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A Chromatographic Study of the Reaction between Trinitro(ammine)ethylenediaminecobalt(III) and (—)-Propylenediamine

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The reaction of trinitro(ammine)ethylenediaminecobalt(III) with (−)-propylenediamine is carried out using carefully purified starting materials. The product is shown to contain six or seven chromatographically distinguishable components. These are identified as trinitrotriamminecobalt(III), *cis*- and *trans*-dinitrobis(ethylenediamine)cobalt(III) species (which are also isolated and identified by elemental analyses), and *cis*- and *trans*-dinitrobis((−)-propylenediamine)cobalt(III) species. It is inferred that the remaining components are the expected *cis*- and *trans*-dinitro(ethylenediamine)((−)propylenediamine)-cobalt(III) species.

Introduction

The singular success of paper chromatography in separating and identifying the closely related components of hitherto inseparable mixtures[2] would suggest that other complicated systems might benefit from the application of this technique.

In particular we have reinvestigated the work of Werner and Smirnoff[3] wherein they describe the laborious separation of the ten predicted isomers[4] of the $[Co(NO_2)_2(en)(pn)]^+$ ion.

The reaction carried out by Werner and Smirnoff[3]

$$[Co(NO_2)_3NH_3(en)] + (-)pn \longrightarrow [Co(NO_2)_2(en)((-)pn)]^+ + NO_2^- + NH_3$$

resembles in some respects the reaction[5] between *cis*-dichlorobis(ethylenediamine)cobalt(III) ion and (−)-propylenediamine. This latter reaction has been shown[5,6] to yield $[Co(en)_3]^{3+}$, $[Co((-)pn)_3]^{3+}$, and all mixed species. In our study of Werner and Smirnoff's reaction therefore we looked especially for disproportionation products such as $[Co(en)_3]^{3+}$, $[Co((-)pn)_3]^{3+}$, $[Co(NO_2)_2(en)_2]^+$, $[Co(NO_2)_2((-)pn)_2]^+$, etc.

We took two precautions in repeating the early work. (1) We recrystallized our starting material $[Co(NO_2)_3NH_3en]$ several times from boiling water until it was analytically and chromatographically pure. (2) We carried out the final synthesis in four separate experiments to show the results are consistent and reproducible.

Results

When the product (RM) of the reaction between $[Co(NO_2)_3NH_3(en)]$ and (−)propylenediamine is chromatographed using *n*-butyl alcohol, pyridine, water, and acetic acid (4:3:2:1) as eluent, six components are clearly visible and a seventh is suggested (*e.g.*, Figure 1D). Separation of the reaction mixture into two parts (fractions F_1 and F_2) by adding ethanol did not achieve any real separation of these six components. Fractional crystallization of F_1 and F_2 as bromide salts never gave fractions with fewer than three components when tested chromatographically.

Analyses of fraction F_1 are consistent with the desired product $[Co(NO_2)_2(en)((-)pn)]NO_2$. *Anal.* Calcd for $CoC_5H_{18}N_7O_6$: C, 18.0; H, 5.4; N, 29.4. Found: C, 17.3; H, 5.0; N, 29.8. However the presence of six components on the chromatogram shows this is certainly not pure.

We were not able chromatographically or spectrally to link any of the components separated from the reaction mixture with any tris(diamine) species. However, tentative identification of some components was achieved chromatographically and confirmed by uv–visible spectral studies. In this way the slowest moving component (C_1) was shown to contain $[Co(NO_2)_3(NH_3)_3]$ (M_1, Figure 1A and B). Since this component is only about 1% of the total product, its presence is neither surprising nor significant.

The second slowest component (C_2) corresponded chromatographically (Figure 1) and spectrally with *trans*-$[Co(NO_2)_2(en)_2]^+$ (M_2), and by running several large paper sheet chromatograms we were able to isolate some of this band as the iodide and confirm its identification by analyses. *Anal.* Calcd for $CoC_4H_{16}N_6O_4I$: C, 12.06; H, 4.02; N, 21.11. Found: C, 12.07; H, 3.87; N, 21.54.

The third slowest component (C_3) parallels *cis*-$[Co(NO_2)_2(en)_2]^+$ (M_3) when eluted with *n*-butyl alcohol, pyridine, water, and acetic acid (4:3:2:1) (Figure 1A) or *sec*-butyl alcohol, *n*-propyl alcohol, water, and acetic acid (35:35:20:10) (Figure 1B). With these latter eluents a partial separation of C_3 appears to be achieved. The uv–visible spectra of C_3 is that of a *trans*-dinitrobis(diamine) species. Isolation of a solid iodide from this component has been achieved in small yield and analysis reveals that this is dinitrobis(ethylenediamine)cobalt(III) iodide. *Anal.*

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[2] (a) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963); (b) F. P. Dwyer, B. L. James, and A. M. Sargeson, *ibid.*, **86**, 590 (1964).

