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# Formation of Transition Metal Sulfides by the Decomposition of Their Dithiolato Complexes

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The thermal behavior of dithiolato complexes of Ni, Co, Fe, and Mo has been investigated. For this purpose simple monoalkyldithiocarbamate, dialkyldithiocarbamate, and xanthate complexes of the metals were used. Since the objective of this study was to ascertain if these complexes could be used to prepare metal sulfides directly, the inorganic residues left after the decomposition of the complexes have been extensively studied. Of the different techniques used (TGA, powder X-ray diffraction, GC/MS, and heated stage XRD), the last was found to be very powerful and the method of choice. With this method the successive decomposition of complexes and, consequently, the pathway for the formation of final sulfides could be established. In this work it was found that the metal, type of ligands, and atmospheric environment are all important parameters in the formation of sulfides upon thermolysis. This study suggests that by judicious selection of these parameters, many desired transition metal sulfides can be prepared by thermolysis of the metal complexes. © 1994 Academic Press, Inc.

## INTRODUCTION

During the past twenty years, several reviews on the thermal behavior, properties, and reactivities of metal dithiocarbamates have been published (1–3). For thermal studies, many techniques including thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), high temperature reflectance spectroscopy, and mass spectrometry (MS) have been used.

Most of the studies have concentrated on *N*,*N*-dialkyl, especially diethyldithiocarbamates of metals (4, 5). In most of these studies, it was concluded that the metal dialkyldithiocarbamates (without any special features in the ligands) are completely volatile in vacuum and partially so in air or nitrogen. Bernard and Borel (6) have shown that unsubstituted dithiocarbamates (DTC) of lead, zinc, and cadmium, of the type $M(H_2DTC)_2$, decompose to give carbon disulfide and ammonium thiocyanate. In one of the very few studies with metal monoalkylDTCs, Venkappayya and Brown (7) have studied thermal behavior of *N*-α-methylbenzylDTCs of Ni, Zn, Cd, Cr, and Co. They concluded that these complexes decompose with the loss of hydrogen sulfide and the formation of isothiocyanate and metal sulfides, which in air give mixtures of metal oxide, sulfide, and sulfate. Apparently more attention has been paid to the characterization of the decomposition products of the organic portion of the complexes rather than those of the inorganic residues as evidenced by the use of Pyrolysis GC/MS (8).

This paper describes the thermal behavior of dithiolato complexes of Ni, Co, and Mo. We have used simple monoalkylDTC, dialkylDTC, and alkoxyalkylxanthate ligands. Our objective was to determine if these complexes could be used to synthesize metal sulfides directly. We have therefore concentrated more on the inorganic part of the complexes left after thermal treatment. Also, we wanted to determine the pathway of the formation of final products as well as their dependence on the environment of the gases employed. The techniques used in this study were TGA, GC/MS, powder X-ray diffraction (XRD), and heated stage XRD.

## EXPERIMENTAL

### *Thermogravimetric Analysis*

Thermal analysis experiments were carried out on a DuPont 951 TGA using a heating rate of 5 to 40°C/min (typically 20°C/min) under $N_2$ or 7% $H_2/N_2$ atmosphere at a flow rate of 80 $cm^3/min$. The final temperature ranged from 450 to 850°C, depending upon conditions. The TGA residues were analyzed by powder XRD to determine the nature of the decomposition products.

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### *Mass Spectrometry (MS)*

A Finnigan 4000 quadrupole mass spectrometer was used to identify volatile breakdown products of metal dithiocarbamates. Pure compounds were analyzed with the solid probe inlet. Approximately 1-mg samples were heated from 30 to 300°C at 50°C/min. Helium (20-psi head pressure) was used as carrier gas. The mass spectrometer was operated using 70-eV ionization.

### *Heated Stage XRD*

(*a*) *Equipment.* The heated stage XRD equipment unit consists of a heated Pt strip in a gas-tight housing supplied with Be–Mylar X-ray windows. The sample is spread evenly across the surface of the Pt strip where it is exposed to the X-ray beam. An XRD pattern of the sample may be obtained at room temperature and at any selected temperature up to 1200°C at atmospheric pressure or 1600°C in a vacuum. Any noncorrosive gas atmosphere may be employed, but experiments must be conducted at or below atmospheric pressure using pure gases or gas mixtures which do not condense on the Pt surface at room temperature. Data acquisition is by a strip chart recorder. The temperature of the sample stage is adjusted and may be held indefinitely within 1°C.

