Crystal and Molecular Structure of a New Linear Chain Compound: Bis(diphenylglyoximato)platinum(III)perchlorate

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Platinum(III) Compound, Structure

The reaction of bis(diphenylglyoximato)platinum(IV) diiodide with AgClO₄ in benzene yields red brown needles of the compound bis(diphenylglyoximato)platinum(III) perchlorate (A) and crystals of bis(diphenylglyoximato)platinum(III) perchlorate which contains additionally between one and one and a half moles of benzene per formula unit (B). Both compounds are highly hygroscopic and instantaneously change their color to black-green in a humid atmosphere. Crystals of A are tetragonal, a = 20.325(2), c = 6.519(4) Å, space group D₄h-P4/nnc, Z = 4. The structure consists of stacks of [Pt(dpg)₂] cations with equidistant Pt–Pt separations of 3.259(4) Å. The perchlorate ions are disordered in channels formed by the cation columns. Crystals of B are triclinic, a = 14.29(3), b = 13.54(2), c = 10.34(3) Å, α = 85.2(2), β = 113.2(2), γ = 93.9(2).°

Introduction

Linear chain transition metal compounds have found considerable interest during the last few years and an appreciable number of reviews have appeared describing their physical and chemical properties [1–10]. The efforts to prepare new materials have concentrated on the mixed valence derivatives of these materials because some of these solids have been shown to be highly conducting electrically [1–10]. Some others may serve as a basis for an excitonic superconductor model compound [11, 12].

The possibility of crystallizing mixed valence (or non-integral oxidation state, "NOS") linear chain metal complexes from solution depends on the solubilities and on the relative donor or acceptor capabilities of the species present in the system. These are:

(i) the dissolved higher valent metal complex molecules (like "square planar" platinum(IV) in the mixed valence bis(oxalato)platinum(II, IV) or tetracyanoplatinum(II, IV) compounds [13, 14]) behaving as Lewis acids.

(ii) the lower valent planar metal complexes (planar platinum(II) species in the above mentioned case) acting as Lewis bases.

(iii) other electron pair donors like solvent molecules (H₂O, EtOH, ether etc.) or halide ions if the compounds are reacted with halogens.

A "piling up" of complex molecules in stacks with direct metal-to-metal contacts ("M–M" stacks, like the "Krogmann's Salts") which can be viewed as a donor-acceptor reaction leads to a less soluble "polymer". The reaction occurs solely if the donating low valent species (ii) is able to substitute the solvent or halide ligands which are bonded in a Lewis acid-base fashion to the axial positions of the higher valent complex molecule (i). In some rare cases like the tetracyanonplatinates(II, IV), bis(oxalato)platinates(II, IV), or dicarbonyldihalo-ridates(I, III) [15] the mixed valence solids can even be crystallized from polar solvents like water, which contain rather strongly donating solvent molecules.

These principal chemical problems in the preparation of mixed valence solids from solution was discussed in detail earlier [16, 17]. We recently prepared some new linear chain compounds with varying oxidation states [18–21] and investigated [22] other well-known solids [23–26] of this type. All these materials are crystallized in the presence of the comparatively weakly coordinating I₃⁻ ions but the versatility of the reaction should improve in avoiding any kind of donating species in the system. We used the almost "non-coordinating" [27] perchlorate, ClO₄⁻, as a counter ion, therefore. This leads to new types of mixed valence linear chain complexes one of which is described in the following.

Experimental

Starting materials

Bis(diphenylglyoximato)platinum(II) was obtained as described earlier [28]. This was oxidized to
bis(diphenylglyoximato)platinum(IV) diiodide with molecular iodine in 1,2-dichlorobenzene using a known procedure [29, 30].

Anhydrous silver perchlorate was prepared through azeotropic drying of a benzene solution of AgClO₄ • H₂O according to ref. [31].

A solution of 10 g AgClO₄ in 1 l of dry toluene served as reagent to prepare the compounds.

**Preparation of the compounds**

The reactions were carried out under inert gas atmosphere using standard Schlenk-tube techniques. The reaction vessels were heated before the reactions with a Bunsen burner to remove traces of moisture which were absorbed on the glass surface. The solvents and reagents were carefully dried and stored under nitrogen.

463.7 mg of bis(diphenylglyoximato)platinum(IV)diiodide (0.5 mmole) were dissolved in 1.6 l of boiling dry benzene free of thiophene. To this yellow solution 20.7 ml of a 0.048 M solution of silver perchlorate in dry toluene (1 mmole) were added with a pipette.

