Inorganica Chimica Acta 425 (2015) 247–254

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Co(II), Cu(II), Mn(II) and Ni(II) complexes of maleic hydrazide

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form 14 September 2014
Accepted 23 September 2014
Available online 2 October 2014

Keywords:
Maleic hydrazide
Crystal structure
Copper
Cobalt
Nickel
Manganese

ABSTRACT

The binding of 3d transition metals to maleic hydrazide (3,6-dihydroxypyridazine) has been investigated. Cobalt(II), copper(II), manganese(II) and nickel(II) complexes of maleic hydrazide have been prepared, crystallized and studied by various spectroscopic techniques. X-ray crystallographic structures of $ML_2\cdot nH_2O$ complexes with all four metal ions have been obtained. In all of the complexes two maleic hydrazides bind as unidentate ligands. Water molecules occupy the remaining coordination sites. In the cobalt(II) and nickel(II) complexes, which are isomorphous, the ligand binds through a single ligand nitrogen atom whereas in the manganese(II) and copper(II) complexes the ligand binds through a ligand oxygen atom. The metal ions all have six coordinate octahedral geometries except the copper(II) complex which has a five-coordinate square pyramidal geometry.

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1. Introduction

Metal binding to heterocycles containing more than one nitrogen atom, particularly those able to mimic pyrimidines or purines, has been a topic of continuing interest, especially for the hydroxylated derivatives. In recent years a variety of transition metal complexes of hydroxylated pyrimidines and purines have been characterized [1–3], but few for related ligands that are not normally present in natural systems.

3,6-Dihydroxypyridazine, maleic hydrazide, MH, is widely used as a growth inhibitor in agriculture. Although studies have shown that MH is bound in seedling roots, and that it interferes with uracil (2,4-dihydroxypyrimidine) uptake [4], the mechanism of growth inhibition has not been well characterized. Studies have shown that MH interacts with gibberellic acid (GA), a plant hormone promoting growth and elongation of cells, by blocking some essential reaction at a stage preceding the step where GA normally exerts its influence, resulting in blocking of cell division but not cell elongation [5,6]. Although MH induces genotoxic effects in plants, this does not appear to be the result of DNA cleavage [7]. Cytotoxicity, mitotic inhibition and unbalanced growth has been reported in cultured mammalian cells [8] but there has been no clear evidence of toxicity in mammals and the US Environmental Protection Agency has concluded that the genotoxic hazard of MH is negligible. Because seeds are frequently treated both with metal salts and MH, and because there have been some reports of an effect of metals on the genotoxicity of MH [9–11], we decided to study the interaction of metal ions with MH.

The crystal structures of three polymorphs of MH have been reported [12–15]. MH has also been co-crystallized with 3-methyluracil [16] and cytosine [17]. In every case in the solid state the ligand has the structure I, the tautomeric state where one of the hydroxyl hydrogens has migrated to the hydrazide moiety, rather than the dihydroxy structure. There is also extensive spectroscopic and computational evidence for this both in the solid state and in solution [18]. Cradwick [19] analyzed the crystal structure to conclude that MH can act as either a pyrimidine or a purine analog. In solution, the ligand readily loses one proton with a pK_a of 5.65 [20] and the crystal structure of the sodium salt of MH [21] shows that this is from loss of the OH proton.

There have been few studies of metal complexation of MH and the only crystal structure determinations have been of complexes in which MH is a chelating and bridging ligand between pairs of molybdenum or tungsten atoms in molecules containing a quadruple metal–metal bond [22–24]. It has been reported that in the presence of heavy metals and iron, zinc, calcium and magnesium ions, sparingly-soluble salts are formed [25] and that MH binds to metal ions on mineral surfaces [26]. Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been reported to form 1:1 and 1:2 metal:MH complexes and stability constants have been determined [27]. Bidentate four-membered metal-containing ring structures have been

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http://dx.doi.org/10.1016/j.ica.2014.09.030
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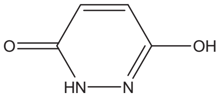
proposed for Cr(III), Mo(VI) and Ru(0) compounds but not validated by crystal structures [28]. Polarographic studies of Mn(II) MH solutions have been carried out [29], but to our knowledge no complexes have been isolated and no structural information has been reported. In this paper, we present the structures and spectroscopic data for complexes of MH with four 3d transition metal ions.



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2. Experimental

Solvents and reagents were of commercial grade and used without further purification. Maleic hydrazide and metal salts were obtained from Sigma–Aldrich Co. Infrared spectra of KBr pellets and of powdered crystals were obtained using a Perkin Elmer Spectrum 100 FTIR instrument with a reflectance attachment. Absorption spectra of aqueous solutions and reflectance spectra of the powdered crystals on a $BaSO_4$ supporting matrix were obtained using a Perkin Elmer Lambda 35 spectrophotometer equipped with a reflectance accessory. EPR spectra were acquired with a Bruker X-band EMX instrument. Magnetic susceptibilities were determined at room temperature using a Johnson Matthey magnetic susceptibility balance and were corrected for diamagnetic contributions. Thermogravimetric analyses (TGA) of powdered crystals were carried out on a TA Instruments Inc. Q500 V20.13 thermogravimetric analyzer. Samples were heated from 25 to 500 °C under an argon atmosphere with a heating rate of 10° min^{-1}. Powder X-ray diffraction patterns (XRD) were obtained using a Bruker D8 focus instrument with Cu Kα radiation. Data were collected between 5° and 45° with increments of 0.04° at a rate of five sec per increment. Diffraction data were obtained of all complexes at 20 °C and, for the Mn(II) complex, after heating at 175 °C overnight. Data were fit with the Bruker TOPAS2.1 software except for the heated Mn(II) complex, which were fit with the EVA software.

