DERIVATOGRAPHIC STUDY
OF METAL PYRIDINE RHODANIDE PRECIPITATES

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Pyridine and similar compounds containing nitrogen form coordination complexes insoluble in water with rhodanides of the following metal ions: copper, cobalt, nickel, cadmium, zinc and manganese. Precipitate formed with pyridine has a well defined composition, $Me(SCN)_2 Py_n$, where n is equal to 2 or 4. Number of coordinated pyridine molecules in the case of nickel, cobalt and manganese is 4 and in the case of cadmium, zinc and copper 2.

The advantage of determinations carried out in the form of pyridine rhodanide that precipitates formed can be dried to constant weight already at room temperature and can be weighed, and that error originating from the weighing is negligible because of their low stoichiometric factor. They have, moreover, the advantageous property of having a product of stoichiometric composition formed by the thermal decomposition, which can also be used as weighing form.

Within systematic study of the analytical precipitates [1—5] thermal stability of the pyridine rhodanide precipitates, changes proceeding by the effect of temperature, the proceeding of a thermal decomposition was investigated. Besides, it was also studied in which temperature interval are the precipitates suitable for gravimetric analytical determinations.

Thermal studies were carried out by derivatograph, the operation of which was treated in a former paper [6].

Experimental

The investigations were carried out in small size porcelain crucibles in order to avoid corrosion of platinum. As a consequence of this DTA curve showing the enthalpy changes could not be obtained.

Curves taken automatically, as functions of time, have been re-drawn as functions of temperature, in order to make the results more readily understandable. Weight of the substance in each precipitate was expressed in per cent of the sample weighed with a similar purpose. Real weights of the precipitates are also presented in the figures.

Investigation was carried out in an air-atmosphere, the heating rate was 10° C/minute in all cases.

In all cases a-Al_2O_3 ignited at 1500° C was used as inert substance.

Precipitates investigated were precipitated according to the literature cited and were dried in vacuum desiccator.

Precipitates dried in vacuum desiccator as stoichiometric values were taken as reference bases.

a) *Nickel pyridine rhodanide*

Pyridine forms an insoluble complex in a neutral solution of nickel rhodanide, the composition being $Ni(C_5H_5N)_4(SCN)_2$. The method was elabor-
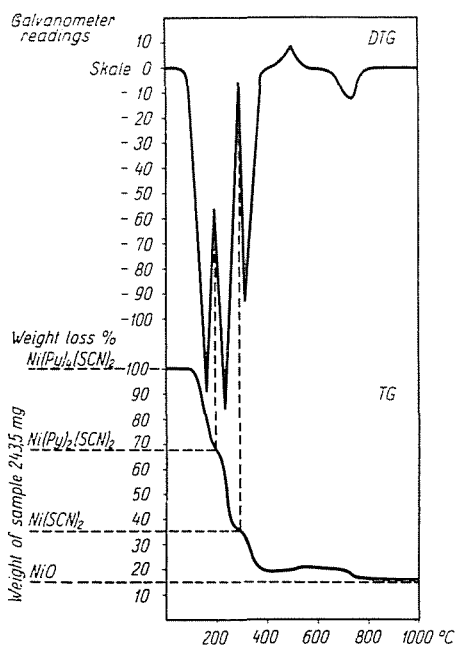

Fig. 1

ated for quantitative determination of nickel by SPACU [7], respectively SPACU and DICK [8].

Precipitate applied for derivatographic investigations was prepared as follows: ammonium rhodanide was added to the neutral solution of nickel salt, the precipitation was carried out with 1—2 ml pyridine. The precipitate was formed within several seconds in the form of azure blue crystalline prisms. The precipitate could be readily filtrated and quickly dried in a vacuum desiccator at room temperature after washing with organic reagents, first with

25 per cent alcohol containing rhodanide and pyridine, then with absolute alcohol containing pyridine, after it with ether containing pyridine.

Fig. 1 shows thermogravimetric and derivative thermogravimetric curves of nickel pyridine rhodanide.

