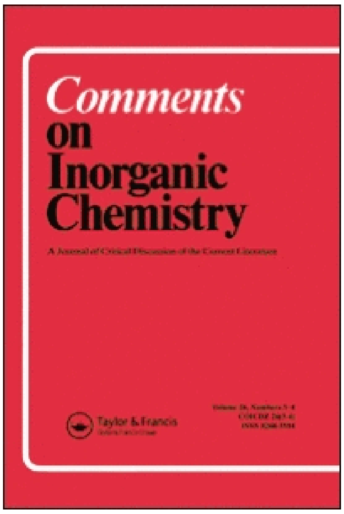
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Olation and Structure

Michael Ardon[a]
[a] Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, Israel

**To cite this Article** Ardon, Michael(1989) 'Olation and Structure', Comments on Inorganic Chemistry, 8: 5, 221 — 232
**To link to this Article: DOI:** 10.1080/02603598908035796
**URL:** http://dx.doi.org/10.1080/02603598908035796

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Olation and Structure

MICHAEL ARDON
*Department of Inorganic and Analytical Chemistry,*
*The Hebrew University,*
*Jerusalem, Israel*

**Key Words:** *olation, $H_3O_2$-bridging ligand*

Formation of ol or μ-(OH) bridging ligands between metal atoms as in

$$\begin{aligned}&(H_2O)_5M(H_2O)^{n+} + (HO)M(H_2O)_5^{(n-1)+}\\ &\rightarrow (H_2O)_5M(OH)M(H_2O)_5^{(2n-1)+} + H_2O\end{aligned} \qquad (1)$$

is known as *olation*. The reaction of olation plays a key role in precipitation of metal hydroxides from aqueous solution by $OH^-$ ions and in subsequent "aging" of these precipitates. The decrease in solubility occurring during these processes is due to structural changes in these species. Heavy metal hydroxides are not mononuclear, as the formulation $M(OH)_n$ implies, but consist of polynuclear networks of metal atoms bridged by μ(OH) "ol" or μ-(O) "oxo" ligands.[1] The insolubility of metal hydroxides, which increases with aging, is the result of these structures. The primary

---

*Comments Inorg. Chem.*
1989, Vol. 8, No. 5, pp. 221–232
Reprints available directly from the publisher

Printed in Great Britain

polynuclear species formed in solution are of low molecular weight and extreme solubility, such as the "diol" of Fe(III).

$$\begin{aligned} 2OH^- + 2Fe(H_2O)_6^{3+} &\rightarrow 2Fe(H_2O)_5OH^{2+} + 2H_2O \\ (H_2O)_4Fe(OH)_2Fe(H_2O)_4^{4+} &+ 4H_2O \end{aligned} \qquad (2)$$

The diols may not be separated from the mononuclear and other related species in solution because of the rapid equilibration of (2) and similar reactions.

Notable exceptions are the hydrolytic products of $Cr(H_2O)_6^{3+}$ which are relatively stable kinetically, and may be separated by ion exchange chromatography.[2-4] Species such as the "chromic dimer"[2] $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, the "trimer," "tetramer," "pentamer" and "hexamer"[4] were separated from aqueous solution and served as a basis for some interesting views on the nature of the aging processes.[4b] But even in the favorable case of Cr(III), the extreme solubility and relative lability of the hydrolytic species make their isolation as crystalline salts extremely difficult. The only species isolated so far as a single crystal and studied by X-ray diffraction[4c] was

$$[(H_2O)_4Cr(OH)_2Cr(OH_2)_4]\ [((H_3C)_3C_6H_2SO_3]_4 \cdot 4H_2O$$

The lower solubility and higher kinetic stability of *hydroxoaqua ammines* of Cr(III), Co(III), Rh(III), etc. make them more suitable than the corresponding aqua ions for detailed studies of the mechanism of olation.

