tals with the decrease in oxidation state and the intensity decrease is consistent with a decreased porphyrin π character in the dπ metal orbital. This results from a decreased metal–porphyrin π interaction in manganese(II) over manganese(III). It is interesting to note the enhanced intensity and sharpening of the visible absorption bands when going from manganese(III) to manganese(II). This is consistent with the notion that there is considerable charge-transfer character in the bands of manganese(III) but very little for manganese(II). Although it may be coincidental, band IV of the manganese(III) derivatives appears at exactly the same frequency as the β band of the manganese(II) complex. Substituting one porphyrin for another produces shifts in all the band frequencies. The order of the band position agrees with that observed for other divalent metalloporphyrins[26] and also for manganese(III) porphyrins.[11] The redox potentials for the first and second porphyrin reduction also parallel the spectral order. This is undoubtedly related to the identity of the substituents on the porphyrin macrocycle. Electron-donating alkyl groups increase the electron density in the ring and it is more difficult to add on another electron during reduction. This accounts for the increase in $-E_{1/2}$ of 0.29 V in going from the β-hydrogen substituents of tetraphenylporphine to the alkyl substituents of etioporphyrin I. The exocyclic ring and the reduction of ring IV in methyl pheophorbide$_a$ also lower the redox potential.[23]

The normal visible spectrum of manganese(II) porphyrins in contrast to the unusual nature of the spectrum of manganese(III) porphyrins implies that the special interaction (and/or geometry) of the latter is not present in the former. Manganese(II) is a high-spin d^5 case with symmetrically half-filled d orbitals. The fact that the d$_{x^2-y^2}$ orbital is singly occupied in these materials is consistent with the notion that the metal is out of the plane of the porphyrin. Indirect evidence for this is the result of molecular orbital calculations which show that a planar configuration would give rise to an intermediate spin state for manganese(II).[32] More to the point, it is known that the isoelectronic iron(III) porphyrins adopt a nonplanar configuration when the metal is in the high-spin state.[33] The marked instability of the manganese(II) porphyrins to dissociation in aqueous solution[20] is consistent with a structure in which the manganese metal is considerably out of the plane of the porphyrin. In this configuration the porphyrin retains a high negative charge and the metal retains a high positive charge.[32] The high potential of the manganese(II) porphyrin ligand reductions is consistent with this description. Further, the relatively strong binding of an axial ligand (more strongly bound than to manganese(III)) is in line with the relatively high positive charge on the metal.[7] The strong axial interaction is also displayed in the esr spectra of manganese(II) porphyrins which show a relatively low zero-field parameter.[22] This can be interpreted as due to axial interactions which are comparable in magnitude to the porphyrin interaction.

Acknowledgment.—Acknowledgment is made to the National Science Foundation for partial support of this research. The authors wish to express their gratitude to Professor T. Yonetani, University of Pennsylvania, and Professor Martin Gouterman, University of Washington, for supplying their papers prior to publication.

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Iodonium Salts of Complex Anions. III.[1] Isolation and Reactions of Diphenyliodonium Tris(*N*-cyanodithiocarbimato)cobalt(III)

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Received February 5, 1970

Isolation and reactions of diphenyliodonium tris(*N*-cyanodithiocarbimato)cobalt(III), $(dpi)_3[Co(cdc)_3]$ (I) have been carried out. Pyrolysis reactions of I show that the reactive sites in the anion are the coordinated sulfur atoms of the same ligand. Partial reduction of the metal ion to the bivalent state and liberation of iodobenzene and phenyl disulfide occur simultaneously. In pyridine solution also ligand phenylation occurs; however, arylated ligand decomposes under these reaction conditions. Nonarylated ligand dissociates into thiocyanate and reduction of metal ion to cobalt(II) also occurs in the pyridine reaction. From this solution $Co(py)_4(NCS)_2$ has been isolated; this complex has been converted into the corresponding *o*-phenanthroline and α,α'-dipyridyl complexes. The electronic spectra of the compounds have been recorded.

Introduction

Recently studies of the reactions of chelated ligands have assumed a place of considerable interest in the field of coordination chemistry.[2,3] Almost all the reactions studied make use of an external reagent and a suitable complex under specific conditions. The di-

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phenyliodonium (dpi) salts of complex anions possess the inherent property of undergoing a new class of ligand reactions both in the solid state at their decomposition temperature and in solution.