The precipitate has a constant weight up to 80° C, the removal of pyridine begins here. Pyridine is lost stepwise in two stages according to the thermal curves. The two decomposition processes overlap, but by projecting minimum of the DTG curve on TG curve it can be established that 2—2 moles of pyridine are lost, in both the first and the second decomposition stage. This is also proved by Table 1, which shows that the value of weight belonging

Table 1

Ni-pyridine rhodanide	Theoretical, %	Experimental, %
$Ni(Py)_4(SCN)_2$	100,00	
$Ni(Py)_3(SCN)_2$	83,89	—
$Ni(Py)_2(SCN)_2$	67,79	69,27
$Ni(SCN)_2$	35,59	36,01
NiO	15,20	15,25

to the minimum agrees well with $Ni(Py)_2(SCN)_2$ composition. All these do not agree with DUVAL's results [9], who observed a compound of $Ni(Py)_3(SCN)_2$ composition which is constant between 110 and 130° C, and can be used as a weighing form. According to our studies there was no region under 820° C which would mean constancy of weight, and therefore was suitable as weighing form.

After removal of pyridine, which lasts up to 290° C the decomposition of nickel rhodanide begins. During this process a mixture of nickel sulphide and nickel oxide is formed, dicyan, sulphur and sulphur dioxide being removed. On increasing the temperature nickel sulphide is oxidized to nickel sulphate. This partial oxidation is shown by the increase of weight at 500° C, and by maximum of the DTG curve. Extent of oxidation is not constant, it depends on the conditions. Parallel measurements have shown that extent of oxidation depends on the weight of the examined sample, on the crucible, on the ventilation of the furnace etc. but oxidation may proceed in every case, only the extent of increase in weight varies. At higher temperatures also the nickel sulphate decomposes. The process may last to 800—900° C, depending on the amount of nickel sulphate, and NiO of stoichiometric composition is formed. In the case shown in the figure, a NiO of constant weight remains back already at 820° C.

It can be concluded from the thermal curves that to 80° $Ni(Py)_4(SCN)_2$, above 900° C NiO can be used as weighing form. Intermediate product formed during decomposition cannot be used for analytical determinations because of the overlapping of decompositions.

b) *Cobalt pyridine rhodanide*

Cobalt rhodanide, similarly to nickel rhodanide forms a complex with pyridine of $Co(Py)_4(SCN)_2$ composition, insoluble in water. This compound was applied for quantitative determination of cobalt by SPACU and DICK [10].
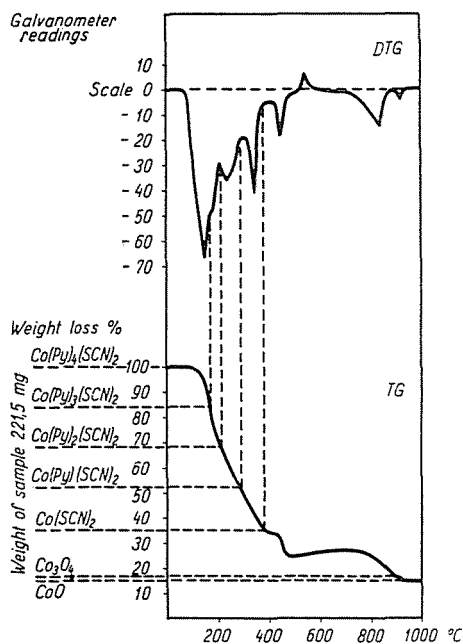

Fig. 2

Preparation of the precipitate: ammonium rhodanide was added to neutral solution of cobalt salt, solution was warmed to boiling point and the precipitate consisting of pink prisms was formed by addition of 1—2 ml pyridine under rapid stirring. The precipitate could be readily filtrated, it was washed with water containing rhodanide and pyridine, then with 10 per cent alcohol containing pyridine and rhodanide, last with ether containing pyridine. The precipitate could easily be dried in a vacuum desiccator at room temperature.