Formation of diols from hydroxoaqua metal ammines by heating their salts, e.g.,

$$2[Co(NH_3)_4(H_2O)(OH)]Cl_2 \xrightarrow{110^\circ} [(NH_3)_4\,Co(OH)_2Co(NH_3)_4]Cl_4 + 2H_2O \qquad (3)$$

was studied at the beginning of this century mainly by Werner and Pfeiffer.[5] Werner noted that only *cis*-hydroxoaqua complexes olate as in (3) at temperatures of 100–150°C while the *trans* isomers do not react before they decompose, at higher temperature (>250°C).

He made use of this difference, as a classical tool, to distinguish between *cis* and *trans* isomers of these complexes and their derivatives.

Olation of hydroxoaqua complexes also occurs in aqueous solution. Reactions such as

$$2[Cr(en)_2(H_2O(OH)]^{2+} \rightleftharpoons (en)_2Cr(OH)_2Cr(en)_2]^{4+}\ 2H_2O \qquad (4)$$

are reversible in solution. The equilibrium may be shifted to the left by increasing the $H^+$ concentration

$$[(en)_2Cr(OH)_2Cr(en)_2]^{4+} + 2H_2O + 2H^+ \rightarrow 2[(en)_2(Cr(H_2O)_2]^{3+} \qquad (5)$$

Springborg[6] studied the de-olation reaction of this diol and proved that it proceeds in two steps: in the first, relatively fast, step a mono-ol is formed. In the second, much slower, reaction the second μ-OH bridge is broken and the mononuclear hydroxoaqua ion formed:

$$H_2O + [(en)_2Cr(OH)_2Cr(en)_2]^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(HO)(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+} \qquad (6a)$$

$$H_2O + [(OH)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{4+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr(en)_2(H_2O(OH)]^{2+} \qquad (6b)$$

The intermediate mono-ol accumulates in the solution since $k_1 >> k_2$ and may be isolated as a solid salt.[6] The structure of one mono-ol was determined by a single crystal X-ray study.[7]

Single crystal X-ray studies of chromium(III) and cobalt(III) hydroxoaqua complexes, conducted since 1983,[8-11] shed new light on the mechanism of olation reactions, especially the solid state reaction. It was established that the structures of the so-called hydroxoaqua ions differed considerably from their classical formulation. These ions are not mononuclear species with distinct hydroxo and aqua ligands: the *trans* "hydroxoaqua" ion consists of a polynuclear chain of metal atoms separated by approximately 5.7 Å. They are linked to each other by $H_3O_2^-$ ligands (Fig. 1). *Cis* hydroxoaqua ions are, in fact, dimers in which two metal atoms (appr. 5.0 Å apart) are bridged by *two* $H_3O_2$ bridges as in Fig. 2. The $H_3O_2$ bridging ligand is formed by means of a hydrogen bond

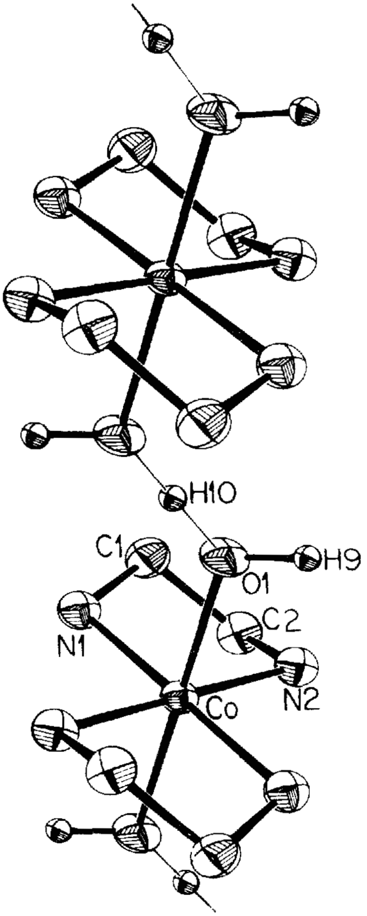


FIGURE 1 The *trans*-polynuclear chain of $[Co(en)_2(H_3O_2)]_n^{2n+}$. Reprinted with permission from Inorganic Chemistry [Ref. 8(b)].

