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PdCl(NO) – an iconic compound

with corrugated Pd₄Cl₄ octagons built up by Pd₂Cl₂(NO)₂ moieties

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Dedicated to Prof. Dr. R. Hoffmann in recognition of his outstanding contributions to
general chemistry.

Abstract. During outstanding research in the late 1950s in Munich, which led to the development of the Wacker process for converting ethene into acetaldehyde by catalysis of PdCl₂, black insoluble nitrosyl-palladium chloride (PdCl(NO)) was obtained. More than sixty years after its first synthesis, its crystal structure was now determined by X-ray diffraction. PdCl(NO) (*mP*16, *P*2₁/*c*, *a*=10.2684(5), *b*=4.0737(2), *c*=7.8456(4) Å, *β*=111.125(1)°, *wR*2=0.0572) consists of distorted Pd₄Cl₄ octagons in chair arrangement to which four distorted Pd₂Cl₂ squares are annulated on every second edge. In this arrangement each of the two Pd atoms of the squares are connected to one N-O group, bonded alternatively up and down to the Pd atoms with a Pd-N-O angle of 129°. Such a square has the composition of the dimer which was found in the mass spectrum at 343.6 m/e. The octagons with four squares are interconnected to corrugated layers in the *b-c*-plane as a two-dimensional polymer.

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Introduction

At the end of the 1950s, outstanding research was performed on alkene oxidation with palladium(II) chloride as a catalyst at the Wacker Chemie company in Munich. Leading scientists in this field were J. Smidt, R. Jira and K. Hafner. Their results led to the Wacker process for industrial converting ethene into acetaldehyde ^[1,2]. Smidt and Jira observed that metallic palladium is obtained after streaming ethene through a slightly acidified PdCl₂ solution. Performing the experiment with a solution to which small amounts of sodium nitrite were added, instead of palladium, a black chloride-nitrosyl-palladium complex **1**, PdCl(NO) was obtained ^[3]. However, due to the lack of suitable single crystals, a structural investigation on **1** failed over a period of more than sixty years.

As continuation of our studies of nitrosyl metal halides that has been summarized in ^[4] we here report on the structure **1**. It was synthesized according to Smidt and Jira ^[3] from nitrite and ethene with palladium(II) chloride compound in water which was slightly acidified with sulfuric acid. Strict absence of air was applied. After several unsuccessful attempts ^[4] dark brown crystals were obtained as thin ribbons. Although the ribbons were twinned and disordered, a structural investigation could be performed and solved.

Previously, **1** has found the interest of several groups by Kurasov ^[5-7], Trogler ^[8,9] and Stromnova ^[10] and their coworkers. [Fe(NO)₂X]₂, Fe(NO)₃X, [Co((NO)₂X]₂, Ni(NO)X, Pd(NO)X may be compared with the Seel-Hieber isoelectronic carbonylnitrosyl metal complexes ^[11,12], Cr(NO)₄ ^[13], [Mn(NO)₄]⁺ ^[14], Mn(CO)₄NO, Mn(NO)₃(CO)₂, Fe(CO)₂(NO)₂, Co(CO)₃NO, Ni(CO)₄. For **1** diamagnetic behaviour has been reported ^[3] and the dimer Pd₂Cl₂(NO)₂ was detected in its mass spectrum after direct insertion probe/electron impact ^[4].

Results and Discussion

Figure 1 shows five *Diamond2* views ^[15] of the molecular structure of PdCl(NO). The structure consists of distorted Pd₂Cl₂ squares where each Pd atom is additionally connected to an N-O group. This arrangement has the composition of the dimer Pd₂Cl₂(NO)₂ (Figure 1(a)). Dimers have been identified in an earlier investigation in the mass-spectrum (EI⁺ mode, 70 eV, 343.6 m/e) ^[4]. Four distorted squares are connected to

a corrugated octagon in chair arrangement (Figure 1(b)). In [100] direction only weak van-der-Waals bonds are present. The strong bonds in the (011) plane create via corrugated layers a two-dimensional polymer which causes the insolubility of PdCl(NO) in common solvents. (Figure 1(c)). The Pd-N-O bond angle is determined to be 129° at Pd-N distances of 1.83(2) and 1.87(2) Å (Table 2). In Table 1 distances and in Table 2 angles are summarized.

Table 1. Distances in Å with uncertainties of the last digit.

