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Xanthine 3d Metal Complexes Characterized by High Ligand to Metal Ion Ratios*

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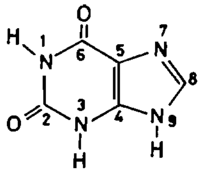
During earlier work in these laboratories, a complex of the $Cu(xn)_2 \cdot 2EtOH$ type was prepared by refluxing for a week a mixture of xanthine (xnH; I) and hydrated $Cu(ClO_4)_2$ in ethanol-triethyl orthoformate (teof) [2]. More recently, reactions of xnH with other 3d metal perchlorates ($M = Cr^{3+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}) were performed, under similar synthetic conditions, and the solid complexes formed are currently being characterized by means of spectral and magnetic studies. Subject of the present letter are the somewhat unusually high xanthine to metal ion molar ratios of most of the new complexes and the discussion of some of the characterization data available. It should be mentioned here that interest in studies of metal complexes with xanthine (a minor constituent of RNA) and derivatives has been steadily increasing in recent years [2–11].



I

The synthetic procedure employed was essentially similar to that used for the preparation of $Cu(xn)_2 \cdot 2EtOH$ [2], *i.e.*: 1.25 mmol hydrated metal perchlorate is admixed with 2.5 (for M^{2+}) or 3.75 (for M^{3+}) mmol xnH and added to a mixture of 35 ml absolute ethanol and 15 ml teof. The resultant mixture is swirled for 5–10 min and then refluxed for a period of 5–25 days (depending on the speed of accumulation of a substantial amount of the solid metal complex produced). Following the refluxive step, the solid products are separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. Under these conditions, Mn^{2+} and Fe^{2+} perchlorates behaved in the same manner as $Cu(ClO_4)_2$ [2], yielding products involving complete substitution of the ClO_4^- ions by the monodeprotonated xn^- anionic ligand. The yellow brown Fe^{2+} complex is of the $Fe(xn)_2$ type and has a room temperature magnetic moment of 4.68 μB, but the white Mn^{2+} compound contains two anionic xn^- and two neutral xnH ligands, *i.e.*, $Mn(xn)_2(xnH)_2$ ($\mu_{eff} = 5.84$ μB). In the rest of the cases investigated, only partial substitution of xn^- for ClO_4^- occurred, while all the complexes contain both xn^- and xnH ligands, *viz.* (colors and magnetic moments at 298 K given in parentheses): $M(xn)_2(xnH)_2ClO_4 \cdot H_2O$: M = Cr (drab green; $\mu_{eff} = 3.78$ μB); M = Fe (orange brown; $\mu_{eff} = 5.93$ μB); and $M(xn)(xnH)_2ClO_4 \cdot 2EtOH$: M = Co (pink; $\mu_{eff} = 4.71$ μB); M = Ni (pale green; $\mu_{eff} = 2.99$ μB); M = Zn (white). The d–d transition spectra of the Cr^{3+}, Co^{2+} and Ni^{2+} complexes are compatible with low symmetry hexacoordinated configurations [12], *i.e.*, nm: Cr^{3+}: $^4A_{2g}(F) \rightarrow {^4T_{1g}(F)}$ 440; $\rightarrow {^4T_{2g}(F)}$ 561,606,660 (approximate Dq = 1642 cm^{-1}); Co^{2+}: $^4T_{1g}(F) \rightarrow {^4T_{1g}(P)}$ 452; $\rightarrow {^4A_{2g}(F)}$ 505,520; $\rightarrow {^4T_{2g}(F)}$ 1150 (approximate Dq = 1040 cm^{-1}); Ni^{2+}: $^3A_{2g}(F) \rightarrow {^3T_{1g}(P)}$ 428; $\rightarrow {^3T_{1g}(F)}$ 650,702; $\rightarrow {^3T_{2g}(F)}$ 960,1130 (approximate Dq = 957 cm^{-1}). On the other hand, the spectrum of $Fe(xn)_2$ (600(sh), 737, 970(sh) nm) is consistent with a flattened tetrahedral configuration [13].

The IR spectra of the new complexes do not exhibit any significant shifts of the $\nu_{C=O}$ modes, which appear at 1700 and 1660 cm^{-1} in free xnH [2], so that it can be concluded that none of the C=O oxygens of the xanthine ligands is involved in coordination [2, 14]. On the other hand, significant shifts and occasional splittings of various $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of xnH at 1600–1100 cm^{-1} (1569, 1455, 1437, 1411, 1332, 1250, 1195, 1145, 1111) [2] are observed in the spectra of the new complexes, and it can be concluded that the xanthine ligands bind through one or more ring nitrogens [2, 14]. The ν_{OH} bands of coordinated water or ethanol appear at 3500–3300 cm^{-1} [15], while the perchlorate group is ionic for $M = Co^{2+}$, Ni^{2+}, Zn^{2+} (single ν_3 band at *ca.* 1080 cm^{-1}) and unidentate coordinated ($-OClO_3$) for $M = Cr^{3+}$, Fe^{3+} (ν_3 appears as a doublet at *ca.* 1130, 1050 cm^{-1}) [16]. The new complexes are either very sparingly soluble or insoluble in organic media.

