Oxamide Oxime Complexes: The Structure of the Complex Bis(oxamide-oximato)nickel(II)-Hydrogen Chloride-Water, and the Characterization of the Analogous Platinum(II) Complex

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Experimental

Oxamide oxime (diaminoglyoxime, oaoH₂) [1] forms a wide variety of complexes with Ni(II), Pd(II), and Pt(II). Depending on pH value and on the concentration of other ions in the mother liquid, different molecular and crystal structures form [2]. In some aspects these structures follow the trends normally observed in 1,2-dioximato complexes of the Ni triad [3], but additional structural features connected with the reduced acidity of the oxime H atoms often modify the otherwise common structural patterns. Another source of structural variations lies in the capability of the free amino groups to form H bridges. In this paper two members of the family of oxamide oxime complexes of the Ni triad are described which illustrate the trends observed previously [3].

Introduction

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Experimental

1. Preparations

Ni(oaoH₂)·HCl·H₂O is obtained as brick-red crystals on dissolving [Ni(oaoH₂)₂]Cl₂·1/2H₂O [4, 5] in hot desalted water, adding an equal volume of hot ethanol, and allowing the blue solution to evaporate on standing. Sometimes the compound precipitates already from the aqueous solution, or shortly after the addition of ethanol. When the crystals form on evaporation of the solution, they may be contaminated with large blue crystals of the parent complex, and sometimes they do not form at all. The reason for this is the subtle equilibrium between blue [Ni(oaoH₂)₂]Cl₂, brick-red Ni(oaoH₂)₂·HCl, and chloride-free Ni(oaoH₂)₂ [6], depending on small pH changes. If the solution is slightly acidic, the blue octahedral [Ni(oaoH₂)₂]₂⁺ complex cation is the stable form. Raising the pH, e.g. by just adding ordinary water, the brown-yellow planar complex Ni(oaoH₂)₂ precipitates. The title compound is obtained in the a pH range which is reached by adding ethanol to the [Ni(oaoH₂)₂]Cl₂ solution. The Pt complex of the same composition, Pt(oaoH₂)·HCl·H₂O, forms in low yield, contaminated with Pt(O), when an aqueous solution of K₂PtCl₄ is added dropwise to a refluxing aqueous solution of oxamide oxime, acetylated by adding diluted acetic acid or ammonium chloride. It may be prepared in a more pure form as dark-red needles with a green lustre, when yellow Pt(oaoH₂)₂Cl₂ [7], which is obtained from HCl solution, is recrystallized from water. Here again the effect of changes in acid concentration on the product formed becomes evident. The composition is supported by elemental analysis*:

Found C 10.01 H 2.95 Cl 7.36 N 23.45 O 16.6
Pt (residue from CH-determination) 40.48, (atomic absorption) 40.1.

Caled C 9.93 H 2.71 Cl 7.32 N 23.16 O 16.54 Pt 40.33.

2. X-ray investigations

Lattice constants of the Ni compound were derived from the setting angles of 25 reflections centered on a diffractometer (Syntex R 3, mono-

* Elemental analysis for C, H, N was carried out by the microanalytical laboratory of the institute, for Pt, O, Cl by Microanalytical Laboratory F. Pascher, Bonn (FRG).
chromatic MoKα radiation). Data collection (θ—2θ scans background–peak–background, 2θ < 60°) yielded 1957 observed (1 > 1.5σ(10)) independent reflections which were subjected to an empirical absorption correction (y-scans). Calculations were carried out on a NOVA 3 computer, plots were drawn on a Tektronix plotter. The program package was SHELXTL [8], which uses atomic scattering factors from International Tables for X-ray Crystallography [9] and takes into account anomalous dispersion.

The dark red crystals of Pt(oaoH)₂ · HCl · H₂O are always twinned and cutting did not result in a non-twinned specimen. As the twinning results in a partial overlap of several groups of reflections, a complete structure determination was not possible. Lattice parameters have been calculated applying a least squares routine [10] to the θ values of 78 reflections centered on a diffractometer.

