

## Iodonium Salts of Complex Anions. IV.<sup>1</sup> The Autophenylation of Diphenyliodonium *trans*-Dicyanobis(dimethylglyoximate)cobalt(III)<sup>2</sup>

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Diphenyliodonium *trans*-dicyanobis(dimethylglyoximate)cobalt(III),  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$ , has been prepared and characterized. Reactions of this salt have been studied in solution and in the solid state. In coordinating solvents X (where X = pyridine (py), aniline, or 3,5-lutidine), cyanide substitution products  $Co(CN)X(DMG)_2$  were produced. The mechanism of these reactions has been discussed in terms of nucleophilic attack by the nitrogen end of a coordinated cyanide on the 1 carbon of  $(C_6H_5)_2I^+$  to give the complex phenyl isocyanide intermediate  $Co(CN)(CNC_6H_5)(DMG)_2$  and iodobenzene. Substitution of phenyl isocyanide by X then produced  $Co(CN)X(DMG)_2$  and free phenyl isocyanide.  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$ , in a noncoordinating, nonreactive solvent (dimethylacetamide), produced the cyano-bridged, anionic complex  $(NC)(DMG)_2Co-CN-Co(DMG)_2(CN)^-$ . In reactive solvents Y (where Y = pyridine, 3-picoline, or 4-picoline),  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  produced phenylated solvents,  $YH[Co(CN)_2(DMG)_2]$ , and iodobenzene. Brief characterization of the products from the solid-state decomposition of  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  indicated that phenylation of the dimethylglyoximate rather than the cyano groups occurred. The charge-transfer spectra of the compounds are discussed.

### Introduction

In recent publications<sup>1,3,4</sup> the utility of the diphenyliodonium ion in ligand reactions and for synthetic coordination chemistry has been demonstrated. This paper describes a continuation of a study of the phenylation of complex anions by the diphenyliodonium ion. In the present work we chose to investigate the reaction between  $(C_6H_5)_2I^+$  and  $Co(CN)_2(DMG)_2^-$ . The reactions with other cyano complexes are presently under investigation. Our choice of  $Co(CN)_2(DMG)_2^-$  stems from the reported stability of the square-planar  $Co(DMG)_2$  group with respect to alkylation reactions at the dimethylglyoximate site<sup>5</sup> and from the nature of the 1:1 electrolyte, both effects simplifying the diphenyliodonium reaction.

### Experimental Section

**Purification of Solvents.**—All solvents were of reagent quality and were further purified and dried by standard procedures.

**Physical Measurements. Electronic Spectra.**—A Cary Model 14 recording spectrophotometer was used to obtain electronic spectra. All measurements were performed on solutions in Beckman quartz cells with 1-cm path lengths.

**Infrared Spectra.**—The infrared spectra from 700 to 3500  $cm^{-1}$  of the complexes were obtained on a Perkin-Elmer Infracord spectrophotometer. Mineral oil mulls of the solids between sodium chloride or cesium bromide plates or potassium bromide pellets of the solids were employed.

**Magnetic Measurements.**—These measurements were performed by either the Gouy or the Faraday methods. All samples were run at two field strengths (approximately 4 and 8 kOe) and in all cases, magnetic susceptibility was independent of field strength. Both apparatuses were standardized using  $Hg[Co(SCN)_4]$ .<sup>6</sup> Data were recorded at room temperature. Corrected magnetic susceptibilities and moments are reported for the metal ions, corrected for the diamagnetism of the ligands using Pascal's constants.<sup>7</sup> A Nobatron DCR 80-10 power supply, Metler semimicro balance, and an electromagnet were used for the Gouy measurements. A Magnion HS105B power supply, Magnion electromagnet, and Cahn RG electrobalance were used as the Faraday apparatus.

**Conductance Measurements.**—Conductivity data were obtained at 20° using an Industrial Instruments Inc. conductivity bridge, Model RC 16B2. Conductances were corrected for the conductance due to solvent.

**Thin Layer Chromatography (Tlc).**—All tlc plates (5 × 20 cm) were prepared from indicating Silica Gel GF-254 (E. Merck Co., Darmstadt, Germany), with 0.25 mm thick layers. In all cases spots were eluted with acetone and visualized both with ultraviolet light (350 and 254  $m\mu$ ) and by staining with iodine.