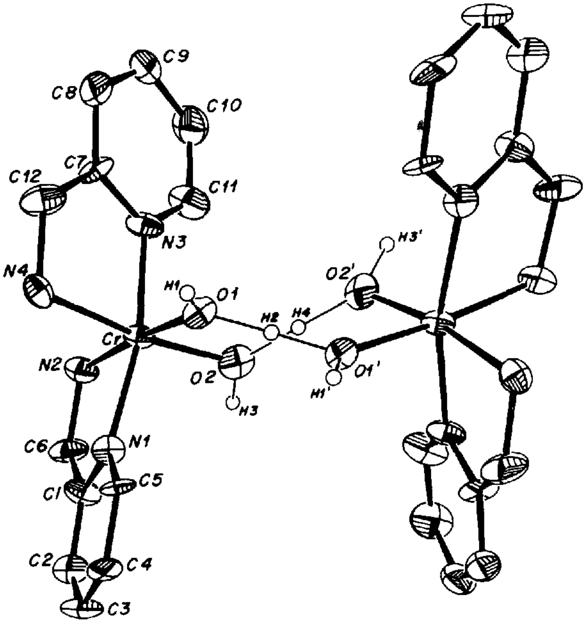
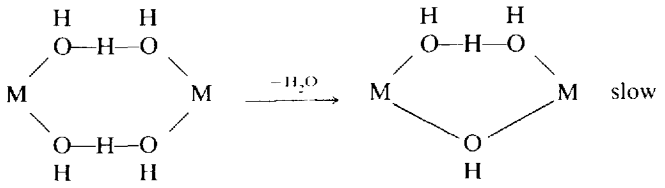


FIGURE 2 The *cis*-dimer $[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]^{4+}$. Reprinted with permission from Journal of the American Chemical Society [Ref. 10].

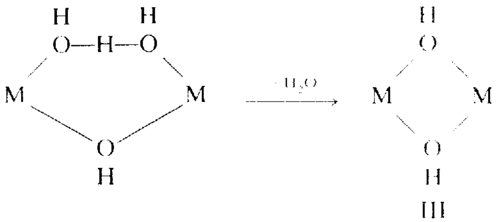
between a hydroxo ligand of one metal atom and an aqua ligand of the other metal atom. This centered H-bond is very strong ($\approx$100 kJ) and short (<2.50 Å) and makes a distinction between an OH ligand and an $H_2O$ ligand, meaningless in most of these compounds.

On the basis of these structures, a two step mechanism for the solid state olation reactions of *cis* hydroxoaqua complexes was proposed[10]:



I II

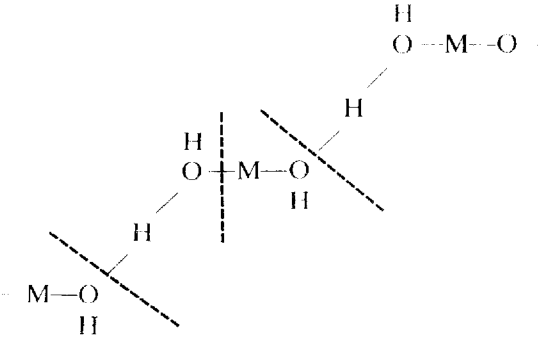
(7)



(8)

III

This mechanism offers a solution to the classical problem of olation: Why do only *cis* isomers olate and *trans* isomers do not? This difference in reactivity is due to the much lower activation energy required for olation of the *cis* isomer (reaction (7)), as the following consideration shows: In reaction (7) one water molecule is eliminated and the distance between the metal atoms shrinks from 5.0 Å to 3.8 Å. In this reaction one M–O bond and one strong H-bond have to be broken. This is also true for the second step (reaction (8)). Olation of a *trans* isomer would require the breaking of an *additional* H-bond: One M–O bond and two H-bonds have to be broken in order to form a mono-ol by elimination of a water molecule and decreasing the separation of the metal atoms from 5.7 Å to 3.8 Å.



