Annual meeting of the Danish Chemical Society August 18, 2022

A historic collection of compounds from the birth of coordination chemistry

Asbjørn Petersen & Ture Damhus

The Danish Society for the History of Chemistry

(adapted from presentation given by AP at the virtual ICHC May 2021)

P.S. Krøyer's draft of a portrait of Jørgensen.
Courtesy of professor Jens Ulstrup.
DTU is the current owner of this painting.

Sophus Mads Jørgensen (1837–1914)

1867 : Head of Chemical Laboratories at the Polytechnical University

1871 : Lecturer in chemistry at University of Copenhagen

1871 / 1887 : Professor in chemistry (until 1908)

Processed *Gmelin Handbuch der Chemie*

Large number of positions in public and industrial boards.

Was the first chairman of the Danish Chemical Society, founded in 1879.

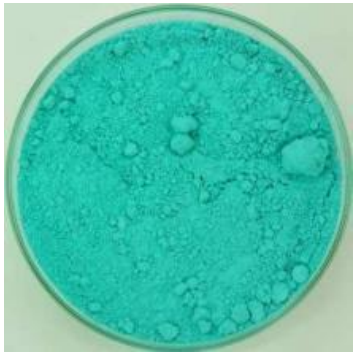
P. S. Krøyer : *Men of the Industry* (1903–1904).

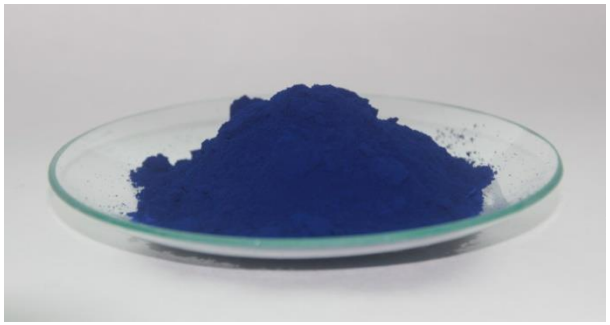
S.M. Jørgensen is there. The painter has imagined a gathering in the newly erected Østre Elektricitetsværk, which supplied power to the new electrical trams in Copenhagen.

The painting was commissioned by the influential Danish chemist and industrialist G.A. Hagemann.

Coordination compounds

antiquity	alum ≈ $AlK(SO_4)_2 \cdot 12\ H_2O$
13th century	copper vitriol = $CuSO_4 \cdot 5\ H_2O$
ca. 1706–1710	Prussian blue ≈ $KFeFe(CN)_6$
1752	yellow prussiate of potash = $K_4Fe(CN)_6 \cdot 3\ H_2O$
1822	red prussiate of potash = $K_3Fe(CN)_6$
1822	Schweinfurt green = $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$





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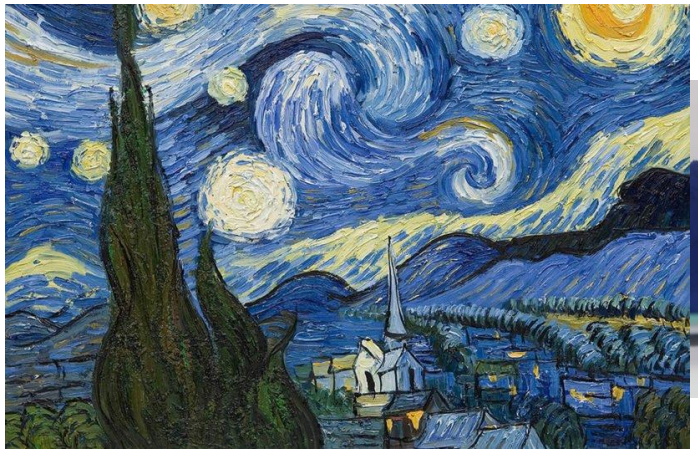
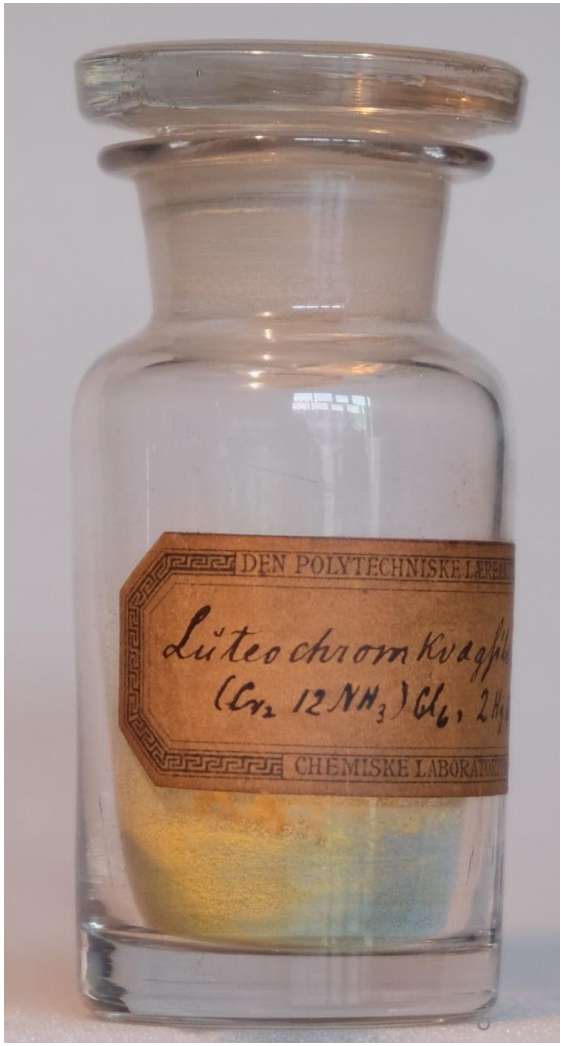


New coordination compounds synthesized ~ 1850–1860

(F. Genth, W. Gibbs, E. Fremy)