In this paper we report the synthesis of diphenyliodonium tris(*N*-cyanodithiocarbimato)cobalt(III) and a study of its autoarylation both in the solid state and in solution.

Experimental Section

Chemicals.—Cyanamide (50% aqueous solution, American Cyanamid Co.), phenyl disulfide (mp 60°, Eastman Organic Chemicals, Rochester, N. Y.), iodobenzene (Matheson Coleman and Bell, East Rutherford, N. J.), and α,α'-dipyridyl and *o*-phenanthroline monohydrate (Aldrich Chemical Co., Milwaukee, Wis.) were purchased and used directly without purification. All other chemicals were of reagent grade.

Diphenyliodonium chloride[4] (dpiCl), $Na_3[Co(CO_3)_3]\cdot 3H_2O$,[5] and solutions containing diprotic *N*-cyanodithiocarbimate ions[1,6] (cyanodithioimidocarbonate ions) were prepared by procedures given in the literature.

Diphenyliodonium Tris(*N*-cyanodithiocarbimato)cobalt(III), $(dpi)_3[Co(cdc)_3]$ (I).—To a suspension of 1.81 g of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (5 mmol) in 15 ml of water, 9 ml of solution containing cdc^{2-} ions was added. The dark green mixture was heated on a steam bath for 15 min. The contents of the beaker were brought to room temperature, cooled in ice for 15 min, and filtered to remove a small amount of brown residue. Then the filtrate was added to a solution of 4.75 g of dpiCl (15 mmol) in 450 ml of water at 40°. A green product separated immediately. After complete addition maintaining the temperature the mixture was stirred for 2–3 min (for coagulation), the green product was allowed to settle, and the colorless supernatant liquid was decanted. The product was transferred to a filter, washed thoroughly with water at 40°, and air dried in diffused light; yield 4.35 g (69.6%) of I. *Anal.* Calcd for $C_{42}H_{30}I_3N_6S_6Co$: C, 40.34; H, 2.40; N, 6.72; S, 15.39. Found: C, 40.15; H, 2.28; N, 6.70; S, 15.22.

The photosensitive product decomposes on heating in a melting point tube at 72°. It is soluble in methanol, acetone, chloroform, nitromethane, acetonitrile, py, DMF, and DMSO. When a yellowish green acetone solution of the dpi salt and sodium iodide are mixed, the relatively insoluble dpiI precipitates, confirming the presence of the dpi ion.

Infrared spectrum: 3010 (w), 2400 (vw, br), 2140 (vs), 1640 (w, br), 1575 (w), 1552 (w), 1462 (m), 1433 (s), 1418 (sh), 1405 (sh), 1398 (sh), 1380 (vs), 1364 (sh), 1318 (sh), 1272 (vw), 1170 (w, br), 1150 (w), 1082 (vw), 1056 (vw), 1025 (w), 986 (sh), 981 (s), 738 (sh), 732 (sh), 728 (s), 673 (m), 642 (m), 620 (w), 567 (m), 525 (m), 462 (s), 438 (m), 376 (m, br), 348 cm^{-1} (m, br).

Electronic spectrum (mineral oil mull): 9663, 10,410, 15,380 (sh), 22,220, 26,670 (sh), 41,110, 42,680, 49,850 cm^{-1}.

Pyrolysis Reactions.—The procedure adopted was the same as that employed in earlier work.[1] About 2 g of I was heated at 72–80° for several days under reduced pressure until the sample lost weight equivalent to 3 mol of iodobenzene. A product (II) having a darker green shade than the parent complex was obtained. Elemental analysis of II obtained from two separate reactions indicated triarylation to have occurred. *Anal.* Calcd for $C_{24}H_{15}N_6S_6Co$: C, 45.12; H, 2.37; N, 13.16; S, 30.20; Co, 9.23. Found for II: C, 42.14, 41.31; H, 2.31, 2.33; N, 12.46, 12.02; S, 27.46, 27.41; Co, 8.75.

The products which distilled off had the same characteristics and composition as observed[1] in the pyrolysis of the nickel complex; iodobenzene and phenyl disulfide were isolated and identified. *N*-Cyanodiphenyldithiocarbimate (cddc) is absent in the distillate.

Electronic spectrum of II (mineral oil mull): 10,330, 10,720 (sh), 14,190 (sh), 16,330 (sh), 23,020, 41,620 cm^{-1}.

