

The shifts at the 1-methylene position of the coordinated ligands are a combination of contact and dipolar effects of similar magnitude in many of the cobalt and iron complexes. The temperature dependence of the dipolar effect in these systems is apparently much greater than that of the contact effect and this leads to unusual temperature dependencies when the effects are opposed. For example in  $\text{Co}(4\text{-Etpy})_4\text{Br}_2$ ,  $\text{Fe}(4\text{-Etpy})_4\text{Cl}_2$ , and  $\text{Fe}(4\text{-Etpy})_4\text{Br}_2$  the shifts at the 1-methylene position decrease with decreasing temperature and in  $\text{Co}(4\text{-}n\text{-Prpy})_4\text{Br}_2$  the shift at the 1-methylene position changes sign with a change in temperature.<sup>22</sup>

The inversion in the sign of magnetic anisotropy in the iron(II) complexes could be significant with respect to a recent study<sup>23</sup> of the Mossbauer spectra of octahedral iron(II)-pyridine complexes. Merrithew, *et al.*, inter-

(22) While this overlap of contact and dipolar effects makes definitive interpretation difficult, it is likely that there is an inversion in the sign of the contact effect at the 1-methylene position in the series of iron(II) complexes in addition to the sign inversion in the dipolar effect. In the majority of pyridine and 4-picoline complexes studied the contact effect gives rise to downfield 4-proton shift and an upfield 4-CH<sub>3</sub> shift (see ref 7 and 9 and references therein). However, tetrahedral cobalt(II) complexes manifest contact shifts in the opposite direction at the 4 position: B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 4597 (1966); G. N. La Mar, *Inorg. Chem.*, **6**, 1939 (1967). Thus, there is some precedence for a variability in sign of the contact effect at the 4 position of pyridine and substituted-pyridine complexes. However, this appears to be the first time such a variation has been found in a closely related series and suggests radical differences in the ground states of the iron(II) complexes.

(23) P. B. Merrithew, P. G. Rasmussen, and D. H. Vincent, *Inorg. Chem.*, **10**, 1401 (1971).

preted their data on  $\text{Fe}(\text{py})_4\text{Cl}_2$  and  $\text{Fe}(\text{py})_4\text{I}_2$  to indicate that the iodide adopted a trans structure whereas the chloride was cis. Elsewhere we have shown<sup>24</sup> that the chloride is in fact also trans. Since in this work we have shown that the chloride and iodide complexes display magnetic anisotropy of opposite sign without a geometric change, it appears likely that a major ground-state change is responsible for both phenomena.

### Conclusions

Dipolar effects are manifested in the nmr spectra of solutions of the iron(II)- and cobalt(II)-substituted-pyridine complexes in the resonances of the coordinated ligand, solvent, and free ligand. The magnetic anisotropy responsible for the dipolar effects in the iron and cobalt series  $\text{ML}_4\text{X}_2$  varies in sign with changes of the anion X.

**Registry No.** Table I  $\text{NiL}_4\text{Cl}_2$ , 36503-14-7;  $\text{NiL}_4\text{Br}_2$ , 36503-15-8;  $\text{NiL}_4\text{I}_2$ , 36503-16-9;  $\text{NiL}_4(\text{NCS})_2$ , 36503-17-0;  $\text{CoL}_4\text{Cl}_2$ , 36537-22-1;  $\text{CoL}_4\text{Br}_2$ , 36503-18-1;  $\text{CoL}_4\text{I}_2$ , 36502-94-0;  $\text{CoL}_4(\text{NCS})_2$ , 36502-95-1;  $\text{FeL}_4\text{Cl}_2$ , 36502-96-2;  $\text{FeL}_4\text{Br}_2$ , 36502-97-3;  $\text{FeL}_4\text{I}_2$ , 36502-98-4;  $\text{FeL}_4(\text{NCS})_2$ , 36502-99-5. Table II  $\text{NiL}_4\text{Cl}_2$ , 36503-00-1;  $\text{NiL}_4\text{Br}_2$ , 36503-01-2;  $\text{NiL}_4\text{I}_2$ , 36503-02-3;  $\text{NiL}_4(\text{NCS})_2$ , 36503-03-4;  $\text{NiL}_4(\text{NCO})_2$ , 36503-04-5;  $\text{NiL}_4(\text{N}_3)_2$ , 36503-05-6;  $\text{CoL}_4\text{Cl}_2$ , 36503-06-7;  $\text{CoL}_4\text{Br}_2$ , 36503-07-8;  $\text{CoL}_4\text{I}_2$ , 36503-08-9;  $\text{CoL}_4(\text{NCS})_2$ , 36537-21-0;  $\text{CoL}_4(\text{NCO})_2$ , 36503-09-0;  $\text{CoL}_4(\text{N}_3)_2$ , 36503-10-3;  $\text{FeL}_4\text{Cl}_2$ , 36503-11-4;  $\text{FeL}_4\text{Br}_2$ , 36503-12-5;  $\text{FeL}_4\text{I}_2$ , 36563-76-5;  $\text{FeL}_4(\text{NCS})_2$ , 36503-13-6.

