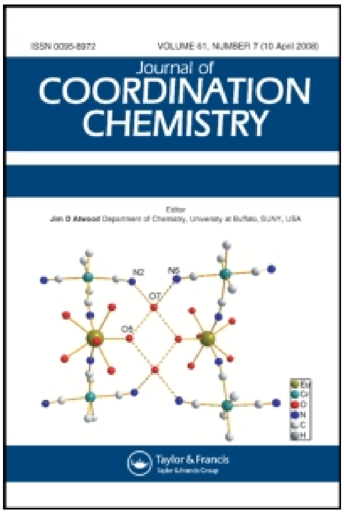

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SOME FIRST ROW TRANSITION METAL COMPLEXES USING THIOSULPHATE AS A LIGAND

James R. Lusty[a]
[a] Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

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SOME FIRST ROW TRANSITION METAL COMPLEXES USING THIOSULPHATE AS A LIGAND

JAMES R. LUSTY

Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

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A range of metal thiosulphate complexes of the type $[ML_nS_2O_3]^{x+}$ has been prepared, where M = Ni(II), Co(II) or Co(III), L = variety of nitrogen ligands. They have been characterised by i.r. and visible spectroscopy and by the measurement of magnetic moments. A complex using 1,2-diamino-2-methyl propane was prepared, $[Ni(mepn)_2S_2O_3]$ which was a diamagnetic square planar complex; on standing it underwent rapid conversion to a distorted octahedral paramagnetic complex. A novel complex $[Co\ py_{2.5}S_2O_3]$ was also prepared and its possible structure is discussed. Thermal analysis was conducted on several complexes.

INTRODUCTION

The thiosulphate group $S_2O_3^{2-}$, has been extensively studied.[1,2] Metal thiosulphate complexes have long been reported especially those of copper[3] and silver.[4] The interest in silver thiosulphate and its complexes probably originates from its use in the photographic industry.[5] Thiosulphate is well known as a reducing agent and most preparations of copper complexes involve the reduction of copper (II) to copper (I) by adding an excess of sodium thiosulphate and precipitating, using a simple sodium or potassium salt, usually the chloride.

Early infrared studies were concerned with simple metal thiosulphates such as sodium and barium,[6,7] or the amine complexes of cobalt thiosulphates.[8,9] A comparison of the infrared spectrum of thiosulphate with other sulphur containing anions has been reported[10] and more recently infrared spectra have been used to distinguish between monodentate and bidentate thiosulphate complexes, and the nature of the donor atom present.[11]

In the present work a range of metal thiosulphates and their complexes were prepared and studied.

EXPERIMENTAL

The compounds are listed with their analytical data in Table I.

(a) Metal thiosulphates

Cobalt, nickel and barium thiosulphates have been prepared. The nickel species decomposed very rapidly, and the cobalt compound was prepared with cobalt sulphide impurities, which proved impossible to separate.

(i) $BaS_2O_3.H_2O$ Sodium thiosulphate (35.5 g) was added to a solution of barium chloride dihydrate (35 g) in water (100 cm^3), and stirred for one hour. The $BaS_2O_3.H_2O$ which precipitated was suction filtered, washed with ice-cold water and 95% ethanol and dried at 40°C. $BaS_2O_3.H_2O$ was made for use in metathetical preparations of other metal thiosulphates and their complexes (1).

$$M(II)SO_4 + BaS_2O_3 \rightarrow M(II)S_2O_3 + BaSO_4 \qquad (1)$$

(ii) $NiS_2O_3.xH_2O$ Barium thiosulphate monohydrate (5 g) was added to a solution of $NiSO_4.7H_2O$ (4.5 g) in water (25 cm^3). The $BaSO_4$ was filtered off and the solution left to evaporate. When the compound had nearly solidified it was dried *in vacuo*, and decomposed as it crystallised out.

(iii) $CoS_2O_36H_2O$ $CoSO_4.7H_2O$ (7 g) was warmed in water (20 cm^3) at 50°C and $BaS_2O_3.H_2O$ (6.7 g) added. The solution was stirred for 30 minutes and filtered. Acetone was added in large excess until the oily layer solidified. The brown-red solid which separated out was filtered and air dried. Decomposition occurred very slowly.

