)}₃(μ₃-N)] with silver(I) trifluoromethanesulfonate in different molar ratios gives the ionic compounds [Ag{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)}₂][O₃SCF₃] and [Ag{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)}₂][O₃SCF₃] or the triangular silver cluster [(CF₃SO₂O)₃Ag₃{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)}₂(μ₃-N)] in which each face is capped by a metalloligand.
As part of a program related to the synthesis of polynuclear nitrido complexes,\(^1\) we have been studying the coordination chemistry of the trinuclear imido-nitrido complex \([\{Ti(\eta^5-C_5Me_5)(\mu-NH)\}_{3}(\mu_3-N)\}]^2\) (1) with a variety of main-group and transition metals.\(^3\) In those studies, we have noted that 1 is prone to act as tridentate chelate to a single metal (e.g. Ti, Sn, Zn, Cu) through the basal NH imido groups, although in some solid-state structures coordination by only one NH group to the metal center (Sn, Zn, Al, Ga, In) has been observed. In many aspects the metalloligand 1 resembles other well-known tridentate nitrogen ligands in coordination chemistry as tris(pyrazolyl)borates,\(^4\) tris(pyrazolyl)methanes,\(^5\) 1,4,7-triazacyclononanes,\(^6\) and especially 1,3,5-triazacyclohexanes.\(^7\) However, the existence of the \(\mu_3-N\) nitrido apical group confers a more rigid conformation to 1 when compared with those systems. Here we report the preliminary study about the interactions of silver(I) salts with our metalloligand. The conventional tridentate chelate coordination mode of 1 is observed for several ionic complexes while an unprecedented bridging mode (\(\mu_3-\eta^1;\eta^1;\eta^1\)) has been structurally characterized in the triangular silver(I) cluster \([\{(CF_3SO_2O)_{3}Ag_3\{\mu_3-NH\}_3Ti_3(\eta^5-C_5Me_5)\}_{3}(\mu_3-N)\}]_2\).

The results obtained in the treatment of \([\{Ti(\eta^5-C_5Me_5)(\mu-NH)\}_{3}(\mu_3-N)\}]\) (1) with silver(I) trifluoromethanesulfonate in different ratios are summarized in Scheme 1. The reaction of 1 with half equivalent of \([Ag(O_3SCF_3)]\) in dichloromethane at room temperature in the absence of light led to the corner-shared double-cube ionic complex \([Ag\{\mu_3(NH)_{3}Ti_3(\eta^5-C_5Me_5)_{3}(\mu_3-N)\}]_2[O_3SCF_3]\) (2). Analogous treatment in a 1:1 ratio gave the complex \([Ag\{\mu_3(NH)_{3}Ti_3(\eta^5-C_5Me_5)_{3}(\mu_3-N)\}]_2[O_3SCF_3]\) (3). When the ratio of \([Ag(O_3SCF_3)]\) to the metalloligand was higher than 1.5:1 the trinuclear silver(I) compound \([\{(CF_3SO_2O)_{3}Ag_3\{\mu_3-NH\}_3Ti_3(\eta^5-C_5Me_5)_{3}(\mu_3-N)\}]_2\) (4) was obtained.
Compounds 2-4 were isolated in 50-82% yield as air and light sensitive yellow or orange solids, which are very soluble in halogenated solvents. However, whereas 2 and 3 are scarcely soluble in toluene or benzene, according to an ionic composition, complex 4 exhibits higher solubility in those solvents. The stability of complexes 2-4 in chloroform-d$_1$ was monitored by NMR spectroscopy. Compound 3 is stable for months, but solutions of 2 immediately undergo partial dissociation (ca. 5% conversion) to give 3 and 1. This mixture remains unaltered for long periods of time even after heating at high temperatures. However, addition of [Ag(O$_3$SCF$_3$)] (1 equiv) to this solution at room temperature afforded immediately the complete consumption of 2 and only resonance signals assigned to complex 3 were observed in the NMR spectra. On the other hand, spectra taken after heating of 4 in chloroform-d$_1$ revealed minor resonance signals due to 3, but only upon leaving the NMR tube at 80 °C for 3 days the spectra showed complete consumption of 4 to give complex 3 along with the precipitation of [Ag(O$_3$SCF$_3$)]. Stirring of this mixture at room temperature for 1 day regenerated complex 4.

