# Anhydrous Transition-metal Sulphites. Part II.[1] Preparation of Anhydrous Cobalt(II) and Nickel(II) Sulphates and Pyrosulphates by Oxidation of Anhydrous Cobalt(II) and Nickel(II) Sulphites, using the Mixed Non-aqueous System Dimethyl Sulphoxide–Sulphur Dioxide

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Dimethyl sulphoxide in the presence of sulphur dioxide oxidizes anhydrous cobalt(II) and nickel(II) sulphites to the corresponding pyrosulphates, which are obtained as the crystalline dimethyl sulphoxide complexes, $Co(dmso)_6S_2O_7$ and $Ni(dmso)_6S_2O_7$. Thermal decomposition of the complexes leads to the formation of anhydrous cobalt(II) and nickel(II) pyrosulphates and anhydrous cobalt(II) and nickel(II) sulphates. The constitutions of the products have been investigated by analytical, spectroscopic, and magnetic techniques, and the mechanism of the oxidative process discussed.

A RECENT communication[2] reported the oxidation of anhydrous cobalt(II) and nickel(II) sulphites to the corresponding solvated pyrosulphates, using dimethyl sulphoxide and sulphur dioxide. This paper describes the preparation of anhydrous cobalt(II) and nickel(II) pyrosulphates and sulphates, all of which are obtained by thermal decomposition of the solvated pyrosulphates.

Cobalt(II) sulphite and nickel(II) sulphite, prepared by refluxing the anhydrous metal iodides with tetramethylammonium pyrosulphite in acetone, were treated with a mixture of dimethyl sulphoxide (DMSO) and sulphur dioxide. Both cobalt(II) sulphite and nickel(II) sulphite are insoluble in dimethyl sulphoxide and in liquid sulphur dioxide alone. However, if sulphur dioxide gas is passed through a suspension of cobalt(II) sulphite in dimethyl sulphoxide, the blue solid dissolves to give an orange-red solution, from which a pink crystalline solid can be isolated. Analytical results, i.r. spectra, and chemical tests indicate a solvated pyrosulphate of composition $CoS_2O_7,6DMSO$. When sulphur dioxide gas is passed through a suspension of nickel(II) sulphite in dimethyl sulphoxide, the yellow solid dissolves to give a yellow-green solution, from which a green crystalline solid, $NiS_2O_7,6DMSO$, can be isolated.

These solvated pyrosulphates are very hygroscopic solids. They dissolve readily in water, but, as in the case of the alkali metal pyrosulphates, the pyrosulphate ion is probably hydrolysed to bisulphate. They are quite soluble in dimethyl sulphoxide ($CoS_2O_7,6DMSO > 35$ g $l^{-1}$, $NiS_2O_7,6DMSO > 40$ g $l^{-1}$). The complexes are insoluble in acetonitrile, nitrobenzene, benzene, acetone, and diethyl ether.

Previous work on cobalt(II) and nickel(II) pyrosulphates has been limited to a preparation of nickel pyrosulphate, which was identified as a product from the reaction of sulphur trioxide on nickel trifluoroacetate in trifluoroacetic acid;[3] the analogous reaction with cobalt trifluoroacetate yielded only cobalt sulphate.

The i.r. bands of the complex pyrosulphates are shown in Table 1. The S–O stretching frequency in dimethyl sulphoxide is at 1053 cm$^{-1}$. In the complexes, if the bands at *ca.* 1000 cm$^{-1}$ are assigned to the S–O stretching frequencies, there is a shift of 54 cm$^{-1}$ when dimethyl sulphoxide co-ordinates to cobalt and 53 cm$^{-1}$ when dimethyl sulphoxide co-ordinates to nickel. The shifts, in both cases, are to lower frequencies compared to the free ligand and indicate co-ordination to the metal through oxygen. If the decrease in the strength of the S–O bond is taken as a measure of the increase in the oxygen–metal bond strength, then it would appear that the similarity in S–O stretching frequencies of the two complexes implies comparable bond strengths. Thermogravimetric studies also support this conclusion. The asymmetric C–S stretching frequency is shifted from 697 cm$^{-1}$ in dimethyl sulphoxide to 716 cm$^{-1}$ in both complexes. However, shifts to higher wave numbers are found even when dimethyl sulphoxide is bonded to the metal through sulphur and therefore no significance can be attached to the increase with respect to distinguishing between the two possible modes of co-ordination.