**Elemental Analyses.**—Quantitative elemental analyses were performed by the Baron Consulting Co., Orange, Conn. 06477.

**Preparation of Reagents. Diphenyliodonium Chloride,  $[(C_6H_5)_2I]Cl$ .**—Using the method of Beringer, *et al.*,<sup>8</sup> diphenyliodonium chloride was prepared from  $KIO_3$ , benzene, acetic anhydride, and ammonium chloride (all reagent grade chemicals were from B & A, Morristown, N. J.); yield 68%; mp 207–208°.

**Potassium *trans*-Dicyanobis(dimethylglyoximate)cobalt(III),  $K[Co(CN)_2(DMG)_2]$ .**—This compound was prepared in 35% yield from KCN (reagent grade, Mallinckrodt Chemical Works, Saint Louis, Mo.) and diamminebis(dimethylglyoximate)cobalt(III) chloride, following the procedure given by Maki.<sup>9</sup> A yellow, crystalline by-product of this reaction, incorrectly identified as tris(dimethylglyoximate)cobalt(III) by Maki, was identified as  $Co(CN)(NH_2)(DMG)_2$ ; yield 19%. Its infrared spectrum had characteristic bands for ammonia, cyanide, and dimethylglyoxime. Conductance measurements (Table I) were in agreement with nonelectrolytic behavior. *Anal.* Calcd for  $Co_9H_{17}N_5O_4$ : C, 32.53; H, 5.16; N, 25.30. Found: C, 32.34; H, 5.29; N, 25.20.

$[Co(CN)(NH_2)(DMG)_2]$  is readily converted to the dicyano complex in 48% yield by refluxing with KCN in 1:1 methanol-water. The infrared spectrum of  $K[Co(CN)_2(DMG)_2]$  prepared in this fashion was superimposable on that of  $K[Co(CN)_2(DMG)_2]$  prepared according to Maki. Compounds from both procedures have identical  $R_f$  values (0.35) with tlc.

The tetra-*n*-butylammonium salt may be prepared in 84% yield from aqueous solutions of the potassium salt and tetra-*n*-butylammonium chloride.

**Diphenyliodonium *trans*-Dicyanobis(dimethylglyoximate)cobalt(III),  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$ .**—A warm (45°) solution of 15.00 g (47.4 mmol) of  $[(C_6H_5)_2I]Cl$  in 750 ml of water was added to a warm (45°) solution of 17.97 g (47.4 mmol) of  $K[Co(CN)_2(DMG)_2]$  in 500 ml of water. Within seconds, yellow plates of the product precipitated. However, the best product was obtained when the solution was allowed to cool to room temperature and then stored in an ice chest for 3 days. In this fashion, crystal size increased and the product was obtained as orange crystals.  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  was isolated by filtering, washing three times with 50-ml portions of water, and then drying *in vacuo* over  $P_2O_5$  overnight; yield 26.5 g (90.0%).

(8) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2705 (1953).

(9) N. Maki, *Bull. Chem. Soc. Jap.*, **38**, 2013 (1965).

(1) Part III: K. K. Ramaswamy and R. A. Krause, *Inorg. Chem.*, **9**, 2649 (1970).

(2) Presented to the Graduate School of the University of Connecticut by N. B. E. in partial fulfillment of the requirements for the Ph.D. degree.

(3) G. E. Hunter and R. A. Krause, *Inorg. Chem.*, **9**, 537 (1970).

(4) R. A. Krause, *ibid.*, **4**, 1227 (1965).

(5) W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **22**, 305 (1961).

(6) J. Lewis and R. G. Wilkins in "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 415.

(7) See ref 6, p 403.