[3] A. Werner and A. P. Smirnoff, *Helv. Chim. Acta*, **1**, 5 (1918).

[4] The ten isomers are initially split into two groups of five each by using only (+)pn or (−)pn in the preparation. It was these sets of five which were then separated by fractional crystallization. The two sets should behave identically and we have chosen to study only the set containing (−)pn.

[5] F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **81**, 5269 (1959).

[6] T. E. MacDermott, Ph.D. Thesis, Australian National University, 1962, p 79.

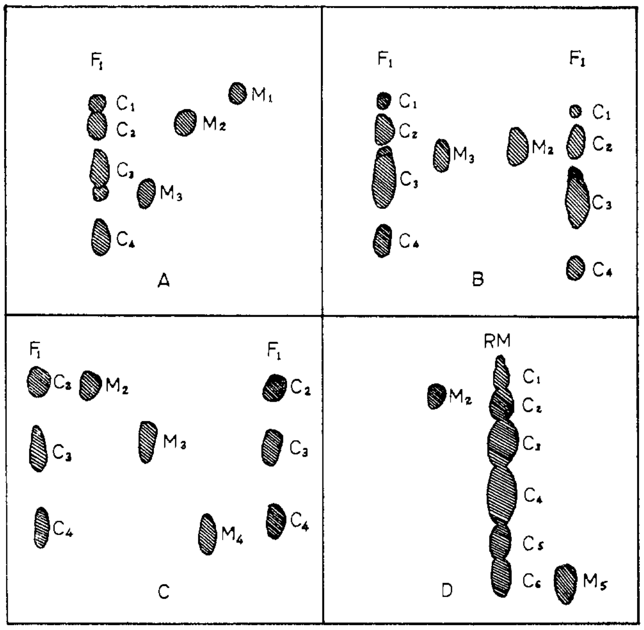

Figure 1.—Details of chromatographic separation (the labels are explained in the discussion). Eluents used: (A) *n*-amyl alcohol, pyridine, water, acetic acid (40:30:20:10); (B) *sec*-butyl alcohol, *n*-propyl alcohol, water, acetic acid (35:35:20:10); (C, D) *n*-butyl alcohol, pyridine, water, acetic acid (40:30:20:10).

Found: C, 12.30; H, 4.46; N, 21.47. We conclude that C_3 contains both *cis*-$[Co(NO_2)_2(en)_2]^+$ and *trans*-$[Co(NO_2)_2(en)((-)pn)]^+$.

The fourth slowest component (C_4) corresponds chromatographically with *trans*-$[Co(NO_2)_2((-)pn)_2]^+$ (M_4, Figure 1C) and its uv–visible spectrum agrees with its identification as this compound.

The fifth slowest component (C_5) is only partially separated from the fourth and is a minor component (about 4%). It may well be *cis*-$[Co(NO_2)_2(en)((-)pn)]^+$. Its position in the chromatogram indicates this and there is a total absence of correspondence with any markers used.

The fastest moving component (C_6) is also a minor component (~2%) and a variety of chromatographic eluents consistently link it to *cis*-$[Co(NO_2)_2((-)pn)_2]^+$ (M_5, *e.g.*, Fig 1D). Its uv–visible spectrum is consistent with this assignment.

Experimental Section

Chromatograms were run in Shandon all-glass chromatography tanks and similar apparatus. The compounds and mixtures to be studied were applied in aqueous solution to Whatman 3-MM paper sheets. Several applications were made in each case—the solvent being allowed to evaporate between applications. Chromatograms were run with a downward displacement of eluent until a satisfactory separation was achieved (usually about 16 hr).

The reaction mixture and its fractions were run variously as the nitrite or bromide. Marker compounds were used as nitrite, bromide, nitrate, or iodide, but no change was observed with a change of anion. The presence of acetic acid in all eluents probably ensured that all materials ran as acetates, especially when pyridine was also present.

Trinitro(ammine)ethylenediaminecobalt(III).—Trinitrotriamminecobalt(III) (20 g) prepared by the method of Schlessinger[7] was treated with ethylenediamine (5 g) according to the method outlined by Werner and Smirnoff.[4] The preparation was repeated ten times and the crude products were combined and recrystallized three times from boiling water. At this point the product (11.0 g, 5% yield) behaved as a single species on paper chromatograms and as a nonelectrolyte in aqueous solution. *Anal.* Calcd for $CoC_2H_{11}N_6O_6$: C, 8.76; H, 4.05; N, 30.67. Found: C, 8.66; H, 4.22; N, 30.70.