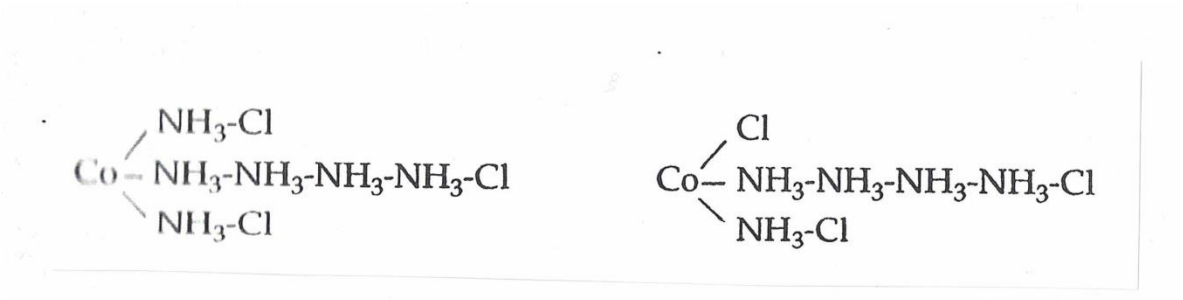
SMJ collection contains mainly chromium, cobalt, rhodium, platinum, and mercury compounds

$Cr(NH_3)_6^{3+}$	luteo	$[Cr(NH_3)_6]^{3+}$
$Co(NH_3)_5Cl^{2+}$	purpureo	$[CoCl(NH_3)_5]^{2+}$
$Co(NH_3)_5(NO_2)^{2+}$	xantho	$[Co(NH_3)_5(NO_2)]^{2+}$
$Rh(NH_3)_5(H_2O)^{3+}$	roseo	$[Rh(NH_3)_5(OH_2)]^{3+}$
$Co(NH_3)_5(OH)^{2+}$	basic roseo	$[Co(NH_3)_5(OH)]^{2+}$
…	…	



Structure of coordination compounds ?

The ”Blomstrand chain model”



”Robust” = kinetically inert

Co^{III} Cr^{III} Pt^{II} Pt^{IV} Rh^{III}

C. W. Blomstrand
(1826–1897)

S. M. Jörgensen: Zur Konstitution der Kobalt-, Chrom- und Rhodiumbasen. VI. Mitteilung. *Z. anorg. Chem.* 7(1) 289–330 (1894).

(pp. 308–309)

Sieht man von der sekundären Reaktion ab, durch welche die aus Ammoniumdiamminnitrit durch Ammoniakaufnahme entstehenden Xantho- und Flavosalze in die Diamminnitrite dieser Salzbasen übergehen, so hat man für diese Umsetzungen folgende einfachen Gleichungen:

$$Co\begin{matrix}\cdot NO_2\\ \cdot NO_2\end{matrix}NH_3.NH_3.NO_2.NO_2.NH_4 + 3NH_3 = Co\begin{matrix}\cdot NO_2\\ \cdot NH_3NO_2\end{matrix}NH_3.NH_3.NH_3.NO_2 + NH_4NO_2$$

Xanthonitrit.

$$Co\begin{matrix}\cdot NO_2\\ \cdot NO_2\end{matrix}NH_3.NH_3.NO_2.NO_2.NH_4 + 2NH_3 = Co\begin{matrix}\cdot NO_2\\ \cdot NO_2\end{matrix}NH_3.NH_3.NH_3.NO_2 + NH_4NO_2$$

Flavonitrit.

$$Co\begin{matrix}\cdot NO_2\\ \cdot NO_2\end{matrix}NH_3.NH_3.NO_2.NO_2.NH_4 + NH_3 = Co\begin{matrix}\cdot NO_2\\ \cdot NO_2\end{matrix}NH_3NH_3.NH_3.NO_2 + NH_4NO_2$$

Dinitrotriamminnitrit.