(b) Complexes of metal thiosulphates.

(i) Nickel complexes Ammonia, pyridine and the following amines were used as ligands (abbreviations

TABLE I
Analytical data (%)

Compound	Original colour	Calculated C	H	N	M	S_2O_3	Found C	H	N	M	S_2O_3
$BaS_2O_3.H_2O$	white										
$CoS_2O_3.6H_2O$	red										
$NiS_2O_3.xH_2O$	green										
$[Ni(mepn)_2S_2O_3]$	yellow	27.7	6.96	16.1	16.9	32.6	27.3	7.15	14.5	15.2	32.4
$[Ni(tn)_3]S_2O_3$	purple	27.6	7.70	21.4	14.9	28.5	27.5	8.10	21.5	13.9	28.4
$[Ni(tn)_2S_2O_3]$	grey-blue	22.6	6.32	17.6			22.3	6.30	16 1		
$[Ni(pn)_3]S_2O_3$	lilac	27.6	7.70	21.4	14.9	28.5	26.4	7.25	20.6	13.3	29.6
$[Ni(en)_2S_2O_3].H_2O$	lilac	15.5	5.86	18.1	18.9	36.3	15.6	5.94	17.0	18.0	37.6
$[Ni(en)_3]S_2O_3$	purple	20.6	6.89	23.9	16.7	31.9	20.5	6.91	23.8	16.9	31.6
$[Ni(py)_4S_2O_3]$	blue-green	47.4	4.97	11.8	11.6	20.9	47.3	4.38	10.9	11.2	25.4
$[Ni(NH_3)_5S_2O_3].2H_2O$	blue		6.51	23.9	20.1			6.19	22.9	22.1	
$[Co(NH_3)_6]ClS_2O_3$	orange		5.84	27.2				6.06	27.0		
$[Co(NH_3)_5Cl]S_2O_3.2H_2O$	brown		5.84	21.4				5.90	21.9		
$[Co(NH_3)_5Cl]S_2O_3$	red		5.18	24.0				5.20	24.3		
$[Co(NH_3)_5S_2O_3]Cl$	deep red		5.18	24.0				5.15	26.0		
$[Co(NH_3)_5S_2O_3]_2S_2O_3$	deep red		4.84	22.4				5.04	21.8		
$[Co(en)_2S_2O_3]Br.2H_2O$	brown	11.8	4.9	13.8			10.9	3.9	11.0		
$[Co(py)_{2.5}S_2O_3]_n$	pink	40.7	3.42	9.49			40.8	3.26	8.88		
$[Co(py)_{1.5}S_2O_3]_n.H_2O$	lilac	30.1	2.85	7.03			29.7	2.76	7.36		
$[Co(py)S_2O_3]_n.H_2O$	lilac	23.2	2.33	5.40			21.0	2.37	5.36		

are in parenthesis:

$NH_2CH_2CH_2NH_2$, ethylenediamine (en),
$NH_2CH_2CH(NH_2)CH_3$, 1,2-diaminopropane (pn),
$NH_2CH_2CH_2CH_2NH_2$, 1,3-diaminopropane (tn),
$NH_2CH_2C(NH_2)(CH_3)CH_3$, 1,2-diamino-2-methylpropane (mepn).

To a solution of nickel thiosulphate, the ligands were added in stoichiometric ratio. The complexes were precipitated with ice-cold acetone or methanol and recrystallised in the same manner.

(ii) Cobalt complexes A number of ammine complexes were prepared together with complexes using pyridine and ethylenediamine as ligands.

$[Co(en)_2S_2O_3]Br.2H_2O$ This was prepared by the method of Schlessinger,[12] involving the conversion of dichlorobis(ethylenediamine)cobalt(III) chloride to the carbonatobis(ethylenediamine)cobalt(III)-bromide which on treatment with barium thiosulphate gave the product.