TABLE I  
MOLAR CONDUCTIVITIES

Species	Solvent	Concn, M	A.	
			mos/cm	Ref
			Exptl	
Co(CN)(NH <sub>3</sub> )(DMG) <sub>2</sub>	DMF	1.00 × 10 <sup>-3</sup>	0.88	This work
Co(CN)(NH <sub>3</sub> )(DMG) <sub>2</sub>	DMF	1.00 × 10 <sup>-3</sup>	2.8	This work
Co(CN)(py)(DMG) <sub>2</sub>	Methanol	1.00 × 10 <sup>-3</sup>	0.48	This work
Co(CN)(an)(DMG) <sub>2</sub>	Methanol	1.00 × 10 <sup>-3</sup>	0.61	This work
Co(CN)(an)(DMG) <sub>2</sub>	Methanol	1.00 × 10 <sup>-4</sup>	0.56	This work
Co(CN)(3,5-lut)(DMG) <sub>2</sub>	Methanol	0.988 × 10 <sup>-3</sup>	0.57	This work
Co(CN)(3,5-lut)(DMG) <sub>2</sub>	Methanol	0.988 × 10 <sup>-4</sup>	2.2	This work
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> As[μ-CN-(Co(CN)(DMG) <sub>2</sub> ) <sub>2</sub> ]	Methanol	1.00 × 10 <sup>-3</sup>	62.8	This work
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	1.04 × 10 <sup>-3</sup>	42.5	This work
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	1.04 × 10 <sup>-4</sup>	39.4	This work
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	1.04 × 10 <sup>-5</sup>	42	This work
K[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	1.00 × 10 <sup>02</sup>	87.3	This work
K[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	1.00 × 10 <sup>-4</sup>	91.9	This work
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I]Cl	Water	1.00 × 10 <sup>-3</sup>	103	This work
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I]Cl	Water	1.00 × 10 <sup>-4</sup>	101	This work
Cl <sup>-</sup>	Water	Inf dil	70	a
K <sup>+</sup>	Water	Inf dil	68	a
			Calcd	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I <sup>+</sup>	Water	Inf dil	31	
Co(CN) <sub>2</sub> (DMG) <sub>2</sub> <sup>-</sup>	Water	Inf dil	24	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> I[Co(CN) <sub>2</sub> (DMG) <sub>2</sub> ]	Water	Inf dil	55	

<sup>a</sup> "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958-1959, p 2608.

The infrared spectrum of this product contained characteristic bands of the diphenyliodonium ion and the dicyanobis(dimethylglyoximate)cobalt(III) ion. Conductance measurements (Table I) are consistent with those of a 1:1 electrolyte;<sup>10</sup>  $\chi_M^{\text{cor}} = 59.1 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}} = 0.37$  BM.

**Reactions in Solvents.**—In general, 5.00 g of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] was dissolved in 50 ml of solvent (pyridine, 3,5-lutidine, 3- or 4-picoline, aniline, tri-*n*-butylamine, or 1:1 pyridine-triethylenediamine (TED)) and heated. On cooling or on evaporation of the solvent product was isolated and recrystallized from ethanol or methanol. The filtrate was examined for phenylated solvent products by use of tlc and isolation of the appropriate picrates. In cases where the product was the protonated solvent salt of the starting anion the identity of (solvent H<sup>+</sup>) was confirmed by treatment with base. The results are summarized in Table II.

**Reaction in Dimethylacetamide.**—A solution of 5.00 g of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] in 50 ml of dimethylacetamide was refluxed for 5 min, filtered to remove a trace of residue, and evaporated at 50° to produce an orange-brown solid. Extraction of the solid with 75 ml of hot ethanol, followed by cooling of the ethanol yielded impure (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[μ-CN-(Co(CN)(DMG)<sub>2</sub>)<sub>2</sub>]. Treatment of a methanolic solution of this compound with KI gave ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I)I, mp 193°,<sup>11</sup> confirming the nature of the cation. The cyano-bridged complex could be purified by conversion to the tetraphenylarsonium salt in methanol. *Anal.* Calcd for Co<sub>2</sub>C<sub>48</sub>H<sub>48</sub>M<sub>3</sub>O<sub>8</sub>As·H<sub>2</sub>O: Co, 11.14; C, 48.82; H, 4.76; N, 14.57. Found: Co, 10.36; C, 48.89; H, 4.79; N, 14.19.  $\chi_M^{\text{cor}} = 28 \times 10^{-6}$  cgsu.

**Solid-State Reaction.**—(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>], 3.00 g (4.82 mmol), was added to a 25-ml, round-bottom glass reaction bulb, sealed to a U-tube trap submerged in a Dry Ice-acetone bath. The system was evacuated to 50 μ and the reaction bulb was brought to 150° over a 4-hr period and then held at 150° for 24 hr. Upon raising the temperature to 170°, 1.80 g of brown residue was produced in the reaction bulb and 0.67 g of red-orange distillate was collected in the cold trap. *Anal.* Found for the residue: Co, 12.69; C, 42.61; H, 4.16; N, 18.68. These data can be formulated as Co<sub>0.97</sub>C<sub>16.0</sub>H<sub>18.6</sub>N<sub>6.00</sub> suggesting

(10) R. K. Murmann in "Inorganic Complex Compounds," Reinhold, New York, N. Y., 1964, p 10.

(11) It is interesting to note that the melting points of [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I]I reported by other workers are much lower than that determined here (193°). Literature melting points for this product were for pale yellow crystals precipitated from ethanol, whereas in this work white needles crystallized from dilute methanolic solution. On standing, the white needles became yellow and the melting points approached that reported by others.