Infrared spectrum of II: 2195 (sh), 2150 (vs), 2050 (w), 1610 (w), 1570 (w), 1460 (s), 1430 (vs), 1390 (vs), 1200 (w), 1170 (w), 1150 (w), 1080 (w), 1060 (w), 1015 (w), 980 (m), 965 (sh), 740 (m), 730 (m), 705 (w), 680 cm^{-1} (m).

Isolation of *N*-Cyanodiphenyldithiocarbimate (cddc).—A stirred suspension of 1 g of II in 60 ml of acetone was boiled for 5 min; during this time about 30 ml of solvent evaporated. The mixture was filtered hot to remove a major greenish brown residue from a dark green filtrate. To the filtrate water was added to produce a permanent cloudiness. On cooling, a solid formed which was recrystallized from acetone–water mixture to obtain white needles of cddc; yield 100 mg; mp 121°. This compound is identical with that characterized earlier.[1]

Reaction of I with Pyridine.—A dark green solution of I in pyridine (5 g in 50 ml) was heated at 72° with stirring. After 16 hr the mixture became brownish red. Heating was continued for a total period of 24 hr. The mixture was filtered; thin layer chromatography of the filtrate indicated that in addition to at least four other components it contained phenyl disulfide in major portion. The filtrate was concentrated (45°) to 10 ml when brownish red crystals started separating. Only pyridine was found to be removed during this concentration. The contents of the flask were cooled in an ice bath for 1 hr, collected by filtration, and washed with ethanol followed by ether and vacuum dried over P_4O_{10}; yield 1.90 g. This complex was identified as *trans*-$Co(py)_4(NCS)_2$. *Anal.* Calcd for $C_{22}H_{20}N_6S_2CO$: C, 53.75; H, 4.10; N, 17.10; S, 13.02; Co, 11.99. Found: C, 53.75; H, 3.97; N, 17.13; S, 13.10; Co, 12.03.

Infrared spectrum: 2052 (vs), 1660 (vw), 1630 (w), 1582 (s), 1566 (w), 1472 (m), 1428 (s), 1342 (vw), 1303 (m), 1232 (w), 1209 (w), 1196 (vw), 1148 (sh), 1142 (w), 1064 (s), 1038 (s), 1032 (s), 1012 (w), 993 (w), 965 (w), 957 (w), 947 (w), 883 (w), 801 (m), 764 (vw), 753 (s), 711 (vw), 697 (vs), 644 (m), 617 (s), 477 (s), 427 (s), 418 (s), 396 cm^{-1} (w).

X-Ray powder pattern (*d* values in Å): 8.50 (vs), 7.34 (m), 6.97 (m), 4.50 (m), 4.43 (m), 4.09 (m), 3.97 (m), 3.91 (s), 3.85 (m), 3.62 (s).

At times the complex is contaminated by an olive green product. In such cases recrystallization from water afforded pure pink $Co(py)_4(NCS)_2$, identical with the authentic compound.

The reddish brown filtrate was added to 125 ml of benzene and stirred for 0.5 hr to obtain a yellow product. It was washed with benzene and ether and vacuum dried over P_4O_{10}; yield 0.39 g. After sublimation this was identified as pyridinium thiocyanate, mp 97–98.5° (lit.[7] mp 99.5–101°). *Anal.* Calcd for $C_6H_6N_2S$: C, 52.14; H, 4.38; N, 20.28; S, 23.20. Found: C, 52.52; H, 4.23; N, 20.01; S, 23.37.

From the benzene filtrate pyridine was removed by repeatedly washing with water (four 40-ml portions). The resulting solution was filtered and dried over Na_2SO_4. Benzene was removed at room temperature and the remaining reddish brown liquid was found to contain iodobenzene and phenyl disulfide.

In order to determine whether phenylation of py occurs, 12.50 g of I in 30 ml of pyridine was treated as above. There was no formation of phenylpyridine picrates on adding picric acid to a hot alcoholic (50 ml) extract of the benzene oil. In the reaction phenylation of pyridine does not take place.[8]

Authentic *trans*-Bis(thiocyanato)(tetrapyridine)cobalt(II).—The complex was prepared according to the method of Logan,[9] *et al.*, with modifications. To an aqueous solution of $CoCl_2\cdot 6H_2O$ (9.52 g in 150 ml), KSCN was added (7.68 g). Pyridine

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[8] However, in the same fashion a mixture of isomeric 2-, 3-, and 4-phenylpyridine picrates has been isolated from the reaction of $(dpi)_2[Ni(cdc)_2]$ with pyridine.

