Alkylation of Nonbridging Thiolato Groups in an S-bridged $Co^{III}Pd^{II}Co^{III}$ Trinuclear Complex: Control of Geometrical Isomerism by Tuning Trans Influence Due to Sulfur Donors

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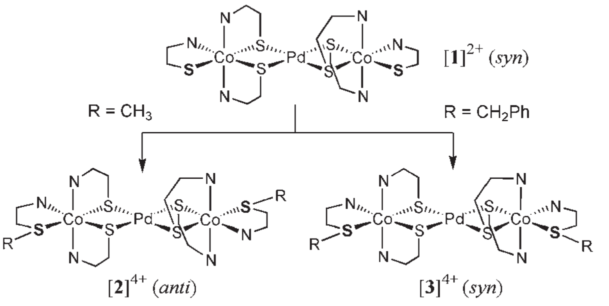
The methylation of two terminal nonbridging thiolato groups in *syn*-$[Pd\{Co(aet)_3\}_2]^{2+}$ (aet = 2-aminoethanethiolate) was accompanied by the syn-to-anti isomerization, while the benzylation proceeded with retention of the syn configuration. The molecular structures of two alkylated $Co^{III}Pd^{II}Co^{III}$ complexes were determined by X-ray crystallography.

It has been recognized that thiolato groups bound to a certain transition-metal center possess relatively high nucleophilicity, which often leads to derivatives modified at sulfur atoms without the cleavage of metal–sulfur bonds.[1,2] For example, oxidation reactions afford coordinated sulfenato and sulfinato species,[1] while alkylation reactions produce various coordinated thioether species.[2] Up to date, these investigations have been extensively made for mononuclear complex systems, such as Co^{III} and Ni^{II},[1a–d,2a–c] and it has been shown that the modification at thiolato donors affects the spectroscopic and stereochemical properties of complexes. On the other hand, the modification at thiolato donors for polynuclear systems has rarely been investigated,[2d] mainly because of the difficulty in isolating polynuclear complexes with nonbridging thiolato groups. In this paper we report on the alkylation reactions of a S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex having two nonbridging thiolato groups at the terminal, $\Delta\Delta/\Lambda\Lambda$-*syn*-$[Pd\{Co(aet)_3\}_2]^{2+}$ ($[\mathbf{1}]^{2+}$), which has been stereoselectively prepared from $[Co(aet)_3]$ and Pd^{II}.[3] A remarkable effect on the syn-anti geometrical isomerism due to the alkylation of thiolato donors is reported (Scheme 1).



Scheme 1.

Treatment of an aqueous solution ($10\,cm^3$) of $[\mathbf{1}]Cl_2{\cdot}5H_2O$ (0.20 g) with dimethyl sulfate ($1\,cm^3$) caused a solution color change from dark brown to red, after stirring at room temperature for 1 h. The red aqueous solution, separated from an organic layer, was chromatographed on an SP-Sephadex C-25 column. Only one red band was eluted with a $0.5\,mol\,dm^{-3}$ aqueous NaCl solution, and from the eluate red crystals ($[\mathbf{2}]Cl_4{\cdot}7H_2O$) were isolated in a reasonable yield (68%).[4] Complex $[\mathbf{2}]Cl_4$ was also obtained by using methyl iodide instead of dimethyl sulfate (60% yield). The elemental analysis of this product is in good agreement with the formula for a methylated species, $[Pd\{Co(aet)_2(mtea)\}_2]Cl_4$ (mtea = methyl-2-thioethylamine). Furthermore, in the ^{13}C NMR spectrum (D_2O) $[\mathbf{2}]Cl_4$ exhibits a sharp signal at δ 17.54, besides six signals in the region δ 35–57, suggestive of the formation of a single symmetrical structure containing methyl groups. Single-crystal X-ray analysis demonstrated that $[\mathbf{2}]^{4+}$ is indeed a methylated derivative of $[\mathbf{1}]^{2+}$, in which two octahedral *mer*(*S*)-$[Co(aet)_2(mtea)]^+$ units are linked by a square-planar Pd^{II} atom through four thiolato S atoms (Figure 1).[5] The S-bridged trinuclear structure in $[\mathbf{2}]^{4+}$ is similar to that in the parental $[\mathbf{1}]^{2+}$,[3b] comprising of two *mer*(*S*)-$[Co(N)_3(S)_3]$-type units with the same chiral configuration. However, $[\mathbf{2}]^{4+}$ adopts the anti geometrical configuration with respect to two terminal S atoms, which is distinct from the syn configuration for $[\mathbf{1}]^{2+}$. This implies that the geometrical isomerization from syn to anti occurred in the course of the methylation reaction of $[\mathbf{1}]^{2+}$. The Co–S (average 2.257(9) Å) and Pd–S (average 2.318(9) Å) bond distances associated with the bridging S atoms trans to the terminal S atoms are shorter than the corresponding distances in $[\mathbf{1}]^{2+}$ (average Co–S = 2.298(2), Pd–S = 2.343(2) Å), while those associated with the bridging S atoms trans to the terminal N atoms (average Co–S = 2.262(9), Pd–S = 2.328(9) Å) are similar to the corresponding distances in $[\mathbf{1}]^{2+}$ (average Co–S = 2.255(2), Pd–S = 2.321(2) Å). As a result, in $[\mathbf{2}]^{4+}$ the Co–S and Pd–S distances trans to the terminal S atoms are comparable with those trans to the terminal N atoms, indicative of the disappearance of a trans influence due to thiolato donors by methylation. The elongated terminal Co–S bonds in $[\mathbf{2}]^{4+}$ (average 2.294(9) Å), compared with those in $[\mathbf{1}]^{2+}$ (average 2.261(2) Å), would be related to this result.