(*b*) *Sample preparation.* Purified crystalline samples of metal dithiolato complexes to be studied were ground and slurried with deionized water prior to application to the Pt stage. Water was used as a convenient slurry medium because these compounds are insoluble in, and not altered chemically at room temperature, by water. Also, the samples are not air-sensitive over the short periods of time required for sample preparation. The heated stage was then enclosed and purged with $N_2$ gas.

(*c*) *Experimental Procedures.* XRD instrumental parameters were set as follows:

Radiation: Cu$K\alpha$ 1.54 Å, 40 kV, 40 ma graphite crystal monochromatization
Starting angle: 2° $2\theta$
Ending angle: 70° $2\theta$
Scan speed: 1°/min
Counts full scale: 1k or 2.5 k
Chart speed: 0.5 in/min

A minimum of seven XRD patterns were acquired: in 7% $H_2/N_2$ atmosphere at room temperature (25°C), 150°C, 350°C, and 450°C, and in dry $N_2$ atmosphere at room temperature and 350°C. In some cases the XRD patterns were obtained only in dry $N_2$ atmosphere; in those cases a minimum of four patterns were acquired: room temperature (25°C), 150°C, 250°C, and 350°C.

### *Preparation of Dithiolato Complexes*

Dialkyl dioxodithiocarbamates of molybdenum were prepared according to the method of Singhal (9). Metal DTCs other than Mo were prepared by one of the general methods given in the review by Coucouvanis (3), or as described by Singhal *et al.* (10). Metal alkoxyalkylxanthates were prepared by the method of Habeeb and Singhal (11). All the complexes were crystallized from suitable solvents to give compounds with sharp melting/decomposition points. All the compounds gave acceptable elemental analysis, and physical characterization such as IR spec. or $H^1$ NMR was consistent with the structure.

*Abbreviations Used for Dithiolato Complexes*

| Compound Name | Abbreviation | Compound Name | Abbreviation |
|---|---|---|---|
| Bis(*N*-butyldithiocarbamato)Ni | NiBuDTC | Bis(*N*,*N*-dibutyldithiocarbamato)Ni | NiDiBuDTC |
| Bis(ethoxyethylxanthato)Ni | NiEEX | Bis(butoxyethylxanthato)Ni | NiBEX |
| Bis(butylxanthato)Ni | NiBuX | Dioxo-bis(dibutyldithiocarbamato)Mo | $MoO_2$DiBuDTC |
| Dioxo-bis(dicyclohexyldithiocarbamato)Mo | $MoO_2$DiCHDTC | Tris(*N*-butyldithiocarbamato)Co | CoBuDTC |
| Tris(*N*,*N*-dibutyldithiocarbamato)Co | CoDiBuDTC | Bis(ethoxyethylxanthato)Co | CoEEX |
| Tris(*N*,*N*-dibutyldithiocarbamato)Fe | FeDiBuDTC | Tris(*N*,*N*-dipropyldithiocarbamato)Fe | FeDiPrDTC |

## RESULTS AND DISCUSSION

Decomposition of Ni complexes was studied in more detail than was that of the complexes of other metals. In the case of nickel, more complexes were used, and more residue characterization techniques were utilized.

### *Thermogravimetric Analysis*

Thermograms obtained in $N_2$ only, or in 7% $H_2/N_2$ were similar; therefore, only the results under $N_2$ are presented. Thermograms of NiBuDTC, NiDiBuDTC, NiEEX, NiBuX, and NiBEX are given in Fig. 1. Table 1