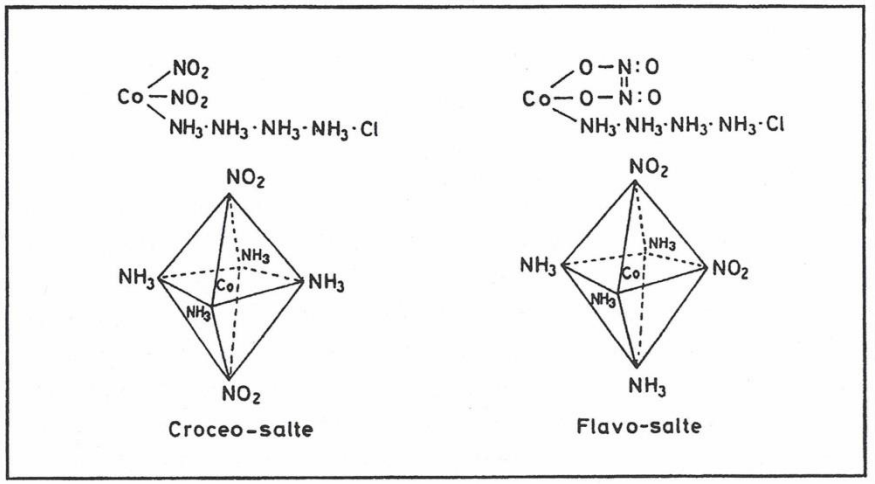
The Jørgensen-Werner controversy

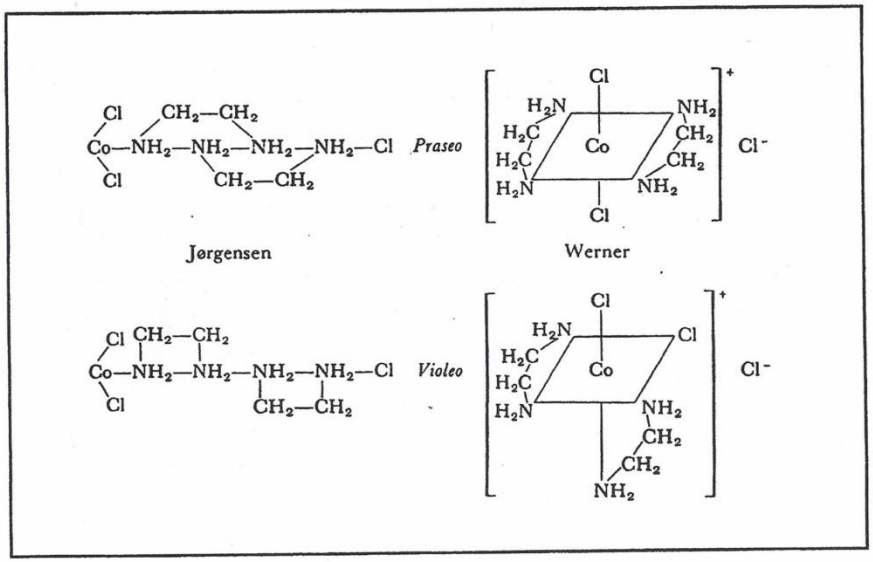
SMJ nominated for Nobel Prize 1907

† 1914

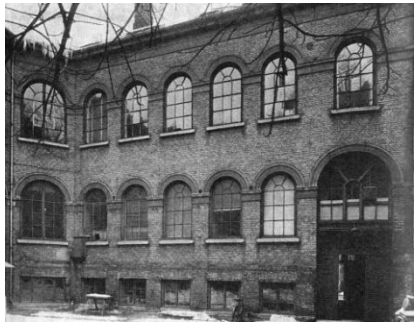
Central (octahedral) metal atom model 1897

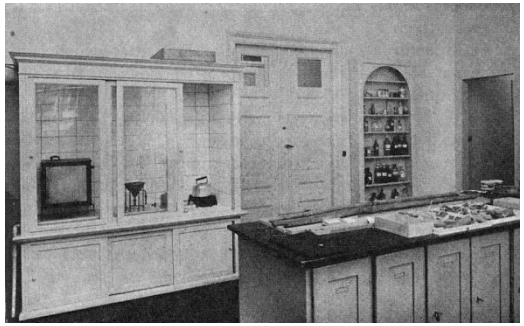
Nobel Prize 1913





Jørgensen's work and compounds





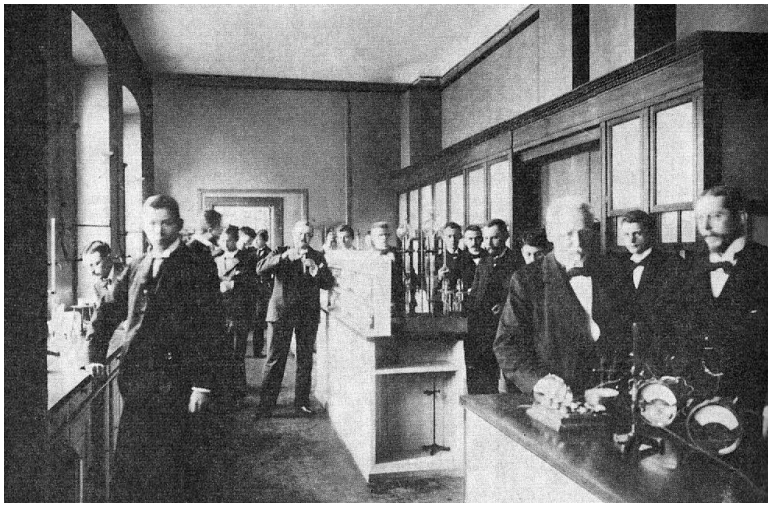
Universitetets Chemiske Laboratorium from ca. 1859
(Ny Vestergade 11)

1892 ↓ ↓ 1890

Universitetets Chemiske Laboratorium
(Øster Voldgade 5)

Polyteknisk Læreanstalt
(Sølvgade 83)

1962–64 ↓

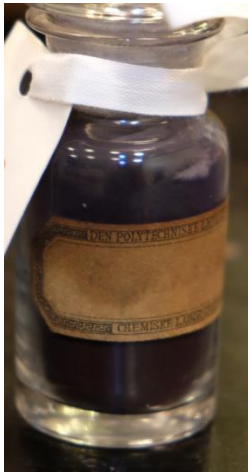


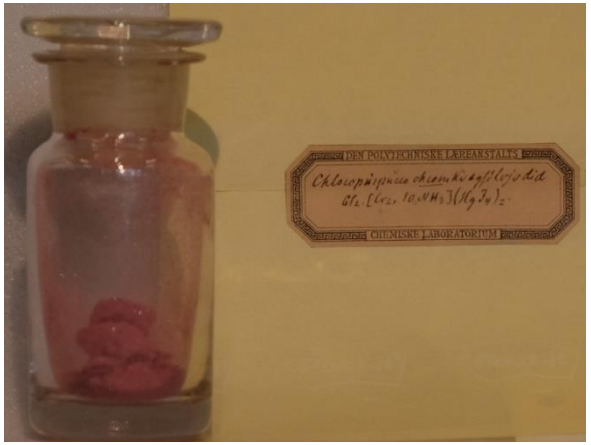
H. C. Ørsted Institute

Technical University of Denmark

”Rediscovery” of the S. M. Jørgensen compounds

Laila Zwisler, science and technology historian at DTU, pointing to boxes containing the Jørgensen samples





Unknown chemical compounds
Open
Public access

Art → No problem

Partially known chemical composition
Closed
No public acces

Chemical → Dangerous waste

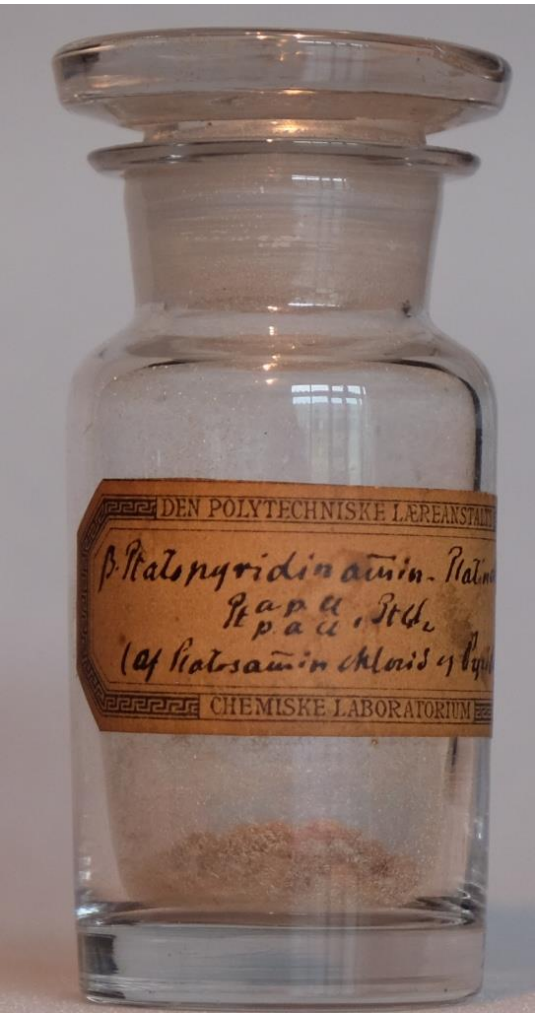
Organization and registration of the S. M. Jørgensen collection