$[Co(NH_3)_6]S_2O_3Cl$, $[Co(NH_3)_5S_2O_3]Cl$, $[Co(NH_3)_5Cl]S_2O_3$, $[Co(NH_3)_5S_2O_3]_2S_2O_3$. These were prepared by the method of Ray.[13] Bis(thiosulphateopentaamminecobalt(III) thiosulphate was prepared by bubbling air through a solution of cobalt(II) hydroxide and ammonium thiosulphate, treated with concentrated ammonia. Recrystallisation was from aqueous ammonia. Hexaamminecobalt(III) thiosulphate chloride and thiosulphateopentaamminecobalt(III) chloride were prepared from a solution of cobalt(II) chloride, ammonium chloride and sodium thiosulphate,treated with concentrated and dilute ammonia respectively and then with a current of air. Chloropentaammine-cobalt(III) thiosulphate was prepared by heating of solution of thiosulphatopentaamminecobalt(III) chloride with a large excess of ammonia, or by adding an excess of sodium thiosulphate to a solution of aquopentaamminecobalt(III) chloride.

$[Co(py)_{2.5}S_2O_3]_{.n}$. Pyridine was added in large excess to a freshly prepared cobalt thiosulphate solution, which was then poured into ice-cold acetone. A pink compound separated out which turned blue-lilac on prolonged standing. A stable lilac compound of formula $[Co(py)_{2.5}S_2O_3]_n$ resulted. On heating other pyridine complexes were prepared. (See later results.)

INSTRUMENTATION

Infrared measurements were made using NaCl, KBr and CsI plates with nujol and hexachlorobutadiene mulls on Perkin Elmer 237, 137 recording spectrophotometers. Reflectance spectra were recorded using Beckmann DK 2A recorder. The Thermal Analysis was conducted on a Stanton

Redcroft thermobalance, model TR fitted with a programmable temperature gradient attachment. Magnetic moments were measured by Gouy method using a Newport Mark II balance.

RESULTS

The reflectance spectra and magnetic moments of the compounds are given in Table II. The infrared spectra of the cobalt and nickel complexes given in Table IV and V respectively. Also included are the spectra of sodium and barium thiosulphate, as these have been shown to contain the ionic thiosulphate group.

DISCUSSION

Electronic properties

In the case of the nickel(II) species the splitting of the bands in the electronic spectra indicated the presence of D_{4h} symmetry. The spectra were assigned thus:

$$
\begin{array}{rl}
{}^3Eg \leftarrow {}^3B_{1g} & \sim 8\ \text{kK} \\
{}^3B_{2g} \leftarrow & \sim 11\ \text{kK} \\
{}^3A_{2g} \leftarrow & \sim 13\ \text{kK} \\
{}^3E_g \leftarrow & \sim 18\ \text{kK} \\
{}^3E_g/{}^3A_{2g} \leftarrow & \sim 27\ \text{kK}
\end{array}
$$

Table II
Electronic spectra and room temperature magnetic moments

Compound	Electronic spectra, kK	μ, BM
$CoS_2O_3.6H_2O$	22.22, 19.80, 19,28ssp, 8.71s, 6.90w	
$Nis_2O_3.xH_2O$	24.80m, 14.70m, 8.81m, 6.74w	
$[Ni(mepn)_2S_2O_3]$	29.81s, 18.62s, 13.11m, 9.71w, 6.49m	2.76
$[Ni(tn)_3]S_2O_3$	29.00s, 18.28s, 11.36s, 7.27w, 6.43m	3.03
$[Ni(tn)_2S_2O_3]$	27.93s, 17.70s, 13.74sh, 8.65s, 7.41sh, 6.56sh	3.26
$[Ni(pn)_3]S_2O_3$	27.93s, 18.87s, 11.75s, 7.27w, 6.47m	2.86
$[Ni(en)_3]S_2O_3$	29.59s, 18.69s, 11.81s, 7.25w, 6.45w	3.09
$[Ni(en)_2S_2O_3].H_2O$	30.03sh, 18.25m, 11.11m, 9.78sh, 7.38w, 6.47m	2.83
$[Ni(py)_4S_2O_3].H_2O$	25.71sh, 15.87s, 9.32m, 8.42sh, 7.34w	2.73
$[Ni(NH_3)_5S_2O_3].2H_2O$	29.41s, 17.76s, 17.30sh, 9.03m, 7.35sh, 6.58m	2.67
$[Co(NH_3)_6]S_2O_3Cl$	21.05s, 14.29sh, 7.94w, 6.90sh, 6.45s	d
$[Co(NH_3)_5Cl]S_2O_3$	22.22, 20.33, 19.23ssp, 8.00w, 6.46m	d
$[Co(NH_3)_5S_2O_3]Cl$	27.00ssp, 19.60s, 18.35s, 10.91w, 8.07w, 6.66s	d
$[Co(NH_3)_5S_2O_3]_2S_2O_3$	19.61s, 11.92sh, 8.21w, 6.47s	d
$[Co(en)_2S_2O_3]Br$	21.98w, 6.85sh, 6.41m	d
$[Co(py)_{2.5}S_2O_3]_n$	18.69, 17.61, 15.85ssp, 7.34bm	4.61