TABLE 1

Infrared bands of cobalt and nickel pyrosulphates (cm$^{-1}$)

| $Co(dmso)_6S_2O_7$ [a] | $CoS_2O_7$ | $Ni(dmso)_6S_2O_7$ [a] | $NiS_2O_7$ | Assignment |
|---|---|---|---|---|
| 430s | 440m | 440s | 440m | DMSO, $S_2O_7^{2-}$ |
| 579s | 570s | 580s | 573s | $S_2O_7^{2-}$ |
| 595sh | 600sh | 596sh | 602sh | |
| 680w | | 680w | | DMSO |
| 716m | | 716m | | |
| 830s | 850s | 835s | 850s | $S_2O_7^{2-}$ |
| 890w | | 890w | | DMSO |
| 902w | | 902w | | |
| 945s | | 942s | | |
| 999s | | 1000s | | |
| 1056s | 1070s | 1056s | 1068s | $S_2O_7^{2-}$ |
| 1152s | 1155s | 1152s | 1155s | |
| 1246s | | 1246s | | |
| 1321s | | 1320s | | DMSO |
| 1405sh | | 1406s | | |

[a] When dimethyl sulphoxide acts as a ligand it is abbreviated to dmso, when free or used as a solvent to DMSO.

Comparisons of the spectra of cobalt and nickel pyrosulphates with the spectrum of anhydrous potassium pyrosulphate and the reported spectrum of sodium pyrosulphate[4] clearly indicate the presence of the pyrosulphate ion. The spectral bands of the complex pyrosulphates in the visible and near i.r. regions are shown in Table 2. The diffuse reflectance spectrum

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[1] Part I, R. Maylor, J. B. Gill, and D. C. Goodall, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1975.

[2] R. Maylor, J. B. Gill, and D. C. Goodall, *Chem. Comm.*, 1971, 671.

[3] G. S. Fujioka and G. H. Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 2451.

[4] A. Simon and H. Wagner, *Z. anorg. Chem.*, 1961, **311**, 102.

and the solution spectrum of the nickel complex are very similar. Comparisons with reported spectra of nickel(II) compounds having known octahedral stereochemistry lead to the conclusion that the nickel is in an essentially octahedral environment. The effect of dissolved sulphur dioxide is negligible, as shown by a comparison of the spectra of $Ni(dmso)_6S_2O_7$ in dimethyl sulphoxide and in a dimethyl sulphoxide–sulphur dioxide mixture. For nickel(II) octahedral complexes, the crystal field splitting parameter, $\Delta_0$, can be obtained directly from the spectrum.[5] From Table 2 it can be seen that the $\Delta_0$ value towards nickel(II) is 7810 $cm^{-1}$. It is usually found that the $\Delta_0$ values in solution are smaller than in the solid,[6] and this is the case for $Ni(dmso)_6S_2O_7$, where $\Delta_0$ (solution) = 7810 and $\Delta_0$ (solid) = 8000 $cm^{-1}$.

TABLE 2

Spectral bands of cobalt and nickel pyrosulphates in the visible and near i.r. region

Diffuse reflectance spectra

| Compound | $\lambda_{max.}/cm^{-1}$ | Assignment |
|---|---|---|
| $Co(dmso)_6S_2O_7$ | 8000 | $^4T_1(F) \longrightarrow {}^4T_2(F)$ |
| | 15,390 | $^4T_1(F) \longrightarrow {}^4A_2(F)$ |
| | 19,220 | $^4T_1(F) \longrightarrow {}^4T_1(P)$ |
| | 20,830 | |
| $CoS_2O_7$ | 7907 | $^4T_1(F) \longrightarrow {}^4T_2(F)$ |
| | 15,160 | $^4T_1(F) \longrightarrow {}^4A_2(F)$ |
| | 19,600 | $^4T_1(F) \longrightarrow {}^4T_1(P)$ |
| | 20,480 | |
| $Ni(dmso)_6S_2O_7$ | 8000 | $^3A_2(F) \longrightarrow {}^3T_2(F)$ |
| | 13,170 | $^3A_2(F) \longrightarrow {}^3T_1(F)$ |
| | 14,290 | $^3A_2(F) \longrightarrow {}^3T_1(F),{}^1E$ |
| | 21,050 | $^3A_2(F) \longrightarrow {}^1T_2$ |
| | 24,240 | $^3A_2(F) \longrightarrow {}^3T_1(P)$ |
| $NiS_2O_7$ | 7770 | $^3A_2(F) \longrightarrow {}^3T_2(F)$ |
| | 12,990 | $^3A_2(F) \longrightarrow {}^3T_1(F)$ |
| | 14,290 | $^3A_2(F) \longrightarrow {}^3T_1(F),{}^1E$ |
| | 23,810 | $^3A_2(F) \longrightarrow {}^3T_1(P)$ |

