

HYPOXANTHINE COMPLEXES WITH 3d METAL PERCHLORATES*

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6-氧基嘌呤与3d金属高氯酸盐的配合物

题配合物的合成是将金属高氯酸盐 1.25 毫摩溶于 35 毫升乙酸乙酯和 15 毫升乙醇-原甲酸三乙酯混合溶剂内, 然后加 6-氧基嘌呤 (hxH) 2.5 毫摩 (对于 M^{2+}) 或 3.75 毫摩 (对于 M^{3+}), 将整个混合物回流 6 小时, 冷至室温后, 加无水乙醚 15—20 毫升, 加微热以使体积减至约 20 毫升, 将固体过滤分出, 用乙醚 30 毫升洗涤, 贮于真空无水 $CaSO_4$ 干燥器内, 所得产物含较高的氧基嘌呤与金属比 (4:1 或 3:1), 根据分析结果, 分下列类型: $[M(hx)(hxH)_3(ClO_4)_2]ClO_4$ ($M = Cr, Fe$), $[M(hx)(hxH)_3(H_2O)]ClO_4$ ($M = Mn, Cu, Zn$), $[M(hx)(hxH)_2(H_2O)(ClO_4)]ClO_4$ ($M = Fe, Ni$) 和 $[Co(hx)(hxH)_3]ClO_4$ 。这些新配合物皆不溶于有机溶剂。光谱表征表明高氯酸根在 $M = Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$ 配合物内皆为外界离子, 而在 $M = Fe^{2+}, Ni^{2+}$ 配合物内则为单齿配体, 在 $M^{3+}(Cr, Fe)$ 配合物内, 一为离子, 另一为单配体。除 Co 为 5 配位外, 余皆为 6 配位。所有这些新配合物皆以 hx 为桥连配体, 通过 N_3, N_7 , 形成链状聚合物。

关键词: 次黄嘌呤 金属高氯酸盐 配合物

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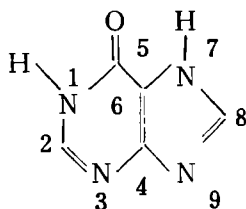
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Hypoxanthine (hxH, 6-oxopurine, I) is a minor constituent of RNA. Several metal complexes with hxH and derivatives (e.g. inosine) have been reported. In the magnetically subnormal $[\text{Cu}_2(\text{hxH})_4\text{Cl}_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ dimer, which involves quadruple hxH bridges between the two Cu^{2+} ions, bidentate hxH binds via N3, N9⁽²⁾. However, in $\text{Cu}(\text{hxH})\text{SO}_4 \cdot \text{H}_2\text{O}$, which is polymeric characterized by the presence of infinite $[-\text{Cu}-(\text{hxH})-]_x$ chains, bridging hxH binds via N3, N7 to adjacent Cu^{2+} ions⁽³⁾. Regarding terminal unidentate hxH, it coordinates through N7 in $\text{M}(\text{hxH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}$)⁽³⁾, but the existence of linkage isomers with either N7- or N9-bound hxH has been demonstrated for $[\text{Ru}(\text{hxH})(\text{NH}_3)_5]\text{Cl}_3 \cdot n\text{H}_2\text{O}$ ($n = 1$ or 1.5)⁽⁴⁾. Moreover, 8-azahypoxanthine binds via N7 in a Cd^{2+} ⁽⁵⁾ and N9 in a Hg^{2+} ⁽⁶⁾ complex. Previous work in these laboratories involved the syntheses and characterization of 3d metal perchlorate complexes with purine⁽⁷⁾ and various biologically important substituted purines, i.e., adenine⁽⁸⁾, guanine^(9,10), xanthine (xnH)^(10,11) and methylsubstituted xanthines^(12,13). The only hypoxanthine complex we had prepared during the course of these studies was $\text{Cu}(\text{hx})\text{ClO}_4 \cdot 4\text{EtOH}$, which was precipitated by refluxing mixtures of ligand and $\text{Cu}(\text{ClO}_4)_2$ in ethanol-triethyl orthoformate (teof) and characterized as polymeric with infinite $[-\text{Cu}-\text{hx}-]_x$ chains and terminal $-\text{OClO}_3$ and EtOH ligands⁽¹⁰⁾. We recently attempted the preparation of hxH complexes with other 3d metal perchlorates from ethanol-teof, but either obtained solid products in very low yields or failed to produce solid complexes. Subsequently, we employed a mixture of ethyl acetate (ea)-teof as the interaction medium⁽¹⁴⁾ and were successful in obtaining crystalline complexes in good yields (60-100% of the theoretical) in all cases investigated. The present letter deals with these complexes.

