Pt(II) and Pd(II) Pyrrolidine-Dithiocarbamates Investigated by XPS

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In the present contribution, a series of four metal dithiocarbamates, namely 1-pyrrolidinecarbodithioate methyl ester (PyDTM) of Pd(II) and Pt(II), $PtCl_2$(PyDTM), $PtBr_2$(PyDTM), $PdBr_2$(PyDTM), $PdCl_2$(PyDTM), were analysed by x-ray Photoelectron Spectroscopy (XPS). Besides the wide scan spectra, detailed spectra for the C 1s, O 1s, N 1s, S 2s, S 2p, Pt 4f (for Pt-based compounds), Pd 3d (for Pd-based compounds), Cl 2p (for Cl containing compounds), Br 3p (for Br containing compounds) regions were acquired and the related data are presented and discussed. © *2011 American Vacuum Society*. [http://dx.doi.org/10.1116/11.20091201]

Keywords: *dithiocarbamates; coordination compounds; metal-sulphur bond; platinum; palladium; sulphur*

PACS: *79.60.Fr, 82.80.Pv*

Accession #s: 01213, 01214, 01215, 01216

Technique: XPS

Host Material: #01213: Pt(II) pyrrolidinedithiocarbamate bromine; #01214: Pt(II) pyrrolidinedithiocarbamate chlorine; #01215: Pd(II) pyrrolidinedithiocarbamate bromine; #01216: Pd(II) pyrrolidinedithiocarbamate chlorine

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci

Major Elements in Spectra: S, Pt, Pd, N, Br, Cl

Minor Elements in Spectra: C

Published Spectra: 12

Spectra in Electronic Record: 30

Spectral Category: technical

INTRODUCTION

Metal-sulphur complexes, in particular in comparison with their oxygen-based analogues, are intriguing due to the higher polarizability of sulphur atoms. Although this class of materials is well established, and a huge number of sulphur-based metal complexes is described in literature (Ref. 1) a thorough investigation of their structure-properties relationships is still lacking.

Among metal-sulphur complexes, metal dithiocarbamates $[R_2NCS_2]_lM$ are well known and several species have been prepared and characterised (Refs. 2–4). In particular, dithiocarbamate complexes of Pd(II) and Pt(II) are under study as chemoprotectants in platinum-base chemotherapy. The well known cisplatin, cis-$(NH_3)_2PtCl_2$ (Ref. 5), the most important drug toward several cell lines (Ref. 6), presents a lot of secondary effects amongst which nephrotoxicity is of particular concern. Dithiocarbamates have shown promising properties for chemical use in modulating cisplatin nephrotoxicity (Refs. 7–10).

Therefore, the investigation of the nature of the metal-ligand electronic interactions in these metal complexes is essential not only to rationalize their complexation behaviour in solution, but particularly for the understanding of their electronic structure, which in turn determines their functional properties, as well as their reactivity and use in cancer therapy. Several spectroscopic studies have been reported in literature on transition metals dithiocarbamates (Refs. 11–16), and two comprehensive reviews have been devoted to the characterization of metal dithiocarbamate complexes with different analytical methods (Ref. 17) and XPS (Ref. 18).

In this work, we thoroughly characterized the four new Pt(II) and Pd(II) dithiocarbamates, based on the 1-pyrrolidinecarbodithioate methyl ester (PyDTM) ligand: [$PtCl_2$(PyDTM)], [$PtBr_2$(PyDTM)], [$PdBr_2$(PyDTM)], [$PdCl_2$(PyDTM)] which had not yet been investigated by XPS. Since the proposed compounds are interesting also as potential chemotherapeutics agents, and since the properties and interactions of these complexes are ruled by their structure but also by their electronic structure, it can be interesting to relate their performances to their composition, and so the presence of different metals (in this case Pd or Pt) and/or different ligands (Br/Cl) could play some role in their efficiency as cancer therapy agents. Therefore, the investigation of the nature of the metal-ligand electronic interactions in these metal complexes is essential not only to rationalize their complexation behaviour in solution, but particularly for the understanding of their electronic structure, which in turns determines their functional properties, as well as their reactivity and use in cancer therapy.

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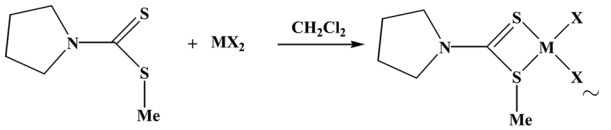
In the following (see History and Significance section), the procedures used for the preparation of the four compounds are extensively described and depicted in the following chart.



PyDTM M = Pd, Pt X = Cl, Br

PyDTM and $[PdCl_2(PyDTM)]$ have been synthetized as reported previously (Ref. 4). $PtCl_2$, $PdCl_2$, $PtBr_2$, $PdBr_2$ and the solvents were purchased by Sigma Aldrich and used as received.

It should be underlined that, for the first two samples, measurements were repeated after 3 hours of X-ray irradiation, showing no remarkable differences with respect to the first acquisition. The samples are stable also in UHV. The complete characterization of the studied compounds is reported in a bigger paper, to which interested readers are referred for more details (R. Wenisch, D. Forrer, S. Gross et al., in preparation).

SPECIMEN DESCRIPTION (ACCESSION #01213, 1 OF 4) —

Host Material: Pt(II) pyrrolidinedithiocarbamate bromine

Host Material Characteristics: homogeneous; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Pt(II) pyrrolidinedithiocarbamate bromine

Source: see History & Significance

Host Composition: $PtBr_2[(CH_2)_4NCS_2CH_3]$

Form: amorphous powder

History & Significance: The complex $[PtBr_2(PyDTM)]$ was prepared by adding $PtBr_2$ (0.92 mmol) to a PyDTM solution in dichloromethane (1.2 mmol in 10 ml) under vigorous stirring (18 h). A dark red solution of the 1:2 adduct formed initially, which reacted slowly with the residual $PdBr_2$ yielding an orange solid. This solid was filtered, washed with CH_2Cl_2 and n-pentane and dried under reduced pressure.

Yield. 85 %. El. Anal. Calcd (%) for $C_6H_{11}NBr_2PtS_2$: C: 14.1; H: 1.8; N: 2.6. Found: C: 14.0; H: 2.1; N: 2.7. ν_{CN} (cm^{-1}) 1579; ν_{PdBr} (cm^{-1}) 237, 218.

As Received Condition: The specimen was supplied as powder and was measured as received

Analyzed Region: same as host material

***Ex Situ* Preparation/Mounting:** sample mounted as received and introduced into the analysis chamber by a fast-entry lock system

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The analysed region was exposed to x-irradiation for alignment for a period no longer than 5 min.

Charge Control: Charge effects were partially compensated by using a charge neutralizer (flood gun). The equipment used to control charge at the specimen is a PHI Model 04-090 neutralizer with 72-030 controller. The flood gun parameters (emission control and electron energy) can be varied only by using the standard PHI V5.4A software. In this experiment they have been set as follows: emission control = 20, electron energy = 19%.