This additional H-bond energy (≈100 kJ) increases the activation energy for olation of a *trans* isomer and therefore prevents its occurrence at temperatures at which the *cis* isomer reacts (100–150°C). At higher temperatures decomposition occurs. The ability of the *cis* isomers to olate is thus ascribed to their dimeric, double bridged structure. In other words, a *cis* isomer that does not have this structure may not olate. Such an irregular *cis* complex was indeed prepared.[13] This complex *cis*-α$[Cr(pico)_2(H_2O)(OH)]S_2O_6$ (pico = 2-picolylammine) consists of a polynuclear chain of Cr atoms linked by asymmetric H-bonds between the OH and $H_2O$ ligands of neighboring Cr atoms.[13b] This compound does not olate even at 200°C[13a] and decomposes at higher temperatures. In order to double-check whether the inability of this *cis* complex to olate was due to its irregular chain structure, another salt of the same complex ion was prepared—the iodide.[10] This salt, *cis*-α$[Cr(pico)_2(H_2O)(OH)]I_2 \cdot H_2O$ was found to have a normal double-bridged, dimeric structure[10] and should be formulated as $[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$. When this iodide was heated to 140°C, olation occurred. The different reactivity of this pair of *cis* complexes strongly supports our mechanism of olation (reactions (7) and (8)). The fact that no detectable quantities of the mono-ol are produced during the solid state olation is due to its very small steady-state concentration—as a result of its slow formation rate (reaction (7)) and faster decomposition rate (reaction (8)). This difference in rates of reaction (7) and (8) may be explained by comparison of the structure of the hydroxoaqua dimer I with that of the mono-ol intermediate II (the data for the mono-ol are taken from Springborg's results[7] for *cis*$[(en)_2Ir(OH)(H_3O_2)Ir(en)_2](S_2O_6)_3 \cdot ClO_4 \cdot 2.75\ H_2O$). The most stable configuration of the $H_3O_2$ bridging ligand is attained by a maximum separation of the two positive metal atoms. This maximum separation is approximately 5.7 Å and exists in the polynuclear chain of the *trans* isomer, in which the spatial relationship of the two M–O bonds of the M–O–H–O–M bridge is "anti" (Fig. 3(a)).

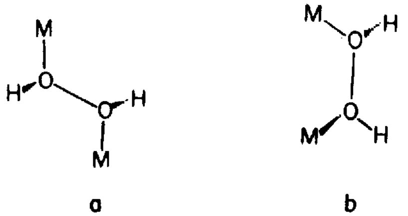


FIGURE 3 (a) Anti and (b) gauche configurations of $H_3O_2$.

In the *cis* dimer such an arrangement is not possible. Its double-bridged structure requires a twisted "gauche" configuration (Fig. 3(b)) with a torsional angle of 60° to 90°. As a result of this somewhat strained configuration of the *cis* dimer, the separation between the metal atoms decreases to approximately 5.0 Å. The highest strain exists in the mono-ol structure II: its $\mu$-(OH) bridge imposes a very short M . . . M separation of approximately 3.8 Å. As a result, the twisted M–O–H–O–M bridge is almost planar,[7] with a dihedral angle between the two M–O bonds of only 7.4°. The destabilization of the mono-ol brought about by this strained structure is expected to decrease the activation energy of reaction (8), compared to that of (7), and make it faster.[9,10]

