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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Dioximato Complexes, Columnar Structure

$[Ni(C_2H_5N_4O_2)_2] \cdot HCl \cdot H_2O$, $C_4H_{10}N_8NiO_4 \cdot HCl \cdot H_2O$, forms triclinic crystals, M_r = 347.36, $P\bar{1}$, a = 7.219(2), b = 7.316(1), c = 11.797(3) Å, α = 73.89(2), β = 86.37(2), γ = 85.71(2)°, V = 596 Å^3, Z = 2, d_c = 1.93 Mgm^{-3}; final R_w = 0.028 for 1957 reflections. The planar complex molecules form equidistant stacks along b, with the molecular planes inclined at ~29° to the stacking axis. Molecules of adjacent stacks are linked along a by an intermolecular H bridge coexisting with the usual intramolecular H bridges. The analogous Pt complex, $C_4H_{10}N_8O_4Pt \cdot HCl \cdot H_2O$, M_r = 483.74, a = 6.480(4), b = 16.115(5), c = 12.194(9) Å, β = 101.27(4)°, V = 1249 Å^3, Z = 4, d_c = 2.57 Mgm^{-3}, $P2_1/a$, crystallizes in a columnar structure with a Pt–Pt separation of $\sim a/2 \approx 3.24$ Å. Due to twinning, faking orthorhombic symmetry, a complete structure determination was not possible.

Introduction

Oxamide oxime (diaminoglyoxime, $oaoH_2$) [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-diondioximato 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].

Experimental

1. Preparations

$Ni(oaoH)_2 \cdot HCl \cdot H_2O$ is obtained as brick-red crystals on dissolving $[Ni(oaoH_2)_3]Cl_2 \cdot 1/2\,H_2O$ [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 $[Ni(oaoH_2)_3]Cl_2$, brick-red $Ni(oaoH)_2 \cdot HCl$, and chloride-free $Ni(oaoH)_2$ [6], depending on small pH changes. If the solution is slightly acidic, the blue octahedral $[Ni(oaoH_2)_3]^{2+}$ complex cation is the stable form. Raising the pH, *e.g.* by just adding ordinary water, the brown-yellow planar complex $Ni(oaoH)_2$ precipitates. The title compound is obtained in the a pH range which is reached by adding ethanol to the $[Ni(oaoH_2)_3]Cl_2$ solution.

The Pt complex of the same composition, $Pt(oaoH)_2 \cdot HCl \cdot H_2O$, forms in low yield, contaminated with Pt(O), when an aqueous solution of K_2PtCl_4 is added dropwise to a refluxing aqueous solution of oxamide oxime, acidified 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 $Pt(oaoH_2)_2Cl_2$ [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.

Calcd 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-

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* 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, $2\theta < 60°$) yielded 1957 observed ($I > 1.5\sigma(I_0)$) independent reflections which were subjected to an empirical absorption correction (ψ-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 $Pt(oaoH)_2 \cdot HCl \cdot H_2O$ 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 0.028 (0.030)*. The weighting scheme was $W = 1/\sigma^2(F)$.

For the Pt complex a Patterson synthesis calculated with 688 reflections having $h = 0, 1, 2$ (where reflections with $h = 1$ and 2 were not affected by twinning, and the contributions of both twins to reflections with $h = 0$ could be resolved by comparing the intensities of the $1kl$ and $2kl$ reflections of both twin components) revealed the Pt position at about .105, .25, .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 $Ni(oaoH)_2 \cdot HCl \cdot H_2O$ 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

* Lists of structure factors are available on request from the author.

Tab. I. Atomic coordinates ($\times 10^4$), H coordinates ($\times 10^3$), isotropic temperature factors ($\times 10^4$) equivalent to the refined anisotropic values, and refined isotropic values ($\times 10^3$) for H. U_{equiv} is defined as $U_{equiv} = 1/3$ trace $\tilde{U}$, $\tilde{U}$ signifying the diagonalized U matrix.