(24) D. Forster and D. J. Dahm, *Inorg. Chem.*, **11**, 918 (1972).

Contribution from the Catedra de Quimica Inorganica de la Facultad de Quimica, Montevideo, Uruguay, and Sektion Chemie der Karl-Marx-Universitat, Leipzig, East Germany

## Synthesis, Characterization and Some Reactions of (Dimethyl sulfoxide)pentaamminecobalt(III) Salts

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$[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  is prepared by reaction of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  with DMSO. The chloride and nitrate of the complex cation are obtained by anionic interchange followed by freeze-drying. Characterization and purity checks are accomplished by analysis, visible spectra, repeated crystallization, ionic interchange behavior, conductivity, tga, and infrared spectra. The use of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}]^{3+}$  as the starting ion for syntheses through substitution reactions in the solid phase or in solution using the DMSO lability is considered. As examples we present the thermal substitution reaction of the DMSO by  $\text{Cl}^-$ , an attempt with  $[\text{Co}(\text{CN})_6]^{3-}$ , and, for the processes in solution, the substitution by  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ , and pyridine. The new method presented for the preparation of  $[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$  derivatives shows advantages over those previously known.

### Introduction

Several cobalt complexes containing DMSO ligand have been described.<sup>2-6</sup> For this central atom the coordination

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(2) H. L. Schlaefler and H. P. Opitz, *Z. Elektrochem.*, **65**, 372 (1961).

(3) F. A. Cotton and R. Francis, *J. Inorg. Nucl. Chem.*, **17**, 62 (1961).

(4) H. L. Schlaefler and H. P. Opitz, *Z. Anorg. Allg. Chem.*, **313**, 178 (1961).

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of the ligand is established through the oxygen atom<sup>7</sup> and considering the steric and polarity characteristics of the DMSO molecule the low strength of Co(III)-DMSO bonds can be inferred. If DMSO is present as a substituting ligand in a Co(III) complex containing other stable bonds, *e.g.*, Co(III)-N, it will be expected that the DMSO functions as a good leaving group. This character has been implicitly recognized by Hurst and Taube<sup>8</sup> when, by comparing the spectra of  $[\text{Co}(\text{NH}_3)_5\text{solv}]^{3+}$  obtained with solutions of (methyl

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(8) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174, (1968).

acetate)pentaamminecobalt(III) perchlorate in different solvents, the rates of substitution of the methyl acetate ligand by other solvents were estimated and found to be in the following order: water > methanol > DMF-TMP > acetone > DMSO > sulfolane. The location of the DMSO in this series as a neighbor of sulfolane, acetone, and TMP is an indication of its good leaving group character. Sulfolane- and TMP-ammine derivatives have been used as synthetic starting materials making use of this property.<sup>8,9</sup> We became interested in the possibilities of DMSO as the sixth ligand in cobalt(III) pentaammine for the same purposes. Such possibilities seem remarkably interesting considering the special solvent properties of DMSO and its relatively high volatility (bp 189°).

The aquopentaamminecobalt(III) derivatives have been used for the synthesis of special compounds by means of water volatilization or in solution by the leaving of the water molecule, a frequent enough event, to allow convenient rates of entering of other groups. Similarly the DMSO-(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup> contains the DMSO group, volatile and presumably labile, thus making it possible to try the thermal and kinetic substitution reactions. For the last type of process we point out that an advantage can be gained by using DMSO as solvent in cases where water is inconvenient.

In the present report we include the preparation, purification, characterization, and some qualitative demonstrations of the ability of the [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]<sup>3+</sup> to behave as explained above. We are currently planning to study the kinetics of DMSO interchange and aquation of the complex to find a deeper foundation for the feasible applications.

### Experimental Section

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O.** Essentially the method consists of the substitution of H<sub>2</sub>O by DMSO in [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](ClO<sub>4</sub>)<sub>3</sub> as described recently by Gould<sup>10</sup> to obtain dimethylformamide and (dimethylacetamide)pentaamminecobalt(III) derivatives. The conditions we found convenient are described as follows. [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](ClO<sub>4</sub>)<sub>3</sub>(aq) (3 g) was poured into a 250-ml round-bottom flask together with 8 g of DMSO and heated to 85° until dissolution. The flask was then connected to a flash evaporating system and kept at 85° for 20 min. This brought about the reaction and at the same time some solvent was distilled off. The reaction was then cooled in an ice bath and 7 ml of 1:3 HClO<sub>4</sub> (2.3 ml of 12.5 M HClO<sub>4</sub> + 4.7 ml of H<sub>2</sub>O) was slowly added. A precipitate was obtained and the system was maintained overnight at 0–4°. Vacuum filtration and washing with small amounts of cold water, alcohol, and ether yielded 2.7 g.