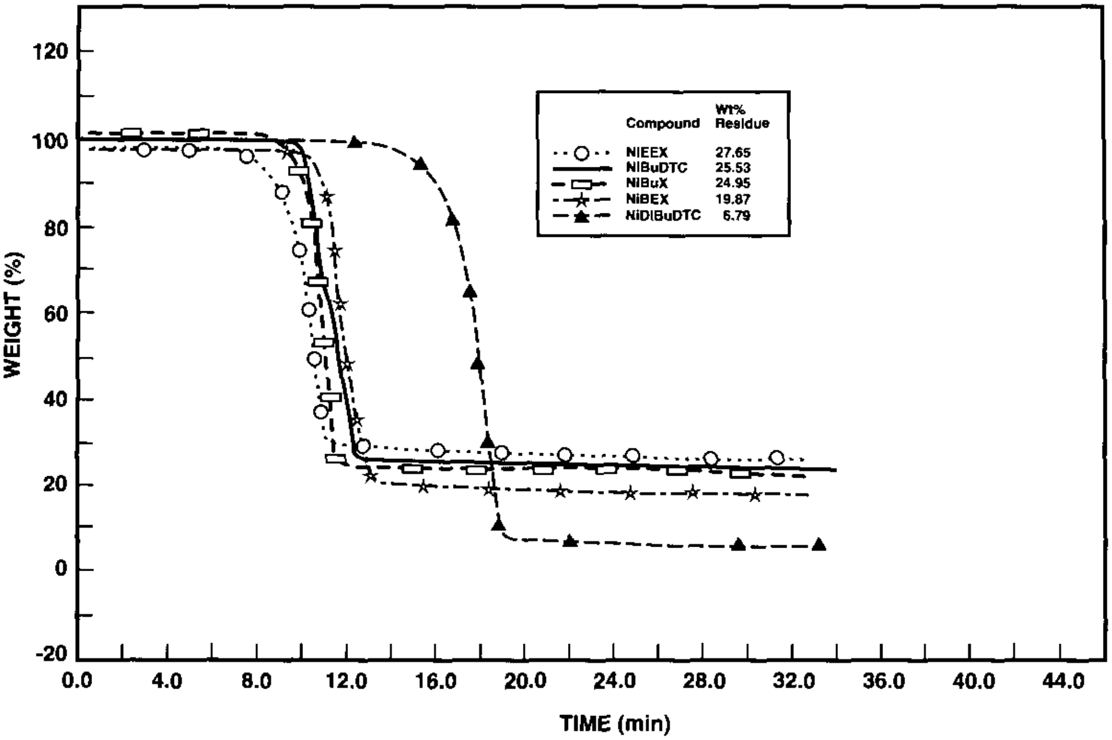

FIG. 1. Thermal decomposition of Ni dithiolato complexes under $N_2$ atmosphere. Heating rate: 20°C/min to 500°C.

gives the calculated and found values for the decomposition of the complex to either metal thiocyanate or metal sulfide. From the results, some general observations can be made. As shown in Fig. 1, Ni complexes, except for NiBuDTC, under the conditions used gave very sharp decomposition patterns. Any significant volatility was observed only for NiDiBuDTC. In almost all cases, the weight of the residue was closer to the weight expected for simple sulfide or a mixture of sulfides. In no case did the residue weight correspond to metal thiocyanates.

For Mo complexes also, our results differ significantly from those given in the literature. It should be pointed out that the DTC complex used by Kumar *et al.* (12) had different hydrocarbyl groups, and Mo was in a different oxidation state than in the complexes used in our study. For $MoO_2$DiBuDTC and $MoO_2$DiCHDTC, formation of thiocyanate and consequent volatility was not observed. As shown by XRD the residues of these complexes consisted primarily of poorly crystalline $MoS_2$.

### *Heated Stage XRD*

Heated stage XRD is a powerful technique for characterizing the decomposition products of complexes. In addition, the decomposition pathway of the complexes with temperature can be easily followed. The decomposition products of NiBuDTC in $H_2/N_2$ are diagrammed as a function of temperature in Fig. 2. Between 100–200°C,

TABLE 1

Comparison of Calculated vs Observed Residues of Dithiolato Complexes from TGA under $N_2$, 20°C/min up to 500°C

| Compound abbreviated name | Compound formula weight | Calculated residue (wt%) | | Actual residue (wt%) |
|---|---|---|---|---|
| | | $M(SCN)_x$ | $MS_x$ | |
| | | $Ni(SCN)_2$ | NiS | |
| NiBuDTC | 355.24 | 49.22 | 25.55 | 25.53 |
| NiDiBuDTC | 467.45 | 37.36 | 19.42 | 6.79 |
| NiEEX | 389.21 | — | 23.32 | 27.65 |
| NiBEX | 445.31 | — | 20.38 | 19.87 |
| NiBuX | 357.21 | — | 25.41 | 24.90 |
| | | $Mo(SCN)_5$ | $MoS_2$ | |
| $MoO_2$DiBuDTC | 536.70 | 71.98 | 29.82 | 34.65 |
| $MoO_2$DiCHDTC | 640.85 | 60.28 | 24.98 | 28.41 |
| | | $Co(SCN)_3$ | CoS | |
| CoBuDTC | 503.75 | 46.28 | 18.06 | 16.71 |
| CoDiBuDTC | 672.08 | 34.69 | 13.54 | 12.91 |
| CoEEX | 554.71 | — | 16.40 | 18.98 |
| | | $Fe(SCN)_3$ | FeS | |
| FeDiBuDTC | 668.99 | 34.39 | 13.14 | 14.26 |
| FeDiPrDTC | 584.83 | 39.33 | 15.03 | 12.35 |