Reaction between Trinitro(ammine)ethylenediaminecobalt(III) and (−)Propylenediamine.—Trinitro(ammine)ethylenediaminecobalt(III) (9.2 g, 0.03 mol) was dissolved in hot water (300 ml) containing (−)propylenediamine (2.2 g, 0.03 mol), obtained by the resolution procedure described by Dwyer and Garvan.[8] The mixture was heated on the water bath at 85° for 1 hr—following exactly the method described by Werner and Smirnoff.[3] About 1 ml of the resulting solution (RM) was used for chromatographic studies. The rest was evaporated to 50 ml and ethanol (200 ml) was stirred in. The solid so formed was collected (F_1) and the filtrate was evaporated to dryness to give F_2. Chromatographic separations of RM and F_1 are shown in Figure 1. Further fractionation of F_1 and F_2 as bromides caused partial separations but no subfraction contained fewer than three components when studied chromatographically.

***trans*-Dinitrobis(ethylenediamine)cobalt(III) Nitrate (M_2).**—This compound was prepared by the method of Holtzclaw, Sheetz and McCarty.[9] *Anal.* Calcd for $CoC_4H_{16}N_7O_7$: C, 14.42; H, 4.84; N, 29.43. Found: C, 14.45; H, 4.90; N, 29.36.

***cis*-Dinitrobis(ethylenediamine)cobalt(III) Nitrite (M_3).**—The racemic compound was prepared by an unpublished method of Dwyer and Reid.[10] Carbonatobis(ethylenediamine)cobalt(III) chloride (274.5 g, 1 mol) was added gradually, with stirring, to 1 l. of 2 *N* hydrochloric acid. After effervescence had ceased, sodium nitrite (241.5 g, 3.5 mol) was added and the solution was set aside for 3 days. The solid which separated was the desired product. It was collected on the filter under suction and washed with ice water (30 ml) followed by 80% ethanol (200 ml) and finally acetone. The yield was 275 g. A further 25–30 g may be isolated from the filtrate and washings as the less soluble iodide.

This racemic compound was resolved by the method of Dwyer and Garvan[11] and the (+) isomer was generally used as M_3. *Anal.* Calcd for $CoC_4H_{16}N_6O_4Br$: C, 13.69; H, 4.59; N, 23.94. Found: C, 14.30; H, 4.79; N, 24.00.

***cis*-Dinitrobis((−)-propylenediamine)cobalt(III) Nitrite (M_5).**—This compound was prepared by a method analogous to that described above for the corresponding ethylenediamine complex, from carbonatobis((−)propylenediamine)cobalt(III) chloride.[12] Recrystallization of the iodide gave a product with $[\alpha]_D$ +57°. It functioned as a single component in all chromatographic separations. *Anal.* Calcd for $CoC_6H_{20}N_6O_4I$: C, 16.91; H, 4.73; N, 19.74. Found: C, 16.87; H, 4.92; N, 19.50.

***trans*-Dinitrobis((−)propylenediamine)cobalt(III) Iodide (M_4).**—When (−)propylenediamine was substituted for ethylenediamine in syntheses known to give *trans*-dinitrobis(ethylenediamine)cobalt(III) salts, only *cis*-dinitrobis((−)propylenediamine)cobalt(III) compounds were obtained. The *trans* compound used in this study is obtained by the method of Bailar, O'Brien, and McReynolds,[13] by refluxing *cis*-$[Co(NO_2)_2((-)pn)_2]I$ (1 g) in water (100 ml) for 26 hr. This process yielded a mixture of *cis* and *trans* isomers and not simply the *trans* as was suggested by these workers. The two isomers were separated by paper chromatography using *n*-butyl alcohol, pyridine, water, and acetic acid (4:3:2:1). R_f values were: *trans*, 0.40; *cis*, 0.60. Identification of the faster moving portion as the *cis* isomer was confirmed chromatographically. The identity of the *trans*

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[7] G. Schlessinger, *Inorg. Syn.*, **6**, 189 (1960).

[8] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 290 (1959).

[9] H. F. Holtzclaw, D. P. Sheetz, and B. D. McCarty, *Inorg. Syn.*, **4**, 177 (1953).

[10] I. K. Reid, private communication, 1962.

[11] F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, **6**, 195 (1960).

[12] F. P. Dwyer and T. E. MacDermott, *Inorg. Chem.*, **2**, 871 (1963).

[13] J. C. Bailar, T. D. O'Brien, and J. P. McReynolds, *J. Am. Chem. Soc.*, **70**, 749 (1948).

isomer was established by its visible and uv spectra, which agreed with that recorded by Basolo for this compound[14] and was almost identical with the spectrum for the *trans*-$[Co(NO_2)_2(en)_2]^+$ ion. A solution of the material recovered from a chromatogram was used as M_4.