Temp. During Analysis: 298 K

Pressure During Analysis: $\sim 1 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01214, 2 OF 4) —

Host Material: Pt(II) pyrrolidinedithiocarbamate chlorine

Host Material Characteristics: homogeneous; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Pt(II) pyrrolidinedithiocarbamate chlorine

Source: see History & Significance

Host Composition: $PtCl_2[(CH_2)_4NCS_2CH_3]$

Form: amorphous powder

History & Significance: The complex $[PtCl_2(PyDTM)]$ was prepared by adding $PtCl_2$ (0.77 mmol) to a PyDTM solution in dichloromethane (1 mmol in 10 ml) under vigorous stirring (18 h). A dark red solution of the 1:2 adduct formed initially, which reacted slowly with the residual $PtCl_2$ yielding a pale yellow solid. This solid was filtered, washed with CH_2Cl_2 and n-pentane and dried under reduced pressure.

Yield. 72%. El. Anal. Calcd (%) for $C_6H_{11}NCl_2PtS_2$: C: 17.3; H: 2.4; N: 3.3. Found: C: 16.9; H: 2.6; N: 3.3. ν_{CN} (cm^{-1}) 1583; ν_{PdBr} (cm^{-1}) 325, 313.

As Received Condition: not specified

Analyzed Region: same as host matetrial

***Ex Situ* Preparation/Mounting:** sample mounted as received and introduced into the analysis chamber by a fast-entry lock system

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The analysed region was exposed to x-irradiation for alignment for a period no longer than 5 min.

Charge Control: Charge effects were partially compensated by using a charge neutralizer (flood gun). The equipment used to control charge at the specimen is a PHI Model 04-090 neutralizer with 72-030 controller. The flood gun parameters (emission control and electron energy) can be varied only by using the standard PHI V5.4A software. In this experiment they have been set as follows: emission control = 20, electron energy = 19%.

Temp. During Analysis: 298 K

Pressure During Analysis: $\sim 1 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01215, 3 OF 4) —

Host Material: Pd(II) pyrrolidinedithiocarbamate bromine

Host Material Characteristics: homogeneous; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Pd(II) pyrrolidinedithiocarbamate bromine

Source: see History & Significance

Host Composition: $PdBr_2[(CH_2)_4NCS_2CH_3]$

Form: amorphous powder

History & Significance: The complex $[PdBr_2(PyDTM)]$ was prepared by adding $PdBr_2$ (1.66 mmol) to a PyDTM solution in dichloromethane (1.80 mmol in 7 ml) under vigorous stirring

(18 h). A red solution of the 1:2 adduct formed initially, which reacted slowly with the residual $PdBr_2$ yielding an orange solid. This solid was filtered, washed with CH_2Cl_2 and n-pentane and dried under reduced pressure.

Yield. 75 %. El. Anal. Calcd (%) for $C_6H_{11}Br_2NPdS_2$: C: 17.1; H: 2.3; N: 3.2. Found: C: 16.9; H : 2.6; N: 3.3. ν_{CN} (cm^{-1}) 1560; ν_{PdBr} (cm^{-1}) 248, 216.

As Received Condition: The specimen was supplied as powder and was measured as received.

Analyzed Region: same as host material

***Ex Situ* Preparation/Mounting:** sample mounted as received and introduced into the analysis chamber by a fast-entry lock system

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The analysed region was exposed to x-irradiation for alignment for a period no longer than 5 min.

Charge Control: Charge effects were partially compensated by using a charge neutralizer (flood gun). The equipment used to control charge at the specimen is a PHI Model 04-090 neutralizer with 72-030 controller. The flood gun parameters (emission control and electron energy) can be varied only by using the standard PHI V5.4A software. In this experiment they have been set as follows: emission control = 20, electron energy = 19%.

Temp. During Analysis: 298 K

Pressure During Analysis: $\sim 1 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01216, 4 OF 4)

Host Material: Pd(II) pyrrolidinedithiocarbamate chlorine

Host Material Characteristics: homogeneous; unknown crystallinity; dielectric; inorganic compound; powder

Chemical Name: Pd(II) pyrrolidinedithiocarbamate chlorine

Source: see History & Significance

Host Composition: $PdCl_2[(CH_2)_4NCS_2CH_3]$

Form: amorphous powder

History & Significance: The complex $[PdCl_2(PyDTM)]$ was prepared by adding $PdCl_2$ (1.66 mmol) to a PyDTM solution in dichloromethane (1.80 mmol in 7 ml) under vigorous stirring (18 h). A dark brown solution of the 1:2 adduct formed initially, which reacted slowly with the residual $PdBr_2$ yielding an orange solid. This solid was filtered, washed with CH_2Cl_2 and n-pentane and dried under reduced pressure.

As Received Condition: The specimen was supplied as powder and was measured as received.

Analyzed Region: same as host matetrial

***Ex Situ* Preparation/Mounting:** sample mounted as received and introduced into the analysis chamber by a fast-entry lock system

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The analysed region was exposed to x-irradiation for alignment for a period no longer than 5 min.

Charge Control: Charge effects were partially compensated by using a charge neutralizer (flood gun). The equipment used to control charge at the specimen is a PHI Model 04-090 neutralizer with 72-030 controller. The flood gun parameters (emission control and electron energy) can be varied only by using the standard PHI V5.4A software. In this experiment they have been set as follows: emission control = 20, electron energy = 19%.

Temp. During Analysis: 298 K

Pressure During Analysis: $\sim 1 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Perkin Elmer, Physical Electronics PHI 5600ci

Analyzer Type: spherical sector

Detector: Multichannel detector, part no. 619103

Number of Detector Elements: 16

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ *Spectrometer*

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): N=1

Throughput Comment:

Excitation Source Window: 1.5 μm Al window

Excitation Source: Al K_α

Source Energy: 1486.6 eV

Source Strength: 250 W

Source Beam Size: $>25000\ \mu m \times >25000\ \mu m$

Signal Mode: multichannel direct

■ *Geometry*

Incident Angle: 45°

Source to Analyzer Angle: 53.8°

Emission Angle: 45°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 14° × 14°

DATA ANALYSIS METHOD

Energy Scale Correction: Charge has been corrected by lining up the C 1s peak with 284.5 eV (value given by the instrument's manufacturer)

Recommended Energy Scale Shift: Varies for the different samples. We suggest a charge correction of −4.3 eV for $PtBr_2$(PyDTm) (Accession #1213), −4.1 eV for $[PdCl_2(PyDTm)]$ (Accession #1216), −4.7 eV for $[PdBr_2(PyDTm)]$ (Accession #1215), and −2.5 eV for $[PtCl_2(PyDTm)]$ (Accession #1214).

Peak Shape and Background Method: The fitted peaks are mostly of the Gaussian type. Particularly well resolved and narrow peaks were fitted with a mix of Lorentzian and Gaussian functions (however, the Gaussian percentage always outweighed the Lorentzian one).

Quantitation Method: The atomic concentrations were calculated by using sensitivity factors taken from standard PHI V5.4A

software. The peak areas were measured above an integrated background.