$Fe(xn)_2$ is characterized by a subnormal room temperature magnetic moment (4.68 μB), owing presumably to magnetic exchange between adjacent ferrous ions in a bi- or poly-nuclear, xn-bridged structure. Possible structural types include $[Fe(xn)_4Fe]$, which is analogous to the structures of several magnetically subnormal binuclear Cu^{2+} complexes with quadruple nucleobase bridges [2, 17–20], and a

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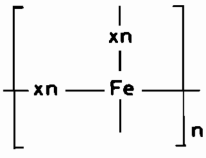
polymeric structure of type **II** [21]. The binding sites of bidentate bridging xn^- for the ferrous complex would include N(9) [6, 17] and either N(3) [2, 17] for the [Fe(xn)$_4$Fe] dimer or N(7) [22] for the single-bridged polymer **II**. It is, nevertheless, possible that the presence of the carbonyl oxygen at C(2) may be introducing sufficient steric hindrance [23] as to prevent binding of xn^- through N(3) and force the use of N(7) as the second binding site in species such as [Fe(xn)$_4$Fe] or [(EtOH)Cu(xn)$_4$-Cu(EtOH)]·2EtOH [2, 22, 23].



II

The rest of the new complexes prepared involve higher than usual xanthine to metal ion ratios. Previous work on adenine (adH) or guanine (guH) complexes with 3d metal perchlorates, synthesized also by refluxing mixtures of ligand and salt in ethanol–teof, resulted, with one exception (Fe(adH)$_2$(ad)-(ClO$_4$)$_2$), in complexes involving nucleobase to metal ion molar ratios of 1 or 2 [20, 24]. On the other hand, Guichelaar and Reedijk have reported that, during synthetic attempts at the preparation of adH or 9-methyladenine complexes with 3d metal salts, by refluxing mixtures of ligand and salt in ethanol alone, they obtained mixtures of the metal complex with uncomplexed ligand in some occasions [25]. However, the stoichiometries of the new xanthine complexes involve (xnH + xn^-) to metal molar ratios that are very close to an integer (analytical results), *i.e.*, 4 for M = Cr^{3+}, Mn^{2+}, Fe^{3+} and 3 for M = Co^{2+}, Ni^{2+}, Zn^{2+}. Hence, it is most likely that these are well-defined complexes rather than random mixtures of xanthine metal complexes and uncomplexed xnH. In view of their poor solubility in organic media, these complexes are most probably linear chainlike polymeric species involving single-bridged -(M–xanthine)-_n chains, with the coordination sphere around each metal ion being completed by the presence of terminal unidentate xanthine and aqua, ethanol or $-OClO_3$ ligands [2, 20, 24, 26]. The fact that the ambient temperature magnetic moments of these complexes are normal or near–normal does not rule out such structural types. In fact, previous studies have established that [M(puH)(OH$_2$)$_3$](ClO$_4$)$_2$ complexes (puH = purine; M = Co, Ni, Cu) exhibit normal room temperature magnetic moments, but show evidence in favor of magnetic exchange interactions at temperature below 110 K, and linear polymeric structures with single-bridged -(M–puH)-_n chains were proposed for these compounds [26]. The bidentate bridging xanthine ligands would be probably N(7), N(9)-bonded [22], and the terminal unidentate xanthine would coordinate through N(9) [2, 6, 20, 24, 26, 27]. It should be noted, however, that alternative structural possibilities exist for the new complexes with high xanthine to metal ratios. In fact, it is established that caffeine (caf; 1,3,7-trimethylxanthine), which usually acts as a unidentate N(9)- [28–30] or C(8)- [31] bonded ligand, forms also the molecular complexes [Mg(OH$_2$)$_6$]Br$_2$·2caf and [Mn(OH$_2$)$_6$]I·I$_3$·2-caf, which contain octahedral hexaaquametal(II) cations, uncoordinated caf and halide anions held together by a network of hydrogen bonds [32]. It is, thus, not inconceivable that in some of the complexes under discussion part of the xnH molecules are not coordinated to the metal ion, but form H-bonds through their ring nitrogens and their exocyclic pyrimidine oxygens (O(2) and O(6)) with the coordinated aqua or ethanol ligands (RO–H...N and RO–H...O bonds; R = H, C_2H_5) [32]. Further characterization work, aimed at the elucidation of the role of the xn^- and xnH groups in the new Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+} complexes is currently underway, and our results will be reported in the near future in a detailed publication.

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