Let us now turn to the steric course of the olation reaction in the solid state. In chiral complexes such as *cis*$[Cr(en)_2XY]^{2+}$, which exist as a recemic mixture of Δ and Λ enantiomers, two configurations of the double-bridged dimer are possible: a meso (Δ,Λ) and a racemic (ΔΔ,ΛΛ) configuration. Both configurations exist. The $[(en)_2Co(H_3O_2)_2(Co(en)_2](S_2O_6)$ dimer has a meso (Δ,Λ) configuration[11] while $[(pico)_2(Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$ has a racemic (ΔΔ,ΛΛ) configuration[10] with (ΔΔ) and (ΛΛ) dimers in the crystal lattice. On the basis of our two step olation mechanism one would expect a retention of this configuration in reactions (7) and (8). Therefore evidence for this reaction scheme would be strengthened if a meso dimer indeed yielded a meso diol and a racemic dimer, a racemic diol. This conclusion was tested in the following way: The racemic $[(pico)_2(Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$ complex was heated to 140°, the powdered diol product was dissolved in water and crystalized from solution as the dithionate $[(pico)_2Cr(OH)_2Cr(pico)_2](S_2O_6)_2 \cdot 2\frac{1}{2} H_2O$. A single crystal X-ray study of this diol proved that it consists of racemic pairs of (ΔΔ) and (ΛΛ) diols as expected.[10] An objection to the validity of this test could be raised: The diol was first dissolved and then recrystalized from solution; therefore isomerization could eventually take place in solution. The fact that the final crystal was racemic does not prove that the primary powdered diol, produced by heating, had the same configuration. In order to eliminate this uncertainty, another procedure was used: meso (Δ,Λ) $[(en)_2Co(H_3O_2)_2Co(en)_2](S_2O_6)_2$ was olated by heating to 120° and an X-ray diffraction spectrum of the powdered diol was recorded. The powder was then dissolved in water and recrystallized from solution. The structure of a single crystal obtained in this way was determined and found to have a meso configuration, just as the reactant had. The data from this single crystal were used to simulate a powder diffraction spectrum and this was compared to the spectrum obtained experimentally from the powdered diol before it was dissolved. The two spectra were identical, thus proving the meso structure of the primary diol product.[11]

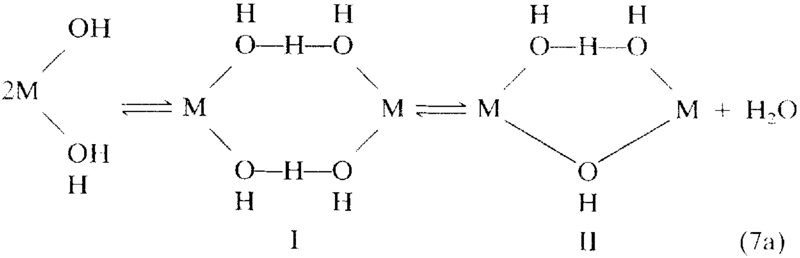
Olation in solution may proceed by a similar two step mechanism as olation in the solid state, namely by reaction (7) and (8), but evidence is in this case only partial and some of it ambiguous. The mechanism of the second step, which involves the mono-ol-diol equilibrium in solution, is well established and conforms to reaction (8). Springborg proved that the mono-ol, with one ($\mu$-OH) and one ($\mu$-$H_3O_2$) bridge, exists not only in the solid state but also in solution. In fact, evidence for very strong H-bonding between the $OH^-$ and $H_2O$ ligands of the mono-ol in solution[6] was discovered long before it was found in the solid state.[7] This evidence is based on the unusual difference between $pK_{a_1}$ (0.67) and $pK_{a_2}$ (7.94) of $(H_2O)(en)_2Cr(OH)(en)_2H_2O)^{5+}$. This difference points to a high stabilization of the species $(HO)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$ and is caused by a very strong H-bond between the terminal $OH^-$ and $H_2O$ ligands.