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(13 ml, slightly more than equivalent) was added with stirring. The rose-colored product which separated was extracted with chloroform (200 ml) and the chloroform was dried over Na_2SO_4. Evaporation of the solution yielded the product which was air-dried for 1 week; yield 16.0 g (81.2%).

Reaction of II with Pyridine.—In order to learn more about the pyrolysis product, II, it was dissolved in the minimum quantity of hot pyridine, treated with decolorizing charcoal, and precipitated by the addition of 3 volumes of chlorobenzene. After repeating this procedure the infrared spectrum of the dark green product showed only the $-C{\equiv}N$ mode for cdc and none of that for thiocyanate. This compound could not be purified to constant composition but it approximated $Co(cdc)(py)_2$. *Anal.* Calcd for $C_{12}H_{10}N_4S_2Co$: C, 43.3; H, 3.03; N, 16.8; S, 19.3. Found: C, 41.89; H, 2.79; N, 17.52; S, 18.22.

The addition of K_2cdc to an aqueous pyridine solution of cobalt chloride gave a similar material. This experiment demonstrates the presence of cdc in pyrolyzed compound II.

Preparation of $Co(dipy)_2(NCS)_2$ and $Co(o\text{-}phen)_2(NCS)_2$.—In our early attempts to determine if $Co(py)_4(NCS)_2$ was a thiocyanato or cdc complex we treated this compound with several other ligands, including α,α'-dipyridyl and *o*-phenanthroline. These complexes were prepared by adding methanol solutions of α,α'-dipyridyl or *o*-phenanthroline to a methanol solution of $Co(py)_4(NCS)_2$. The *o*-phen complex was recrystallized from hot dimethyl sulfoxide. *Anal.* Calcd for $C_{26}H_{16}N_6S_2Co$ [$Co(o\text{-}phen)_2(NCS)_2$]: C, 58.32; H, 3.01; N, 15.70; S, 11.98. Found: C, 57.49; H, 3.17; N, 15.52; S, 12.85.

Infrared spectrum: 2064 (sh), 2040 (vs), 1616 (w), 1570 (w, br), 1501 (s), 1481 (s), 1414 (s), 1402 (s), 1392 (vw), 1330 (w), 1308 (w), 1298 (vw), 1220 (w), 1204 (vw), 1140 (sh), 1134 (w), 1098 (w), 1088 (w), 1046 (vw), 1010 (vw), 988 (vw), 963 (sh), 960 (w, br), 864 (m), 845 (vs), 800 (w), 762 (m), 723 (vs), 632 (s), 507 (w), 492 (w), 475 (m), 469 (m), 430 (w), 417 cm^{-1} (m).

X-Ray powder pattern (*d* values in Å): 8.61 (s), 7.90 (s), 7.19 (s), 5.85 (w), 5.00 (w), 4.67 (s), 4.11 (w), 3.99 (w), 3.89 (m), 3.80 (vs), 3.65 (vw), 3.41 (w), 3.29 (m), 3.23 (w), 3.18 (m), 3.07 (w), 2.74 (w), 2.60 (w), 2.54 (vw), 2.51 (vw), 2.17 cm^{-1} (w).

Anal. Calcd for $C_{22}H_{16}N_6S_2Co$ [$Co(dipy)_2(NCS)_2$]: C, 54.20; H, 3.31; N, 17.25; S, 13.16. Found: C, 53.50; H, 3.23; N, 17.20; S, 13.54.

Infrared spectrum: 2900 (w), 2040 (vs), 2033 (sh), 1590 (s), 1575 (m), 1552 (m), 1480 (m), 1460 (s), 1428 (vs), 1420 (sh), 1404 (vw), 1303 (m), 1243 (m), 1210 (w), 1172 (sh), 1162 (w), 1152 (w, br), 1111 (vw), 1098 (w), 1068 (vw), 1053 (w), 1036 (w), 1014 (m), 975 (vw), 955 (w, br), 896 (w), 810 (vw), 797 (m), 772 (sh), 763 (vw), 757 (sh), 733 (s), 644 (s), 621 (m), 472 (m), 432 (w), 411 cm^{-1} (vs).