Dimethyl sulphoxide solution spectra

| Compound | $\frac{\lambda_{max.}}{cm^{-1}}$ | $\varepsilon_{max.}$ [a] | Assignment |
|---|---|---|---|
| $Co(dmso)_6S_2O_7$ | 7250 | 2·33 | $^4T_1(F) \longrightarrow {}^4T_2(F)$ |
| | 14,500 | 0·635 [b] | $^4T_1(F) \longrightarrow {}^4A_2(F)$ |
| | 18,690 | 11·30 [b] | $^4T_1(F) \longrightarrow {}^4T_1(P)$ |
| | 20,830 | 5·70 [b] | |
| $Ni(dmso)_6S_2O_7$ | 7810 [c] | 3·48 | $^3A_2(F) \longrightarrow {}^3T_2(F)$ |
| | 12,940 | 3·58 [b] | $^3A_2(F) \longrightarrow {}^3T_1(F)$ |
| | 14,390 | 2·48 [b] | $^3A_2(F) \longrightarrow {}^3T_1(F),{}^1E$ |
| | 20,830 | 1·06 [b] | $^3A_2(F) \longrightarrow {}^1T_2$ |
| | 24,100 | 10·11 | $^3A_2(F) \longrightarrow {}^3T_1(P)$ |

[a] $\varepsilon$ Given in l $mol^{-1}$ $cm^{-1}$. [b] Apparent extinction coefficient. [c] Equivalent to $\Delta_0$, the crystal field splitting parameter.

The diffuse relectance spectrum and the solution spectrum of the cobalt complex are very similar. Comparisons with the reported spectra of cobalt(II) compounds having known octahedral stereochemistry indicate that the cobalt is in an essentially octahedral environment. There is a small difference between the solid state spectrum and the spectrum in dimethyl sulphoxide solution, and this would seem to indicate a certain amount of distortion of the octahedral arrangement of six dimethyl sulphoxide molecules around the cobalt in the solid state. As with the solution spectrum for the nickel complex, there is no evidence to suggest that the presence of dissolved sulphur dioxide alters the spectrum in any way.

Conductivity measurements were undertaken on dimethyl sulphoxide solutions of the complexes. The molar conductivities of the complexes were, respectively, 76·5 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ for $Co(dmso)_6S_2O_7$, and 77·2 $\Omega^{-1}$ $cm^{-2}$ $mol^{-1}$ for $Ni(dmso)_6S_2O_7$. These values indicate the presence of the ions $M(dmso)_6{}^{2+}$ and $S_2O_7{}^{2-}$.

Room-temperature magnetic moments for the complexes are shown in Table 3, along with values for the Weiss constant, $\theta$. Both complexes have $\mu_{eff.}$ and $\theta$ values which are consistent with the metal ion being in an octahedral environment.

TABLE 3

Magnetic measurements on the dimethyl sulphoxide complexes

| Complex | $\mu_{eff.}$/B.M. | $T$/K | $\theta$/K |
|---|---|---|---|
| $Co(dmso)_6S_2O_7$ | 4·78 | 301 | 9·5 |
| $Ni(dmso)_6S_2O_7$ | 3·21 | 299 | 2 |

