Reaction of $[Mo_2]^{4+}$ Aminoacid Complexes with Quadruple Bond in Liq. NH_3; Characterization of New Homoleptic Decaammine Complexes

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Introduction

Recently we presented[1] a series of three novel decaammine complexes with $[Mo_2]^{4+}$ core, namely $[Mo_2(NH_3)_{10}][O_2CH]_4$, $[Mo_2(NH_3)_{10}][O_2CCH_3]_4 \cdot 2NH_3$, $[Mo_2(NH_3)_{10}][O_2CC_6H_5]_4 \cdot 2NH_3$ and reported their single crystal x-ray structure determinations. These cationic ammine complexes consist of a central molybdenum-molybdenum quadruple bond and as essential part their $[Mo_2]^{4+}$ centers are in homoleptic ligand environment of ten ammonia molecules, with eight equatorial ligands arranged in ecliptic conformation and characteristic bond lengths. The reaction of Mo(II)carboxylates, $Mo_2(O_2CR)_4$, with liquid ammonia led to a complete exchange of labile carboxylate ligands on the „Paddlewheel“ precursors against NH_3 molecules. With increasing size of the aliphatic groups, $Mo_2(O_2CR)_4$ afforded the respective $[Mo_2(NH_3)_{10}][O_2CR]_4$ compounds only in the form of fine powders, unsuitable for single crystal x-ray work due to decreasing solubility in liq. NH_3. Subsequently we have chosen appropriate Paddlewheel precursors, containing amino acids, which possess good crystallization properties and also good solubilities of the precursors in liquid ammonia.

Results and Discussion

$[Mo_2(ß\text{-alaH})_4]Cl_4$ **A** and $[Mo_2(ß\text{-alaH})_4]Br_4$ **B**, were synthesized from $K_4[Mo_2Cl_8]$[2] and $(NH_4)_4[Mo_2Br_8]$[3] by halogen exchange against ß-alanine. Within two weeks at –40°C in liquid NH_3, orange colored single crystals of the moderately soluble decaammine complexes $[Mo_2(NH_3)_{10}][ß\text{-ala}]_2Cl_2 \cdot 6NH_3$ **(I)** and $[Mo_2(NH_3)_{10}][ß\text{-ala}]_4 \cdot 2NH_3$ **(II)** were obtained.

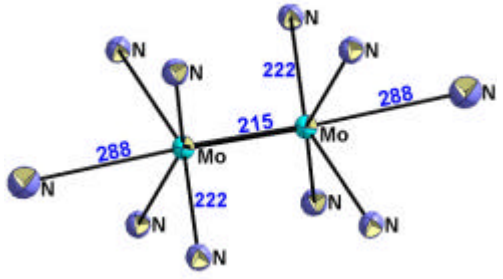

Figure 1.
Structure of the complexes **$[Mo_2(NH_3)_{10}]^{4+}$** in **I** and **II**

(Bond lengths in pm)

(I) (monoclinic, ***P2₁/n***, *a*=848.17(1), *b*=1185.02(1), *c*=1623.14(2) pm), *ß*=91.732(1)°; **(II)** (monoclinic, ***P2₁/c***, *a*=1300.37(7), *b*=1378.10(8), *c*=943.96(2) pm); Tentatively $K_4[Mo_2Cl_8]$ was also reacted in liquid ammonia for three month under same conditions, but no ligand exchange reaction occurred. Surprisingly, little dark-red single crystals of $K_4[Mo_2Cl_8]$ **(III)** itself could be obtained instead. **(III)** (tetragonal, ***I4/mmm***, *a*=1016.2(2), *b*=773.4(3) pm). All samples were manipulated below -50°C[4]. In **(I)** and **(II)** H-bonding is the dominant interaction between the NH_3 ligands of the $[Mo_2]^{4+}$ core and the oxygen atoms of the carboxylate counter ions. But only in **(I)** there is additional chlorine involved which is not present in **(II).** This is surprising, as both were derived from the very similar precursors **A** and **B**.

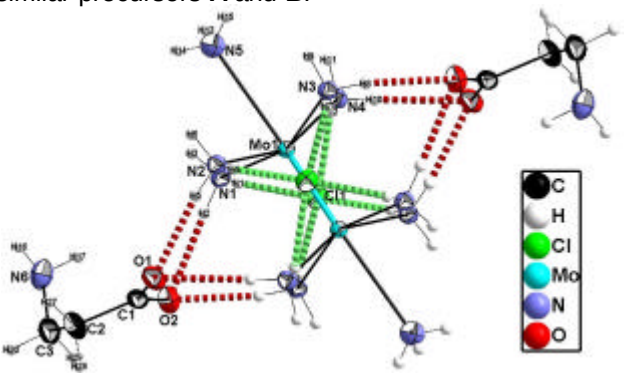

Figure 2. Constitution and H-bonding for **(I)**

Conclusion

Two new ammine complexes with Mo≡Mo quadruple bond and ß-alaninate as counter ion are reported. The amino acid complexes of $[Mo_2]^{4+}$ undergo ligand exchange in liquid NH_3, forming $[Mo_2(NH_3)_{10}]^{4+}$ units with the typical staggered structure. $[Mo_2(NH_3)_{10}][ß\text{-ala}]_2Cl_2 \cdot 6NH_3$ differs from all its relatives by the presence of two Cl^- ions, making it much more useful for subsequent reactions in liquid ammonia.

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[1] 13th Brazilian Meeting on Inorganic Chemistry, Fortaleza, Brazil, **2006**.

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