Conclusion

This study does not destroy any of Werner's actual work but merely moderates the interpretation he placed on some of this work. We conclude that all such synthetic procedures should be viewed with a great deal of caution and should be monitored, wherever possible, by chromatographic processes.

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[14] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

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Organometallic Compounds with Metal–Metal Bonds. XV. Synthesis and Infrared Spectra of Mono(tetracarbonylcobalt) Derivatives of Tin, Tetrakis(tetracarbonylcobalt)tin(IV), and Related Compounds[1]

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The syntheses and infrared spectra of a series of mono(tetracarbonylcobalt)tin(IV) derivatives of the general formula $R_nX_{3-n}SnCo(CO)_4$ [$R = C_6H_5$; X = Cl, Br, I; n = 0, 1, 2] are reported. Several triphenylphosphine complexes are also described. Assignments are suggested for the carbonyl stretching bands. Cobalt carbonyl reacts with tin(II) fluoride to form $FSn[Co(CO)_4]_3$ and with tin(II) acetate to yield $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $(CH_3CO_2)Sn[Co(CO)_4]_3$. The preparation of $Sn[Co(CO)_4]_4$ is also reported.

Introduction

In an earlier paper of this series,[2] we described the synthesis of an extensive series of derivatives of the type $R_nX_{3-n}GeCo(CO)_4$ [$R = C_6H_5$, CH_3; X = Cl, Br, I; n = 0, 1, 2, 3]. The infrared spectra of these germanium compounds in the carbonyl stretching region were also discussed.

We now report on an extension of this work to tin and describe the synthesis and infrared spectra of the series $R_nX_{3-n}SnCo(CO)_4$. The preparation of $Sn[Co(CO)_4]_4$, also described in this paper, completes a very extensive series of tin–cobalt compounds which may be represented by the general formula $R_nX_{m-n}Sn[Co(CO)_4]_{4-m}$ (m = 0, 1,[3] 2,[2,4] 3; $n \le m$).

Experimental Section

All reactions were carried out under a static nitrogen atmosphere, and solid products were handled with minimum exposure to air. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded on a Texas Instruments Servo-Riter with calibration as described previously.[5] Microanalyses were performed by Alfred Berhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Mass spectra were measured with an AEI MS-9 spectrometer with direct introduction of solid samples.

Tribromo(tetracarbonylcobalt)germanium(IV), $Br_3GeCo(CO)_4$.—A solution of 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in THF was added to 2.0 g (5.1 mmoles) of $GeBr_4$ in the same solvent and the mixture was stirred at room temperature. The solution became dark green and CO was rapidly evolved. THF was removed at reduced pressure when CO evolution had ceased, and the residue was extracted with *n*-pentane. Concentration and cooling of the extract to −20° afforded yellow crystals of product. Recrystallization from *n*-pentane gave 0.4 g of product. **Triiodo(tetracarbonylcobalt)germanium(IV), $I_3GeCo(CO)_4$,** was prepared in the same way from 2.9 g (5.0 mmoles) of GeI_4 and 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in THF (yield 1.4 g).

Trichloro(tetracarbonylcobalt)tin(IV), $Cl_3SnCo(CO)_4$.—A solution of 10 g (29 mmoles) of $Co_2(CO)_8$ in 200 ml of benzene was added dropwise over the course of 1 hr to 25 g (96 mmoles) of $SnCl_4$ in 100 ml of benzene stirred at room temperature. Carbon monoxide was evolved and a pale blue gelatinous precipitate formed. When CO evolution had ceased, the solution was filtered and evaporated to dryness *in vacuo*. The residue was extracted with *n*-pentane and the solution was concentrated and cooled to −20°, affording yellow crystals. Recrystallization from *n*-pentane yielded 1.1 g.

Tribromo(tetracarbonylcobalt)tin(IV), $Br_3SnCo(CO)_4$.—A solution of 5.2 g (16.4 mmoles) of $Co_2(CO)_8$ in 150 ml of benzene was added dropwise over the course of 30 min to a room-temperature solution of 13.0 g (29.7 mmoles) of $SnBr_4$ in 70 ml of benzene. When CO evolution had ceased, the solution was filtered free of precipitated cobalt bromide and evaporated to dryness under vacuum. The residue was dissolved in ~150 ml of *n*-pentane and the solution was cooled to −20°. A mixture of red and orange

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[1] Part XIV of this series: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

[2] D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967), where references to earlier literature are also given.

[3] D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 2222 (1966).

[4] D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966).

[5] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).