The synthetic procedure followed was: 1.25 mmol hydrated metal perchlorate is dissolved in a mixture of 35 ml ea and 15 ml teof, 2.5 (for M^{2+}) or 3.75 (for M^{3+}) mmol hxH are added, and the resultant mixture is refluxed for 6h or until no further significant change in appearance is noted. After cooling to room temperature, 15-20 ml anhydrous diethyl ether are added to the mixture and the volume is then reduced at low heat to ca. 20 ml. The solid residue is separated by filtration, washed with 30 ml diethyl ether and stored *in vacuo* over anhydrous CaSO_4 . As was also the case with the corresponding xnH complexes^(11,15) the new metal complexes involve relatively high hypoxanthine to metal ion ratios (4:1 or 3:1), being of the following types (analytical data): $\text{M}(\text{hx})(\text{hxH})_3(\text{ClO}_4)_2$ ($\text{M} = \text{Cr}, \text{Fe}$), $\text{M}(\text{hx})(\text{hxH})_3\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Cu}$,

Zn), $M(hx)(hxH)_2ClO_4 \cdot H_2O$ ($M = Fe, Ni$) and $Co(hx)(hxH)_3ClO_4$. It is noteworthy that in all cases investigated, substitution of one anionic hx^- ligand for one ClO_4^- group occurred during the synthesis. The new complexes are generally insoluble in organic media. Characterization studies are currently in progress.

From the characterization data available thus far it is clear that



the hypoxanthine ligands coordinate exclusively via ring nitrogens in the new complexes. The $\nu_{C=O}$ mode of free hxH (1665 cm^{-1}) is relatively insensitive to complex formation, appearing at $1675\text{--}1660\text{ cm}^{-1}$ in the spectra of the complexes, while the ν_{C-C} , ν_{C-N} and ring vibrations of the ligand at $1605\text{--}1200\text{ cm}^{-1}$ undergo more significant shifts and occasional splittings upon metal complex formation^(9-13,15). The perchlorate group is exclusively ionic for $M = Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$ and unidentate coordinated ($-OClO_3$) for $M = Fe^{2+}, Ni^{2+}$, as indicated, respectively, by single (*ca.* 1090 and 620) and doubly split ($1095, 1080$ and $635, 617\text{ cm}^{-1}$) ν_3 and $\nu_4(ClO_4)$ bands^(16,17). The M^{3+} (Cr, Fe) complexes exhibit triply split ν_3 ($1140, 1105, 1080$) and ν_4 ($650, 635, 620\text{ cm}^{-1}$) ClO_4 bands and contain, therefore, both ionic ClO_4^- and unidentate coordinated $-OClO_3$ ligands^(16,17). The ν_{OH} mode of coordinated water appears at $3400\text{--}3380\text{ cm}^{-1}$ in the spectra of the hydrated complexes⁽¹⁸⁾. With the exception of the Co^{2+} complex, which is pentacoordinated, the new complexes are hexacoordinated. The Co^{2+} complex shows ν_{Co-N} bands at 273 and 252 cm^{-1} ⁽¹⁹⁾ and its $d-d$ transition spectrum is characterized by multiple maxima ($437, 464, 500, 535, 582, 617, 771, 890, 1010, 1900\text{ nm}$) as is typical for pentacoordinated compounds of this metal ion^(20,21). The hexacoordinated Cr^{3+} and Fe^{3+} complexes show the $\nu_{M-O}(OClO_3)$ and ν_{M-N} modes at $340\text{--}330$ ⁽²²⁾ and *ca.* 285 cm^{-1} ^(8,9,11,13), respectively. The $d-d$ transition spectrum of the Cr^{3+} complex (${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 433, 455, $\rightarrow {}^4T_{2g}(F)$ 535, 573, 610 nm; $D_q = 1746\text{ cm}^{-1}$) is compatible with a CrN_5O chromophore⁽¹¹⁾. The $\nu_{M-O}(\text{aqua})$ mode in the hydrated M^{2+} complexes appears at $423\text{--}404\text{ cm}^{-1}$ ^(7,13,19,23), whilst ν_{M-N} occurs as a doublet at $257\text{--}241$ and $240\text{--}227\text{ cm}^{-1}$ ^(7-9,11,13,19). The frequencies of both these modes show the expected trends of decrease (Irving-Williams series, i.e., $Cu^{2+} > Ni^{2+}$