Co(CN)<sub>2</sub>(DMG)((DMG)C<sub>6</sub>H<sub>5</sub>) (theoretical CoC<sub>16</sub>H<sub>18</sub>N<sub>6</sub>O<sub>4</sub>). The infrared spectrum had bands corresponding to dimethylglyoxime and terminal (2140 cm<sup>-1</sup>) and bridging (2190 cm<sup>-1</sup>) cyanide;  $\chi_M^{\text{cor}} = 710 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}} = 1.30$  BM. This value for the magnetic susceptibility indicates a Co(II) impurity. Tlc and vpc data of the distillate showed five and four components, respectively, one of which (iodobenzene) was identified. Neither benzonitrile nor phenyl isocyanide were present in the distillate.

**Displacement Reactions of Co(CN)<sub>2</sub>(DMG)<sub>2</sub><sup>-</sup>.**—(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Co(CN)<sub>2</sub>(DMG)<sub>2</sub> was heated in pyridine, aniline, and 3,5-lutidine under the identical conditions (time, temperature, and concentration) as those for the diphenyliodonium salt. More than 99% of the starting material was recovered unchanged from the solutions.

## Results

Two different modes of attack are observed in the reaction of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] in solvents. Either cyanide ion is displaced by the solvent or the complex anion is precipitated by a protonated solvent cation, (solvh)[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>].

In pyridine, 3,5-lutidine, or aniline, products of the type [Co(CN)(solv)(DMG)<sub>2</sub>] were formed. Stretching frequencies for terminal cyanide bonded to cobalt(III) (2130 cm<sup>-1</sup>) (also found in K<sub>3</sub>[Co(CN)<sub>6</sub>]<sup>12</sup> and K[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] (this work)) and the dimethylglyoximate anion (2330 (w), 1750 (w), 1560 ± 10 (m), 1430 ± 10 (m), 1365 ± 5 (m), 1240 (s), 1090 (s), 980 ± 5 (m) cm<sup>-1</sup>) (in agreement with frequencies reported by Nakamoto<sup>13</sup>) were common to these three compounds. Characteristic dimethylglyoximate bands were also found for K[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>], (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>], and Co(CN)(NH<sub>3</sub>)(DMG)<sub>2</sub>. In addition to these bands, stretching frequencies characteristic of the individual solvent ligands were present. Conductance measurements (Table I) were in agreement with a nonelectrolyte, thereby distinguishing Co(CN)X(DMG)<sub>2</sub> from its coordination polymeric isomer [CoX<sub>2</sub>(DMG)<sub>2</sub>][Co(CN)<sub>2</sub>(DMG)<sub>2</sub>]. Corrected magnetic moments were in the range 0.1-0.5 BM. Similar solubilities (soluble in hot methanol and ethanol, slightly soluble in methanol and ethanol at room temperature, insoluble in water and nonpolar solvents) were noted for the compounds Co(CN)X(DMG)<sub>2</sub>. *R<sub>f</sub>* values (0.60) with tlc were identical (distinguishable from the parent anion, Co(CN)<sub>2</sub>(DMG)<sub>2</sub><sup>-</sup>, at *R<sub>f</sub>* 0.35).

In the reactions of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] in 3,5-lutidine and aniline, neither phenylated solvent nor phenyl isocyanide were detected. (However, after adding an authentic sample of phenyl isocyanide to 3,5-lutidine and heating the resulting mixture at reflux for 5 min, phenyl isocyanide could not be detected.) In the reaction of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] with pyridine, phenylation of pyridine did occur, but phenyl isocyanide was not detected. In the solvents pyridine, pyridine-TED, 4-picoline, 3-picoline, and tributylamine the products isolated were solvh[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] and phenylated solvent. In the mixed-solvent system pyridine-TED, the cation was derived from the stronger base TED. In the experiments with pyridine, pyH[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] was never isolated, but tlc of the filtrate of the reaction mixture indicated the presence of Co(CN)<sub>2</sub>(DMG)<sub>2</sub><sup>-</sup> (*R<sub>f</sub>* 0.35). The presence of the pyridinium ion can only be inferred by comparison to the 3- and 4-picoline systems.

(12) K. Nakamoto in "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 166.

(13) See ref 12, p 194.