Bond	distance	
Pd - Cl	2.531(1)	
	2.545(1)	(x, 3/2-y, -1/2+z)
	2.596(1)	(1-x, 1/2+y, 3/2-z)
Pd - N1	1.83(2)	
Pd - N1B	1.87(2)	
Pd - O1	2.57(2)	
O1 - N1	1.00(2)	
O1B - N1B	0.99(3)	

Table 2. Angles with uncertainties of the last digit (°).

Angle	
Pd1 - N1 - O1	129.2(2)
Pd1 - N1B - O1B	128.8(2)
Pd - Cl - Pd	96.32(3), 101.38(3)
Cl - Pd - Cl	83.68(3), 88.95(3), 169.89(2)

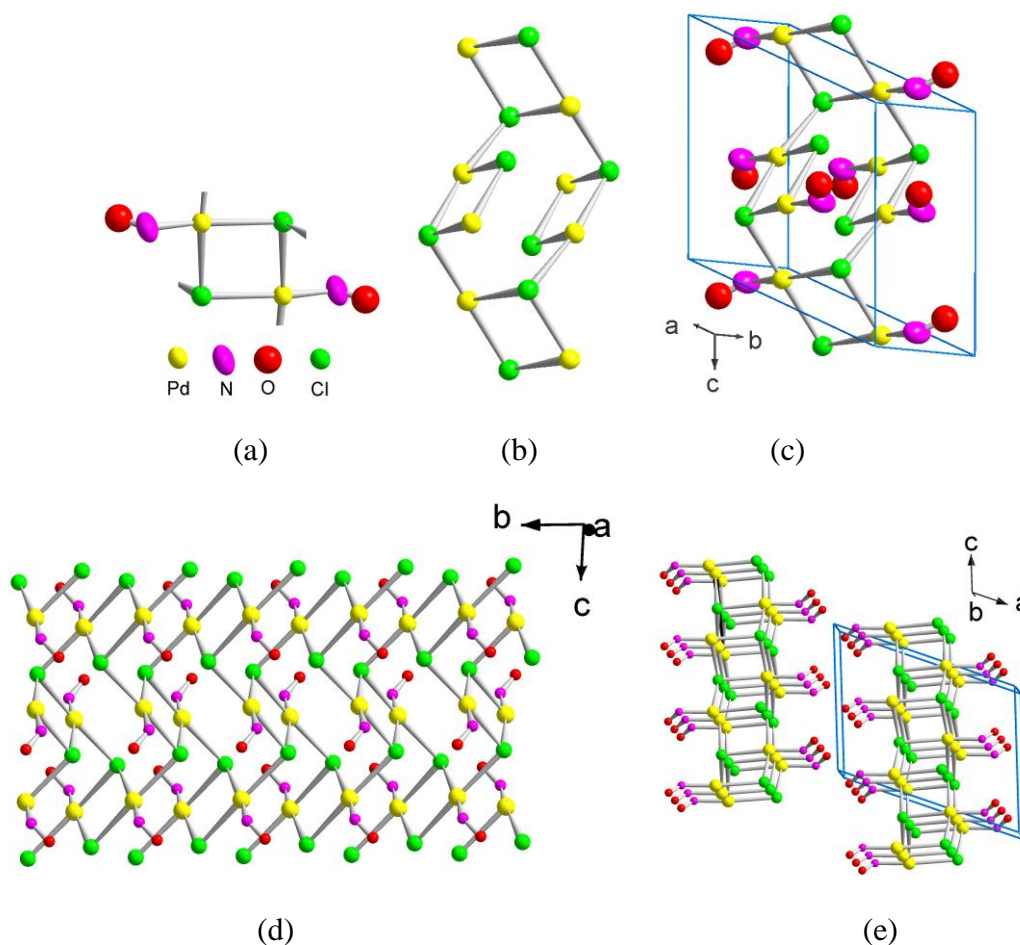
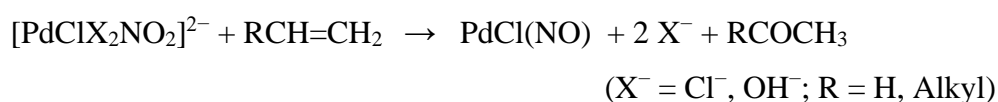