d = diamagnetic

The yellow colour of $[Ni(mepn)_2S_2O_3]$ is indicative of further distortion of D_{4h} symmetry resulting in a diamagnetic complex showing only 1 band in its electronic spectrum. An approximate Dq value for $S_2O_3^{2-}$ was obtained[†] by a comparison of the $[Ni(en)_3]^{2+}$ and $[Ni(en)_2S_2O_3]$ spectra and was found to be 11.6 kK. This would suggest oxygen coordination.

Apart from thiosulphatobis(-1,2-diamino-2-methylpropane)nickel(II) all the magnetic moments for the nickel complexes were consistent with octahedral stereochemistry, with two unpaired electrons, all falling within the range 2.7–3.8 BM.

These complexes showed interesting colour changes during and subsequent to their preparation. $[Ni(mepn)_2S_2O_3]$ changed rapidly from a yellow compound to a purple compound indicating that a rearrangement had occurred (2). This was confirmed by the electronic and infrared spectra

$$
\begin{array}{l}
\text{Ni(II), } D_{4h}\text{, square planar, } \rightleftharpoons \\
\quad \text{diamagnetic yellow} \\
\qquad\qquad \text{Ni(II), } D_{4h}\text{, distorted octahedral,} \\
\qquad\qquad\qquad \text{paramagnetic purple}
\end{array}
\qquad (2)
$$

of the paramagnetic complex on which all determinations were carried out.

The bis(diaminopropane) and bis(ethylenediamine) complexes darkened on standing and eventually decomposed to give black nickel sulphide. Thiosulphatopentaamminenickel(II) was prepared as a light blue complex but gave green nickel hydroxide in the air or on the addition of water.

All the cobalt(III) complexes were octahedral or distorted octahedral and showed two or three main bands in their spectra. These were assigned thus:

$$
\begin{array}{rl}
{}^3T_{1g} \leftarrow {}^1A_{1g} & 13\ \text{kK} \\
{}^3T_{1g}(F) \leftarrow & 21\ \text{kK} \\
{}^1T_{1g}(P) \leftarrow & 29\ \text{kK}
\end{array}
$$

Of particular interest was the dimeric or polymeric cobalt(II) complex, $[Co(py)_{2.5}S_2O_3]_n$ which was

[†] using formula $10\,Dq(S_2O_3{}^{2-}) = 4/6.10\,Dq(en)^a + 2/6.10\,Dq(S_2O_3{}^{2-})^b$
^{a}of Ni $(en)_3{}^{2+}$ ^{b}of Ni $(en)_2S_2O_3$