Mission:

- registration of name and/or formula of substance on label
- note dangerous elements or components (Hg, picrate, *etc.*)

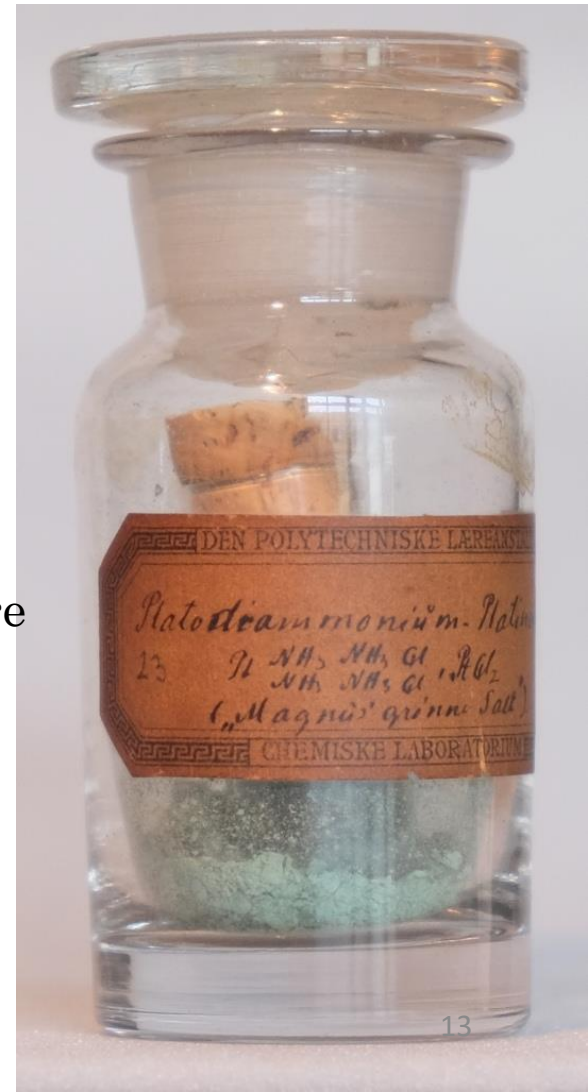
Registration took place in the period 2018–2022 with 12 visits to DTU

#82



β.Platopyridinaāmin – Platinchlorŭre
(af Platosaāminchlorid og Pyridin)

$$\begin{matrix} a \bullet p \bullet Cl \\ Pt \qquad\qquad , PtCl_2 \\ p \bullet a \bullet Cl \end{matrix}$$

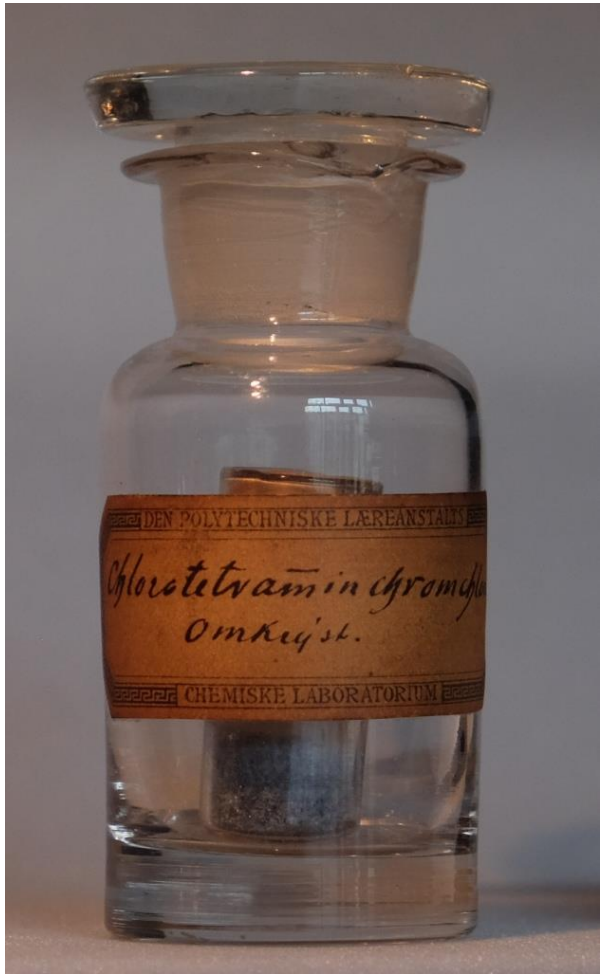


Platodiammonium – Platinchlorŭre

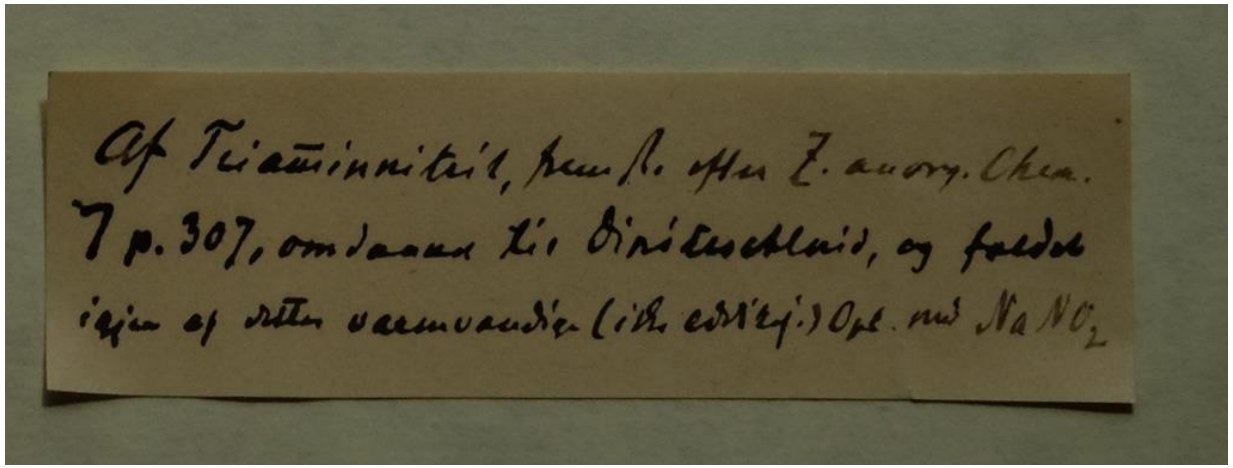
$$23 \quad \begin{matrix} NH_3 \quad NH_3 \quad Cl \\ Pt \qquad\qquad\qquad , PtCl_2 \\ NH_3 \quad NH_3 \quad Cl \end{matrix}$$