Curves of thermal decomposition of cobalt tetra pyridine rhodanide precipitate are shown in Fig. 2. It can be exceedingly well seen on DTG curve that removal of pyridine proceeds in four stages. The decompositions overlap, but

it can be established that each of the decomposition stages corresponds to the removal of 1—1 pyridine. In order to prove digressing from the usual, not minima of DTG curve were projected on to TG curve, but the corresponding theoretical values up to the DTG curve. Therefore, vertical lines drawn from the intersection of the TG curve and the theoretical values are not exactly at the minima.

Table 2

Co-pyridine rhodanide	Theoretical, %	Experimental, %
$Co(Py)_4(SCN)_2$	100,00	
$Co(Py)_3(SCN)_2$	83,90	84,53
$Co(Py)_2(SCN)_2$	67,81	69,54
$Co(Py)(SCN)_2$	51,71	50,12
$Co(SCN)_2$	35,62	34,26
Co_3O_4	16,33	16,42
CoO	15,23	15,29

It is also shown by Table 2 that theoretical and experimental values of weights of products formed during decomposition are in quite good agreement.

Removal of two pyridine molecules follows each other closely, there is only a small difference between their bond strengths, only an inflexion point can be observed even on a derivative curve. Third and fourth pyridine molecules are removed more separately. After stepwise removal of pyridine decomposes the remaining $Co(SCN)_2$. Product formed during decomposition — similarly to nickel pyridine rhodanide — is partly oxidized to cobalt sulphate immediately, partly after the ending of decomposition. This process is followed by an increase in weight, but does not proceed quantitatively and its extent depends on experimental conditions.

On further increase of temperature cobalt sulphate decomposes and Co_3O_4 remains, sulphurtrioxide being removed. This conversion may last to 900° C depending on the amount of cobalt sulphate. This is followed at 920° C by $Co_3O_4 \rightarrow CoO$ conversion also observed at decomposition of cobalt anthranylate. Above 920° C CoO is a stable form applicable for determination.

It can be established that cobalt pyridine rhodanide is stable to 80° C, and loosens pyridine stepwise on increase of temperature. On heating to between 700 and 900° C the Co_3O_4, above 920° C the CoO is the suitable weighing form

c) *Manganese pyridine rhodanide*

Manganese pyridine rhodanide is precipitated from manganese solutions containing rhodanide on the effect of pyridine. The precipitate is slightly

soluble in water (the most among the pyridine rhodanide precipitates). Method applied for analytical determination was elaborated by SPACU and DICK [11].

The precipitate was formed from manganese sulphate solution by addition of ammonium rhodanide and pyridine under stirring. The $Mn(Py)_4(SCN)_2$ precipitate was washed with various solutions containing rhodanide or pyridine according to prescriptions [10], then dried in vacuum desiccator at room temperature.
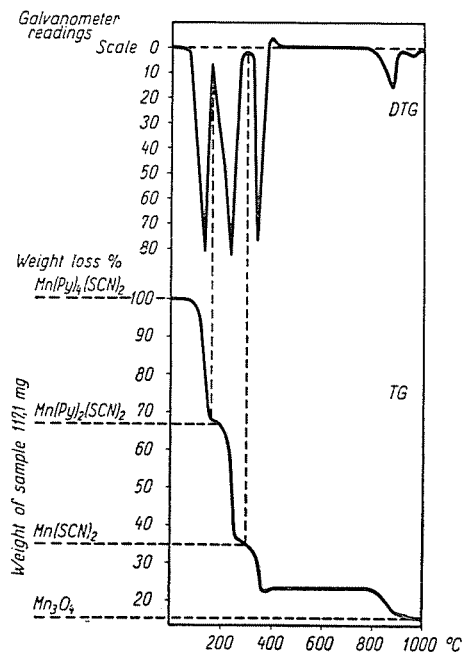

Fig. 3

Thermogram of the precipitate is shown in Fig. 3, according to which pyridine is removed in two stages. Both stages correspond to the removal of 2 molecules of pyridine (see Table 3), which also means at the same time that