It is important to consider the steps involved in the oxidation of sulphite to pyrosulphate. As one of the products of the reaction is dimethyl sulphide, the dimethyl sulphoxide is clearly acting as an oxidizing agent and not merely as an inert solvent. Although no case seems to have been reported where dimethyl sulphoxide has oxidized an inorganic anion, the oxidizing properties of dimethyl sulphoxide have been used in organic chemistry for some time. Except possibly at very high temperatures, dimethyl sulphoxide cannot oxidize cobalt sulphite in the absence of sulphur dioxide. Solutions of cobalt sulphite in dimethyl sulphoxide, prepared by heating to 140°, contain little, if any, cobalt sulphate, and a compound of formula $CoSO_3$,2DMSO, established by analysis, can be isolated from the solution. I.r. studies and chemical tests confirm that this compound is a sulphite. Similarly, the undissolved residue, left from the preparation of the cobalt sulphite solution, is mostly unchanged cobalt sulphite.

When sulphur dioxide is passed into a suspension of anhydrous cobalt sulphate (prepared by heating the heptahydrate at 400°) in dimethyl sulphoxide, some of the solid dissolves, forming a pink solution. When this solution was filtered, and diethyl ether added to the filtrate, pink crystals of $Co(dmso)_6S_2O_7$ were obtained.

Anhydrous sodium sulphite is not oxidized to sodium pyrosulphate by dimethyl sulphoxide and sulphur dioxide. When sulphur dioxide was passed through a suspension of sodium sulphite in dimethyl sulphoxide, the solid did not dissolve, and i.r. studies and chemical tests indicated that most of the sodium sulphite had been converted to sodium pyrosulphite. These results suggest that pyrosulphite is a likely intermediate in the conversion of $MSO_3$ (M = Co or Ni) to $MS_2O_7$, and that the nature of the metal has a profound effect on the course of the reaction.

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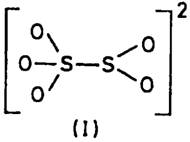
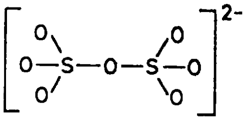
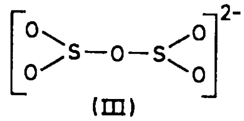
C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.*, 1955, **29**, No. 8.

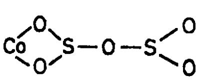
[6] P. van Leeuwen and W. L. Groeneveld, *Rec. Trav. chim.* 1967, **86**, 1219.

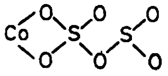
Sulphite and sulphur dioxide readily form pyrosulphite, in which sulphur dioxide acts as an electron acceptor, *i.e.* $^{2-}O_3S\colon \longrightarrow SO_2$. Thus, the presence of sulphur dioxide in the dimethyl sulphoxide would be expected to promote pyrosulphite formation, and the isolation of sodium pyrosulphite from the suspension of sodium sulphite in the dimethyl sulphoxide–sulphur dioxide solvent mixture is evidence for this. However, the structures of the pyrosulphite ion (I) [7,8] and the pyrosulphate ion (II) [9] are known, and are quite different:


(I)


(II)

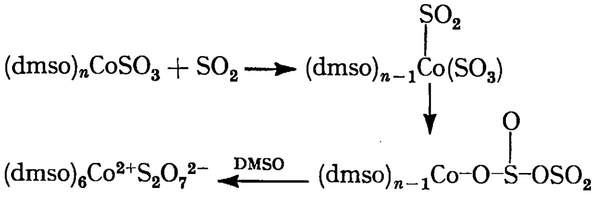

(III)


(IV)


(V)