Scheme 1. Reactions of 1 with [Ag(O$_3$SCF$_3$)]. [Ti] = Ti(η$^5$-C$_5$Me$_5$).
Compounds 2-4 were characterized by analytical and spectroscopic methods, as well as by X-ray crystal structure determinations for 2 and 4. ¹ IR spectra (KBr) of complexes 2-4 show two $v_{\text{NH}}$ vibrations, between 3357 and 3261 cm$^{-1}$, in a similar range to the value determined for 1, ² 3352 cm$^{-1}$. Information regarding the possible interaction of the triflate anion with a metal center may be obtained from the solid IR spectra in the 1350-1000 cm$^{-1}$ range. ⁸ While in 2 the $v_{\text{as}}(\text{SO}_3)$ band is observed at 1274 cm$^{-1}$, which is closely similar to that found for the free CF$_3$SO$_3^-$ ion, ⁸b the analogous stretching mode in 3 splits into two bands at 1276 and 1263 cm$^{-1}$, indicating some interaction of the triflate ion with the silver cation in the solid state. ⁸c,d The splitting in two well-defined bands at 1290 and 1236 cm$^{-1}$ found in compound 4 may agree with the coordination of the triflate groups. The $^1$H and $^{13}$C($^1$H) NMR spectra in chloroform-d$_1$ of 2 and 3 at room temperature show resonance signals for equivalent NH and $\eta^5$-C$_5$Me$_5$ groups, suggesting a highly symmetrical structure or very fast exchange processes in solution, as those observed previously in other adducts of 1. ³ The NH resonance signals, $\delta = 12.12$ (2) and 12.25 (3), in the $^1$H NMR spectra are shifted to higher field with respect to that found for 1 ($\delta = 13.40$), suggesting a tridentate coordination of the ligand to the silver(I) ion. ⁳d Thus, the NMR data for 2 would be consistent with a trigonally distorted octahedral geometry around the silver center, as determined previously for other silver(I) ionic complexes with two tridentate nitrogen ligands. ⁶b,⁹ However, the solid-state structure of 2 determined by an X-ray analysis reveals a linear two-coordinate environment for the silver center in the cationic fragment (Figure 1). The silver atom lies on an inversion center and exhibits two silver-nitrogen distances, Ag(1)-N(13) 3.240(4) Å and Ag(1)-N(12) 2.900(4) Å, clearly longer than that to N(23) 2.205(4) Å but still shorter than the sum of the van der Waals radii (3.30 Å). ¹⁰
Geometrical parameters of the organometallic ligand are similar to those of the parent compound 1.²

![Diagram of complex 2](image)

**Figure 1.** Cationic fragment of the crystal structure of complex 2 (thermal ellipsoids at the 50% probability level). The prime character in the labels indicates that these atoms are at equivalent position (-x,-y,-z). Selected lengths (Å) and angles (°): Ag(1)-N(23) 2.205(4), Ag(1)-N(13) 3.240(4), Ag(1)-N(12) 2.900(4), Ag(1)···Ti(1) 3.784(1), Ag(1)···Ti(2) 3.102(1), Ag(1)···Ti(3) 3.377(1), averaged values for N(1)-Ti 1.93(1), Nbasal-Ti 1.96(2), Ti···Ti 2.848(5), N(23)-Ag(1)···N(23)' 180.0, Ti-Nbasal-Ti 93(1), Ti-Napical-Ti 94.9(5), Nbasal-Ti-Nbasal 106.6(9), Nbasal-Ti-Napical 85.6(5).