A sample for elemental and spectral analysis was obtained upon recrystallization; 2.5 g of crystals was dissolved in 11 ml of water and 1.5 ml of concentrated HClO<sub>4</sub> was slowly added. The crystals are then filtered and washed with small amounts of cold water, alcohol, and ether; yield ~ 65%. *Anal.* Calcd for [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O: Co, 10.59; NH<sub>3</sub>, 15.27; ClO<sub>4</sub><sup>-</sup>, 53.62; C, 4.31; S, 5.75; H, 4.50. Found: Co, 10.8; NH<sub>3</sub>, 15.5; ClO<sub>4</sub><sup>-</sup>, 53.9; C, 5.47; S, 6.51; H, 4.40.

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]Cl<sub>3</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O.** Our attempts to obtain these salts by the same procedure were unsuccessful; notwithstanding, we prepared them from the perchlorate by anion exchange followed by freeze-drying. In a typical experiment 0.8 g of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O dissolved in 25 ml of water was treated by ionic interchange passing through a 20 cm high and 1 cm in diameter column of Amberlite 400 (20–50 mesh), previously prepared as chloride or nitrate. The effluent was freeze-dried and the recovered crystals were kept overnight over CaCl<sub>2</sub>. The chloride is hygroscopic. *Anal.* Calcd for [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]Cl<sub>3</sub>: Co, 17.94; NH<sub>3</sub>, 25.92; Cl, 32.38. Found: Co, 18.1; NH<sub>3</sub>, 25.8; Cl, 31.8. Calcd for [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O: Co, 13.27; NH<sub>3</sub>, 19.15; N(total), 25.91; H, 5.67; S, 7.20; C, 5.41. Found: Co, 13.4; NH<sub>3</sub>, 18.7; N, 26.05; H, 5.66; S, 6.64; C, 7.73.

(9) G. E. Dolbear and H. Taube, *Inorg. Chem.*, 6, 60 (1967).  
 (10) E. S. Gould, *J. Amer. Chem. Soc.*, 90, 1740 (1968).

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](ClO<sub>4</sub>)<sub>3</sub>.** This was done according to ref 11. *Anal.* Calcd: Co, 12.80. Found: Co, 12.7.

**Preparation of K<sub>3</sub>[Co(CN)<sub>6</sub>].** This was done according to ref 12. *Anal.* Calcd: Co, 17.76. Found: Co, 17.6.

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO][Co(CN)<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O.** A 5.56-g (0.01-mol) sample of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O dissolved in 400 ml of water was mixed with 3.32 g (0.01 mol) of K<sub>3</sub>[Co(CN)<sub>6</sub>] also dissolved in 400 ml of water. After 3 hr at room temperature, precipitation took place and the crystals were thoroughly washed with water, alcohol, and ether. The product was dried over CaCl<sub>2</sub>. *Anal.* Calcd: Co, 24.91; NH<sub>3</sub>, 17.99; H<sub>2</sub>O, 7.61. Found: Co, 24.2; NH<sub>3</sub>, 17.9; H<sub>2</sub>O, 7.4.

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>py]I<sub>3</sub>·2H<sub>2</sub>O.** [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O (2.5 g) dissolved in 10 ml of DMSO was treated with an excess of pyridine (14 g) and heated for 7 min at 100°; the color changed quickly from the red-violet to yellow-brown. The mixture was cooled to 10° and diluted with 15 ml of water, and addition of an excess of saturated solution of NaI in methanol produced, after 1–2 min, precipitation of yellow crystals. These were filtered, washed with alcohol and ether, and dried over silica gel; yield 1.5 g. On standing, the filtrate containing alcohol and ether yielded 1.1 g of second crystallization product; total yield 96%.

Recrystallization was accomplished by dissolution in aqueous NaI solution by heating to 40° and cooling to 0–5°; yield 80%.

*Anal.* Calcd: Co, 9.21; NH<sub>3</sub>, 13.31; I<sup>-</sup>, 59.50; H<sub>2</sub>O, 5.6. Found: Co, 8.9; NH<sub>3</sub>, 13.6; I<sup>-</sup>, 58.5; H<sub>2</sub>O, 5.7. Spectrum of water solution, 5 × 10<sup>-3</sup> M: 474 nm (ε 65.3); 337 nm (ε 107.8). Molar conductivity, 25°, 10<sup>-3</sup> M: 439 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**Preparation of [Co(NH<sub>3</sub>)<sub>5</sub>py](ClO<sub>4</sub>)<sub>3</sub>.** Following the method indicated in ref 13 we transformed the iodide in perchlorate. The anhydrous salt was obtained by vacuum P<sub>2</sub>O<sub>5</sub> drying. *Anal.* Calcd: Co, 11.30; NH<sub>3</sub>, 16.33. Found: Co, 10.9; NH<sub>3</sub>, 16.0. Spectrum of the water solution, 2 × 10<sup>-3</sup> M: 474 nm (ε 65.5); 341.5 nm (ε 58.0). Molar conductivity, 25°, 10<sup>-3</sup> M: 347 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

All other materials used in the present research were reagent grade chemicals.