The evidence for the existence of the first step, i.e., reaction (7) in solution, is on more shaky grounds. The first question to be asked is: Do dimers of hydroxoaqua ions exist in solution? The answer was provided by Three Phase Vapor Tensiometry (TPVT)[12a]: Dimers do exist in concentrated solutions of the *cis* isomer, but not in solution of the *trans* isomer. Titration of $Cr(bipy)_2(H_2O)_2^{3+}$ by $OH^-$ in a saturated $Ba(NO_3)_2$ solution proved that the number of chromium particles decreased during the deprotonation of the first aqua ligand and increased again as the second aqua ligand was deprotonated, as is expected by

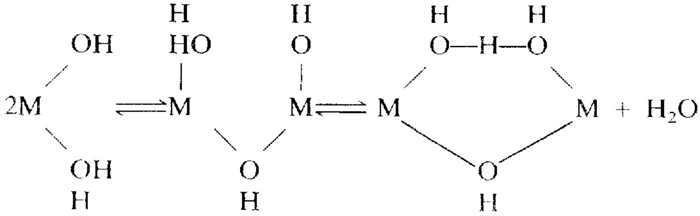
$$2Cr(bipy)_2(H_2O)_2^{3+} + 2OH^- \rightarrow (bipy)_2Cr(H_3O_2)_2Cr(bipy)_2^{4+} + 2H_2O$$

$$(bipy)_2Cr\ (\mu\text{-}H_3O_2)_2Cr(bipy)_2^{4+} + 2OH^- \rightarrow 2Cr(bipy)_2(OH)_2^{+} + 2H_2O$$

However, dimerization is not complete and a monomer–dimer equilibrium exists in moderately concentrated solutions (~0.1 M). In very dilute solutions the concentration of the dimer is negligible. Similar TPVT measurements showed no evidence for association of the *trans* isomer even in concentrated solution.[17] The difference between the stability of the *cis* and *trans* dimers was ascribed to the chelate effect which stabilizes the former. The existence of a monomer–dimer equilibrium of the *cis* isomer in solution raises the possibility that reaction (7) takes place in solution. This mechanism is supported by an early kinetic study of Grant and Hamm[14] on the olation of *cis*-$Cr(C_2O_4)_2H_2O(OH)^{2-}$. They found that olation is second order in dilute solutions and first order in concentrated solutions. This change of order with concentration is a direct result of a monomer–dimer equilibrium. In his recent study[15] on olation of $Rh(en)_2(H_2O(OH)^{2+}$, Springborg pointed out two alternative reaction schemes for the first step of olation in solution:



(7a)



(7b)

He tends to prefer the scheme (7b), with a non-H-bonded transition state, but presents no firm evidence which may enable a clear decision between these alternative paths.

The mechanism of reaction (7) is only one of the unsolved problems of olation in solution and in the solid state. Another interesting question concerns the reactivity of the double-bridged *cis*-dimer. While it is true that only double-bridged dimers may olate in the solid state, we observed that not all of these dimers do, in fact, olate. In other words, the existence of a double-bridged dimer is a necessary but not sufficient condition for olation. Complexes such as meso-$[(phen)_2Cr(H_3O_2)_2Cr(phen)_2]Br_4 \cdot 4H_2O$ or meso-$[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2](S_2O_6)_2(NO_3)_2 \cdot 2H_2O$ or racemic $(\Delta\Delta,\Lambda\Lambda)$-$[(bipy)_2Cr(H_3O_2)_2Cr(bipy)_2](NO_3)_4 \cdot 2H_2O$ do not olate at elevated temperatures, although they have a regular, double-bridged structure.[11] This failure to react may be due to some specific differences in the reactivity of certain racemic and meso mono-ols. Such a difference was observed in one case by Springborg.[6] The racemic-meso isomerization in solution may explain the fact that the hydroxoaqua dimers mentioned above olate in solution,[11] although they fail to do so in the solid state.

Another problem, which may be intimately linked with the former, concerns the steric course of olation: Is retention of the configuration (meso or racemic) a general feature of the solid state olation reaction? While the evidence reported here supports this generalization, it does not prove it. The remarkable stability of the racemic mono-ol $[(en)_2Cr(OH)(H_3O_2)Cr(en)_2]Br_4 \cdot H_2O$, compared to that of the meso-isomer,[6] may be a good starting point for further studies of the steric course of olation.

