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Trans Dinitrobis((-)propylenediamine)cobalt (III) Ion - its Existence and Spectroscopic Properties

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Receveid March 13, 1969

The oxidation of cobalt(II) chloride in the presence of sodium nitrite and (—)propylenediamine yields a product which can be separated into three components chromatographically, and incompletely into four components by fractional crystallization. The two slower chromatographic components appear to be a single trans *dinitrobis((—)propylenediamine)cobalt(III) species whose separation is due to an ion-pair effect. This isomer is characterized by its p.m.r. and u.v. spectra, and its c.d. spectrum is also discussed. The three less soluble components of the fractional crystallization appear to be different* cis *isomers of the same cation. The least soluble of these is characterized as* cis-*dinitro(*trans *methyls) bis ((—)propylene - diamine) cobalt(III) chloride.*

Introduction

As has recently been pointed out[1] there is considerable confusion in the literature concerning the existence of compounds of the *trans*-dinitrobis((—)propylenediamine)cobalt(III) ion. It is not possible unambiguously to distinguish *trans* from *cis* isomers in this system by appearance — since the visible spectra are extremely similar, nor by optical activity since both will show some optical activity.

In this work we use two reliable methods for distinguishing these isomers: 1. The chromatographic behaviour; 2. The ultra-violet spectra. We have already shown[2] that chromatography distinguishes various *cis* and *trans* isomers of this type. It is also a consistent observation[2] that in cellulose partition chromatography the *cis* isomer moves ahead of the *trans.*

Previously we have shown[3] that the reaction mixture $[Co(NO_2)_2(-)pn_2]Cl$ could be separated by paper chromatography into three components using n-butyl alcohol, water and acetic acid (70:20:10). In that work we also showed that the least soluble fraction corresponded with the fastest moving chromatographic component and was chromatographically "pure". This fraction was subsequently studied by X-ray crystallography[4] and shown to be the *L-cis-dinitro* (*trans*-methyls)bis((—)propylenediamine)cobalt(III) ion.

The application of UV-visible spectra in distinguishing *cis* dinitro from *trans*-dinitrobis(diamine)cobalt(III) species has been well established[5] and there appear to be no exceptions to the rule that dinitrotetraminecobalt(III) species have absorption maxima at approximately:

cis	240 mμ	325 mμ	437 mμ
trans	251 mμ	340 mμ	433 mμ

Now while the splitting is greatest in the bands in the near UV the sharpness of the bands at 240 and 250 mμ make these even more diagnostic.

Experimental Section

Preparation of a mixture of Isomers of $[Co(NO_2)_2$-$(-)pn_2]Cl$. Cobalt(II) chloride hexahydrate (12.0 g) was dissolved in 10 ml of 1 N hydrochloric acid and a solution of sodium nitrite (7.5 g) in 16 ml of aqueous optically pure (—)propylenediamine (46.6% w/v) was quickly added. Air was bubbled through the solution for 3-4 hours.

This *reaction mixture* was then treated in one of two ways:

(a) It was directly applied to a paper sheet and chromatogrammed using n-butyl alcohol, water and acetic acid (70:20:10) as eluent as described above. From such preparative chromatograms pure *trans* $[Co(NO_2)_2(-)pn_2]ClO_4$ was isolated by extracting either the middle band or the slowest band into water and adding sodium perchlorate to the filtered solution. The perchlorate salt crystallized when the sides of the flask were rubbed with a glass rod. It was collected at the pump and washed with ethanol and air dried.

Anal. Calcd. for $CoC_6H_{20}N_6O_8Cl$: C, 18.07; H. 5.02; N. 21.20. Found: C, 17.90; H. 5.12; N, 20.60.

(b) The filtrate was exaporated to a small volume and the solid material (Fraction 1, 3.15 g) collected by filtration, washed with ethanol and air dried. The filtrate was further evaporated and ethanol stirred in to precipitate Fraction 2 (2.75 g). Fractions 3 (10.8 g), 4 (4.8 g), 5 (2.55 g) and the residue Fraction 6 (0.2 g) were collected in a similar way. Further fract-

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[1] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, *7*, 921 (1968).