**Measurements.** Visible spectra were measured with a Beckman DB recording spectrophotometer. Infrared spectra were measured with a Perkin-Elmer spectrophotometer. Conductivity measurements were carried out at 25° with a 221-3 RLC Universal conductivity bridge; tga experiments, by using Netzsch equipment 404.<sup>14</sup>

**Analytical Methods.** Cobalt was titrated with EDTA after H<sub>2</sub>SO<sub>4</sub> attack on the samples. Ammonia was analyzed by treating the complexes with arsenic(III) oxide and sodium hydroxide and titrating the distilled ammonia fixed on saturated boric acid solution. Perchlorate anion was transformed to KClO<sub>4</sub> by eliminating the complex cation using a cationic resin (Amberlite 120, H<sup>+</sup> form), neutralizing with KOH and insolubilizing the KClO<sub>4</sub> by evaporating to dryness, treating with alcohol, drying at 105°, and weighing.

H, C, and S elementary analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by R. Martin, Sektion Chemie, Karl-Marx-Universität, Leipzig.

The H<sub>2</sub>O content of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO][Co(CN)<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O was determined by heating to constant weight at 120°; that of [Co(NH<sub>3</sub>)<sub>5</sub>py]I<sub>3</sub>·2H<sub>2</sub>O, by using vacuum over P<sub>2</sub>O<sub>5</sub>. In all other cases it was found by analytical coincidence of other radicals and tested by tga curves. The chloride content in [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]Cl<sub>3</sub> and its transformation products was found gravimetrically as AgCl after use of ion exchange to transform the chloride in the complex salt into HCl.

Iodide in [Co(NH<sub>3</sub>)<sub>5</sub>py]I<sub>3</sub>·2H<sub>2</sub>O was determined gravimetrically as AgI.

### Results and Discussion

**Characterization of Complexes.** When an excess of DMSO is added to [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](ClO<sub>4</sub>)<sub>3</sub> and heated as explained in our main preparation, a change in color takes place. The original solution spectrum [490 nm (ε 48.3), 340 nm (ε 44.7)]<sup>15</sup> shifts the absorption maxima to 515 and 352 nm, respectively. This second band shows the influence of a more intense absorption near the ultraviolet region. The

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Table I. Infrared Spectral Correlation and Assignments<sup>a</sup>

Assignment	[Co(DMSO) <sub>6</sub> ] <sup>2+</sup> [CoCl <sub>4</sub> ] <sup>2-</sup> <sup>7</sup>	[Co(NH <sub>3</sub> ) <sub>5</sub> - DMSO]Cl <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>5</sub> DMSO]- (ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	[Co(NH <sub>3</sub> ) <sub>5</sub> DMSO]- (NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	[Co(NH <sub>3</sub> ) <sub>5</sub> DMSO]- [Co(CN) <sub>6</sub> ] <sup>3-</sup> ·2H <sub>2</sub> O
$\nu_{as}(C-S)$	714 w	720 vw	719 vw	713 vw	720 vw
$\nu(S-O)$	950 vs	943 } vs 929 } vs	937 vs	956 s	942 vs
$\rho_r(CH_3)$	1009 } sh 999 } s	1026 } w 980 } m	Overlapped $\nu_3(ClO_4)$	990 m	1020 } w 980 } m
$\delta_s(CH_3)$	1314 } w 1292 } w	Overlapped $\delta_s(NH_3)$	Overlapped $\delta_s(NH_3)$	Overlapped $\delta_s(NH_3)$ and $\nu_s(NO_3)$	Overlapped $\delta_s(NH_3)$
$\delta_{as}(CH_3)$	1416 b	1405 } w, b 1418 } w, b	1398 } w, b 1411 } w, b	Overlapped $\delta_s(NH_3)$ and $\nu_s(NO_3)$	1400 } w, b 1413 } w, b
$\nu_s(C-H)$	2906 m	2900 m, sh	2900 m, sh	2922 vw	2900 m, sh
$\nu_{as}(C-H)$	3002 m	2990 m	2990-3000 m	2995 w	2990 m

<sup>a</sup> Abbreviations:  $\nu$ , stretching;  $\delta$ , deformation;  $\rho_r$ , rocking; as, asymmetric; s, symmetric; s, strong; vs, very strong; w, weak; sh, shoulder; vw, very weak; m, medium; b, broad.

new spectrum maintains the characteristics corresponding to a cobalt(III) pentaammine.