ACKNOWLEDGMENTS

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ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
29	Au $4f_{7/2}$	83.7	1.5	35325	···	···	metallic gold
30	Cu $2p_{3/2}$	932.7	1.6	86973	···	···	metallic copper

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01213-06[a]	Br $3p_{3/2}$	181.4	3.0	93200	1.398	10.2	···
01213-06[a]	Br $3p_{1/2}$	188.0	2.8	26100	1.398	10.2	···
01213-02[b]	C 1s	284.5	2.4	30000	0.296	71.1	C in sample and advent. contamin
01213-03	N 1s	399.8	1.9	19300	0.477	8.8	···
01213-04	S 2p	163.5	3.1	51500	0.666	8.8	···
01213-07[c]	Pt $4f_{7/2}$	72.2	2.0	177000	5.575	4.8	Pt(II)
01213-07[c]	Pt $4f_{5/2}$	75.5	2.0	110000	5.575	4.8	Pt(II)
01214-07[d]	Cl $2p_{3/2}$	197.3	2.1	16666	0.891	7.3	···
01214-07[d]	Cl $2p_{1/2}$	199.1	1.8	8333	0.891	7.3	···
01214-03[b]	C 1s	284.5	1.9	1562	0.296	70.5	C in sample and advent. contamin
01214-04	N 1s	399.6	2.1	3140	0.477	6.78	···
01214-05	S 2p	163.4	3.2	7605	0.666	9.9	···
01214-02[c]	Pt $4f_{7/2}$	72.0	2.1	20991	5.575	5.5	Pt(II)
01214-02[c]	Pt $4f_{5/2}$	75.3	2.2	16782	5.575	5.5	Pt(II)
01215-03[a]	Br $3p_{3/2}$	181.2	3,4	14658	1.398	11.3	···
01215-03[a]	Br $3p_{1/2}$	187.9	3.0	3882	1.2989	11.3	···
01215-05[b]	C 1s	284.5	2.8	9660	0.296	71.2	C in sample and advent. contamin
01215-02	N 1s	399.9	2.3	2113	0.477	5.7	···
01215-06	S 2p	163.5	3.4	7140	0.666	7.9	···
01215-04[e]	Pd $3d_{5/2}$	337.2	2.3	19867	5.356	3.9	Pd(II)
01215-04[e]	Pd $3d_{3/2}$	342.5	2.5	15752	5.356	3.9	···
01216-05[d]	Cl $2p_{3/2}$	197.4	2.1	2132	0.891	11.3	Pd(II)
01216-05[d]	Cl $2p_{1/2}$	199.0	2.2	1354	0.891	11.3	···
01216-02[b]	C 1s	284.5	2.3	18567	0.296	66.1	C in sample and advent. contamin
01216-06	N 1s	399.9	2.2	2684	0.477	10.1	···
01216-03[d]	S 2p	163.5	3.3	9072	0.666	13.7	···
01216-07[e]	Pd $3d_{5/2}$	337.2	2.1	25135	5.356	3.6	Pd(II)
01216-07[e]	Pd $3d_{3/2}$	342.6	2.2	16937	5.356	3.6	Pd(II)

[a] Amplitude and sensitivity factor refer to both sub-peaks. Therefore the concentration has been calculated using both the $3p_{1/2}$ and the $3p_{3/2}$ transitions.
[b] This reference peak for charge correction has been set to 284.5 eV.
[c] Amplitude and sensitivity factor refer to both sub-peaks. Therefore the concentration has been calculated using both the $4f_{5/2}$ and the $4f_{7/2}$ transitions.
[d] Amplitude and sensitivity factor refer to both sub-peaks. Therefore the concentration has been calculated using both the $2p_{1/2}$ and the $2p_{3/2}$ transitions.
[e] Amplitude and sensitivity factor refer to both sub-peaks. Therefore the concentration has been calculated using both the $3d_{3/2}$ and the $3d_{5/2}$ transitions.

Footnote to Spectrum 01215-03: The Br 3p region showed two clearly distinct peaks attributable to the $3p_{3/2}$ and $3p_{1/2}$ transitions respectively. This is true for both Br containing compounds.

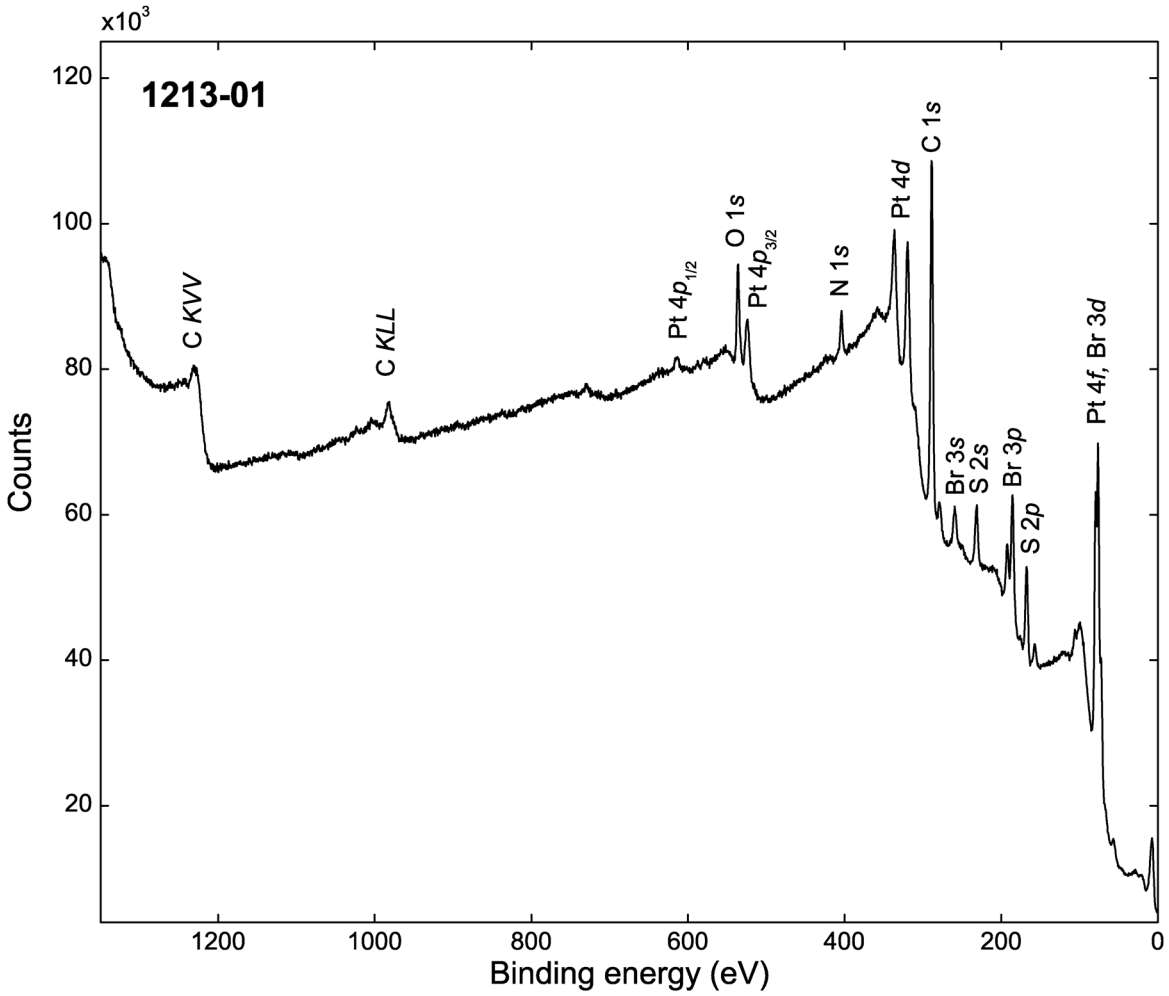
Footnote to Spectrum 01216-02: The C 1s peak is broadened because of the 4 distinct chemical environments present. Also, adventitious carbon contamination superimposes the signal making a reliable deconvolution practically impossible.
The C 1s peak was used to determine the charging of the sample. We compared the peak position to the reference value of 284.5 eV as given by the instrument's manufacturer.