Figure 1. *Diamond2* plots ^[15] of **1** are shown for Pd-, Cl- and N-atoms with anisotropic displacement parameters at 50% probability, for O-atoms, large ellipsoids due to disorder are omitted and the isotropic displacement parameter is set to $U=0.08 \text{ \AA}^2$ for (a) to (c). For (d) and (e) isotropic displacement parameters are used for all atoms. (a) A distorted Pd₂Cl₂ square is shown where the Pd atoms are bonded to N-O groups, alternatively orientated up and down, with a bent Pd-N-O linkage of 129°. (b) The distorted squares are planar and parallel to the opposite one. Four Pd₂Cl₂ edge-connected squares build up a distorted Pd₄Cl₄ octagon in chair arrangement. (c) A distorted octagon with eight N-O groups is shown in the monoclinic unit-cell. (d) A view along [100] on one layer with four octagons building up a two-dimensional layer structure in the *b-c*-plane is shown in (d). View down [010] showing two corrugated layers of **1** in the (011) plane stacked in [100] direction is shown in (e). The layers are shifted to each other due to the monoclinic angle of 111°.

By shaking an aqueous solution of palladium(II) chloride in an atmosphere of nitrogen(II) oxide Smidt et al. [3] obtained a dark-brown, crystalline precipitate with composition PdCl(NO), insoluble in common solvents:



PdCl(NO) is also obtained by reaction of equimolar solutions of palladium(II) chloride and nitrite with alkenes [3]:



Alkenes are oxidized to carbonyl compounds, e.g. ethene, propene, butene to ethanal, acetone, methylethylketone, respectively [3].

In the following investigations of this substance we try to enlighten the bonding situation in PdCl(NO). For this purpose, vibrational, electronic and X-ray absorption spectroscopy (XAS) measurements were undertaken. Furthermore, in an accompanying publication [16], various quantum-chemical tools are used to answer the question, whether PdCl(NO) - in terms of electron count - might be a $\{\text{PdNO}\}^{10}$ species in the Enemark-Feltham notation [17]. In this work, particular attention is also paid to the bent Pd-N-O function in **1**.

Vibrational and electronic spectroscopies

To enhance the knowledge on the bonding in PdCl(NO) a vibrational spectroscopic study was performed. Vibrational frequencies and force constants serve as excellent measures to estimate the force required to stretch a bond connecting two atoms [18]. In the diamond ATR-FTIR spectrum broad signals around 1740 and 1576 cm^{-1} were found, but these were only poorly analysable. Due to apparent "negative" absorptions, we assume a refractive index of a semiconductor compound that is larger than that of the diamond used for the ATR measurement. This leads to only limited total reflection in the ATR-IR spectrum. To overcome this problem, further vibrational spectroscopic investigations were carried out using Raman spectroscopy.

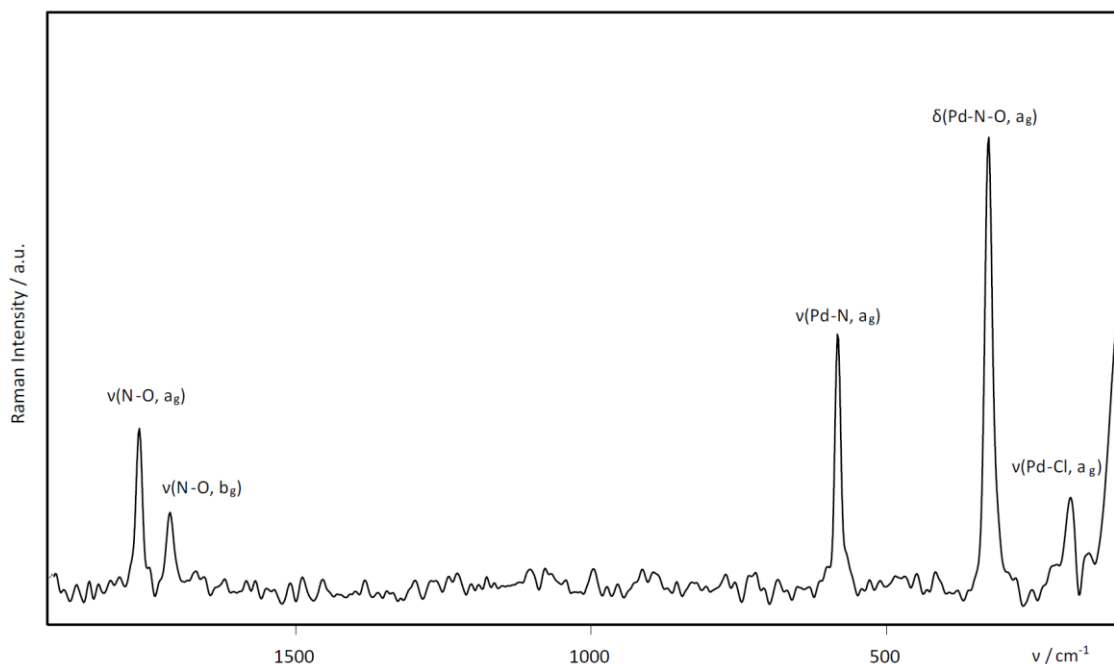


Figure 2: FT-Raman spectrum of PdCl(NO) (excitation wavelength 1064 nm).