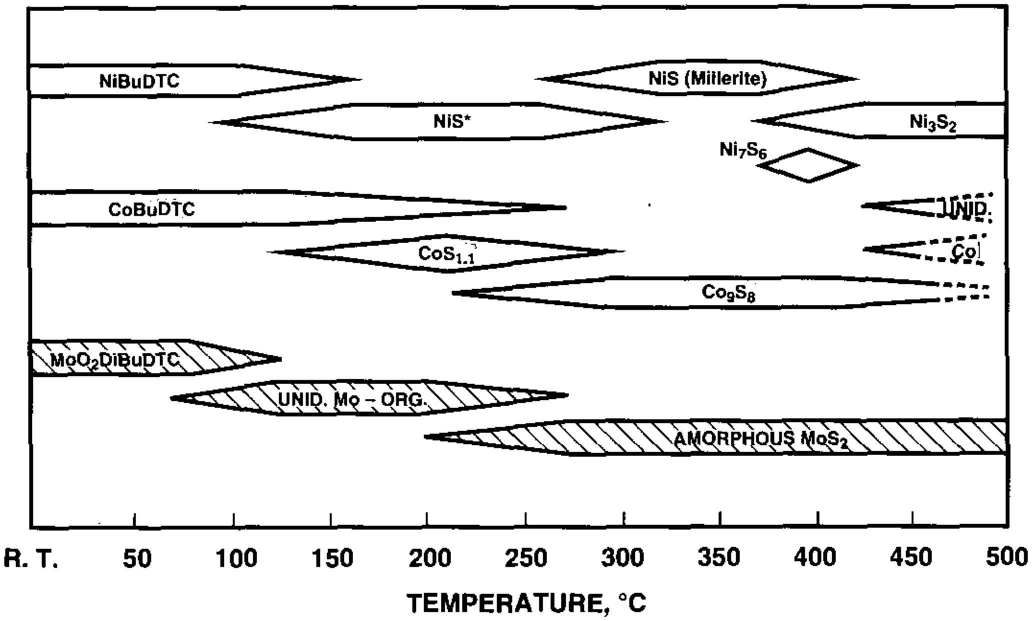

FIG. 2. Decomposition products of metal DTC complexes under 7% $H_2/N_2$.

crystalline NiBuDTC decomposes to yield NiS*. This form of nickel sulfide is not the well-known and well-characterized form, millerite. It is a poorly known form represented in the Joint Committee on Powder Diffraction Studies (JCPDS) file of XRD patterns with unindexed card number 2-1280. In the temperature range from 250–300°C, NiS* undergoes a structural rearrangement to become the more familiar NiS phase millerite. Above 350°C, millerite loses some sulfur to produce godlevskite ($Ni_7S_6$) and heazlewoodite ($Ni_3S_2$):

$$7NiS + H_2 \longrightarrow Ni_7S_6 + H_2S$$
$$3NiS + H_2 \longrightarrow Ni_3S_2 + H_2S$$
$$3Ni_7S_6 + 4H_2 \longrightarrow 7Ni_3S_2 + 4H_2S.$$

Decomposition products of CoBuDTC in $H_2/N_2$ are also given in Fig. 2. The initial product is a CoS phase having a stoichiometric excess of sulfur. "Cobaltian pentlandite," $Co_9S_8$, forms above 200°C. Subsequent desulfurization of $Co_9S_8$ produces metallic Co and an unidentified cobalt sulfide phase. It is interesting to note that there is no pure Ni analog of pentlandite, $Ni_9S_8$, and the Co analog of heazlewoodite, $Co_3S_2$, is similarly unreported.

Figure 2 also presents the decomposition products of $MoO_2$DiBuDTC in $H_2/N_2$. Near 150°C, the original complex decomposes to yield a second crystalline metal organic compound with a relatively large maximum *d*-spacing of 8.85 Å. This second compound decomposes above 250°C, to yield a very poorly crystalline residue. The XRD pattern of this residue above 300°C consists of broad humps corresponding to the *d*-spacings of molybdenite ($MoS_2$). Therefore, it is very probable that the residue contains $MoS_2$ or consists entirely of $MoS_2$ in a poorly crystalline form. The residue is the color of blue steel, as is $MoS_2$.