The formation of pyrosulphate by the oxidation of the pyrosulphite ion of $C_s$ symmetry would involve breaking the S–S linkage. Although this is possible, further difficulties arise when postulating a mechanism to account for the formation of pyrosulphate from cobalt sulphate, and in this case the only suitable intermediate species would be one with an S–O–S linkage. A more likely explanation of the oxidation is possible if an intermediate pyrosulphite species with an S–O–S linkage (III) is considered to be formed. Although a pyrosulphite structure with an S–O–S linkage has been shown to be incorrect for the free anion,[10] the presence of free pyrosulphite ions in the dimethyl sulphoxide solution is not necessary for any postulated mechanism. Thus a transitionary pyrosulphite of cobalt or nickel could have an S–O–S linkage if there was a large measure of covalent bonding between the pyrosulphite and the metal. Such an intermediate (IV) could be formed where a sulphur dioxide molecule has acted as an acceptor and the cobalt sulphite as a donor species. This intermediate is then oxidized by two dimethyl sulphoxide molecules to form the pyrosulphate. With this mechanism, the observed conversion of cobalt sulphate to pyrosulphate is also easily explained and no rearrangements need be postulated; an intermediate (V) could be formed, where once again a sulphur dioxide molecule acts as an acceptor. This intermediate only requires to be oxidized by one dimethyl sulphoxide molecule to give the pyrosulphate, compared with two dimethyl sulphoxide molecules for anhydrous cobalt or nickel sulphites. The involvement of a pyrosulphite intermediate having an S–O–S linkage in the oxidative process seems all the more likely, since sodium sulphite cannot be converted beyond the pyrosulphite stage. Presumably this is because it contains pyrosulphite having the S–S linkage, which apparently resists oxidation by dimethyl sulphoxide.

Another possible mechanism for the oxidation of sulphite to pyrosulphate is that which involves insertion of sulphur dioxide between the transition metal and sulphite. The compound of formula $CoSO_3,2DMSO$ formed when cobalt sulphite dissolves in dimethyl sulphoxide, is thought, from examination of its i.r. spectrum, to contain sulphite as a bidentate group in the inner co-ordination sphere. A possible reaction of solvated cobalt sulphite with sulphur dioxide may occur as follows:



$$(dmso)_nCoSO_3 + SO_2 \longrightarrow (dmso)_{n-1}\overset{\displaystyle SO_2}{\overset{|}{Co}}(SO_3)$$

$$\downarrow$$

$$(dmso)_6Co^{2+}S_2O_7^{2-} \xleftarrow{\text{DMSO}} (dmso)_{n-1}Co\text{–}O\text{–}\overset{\displaystyle O}{\overset{|}{S}}\text{–}OSO_2$$

This mechanism is thought to be less likely than the mechanism first suggested, since it involves replacement of bidentate sulphite with monodentate sulphur dioxide.

The thermal decomposition of $Co(dmso)_6S_2O_7$ and $Ni(dmso)_6S_2O_7$ has been studied up to 1000°. The thermograms are very similar. Decomposition to unsolvated metal sulphate proceeds with the intermediate formation of the unsolvated metal pyrosulphate. The existence of these intermediates has been confirmed by analysis and spectral studies. $Co(dmso)_6S_2O_7$ begins to lose dimethyl sulphoxide at 160°, and at 270°, $CoS_2O_7$ is obtained. No evidence was obtained for any intermediate dimethyl sulphoxide complexes. Further heating results in the loss of sulphur trioxide, and cobalt sulphate exists from 320 to 730°. Further heating leads to the formation of cobalt oxide. The decomposition temperature for cobalt sulphate is identical to the temperature indicated on a thermogram of $CoSO_4,7H_2O$.

$Ni(dmso)_6S_2O_7$ begins to lose dimethyl sulphoxide at 150°, and at 250°, $NiS_2O_7$ is obtained. No evidence was obtained for any intermediate dimethyl sulphoxide complexes. Further heating results in the loss of sulphur trioxide, and nickel sulphate exists from 320 to 740°. Further heating leads to the formation of nickel oxide.

The anhydrous pyrosulphates are very hygroscopic. The cobalt compound is obtained as a purple-pink amorphous solid, and the nickel compound as a pale green amorphous solid. The i.r. bands for anhydrous cobalt and nickel pyrosulphates are given in Table 1, and the diffuse reflectance spectra in Table 2. The i.r. spectra indicate the presence of the pyrosulphate ion. The spectra of the two compounds in the visible

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[7] S. Zachariasen, *Phys. Rev.*, 1932, **40**, 113, 923.

[8] I. Lindqvist and M. Mörtsell, *Acta Cryst.*, 1957, **10**, 406.

[9] H. Lynton and M. R. Truter, *J. Chem. Soc.*, 1960, 5112.

[10] A. W. Herlinger and T. V. Long, *Inorg. Chem.*, 1969, **8**, 2661.

region suggest that the metal is surrounded octahedrally by oxygen atoms in the pyrosulphate group. The situation is probably similar to that which exists for the anhydrous metal sulphates.

