An Intracomplex Compound of Divalent Platinum with Methionine

1962

SovietRxiv

Abstract

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Chemistry

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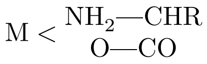
An Intracomplex Compound of Divalent Platinum with Methionine

(Presented by Academician A. A. Grinberg, 7 X 1961)

Platinum compounds with methionine* (α-amino-γ-methylmercaptobutyric acid) have not yet been described. Among the other metals, only for iron has a compound with methionine been described, isolated in the individual state. Bilig and Bayer (^{1}) obtained the solid compound $[Fe(MtH)_2(OH)_2]Cl$, in which, according to the authors, MtH is bound to Fe(III) only through the amino group. For many metals (Ni, Cu, Zn, etc.), physicochemical methods have revealed the formation in solutions of complexes with methionine (^{2}-^{4}), their composition has been established (for example, $ZnMt^+$, $ZnMt_2$), and instability constants (K) have been determined. These complexes, according to the authors' data, contain negative ions Mt^-, which form with cations M five-membered rings



$$\mathrm{M} < \begin{matrix} \mathrm{NH_2{-}CHR} \\ \mathrm{O{-}CO} \end{matrix}$$

the same as in complexes with α-amino acids (glycocol and its analogs), which do not contain additional functional groups in R (in their general form these amino acids are denoted below as ZH). For example, Peltier (^{4}) determined the stepwise instability constants of Ni complexes with valine, serine, and methionine, found an almost complete agreement of the values of $\lg K$ for complexes of the same type of the three α-amino acids, and considers it beyond doubt that in all three cases the groups $-NH_2$ and $-COO$ participate in ring formation, while the $-OH$ group of serine and the $-S-$group of methionine are not bound to Ni.

On the basis of the foregoing, it could be assumed that methionine with Pt(II) should form the intracomplex salt $[PtMt_2]$, analogous to the salts $[PtZ_2]$, previously synthesized (^{5}-^{9}) for many ZH. One could also expect the preparation of noncyclic compounds with MtH of the type $[Pt(MtH)_2Cl_2]$, similar to the numerous compounds $[Pt(ZH)_2Cl_2]$, in which the ZH molecules are bound to Pt(II) only through amino groups (^{5}-^{9}). However, the very first experiments showed that the interaction of potassium chloroplatinite with MtH differs sharply from the interaction of K_2PtCl_4 with ZH. It turned out that in the case of MtH, a bond of Pt(II) with the $-S-$group very readily arises. The present communication describes the first of the peculiar Pt(II) compounds with methionine synthesized by us.

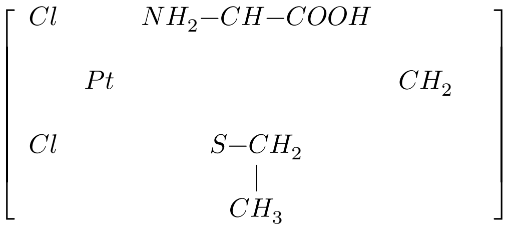
Usually, for reactions of platinite with ZH, an excess of ZH is taken (the number of moles of ZH or MtH taken per 1 mole of K_2PtCl_4 is denoted below by n) and the mixture is heated on a water bath; even at $n \geq 4$ the color of the platinite disappears slowly (after ~30 min of heating). At $n = 2$, disappearance of the platinite color in the case of ZH occurs only after heating for many hours; bright-yellow solutions are then obtained. Meanwhile, in the case of MtH the disappearance of the platinite color occurs in the cold within a few minutes, not only at $n = 4$, but also at $n = 2$; almost colorless solutions are then obtained. A second difference in the reactions with MtH is that at $n = 4$ (and $n = 2$) even very prolonged heating does not lead to the formation of any precipitate, whereas in the case of ZH, at $n = 4$, white precipitates $[PtZ_2]$ gradually form.