Raman spectra were obtained with a Bruker Senterra II Raman microscope using a 532 nm excitation laser. However, only the decomposition of PdCl(NO) on the surface of the single crystals to palladium oxide PdO^[19] was observed: it shows a very intense resonance Raman enhanced signal at 630 cm⁻¹ as well as different weaker signals of partially second order^[20]. This behaviour was suppressed when recording the spectrum by means of an excitation wavelength of 1064 nm using a FT-Raman spectrometer Bruker MultiRam II. The Raman spectrum is shown in Figure 2. Based on their equal intensity behaviour in different spectra the recorded five bands can be assigned to one species that are attributed to the vibrational modes $\nu(\text{N-O}, a_g)$, $\nu(\text{N-O}, b_g)$, $\nu(\text{Pd-N}, a_g)$, $\delta(\text{Pd-N-O}, a_g)$, and $\nu(\text{Pd-Cl}, a_g)$ of solid PdCl(NO) in space group $P2_1/c$ (Table 3). The energies of the former four signals are in good agreement with the infrared spectrum of molecular PdNO studied experimentally using the matrix isolation technique ($\nu(\text{N-O}) = 1661$, $\nu(\text{Pd-N}) = 522$, $\delta(\text{Pd-N-O}) = 230$ cm⁻¹, $\nu(\text{N-O}) = 1220$, $\nu(\text{Pd-N}) = 315$, $\nu(\text{Pd-N-O}) = 50$ N m⁻¹^[21]).

Factor group analysis of solid PdCl(NO) based on space group $P2_1/c$ and Laue group $2/m$ (C_{2h}) results in 3 translational and 45 optical modes (Ra Raman, IR infrared, a. active, i. inactive):

$$\Gamma_{\text{opt}} = 12 a_g (\text{Ra a.}, \text{IR i.}) + 12 b_g (\text{Ra a.}, \text{IR i.}) + 11 a_u (\text{Ra a.}, \text{IR i.}) + 10 b_u (\text{Ra a.}, \text{IR i.}).$$

Table 3. Experimental and calculated Raman frequencies of solid PdCl(NO).

mode (exp.)	$\nu_{\text{exp.}} / \text{cm}^{-1}$	mode (calc.)*	$\nu_{\text{calc.}} / \text{cm}^{-1}$
$\nu(\text{N-O}, a_g)$	1767	$\nu(\text{N-O}, a_g)$	1765
$\nu(\text{N-O}, b_g)$	1715	$\nu(\text{N-O}, b_g)$	1712
$\nu(\text{Pd-N}, a_g)$	584	$\nu(\text{Pd-N}, a_g)$	590
$\delta(\text{Pd-N-O}, a_g)$	329	$\delta(\text{Pd-N-O}, a_g)$	342
		$\nu(\text{Pd-Cl}(\text{d3}), a_g)$	271
$\nu(\text{Pd-Cl}, a_g)$	189	$\nu(\text{Pd-Cl}(\text{d1}), a_g)$	211
		$\tau(\text{Cl-Pd-N-O}, a_g)$	124

* calculated structural data: space group $P2_1/c$ (C_{2h}^4), $a = 9.994$, $b = 3.423$, $c = 8.900$ Å, $\beta = 106.4^\circ$, $r(\text{Pd-Cl})$ 2.527, 2.690, 3.045, 3.064, 2.630, $r(\text{Pd-N})$ 1.891, $r(\text{N-O})$ 1.173 Å, $\angle(\text{Pd-N-O})$ 123.6° , $V = 292$ Å³; partial charges (QTAIM/Hirshfeld)/e: Pd +0.59/+0.34, NO -0.09/-0.05, local force constants $k_a/\text{N m}^{-1}$: Pd-N 206, N-O 1294.