Table 3

Mn-pyridine rhodanide	Theoretical, %	Experimental, %
Mn(Py)$_4$(SCN)$_2$	100,00	
Mn(Py)$_2$(SCN)$_2$	67,54	68,32
Mn(SCN)$_2$	35,09	35,31
Mn$_3$O$_4$	15,64	15,69

no energetical difference can be made between the two removed pyridine mole-cules. Peaks which are well separated on the derivative curve even so partly overlap, therefore, $Mn(Py)_2(SCN)_2$ formed at about 150° C is only a transitional product and according to our opinion it can not be applied as a form of de-termination. According to DUVAL [9] $Mn(Py)_2(SCN)_2$ formed in the course of decomposition of the precipitate is of constant weight between 84 and 92° C, and gives a horizontal region in TG curve which is suitable for determination. This interval is, however, so narrow that the determination involves a possi-bility of great error.

Removal of pyridine is followed by decomposition of the remaining manganese rhodanide, which proceeds similarly to that of nickel or cobalt rhodanide. During thermal decomposition also simultaneous reactions are proceeding, resulting first various mixtures of manganese sulphide, sulphate and various manganese oxides, then manganese sulphide is oxidized to sul-phate [12]. The reaction is not quantitative in this case either, therefore, the horizontal region being between 400 and 760° C is not suitable for analytical determination. Above 760° C decomposition of manganese sulphate begins which may last to 900° C, according to the amount of sulphate. Above this temperature also conversion of Mn_2O_3 proceeds — this is often formed in the oxidation process — to Mn_3O_4 and in this form can be weighed above 940° C in every case.

It can be established from the above results that $Mn(Py)_4(SCN)_2$ can be used for determination of Mn up to 60° C. Removal of pyridine proceeds in two steps, but neither transitional nor residual manganese rhodanides are suitable as weighing forms. Above 940° C Mn_3O_4 can be applied for analytical determin-ations as weighing form.

d) *Cadmium pyridine rhodanide*

Cadmium ions can be precipitated by means of pyridine from a solution containing rhodanide. Procedure used for analytical determination was elabor-ated by SPACU and DICK [13]. They have observed that if precipitation was not carried out in a boiling solution, then a precipitate of not $Cd(Py)_2(SCN)_2$ composition was formed. If precipitation is carried out in a cold solution in presence of much pyridine, then a precipitate of $Cd(Py)_4(SCN)_2$ composition is formed, which is, however, not stable in air and loses 2 molecules of pyridine even at lower temperatures [14].

For our purposes the precipitate was formed in a warm cadmium sul-phate solution by means of ammonium rhodanide and pyridine according to the prescriptions of SPACU. The precipitate — which was formed only after cooling, and was readily filterable — was washed with solutions according to prescriptions.

Fig. 4 shows thermogram of a precipitate which was not dried well and contained significant amount of pyridine, which was removed with a maximum at 130° C. After this process did the decomposition of the precipitate itself proceed, which was however retarded by higher partial pressure of pyridine inside of the sample. Decomposition of the precipitate appears only above 220° C, because of the overlapping of the two processes. Decomposition of the pure, well dried cadmium pyridine rhodanide begins at markedly lower temperature.
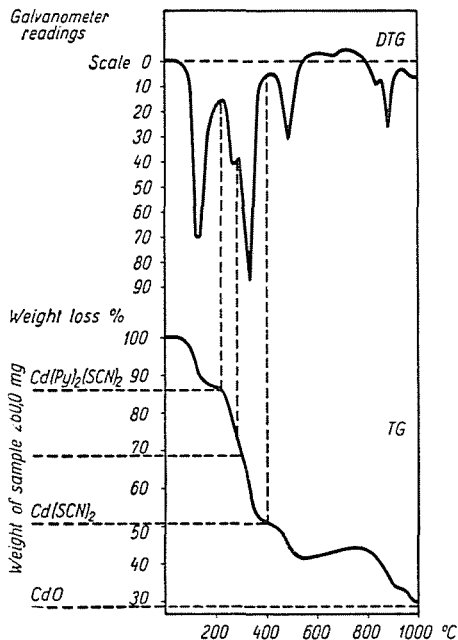

Fig. 4

Decomposition of the precipitate is made reproducible in two stages, with maximums at 260 and 320° C. Projecting the minimum on TG curve, that is establishing the weight difference, it comes out that not quite 1—1 molecule pyridine is removed during the two decomposition processes (see Table 4).