The analytical results as well as the spectrum are reproducible through the recrystallizations.

We have obtained crystals of the same analytical and spectral results by a completely independent method using the reaction of [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> with NOClO<sub>4</sub> in DMSO.<sup>16</sup> Obviously the simplicity of the H<sub>2</sub>O substitution method justifies our selection for preparation purposes.

The measured molar conductivities of the prepared salts were as follows (10<sup>-3</sup> M, 25°) (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>): [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O, 434.0; [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]Cl<sub>3</sub>, 441.0; [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O, 408.3; which corresponds to 3:1 electrolytes.

In the case of [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O we further studied the conductivity behavior in water solution by use of the Onsager equations<sup>17</sup> and found the parameters  $B = 412$  and limiting cation conductance at 25°,  $\Lambda_0 = 101.6$  ohm<sup>-1</sup> cm<sup>2</sup> equiv<sup>-1</sup>. These results at 10<sup>-3</sup>-10<sup>-5</sup> M concentrations are higher than expected and can be primarily related with association processes of the complex.

In our syntheses attempts we experimented on the reaction of [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](NO<sub>3</sub>)<sub>3</sub> with DMSO. Considering the ligand ability of NO<sub>3</sub><sup>-</sup> we expected to be able to obtain [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](NO<sub>3</sub>)<sub>3</sub> by treating [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O](NO<sub>3</sub>)<sub>3</sub> with an excess of DMSO at 85° as in the case of the perchlorate. However, the recovered crystals were [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>. Anal. Calcd: Co, 17.85; NH<sub>3</sub>, 25.79. Found: Co, 17.3; NH<sub>3</sub>, 25.2. Spectrum in water: 500 nm ( $\epsilon$  59.8), 345 nm ( $\epsilon$  55.0).<sup>15</sup> Molar conductivity, 25°, 10<sup>-3</sup> M: 231.6 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

The second precipitation with alcohol produces crystals for which analysis, spectrum, and conductivity seem to correspond to an adduct of the formula [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·DMSO.

In the presence of NO<sub>3</sub><sup>-</sup> and DMSO, the leaving of water seems to be followed by the entry of NO<sub>3</sub><sup>-</sup>. The possibility of the existence of intermediate compounds containing coordinated DMSO must be considered.

This information, together with the fact that the original product [Co(NH<sub>3</sub>)<sub>5</sub>DMSO](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O contains water which cannot be completely eliminated without decomposition, raises the possibility of DMSO being not a first-sphere ligand but a solvate. Such a possibility has been especially considered.

By using anion-exchange resins we obtained solutions of

chloride and nitrate from the perchlorate, which reproduce quantitatively the spectrum giving evidence of the maintenance of chromophore nature through the metathetical reactions. This was also controlled by the analytical results of the recovered solids (see Experimental Section). The anion-exchange substitution of the counterion rules out the solvate possibility because a solvate molecule, loosely bonded, will very probably not maintain its character upon percolation through the resin. The existence of an anhydrous salt [Co(NH<sub>3</sub>)<sub>5</sub>DMSO]Cl<sub>3</sub>, obtained by the same method, also adds to the elimination of the possible solvate composition.

Further evidence of the ligand character of DMSO is obtained from the infrared spectra of the prepared salts. Table I shows the comparison of infrared spectra with the one presented by Cotton, Francis, and Horrocks<sup>7</sup> for [Co(DMSO)<sub>6</sub>][CoCl<sub>4</sub>]. The frequency assignment has been obtained by the same authors using deuteration. The correlation becomes evident from comparative examination. All described bands of the reference spectrum, which is a pure spectrum, appear in our complexes, assuring the presence of DMSO. The small observed differences can be justified by variations in force constants due to the presence of the ammine ligand bound to the Co(III). For the perchlorate salt, the ir spectrum shows overlapping of anion absorptions with  $\rho_r$  and  $\delta_s(CH_3)$  at 1000 and 1200 cm<sup>-1</sup>, but still the  $\nu_{S-O}$  of 937-943 cm<sup>-1</sup> is strong and clearly defined. For the chloride, overlapping is avoided, there remaining only the coexistence of NH<sub>3</sub> vibrations which do not interfere with our identification purposes. The  $\nu_{S-O}$  band in free DMSO is identified at 1055 cm<sup>-1</sup> and shifts to 940 cm<sup>-1</sup> by coordination.<sup>7</sup> Such shifting is considered an indication of coordination through the oxygen atom. When DMSO forms solvates as in the case of PdCl<sub>2</sub>·2DMSO or PtCl<sub>2</sub>·2DMSO, the  $\nu_{S-O}$  band goes to 1116 and 1157, 1134 cm<sup>-1</sup>, respectively, showing a small hypsochromic effect. On the contrary, if DMSO coordinates through oxygen, the polarity change due to the new bond influences the stretching vibration (> S<sup>+</sup>-O<sup>-</sup>) producing a strong bathochromic effect as observed.