(„Magnus grønne Salt")

#161



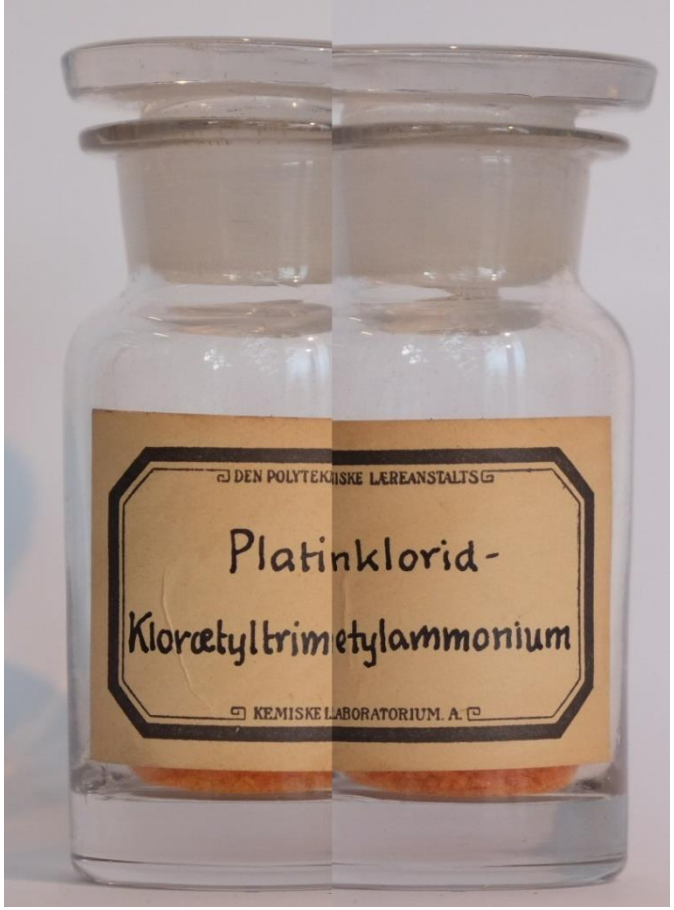
#442



#463

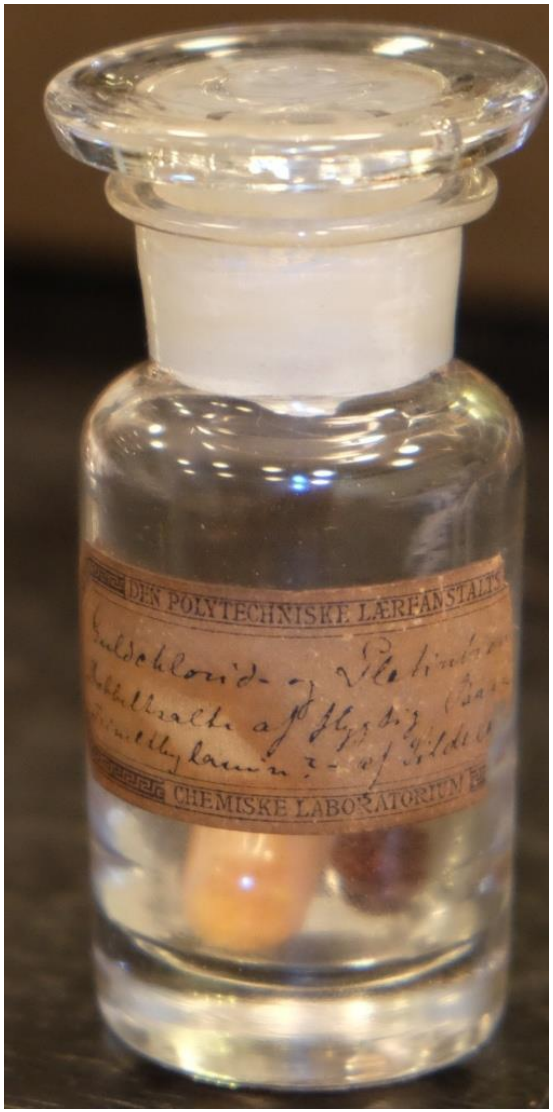
DEN POLYTECHNISKE LÆREANSTALTS
CHEMISKE LABORATORIUM

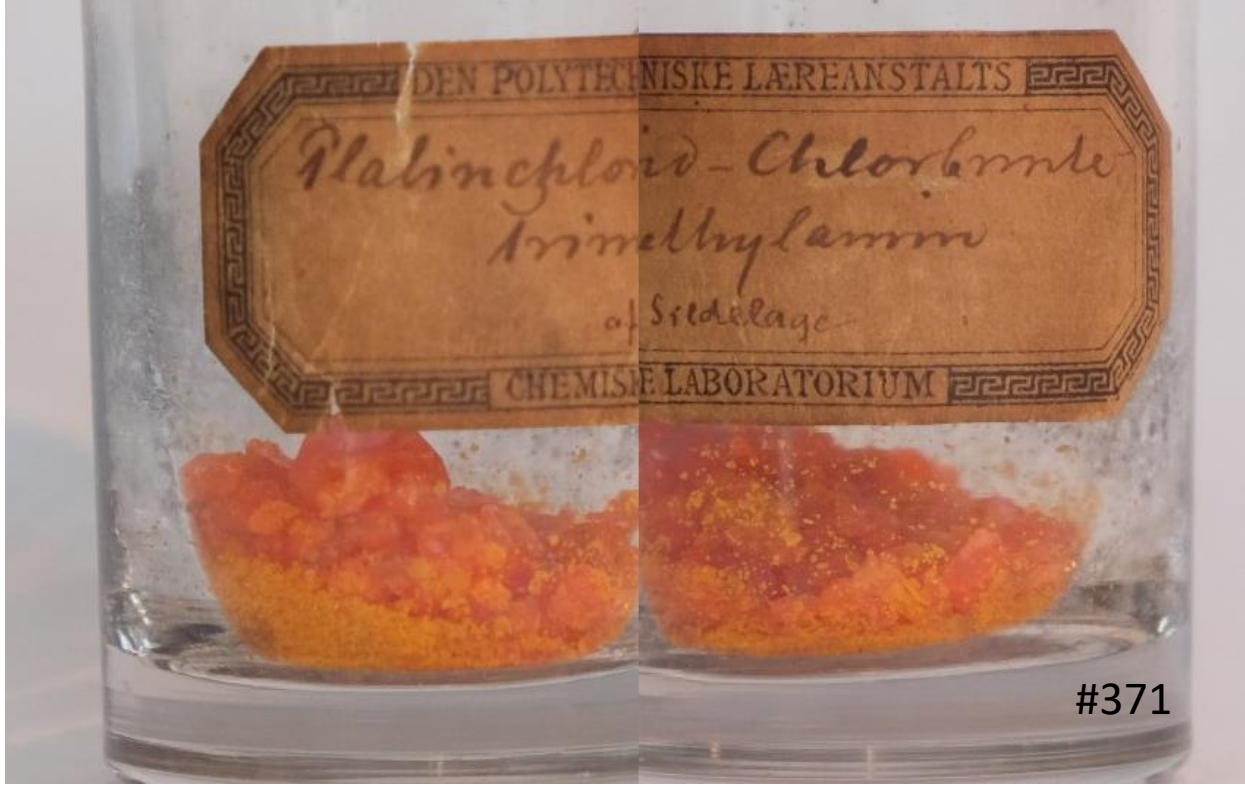
#363



DEN POLYTEKNISKE LÆREANSTALTS