Immediately a light yellow precipitate of silver iodide formed. The reaction mixture was boiled for at least 6 h to coagulate the silver iodide. The reaction mixture was then evaporated by distillation to about 400 ml. The distillate showed traces of molecular iodine. The warm reaction suspension was filtered through a very efficient glass frit to remove the silver iodide and some silver which was formed by photochemical decomposition of the silver iodide. The brown filtrate was allowed to cool to room temperature and orange-brown crystals precipitated from the solution. The reaction product was filtered and dried carefully under high vacuum. The yield was about 300 mg. The compound crystallizes in long, strongly dichroic needles which appear lustrous orange or black depending on the position of the needle axis with respect to the plane of polarized light. Crystals suitable for X-ray investigation were obtained on slow cooling of the warm reaction filtrates.

The elemental analyses show that the reaction products crystallize with variable benzene content and have the general composition of Pt(dpg)₂ClO₄ • 1.0–1.5 C₆H₆. Typical elemental analyses are shown in Table I. Upon standing in a dessicator for some days the compound loses considerable amounts of benzene.

The varying ratio of benzene can be accounted for by the fact that a small number of tetragonal crystals (benzene free) can be found in the samples together with a large number of triclinic crystals containing benzene. A tetragonal crystal was chosen for the structure determination, as it was most likely to show a columnar structure of the platinum complexes. The triclinic crystals were characterized by their lattice parameters: \(a = 14.29(3)\), \(b = 13.54(2)\), \(c = 10.34(3)\) Å, \(\alpha = 85.2(2)\), \(\beta = 113.2(2)\), \(\gamma = 93.9(2)\)°.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>C</th>
<th>H</th>
<th>Cl</th>
<th>N</th>
<th>O</th>
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</table>

Up to now no triclinic crystal suitable for a structure determination could be found.

**Spectra**

Infrared spectra were obtained using a Beckmann spectrometer. The IR spectra of the samples obtained are very similar to the IR spectra of the complex Pt(dpg)₂. There is just one striking difference in the spectra, namely two additional bands, one broad and very strong absorption at about 1100 cm⁻¹ and one band of medium intensity at 637 cm⁻¹ (sometimes as a shoulder). These can be attributed without any doubt to the ClO₄⁻ ions. According to Nakamoto [32] two IR frequencies at 1060–1160 cm⁻¹ and 620–640 cm⁻¹ should be characteristic for a perchlorate ion. The IR evidence, therefore, supports the conclusion that the reaction products consists of a Pt(dpg)₂ unit with additional perchlorate ions. Neither the solutions of the reaction products nor the crystalline samples show any EPR absorption.

**Behaviour of the compounds in water**

Crystalline samples of Pt(dpg)₂ClO₄ are highly moisture sensitive. The crystals turn black in a few seconds when exposed to air. Therefore traces of moisture must be avoided during the preparation and handling of the substances. Powdered samples of bis(diphenylglyoximato)platinum(III) perchlorate turn green or black in a few seconds when exposed to air probably as a result of the high reactivity of platinum(III) toward moisture. However, after standing for some days on air or after boiling in solvents like nitromethane not excluding moisture most of the bis(diphenylglyoximato)platinum(III) perchlorate reacted to the violet divalent platinum complex Pt(dpg)₂, which was identified by IR spectroscopy. Until now we could not find out whether Pt(dpg)₂ is formed through disproportionation of the Pt(dpg)₂ClO₄ into the divalent Pt(dpg)₂ and a tetravalent platinum compound or through reduction of the Pt(dpg)₂ClO₄ with water or other...
reducing agents. The final formation of Pt(dpg)$_2$ from the trivalent species proves that on the reaction of the bis(diphenylglyoximato)platinum(IV) diiodide with silver perchlorate and then by the reaction of the bis(diphenylglyoximato)platinum(III) perchlorate with water the planar moiety remains unchanged whereas the occupation of the axial positions and the oxidation state of the central metal is changed.

X-ray investigations

The crystal was sealed under dry nitrogen in a glass capillary containing P$_2$O$_5$. Rotating crystal and Weissenberg photographs (CuK$_x$ radiation) showed the crystals to be tetragonal and yielded approximate lattice parameters. The systematic absences determined space group D$_h^8$-P$_4$/ncc uniquely. Precise lattice constants were calculated from the $\theta$ values of 40 reflections, centered on an automatic single crystal diffractometer (Siemens), by a least squares routine [33]. They are summarized in Table II. Intensity measurements were carried

Table II. Crystal data.