Footnote to Spectrum 01216-03: The S 2p peaks of both sulphur atoms coincide partially. Namely the S $2p_{3/2}$ transition of one of the S atoms overlaps with the S $2p_{1/2}$ transition of the other. This lets us expect 3 distinct subpeaks. However fitting this configuration remained ambigous thus we show merely a single broad peak.

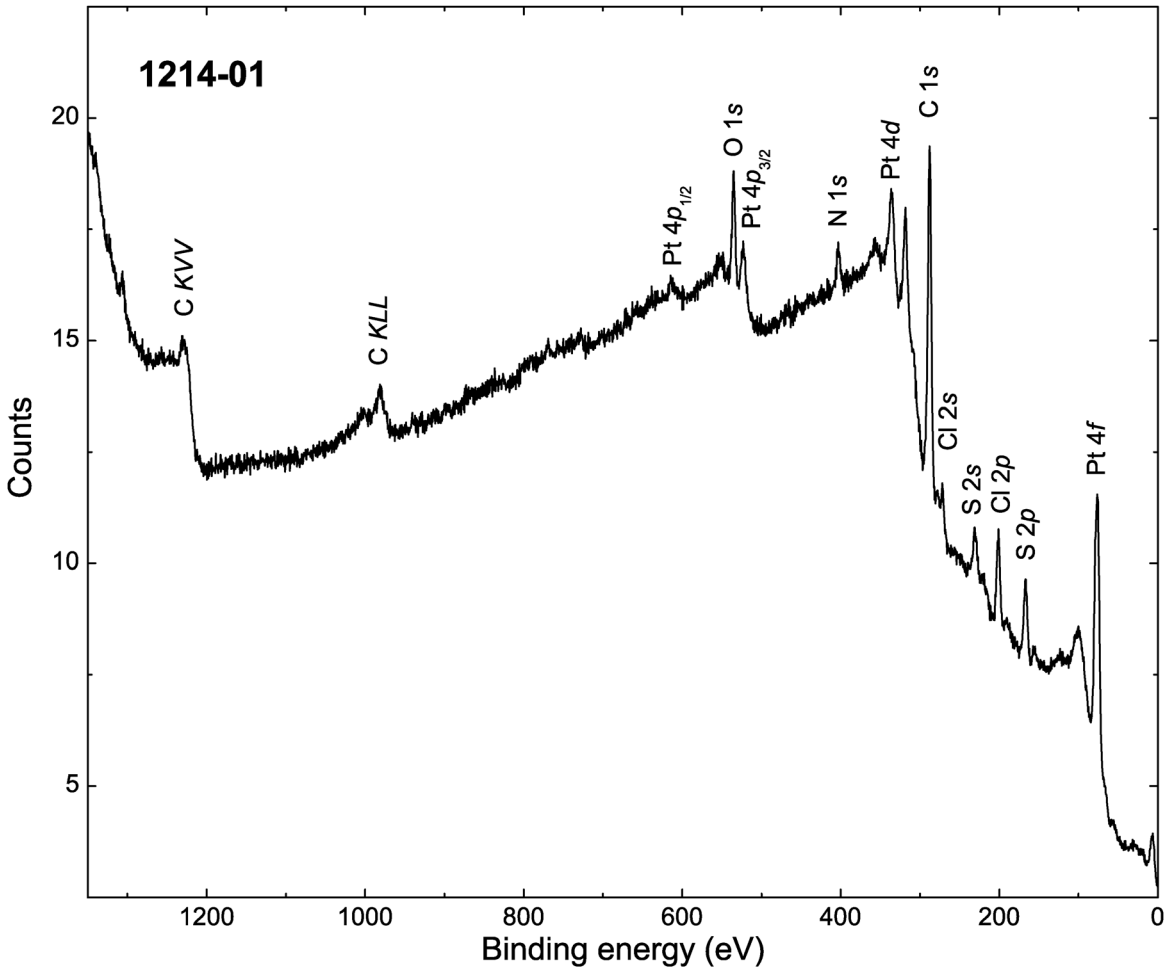
Footnote to Spectrum 01216-05: The Cl peaks could be decomposed as depicted for both Cl containing compounds. However, the individual Cl atoms remained indistinguishable as their BEs were nearly identical.

GUIDE TO FIGURES					
Spectrum (Accession) #	**Spectral Region**	**Voltage Shift***	**Multiplier**	**Baseline**	**Comment #**
1213-01	survey	4.3	1	0	1
1214-01	survey	2.5	1	0	2
1215-01	survey	4.7	1	0	3
1216-01	survey	4.1	1	0	4
1216-02	C 1s	4.1	1	0	4
1215-02	N 1s	4.7	1	0	3
1216-03	S 2p	4.1	1	0	4
1216-04	S 2s	4.1	1	0	4
1216-05	Cl 2p	4.1	1	0	4
1215-03	Br 3p	4.7	1	0	3
1214-02	Pt 4f	2.5	1	0	2
1215-04	Pd 3d	4.7	1	0	3
1213-02 [NP]**	C 1s	4.3	1	0	1
1213-03 [NP]	N 1s	4.3	1	0	1
1213-04 [NP]	S 2p	4.3	1	0	1
1213-05 [NP]	S 2s	4.3	1	0	1
1213-06 [NP]	Br 3p	4.3	1	0	1
1213-07 [NP]	Pt 4f	4.3	1	0	1
1214-03 [NP]	C 1s	2.5	1	0	2
1214-04 [NP]	N 1s	2.5	1	0	2
1214-05 [NP]	S 2p	2.5	1	0	2
1214-06 [NP]	S 2s	2.5	1	0	2
1214-07 [NP]	Cl 2p	2.5	1	0	2
1215-05 [NP]	C 1s	4.7	1	0	3
1215-06 [NP]	S 2p	4.7	1	0	3
1215-07 [NP]	S 2s	4.7	1	0	3
1216-06 [NP]	N 1s	4.1	1	0	4
1216-07 [NP]	Pd 3d	4.1	1	0	4