Therefore, two of the four N-O valence vibrations (irreducible representations a_g and b_g) should be Raman active. The Raman bands at 1767 and 1715 cm^{-1} correlate well with IR absorptions at 1759 and 1715 cm^{-1} [3] (normal modes of a_g and b_g symmetries are Raman-active and IR-inactive).

To confirm the experimental findings, orientational quantum chemical DFT calculations of the solid were performed using the quantum chemistry package *AMS/BAND* (functional *TPSS*, Grimme dispersion correction, basis sets of *TZP* quality for all atoms, “small” frozen cores [22]). The geometry and the lattice parameters were optimized while keeping the experimental symmetry. With the exception of the torsion angle Cl-Pd-N-O the obtained structural data (Table 3) agree well with the experimental values. The calculated cell volume of 292 Å³ differs by 4.5 % from the experimental cell volume (306 Å³). Furthermore, the calculation confirms the behaviour of PdCl(NO) as a semiconductor with a low band gap. The absorption behaviour was calculated by means of the TD-CDFT routine of the *AMS/BAND* program package. The calculated band gap close to 0.5 eV is associated to the excitation in the Pd-Cl backbone, whereas the increase of the absorption near 1.5 eV is in line with an excitation of the Pd-N-O system

(Figure S2 in the ESI). These findings are based on the Hirshfeld induced densities attributed to these energies. Using UV/VIS spectroscopy, the direct band gap of PdCl(NO) was determined experimentally. By means of a Tauc plot ^[23] (Figure S1 in the ESI) the transition was determined to be 2.39 eV. The indirect band gap in the infrared region could not be detected due to instrumental reasons. Although for comparable compounds like PdCl₂ or PtCl₂ data are not known to date, this value seems plausible, as the band gap of TcCl₂ was determined experimentally to be 0.12 eV ^[24]. For PdCl₂ a band gap of 0.59 eV was calculated before ^[25].

The calculated Raman active vibrational modes are in good agreement with the experimental data (Table 3). The character of the motions was obtained from the eigenvector values of the calculated hessian matrix. We assume that the fully symmetric modes of *a_g* symmetry are those of the highest Raman intensities. The Hirshfeld atomic charges are consistent with the expectation of a polar Pd/Cl backbone (q(Pd) 0.34, q(Cl) -0.29). The NO group is slightly negatively charged (q(N) -0.02, q(O) -0.03).

To estimate the bonding in solid PdCl(NO) we compared the vibrational frequencies as well as the force constant values especially of the Pd-N and the N-O bonds. The energy of the N-O stretching vibration of the ligand NO fits nicely to that of a slightly negatively charged diatomic molecule NO (NO⁻: 1363 cm⁻¹, 818 N m⁻¹, NO: 1904.20 cm⁻¹, 1595 N m⁻¹, NO⁺: 2376.42 cm⁻¹, 2484 N m⁻¹) ^[26].

The strength of the Pd-N bond is more difficult to estimate by means of vibrational spectroscopy due to a lack of suitable data. By means of a local force constant analysis using the *program lmodeA-nano* ^[27] the value for the Pd-N force constant is determined to be in the range around 206 N m⁻¹ ^[28]. This size is attributed to predominantly covalent forces similar to the situation of the Pd bond in Pd-CO, Pd-SiO or Pd-NO (precise values obtained by normal coordinate analyses: f(Pd-C) = 285, f(Pd-Si) = 245 ^[29], f(Pd-N) = 315 N m⁻¹ ^[21]).

X-ray absorption spectroscopy

To enhance the knowledge on the chemical state of the Pd atom in PdCl(NO) ex-situ X-ray absorption (XAS) measurements on Pd K-edge (24.350 keV) were performed. The measurements were done at CAT-ACT beamline at KIT Light Source ^[30] in transmission mode on pelletized powders, PdCl₂ and PdO were used as references. The

shape of the near edge absorption (XANES) spectrum and the energy positions of the absorption features are finger-prints of the chemical bond formed in the compounds. The shape and the position of the absorption edge of the XANES spectrum of PdCl(NO) hint to the presence of both Pd-Cl and Pd-O or Pd-N bonds in PdCl(NO), the charge of Pd being an intermediate between the states in chloride and oxide (Figures 3 and 4). The analysis of the extended X-ray absorption fine structure (EXAFS) of Pd K-edge, reflecting the geometrical arrangement of neighbors around Pd atom, revealed well defined Pd-Cl bonds at about 2.32 Å, probably closer than in PdCl₂ (Figure S3 in the ESI). The Pd-O or Pd-N bond appeared less determined, the number of oxygen or nitrogen atoms is significantly less than chlorine.