## EXPERIMENTAL

All operations were carried out in a closed system under dry nitrogen. Nitrogen was dried by passing the gas through concentrated sulphuric acid. Sulphur dioxide was dried by passing the gas through concentrated sulphuric acid and phosphorus(V) oxide. Filtrations were carried out under a nitrogen stream, using a sinter-tube. Anhydrous cobalt(II) sulphite was prepared as described elsewhere.[1] Anhydrous nickel(II) sulphite was prepared in a similar way starting from anhydrous nickel(II) iodide. The same difficulties were experienced in the purification. Sublimation proved to be of no value as a method of purification, since the yellow amorphous compound is involatile, and decomposes to form nickel oxide at high temperatures. However, it is not necessary to use the pure sulphites for the subsequent oxidation with dimethyl sulphoxide.

$Co(dmso)_6S_2O_7$.—Cobalt(II) sulphite (2·0 g) was added to freshly distilled dimethyl sulphoxide (60 ml) and sulphur dioxide passed through the suspension for 10 min. The orange-red solution was filtered and ether (60 ml) added to the filtrate. A pink crystalline solid precipitated. After 1 h the product was filtered off, washed with diethyl ether (5 × 20 ml), and pumped for 4 h (Found: C, 20·45; H, 5·3; Co, 8·3; Calc. for $C_{12}H_{36}O_{13}S_8Co$: C, 20·45; H, 5·15; Co, 8·35%).

$Ni(dmso)_6S_2O_7$.—Nickel(II) sulphite (1·8 g) was added to freshly distilled dimethyl sulphoxide (100 ml), and the method described above for the corresponding cobalt complex followed. The green crystalline solid obtained was pumped for 3 h (Found: C, 20·3; H, 5·3; Ni, 8·3. Calc. for $C_{12}H_{36}O_{13}S_8Ni$: C, 20·45; H, 5·15; Ni, 8·35%).

$CoS_2O_7$.—$Co(dmso)_6S_2O_7$ (1·28 g) was heated to 275—280° on a Stanton thermogravimetric balance, in an atmosphere of dry nitrogen. The pink residue (0·40 g) was transferred immediately to a dry-bag filled with nitrogen (Found: S, 27·0; Co, 25·5. Calc. for $O_7S_2Co$: S, 27·25; Co, 25·1%).

$NiS_2O_7$.—$Ni(dmso)_6S_2O_7$ (1·41 g) was heated to 245—255° on a Stanton thermogravimetric balance, in an atmosphere of dry nitrogen. The pale green residue (0·42 g) was transferred immediately to a dry-bag filled with nitrogen (Found: S, 26·9; Ni, 24·85. Calc. for $O_7S_2Ni$: S, 27·25; Ni, 25·1%).

$CoSO_3$,2DMSO.—Cobalt(II) sulphite (0·1 g) was suspended in freshly distilled dimethyl sulphoxide (100 ml), and the suspension heated to 140°. A purple solution was obtained. The cooled solution was filtered, and diethyl ether added to the filtrate. A light blue amorphous solid precipitated (Found: C, 15·75; H, 3·7; Co, 20·3. Calc. for $C_4H_{12}O_5S_3Co$: C, 16·25; H, 4·05; Co, 20·0%). The i.r. spectrum and chemical tests confirmed the presence of sulphite.

*Physical Measurements*.—I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer as Nujol mulls. Since the compounds handled were moisture-sensitive, the mulls were prepared by grinding the solids finely and mixing them with sodium-dried Nujol in a dry-bag. The mull was placed between potassium bromide discs, and a lead washer (0·05 mm thickness) used to provide a seal to exclude atmospheric moisture.

Spectra in the visible and u.v. region were recorded on a Unicam SP 700 spectrophotometer. Solutions were prepared, and the cells filled, under dry nitrogen. Diffuse reflectance spectra were obtained by using an SP 735 diffuse reflectance attachment.

Magnetic measurements were carried out using a Gouy balance. Thermogravimetric curves were obtained using a Stanton thermobalance.

*Analysis*.—Cobalt was determined spectrophotometrically as tetrachlorocobalt(II). Nickel was determined gravimetrically as dimethylglyoximatonickel(II). C, H, N, and S were determined by Mr. A. Hedley of this department.

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