Table 4

Cd-pyridine rhodanide	Theoretical, %	Experi-mental, %
Cd(Py)$_2$(SCN)$_2$	85,95	
Cd(Py) (SCN)$_2$	68,38	(73,47)
Cd(SCN)$_2$	50,80	50,96
CdO	28,53	—

Contrary to DUVAL [9] in our measurements such a horizontal region was experienced between 77 and 107° C, in which $Cd(Py)_2(SCN)_2$ of stoichiometric composition was present. According to our experiences decomposition of the precipitate begins only above the latter temperature. After removal of pyridine proceeds decomposition of the rhodanide at the end of which cadmium sulphide — formed transitionally — is partly oxidized to cadmium sulphate. This latter is converted quantitatively into CdO only above 1000° C. In the course of thermal decomposition of the compound there is no intermediate product up to 1000° C, which is of constant weight for a longer time and of stoichiometric composition. $Cd(Py)_4(SCN)_2$ precipitated in cold solution with much pyridine was also investigated. Deviation in the shape of thermal curves is only that a further peak appears with a maximum of 100° C, at which not quite 2 molecules of pyridine are removed.

It can be established that decomposition of $Cd(Py)_2(SCN)_2$ precipitate proceeds in two stages, but — contrary to other pyridine rhodanide precipitates — through intermediate products of not stoichiometric compositions. Cadmium rhodanide and other products formed in course of decomposition to 1000° C are not suitable as weighing forms.

e) *Zinc pyridine rhodanide*

Also zinc ions can be precipitated with pyridine from a solution containing rhodanide. Procedure applicable for analytical determination was elaborated by SPACU and DICK [15]. The precipitate was formed from zinc sulphate solution at room temperature by means of ammonium rhodanide and pyridine under stirring. Colourless needle-shaped prisms were immediately formed. The precipitate was washed after standing for 15 minutes according to prescriptions with alcohol containing rhodanide and pyridine, then with absolute alcohol containing pyridine, with ether containing pyridine, finally it was dried in a vacuum desiccator at room temperature.

Thermogram of the precipitate of $Zn(Py)_2(SCN)_2$ composition is shown in Fig. 5. It can be seen in the figure that the precipitate is constant weight up to 120° C. Decomposition begins at higher temperatures and proceeds in one stage according to the Figure and Table 5. It means that no difference

Table 5

Zn-pyridine rhodanide	Theoretical, %	Experimental, %
$Zn(Py)_2(SCN)_2$	100,00	
$Zn(Py)(SCN)_2$	76,71	—
$Zn(SCN)_2$	53,43	54,51
ZnO	23,95	24,20

exists between the bond strengths of the two coordinated pyridine molecules
(it is a deviation from cadmium pyridine rhodanide). Removal of the bound
pyridine is followed by decomposition of the remaining zinc rhodanide. Zinc
sulphide formed in course of decomposition is partly oxidized immediately
to zinc sulphate. A deviation from the other pyridine rhodanides is that in
this case reaction accompanied by increase of weight was never observed.
Formation of sulphate already begins at 400° C [12], at a temperature at which
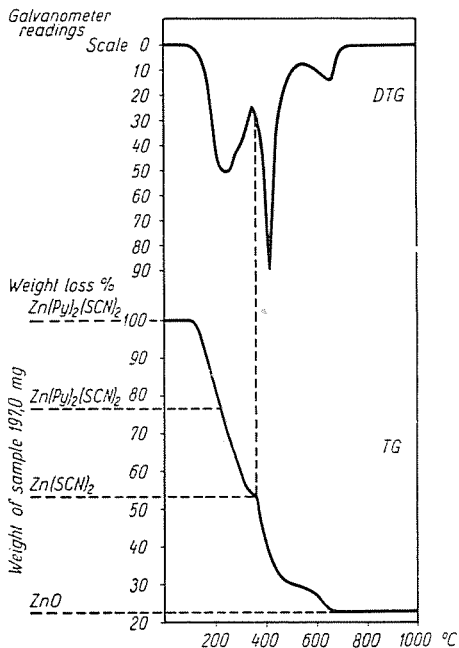

Fig. 5

zinc sulphide was still formed as a result of decomposition of rhodanide. The
two processes, decomposition and sulphate formation proceed at the same time,
and sulphate formation does not appear as a new, separate process.