KEMISKE LABORATORIUM A

#362



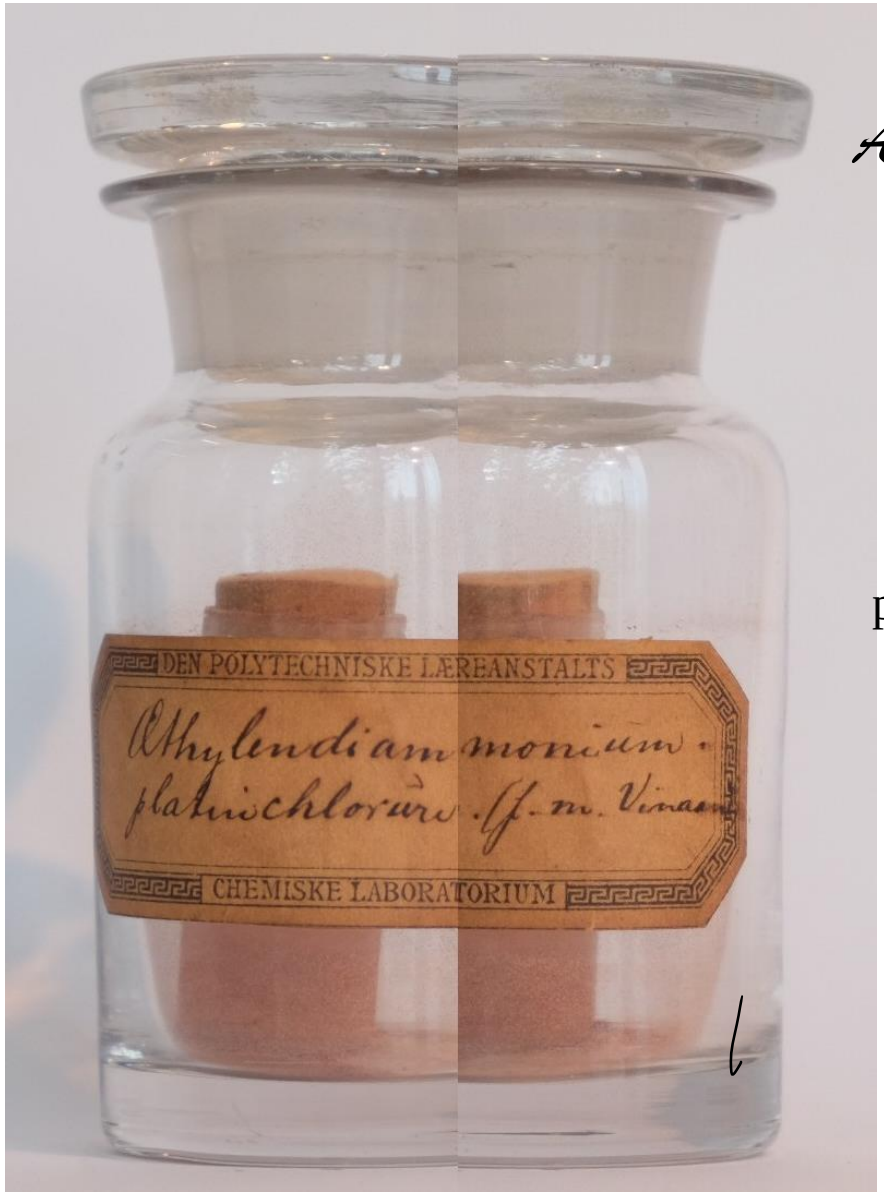


Platinchlorid-Chlorbrinte
trimethylamin
af Sildelage

sild = herring lage ≈ marinade

Guldchlorid og Platinbrom...
Dobbeltsalte af flygtig Base
Trimethylamin ? – af Sildela

