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, , c = 6.519(4) Å, space group P4/ncc, Z = 4. The structure consists of stacks of \([\text{Pt}(dpg)_3]^+\) 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 = 13.54(2), b = 13.54(2), c = 10.34(3) Å, α = 85.2(2), β = 113.2(2), γ = 93.9(2)°.

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 tetracyanonплатинатеs(II, IV), bis(oxalato)platinate(II, IV), or dichromylhalo-

iridates(I, III) [13, 14] 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 1.61 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: \(a = 14.29(3), b = 13.54(2), c = 10.34(3) \text{ Å}, \alpha = 85.2(2), \beta = 113.2(2), \gamma = 93.9(2)^\circ\).

**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)platin(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

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**Table I. Analytical data for Pt(dpg)₂ClO₄ · xC₆H₆.**

<table>
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<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>Cl</th>
<th>N</th>
<th>O</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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Up to now no triclinic crystal suitable for a structure determination could be found.

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reducing agents. The final formation of Pt(dpg)2 from the trivalent species proves that on the reaction of the bis(diphenylglyoximato)platinum(IV) diodide 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 P2O5. Rotating crystal and Weissenberg photographs (CuKα radiation) showed the crystals to be tetragonal and yielded approximate lattice parameters. The systematic absences determined space group D₄h-P₄/ncc uniquely. Precise lattice constants were calculated from the θ 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 out on the Siemens diffractometer with MoKα radiation, a "fine value method" and θ—2θ scans up to 2θ = 55°. 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 2.5σ 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].

**Table II. Crystal data.**

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<th>Formula</th>
<th>Pt(C₁₆H₁₁N₂O₂)₂ClO₄</th>
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<tr>
<td>Space group</td>
<td>D₄h-P₄/ncc</td>
</tr>
<tr>
<td>a</td>
<td>20.325(2) Å</td>
</tr>
<tr>
<td>c</td>
<td>6.519(4) Å</td>
</tr>
<tr>
<td>v</td>
<td>3692.9 Å³</td>
</tr>
<tr>
<td>Number of formula units</td>
<td>Z = 4</td>
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<tr>
<td>Density (sealed)</td>
<td>1.90 g/cm³</td>
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**Table III. Atomic parameters (× 10³).** The expression for the temperature factors is:

\[ T = \exp[-2π²(U_{11}h²a²* + U_{22}b²* + U_{33}c²* + 2 U_{12}hka*b* + 2 U_{13}hla*c* + 2 U_{23}klb*c*)] \]

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<th></th>
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<td>9(2)</td>
<td>0.3(16)</td>
<td>4(2)</td>
<td>0(1)</td>
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</table>

**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
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 43° 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.

Fig. 1. Projection of the structure parallel to the
stacking axis (c-axis).

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 orienta-
tions of the ClO₄⁻ tetrahedra. Furthermore the z
parameter for the chlorine atom is not well charac-
terized and the Uₓₘ 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-diondioximato
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 polyiodide 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 meta-
lion forming a columnar structure with direct meta-
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-diondioximato 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 steri-
cally less hindered o-benzoquinonedioxime(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 tetracyanoplatinate(II, IV) [13, 14] are due to only weak repulsive forces between the ligands. Therefore the consequences of the mixed valence state on the metal-metal distances are much more pronounced than in the above described dioximato complexes.

Only 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) $\text{Pt}^{IV}(\text{dpg})_2\text{I}_2 + 2 \text{AgClO}_4 \rightleftharpoons \text{Pt}^{IV}(\text{dpg})_2\text{ClO}_4 + 2 \text{AgI}$

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

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

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 Pt²⁺-dpg reacting readily with Lewis bases like H₂O and other planar platinum(II) species.

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