[2] T. E. MacDermott and L. A. P. Kane-Maguire, *Inorg. Chem.*, *7*, 769 (1968).

[3] T. E. MacDermott, Ph. D. Thesis A.N.U. 1962, p. 125.

[4] G. A. Barclay E. Goldshmied, N. C. Stephenson, and A. M. Sargeson, *Chem. Comm.*, *1966*, 540.

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

Table I. Uv-visible Spectral Features of chromatographic Bands

	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$
Band 1	433 mμ	2.25	340	3.55	250	4.30	203	4.36
Band 2	433 mμ	2.25	340	3.49	250	4.28	203	4.41
Band 3	437 mμ	2.25	322	3.54	241	4.33	200	4.33

ionation of 1 into 1 (a) (b) and (c), 3 into 3 (a) and (b), 4 into 4 (a) (b) (c) and (d) was achieved by a similar process. From comparative chromatograms using the system mentioned in (a) above, it was shown that Fractions 1 (a), (b), (c), 3 (a), 4 (a), (b), contained mostly *cis* isomers while the other fractions contained mostly *trans* with a small *cis* impurity. From X-ray powder patterns it was clear by comparing the values of 2 Θ observed with those computed from the unit cell dimensions[4] that Fraction 1 (a) and (b) contained almost entirely *cis* dinitro(*trans* methyls)bis((—)propylenediamine)cobalt(III) chloride. Fraction 1 (c) gave a distinct powder pattern and Fractions 3 (a), 4 (a) and 4 (b) gave a third pattern. Since there are six possible *cis* isomers no assignment nor tentative assignment can yet be made for the configuration of the two new *cis* isomers.

The fractions containing the *trans* species have been subject to further fractionation but with no evidence so far of the existence of a second *trans* isomer.

Chromatographic Study. The chromatograms were run in Shandon all-glass tanks. Separations were carried out on Whatman 3MM and 3MC paper sheets by downward displacement of eluent. The best results were achieved with the 3MC paper probably because it is carboxylate free and so there is no competitive ion exchange chromatography which would favour the reverse order of elution. The material to be separated was aplied in fairly concentrated aqueous solution using a capillary tube. The paper was dried (the band being no more than 1 cm wide) and the elution allowed to proceed until a good separation was achieved — usually from 4 to 16 hours.

The three bands observed in this study had Rf values of 0.19, 0.28, 0.38 respectively.

UV-visible Spectra were recorded on a Cary 14 recording spectrophotometer. The spectra of the three bands from the chromatogram were recorded by extracting each band as completely as possible from the chromatogram with water, filtering and diluting to a measurable concentration. By puting the extinction coefficient of the band in the visible at $\log \varepsilon = 2.25$ (in agreement with Basolo[5]) the values of $\log \varepsilon$ for the other absorptions have been calculated and are presented in Table I.

Band 1 agrees well with the spectrum measured on the isolated *trans* $[Co(NO_2)_2(—)pn_2]ClO_4$ which is shown in Figure 2, while Band 2 may still contain a small amount of the *cis* isomer as an impurity and this would tend to depress the absorption maxima of the bands at 340 and 250 mμ.

These trans spectra agree well that of Basolo[5] and since he refers his synthesis for this compound to Watts[6] we presume that the earlier worker had also isolated a compound having the correct constitution.

It is interesting to note that very intense absorption bands occur for both the *cis* and *trans* isomers at about 200 mμ. In the case of the *cis* isomer this absorption is of equal intensity with the band at 241 mμ while for the *trans* isomer this highest energy band is also the most intense.

