Oxovanadium(IV) Complexes of Halogenated Oxines

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Summary. Six VO$_2^+$ complexes of 8-hydroxyquinoline (oxine) and of some of its mono- and dihalogenated derivatives have been prepared. The complex of 5-chloro-oxine is very unstable and oxidizes rapidly, generating a V(V) complex of stoichiometry VO(OCl)$_2$OH which could also be prepared in pure form. The infrared spectra of all complexes have been recorded and are discussed in detail. The complexes containing halogenated ligands appear as polymeric species, interacting through V=O···V=O bridges. The magnetic moments, investigated at room temperature, indicate completely quenched orbital contributions. The analysis of the electronic spectra reveals very complex solution behaviour including, oxidation phenomena, ligand loss, and interaction with the solvent.

Keywords. Vanadyl(IV); Oxine; Halogenated oxines; IR; Magnetic susceptibilities; Electronic spectra; Solution behaviour.

Oxovanadium(IV)-Komplexe von halogenierten Oxinen


Introduction

Increasing evidence on the biological relevance of vanadium has been accumulated during the last years [1–4], and its essentiality, distribution, and toxicity as well as its biological and pharmacologic activity are areas of great interest. Nevertheless, the role of vanadium in higher organisms is still unclear. Up to now, the best evidence for a biological role of this element comes from bacteria (vanadium
containing nitrogenase in Azotobacter species [5, 6]) and from plants (vanadium dependent haloperoxidases in algae and lichens [7]). On the other hand, and although the accumulation of vanadium in tunicates and in the toadstool Amanita muscaria has been well established, the possible functions of the systems containing the metal (hemovanadine and amavadin, respectively) remain obscure [8].

As part of our studies about simple inorganic models of interest for the development of the bioinorganic chemistry of vanadium [9–16], we have started investigations on VO$^{2+}$ complexes with 8-hydroxyquinoline (oxine) and some of its halogenated derivatives which appear to be suitable models due to the preference of oxovanadium(IV) for oxygen and nitrogen donors in biological systems.

Oxine, which forms particularly stable complexes with many metal cations [17–19], has been used as a ligand in previous studies belonging to this general project, involving V(III) [10] and VO$_2^+$ [12] as central cations.

In the present paper, we analyze the infrared and electronic spectra as well as the magnetic behaviour of the VO$^{2+}$ complexes of 8-hydroxyquinoline and its following halogenated derivatives: 5-chloro, 5,7-dichloro, 5,7-dibromo-, 5,7-diiodo-, and 5-chloro-7-iodo-8-hydroxyquinoline. The structures of the ligands are depicted schematically in Fig. 1, including a general diagram of the metal-ligand interactions supported by experimental evidences discussed in the following sections. Some of these compounds have been described earlier [20, 21], but their spectroscopic and magnetic behavior has not been investigated in detail. The complexes derived from 5-chloro-8-hydroxyquinoline and 5-chloro-7-iodo-8-hydroxyquinoline as well as the vanadium(V) complex of the first of these ligands (whose probable structure is also given in Fig. 1) are reported here for the first time.

Some unexpected results, related to the oxidation behavior of the central cation, apparently depending on the nature of the ligands, are also discussed.

### Results and Discussion

**Synthesis of the complexes**

Oxobis(8-hydroxyquinolinate)vanadium(IV) (VOQ$_2$) was obtained according to the procedure described by Doadrio and Martínez [20]. In contact with air, the obtained greenish precipitate oxidizes immediately, turning its colour to black.

\[ \text{Fig. 1. a: Schematic structure of the ligands (oxine } X = X' = H); \text{ b: diagram of the VO}^{2+} \text{ ligand interactions; c: probable structure of the V(V) complexes of 5-chloro-8-hydroxyquinoline} \]