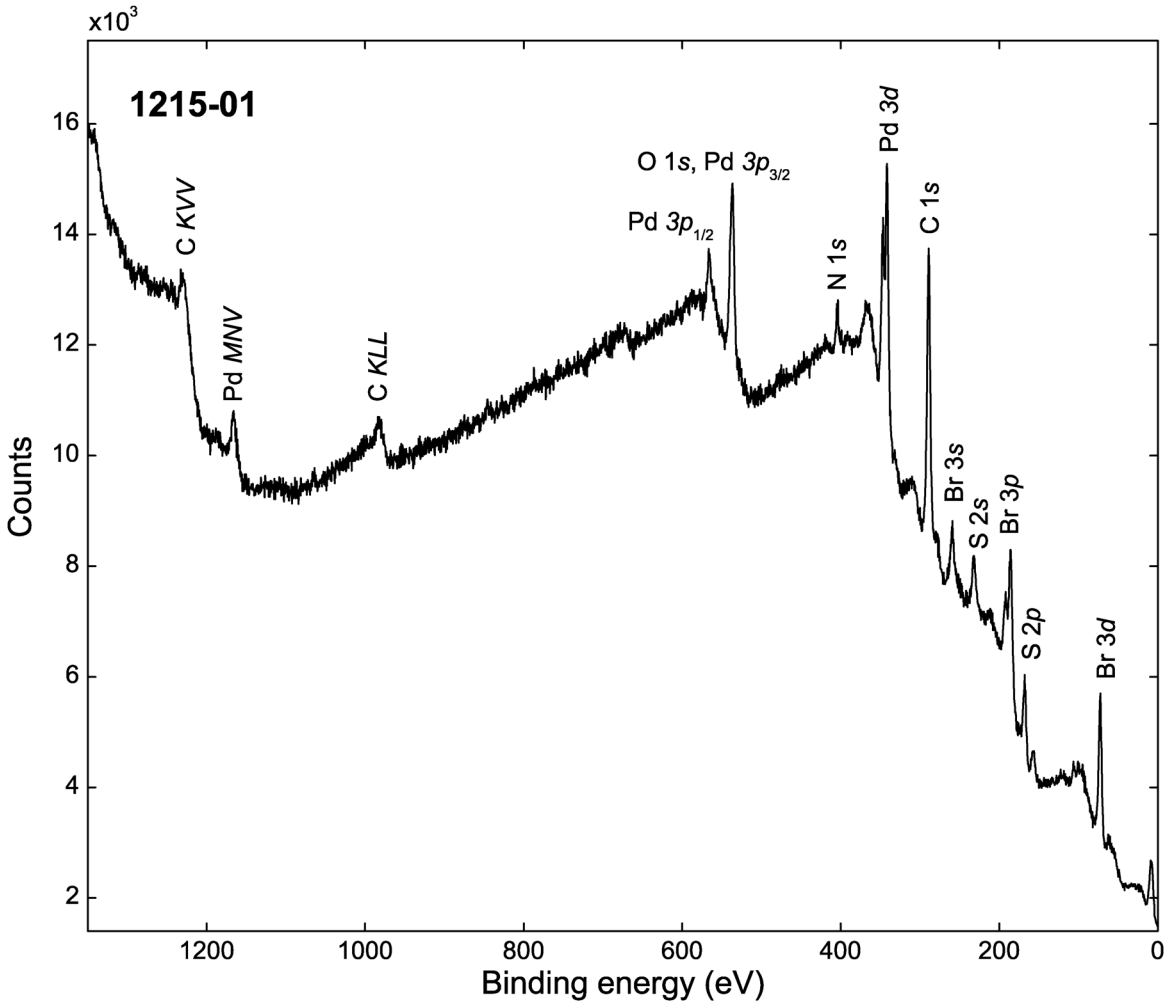
* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.
** [NP] signifies not published; digital spectra are archived in *SSS* database but not reproduced in the printed journal.
1. Pt(II) pyrrolidinedithiocarbamate bromine
2. Pt(II) pyrrolidinedithiocarbamate chlorine
3. Pd(II) pyrrolidinedithiocarbamate bromine
4. Pd(II) pyrrolidinedithiocarbamate chlorine



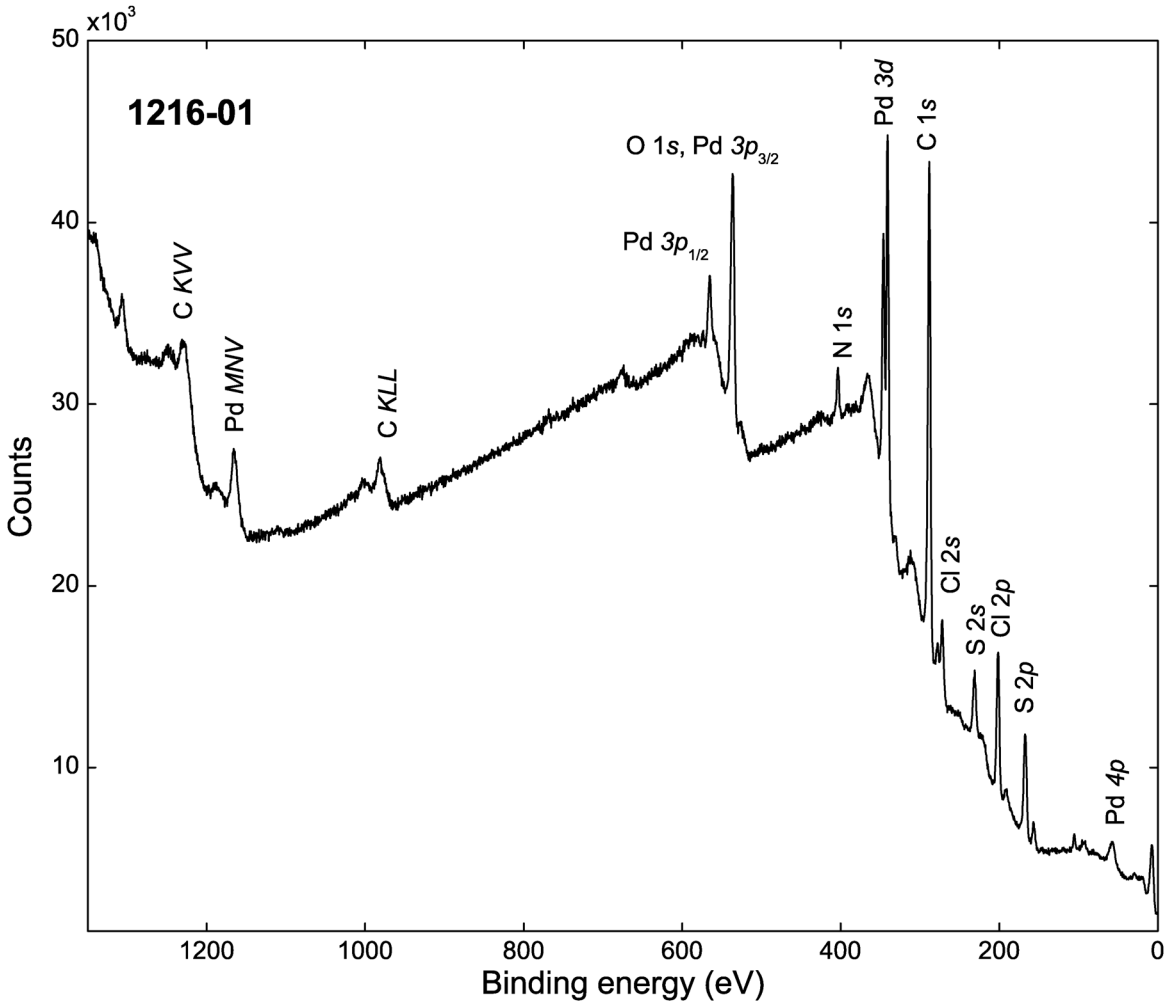
Accession #	01213–01
Host Material	Pt(II) pyrrolidinedithiocarbamate bromine
Technique	XPS
Spectral Region	survey
Instrument	Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source	Al K_α
Source Energy	1486.6 eV
Source Strength	250 W
Source Size	$>$25 mm $\times$ $>$25 mm
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy:	187.85 eV
Analyzer Resolution	1.9 eV
Total Signal Accumulation Time	2768.5 s
Total Elapsed Time	not specified
Number of Scans	41
Effective Detector Width	1.9 eV