Atom	x	y	z	U_{equiv}
Ni	− 7.0(6)	2547.7(7)	9975.9(4)	188(1)
N(1)	2307(3)	2779(3)	9154(2)	215(8)
N(2)	− 714(4)	4436(4)	8629(2)	225(9)
N(3)	−2332(3)	2331(3)	10785(2)	208(8)
N(4)	674(4)	627(4)	11318(2)	241(10)
N(5)	3835(4)	4165(4)	7336(2)	339(11)
N(6)	243(4)	6198(4)	6736(2)	340(11)
N(7)	−3944(4)	880(4)	12547(2)	332(11)
N(8)	− 321(4)	−1156(4)	13194(2)	314(10)
O(1)	3946(3)	1672(3)	9512(2)	258(7)
O(2)	−2477(3)	5335(3)	8380(2)	315(9)
O(3)	−3936(3)	3409(3)	10396(2)	256(7)
O(4)	2430(3)	− 267(3)	11588(2)	321(9)
C(1)	2367(4)	3914(4)	8088(3)	213(11)
C(2)	526(4)	4933(4)	7767(3)	215(11)
C(3)	−2416(4)	1144(5)	11832(3)	222(11)
C(4)	− 580(4)	129(5)	12168(3)	217(11)
Cl	3456(1)	7300(2)	4657(1)	431(3)
O(5)	−2695(4)	8412(4)	5328(2)	476(10)
H(1)	− 310(6)	486(6)	899(3)	74(13)
H(2)	296(6)	13(6)	1100(3)	53(14)
H(3)	469(5)	357(5)	759(3)	44(10)
H(4)	395(6)	503(6)	651(3)	76(13)
H(5)	106(5)	641(5)	620(3)	43(10)
H(6)	− 86(6)	680(5)	655(3)	65(12)
H(7)	− 498(6)	143(5)	1218(4)	75(13)
H(8)	− 401(5)	1(5)	1313(3)	27(10)
H(9)	− 108(5)	− 114(5)	1376(3)	47(12)
H(10)	79(5)	− 158(5)	1335(3)	29(10)
H(11)	− 298(5)	974(5)	538(3)	59(12)
H(12)	− 346(5)	797(5)	528(3)	40(10)
H(13)	479(6)	248(6)	988(4)	96(15)

Anisotropic temperature factors ($\times 10^3$).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	13.2(2)	22.2(2)	18.1(2)	−1.2(1)	−2.0(1)	0.6(1)
N(1)	13(1)	26(1)	22(1)	−2(1)	−3(1)	2(1)
N(2)	14(1)	28(2)	23(2)	−2(1)	−4(1)	2(1)
N(3)	15(1)	26(1)	18(1)	−2(1)	−2(1)	4(1)
N(4)	14(1)	30(2)	25(2)	−2(1)	−3(1)	3(1)
N(5)	20(2)	48(2)	26(2)	1(1)	4(1)	6(1)
N(6)	26(2)	41(2)	23(2)	9(1)	0(1)	5(2)
N(7)	21(2)	46(2)	25(2)	3(1)	3(1)	0(2)
N(8)	23(2)	40(2)	24(2)	3(1)	−2(1)	3(2)
O(1)	14(1)	31(1)	30(1)	−4(1)	−6(1)	5(1)
O(2)	16(1)	38(2)	31(1)	4(1)	−3(1)	6(1)
O(3)	15(1)	30(1)	27(1)	−2(1)	−3(1)	5(1)
O(4)	17(1)	42(2)	29(1)	3(1)	−2(1)	8(1)
C(1)	18(2)	25(2)	20(2)	−4(1)	−1(1)	−2(2)
C(2)	18(2)	24(2)	21(2)	−4(1)	−1(1)	−2(2)
C(3)	17(2)	28(2)	23(2)	−8(1)	−3(1)	−2(2)
C(4)	21(2)	26(2)	18(2)	−4(1)	−6(1)	0(2)
Cl	32.4(5)	57.6(6)	29.2(4)	1.6(4)	0(4)	8.6(4)
O(5)	29(1)	55(2)	50(2)	−1(1)	−2(1)	1(1)