A reaction related to olation is "ammine-olation," i.e., formation of a μ-amido bridge by condensation of $NH_3$ from an ammino-amido complex, e.g.,

$$2(Pt(NH_3)_5(NH_2)]^{3+} \rightarrow \underset{\text{V}}{(NH_3)_4Pt(NH_2)_2Pt(NH_3)_4^{6+}} + 2NH_3 \qquad (9)$$

The existence of an ammine analogue of $H_3O_2^-$, namely an $H_5N_2^-$ bridging ligand was suspected on the basis of the remarkable acidity of V ($pK_a = 1.9$, compared to $pK_a = 7.0$ of $Pt(NH_3)_6^{4+}$).[16] The stabilization of the deprotonated dimer $[(NH_2)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_4]^{5+}$ was attributed to a very strong H-bond between the terminal amido and ammine ligands of the two Pt atoms, i.e., by an $H_5N_2^-$ bridging ligand. A single crystal X-ray study confirmed this expectation.[16] In addition to the two μ-$NH_2$ bridges there exists a third, μ-$H_5N_2$ bridge in

$[(NH_3)_3Pt(NH_2)_2(H_5N_2)\,Pt(NH_3)_3](ClO_4)_5.4H_2O$. It is not yet clear whether the $H_5N_2^-$ ligand plays any role in the ammine olation reaction (9).

## References

1. C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations* (Wiley, New York, 1976), pp. 419–430.
2. M. Ardon and R. A. Plane, J. Am. Chem. Soc. **81**, 3197 (1959).
3. M. Thompson and R. E. Connick, Inorg. Chem. **20**, 2279 (1981).
4. (a) H. Stunzi and W. Marty, Inorg. Chem. **22**, 2145 (1983); (b) L. Spiccia and W. Marty, Inorg. Chem. **25**, 266 (1986); (c) L. Spiccia, H. Stoeckli-Evans, W. Marty and R. Gioanoli, Inorg. Chem. **26**, 474 (1987); (d) L. Spiccia, W. Marty and R. Giovanoli, Inorg. Chem. **27**, 2660 (1988).
5. (a) A. Werner, Chem. Ber. **40**, 4439 (1907); (b) P. Pfeiffer, Z. Anorg. Chem. **58**, 272 (1908).
6. J. Springborg and H. Toftlund, Acta Chem. Scand. **A30**, 171 (1976).
7. F. Galsbøl, S. Larsen, B. Rasmussen and J. Springborg, Inorg. Chem. **25**, 290 (1986).
8. (a) M. Ardon and A. Bino, J. Am. Chem. Soc. **105**, 7748 (1983); (b) M. Ardon and A. Bino, Inorg. Chem. **24**, 1343 (1985).
9. M. Ardon and A. Bino, Structure and Bonding **65**, 1–28 (1987).
10. M. Ardon, A. Bino and K. Michelsen, J. Am. Chem. Soc. **109**, 1986 (1987).
11. I. Benori, E. Benori, A. Bino and M. Ardon, unpublished results.
12. (a) M. Ardon and B. Magyar, J. Am. Chem. Soc. **106**, 3359 (1984); (b) R. D. Lorentz, A. Bino and J. E. Penner-Hahn, J. Am. Chem. Soc. **108**, 8116 (1986).
13. (a) K. Michelsen, Acta Chem. Scand. **A26**, 1517 (1972); (b) S. Larsen, K. B. Nielsen and I. Trabjerg, Acta Chem. Scand. **A37**, 833 (1983).
14. D. M. Grant and R. E. Hamm, J. Am. Chem. Soc. **78**, 3006 (1956).
15. K. Kaas and J. Springborg, Inorg. Chem. **26**, 387 (1987).
16. L. Heck, M. Ardon, A. Bino and J. Zapp, J. Am. Chem. Soc. **110**, 2691 (1988).
17. A differential anomalous X-ray scattering study (Ref. 12(b)) does, however, prove the existence of single $H_3O_2^-$ bridging in solutions of trinuclear tungsten clusters.