TABLE II  
 SUMMARY OF REACTIONS OF  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  IN SOLVENTS

Solvent	Conditions	Product (yield)	Presence of Phenylated Solvent	10% cgsu	Analyses, %							
					C		H		N		Co	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Pyridine	Reflux, 1 week	$[Co(CN)(py)(DMG)_2]$ (60-80%)	Yes	7.0	15.0	14.59	4.86	4.68	21.3	21.59	15.0	14.59
3,5-Lutidine	Reflux, 5 min	$[Co(CN)(lut)(DMG)_2]$ (53%)	None	101	45.5	45.39	5.49	5.36	19.9	20.01		
3-Picoline	Reflux, 5 min	$(picH)[Co(CN)_2(DMG)_2]$ (67%)	Yes									
4-Picoline	Reflux, 5 min	$(picH)[Co(CN)_2(DMG)_2]$ (92%)	Yes		44.2	44.39	5.09	5.04	22.5	22.34		
Aniline	150°, 5 min	$[Co(CN)(an)(DMG)_2]$ (54%)	<i>b</i>	44.0	43.2	43.19	5.31	4.97	20.1	20.11	14.1	13.7
Tributylamine	150°, <sup>a</sup> 1 hr	$(amH)[Co(CN)_2(DMG)_2] \cdot 0.5H_2O$	<i>b</i>		49.4	49.21	7.73	7.67	18.3	18.45	11.0	10.60
py-TED	112°, 5 min	$(TEDH)[Co(CN)_2(DMG)_2]$ (89%)	Yes		42.3	42.88	5.99	6.27	24.7	24.39		

<sup>a</sup> In suspension, product recrystallized from hot water. <sup>b</sup> Product isolated by evaporation of solvent and then recrystallized.

It is of interest to recognize that pyridine is unique among the solvents studied, being reactive toward phenylation and being a ligand for the substitution reaction.

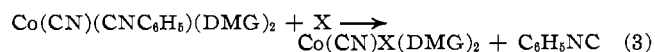
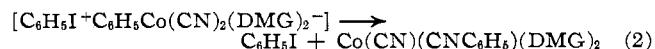
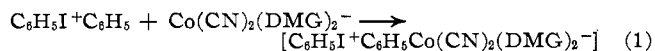
The effect of the diphenyliodonium ion in these systems is demonstrated by employing tetra-*n*-butylammonium salts instead. When  $(C_6H_5)_4N[Co(CN)_2(DMG)_2]$  was refluxed in pyridine, 3,5-lutidine, or aniline, no substitution of coordinated cyanide occurred, in contrast to the results with the diphenyliodonium salt.

Heating  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  in dimethylacetamide produces  $(C_6H_5)_2I[\mu-CN-(Co(CN)(DMG)_2)_2]$  and phenyl isocyanide. The infrared spectrum of  $(C_6H_5)_2I[\mu-CN-Co(CN)(DMG)_2]$  is identical with that of the starting material except in the cyanide stretching region where the starting material has only one cyanide stretch ( $2130\text{ cm}^{-1}$ ), expected for terminal cyanide bonded to cobalt(III).  $(C_6H_5)_2I[\mu-CN-Co(CN)(DMG)_2]$  has two cyanide stretching vibrations: terminal ( $2130\text{ cm}^{-1}$ ) and bridging ( $2180\text{ cm}^{-1}$ ) cyanide. This compound was purified by conversion to its tetraphenylarsonium salt.

### Discussion

**Reactions in Solvents.**—Decomposition of the diphenyliodonium ion and subsequent phenylation has been shown to proceed by two mechanisms: radical attack by  $C_6H_5^{\cdot}$ <sup>14</sup> and nucleophilic attack by organic and inorganic bases.<sup>15</sup> The path of phenylation by the diphenyliodonium ion is dependent upon the nature of the reacting species. Beringer, *et al.*,<sup>15</sup> have shown that phenylation of inorganic and organic bases ( $Cl^-$ ,  $CN^-$ ,  $NO_2^-$ , etc.) proceeds by nucleophilic attack of the base on the 1 carbon of the diphenyliodonium ion. Furthermore, they reported that the diphenyliodonium ion exists with the base as an ion pair in solution prior to reaction.

By analogy with the reasoning of Beringer, *et al.*, it is reasonable to propose that the following steps occurred in the conversion of  $(C_6H_5)_2I[Co(CN)_2(DMG)_2]$  to  $Co(CN)X(DMG)_2$



(14) R. B. Sandin and R. K. Brown, *J. Amer. Chem. Soc.*, **69**, 2253 (1947).