Zinc sulphate decomposes at a further increase of temperature, and the
oxide of constant weight is formed at the lowest temperature among the studied
precipitates, already above 700° C ZnO can be used as weighing form.

It can be established that $Zn(Py)_2(SCN)_2$ precipitate is of constant weight
up to 120° C, then after simultaneous removal of two molecules of pyridine
rhodanide also decomposes. The residual ZnO can be used for analytical de-
termination above 700° C.

f) *Copper(II)pyridine rhodanide*

From solution of copper(II) ions a copper(II)pyridine rhodanide pre-
cipitate (insoluble in water) is formed by the effect of ammonium rhodanide
and pyridine. This phenomenon was used by SPACU and DICK [16, 17] for gravi-
metric determination of copper(II) ions.

The precipitation was carried out from a copper sulphate solution. On
the effect of pyridine an azure blue complex was formed, and after addition
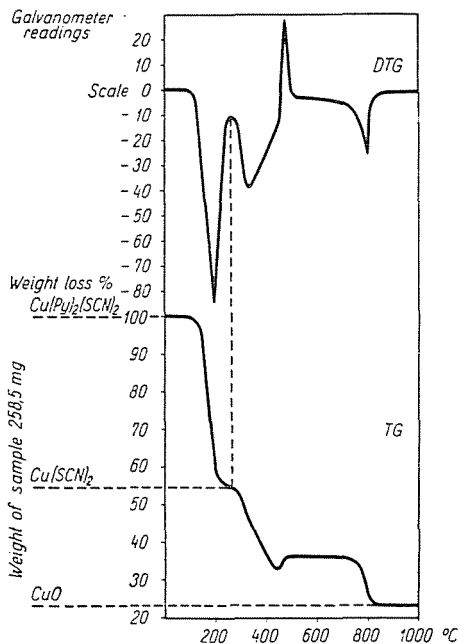

Fig. 6

of ammonium rhodanide under stirring a green precipitate of $Cu(Py)_2(SCN)_2$
composition was immediately formed. The precipitate was filtrated and washed
with 75 per cent alcohol containing pyridine and rhodanide, then with absolute
alcohol containing pyridine, last with ether containing pyridine. The precipitate
was dried in a vacuum desiccator at room temperature.

Thermogram of the precipitate is shown in Fig. 6. It is clear from the
figure that the precipitate is of constant weight to 110° C. Removal of pyridine
proceeds in one step. The remaining copper(II)rhodanide begins to decompose
on increase of temperature. The decomposition also proceeds here similarly
to the other pyridine rhodanides. Copper sulphide temporarily formed is partly
oxidized to copper sulphate [12]. Reaction accompanied by the increase of
the weight proceeds between 450 and 500° C. Between 500 and 700° C there is

no thermal change, above 700° C copper sulphate begins to decompose. Removal of sulphur trioxide — depending on the amount of copper sulphate — ends at about 820° C. Above this temperature CuO of stoichiometric composition is present which can be used as weighing form (see Table 6). It should be mentioned that about 1000° C begins $CuO \rightarrow Cu_2O$ conversion.

Table 6

Cu-pyridine rhodanide	Theoretical, %	Experimental, %
$Cu(Py)_2(SCN)_2$	100,00	
$Cu(Py)(SCN)_2$	76,58	—
$Cu(SCN)_2$	53,16	54,41
CuO	23,54	23,72

It can be established that $Cu(Py)_2(SCN)_2$ precipitate is of constant weight up to 110° C, and the removal of pyridine proceeding in one step is followed by decomposition of copper(II)rhodanide. As a result these various compounds are formed one beside the other. After the decomposition of these products between 820 and 970° C CuO, a form suitable for determination is present.