X-Ray powder pattern (*d* values in Å): 8.34 (s), 7.90 (s), 6.85 (s), 5.76 (s), 4.42 (s), 4.33 (m), 3.92 (vs), 3.75 (m), 3.75 (m), 3.48 (s), 3.23 (w), 3.13 (w).

Thin Layer Chromatography.—Chromatograms were run on glass plates coated with silica gel GF-254.

Physical Measurements.—Infrared spectra of the solid samples were scanned on a Perkin-Elmer Infracord Model 137 as Nujol and Halocarbon mulls (unless stated otherwise) between NaCl plates. Polystyrene film was used for calibration. Liquid films were employed in suitable cases. For the CsBr region the spectra were recorded on a Beckman IR-5A CsBr instrument as Nujol mulls between CsBr plates. The values of the absorption bands reported in this paper are in cm^{-1} and their relative intensities are given as s (strong), m (medium), w (weak), and sh (shoulder).

Electronic spectra were obtained on a Cary Model 14 recording spectrophotometer. The solution spectra were scanned using 1-cm matched quartz cells. The spectra of the solid samples were run as mineral oil mulls of varying thickness sandwiched between quartz plates. The positions of the absorption bands listed in this paper are in cm^{-1} and ϵ values are given in parentheses.

Magnetic susceptibility of the compounds was determined at room temperature (297°K) by the Gouy technique,[10] using $Hg[Co(NCS)_4]$ as calibrant.[11] The observed values are independent of field strength.

X-Ray powder data were obtained on a General Electric XRD-5 diffractometer using nickel-filtered copper radiation.

Analyses were performed by Baron Consulting Co., Orange, Conn., and Galbraith Laboratories Inc., Knoxville, Tenn.

Results and Discussion

Previous workers have isolated a number of complexes of the *N*-cyanodithiocarbimate (cdc) ion[6,12] but to date no report has appeared on the cobalt(III) complex. We have been successful in isolating $Co(cdc)_3^{3-}$ by precipitation with the diphenyliodonium ion. We have found this cation to be quite useful in the isolation of a number of complex anions.

The diphenyliodonium ion is known to phenylate sulfur compounds. Sandin, *et al.*, observed the decomposition of diphenyliodonium sulfide[13] and also the reaction of diphenyliodonium ion with sulfhydryl groups.[14] It is consequently no surprise then to observe S-phenylation of the cdc ligands in this work. On heating I both in the solid state and in pyridine solution a reaction occurs between cation and anion as anticipated. In pyridine phenylation of cdc occurs but the resulting cddc is never detected, decomposing into phenyl disulfide. Cobalt(III) is reduced to cobalt(II) and the cdc remaining after phenylation cleaves to give thiocyanate. The reduction of cobalt(III) is not surprising; with the lowered ligand field produced by cddc cobalt(III) is less stabilized than in the cdc complex. An electron is then readily lost to the dpi ion resulting in its radical cleavage. However the cleavage of cdc to yield thiocyanate was quite unanticipated.

Our first indication of the actual nature of the derivatives isolated from the reaction in pyridine was from their infrared spectra. All of the reported compounds containing cdc (with one exception) have the "$-C{\equiv}N$" stretching mode in the range 2130–2185 cm^{-1}. The presumed "$Co(py)_4cdc$" (in actuality $Co(py)_4(NCS)_2$) and the *o*-phen and dipy derivatives show this mode near 2050 cm^{-1}. Comparison of the pyridine complex with authentic $Co(py)_4(NCS)_2$ confirmed the nature of the reaction product in pyridine solution.

The one compound claimed to contain cdc and having an infrared absorption below the range indicated above is "$[(C_6H_5)_4As]_2cdc$," obtained by Cotton and McCleverty.[12] We have isolated $(C_6H_5)_4AsSCN$ using the procedure employed by Cotton and McCleverty for the cdc salt but starting with thiocyanate in place of cdc solution. Our thiocyanate is identical with their presumed "$[(C_6H_5)_4As]_2cdc$," thus the reason for the apparent infrared anomaly. The apparent lability of cdc should be a matter of concern to workers in this field.