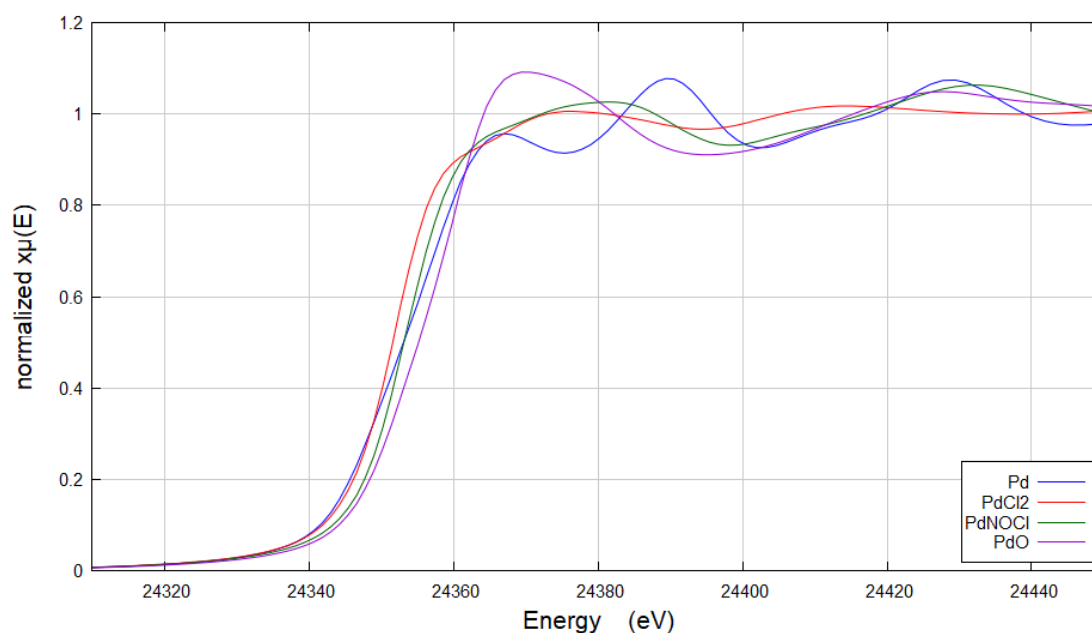


Figure 3: Normalized x-ray absorption spectrum of PdCl(NO), PdO, PdCl₂ and Pd.

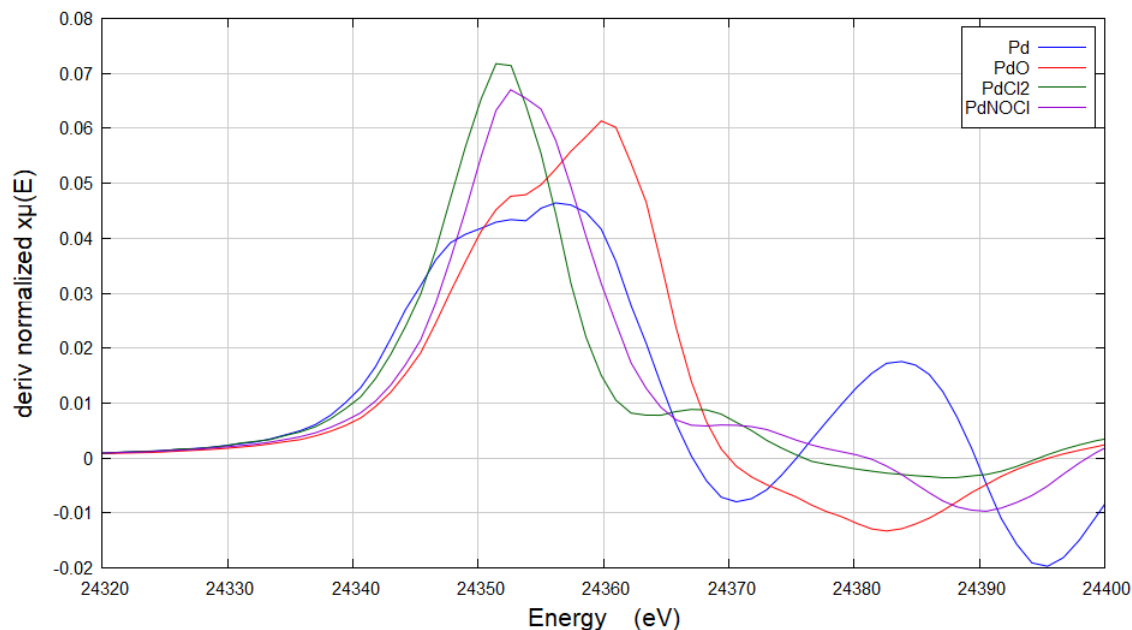


Figure 4: Derivative of the normalized x-ray absorption of PdCl(NO), PdO, PdCl₂ and Pd.