#87



Ethylendiammonium -

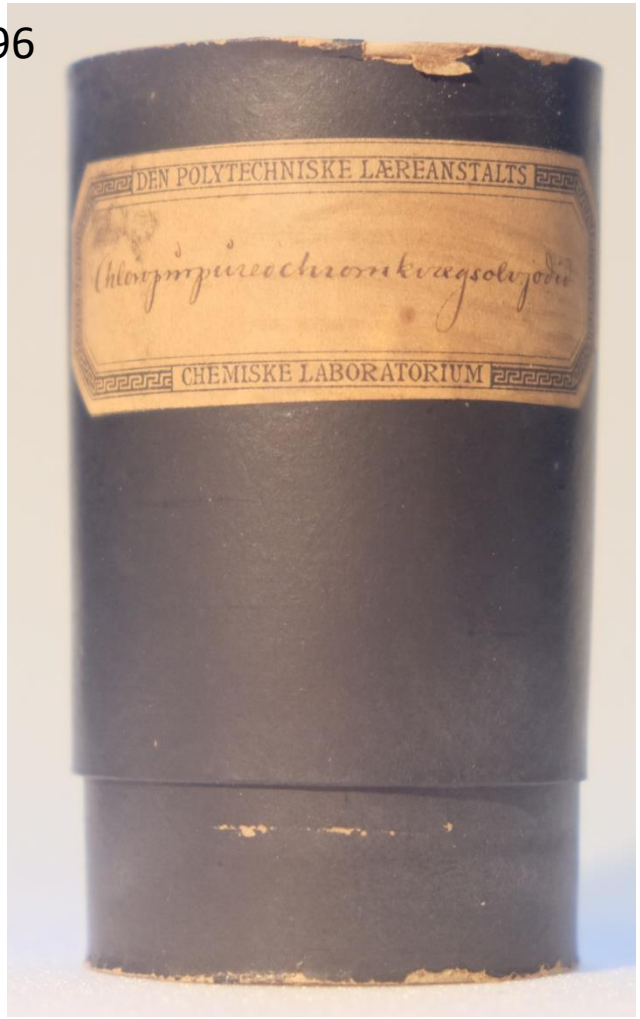
Platinchlorür . (f. m. Vinaand)

platinum(II) chloride ethanol (spirit of wine)

#372

#396


DEN POLYTECHNISKE LÆREANSTALTS
CHEMISKE LABORATORIUM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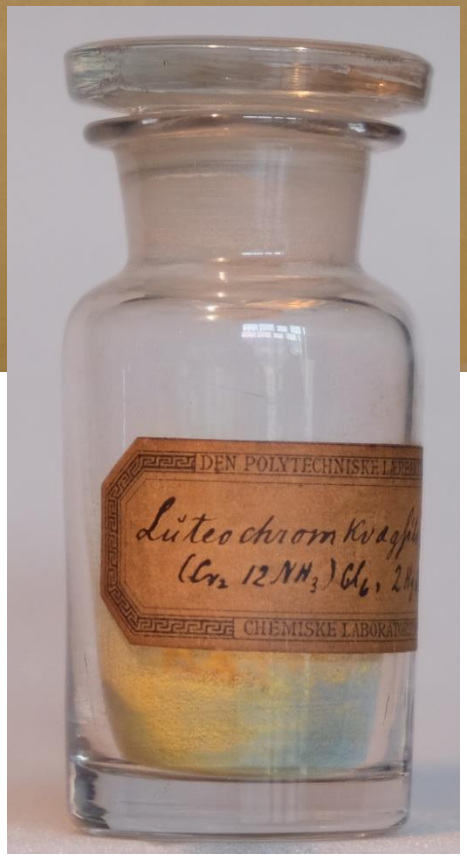
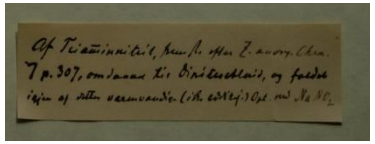
CHEMISKE LABORATORIUM


DEN POLYTECHNISKE

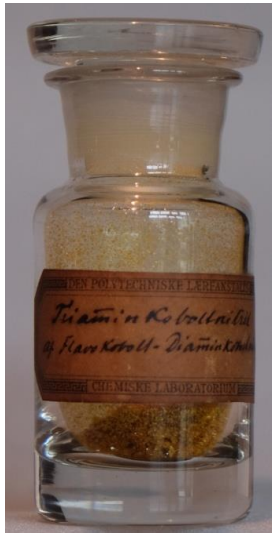
#447

Triaminkoboltnitrit

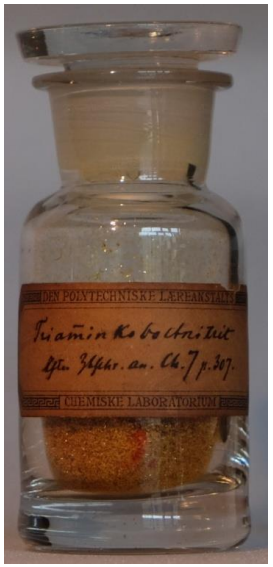


#463

#456



#459



#472

#457

af FlavoKobolt-Diaminkoboltnitrit

efter Erdmann

Af Triaminnitrit, fremst. efter Z. anorg. Chem. 7 p.307, omdannet til Dinitrochlorid, og fældet igjen af (xxxx) varmvandige (xxxx) Opl. med $NaNO_2$.

efter Ztschr. an. Ch. 7 p.307.

Asbjørn Petersen, Ture Damhus, Danish Society for the History of Chemistry
Version of August 2022

The collection of S.M. Jørgensen's experimental samples at History of Technology, DTU.

Bottle labels (large ones as well as small ones) with few exceptions carry a preprinted text: Den Polytechniske Læreanstalts Chemiske Laboratorium (spelled like this unless otherwise stated in the comments field).

It has been attempted to imitate the handwriting on the labels to some extent using special symbols such as m̃, ũ, 𝒩, n, m, ε, ∂, 𝒢. It is obvious that several persons have been involved in writing on the labels. Everything on the labels has been written using pen and ink, unless it is explicitly noted here that text was added in pencil..

Editorial comments in the second and third columns have been added in the format **[boldface]**, say, *e.g.*, **[on small label inside the bottle]**. The symbols *) and **) are used when referring to comments givn in the last column to the right in the table.