However, mention should be made of a different interpretation of the coordination shift that has been proposed by Drago and Meek.<sup>18</sup> These authors assigned the 950-cm<sup>-1</sup> band to shifted  $\rho_r(CH_3)$  and 990 cm<sup>-1</sup> to  $\nu_{S-O}$ . The spectra of our complexes show a marked difference in the intensities of 940 and 990 cm<sup>-1</sup> which favors the assignment of 940 cm<sup>-1</sup> to  $\nu_{S-O}$ , in agreement with ref 7.

**Substitution Processes.** According to the purposes stated

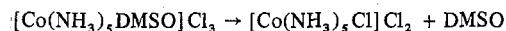
(16) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

(17) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(18) R. S. Drago and D. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

in the Introduction, we explored the possibilities of using  $[\text{Co}(\text{NH}_3)_5\text{DMSO}]^{3+}$  derivatives for substitution reactions of DMSO by other ligands. Our experiments refer to the thermal elimination of DMSO in the solid phase as well as to the leaving of the ligand in water, DMSO, and other solvents with substitution by some typical ligands.

**Thermal Reactions.** First we studied the thermal elimination from the chloride according to the reaction



To establish the conditions for a preparation we used the tga information. At the heating rate of  $1^\circ/\text{min}$  the first process starts at  $40^\circ$  and finishes at  $75^\circ$  producing a zone of constant weight up to  $125^\circ$ . This process,  $40\text{--}75^\circ$ , is identified as the volatilization of the small water content due to hygroscopicity of the substance. The next weight loss takes place from  $125$  to  $165^\circ$ , corresponding to 81% of the total DMSO present in the sample. This figure increases to 90% by means of smaller losses observed up to  $200^\circ$ . From  $200^\circ$  up, the weight decreases faster showing a little plateau at  $265^\circ$ ; at  $350^\circ$  constant weight is attained. This corresponds to the  $\text{CoCl}_2$  stability zone (end of the run,  $450^\circ$ ). This part of the tga curve shows good agreement with the known thermal decomposition of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .<sup>19</sup> The initial decomposition temperature,  $200^\circ$ , and that at the beginning of  $\text{CoCl}_2$  constant weight,  $350^\circ$ , are coincident. The resolution of decomposition in two steps has not been reported for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  tga, but two endothermic peaks are present in dta assigned<sup>20</sup> to the loss of four  $\text{NH}_3$  groups with reduction of  $\text{Co(III)}$  followed by  $\text{NH}_4\text{Cl}$  sublimation. Although our rate of heating was quite slow and the observed weight losses do correspond to such a scheme, the existence of some small side process must be recognized (see in advance) and it can be considered responsible for the difference. Further studies would be necessary but they are not included in our present purposes.

On the basis of such information we programmed the heating of a sample in the tga furnace up to  $150^\circ$  maintaining such temperature to constant weight. The constancy is attained when the loss becomes equal to 80% of the weight of DMSO present in the sample. The crystals turn purple showing the spectrum: 530 nm ( $\epsilon$  44.3), 364 nm ( $\epsilon$  46). This spectrum resembles, in its position, shape, and relative intensity of the bands, the spectrum of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  [534 nm ( $\epsilon$  51.3), 363 nm ( $\epsilon$  52.4)].<sup>21</sup> The chemical analysis shows high Co (26.9%) and low  $\text{NH}_3$  (30.9%) contents, confirming the existence of some impurities. Accordingly, we deduce that the thermal leaving of DMSO is not the only process. Considering that 20%, at least, of the weight of DMSO remains in the solid, the existence of some side reaction fixing part of the DMSO is confirmed.

We further experimented with higher amounts of substance by static warming in a furnace at  $140^\circ$ . After approximately 2 hr the velocity of weight loss falls down, corresponding to the 82% required by DMSO stoichiometry. The crystals become purple and after triple recrystallization from 2 M ammonia<sup>22</sup> each time with a yield better than 90% and washing with concentrated HCl, the following re-

sults are obtained. *Anal.* Calcd for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ : Co, 23.56;  $\text{NH}_3$ , 33.96;  $\text{Cl}^-$  (not coordinated), 28.35. Found: Co, 23.2;  $\text{NH}_3$ , 33.6;  $\text{Cl}^-$  (not coordinated), 28.6. Visible spectrum, water solution: 531 nm ( $\epsilon$  52.9), 364 nm ( $\epsilon$  49.6), and a shoulder at 469 nm. Molar conductivity,  $25^\circ$ ,  $10^{-3} M$ :  $318 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , corresponding to a fairly pure sample of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .