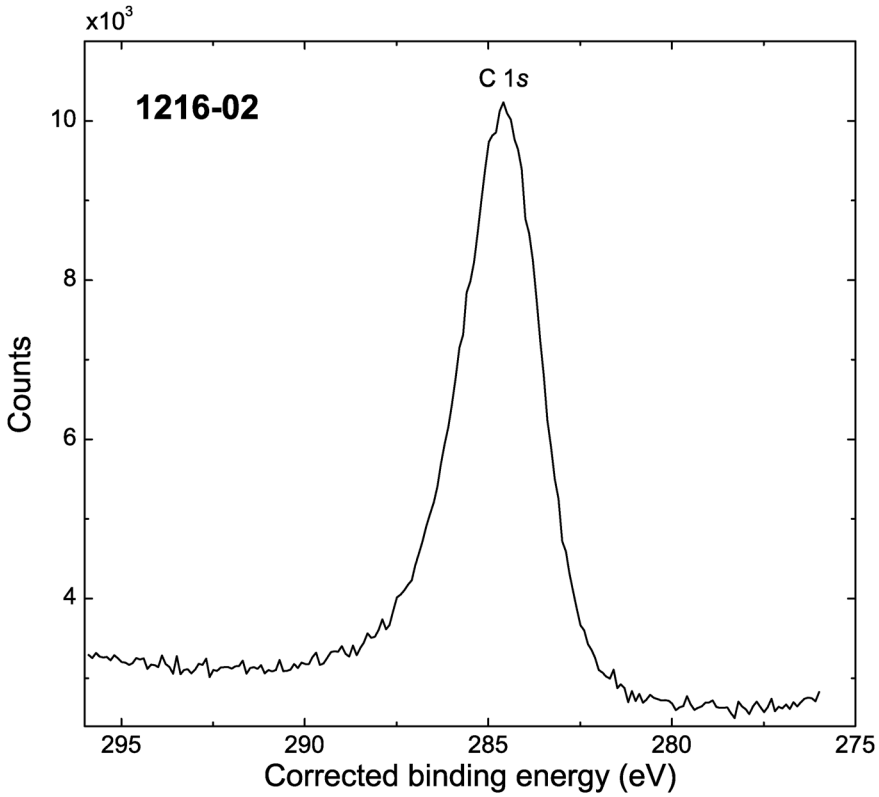
Accession #	01214–01
Host Material	Pt(II) pyrrolidinedithiocarbamate chlorine
Technique	XPS
Spectral Region	survey
Instrument	Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source	Al K_α
Source Energy	1486.6 eV
Source Strength	250 W
Source Size	>25 mm × >25 mm
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy:	187.85 eV
Analyzer Resolution	1.9 eV
Total Signal Accumulation Time	2228.3 s
Total Elapsed Time	not specified
Number of Scans	33
Effective Detector Width	1.9 eV



Accession #	01215–01
Host Material	Pd(II) pyrrolidinedithiocarbamate bromine
Technique	XPS
Spectral Region	survey
Instrument	Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source	Al K_α
Source Energy	1486.6 eV
Source Strength	250 W
Source Size	$>$25 mm $\times$ $>$25 mm
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy:	187.85 eV
Analyzer Resolution	1.9 eV
Total Signal Accumulation Time	1350.5 s
Total Elapsed Time	not specified
Number of Scans	20
Effective Detector Width	1.9 eV

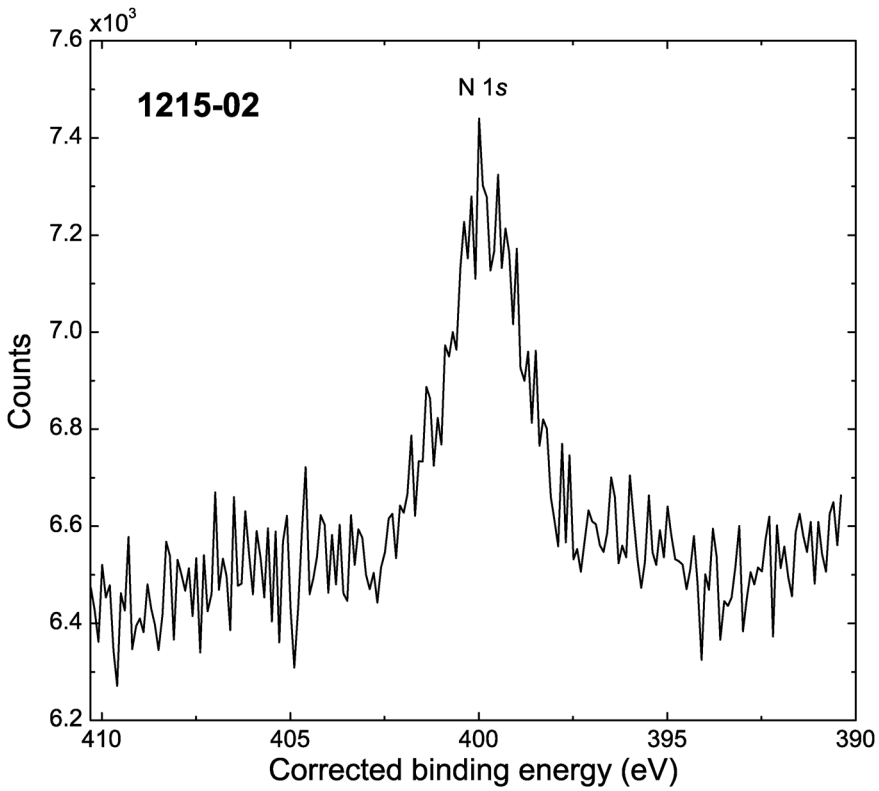


Accession #	01216–01
Host Material	Pd(II) pyrrolidinedithiocarbamate chlorine
Technique	XPS
Spectral Region	survey
Instrument	Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source	Al K_α
Source Energy	1486.6 eV
Source Strength	250 W
Source Size	>25 mm × >25 mm
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	45°
Analyzer Pass Energy:	187.85 eV
Analyzer Resolution	1.9 eV
Total Signal Accumulation Time	1890.7 s
Total Elapsed Time	not specified
Number of Scans	28
Effective Detector Width	1.9 eV



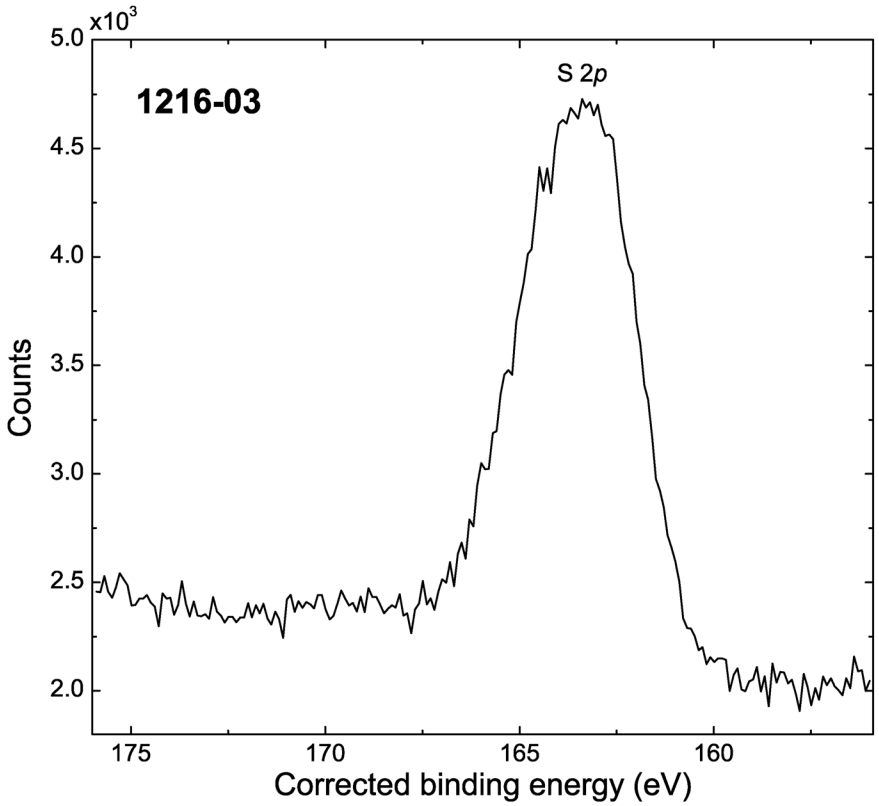
- **Accession #:** 01216–02
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate chlorine
- **Technique:** XPS
- **Spectral Region:** C 1*s*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 150 s
Total Elapsed Time: not specified
Number of Scans: 15
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.