Decomposition products of FeDiPrDTC in a reducing atmosphere of $H_2/N_2$ also show a distinct transition from one sulfide to another. An unknown metal-organic complex appears at 150°C in addition to the initial crystalline pattern. At 250°C, it passes mainly to an amorphous phase with marcasite ($FeS_2$) and troilite (FeS) being present. Between 250–350°C, transition to troilite is complete. At temperatures of 450°C and higher, iron starts to form alloys with Pt; mixed Pt/Fe sulfides and troilite are also present.

## *Ligand Dependency of the Decomposition Products:*

The decomposition of NiBuX in $H_2/N_2$ is compared with the decomposition of NiBuDTC in Fig. 3. The results illustrate the ligand dependency of the decomposition products. For reasons as yet unclear, desulfurization of the NiS* product of NiBuX progressed more rapidly and completely than the desulfurization of NiS* from Ni BuDTC as the temperature was raised beyond 250°C. Above 400°C metallic Ni was formed, some of which alloyed with the Pt stage.

## *Combined Magnetic Measurements and Thermogravimetric Analysis*

NiBuDTC and NiEEX were also studied by the technique of Wold and co-workers (13) to determine the tem-

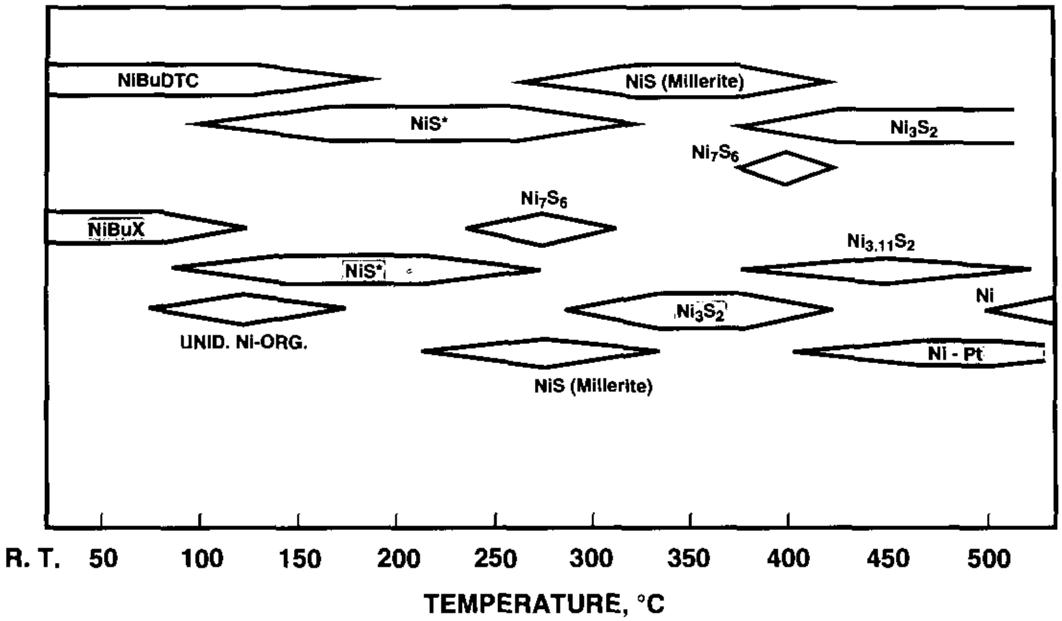

FIG. 3. Comparison of decomposition pattern of NiBuDTC and NiBuX.

perature of Ni° formation. In these experiments, the flow rate of $H_2$ (15%)/Ar was maintained at 50 cm$^3$/min and the heating rate was 30°C/hr. Ni° was detected at 550°C for the NiBuDTC and at 500°C for the NiEEX. XRD examination of both residues showed that the major component was $Ni_3S_2$ (heazlewoodite) with a small amount of Ni° metal (14). No other crystalline solids were detected.

### *Heated Stage XRD in $N_2$ Atmosphere*

The decomposition of DTC and xanthate metal complexes in hydrogen atmosphere and at high temperature leads to the reduction of metal sulfides to give metals. These metals react with Pt to give Pt alloys and Pt–metal–sulfur composites, resulting in the eventual cracking of the Pt strip. In order to avoid these complications thermal decomposition of complexes was studied in pure $N_2$.