Conclusion

1 was characterized by single crystal structural X-ray investigation and identified as two-dimensional polymer built up by corrugated layers in the (011) plane. Perpendicular to the layers only van-der-Waals bonds are present. The layers are built up by distorted squares of **1**, with the composition of the dimer, forming distorted Pd₄Cl₄ octagons. In an earlier investigation, dimers have been identified in the mass-spectrum. The N-O groups in the squares are bonded alternatively up and down with bent bonds of 129° to the Pd atoms at a Pd-N distance of 1.83(2) and 1.87(2) Å. FT-Raman spectroscopy of **1** supports strong covalent contributions to the Pd-N and N-O bonds. By comparing the NO vibrational frequency with those of the diatomic species NO^{+0/-} the NO-ligand is expected to be slightly negatively charged in **1**. According to the XAS spectrum the charge located at palladium is comparable to that of PdCl₂ or PdO.

Experimental Section

Preparation

PdCl(NO) was prepared according to Smidt and Jira^[3], starting from a 0.1 M PdCl₂ solution. 887 mg of commercially available γ -PdCl₂ (Strem Chemicals Inc., USA, #45-1850, purity with respect to Pd 99.9 %) was dissolved in 50 mL water with 1 mL conc. H₂SO₄. The slightly brown slurry in the solution was removed by streaming it through a folded filter. In 20 mL of the clear PdCl₂ solution 125 mg NaNO₂ was dissolved. This solution was diluted with 30 mL water. Into a 100 mL round bottom flask, with three sleeves, purified nitrogen was streamed from sleeve 1, ethene from sleeve 2. Gas outlet was sleeve 3. For a few minutes both gases were streamed into the round bottom flask to replace completely air. Then ethene streaming was stopped and during continuously streaming of nitrogen the prepared 100 mL PdCl₂ solution was poured into round bottom flask. All sleeves were tightened and nitrogen was streamed in while the solution was magnetically stirred for five minutes. Then stirring was stopped and the streaming of ethene was started for one hour with two bubbles per second. In this time the solution changed its colour from yellow brown to dark brown and then to black brown near the surface of the solution. There ethene reduces Pd²⁺ to Pd⁰ and reacts to PdCl(NO) with a density $\rho=3.7303 \text{ g}\cdot\text{cm}^{-3}$, more than three times heavier than the diluted aqueous solution. During growing the crystal is permanently dragged down under the influence of gravity with the result that crystals of lower quality, including twinning and disorder, are obtained. (Figure 5(a)). The crystals were filtered and washed several times with water, ethanol and acetone. The yield was 85 mg in the form ribbons. Closer inspection of the ribbons showed that they deviate from a regular habitus. Some of them show a curved form (Figure 5(b)). With increased magnification it is evident that the ribbons consist of small blocks which are grown together as zigzag lines (Figure 5 (c)). It was a hard job to find a single crystal for structural investigation.

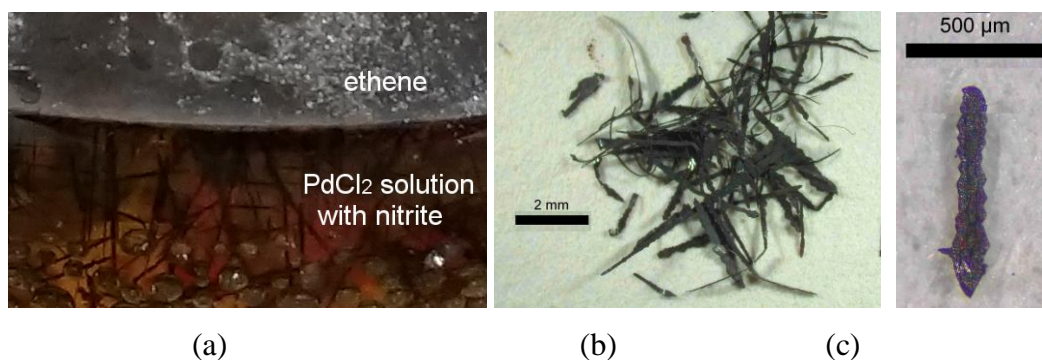


Figure 5. (a) Growing conditions for PdCl(NO) crystals. (b) Dark black ribbons of PdCl(NO). One side is broad, the other very thin. Also crystals with curved forms are observed. (c) With increased magnification it is shown that smaller blocks of ribbons are grown together forming zigzag lines.