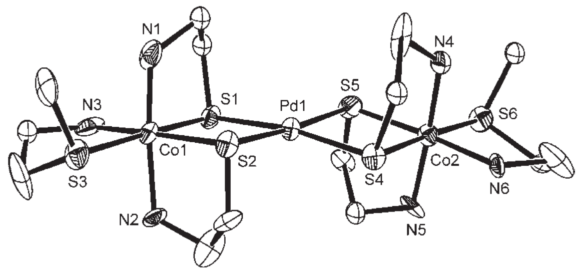


Figure 1. A perspective view of one of the two independent complex cations $[\mathbf{2}]^{4+}$ with the atomic labeling scheme. The $\Delta\Delta$ isomer is selected.

A similar alkylation reaction of $[\mathbf{1}]^{2+}$ using benzylbromide also gave a red reaction solution, from which red crystals

($[\mathbf{3}]Cl_4\cdot 9H_2O$) were isolated (73% yield) by the same procedure adopted for $[\mathbf{2}]Cl_4$.[6] Complex $[\mathbf{3}]Cl_4$ was confidently assigned to a benzylated species, $[Pd\{Co(aet)_2(bztea)\}_2]Cl_4$ (bztea = benzyl-2-thioethylamine), based on (i) the elemental analysis that is consistent with the proposed formula, (ii) the ^{13}C NMR spectroscopy that shows a single set of aromatic carbon signals, besides a single set of methylene carbon signals, and (iii) the electronic absorption spectroscopy, the spectral feature of which corresponds well with that of $[\mathbf{2}]Cl_4$. X-ray analysis established that $[\mathbf{3}]^{4+}$ has an expected S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear structure in $[Pd\{Co(aet)_2(bztea)\}_2]^{4+}$, which is composed of two *mer*(*S*)-$[Co(aet)_2(bztea)]^+$ units with the same chiral configuration (Figure 2).[7] Of note is the syn arrangement of two terminal S atoms in $[\mathbf{3}]^{4+}$, implying the retention of the geometrical configuration during the benzylation reaction of $[\mathbf{1}]^{2+}$. The Co–S (average 2.263(2) Å) and Pd–S (average 2.340(2) Å) bond distances associated with the bridging S atoms trans to the terminal thioether S atoms are ca. 0.03 Å longer than those with the bridging S atoms trans to the terminal N atoms (average Co–S = 2.238(2), Pd–S = 2.307(2) Å). This indicates that the terminal benzylated S atoms in $[\mathbf{3}]^{4+}$ exert a trans influence, unlike the methylated S atoms in $[\mathbf{2}]^{4+}$. Compatible with this, the terminal Co–S bonds in $[\mathbf{3}]^{4+}$ (2.277(2) Å) are shorter than those in $[\mathbf{2}]^{4+}$.

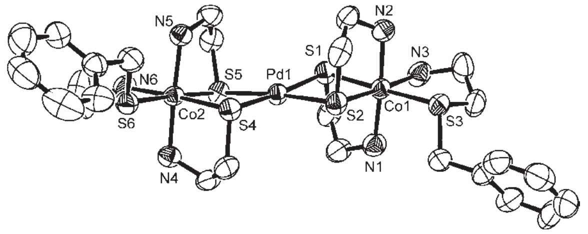


Figure 2. A perspective view of $[\mathbf{3}]^{4+}$ with the atomic labeling scheme. The $\Delta\Delta$ isomer is selected.