The recrystallization from 2 M ammonia yields blue liquors, which suggests the hypothesis that the side process implies  $\text{Co(III)}$  reduction, the product of which forms tetrahedrally  $\text{Co(II)}$ -coordinated species upon solution. This has been confirmed because the original crystals washed with concentrated HCl maintain their purple color giving a blue solution absorbing at 685, 662, 623, and 611 nm.

As a conclusion our experiments show that the thermal substitution of DMSO by  $\text{Cl}^-$ , in the solid phase, takes place mainly as the reaction above.

Another reaction by thermal elimination of DMSO which we studied was the heating of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}][\text{Co}(\text{CN})_6 \cdot 2\text{H}_2\text{O}]$ , with the purpose of checking the possible formation of the dinuclear species  $[(\text{NH}_3)_5\text{CoNCCo}(\text{CN})_5]$ .<sup>23</sup> The tga of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}][\text{Co}(\text{CN})_6 \cdot 2\text{H}_2\text{O}]$  indicates that the DMSO thermal leaving could be a dominant process in the zone  $185\text{--}235^\circ$  although overlapping from some other decomposition shows up through slope changes toward the end of the zone.

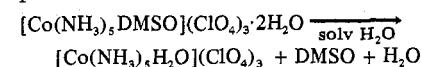
The static heating at  $190^\circ$  seems to offer the best chance to obtain the dinuclear product, maintaining the system as far as possible from the decomposition temperature. The experiments of stove heating at  $190^\circ$ , using different periods, produce blue solids showing the impossibility of isolation of the dinuclear formation process or at least of making it dominant. By lowering the heating temperature to the zone  $120\text{--}150^\circ$  the weight loss rate becomes too low, producing no evidence of formation of uncharged, slightly soluble, and yellow products. The blue solids when treated with water change to orange-rose insoluble powders.

*Anal.* Found: Co, 31.6;  $\text{NH}_3$ , 2.5.

It was not possible to find conditions for the production of the dinuclear compound. The heating decomposes the original complex producing a large loss of ammonia and reducing the  $\text{Co(III)}$ . We interpret this to mean that the thermal leaving of DMSO occurs at too high a temperature to be able to isolate the desired process from decomposition reactions.

From both described experiments on the thermal substitution of DMSO in the solid phase, criteria can be formulated to direct further applications involving not only the relative donor character but also the thermal stability of molecular parts at the corresponding temperatures.

**Solution Reactions.** In reference to the DMSO substitution in homogeneous media, we first investigated the process



By heating at  $90^\circ$  a solution of 1.35 g of the DMSO complex in 10 ml of water, the color changes quickly from red-violet to red-rose. The solution, the volume of which was reduced by evaporation, spontaneously yields pink crystals. The precipitation is completed by adding one-fifth of its volume of concentrated  $\text{HClO}_4$ ; yield 1.1 g (99%). *Anal.* Calcd for  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ : Co, 12.80;

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(22) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962 p 213.

(23) R. A. de Castello, C. R. P. Mac-Coll, and A. Haim, *Inorg. Chem.*, **8**, 699 (1969).

$\text{NH}_3$ , 18.49. Found: Co, 12.7;  $\text{NH}_3$ , 18.2. Spectrum of water solution: 490 nm ( $\epsilon = 47$ ), 347 nm ( $\epsilon = 43.5$ ), in good agreement with pure  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ .<sup>15</sup> We concluded that the substitution of DMSO by  $\text{H}_2\text{O}$  takes place completely in these conditions.

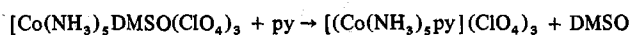
We have begun some preliminary kinetic aquation studies. The absorbance at 260 nm can be used to follow the extent of the reaction and our measurements at 45° indicate that the reaction is completed in nearly 3 hr.

We also studied the substitution of DMSO by  $\text{Cl}^-$  in DMSO solution



The starting salt is only slightly soluble in DMSO. Saturation at 20° is obtained at ~1 g/1000 ml. The color of the solution is red but it turns purple when heated at 65°. The spectral changes are from 516 to 534 nm and from 351 to 363 nm.<sup>21</sup> This maxima shift is not the only change observed. Absorptions at 660, 610, and 595 nm build up more slowly and correspond to the development of a blue tone. The position and shape of such absorptions indicate the formation of tetrahedral Co(II) species, again denoting the existence of a reduction process consuming some of the octahedral Co(III). Under the relatively high dilution used in the experiments, the reduction process does stop after 1 hr at 70°. According to the observed spectral maxima reduction, the concentration lowering of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  is very small. This reduction process observed in DMSO solution can be related to the above mentioned in the similar thermal reaction and the failure of the stoichiometric leaving of DMSO. We are planning further experimental work to study the course of these side reactions.