General coordination-chemistry terms

croceo = *trans*-tetraamminedinitro*	[** crŏceŭs (Latin), saffron-yellow]
flavo = *cis*-tetraamminedinitro*	[**,† flāvus (Latin), light yellow, golden yellow]
luteo = hexaammine	[** lūteus (Latin), egg-yellow]
praseo = *trans*-tetraamminedihalogenido	[** prasios (Greek), leek-green]
purpureo = pentaamminehalogenido	[** purpŭreus (Latin), purple]
roseo = pentaammineaqua	[** rŏseus (Latin), rose-red]
violeo = *cis*-tetraamminedihalogenido	[** viola (Latin), violet (the flower)]
xantho = pentaamminenitro*	[** xanthos (Greek), yellow]

Two ammonia ligands can be replaced by one chelating diamine such as en = ethane-1,2-diamine.

* 'nitro' has been stated as nitrito-κ*N* in the contemporary names below; binding through nitrogen is an editorial assumption
** According to Schläfer & Gliemann: *Einführung in die Ligandenfeldtheorie* (Akademische Verlagsgesellschaft 1967), these prefixes were coined by Fremy in *Ann.chim.phys.* [3], **35** (1852) 257. (S & G do not seem to mention xantho compounds).
† S & G list 'flavo' as meaning 'braun'.

Chromium compounds are probably in many cases light-sensitive, and some parts of samples are seen to have changed color.

References

1. S.M. Jörgensen: Beiträge zur Chemie der Kobaltammoniakverbindungen; II. Ueber die Bromopurpureokobaltsalze. *J. prakt. Ch.* 19 (2) 49–69 (1879).
2. S.M. Jörgensen. Zur Konstitution der Kobalt-, Chrom- und Rhodiumbasen. VI. Mitteilung. *Z. anorg. Ch.* 7 (1) 289–330 (1894).

#	Name etc. on label on outer bottle (unless otherwise stated)	Formula on label on outer bottle (unless otherwise stated)	Contemporary name for the compound assumed to be in the bottle The sign = is used when a name that has to be divided over two lines is not otherwise to contain a space at that place	Metals; (but not group 1,2); fluorine; selenium	Appearance of sample pwv. = powder cryst. = crystals, crystalline	Comments (AP + TD)
	April 4th, 2018					
1	Nitratopurpur(e)okoboltpikrat	–	pentaammine(nitrato-κ*O*)cobalt(III) 2,4,6-trinitrophenolate	Co	curry-yellow pwd.	picrate
2	Chlorotetramĩnkoboltbromid	$Cl.Co.(4NH_3,OH_2)Br_2$	tetraammineaquachloridocobalt(III) bromide	Co	purple pwd.	
3	Bromopūrpūreokoboltplatinchlorid	$Br_2[Co_2, 10NH_3]_2PtCl_6$	pentaamminebromidocobalt(III) hexachloridoplatinate(IV)	Co, Pt	brown pwd. SMJ in Ref. 1 states: 'havanna-braun oder graubraun'	formula not correct if it is platinum(IV); is it platinum (II)?
4	AqvotetramĩnxanthoKobolt Bromid	–	pentaammine(nitrito-κ*N*)cobalt(III) bromide	Co	red-purple pwd.	
5	XanthoKoboltoxalat	–	pentaammine(nitrito-κ*N*)cobalt(III) oxalate	Co	curry-yellow pwd.	
6	Bromopūrpūreokoboltoxalat	$Br_2[Co_2, 10NH_3]2C_2O_4$	pentaamminebromidocobalt(III) oxalate	Co	blue-purple pwd. SMJ in Ref. 1 states: 'schöne, mehrere Millimeter lange, violette Nadeln'	**Note that the entire formula has been multiplied by 2 (this is common all the way through the collection)**

mental samples at History of Technology, DTU.

General coordination-chemistry terms

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xantho = pentaamminenitro*	[** xanthos (Greek), yellow]

Two ammonia ligands can be replaced by one chelating diamine such as en = ethane-1,2-diamine.

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in *Ann.chim.phys.* [3], **35** (1852) 257. (S & G do not seem to mention xantho compounds).
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2	Chlorotetram̄inkoboltbromid	$Cl.Co.(4NH_3,OH_2)Br_2$
3	Bromopūrpūreokoboltplatinchlorid	$Br_2[Co_2, 10NH_3]_2PtCl_6$
4	Aqvotetram̄inxanthoKobolt Bromid	–
5	XanthoKoboltoxalat	–
6	Bromopūrpūreokoboltoxalat	$Br_2[Co_2, 10NH_3]2C_2O_4$

er	**Contemporary name for the compound assumed to be in the bottle** The sign = is used when a name that has to be divided over two lines is not otherwise to contain a space at that place	**Metals; (but not group 1,2); fluorine; selenium**	**Ap pv cr**
	pentaammine(nitrato-κ*O*)cobalt(III) 2,4,6-trinitrophenolate	Co	cu
	tetraammineaquachloridocobalt(III) bromide	Co	pu
	pentaamminebromidocobalt(III) hexachloridoplatinate(IV)	Co, Pt	br SM br
	pentaammine(nitrito-κ*N*)cobalt(III) bromide	Co	re
	pentaammine(nitrito-κ*N*)cobalt(III) oxalate	Co	cu
	pentaamminebromidocobalt(III) oxalate	Co	bl SM m vi

	Appearance of sample pwv. = powder cryst. = crystals, crystalline	Comments (AP + TD)
	curry-yellow pwd.	picrate
	purple pwd.	
	brown pwd. SMJ in Ref. 1 states: 'havanna-braun oder graubraun'	formula not correct if it is platinum(IV); is it platinum (II)?
	red-purple pwd.	
	curry-yellow pwd.	
	blue-purple pwd. SMJ in Ref. 1 states: 'schöne, mehrere Millimeter lange, violette Nadeln'	**Note that the entire formula has been multiplied by 2 (this is common all the way through the collection)**

Future work on the collection?

Make connections to original articles

New (legal) labels on bottles

Analyses of content

Exibition at DTU of some of the 805 bottles

Official recognition of the historical value of the collection

#2018.1.1