Discussion

The advantage of determinations carried out in the form of pyridine rhodanide is that the method is very rapid, can be easily carried out and error occurring from weighing can be neglected because of the low stoichiometric factors, and the method makes possible the determination of small amounts of metal ions. The method is applicable for the rapid determination of listed metal ions chiefly beside cations of IV. and V. groups.

Thermal stability of the pyridine rhodanide precipitates is not nearly so high as that of anthranylate precipitates. Pyridine molecules are bound only coordinatively to the metal ion, therefore, the bond is relatively weak. On increasing the temperature the bond splits and the pyridine is removed.

By studying the precipitates it can be established that pyridine rhodanide precipitates containing only two molecules of pyridine (Cd, Zn, Cu) are more stable, and begin to decompose only at higher temperatures than those containing four molecules. While the beginning of decomposition of the former is about 110° C, the latter are of constant weight only up to 60—80° C.

In the case of compounds containing two molecules of pyridine one can not be distinguished from the other when they are removed. Their removal proceeding in one step shows that no difference exists between the bond strengths of the two molecules. At Ni and Mn complexes containing four moles of pyridine, it was observed that first two moles then at somewhat higher temperature

further two moles of pyridine were removed. The 2—2 pyridines, splitting off at the two temperatures are bound very likely with identical strengths to the complex which is proved by their simultaneous removal. Only at cobalt pyridine rhodanide precipitate could it be shown that the four pyridine molecules were separately removed, that is, differences existed between their bond strengths.

It can also be established from the diagrams that only precipitation form and oxide of the pyridine rhodanide complexes are applicable for analytical determination. Contrary to reports of DUVAL, in our investigations in the course of the removal of pyridine no weighing forms containing one or more pyridine molecules have been found. Removal of pyridine is followed at each pyridine rhodanide by the decomposition of the remaining metal rhodanide. Meanwhile more decomposition processes are proceeding simultaneously. Therefore, the process is never univocal, products of varying composition are always formed, depending on experimental conditions. It can be established, however, in each case that the sulphides formed are partly oxidized to sulphates at about 4—500° C. This — excepting Zn — is always accompanied by various increases in weights. At higher temperatures the sulphates decompose and the corresponding oxides remain.

The fact that all the pyridine rhodanides have another weighing form, the corresponding metal oxide applicable for analytical determination, makes possible the simultaneous determination of two components one beside the other, by indirect analysis. When weighing the precipitate of the two metal ions formed together, first after drying and for the second time after ignition, ratio of components can be determined from the two data.

It was established that if the precipitate was not dried out well, pyridine adsorbed on the surfaces was removed between 100 and 200° C depending on its amount. Decomposition of the complex is shifted by this fact towards higher temperatures.

Table 7

	$-(Py)_4(SCN)_2$ °C	$-(Py)_3(SCN)_2$	$-(Py)_2(SCN)_2$ °C	$-(Py)(SCN)_2$	$-(SCN)_2$	Oxide °C
Ni	20—80	—	+	—	+	>900 NiO
Co	20—80	+	+	+	+	<900 Co_3O_4 >920 CoO
Mn	20—60	—	+	—	+	>940 Mn_3O_4
Cd			20—110	—	+	>1000 CdO
Zn			20—120	—	+	>700 ZnO
Cu(II) ..			20—110	—	+	820—970 CuO

Sign + indicates that the compound is transitionally formed during decomposition, while — if it is not.

Summary

Thermal stability, proceeding of thermal decomposition of Ni, Co, Mn, Cd, and Cu(II) pyridine rhodanide precipitates used in gravimetric analysis was investigated. Nature of the transitional products formed in the course of decomposition, and temperature intervals, within which weighing forms are present, applicable for gravimetric determinations were also studied. Summarized results of the studies are given in Table 7.

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