(15) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

Following the initial ion-pair formation of  $(C_6H_5)_2I^+$  with  $Co(CN)_2(DMG)_2^-$  (step 1), nucleophilic attack of the lone pair on the nitrogen of a coordinated cyanide at the 1 carbon of the diphenyliodonium ion leads to the formation of iodobenzene and the (unstable) coordinated phenyl isocyanide intermediate (step 2). In step 3, substitution of phenyl isocyanide by solvent X occurred and the neutral species  $Co(CN)X(DMG)_2$  were formed. Overall, iodobenzene and phenyl isocyanide should be among the products. Iodobenzene was detected in each of those reactions. Phenyl isocyanide was not detected; however, it was demonstrated that phenyl isocyanide reacts immediately and completely with 3,5-lutidine. This accounts for its absence in the reaction products of the present work. We have evidence however that the course of the reaction of  $(C_6H_5)_2I^+$  with  $Co(CN)_2(DMG)_2^-$  was through the formation of a coordinated phenyl isocyanide intermediate. Thus, phenyl isocyanide was detected on heating this salt in aqueous solution, in a solution of DMAC, and in suspension with 1,1,2,2-tetrachloroethylene.

The possibility that the overall conversion (in 50-60% yield)  $Co(CN)_2(DMG)_2^- \rightarrow Co(CN)X(DMG)_2$  proceeded by cyanide substitution by X was dismissed since solutions of  $(C_6H_5)_4N[Co(CN)_2(DMG)_2]$  heated under identical conditions as for the diphenyliodonium salt gave essentially no conversion.

The course of the reaction in DMAC was very much like those in pyridine, aniline, and 3,5-lutidine, with one exception: DMAC did not enter the coordination sphere of cobalt(III) following the initial phenylation of coordinated cyanide and subsequent loss of phenyl isocyanide. DMAC is stable with respect to reaction with the diphenyliodonium ion and is a poor donor group for transition metals. In this reaction, cobalt(III) was able to satisfy its coordination requirement by bonding with the nitrogen end of a coordinated cyanide of an unreacted  $Co(CN)_2(DMG)_2^-$  ion to give the cyano-bridged, anionic species  $\mu-CN-(Co(CN)(DMG)_2)_2^-$ , precipitated as the diphenyliodonium salt. The reaction pathway would be the same as that proposed above except that step 3 involves displacement of coordinated phenyl isocyanide by the nitrogen end of cyanide in  $Co(CN)_2(DMG)_2^-$ . Free phenyl isocyanide, detected in this reaction, lends substance to our proposal of its existence in an intermediate.

Although  $(C_6H_5)_2I[\mu-CN-(Co(CN)(DMG)_2)_2]$  does not represent the first example of a discrete unit containing a bridging cyanide group, only three other examples of such compounds have been reported and

these have been within the past decade.<sup>16,17</sup> In a detailed study of the position of the cyanide stretch, Dows, *et al.*,<sup>18</sup> have shown that upon cyanide bridging, the cyanide stretching increases about 50 cm<sup>-1</sup> as we have observed in the present work.

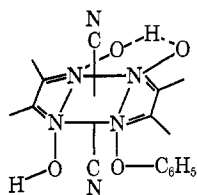
Several solvents were observed to function in a fashion different from the reactions discussed above. In these the products were (solvH)[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>], the protonated solvent being produced in the radical phenylation of solvent. The reaction in pyridine occurs both ways, as indicated by our isolation of substituted complex, Co(CN)(py)(DMG)<sub>2</sub>, and also phenyl-substituted pyridines from this reaction.

Sandin and Brown<sup>14</sup> proposed a radical mechanism for the phenylation of pyridine with the diphenyliodonium ion. Although Sandin and Brown explained the radical mechanism using a diphenyliodonium hydroxide intermediate to give the phenyl radical, we observed all three isomeric phenylpyridines in the reaction of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] in pyridine (without NaOH) and therefore it seems likely that hydroxide catalysis is not necessary for phenyl radical attack on the pyridine ring. Whereas Sandin and Brown reported an immediate reaction of the diphenyliodonium ion with pyridine following the addition of NaOH, we observed the reaction of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I[Co(CN)<sub>2</sub>(DMG)<sub>2</sub>] in pyridine to require about 1 week for completion. This is consistent with their theory of catalysis.

In view of the mechanism of hydroxide-catalyzed phenylation of pyridine, it appears plausible to include an intermediate complex of pyridine and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>I<sup>+</sup> in this reaction. Beringer, *et al.*,<sup>19,20</sup> reported that reduction of the diphenyliodonium ion must occur prior to the generation of phenyl radical. Such an intermediate would allow the requisite electron transfer. Experimentally, the isomeric phenylpyridines, characteristic of a radical reaction, were detected.