<table>
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<th>Formula</th>
<th>Molecular weight</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Cell parameters</th>
<th>Number of formula units</th>
<th>Density (sealed)</th>
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<tr>
<td>Pt(C$<em>{13}$H$</em>{11}$N$_2$O$_2$)$_2$ClO$_4$</td>
<td>760.9</td>
<td>tetragonal</td>
<td>D$_h^8$-P$_4$/ncc</td>
<td>$a = 20.325(2)$ Å, $c = 6.519(4)$ Å, $v = 3692.9$ Å$^3$</td>
<td>$Z = 4$</td>
<td>1.90 g/cm$^3$</td>
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out on the Siemens diffractometer with MoK$_x$ radiation, a “fine value method” and $\theta - 2\theta$ scans up to $2\theta = 55^\circ$. During the measurement the crystal was treated as “orthorhombic”, corresponding intensities were then averaged to give a “tetragonal” data set of 636 observed independent intensities. Reflections with an intensity less than 2.58 standard deviations were classified as unobserved. The observed intensities were corrected for Lorentz and polarization factors only. Calculations were carried out with Siemens 301 (Anorganisch-Chemisches Institut der Universität) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) computers with programs of the X-ray System [34]. Scattering factors were those of Hanson et al. [35].

Structure determination and refinement

A Patterson synthesis revealed the special positions of the platinum atoms. As these heavy atoms define a cell of only half the size of the true one, a Fourier synthesis gives a projection of the whole unit cell into a cell with only half the size. As this projection could not be resolved unambiguously, a new data set was generated by subtracting the platinum contributions from the observed intensities. Direct methods were applied to this new data set using the program MUL TAN [36] and a phase combination could be found which reproduced the platinum positions (for the subtraction of the platinum contributions were incomplete because of the inaccurate temperature factor), chlorine positions which corresponded to vectors on the Patterson map, and light atom positions for the ligand which could be refined successfully. The oxygen positions of the perchlorate ion were eventually detected on difference Fourier syntheses. Hydrogen was ignored. Refinement with isotropic temperature factors converged at $R = 0.107$ ($R = \Sigma|F_o| - |F_c|)/|F_o|$). Refinement with anisotropic temperature factors yielded $R = 0.079$ with a maximum shift/error of 0.7, average shift/error = 0.2. Atomic parameters are listed in Table III.

Description of the structure

Platinum occupies a crystallographic 222 position, so that the asymmetric unit of the [Pt(dpg)$_2$]$^+$ complex molecule consists of one quarter of the molecule. The coordination around the Pt is not exactly planar, but the two planes through Pt and

Table III. Atomic parameters ($\times 10^3$). The expression for the temperature factors is:

$$T = \exp[-2\pi^2(U_{11}h^2a^2 + U_2k^2b^2 + U_3l^2c^2 + 2U_{12}hka*b* + 2U_{13}hla*c* + 2U_{23}kcb*c*)].$$

<table>
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<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
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<td>11(3)</td>
<td>19(6)</td>
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<td>94(9)</td>
<td>11(4)</td>
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<td>9(2)</td>
<td>0.3(16)</td>
<td>4(2)</td>
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</table>
the two nitrogen atoms of each dpg ligand form a dihedral angle of 7°. The most relevant distances and angles in the complex are shown in Fig. 2. For steric reasons the phenyl groups are not coplanar with the central part of the complex molecule, but are tilted by 4° out of the “mean” plane through Pt and the four nitrogen atoms. Thus they form a propeller like arrangement. The complex units are stacked on top of each other to form columns with equidistant Pt–Pt separations of 3.259(4) Å. Two adjacent complex units of one column are twisted by 90° with respect to each other, imposed by symmetry. Thus, the phenyl groups of the upper molecule fit into the gaps between those of the lower one. A projection of the structure along the columnar stacks (c-axis) is shown in Fig. 1.

The [Pt(dpg)₂]⁺ stacks are arranged in a way to form parallel channels. These channels are occupied by the perchlorate ions, which are disordered in two ways: the chlorine atom is located on a fourfold symmetry axis, so there are two possible orientations of the ClO₄⁻ octahedra. Furthermore the z parameter for the chlorine atom is not well characterized and the U₃₃ component of the temperature factor is abnormally high, reflecting the fact that the perchlorate ions are disordered in the channel direction. This fact surely contributes to the relatively high discrepancy factor.