Optical Rotatory Dispersion curves for aqueous extracts of the three chromatographic components were measured using a Perkin Elmer P22 Spectropolarimeter. The curves for Bands 1 and 2 are almost superimposable, crossing the zero rotation line at 470 mμ and having a maximum at 434 mμ and a minimum at 493 mμ. The ratio max: min is 4.4. The curve for Band 3 is also very similar having a maximum at 436 mμ and a minimum at 495 mμ and zero rotation at 473 mμ. The ratio max: min is 6.8. In the case of the *cis* isomer the band at 495 mμ is known[3] to represent a molecular rotation of —1000° so the maximum at 434 mμ is $[M] = +6800°$. All three curves resemble $L[Coen_3]^{3+}$ although it is difficult to interpret this trend for the *trans* isomer.

Circular Dichroism. The circular dichroism spectrum for the *trans* $[Co(NO_2)_2(—)pn_2]ClO_4$ was run on a Jouan Dichrographe using a 6.64×10^{-3} *M* solution in a 1 cm cell with the sensitivity at 1.5×10^{-4}. This gave a max = 0.84 at 465 mμ and min = —0.47 at 405 mμ (Figure 2). This spectrum essentially mirrors the

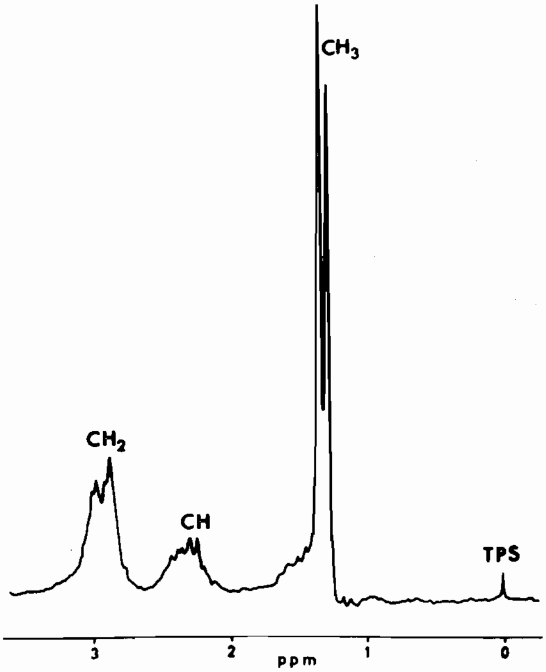

Figure 1. 100 Mc spectra of *trans*$[Co(NO_2)_2(—)pn_2]Cl$ (Slowest chromatographic band).

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[6] E. Watts Dissertation Zurich 1912.

c.d. spectrum for the *L-cis*-dinitro(*trans* methyls)bis((—)-propylenediamine)cobalt(III) ion[4] although the peak heights are not so great.

p.m.r. Spectra were measured on a varian H.A. 100 in neutral D_2O solution and are shown in Figure 1. From the integration it is easy to assign the sharp doublet 1.30 ppm downfield from TPS to the methyl groups, the multiplet centred at 2.33 ppm downfield from TPS as due to the methine protons and the quartet 2.91 ppm downfield from TPS to the methylene groups. The simplicity of the spectrum suggests two identical propylenediamine residues but does not distinguish the two possible *trans* species.

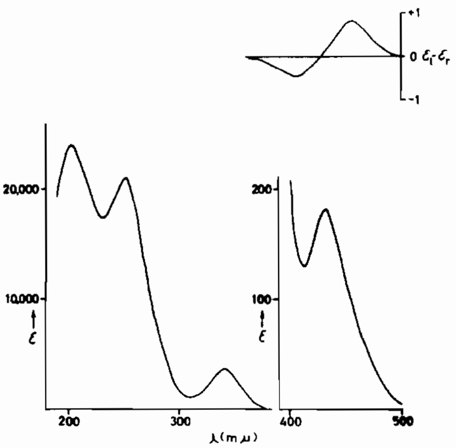

Figure 2. Uv-visible and C.D. spectra of *trans*$[Co(NO_2)_2(-)pn_2]Cl$. Slowest chromatographic band).