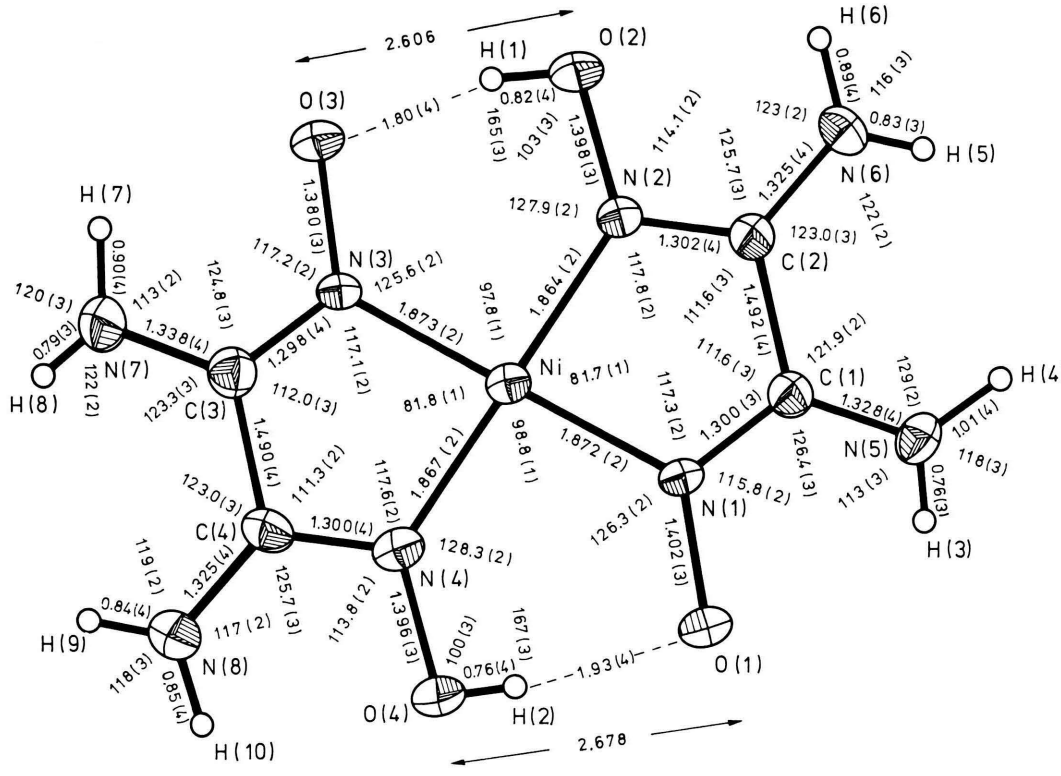

Fig. 1. Numbering scheme, bond distances (Å) and angles (°) in the $Ni(oaoH)_2$ complex molecule. Thermal ellipsoids are at the 50% probability level, H atoms are drawn as spheres with an arbitrary radius.

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 $Ni(oaoH)_2 \cdot 2\ H_2O$ [6], where the Ni–N(apical) distances are considerably longer (3.478(3) Å). Shorter distances (3.04 Å) occur in $Ni(oaoH)_2 \cdot oaoH_2$ [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

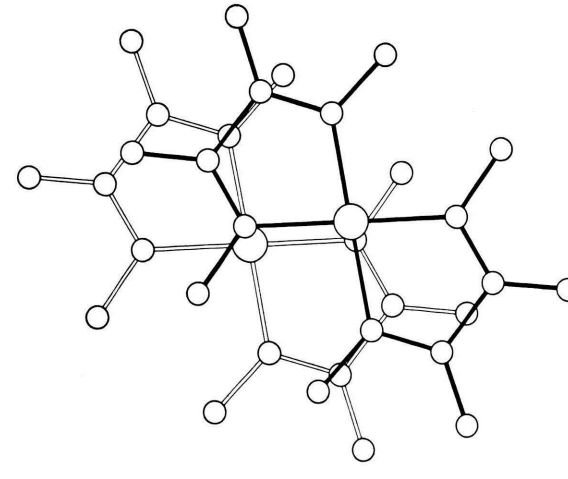

Fig. 2. Perpendicular projection of two adjacent molecules of a stack onto each other.