TABLE 2

Comparison of Decomposition Products under 7% $H_2/N_2$ and $N_2$

| Compound | Decomposition products at 350°C | |
|---|---|---|
| | 7% $H_2/N_2$ atmosphere | $N_2$ atmosphere |
| NiBuDTC | NiS(millerite) | NiS* + minor unknown + NiS(millerite) |
| NiBu*X* | $Ni_3S_2$ (heazlewoodite) | $Ni_7S_6$ (godlevskite) + $\alpha$ $Ni_7S_6$ + NiS[a] + $NiS_{1.03}$ + $Ni_{2.82}S_2$[b] |
| CoBuDTC | $Co_9S_8$ | Mostly amorphous + minor $Co_9S_8$ |

[a] Poorly characterized form of NiS.

[b] Only product remaining at 450°C under $N_2$ atmosphere.

The decomposition products of NiBuDTC and NiBuX varied depending on whether an atmosphere of $H_2/N_2$ or pure $N_2$ was employed (Table 2). Although the $N_2$ atmosphere was used only at one temperature (to minimize the length of experiments), enough data were obtained to show that the two starting materials produced widely different decomposition products in $H_2$-containing vs $H_2$-free atmospheres. As expected, the use of pure $N_2$ minimized the desulfurization of the initial NiS* product from NiBuX particularly. Decomposition of this compound at 350°C under $H_2/N_2$ atmosphere produced only heazlewoodite. Decomposition of the same material in $N_2$ atmosphere gave several crystalline phases, none having a Ni : S ratio as high as 3 : 2.

Decomposition products of other dithiolato complexes that were studied in pure $N_2$ atmosphere are given in Table 3. An unknown compound crystallized from $MoO_2$DiBuDTC upon heating to 250°C. It is presumed to be another metal-organic compound, an intermediate in the reaction path to $MoS_2$ at 350°C. Decomposition of NiEEX and CoEEX yielded a variety of metal sulfides above 150°C. In the case of NiEEX, the sulfide having the highest metal : sulfur ratio was heazlewoodite, $Ni_3S_2$. However, other sulfides having much lower metal : sulfur ratios were also present. The decomposition of CoDiBu DTC produced five different sulfide phases at 350°C. Among these cobalt sulfides the metal : sulfur ratio ranged from 1 : 2 to 4 : 3. Clearly, this was a nonequili-

TABLE 3

Decomposition Products of Other Thiolato Complexes under $N_2$

| Temperature (°C) | $MoO_2$DiBuDTC | NiEEX | CoEEX | CoDiBuDTC[a] |
|---|---|---|---|---|
| Room (25) | $d_{max} = 13.6$ Å | $d_{max} = 11.8$ Å | $d_{max} = 11.1$ Å | $d_{max} = 11.2$ Å |
| 150 | Amorphous | Amorphous + trace NiS | Amorphous | Same + small amounts of $Co_9S_8 + Co_4S_3 + CoS_2$ |
| 250 | Unknown compound $d_{max} = 16.7$ Å | Major – $NiS_{1.03}$ | $Co_3S_4 + Co_4S_3$ | Minor amounts of $Co_9S_8 + Co_4S_3 + CoS_2$ |
| 350 | Poorly crystalline $MoS_2$ | Minor – $NiS_{1.03} + Ni_3S_2 + Ni_7S_6$ | $Co_4S_3$ | $Co_9S_8 + CoS_{1.04} + Co_3S_4 + Co_4S_3 + CoS_2$ |

[a] It should be emphasized that since several cobalt sulfides have nearly same *d*-spacings these assignments are not absolute.

brium mixture and, given sufficient reaction time at this temperature, further transformation would have produced a simpler assemblage of sulfides with higher metal : sulfur ratios.

## CONCLUSIONS

Thermal decomposition of transition metal dithiolato complexes results in the formation of transition metal sulfides. Comparing our results with those given in the literature, it seems clear that the metal, type of ligands, and atmospheric environment (oxidizing, reducing, or inert) are all important parameters in the formation of the sulfides on thermolysis. Thus the oxides and thiocyanates of metals observed by other investigators were never obtained in this research.

Heated stage XRD is one of the most powerful techniques to study the decomposition products of dithiolato complexes. However, in a reducing environment such as $H_2/N_2$ atmosphere and at high temperatures, decomposition of dithiolato complexes can result in the formation of metals which have a tendency to alloy with the Pt strip. Thus under a reducing environment, only lower (<400°C) temperatures should be used. Our work suggests that by judicious selection of metals, ligands, gaseous environment, and temperature, many desired transition metal sulfides can be prepared.

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