prepared several times with constant composition. The thermal analysis (numerical results follow) indicated the formulation to be correct, as it lost one mol and one half mol of pyridine in successive steps, to give the complexes $[Co(py)_{1.5}S_2O_3]_n$ and $[Co(py)S_2O_3]_n$ respectively. The colour of the complex changed on standing from pink to lilac. In solution it was pink but small quantities of water absorbed onto the surface gave an intense purple colour. This is unusual for cobalt(II) compounds, hydrated salts being red or pink and containing the octahedrally coordinated cobalt(II) ion. The electronic spectrum (Table II) and magnetic moment showed the complex to be tetrahedral. Two bands, the ${}^4T_1(F) \leftarrow {}^4A_2(F)$ and ${}^4T_1(P) \leftarrow {}^4A_2(F)$ were observed at 7.3 and 17.6 kK respectively. The latter band showed considerable splitting. A further possibility is that the bidentate behaviour sometimes observed in cobalt(II) complexes, giving six coordinate pseudo-tetrahedral complexes, is present here, with thiosulphate occupying two of the octahedral sites. This type of behaviour is well known for cobalt complexes of the type $CoX_3(Ln^+)$ and $CoX_2Y(Ln^+)$ where X = Cl, Br, I; Y = Cl, Br, I; X ≠ Y. A recent publication[14] in which L_n^+ was monoprotonated 1-methyl and 2-methyl piperazine assigned pseudotetrahedral symmetry to all the complexes. Comparing the magnetic moments of the pyridine (4.61 BM) and piperazine complexes (4.40–4.72) it would appear that the contribution to the "spin-only" value, of the $S_2O_3^{2-}$ ion, is similar to that of the Br^- ion. The ligand field strength would thus decrease,

$$I^- < Br^- \sim S_2O_3^{2-} < Cl < NO_3^- \sim SCN \text{ etc.}^{15}$$

It is also worth noting that pseudotetrahedral complexes of nitrate complexes have been reported and it is thus expected that thiosulphate would appear at this position in the spectrochemical series.

Table III

Infrared spectra, barium and sodium thiosulphates. (Free thiosulphate ion)

Assignment	$BaS_2O_3.H_2O$	$Na_2S_2O_3$[a]
ν_{as} asymmetric (S—O)	1120 s	1160 sh
	1100 s	1130 s
stretch	1080 s	
ν_s symmetric (S—O)	998 s	1002 s
stretch	981 s	
δ_s symmetric (S—O)	685 s	680 sh
deformation	668 s	668 s
δ_{as} asymmetric (S–O)	561 s	555 m
	542 s	535 m
deformation	507 s	

[a] reference 11

Infrared Spectra

The free thiosulphate ion, of symmetry C_{3v} has six infrared active modes of vibration. These are symmetric and asymmetric stretching and bending vibrations, a sulfur–sulfur stretch and a rocking mode. Splitting of the free thiosulphate fundamentals can occur in the solid state and this will be greatest for the ν_{as} (S—O) and δ_{as} (S—O) modes. Freedman and Straughan[11] suggested that when sulfur is coordinated the spectra exhibits a lowering of the ν(S–S) and an increase in the ν_{as}(S–O) and ν_s(S–O) frequencies compared to the fundamental frequencies of sodium thiosulphate. Oxygen coordination causes a shift in the opposite direction. The infrared assignments are given in Tables III–V. It can be seen from the spectrum of $[Co(NH_3)_5S_2O_3]Cl$ that the possibility of linkage isomers exists. The ν_{as}(S—O) at 1141 cm^{-1} implies M—S coordination and the two bands below 1000 cm^{-1} suggest M—O coordination. A similar conclusion based on a rigorous kinetic study was reached independently by workers in this field.[9,16] Bis(thiosulphatopentaamminecobalt(III) thiosulphate has both coordinated and ionic thiosulphate present with ν_{as}(S—O) bands occurring at 1150 and 1095 cm^{-1} respectively. The ν_s(S—O) mode was split into two strong bands, δ_s(S—O) into three bands and δ_{as}(S—O) also showed a doublet. While the stretching and asymmetric deformation modes of the NH_3 groups were similar throughout, the symmetric deformations and rocking modes varied, the lower frequency denoting coordination. The spectrum of $[Co(en)_2S_2O_3]Br$ was, like most of the ethylenediamine complexes, difficult to interpret. Bands at 1125 cm^{-1} (ν_{as}(S—O)) and 628 cm^{-1} (δ_s(S—O)) signified thiosulphate coordination, although it was difficult to determine whether it was S- or O-bonded. The broad band at 1125 cm^{-1} could indicate isomeric forms. Indeed recent evidence suggests a mixture of compounds are formed using this method of preparation.[17] The spectrum of $[Co(py)_{2.5}S_2O_3]_n$ suggested both sulfur bridging and M—O coordination. The bridging band at 1192 cm^{-1} was much reduced in $[Co(py)_{1.5}S_2O_3]_n$.