No phenylated pyridines could be detected in the

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TABLE I

SPECTRAL AND MAGNETIC DATA[a]

	$10^6\chi_m$, cgsu	μ_{eff}, BM	Spectral bands, cm^{-1}							
$Co(py)_4(NCS)_2(s)$	10,390	4.98	9,440 w, br	10,400 w		18,700 sh	19,600 sh	20,400		
In $CHCl_3$ + py						18,300 (11)		20,200 (24)	22,600 sh (7)	
In DMSO					16,200 (11)	18,600 (24)	19,900 (15)			
In DMSO + py						19,100 (26)	20,500 (21)	21,700 sh (8)		
$Co(dipy)_2(NCS)_2(s)$	9,480	4.77		10,400 w, br	11,900 w	18,600 sh		20,600		27,800
In DMSO			9,570 sh (31)	10,100 (40)		18,900 sh (34)		20,800 (50)		35,400 (10^4)
$Co(o\text{-phen})_2(NCS)_2(s)$	9,800	4.85	9,770 w, br	10,500 w				20,400		
In DMSO			9,350 sh (22)	10,200 (40)	11,600 sh (20)			20,900 (48)		28,800 (10^3), 37,300 (10^4)
$Co(py)_4(NCS)_2$ in $CHCl_3$[b]			10,500	15,900	16,800	18,000	20,000 sh			

[a] Complexes 10^{-2} *M* in indicated solvents. Pyridine, where added, to give solutions 0.05 *M* in this reagent. Molar extinction coefficients are in parentheses. [b] Sample not completely soluble.

solution reaction in this solvent. $Co(cdc)_3^{3-}$ is apparently, then, quite reactive toward phenylation. If it were not, the solvent would be phenylated. We have prepared a number of different diphenyliodonium salts of complex anions and observe a wide range of behavior in this respect.[15]

From the pyridine solution reaction the principal product isolated is *trans*-$Co(py)_4(NCS)_2$. This complex has been known for some time.[16] We have also prepared two other complexes from the pyridine compound, $Co(dipy)_2(NCS)_2$, and $Co(o\text{-phen})_2(NCS)_2$. Both have been reported—the dipyridyl (dipy) complex by Pirtea, *et al.*,[17] and the *o*-phenanthroline (*o*-phen) complex by Cambi and Cagnasso.[18] Neither appears to be well characterized and we report electronic spectral and magnetic data in Table I.

In chloroform solution $Co(py)_4(NCS)_2$ exhibits the spectrum of a tetrahedral species. The octahedral → tetrahedral change for $Co(py)_4X_2$ complexes is well documented[19] and undoubtedly occurs for this compound. On the addition of pyridine to the solution the spectrum shifts back to that of an octahedral species. In DMSO solution all three complexes display octahedral spectra. Pyridine is undoubtedly displaced from $Co(py)_4(NCS)_2$ in DMSO as evidenced by the slight spectral shift on adding excess pyridine to this solution.

In the solid-state reaction a different substance is formed. Product II is impure, but the formula approximates $Co[(C_6H_5)S_2C_2N_2]_3$. A low magnetic moment for this substance (*ca.* 2.6 BM) indicates some amount of cobalt(II) (probably 25%) to be present in the sample.

The infrared spectrum of II clearly shows a weak peak at 2050 cm^{-1} assignable to thiocyanate, in addition to the strong cdc and cddc modes in the 2150-cm^{-1} region. Some slight cleavage of cdc must occur in the solid-state reaction. Further evidence for the presence of cdc in II is the isolation of an impure form of $Co(cdc)(py)_2$ from a pyridine solution of II.

As in our earlier work,[1] diphenylated ligand (cddc) could be isolated from the pyrolysis product II. This compound undoubtedly functions as a ligand in II since it does not sublime out of the product *in vacuo* at 72°. All of the evidence points toward II as being a compound of the general type $[Co(cddc)_2(cdc)][Co(cddc)(cdc)_2]$.

The solid-state and solution reactions appear to follow the same course, the latter simply proceeding further. In both situations cdc is phenylated by the diphenyliodonium ion. In solution cddc decomposed completely to phenyl disulfide while in the solid reaction this decomposition is much less evident. (The formation of SCN^- from cdc is not restricted to the use of pyridine as a solvent. We have observed a similar occurrence in dimethylformamide solution). In the solid reaction dissociation of cdc into SCN^- is much less pronounced while in pyridine the dissociation appears to be complete.

Acknowledgment.—We are grateful to the National Institutes of Health for support of this work under Grant GM 14080.

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