Results and Discussion

In this investigation we have carried out preparative scale separations of the dinitrobis((—)propylenediamine)cobalt(III) chloride reaction mixture on paper sheets using n-butyl alcohol, water and acetic acid (70:20:10) and again found the three components described previously.[3] The fastest band was fractionally crystallized as the chloride, crystals were grown and shown by X-ray powder studies and the computation of values of 2 Φ to be identical to the compound whose X-ray structure has been determined,[4] *i.e. L-cis*-dinitro(*trans*-methyls)bis((—)prophylenediamine)cobalt(III) chloride. The middle band and the slowest band have almost identical UV-visible spectra with absorption maxima at 251, 340 and 433 mμ. They are therefore assigned the *trans* configuration. Now on rechromatogramming the slowest chromatographic component using the same eluent a second separation occurs and the faster of the two new components corresponds precisely with the middle band of the original separation. This process can be repeated several times. However, if only a small amount of material is applied to the paper it all runs as the faster component.

The p.m.r. spectra show that the faster of the two *trans* components contains one equivalent of acetate when the papers are dried and the band eluted into D_2O. The slower band still persists as the chloride. This unusual separation is concentration-time dependent. When a maximum amount of the *trans* $[Co(NO_2)_2(-)pn_2]Cl$ is applied to the paper the searation into two bands occurs quite suddenly and completely only ofter about 24 hours. The separation seems to depend not only on the relative speeds of elution of the two ion pairs but also on their relative concentrations.

The p.m.r. spectrum of the *trans* chloride or perchlorate derived from either of the two slower chromatographic bands is quite simple and suggests that only a single isomer is present and microscopic examination of the needles in which this compound crystallizes fails to reveal evidence of a second isomer.

As described above eareful fractional crystallisation of the reaction mixture from aqueous solution by the addition of ethanol has indicated two new *cis* dinitro species with distinct X-ray powder patterns. Elucidation of their structures is our continuing endeavour.

The circular dichrograph of our chromatographically pure *trans* species is shown together with the UV-visible spectrum in Figure 2. The form of the c.d. curve is very similar in shape but opposite in sign in the visible region to that for the *L-cis* species.[4] Also the intensities of the absorptions are considerably lower. This measurement does not distinguish these isomers and earlier discussions[7] of the *trans* dinitrobis(propylenediamine)cobalt(III) species are very confused since they are based on studies of the *cis* isomer. Therefore the assignment of *cis* or *trans* geometries to dinitrobis (*act* diamine)cobalt(III) species through a study of their c.d. spectra is quite unacceptable.

One may also presume at this stage that there will be little difference between the *trans* dinitro (*cis* methyls) and (*trans* methyls) as far as their UV-visible and c.d. spectra are concerned. We have already shown[8] that the different relative positioning of the various methyl groups in *cis* and *trans* *L* $[Co(-)pn_3]^{3+}$ causes no discernable differences in these spectra. In this present case also the metal chelate rings will have the identical conformations for the two isomers and the methyl groups should have very little influence.

Since the absolute configuration of (—)propylenediamine is known it is possible do drawn down the configuration of this *trans* product and use the c.d. spectrum as a guide in the assignment of the absolute configuration of other optically active diamines which form similar complexes. Such extensions can be very misleading and must be indulged in with extreme caution. For example both the *trans* dichloro and *trans* dinitrobis(N-methylethylenediamine)cobalt(III) ions which have similar c.d. spectra to the corresponding (—)propylenediamine complexes have the opposite metal-ligand ring conformations.[9]

Acknowledgments. I thank Dr. L. G. Marzilli for continued interest and helpful discussions; Dr. Joyce H. Fildes for the microanalyses; Mr. C. Arandjelovic for the p.m.r. spectra; Dr. C. J. Hawkins for recording the c.d. spectra and Mr. I. Maxwell for writing the program for compunting 2 Θ from the unit cell dimensions.

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(7) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, *4*, 202, (1965).

(8) T. E. MacDermott, *Inorg. Chim. Acta*, 2, 81, (1968).

(9) D. A. Buckingham, L. G. Marzilli, and W. Robinson, unpublished results (1968).