In $[Ni(py)_4S_2O_3]$, $[Ni(tn)_2S_2O_3]$, $[Ni(en)_2S_2O_3]$, $[Ni(mepn)_2S_2O_3]$ and $[Ni(NH_3)_5S_2O_3]$ there was evidence for oxygen and/or bidentate coordination (Table V). The remaining nickel complexes contained only ionic thiosulphate.

TABLE IV

Infrared spectra, cobalt complexes

Assignment	$[RS_2O_3]Cl$	$[RCl]S_2O_3$[a]	$[RCl]S_2O_3$[b]	$[RNH_3]S_2O_3$	$[RS_2O_3]_2S_2O_3$	$[Co(en)_2S_2O_3]Br$	$[Co(py)_{2.5}S_2O_3]_n$	$[Co(py)_{1.5}S_2O_3]_n$
$\nu_{as/s}$ asymmetric and symmetric NH_3 stretch	3100 sb	3140 sb	3150 sb	3150 sb	3200 b			
δ_{as} asymmetric NH_3 deformation	1600 sb	1591 s	1598 s	1600 mb	1603 s			
δ_s symmetric NH_3 deformation	1332 m 1311 w 1294 m 1270 w	1354 w 1311 s	1320 w 1304 m	1352 m 1332 sh 1322 s	1331 s 1318 sh 1292 s			
δ_{as} asymmetric S—O stretch	1141 s	1130 w 1091 s 1070 w	1130 w 1099 s	1101 s	1160 sh 1150 s 1095 s	1125 bs	1192 s 1169 w 1081 s	1190 sh 1118 m 1108 m 1090 sh
ν_s symmetric S—O stretch	996 s 975 sh	978 s	982 s	986 s	993 s 981 s	1008 sh	1002 s	1002 sh
NH_3 rocking	840 sh 825 s	853 s	848 s	863 s	841 s 834 sh			
δ_s symmetric S—O deformation	628 s	647 s	647 s	655 s	645 sh 631 sh 625 s	628 s	655 s 640 s	631 s
δ_{as} asymmetric S—O deformation	533 s	541 s 529 s	534 s	551 s 539 m	538 s 528 s	521 m	530 s 513 s	561 w 531 w
νM—N stretch		491 w	497 w	491 w 451 w	480 w 427 s	460 m		
νS—S stretch	420 s	370 w		380 w	365 sh 360 w			418 w
δN—M—N deformation	320 sb	320 sb		340 sb 325 m	322 w 312 sb			

[a]brown complex; [b] red complex; R = $Co(NH_3)_5$

TABLE V
Infrared spectra, nickel complexes

Assignment	$[Ni(en)_3]S_2O_3$	$[Ni(en)_2S_2O_3]$	$[Ni(tn)_3]S_2O_3$	$[Ni(tn)_2S_2O_3]$	$[Ni(pn)_3]S_2O_3$	$[Ni(mepn)_2S_2O_3]$	$[Ni(py)_4S_2O_3]$	$[RS_2O_3]$
ν(N–H) stretch								3220 bs
δ_{as}asymmetric (NH_3) deformation								1625 sh 1603 s
$\delta_s$symmetric (NH_3) deformation								1250 s 1209 s 1180 s
ν_{as}asymmetric (S–O) stretch	1050 msh					1095 m	1159 s 1101 s	
$\nu_s$symmetric (S–O) stretch	970 sh		986 s	987 s	983 s	992 s	994 w 976 w	992 s 980 s
$\delta_s$symmetric (S–O)				625 sh 612 s	642 s	662 sh 658 s	654 s 640 m	650 s 635 s
δ_{as}asymmetric (S–O) deformation	530 s 520 s	528 w 520 m 505 w	541 sh 530 s	538 s 520 s	531 s 524 m	552 m 521 s	540 bm 520 w	528 s
ν(M–N) stretch								332 m