In summary, the two nonbridging thiolato groups in $\Delta\Delta/\Lambda\Lambda$-*syn*-$[Pd\{Co(aet)_3\}_2]^{2+}$ ($[\mathbf{1}]^{2+}$) were successfully alkylated in aqueous media under moderate conditions. Remarkably, the methylation reaction of $[\mathbf{1}]^{2+}$ is accompanied by the geometrical isomerization from syn to anti to exclusively give the $\Delta\Delta/\Lambda\Lambda$-anti isomer of $[Pd\{Co(aet)_2(mtea)\}_2]^{4+}$ ($[\mathbf{2}]^{4+}$), while the benzylation proceeds with retention of the syn configuration to produce only the $\Delta\Delta/\Lambda\Lambda$-syn isomer of $[Pd\{Co(aet)_2(bztea)\}_2]^{4+}$ ($[\mathbf{3}]^{4+}$).[8] In parallel with this, a trans influence due to terminal S donors found in $[\mathbf{1}]^{2+}$ disappeared in $[\mathbf{2}]^{4+}$, while an appreciable trans influence still remained in $[\mathbf{3}]^{4+}$. Thus, it is reasonable to conclude that the removal of a trans influence due to terminal S donors by methylation leads to the conversion into the thermodynamically favorable anti form that is destabilized by the presence of a 'remote trans influence' in $[\mathbf{1}]^{2+}$, while the syn form in $[\mathbf{1}]^{2+}$ is maintained even after benzylation because of the insufficient removal of a trans influence.[9] Finally, the present results point out that the overall geometries of sulfur-containing polynuclear systems could be controlled by the modification at thiolato donors, which tunes the degree of a trans influence.

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4 Anal. Calcd for $[\mathbf{2}]Cl_4\cdot 7H_2O$: C, 17.17; H, 5.76; N, 8.58%. Found: C, 16.92; H, 5.52; N, 8.47%. ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 17.54 (CH_3S), 35.82, 36.55, 40.97 (CH_2S), 46.32, 56.02, 56.61 (CH_2NH_2). UV–vis spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log\varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 19.35 (2.96), 27.28 (4.4 sh), 30.54 (4.56), 46.38 (4.5 sh).

5 Crystal data for $[\mathbf{2}]Cl_4\cdot 7H_2O$: fw 979.07, monoclinic, $P2_1$, $a = 16.155(2)$, $b = 15.088(3)$, $c = 17.174(2)$ Å, $\beta = 112.31(1)^\circ$, $V = 3873(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.679\,g\,cm^{-3}$, $R(R_w) = 0.033$ (0.102) for 2939 reflections with $> 2.0\sigma(I)$. The asymmetric unit contained two crystallographically independent, but nearly enantiomeric complex cations to form a racemic ($\Delta\Delta/\Lambda\Lambda$) compound.

6 Anal. Calcd for $[\mathbf{3}]Cl_4\cdot 9H_2O$: C, 26.75; H, 5.87; N, 7.20%. Found: C, 26.51; H, 5.82; N, 7.21%. ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 35.85, 36.73, 38.63, 39.43 (CH_2S), 46.14, 56.01, 56.91 (CH_2NH_2), 131.53, 131.88, 132.00, 135.25 (Ph). UV–vis spectrum in H_2O [σ_{max}, $10^3\,cm^{-1}$ ($\log\varepsilon$, $mol^{-1}\,dm^3\,cm^{-1}$)]: 19.22 (2.93), 26.95 (4.4 sh), 30.23 (4.58), 45.45 (4.6 sh).

7 Crystal data for $[\mathbf{3}]Cl_4\cdot 9H_2O$: fw 1167.35, triclinic, $P\bar{1}$, $a = 13.024(2)$, $b = 16.762(3)$, $c = 12.618(2)$ Å, $\alpha = 111.31(1)^\circ$, $\beta = 98.74(2)^\circ$, $\gamma = 104.06(1)^\circ$, $V = 2400(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.615\,g\,cm^{-3}$, $R(R_w) = 0.059$ (0.163) for 5486 reflections with $> 2.0\sigma(I)$.

8 The column chromatographic band for each of $[\mathbf{2}]^{4+}$ and $[\mathbf{3}]^{4+}$ showed a single set of ^{13}C NMR signals that are identical with those of the isolated sample.

9 In the anti form the two terminal S donors are located in a trans position with respect to each other through the central S–Pd–S (trans) line, and it has been assumed that the selective formation of the syn form for $[\mathbf{1}]^{2+}$ is due to the presence of a mutual 'remote trans influence' (trans influence through the central Pd^{II} atom) in the anti form.[3b]

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