Using 3- and 4-picolines as solvents also yielded only solvent phenylation. Since the radical attack is base catalyzed, this route of reaction may be due to the higher base strength of these solvents<sup>21</sup> than that of pyridine. Indeed, by conducting the reaction in pyridine containing the stronger base TED, solvent phenylation was the exclusive reaction occurring.

**Solid-State Reaction.**—Experimental evidence indicates that phenylation of the dimethylglyoximate and not the cyanide groups occurred to (presumably) produce something of the structure



This structure contains both terminal cyanides and a bridging hydrogen, required from the infrared spectrum

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of the residue. These data are in agreement with the residue containing the square-planar bis(dimethylglyoximate) group since the weak bands assigned to the bridging -O-H-O- group were present (1775 and 2350 cm<sup>-1</sup>).<sup>22</sup> Such bands are not present in NaDMG or Co(DMG)<sub>3</sub> which, from structural considerations, cannot contain the hydrogen-bridged group.

Subsequent decomposition of this species with accompanying reduction to Co(CN)<sub>2</sub> could occur, and in this fashion the presence of several substances in the residue would collectively account for the observed magnetic moment and the bridging cyanide absorption band. Phenylation of dimethylglyoxime rather than cyanide is not unreasonable, even though cyanide phenylation occurred in solution, since in the solid state the relative orientation of the diphenyliodonium ion and the anion could be such that the 1 carbon of the former more closely approaches the dimethylglyoxime than it does the cyanide group. Both analytical data and the absence of phenyl isocyanide and benzonitrile from the volatile fraction of the reaction products suggest that reaction occurred in this fashion.

**Electronic Spectra.**—Table III presents absorption

Species	X	$\lambda_{\max}$ , nm ( $\epsilon \times 10^{-4}$ )	
Co(CN)X(DMG) <sub>2</sub>	NH <sub>3</sub>	245 (2.13), 275 sh (0.645)	
		Pyridine	245 (2.28)
		3,5-Lutidine	245 (2.26)
		Aniline	245 (2.25), 283 sh (1.15)
Co(CN)X(DMG) <sub>2</sub> <sup>-</sup>	CN <sup>-</sup>	227 (3.33)	
	Co(CN) <sub>2</sub> (DMG) <sub>2</sub> <sup>-</sup>	243 sh (3.48), 223 (5.81)	

maxima from the electronic spectra of some cobalt(III) complexes. From the intensity of the observed absorption bands the transitions appear to be of the charge-transfer type. None of the lower intensity d-d transitions can be detected in these spectra; presumably, the d-d transitions are covered by the edge of the charge-transfer absorption. We may consider three distinct classes of [CoL<sub>2</sub>(DMG)<sub>2</sub>] complexes, based on the nature of the axial ligands, L. The first class consists of [Co(CN)<sub>2</sub>(DMG)<sub>2</sub>]<sup>-</sup>, with C-bonded cyanides. This compound absorbs at 227 nm (44,800 cm<sup>-1</sup>). Complexes with one C-bonded cyanide and one nitrogen donor in the axial positions constitute the second class; they are observed to absorb at 245 nm (40,800 cm<sup>-1</sup>). A third class of complexes is those with two nitrogen donors in the axial positions. Ripan, *et al.*,<sup>23</sup> reported toluidine complexes of this type to have absorption maxima at 250 nm (40,000 cm<sup>-1</sup>). Thus, the three classes are distinguished (in this small sample) by the location of this band. From Table III it can be seen that the bridging cyano complex  $\mu$ -CN-(CoCN-(DMG)<sub>2</sub>)<sub>2</sub> falls in both the first and second classes, having absorbances at 223 and 243 nm and presumably containing two axial carbon donors on one cobalt and an axial carbon and nitrogen on the other.

In this series of compounds the energy of the charge-transfer band increases as the crystalline field strength

- (22) See ref 12, p197.  
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of the axial ligands increases. Ripan suggested the 250-nm band to be due to the  $\text{Co}(\text{DMG})_2$  moiety only; we feel this to be an insufficient explanation. Instead, we suggest that the charge-transfer band involves a transition from the  $^1A_1$  ground state of cobalt(III) to some higher state of the molecule involving considerable mixing of DMG orbitals. This state is probably at a rather constant energy (with respect to cobalt's field-free atomic term) throughout all the compounds.

As the field strength increases, lowering the  $^1A_1$  ground state of cobalt(III), the separation between ground and charge-transfer state increases. Thus, an increase in strength of axial ligands results in the charge-transfer band appearing at higher energy.