Compound 4 is soluble in toluene or benzene, and its $^1$H, $^{13}$C{$^1$H} and $^{19}$F NMR spectra in benzene-d₆ or chloroform-d₁ at room temperature are very similar. The spectra show resonance signals for equivalent NH and $\eta^5$-C₅Me₅ ligands. The $^1$H NMR spectrum in
chloroform-d\textsubscript{1} reveals \textsuperscript{1}H-\textsuperscript{107,109}Ag couplings (\textsuperscript{2}J\textsubscript{H,Ag} = 6 Hz) for the imido groups, suggesting a static structure in solution. \textsuperscript{13}C{\textsuperscript{1}H} NMR spectrum shows a singlet for the ipso-carbon resonance of the C\textsubscript{5}Me\textsubscript{5} groups at \(\delta = 127.2\), which is ca. 7 ppm shifted downfield with respect to those found in complexes 2 (\(\delta = 119.9\)) and 3 (\(\delta = 120.6\)). These data are consistent with the solid-state structure determined by X-ray crystallography (Figure 2). The complex contains an equilateral triangular cluster of Ag\textsuperscript{1} ions, with Ag-Ag separations of av. 2.978(3) Å; each face of the triangle is capped by a single “\((\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\)” metalloligand which binds to each silver center by one NH imido group. Therefore, every Ag\textsuperscript{1} is coordinated, in addition to the two Ag-Ag interactions, by two NH ligands and one oxygen atom of a triflate group. Thus, the geometry around the silver centers becomes a distorted trigonal-bipyramid with the nitrogen atoms at the axial positions (N-Ag-N 170.7(3)\textsuperscircled{o}) and two silver and the oxygen atoms at the equatorial plane (sum of angles = 357(1)\textsuperscircled{o}). The Ag-N distances (av. 2.175(7) Å) range between those found for two-coordinate [av. 2.11 Å] and six-coordinate [av. 2.27 Å] Ag\textsuperscript{1} ions in trinuclear silver complexes with (\(\mu_3-\eta^1:\eta^1:\eta^1\)) tris(pyrazolyl)borate ligands\textsuperscript{11} and are also similar to that found in complex 2. The Ag-O distance of av. 2.66(3) Å is smaller than the sum of the van der Waals radii of 3.20 Å,\textsuperscript{10} and could be considered to be a coordinative Ag···O interaction,\textsuperscript{12} in good agreement with the IR data. The coordination of the metalloligand to three silver atoms in 4 results in a slightly lengthening of the Ti-N\textsubscript{imido} and Ti···Ti distances, average 2.009(7) Å and 2.879(5) Å respectively, when compared with 1 (average 1.924 Å and 2.802 Å) without any other significant changes in bond lengths and angles.\textsuperscript{2}
Figure 2. Crystal structure of complex 4 (thermal ellipsoids at the 50% probability level).

The methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity. Average of selected lengths (Å) and angles (°): Ag-Ag 2.978(3), Ag-N 2.175(7), Ag-O 2.66(3), Ti-Nbasal 2.009(7), Ti-Napical 1.922(4), Ti···Ti 2.879(5), Ag-Ag-Ag 60.0(1), Ag-Ag-O 149(1), N-Ag-N 170.7(3), N-Ag-Ag 94(4), N-Ag-O 85(7), Ti-Nbasal-Ti 91.5(3), Ti-Napical-Ti 96.9(2), Nbasal-Ti-Nbasal 110.0(7), Nbasal-Ti-Napical 85.4(2), Ti-Ti-Ti 60.0(1).

In conclusion, we have demonstrated that [{Ti(η₅-C₅Me₅)(μ-NH)}₃(μ₂-N)] can interact with both a single silver cation or trinuclear silver clusters through different binding modes. In particular, the unprecedented coordination mode (μ₂-η¹:η¹:η¹) observed in complex 4 should be common for trinuclear systems containing metal-metal bonds or metallophilic interactions and will be the scope of our next investigations.

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Notes and references

‡ Crystal data for 2: C_{61}H_{96}AgF_{3}N_{8}O_{3}STi_{6}, M = 1473.79, triclinic, a = 11.6024(18), b = 11.61.93(11), c = 14.7433(18) Å, α = 109.264(9), β = 111.742(12), γ = 95.191(9), U = 1690.8(4) Å³, T = 200(2) K, space group P-1, Z = 1, μ(Mo-Kα) = 1.042 mm⁻¹. 41498 reflections measured, 7597 unique (R_int = 0.057) which were used in all calculations. R_1(F²) = 0.064 (for 5044 reflections with F_o > 4σ(F_o)) and wR2 = 0.237 for all data.

Crystal data for 4·C_{7}H_{10}Ag_{3}F_{3}N_{8}O_{9}S_{3}Ti_{6}, M = 2079.8, monoclinic, a = 16.058(3), b = 20.694(6), c = 37.507(11) Å, β = 93.956(19), U = 12434(5) Å³, T = 200(2) K, space group P2₁/c, Z = 4, μ(Mo-Kα) = 0.927 mm⁻¹, 117004 reflections measured, 28264 unique (R_int = 0.076) which were used in all calculations. R_1(F²) = 0.051 (for 16649 reflections with F_o > 4σ(F_o)) and wR2 = 0.146 for all data.