2.1. Structure solution and refinement

The structure of the Ni compound was solved by Patterson and Fourier methods. After the location of all the nonhydrogen atoms, refinement with anisotropic temperature factors gave a weighted (unweighted) R of 0.038 (0.039). The highest peaks of a difference Fourier map corresponded to the H positions. These were refined with individual isotropic temperature factors. Final refinement by "cascade matrix" least squares resulted in a weighted (unweighted) R of 0.025 (0.026). The highest peaks in the difference Fourier map corresponded to the H atom from the least squares plane through these atoms is 0.025 Å (0.06 Å for N(5)). They are stacked along b, and adjacent complex molecules are related by inversion centers midway between two Ni positions. The normals of the planes (which are parallel by symmetry) are inclined at 28.6° to the stacking axis. Symmetry would allow for two different twin components) revealed the twin position at about 1.054, 2.5, 0.07. A more detailed structure analysis gave no satisfactory result due to the restricted range of available reflections.

3. Description of the structure and discussion

Atomic coordinates of Ni(oaoH)₂ · HCl · H₂O are listed in Table I, the numbering scheme and bond distances and angles in the complex molecule are shown in Fig. 1. The molecules are practically planar, the mean (maximum) distance of a non-H atom from the least squares plane through these atoms is 0.025 Å (0.06 Å for N(5)). They are stacked along b, and adjacent complex molecules are related by inversion centers midway between two Ni positions. The normals of the planes (which are parallel by symmetry) are inclined at 28.6° to the stacking axis. Symmetry would allow for two different twin components) revealed the twin position at about 1.054, 2.5, 0.07. A more detailed structure analysis gave no satisfactory result due to the restricted range of available reflections.

* Lists of structure factors are available on request from the author.
alternating interplanar distances along a stack, but these are not significantly different, amounting to 3.19(4) and 3.23(4) Å. The same is true for the two independent overlap patterns of adjacent molecules in a stack, which are practically indistinguishable. Fig. 2 shows a perpendicular projection of two adjacent molecules onto each other: The Ni of one complex molecule is nearly perpendicularly above and below the oxime N atoms N(2) and N(4) of the two neighbouring molecules, so that the coordination around each Ni is an elongated tetragonal bipyramid. The apical Ni-N distances are: Ni-N'(2) 3.185(2) and Ni-N'(4) 3.191(2) Å, the N(basal)-Ni-N(apical) angles are between 85.8(1) and 94.3(1)°. This stacking arrangement is reminiscent of the arrangement found in Ni(oaoH)$_2$ • 2 H$_2$O [6], where the Ni-N(apical) distances are considerably longer (3.478(3) Å). Shorter distances (3.04 Å) occur in Ni(oaoH)$_2$ • oaoH$_2$ [11], where amino N atoms of adjacent complex molecules are in the apical positions.

A remarkable structural feature is brought about by the additional H(13) in the lattice, originating from the HCl: It forms an H-bridge between O(1) and O(3) of adjacent molecules in a direction. The distances are: O(1)-H(13) 1.07(5), O(3)-H(13) 1.44(5) Å, the O-H-O angle is 174(4)°. This unusual intermolecular H bridge, indicated in Fig. 3, links the stacks to sheets parallel to the $ab$ plane. Further H-bonding interactions involving the water and the Cl$^-$ ion and connecting the different sheets are illustrated in Fig. 3: the water forms H bridges to
The Ni complex is a typical example of a so-called M-L form of bis(1,2-diondioximato)metal complexes of the Ni triad [3], where the molecular planes are inclined to the stacking axis, and the molecules of a stack are slipped with respect to each other, so that the p_{\pi} and d_{\sigma} orbitals of the metal atoms point at the ligand of the adjacent molecule. As outlined in [3], the heavier metals of the Ni triad exhibit an increasing tendency to have their dioximato complexes arranged in an M-M form, where the molecular planes are perpendicular to the stacking direction and where a direct electronic metal metal interaction may occur.

The compound Pt(oaoH)_{2} • HCl • H_{2}O is another example for this trend: Pt is close to .105, .25, .07, and the symmetry operation 0.5 + x, 0.5 — y, z of space group P2_{1}/a generates a second Pt position at .605, .25, .07, just a/2 above the first one. (As these values were not refined, the true figures may be slightly different.) This means that the Pt atoms are arranged in practically equidistant chains along a, with a Pt–Pt separation close to a/2 = 3.240 Å. This short metal metal distance (as compared to those in the Ni compound, 3.61 and 3.71 Å) is in the range typical for an M–M form. Furthermore, the molecular planes in the Pt complex cannot be inclined too strongly relative to the stacking direction, as otherwise too short an interplanar separation would result. The deep red colour and the green metallic lustre, which are not observed in any other Pt(oaoH)_{2} compound investigated so far, are a further hint at direct electronic metal metal interactions.
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