The interaction of MtH with platinite at $n = 1$ is quite peculiar and especially important; in this case, after 2 min of heating there begins— a yellow precipitate begins to form (for ZH, even prolonged heating at $n = 1$ does not lead to the formation of precipitates). To synthesize the yellow substance, 3 mmol of K_2PtCl_4 were dissolved in 6-7 ml of water, 3 mmol of MtH were added, and the mixture was heated for ~ 30 min on a water bath. The precipitate was filtered off, washed with water, alcohol, and ether, and dried at 60°. Analyses showed that the composition of the precipitate is well reproducible and corresponds to the empirical formula $PtCl_2{\cdot}MtH$. The compound is formed in high yield (85-87%).

Found, %: Pt 47.00; 47.04; N 3.35; 3.44; S 7.63; 7.59; Cl 16.91; 17.01
$PtCl_2 \cdot MtH$. Calculated, %: Pt 47.01; N 3.37; S 7.72; Cl 17.06

From the percentage content of the elements (average figures were taken), the ratio $Pt : N : S : Cl = 1 : 1.002 : 0.98 : 1.99$ was found. For $PtCl_2 \cdot MtH$, the ratio $Pt : N : S : Cl$ should be equal to $1 : 1 : 1 : 2$.

Three structural variants may be proposed for the compound corresponding to the empirical formula $PtCl_2 \cdot MtH$:



$$\left[\begin{array}{llll} Cl & & NH_2{-}CH{-}COOH & \\ & Pt & & CH_2 \\ Cl & & S{-}CH_2 & \\ & & \;| & \\ & & CH_3 & \end{array}\right]$$

(I)

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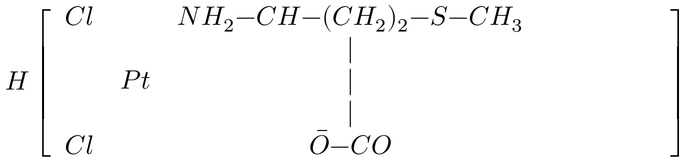
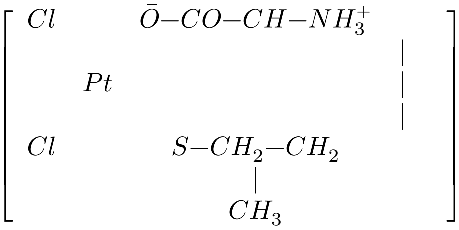
* $NH_2CH(CH_2CH_2SCH_3)COOH$ is denoted MtH.



$$H\left[\begin{array}{lll} Cl & & NH_2-CH-(CH_2)_2-S-CH_3 \\ & & \quad\quad\;\; | \\ & Pt & \quad\quad\;\; | \\ & & \quad\quad\;\; | \\ Cl & & \quad\;\; \bar{O}-CO \end{array}\right]$$

(II)



$$\left[\begin{array}{lll} Cl & & \bar{O}-CO-CH-NH_3^+ \\ & & \quad\quad\quad\quad\quad\;\; | \\ & Pt & \quad\quad\quad\quad\quad\;\; | \\ & & \quad\quad\quad\quad\quad\;\; | \\ Cl & & \;\; S-CH_2-CH_2 \\ & & \quad\quad\; | \\ & & \quad\;\; CH_3 \end{array}\right]$$

(III)

In abbreviated form these variants may be written as $[Cl_2Pt(MtH)]$ (I), $H[Cl_2Pt(\overline{Mt})]$ (II), and $[Cl_2Pt(MtH\pm)]$ (III), i.e., the inner sphere of the complexes contains, respectively, molecules, negative ions, and dipolar ions of methionine. The coordination capacity of methionine in all structural variants is taken as equal to 2 (the following pairs of groups are bound to Pt, respectively: $-NH_2$ and $-S-$; $-NH_2$ and $-CO\bar{O}$; $-S-$ and $-CO\bar{O}$). Obviously, the coordination capacity of methionine cannot be taken as equal to 1 or 3, since the composition of the compound would then be different, markedly differing from that actually found (for example, $H[Cl_3Pt(MtH)]$ or $[ClPt(Mt)]$).