X-Ray Single Crystal Investigation

A crystal ($0.02 \times 0.06 \times 0.08 \text{ mm}^3$) was sealed into a Lindemann glass capillary. On a Bruker D8 Venture TXS system equipped with a multilayer mirror monochromator and a MoK α rotating anode X-ray tube ($\lambda = 0.71073 \text{ \AA}$) the X-ray intensity was measured. The frames were integrated with the Bruker SAINT software [31]. After correction for absorption the structure was solved and refined with the Bruker *SHELXT* software package [32,33].

The investigated crystal is twinned and disordered. Twinning consists of two domains with a refined volume of 0.82 / 0.18. The NO fragment shows also disorder and is described by a split model. The disordered parts have a refined ratio of 0.57 / 0.43.

The crystallographic data, distances and angles are found in [34]. The complete data of this structural investigation can be obtained from the Cambridge Crystallographic Data Centre under CCDC 2159713 free of charge.

X-Ray Powder Investigation

Finely ground material of PdCl(NO) was filled in a Lindemann capillary (0.6 mm diameter, sealed under vacuum) and investigated on a Huber G644 Guinier diffractometer with MoK α_1 radiation ($\lambda = 0.7093 \text{ \AA}$, quartz monochromator). The angle

calibration of the diffractometer was performed with electronic grade germanium ($a=5.6575 \text{ \AA}$). In the 2θ range between 3 and 28° with an increment of 0.04° , 625 data points were collected with a counting time of 60 s for each increment. The Rietveld refinement parameters for PdCl(NO) at 298 K were analysed with the program *FullProf* [35]. Starting parameters were those from the single crystal investigation. These data lead to a good match between observed and calculated diffractograms. The refined Rietveld plot ($a=10.265(6)$, $b=4.038(2)$, $c=7.792(3) \text{ \AA}$, $\beta=111.03(3)^\circ$, $R_w=0.103$, $R_{wp}=0.140$, $R_{Bragg}=0.097$) is shown in Figure 6. Attempts to refine the oxygen positional parameters (x,y,z) with a constraint of 1.15 \AA for the N-O distance, and keeping constantly Pd, Cl and N at their single crystal positional parameters, had no success. The scattering contribution for X-rays of palladium with 46 electrons ($=46^2=2116$) is about 30 times larger than that for oxygen ($=8^2=64$). The complete data of this structural investigation can be obtained from the Cambridge Crystallographic Data Centre under CCDC 2160482 free of charge.

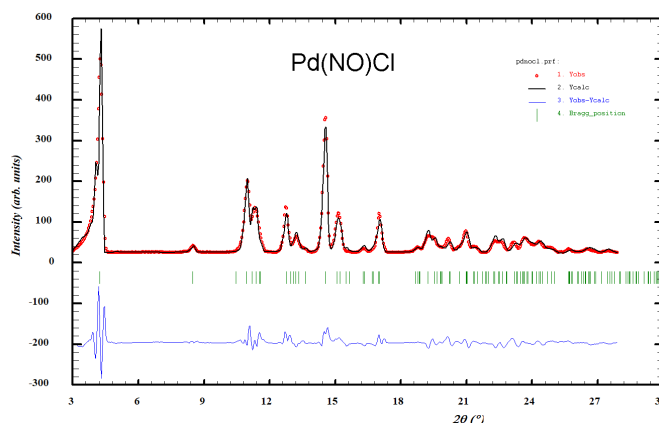


Figure 6. Rietveld plot of the Guinier diffractogram for PdCl(NO), obtained at 298 K using MoK α_1 radiation in the 2-Theta-range from 3 - 28° with increment 0.04° .

Accession Codes

Accession Code CCDC 2159713 contains the supplementary crystallographic data for the single crystal investigation, code CCDC 2160482 the supplementary crystallographic data for the powder investigation by Rietveld technique. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Keywords

Chloridonitrosylpalladium, Seel-Hieber rules, palladium complex, nitrosyl ligands, polymer, solubility, XAS, EXAFS.

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