The complexes were prepared by mixing stoichiometric amounts of aqueous solutions of MH, typically 2 g (18 mmol) in 200 mL water adjusted to a pH of 6, with aqueous solutions of metal sulfates (9 mmol in 10 mL water). The resulting solutions were filtered and set aside for the solvent to slowly evaporate at room temperature (ca. 20 °C) resulting in formation of crystals, which were gathered from the solution, placed on filter paper, and air dried. The pH utilized for crystallization (6.0 for Mn(II), 5.7 for Co(II) and Ni(II) and 5.0 for Cu(II)) was chosen to maximize solubility and to minimize precipitation of metal hydroxides. At lower pH MH is less soluble and at higher pH metal hydroxides formed. Solutions prepared at different stoichiometries gave the same solids, but were contaminated with the starting material present in stoichiometric excess and crystals obtained by complete evaporation of the solvent were also not pure. Thus we chose to stop crystallization at about 25% yield to ensure purity. Elemental analyses of the solid powders were carried out using a Bruker Quantax 50 EDX attachment to a Hitachi TM3000 SEM instrument, and although subject to significant errors for C, N, and O were consistent with the metal:ligand stoichiometries later obtained from X-ray crystallography.

2.1. X-ray crystallography

Selected crystallographic data are given in Tables 1, 3 and 4, and complete results are given in the CIF files and data tables (Supplementary information). Data were collected at 123 K on an Oxford Diffraction (now Agilent) Gemini-R CCD diffractometer with kappa geometry using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). All data were collected to d = 0.55 and all data were used in refinement for all structures although the coverage was only calculated to 25.5° using the instruction ACTA 51 in the *.ins file used for refinement. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXTL97 program package [30]. All non-hydrogen atoms were refined as anisotropic, the hydrogen atomic positions were constrained in an idealized geometry relative to the bonded carbons or nitrogens [C—H at 0.95 and N—H at 0.88 Å with $U_{iso}(H) = 1.2\ U_{eq}(C,N)$]. Water hydrogens were refined isotropically without any constraints. Symmetry transformations used to generate equivalent atoms are given in Table 4. For the Mn(II) complex the data were searched for higher symmetry using PLATON [31]. The Mn(II) complex exhibits pseudo lattice centering but this had no effect on solution or refinement. There were no correlation matrix elements greater than 0.5. For the Cu(II) complex the crystal used was a two-component non-merohedral twin. The orientation matrices for the two components were found and the data were processed generating hklf4 and hklf5 files. The former was used to solve the structure while the latter was used for the final refinement cycles. As a consequence of using an hklf5 type hkl file, the data are not merged and hence R(int) is reported as 0.0 in Table 1. The final refinement gave a BASF value of 0.3774(6) indicating that the two components of the twin are in the ratio of 0.6226(6):0.3774(6).

3. Results and discussion

The complexes formed green (Cu and Ni), yellow (Mn) and red-brown (Co) transparent crystals. The Cu(II) and Ni(II) complexes formed thin plates while the Co(II) and Mn(II) crystals were more elongated. The metal complexes are stable in solution between pH 5 and 9 but poorly soluble above pH 7. The electronic absorption spectrum of MH has a band that shifts from 300 to 330 nm upon deprotonation at a pKa of 5.65 [32] but is little affected by metal binding. Standard additions experiments where aliquots of metal ion were added to a solution of MH at a constant pH of 6.0 indicated a metal:MH stoichiometry of 1:2 in solution with no indication of formation of a 1:1 complex. Isosbestic points were not observed because the free metal ion and the complex are in fast exchange at a pH near 6 and precipitation occurs at higher pH values at the concentrations required to observe the d—d bands. Addition of the metal ions to solutions of MH caused the pH to drop, but only up to a metal:MH stoichiometry of 1:2, also suggesting that the reaction is complete at this point. While our observations do not exclude the possibility of 1:1 complexes forming in solution, we found no evidence for them with the experimental techniques we used. Electronic absorption spectra of solutions and reflectance spectra of the solid complexes indicated that the d–d transitions occurred at 1087 and 475 nm (Co), 1006 and 646 nm (Ni), and 757 nm (Cu). The transitions in the spectra of the Mn(II) complex were too weak to be clearly assigned, as expected for high spin d^5 ions.

3.1. Infrared spectra

Infrared spectra of the metal complexes are generally similar. The broad band observed near 2500 cm^{-1} in MH, attributed to the O—H stretch [21], was lost as was the case in oxo-bridged binuclear Cr and Mo complexes of MH [28], but the broad band observed near 3000 cm^{-1} with contributions from both N—H and O—H stretching modes was retained in all the metal complexes. A medium, broad band near 900 cm^{-1}, assigned as a mixed

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