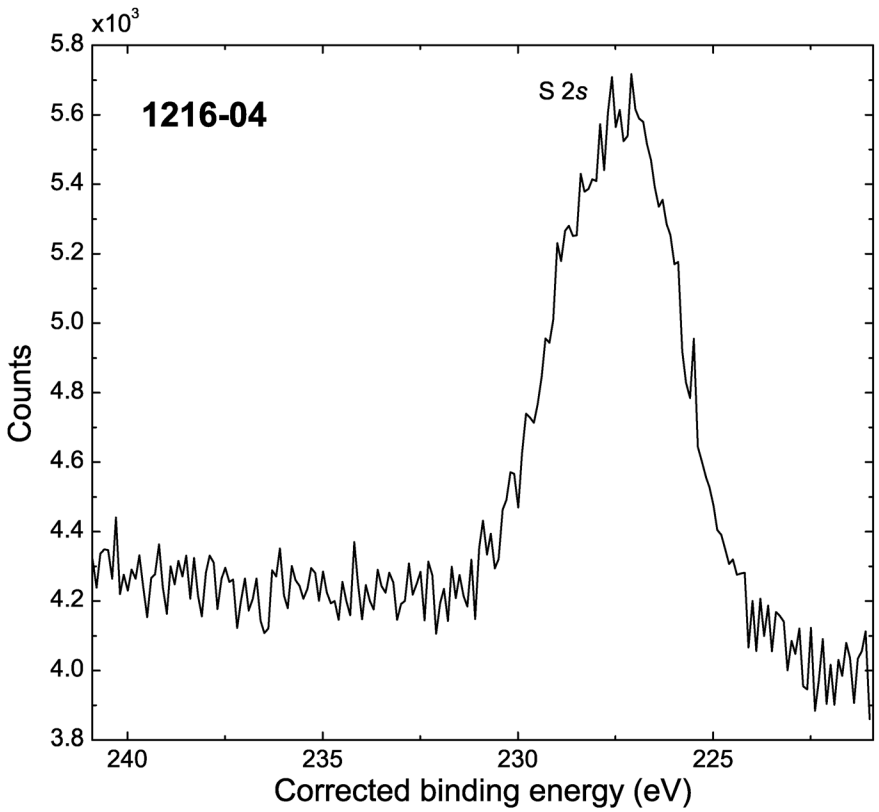
- **Accession #:** 01215–02
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate bromine
- **Technique:** XPS
- **Spectral Region:** N 1*s*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 240 s
Total Elapsed Time: not specified
Number of Scans: 12
Effective Detector Width: 0.6 eV
Comment: The N 1s peak showed little variance for the different species.



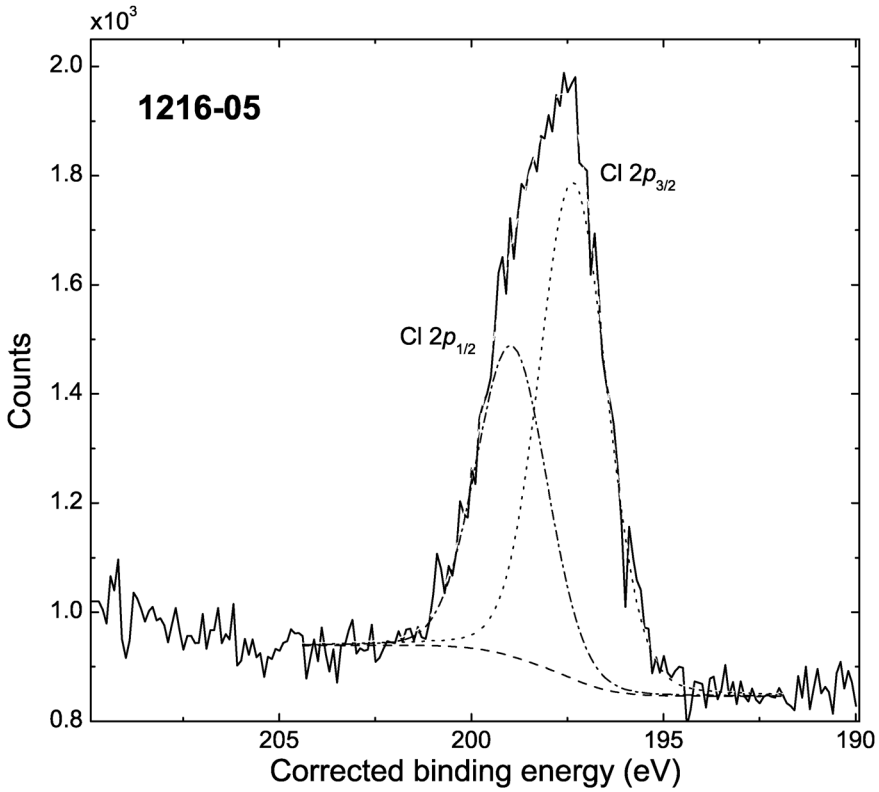
- **Accession #:** 01216–03
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate chlorine
- **Technique:** XPS
- **Spectral Region:** S 2*p*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 300 s
Total Elapsed Time: not specified
Number of Scans: 15
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.