Discussion

The structure shows a remarkable similarity with the oxidation products of Ni(dpg)₂ and Pd(dpg)₂ with iodine, M(dpg)₂I, M = Ni, Pd [24]: practically the same unit cell dimensions, same space groups and very similar atomic coordinates [37]. There are two major differences concerning the composition: Pt(dpg)₂ClO₄ is the first example of a 1,2-dioxi-mato complex of platinum retaining its columnar structure upon oxidation. The second difference concerns the oxidation state of the metal: In M(dpg)₂I the iodine is present as polyanionic anions [38] so that each iodine carries only a fractional negative charge resulting in an oxidation state of the metal between 2 and 2.33. In our case there is one fully charged anion per complex unit, so that the oxidation state of the platinum is 3. Thus this compound is the first example of a d⁷ central metal-ion forming a columnar structure with direct metal-metal interactions (M–M form [39]). The complete absence of an EPR signal shows the pairing of the free electron spins along the chain.

Pt(dpg)₂ClO₄ clearly demonstrates the limits of the concept that short metal metal distances and strong electronic interactions are a simple function of the increasing oxidation state of the metal only. In 1,2-dioxi-mato complexes a shortening of the metal-metal distance on oxidation is always observed [39]. But there is no way to drive the metal-metal distance shorter than a minimum value determined by the steric requirements of the ligand. This minimum distance seems to be in the range of 3.25 Å for the dpg ligand and 3.15 Å for the sterically less hindered o-benzoquinonedioxide(bcd) [21].
It must be stated that these “short” distances can be achieved without oxidation, too, if electron withdrawing substituents are used. For example in the Pd complex of the ligand di(m-chlorophenyl)-glyoxime the metal-metal distance is 3.25 Å [40], and for the smaller and strongly electron withdrawing dichloroglyoxime ligand 3.19 Å [39]. Thus, as we stated earlier [39], the idea to use partial oxidation (“mixed valency”) to increase intermolecular metal-metal interactions in linear chain compounds fails if steric repulsions between the ligands dominate the metal-metal separations. In our opinion the comparatively short metal-metal distances found in the as well partially oxidized dioxalatoplatinates(II, IV) and tetracyanoplatin-ate(II, IV) [13, 14] are due to only weak repulsive forces between the ligands. Therefore the consequences of the mixed valency state on the metal-metal distances are much more pronounced than in the above described dioximato complexes.

Very few complexes with trivalent platinum as central metal are known so far, one thoroughly investigated recent example being the dipotassium-diaquadiplatinum(III)tetrasulfate [41] (Pt–Pt = 2.446 Å).

It is interesting from a chemical point of view that only platinum(III) compounds are isolated in the Pt(dpg)$_2$ system. A hypothetical reaction mechanism can be offered as an explanation:

(i) $\text{Pt}^{IV}(\text{dpg})_2 + 2 \text{AgClO}_4 \rightarrow \text{Pt}^{IV}(\text{dpg})_2\text{(ClO}_4)_2 + 2 \text{AgI}$

(ii) $\text{Pt}^{IV}(\text{dpg})_2\text{I}_2 \rightarrow \text{Pt}^{II}(\text{dpg})_2 + \text{I}_2$

(iii) $\text{Pt}^{II}(\text{dpg})_2 + \text{Pt}^{IV}(\text{dpg})_2\text{(ClO}_4)_2 \rightarrow 2 \text{Pt}^{III}(\text{dpg})_2\text{ClO}_4$

Reaction (i) occurs in the very similar case of bis-(4,4'-dimethoxybenzildioximato)platinum(IV) diiodide [42]. The more “electron donating” ligand 4,4'-dimethoxybenzildioxime stabilizes the tetravalent platinum(IV) diperchlorate derivative, which is obtained as the main product of reaction (i). The bis(benzildioximato)platinum(IV) diperchlorate species discussed here is evidently less stable, reacting immediately with any donors in the solution. It has to be assumed that this donor is $\text{Pt}(\text{dpg})_2$ resulting from reaction (ii). Reaction (ii) is typical for all bis(dioximato)metal(IV) dihalides at elevated temperatures. In the special case of $\text{Pt}^{IV}(\text{dpg})_2\text{I}_2$ reaction (ii) leads completely to iodine and $\text{Pt}^{II}(\text{dpg})_2$ upon heating in boiling toluene. In boiling benzene the disproportionation reaction (ii) occurs only partly.

Reaction (iii) is a typical example of an “Aufbau process” in dissolved linear chain transition metal complexes and needs no further comments. As a typical Lewis acid $\text{Pt}^{III}(\text{dpg})_2\text{ClO}_4$ reacts readily with Lewis bases like H$_2$O and other planar platinum(II) species.

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