$R = Ni(NH_3)_5$

$[Co(py)_{2.5}S_2O_3]_n.H_2O$ lilac
calculated loss, 23%
↓ actual loss, 24%
$[Co(py)_{1.5}S_2O_3]_n$ lilac
calculated total loss, 34%
↓ actual loss, 33%
$[Co(py)S_2O_3]_n$ lilac
(CoS_2O_3) red-lilac
↓
decomposition

FIGURE 1 Thermal analysis of $[Co(py)_{2.5}S_2O_3]n$

Thermal Analysis

Thermal analysis was conducted on most of the complexes but was generally ill-defined.

In hydrated thiosulphatopentaamminenickel(II), water and ammonia were expelled (calculated 37.5%, found 38.1%) to give nickel thiosulphate which decomposed to give the mixed nickel oxide, Ni_2O_3. In the hydrated bis-(1,2-diamino-3-methylpropane) complex, water was expelled. This was followed by ligand expulsion and decomposition to the mixed oxide.

Thermal analysis was conducted on $[Co(py)_{2.5}S_2O_3]_n$. The results are given in Figure 1.

Obviously this complex can not be symmetrical and several possibilities exist. Some of which have be been discussed above. It is also possible that a polymeric complex is formed as sulphur's tendencies to form polymers is well known. However the spectral evidence suggests a pseudotetrahedral complex, probably dimeric with thiosulphate occupying two sites of coordination.

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REFERENCES

1. *Gmelins Handbuch der Anorganischen Chemie., 8th Ed., System 9, Schwefel Te. 1 B. Le. f. 2., Weinheim: Verlag Chemie, 1960.*

2. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green and Co., 1930.
3. *For Example*, H. Bassett and R. G. Durant, *J. Chem. Soc.*, **123**, 1279, (1923), D. Ryabachikov and V. S. Pnichenko, *Bull. Acad. Scr. U.S.S.R., Classe Scr. Chim.*, 1974, 19. K. K. Chatterji, *J. Ind. Chem. Soc.*, **35**, 833, (1958).
4. *For Example*, Y. Zil'berman and I. Khmelnitskaya, *J. Gen. Chem. (USSR)*, **11**, 1190, (1941). H. Chateau and J. Pouradier, *Compt. Rend.*, **240**, 1882 (1955). A. R. Dey, *J. Inorg. Nucl. Chem.*, **6**, 71, (1958).
5. *For Example*, H. Baines, *J. Chem. Soc.*, 1929, 2763.
6. F. A. Miller, G. L. Carlson, E. F. Bentley and W. H. Jones, *Spectrochim. Acta*, **16**, 135, (1960).
7. C. Duval and J. Lecompte, *Compt. Rend.*, **262B**, 1000, (1966).
8. E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *J. Amer. Chem. Soc.*, **81**, 3818, (1959).
9. D. E. Peters and R. T. M. Fraser, *J. Amer. Chem. Soc.*, **87**, 2758, (1965).
10. T. Depuis, *Compt. Rend.*, **242**, 2924, (1956).
11. A. N. Freedman and D. P. Straughan, *Spectrochim. Acta*, **27A**, 1455, (1971).
12. G. G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Co., New York, 1962.
13. P. R. Ray, *Quart. J. Ind. Chem. Soc.*, **4**, 64, (1927).
14. G. Marcotrigiano, L. Manabue and G. C. Pellacini, *Inorg. Chim. Acta.*, **26**, 57, (1978).
15. J. Lewis and R. G. Wilkins, *Modern Coordination Chemistry*, Interscience Publications Inc., New York, 1960.
16. J. R. Lusty, Doctorate Thesis, University of London, 1976.
17. Shamay, Cooper and Barto, *J. Inorg. Nucl. Chem.*, **41**, 121, (1979).