$>Fe^{2+} > Mn^{2+} > Zn^{2+}$) with metal ion variation. The Fe^{2+} and Ni^{2+} complexes exhibit the $\nu_{M-O}(OClO_3)$ mode at *ca.* 300 cm^{-1} ⁽²²⁾. The $d-d$ transition spectra of the latter two complexes are consistent with the presence of a MN_4O_2 absorbing species ^(7,11), *viz.*: $M = Fe^{2+}$ ${}^6T_{2g} \rightarrow {}^6E_g$ 440, 730, 915 cm^{-1} , $D_q = 1216\text{ nm}$; $M = Ni^{2+}$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 432, 450; $\rightarrow {}^3T_{1g}(F)$ 600, 648, 728; $\rightarrow {}^3T_{2g}(F)$ 960, 1020 nm ; $D_q = 1010\text{ cm}^{-1}$. The ${}^2E_g \rightarrow {}^2T_{2g}$ transition in the Cu^{2+} complex is split into three maxima at 552, 590 and 765 (very broad) nm ⁽⁷⁾.

In view of the insolubility of the new complexes in organic solvents and the pronounced tendency of purines to act as bidentate bridging ligands ^(2,3,7-9,11,13,19,24), structures involving linear polymeric $[-M-hx-]_x$ chains seem most probable for the complexes herein reported. The bridging hx^- ligand would most likely bind through N3, N7 to adjacent metal ions, since it is involved in single ⁽³⁾ rather than multiple ⁽²⁾ bridging. Terminal ligands vary from complex to complex as follows: $M = Cr^{3+}$, Fe^{3+} : three hxH and one $-OClO_3$ ligand, with one ionic ClO_4^- per metal ion, *i. e.*, $[-M(hxH)_3(OClO_3)-hx-]_x(ClO_4)_x$; $M = Co^{2+}$: three hxH ligands and ionic ClO_4^- , $[-Co(hxH)_3-hx-]_x(ClO_4)_x$ (CoN_5 chromophore); $M = Fe^{2+}$, Ni^{2+} : two hxH , one aqua and one $-OClO_3$ ligand, $[-M(hxH)_2(OClO_3)(OH_2)-hx-]_x$; and $M = Mn^{2+}$, Cu^{2+} , Zn^{2+} : three hxH and one aqua ligand, and ionic ClO_4^- , $[-M(hxH)_3(OH_2)-hx-]_x(ClO_4)_x$ (MN_5O absorbing species). As regards the binding site of terminal unidentate hxH , either of the imidazole nitrogens (N7 or N9) may act as the primary binding site, as already discussed in the introductory section ⁽³⁻⁶⁾. Protonation of free hxH may occur at N1, N7 or N1 N9 (the former tautomer is shown in I) ^(25,26). IR evidence appearing to favor the N1, N7-diprotonated tautomer in solution has been presented ⁽²⁵⁾. Purines have the tendency to use the imidazole nitrogen which is protonated in the free base as their primary binding site in their metal complexes ⁽²⁴⁾. In view of this and the recent crystal structure determination of $Co(hxH)SO_4 \cdot 5H_2O$, in which terminal hxH binds via N7 ⁽³⁾, it is considered as likely that the terminal hxH ligands in the new complexes also use N7 as their binding site. A full account of the work herein presented will be published upon completion of our characterization studies.

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