From a general point of view, the existence of this side reduction process does not spoil the preparation possibilities, but it must be kept in mind for the planning of other syntheses. Finally, we studied the reaction



following similar paths.

By preparing a dilute solution ( $2.5 \times 10^{-3} M$ ) of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  in pyridine, at room temperature, an immediate change of color is observed. The resulting spectrum is: 479 nm ( $\epsilon = 80.3$ ), 340.5 nm ( $\epsilon = 77.5$ ). For the water solution spectrum of  $[\text{Co}(\text{NH}_3)_5\text{py}](\text{ClO}_4)_3$  we found different reported data in recent literature: 480 nm ( $\epsilon = 46$ ), 340 nm ( $\epsilon = 39$ );<sup>16</sup> 474 nm ( $\epsilon = 63.8$ ), 340 nm ( $\epsilon = 54.4$ );<sup>24</sup> 475 nm ( $\epsilon = 64$ ), 338 nm ( $\epsilon = 52$ ).<sup>25</sup> Our findings coincide in the position of the bands but the molar absorptivity is much higher than reported for the perchlorate in water. The different solvent used (pyridine in our case) may be the one cause for this fact, but the possibility of some reactions that affect the nature of the chromophore must be taken into consideration. This chance is reinforced because, upon heating of the solution, further changes in the spectrum involving position and absorbance show up. The absorbance is sensibly increased.

We also tried the DMSO-py substitution in DMSO as a solvent, using different pyridine concentrations and heating times. The observed shifts and absorbance changes of the

bands appear to be dependent on the pyridine excess. However a neat interpretation does not come from this information alone, because we observed that a DMSO solution of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  not containing pyridine, when heated under the same conditions, also shows spectral changes which we consider to be due to the establishment of the aquation equilibrium.

When the concentration of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  in pyridine is raised to near saturation (~0.26 M), upon dissolution an unusual behavior is observed: The solution obtained by stirring at room temperature yields after a few minutes the precipitation of well-formed, red-violet crystals. These crystals redissolve slowly in the cold and faster by warming. The redissolution corresponds to the formation of an orange hue in the liquid, assigned to the formation of a pyridine-substituted product. The momentarily formed crystals were separated and identified as similar to the initial substance by analysis and spectrum. *Anal.* Calcd for  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3$ : Co, 11.32;  $\text{NH}_3$ , 16.36. Found: Co, 11.3;  $\text{NH}_3$ , 15.6.

Our interpretation of observed phenomena is that the dissolution-crystallization can be assigned to the elimination of crystallization water and the redissolution is related to the substitution itself.

Thus, we decided to attempt the synthesis of derivatives of the ion  $[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$  from  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ . The method described in the Experimental Section has been developed on the basis of criteria derived from some reported procedures for similar cases.<sup>13,24,25</sup>

The direct substitution reaction from  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  using pyridine is inconvenient because of the poor solubility of the  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  in pyridine; the synthesis of the pyridine-substituted compound developed by Nordmeyer and Taube<sup>24</sup> uses the DMF derivative as an intermediate reactant. We tried the similar system  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{DMSO} + \text{pyridine}$ , adopting the same conditions without any significant success.

However, the isolation of  $[\text{Co}(\text{NH}_3)_5\text{py}]\text{I}_3 \cdot 2\text{H}_2\text{O}$  salt, which we completely characterize in the present work, seems to us a very convenient method. The salt  $[\text{Co}(\text{NH}_3)_5\text{py}]\text{I}_3 \cdot 2\text{H}_2\text{O}$  crystallizes well, is pure, and is easily obtained with a high yield. It can be considered a good starting material to produce other counterion derivatives of the complex cation. We prepared the perchlorate whose characterization coincides with the ones reported in ref 24 and 25.

These syntheses are presented as an example of the use of leaving properties of DMSO as sixth ligand in cobalt(III) amines in solution.

**Registry No.**  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ , 35918-75-3;  $[\text{Co}(\text{NH}_3)_5\text{DMSO}]\text{Cl}_3$ , 35918-76-4;  $[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ , 35918-77-5;  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ , 13820-81-0;  $[\text{Co}(\text{NH}_3)_5\text{DMSO}][\text{Co}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ , 35918-79-7;  $[\text{Co}(\text{NH}_3)_5\text{py}]\text{I}_3 \cdot 2\text{H}_2\text{O}$ , 35918-80-0;  $[\text{Co}(\text{NH}_3)_5\text{py}](\text{ClO}_4)_3$ , 15351-76-5;  $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$ , 14404-36-5;  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , 13859-51-3.

**Acknowledgment.** The authors wish to note the important contribution of Professor R. Martres, who ran the tga curves and discussed their results. L. Donangelo contributed partially to early experimental work.

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