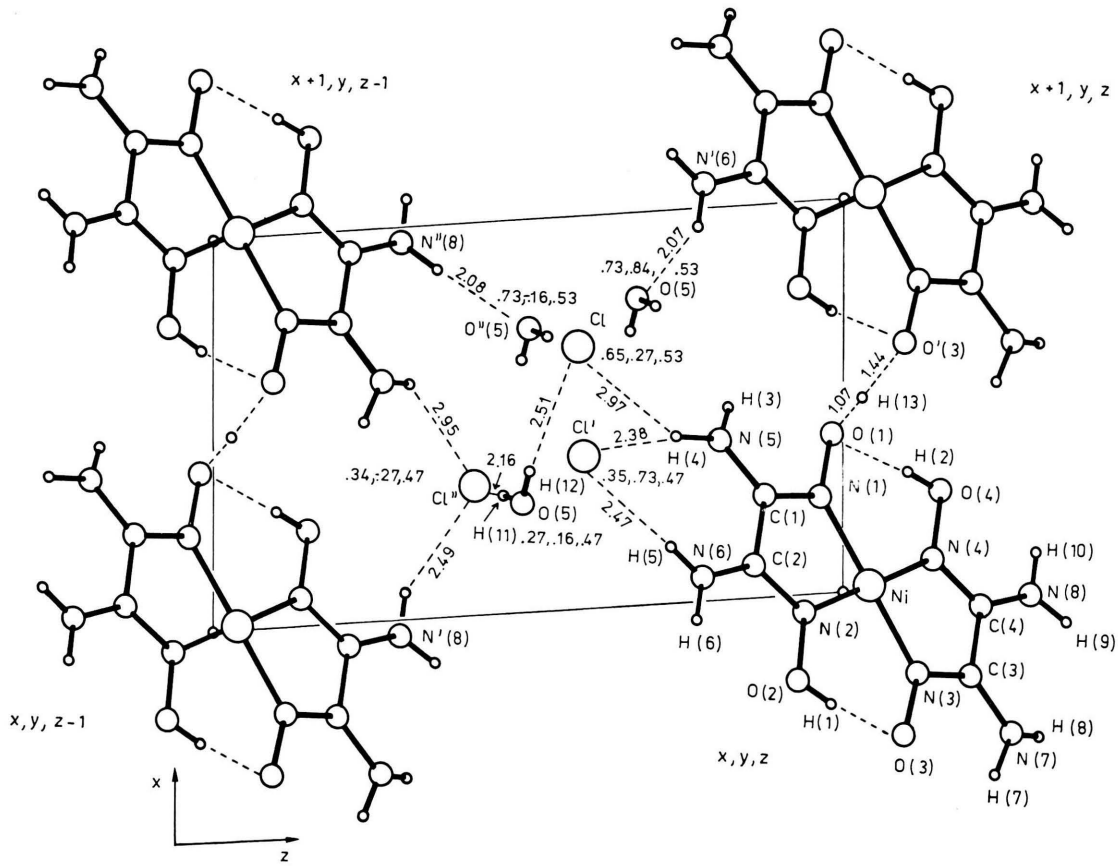

Fig. 3. Projection onto the ac plane showing H bonding interactions. Plotted are four complex molecules with Ni at $y \approx 1/4$ and those Cl^- and water positions (with round-off coordinates) within the unit cell which show H bonding interactions with the complex molecules plotted in the figure. The coordinates of the complex molecules are generated from those given in table I by the indicated unit vector translations. Distances (Å) to H atoms are given in the figure, the corresponding heavy atom distances are: N(5)–Cl 3.317, N(5)–Cl′ 3.364, O(5)–Cl 3.160, N(6)–Cl′ 3.242, N′(8)–Cl″ 3.277, O(5)–Cl″ 3.149; N′(6)–O′(5) 2.885, N″(8)–O″(5) 2.910; O(1)–O′(3) 2.503. Standard deviations may be estimated from Fig. 1.

Cl^- with each of its hydrogens, and Cl^- and water oxygen accept H-bridges from the terminal amino groups.

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_z and d_{z^2} 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 $Pt(oaoH)_2 \cdot HCl \cdot H_2O$ 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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