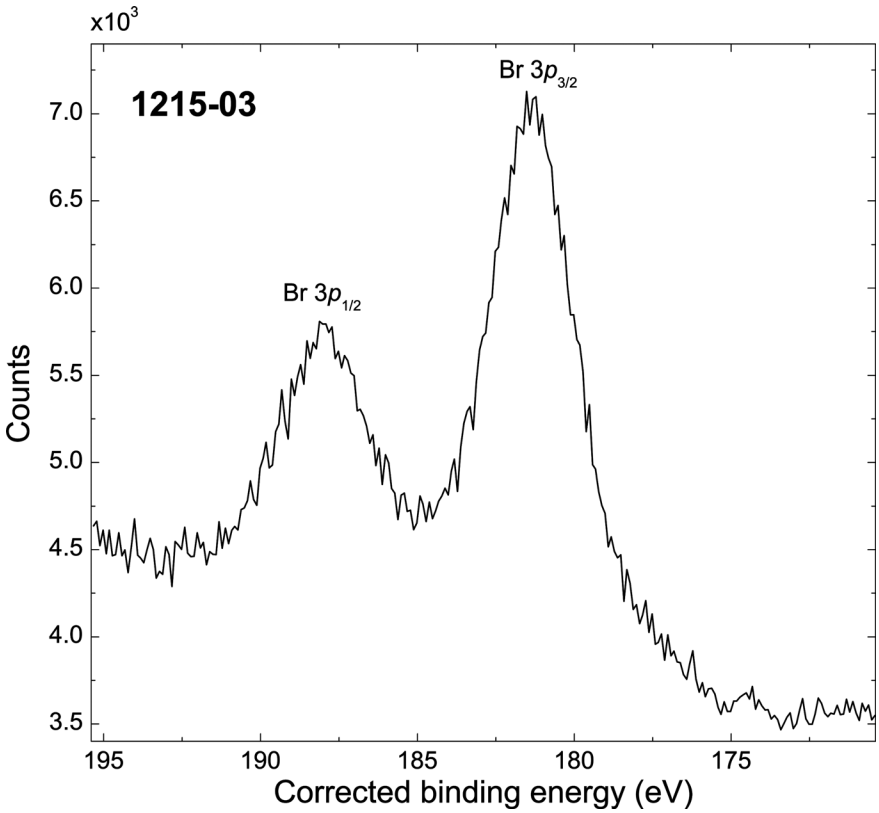
- **Accession #:** 01216–04
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate chlorine
- **Technique:** XPS
- **Spectral Region:** S 2*s*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 300 s
Total Elapsed Time: not specified
Number of Scans: 15
Effective Detector Width: 0.6 eV



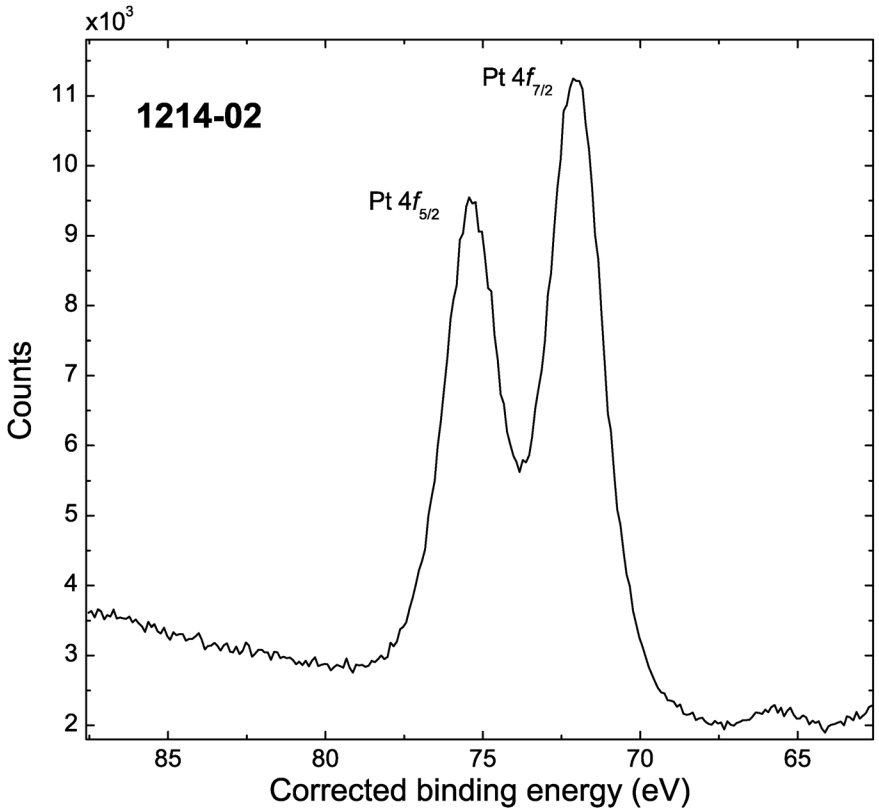
- **Accession #:** 01216–05
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate chlorine
- **Technique:** XPS
- **Spectral Region:** Cl 2*p*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 180 s
Total Elapsed Time: not specified
Number of Scans: 9
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.



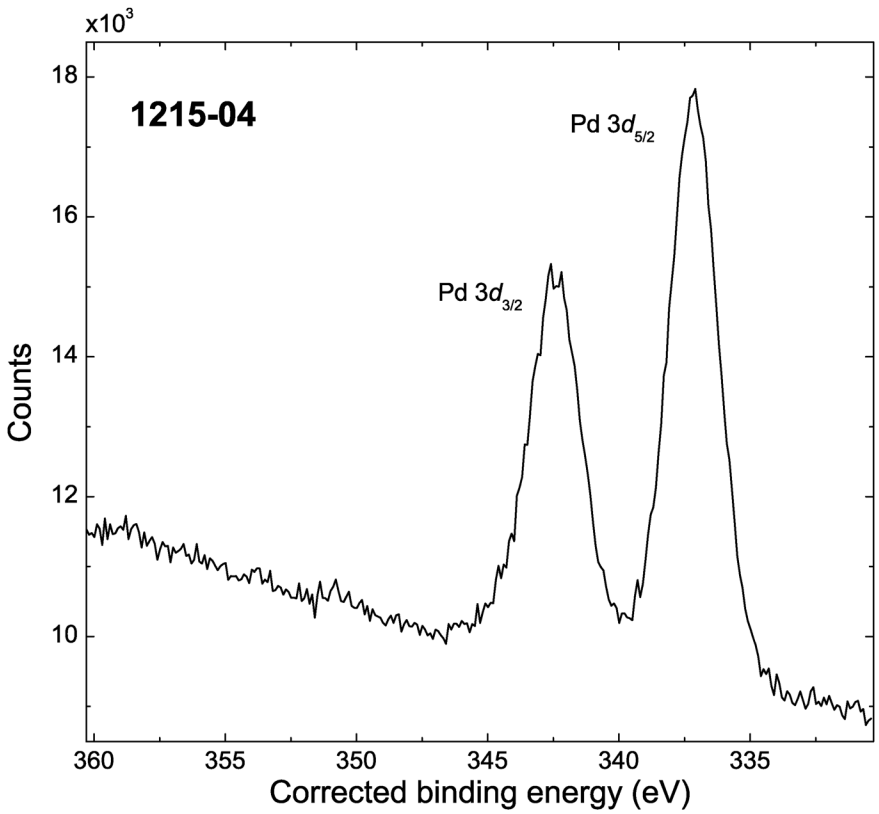
- **Accession #:** 01215–03
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate bromine
- **Technique:** XPS
- **Spectral Region:** Br 3*p*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 400 s
Total Elapsed Time: not specified
Number of Scans: 16
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.



- **Accession #:** 01214–02
- **Host Material:** Pt(II) pyrrolidinedithiocarbamate chlorine
- **Technique:** XPS
- **Spectral Region:** Pt 4*f*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 225 s
Total Elapsed Time: not specified
Number of Scans: 9
Effective Detector Width: 0.6 eV



- **Accession #:** 01215–04
- **Host Material:** Pd(II) pyrrolidinedithiocarbamate bromine
- **Technique:** XPS
- **Spectral Region:** Pd 3*d*

Instrument: Perkin Elmer, Physical Electronics PHI 5600ci
Excitation Source: Al K_α
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 45°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 720 s
Total Elapsed Time: not specified
Number of Scans: 16
Effective Detector Width: 0.6 eV