Variant III is a priori unlikely, since 7-membered rings are usually unstable; variants II and I correspond to more stable 5- and 6-membered rings. Evidence rejecting variant II (and still more III) is furnished by the behavior of the yellow compound toward hydrochloric acid. It is known $^{(5-9)}$ that when all intracomplex salts $[PtZ_2]$ are heated with HCl (1 : 1), the bond of Pt with the carboxyl group is cleaved and noncyclic compounds $[Cl_2Pt(ZH)_2]$ are formed; this transformation is completely finished after 1-2 min of boiling with an excess of acid. In one experiment, 4 ml of HCl (1 : 1) were added to 0.22 g of the yellow compound and the mixture was boiled vigorously for 2 min. Part of the starting substance did not pass into solution, and part separated upon cooling. The precipitate was filtered off, washed, dried, and analyzed. It contained 47.07% Pt; calculated for the starting compound, 47.01% Pt. Evidently, the composition of the substance did not change; moreover (despite unavoidable small losses), 0.17 g of substance was collected, i.e., $\sim 80\%$ of the initial amount. Such treatment could not have been withstood by a compound containing $Pt—OC\bar{O}—$ bonds; evidently, variants II and III are excluded. Only a compound having structure I could remain unchanged under the conditions described.

Also significant is the behavior of the yellow compound (1 mmol) toward free methionine (1 mmol). When MtH is added to a suspension of the yellow compound

···in a small amount of water, dissolution of most of the precipitate already occurs in the cold. After slight heating no precipitate remains, and an almost colorless solution is obtained. The interaction of $PtCl_2 \cdot MtH$ with MtH evidently leads to the formation of a dimethionine complex. It is highly probable that the bonds of the second methionine particle (MtH or Mt^-) with Pt do not differ from the bonds of the first particle, which became attached to Pt in the preparation of the yellow compound from K_2PtCl_4. If the compound $PtCl_2 \cdot MtH$ had structure II, then from it the compound $[PtMt_2]$ would be obtained (both Mt^- would be bound to Pt through the groups —NH_2 and —COO^-). Such a compound should be an analogue of $[PtZ_2]$; it should be sparingly soluble, like all compounds of this type. In fact, however, the action of MtH on $PtCl_2 \cdot MtH$ gives a readily soluble compound. Moreover, the reaction of the yellow compound with MtH proceeds rapidly even in the cold, whereas the interaction of the compound $K[Cl_2PtAn]$ with an excess of free α-alanine (AnH) requires prolonged heating (in the latter case the sparingly soluble salt $[PtAn_2]$ is formed, in which, as in all compounds of the $[PtZ_2]$ type, the bonds of An^- with Pt are effected through the groups —NH_2 and —COO^-).

The high rate of the reactions both in the action of MtH on $PtCl_2 \cdot MtH$,* and in the action of MtH on K_2PtCl_4, is evidently due to the ease of attachment to Pt(II) of the —S— group of methionine.

The totality of the data set forth above leads us to the conclusion that the yellow compound has structure I (dichloromethionineplatinum). The compound is sparingly soluble in water, alcohol, and ether, and dissolves considerably better in hot water; after recrystallization from dilute HCl it forms characteristic crystals (under the microscope–slightly elongated rectangles with sharp outlines). Despite its poor solubility in water, the compound gives a sharply acid reaction with methyl orange (presence of a free carboxyl group). On addition of alkali the compound passes into solution. However, in the presence of phenolphthalein, more than 1 equivalent of KOH is consumed in titration (about 1.6 equivalents; the end point is not entirely sharp). Apparently this is explained by the easy mobility of the chlorine situated trans to the strongly trans-directing —S— group and replaced by OH^- upon addition of KOH (in the presence of an excess of KCl, less alkali is consumed in the titration–about 1.2 equivalents). If the compound had the structure II rejected by us, it would probably titrate sharply and would consume 1 equivalent of KOH (as occurs in the titration, for example, of the compound [Cl(ZH)PtZ], in which Cl is located trans to the amino group of glycine ([9])).

Let us note that the yellow compound has also been synthesized by us by another method (addition of K_2PtCl_4 to a solution prepared by heating K_2PtCl_4 with MtH at $n = 2$); this peculiar reaction will be described in a subsequent communication.

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Received
17 X 1961

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* Study of the soluble product of this reaction, as well as of the product of the action of MtH on K_2PtCl_4 at $n = 2$, is currently being carried out by us.

Note: Figure translations are in progress. See original paper for figures.

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