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## Magnetic Studies on Amino Acid Complexes of Copper(II). II. Novel Interactions in Tetrakis(L-tyrosinato)dicopper(II)<sup>1</sup>

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Tetrakis(L-tyrosinato)dicopper(II) is shown to exhibit spin-spin interactions yielding a triplet ground state with the singlet state at  $19.1 \text{ cm}^{-1}$  above the ground state. The epr spectrum of the half-field region also demonstrates the existence of spin-spin coupling. A value of  $D = 0.0213 \text{ cm}^{-1}$  is calculated from the half-field line. The observed spin interactions are shown to be of a strictly localized fashion within the dimers, but at very low temperatures ( $<17^\circ\text{K}$ ) a weak cooperative phenomenon becomes perceptible. A best fitting procedure of the magnetic susceptibility data yields the following values for the magnetic parameters:  $2J = +19.1 \text{ cm}^{-1}$ ,  $g = 2.17$ , and  $\theta = -2.06^\circ\text{K}$ . A model which accounts for the observed data is proposed. It involves a  $\sigma$ -orbital mechanism *via* the out-of-plane bonds. The carboxyl oxygens of the ligands act as bridges in the mechanism.

### Introduction

Recently we reported<sup>2-5</sup> the possibility of the existence of triplet ground states in coordination compounds of copper(II) where there are spin interactions between isolated pairs of copper ions.

In order to determine the frequency of this relatively rare phenomenon and the properties of the compounds that exhibit it, we have now studied tetrakis(L-tyrosinato)dicopper(II),  $[\text{Cu}(\text{tyr})_2]_2$ , which has been shown<sup>6</sup> to have the copper ions arranged in distinct dimeric units, as depicted in Figure 1. The coordination of the copper ions is made up by the nitrogen and carboxyl oxygen atoms of two tyrosine molecules. The fifth position of coordination is occupied by the oxygen atom of the adjacent half of the molecule while the sixth position is open. Some pertinent distances are given in Figure 1. The out-of-plane bonds (dotted in Figure 1) are longer than the in-plane bonds by about  $0.4 \text{ \AA}$  but still offer a possible pathway for electron delocalization and spin coupling between the copper ions.

Here we report the observation of spin interactions by means of electron paramagnetic resonance measurements and the characterization of the magnetic properties of  $[\text{Cu}(\text{tyr})_2]_2$  by measuring the susceptibility in the temperature range  $2.5\text{--}93^\circ\text{K}$ .

### Experimental Section

Tetrakis(L-tyrosinato)dicopper(II) was synthesized by a method similar to Laurie's,<sup>7</sup> by preparing an equimolar ( $0.125 \text{ M}$ ) aqueous solution of tyrosine and NaOH, warming to  $60^\circ$ , and adding dropwise an aqueous solution of  $\text{CuSO}_4$ . The final volume was about 250 ml. The precipitate which formed immediately was filtered and washed with water and ether. The mauve solid was dried over  $\text{P}_2\text{O}_5$ ; mp  $248\text{--}250^\circ \text{ dec}$ . *Anal.* Calcd for  $\text{Cu}(\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6)_2$ : Cu, 51.00; H, 4.76; N, 6.81. Found: Cu, 51.09; H, 4.76; N, 6.58. The analyses were carried out by Galbraith Laboratories, Inc.

All the physical measurements were carried out using polycrystalline samples of the pure compound. The epr spectra were obtained at room and liquid nitrogen temperatures with a Varian E-3 spectrometer, at a frequency of 9.191 GHz. Diphenylpicrylhydrazyl was used as an internal standard<sup>8</sup> ( $\langle g \rangle = 2.0036$ ). The magnetic susceptibility was measured in the temperature range from 300 to  $77^\circ\text{K}$  using a Faraday balance which has been described previously.<sup>9</sup> For the temperature range from 2.5 to  $77^\circ\text{K}$  a vibrating-sample magnetometer from Princeton Applied Research was used. The sample weight was about 0.1 g. The magnetic field was maintained constant at 10,000 G with a Ventron Instrument Corp. power supply equipped with a field control unit. A high-sensitivity, precalibrated germanium resistance thermometer from Scientific Instruments, Inc., was used to monitor the temperature. Appropriate corrections for the diamagnetism of the sample rod and sample container were applied, as well as corrections for the diamagnetism of the sample<sup>10</sup> ( $213 \times 10^{-1} \text{ cgsu}$ ) and for temperature-independent paramagnetism ( $100 \times 10^{-1} \text{ cgsu}$ ). The calculations were carried out using Fortran IV programs written for a Raytheon 706 computer with an SDT input-output system.

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