ACTA CHEMICA SCANDINAVICA 24 (1970) 924–930

A New Isomerism — Conformational Isomers of *meridional*-Trinitro(ammine)ethylenediaminecobalt(III)

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In the course of a study of nitro-ammine complexes of cobalt(III) we have observed considerable confusion and error in the literature. Here we extend the knowledge of the trinitro triamine type of compound by repeating, reviewing and explaining previous work and by describing two Conformational Isomers of *meridional*-$[Co(NO_2)_3NH_3en]$. The physical properties of these novel isomers are described in detail and rationalised in the light of the results of the X-ray investigations of Gram Jensen, Soling and Thorup.[22] A new simple synthesis for *meridional*-$[Co(NO_2)_3(NH_3)_3]$ is also described.

Isomerism in the case of nitro-ammine complexes of cobalt(III) has hitherto been restricted to Linkage Isomerism as exhibited by the nitro-nitrito isomers of the $[CoNO_2(NH_3)_5]^{2+}$ ion,[1] and Geometric Isomerism as displayed in the *cis* and *trans* isomers of the $[Co(NO_2)_2(NH_3)_4]^+$ ion.[2,3] Such isomerism has not always been found where predicted. Only the *trans* isomer of the $[Co(NO_2)_4(NH_3)_2]^-$ ion has been described [4] while for trinitrotriamminecobalt(III) only the *meridional* isomer [5,6] has been identified by X-ray studies.[7] The various claims for the isolation and identification of the facial isomer of this compound [8–13] are all without foundation.[14–16,25] The compound most often being assigned [10–12] as *facial*-$[Co(NO_2)_3(NO_3)_3]$ is *trans*$[Co(NO_2)_2(NH_3)_4]$ *trans*-$[Co(NO_2)_4(NH_3)_2]$.[15,25]

In one of the earliest studies on trinitrotriamminecobalt(III) Jørgensen [17] has described two crystalline modifications. We have taken the two samples which were actually prepared by Jørgensen himself and have shown that they have identical infra-red spectra and X-ray powder patterns. The difference in crystal appearance must be due to crystal growth along different axes.

In the course of our investigations we have observed a very simple synthesis of *meridional*-$[Co(NO_2)_3(NH_3)_3]$ wherein sodium nitrite reacts with chloropenta-

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amminecobalt(III) chloride in boiling aqueous solution to give the required product in a few minutes. The product which separates as the solution cools is spectroscopically pure. We believe that this will become the preferred method of synthesis for this compound.

Mathieu [15] has recently described a new synthesis for *facial*-$[Co(NO_2)_3(NH_3)_3]$. We have not yet succeeded in reproducing this rather sensitive synthesis wherein one of the intermediates (the blue form of $[CoCl_2H_2O(NH_3)_3]Cl$ is sensitive to moisture reverting to the "dichro" or violet form; and the final product (designated 1,2,3 or *facial* isomer by Mathieu) is sensitive to both moisture and heat — easily reverting to the well known *meridional* or 1,2,6 (or 1,2,4) isomer. Mathieu's evidence is restricted to infra-red studies and we do not consider the designation as definitely proven. Indeed if the *facial* isomer is so unstable it will be most difficult to prove its structure in an unambiguous way.

We note also that trinitrodiethylenetriaminecobalt(III) $[Co(NO_2)_3dien]$, has been described in only one form [18] and X-ray analyses [19] have shown that in the solid state this molecule possesses a true plane of symmetry and is the sterically unfavoured *meridional* isomer.

As an extension of knowledge of isomerism in this system we now describe another similar compound which exhibits an isomerism of a novel type as far as these systems are concerned.

RESULTS AND DISCUSSION

Intermediate between $[Co(NO_2)_3(NH_3)_3]$ and $[Co(NO_2)_3dien]$ is the compound $[Co(NO_2)_3NH_3en]$. We have previously been interested in this compound,[20] as an intermediate in a synthetic study. Now we have reinvestigated the compound with a view to establishing its molecular configuration. In our previous work we obtained this compound in very poor yield as translucent yellow needles. We have now devised a direct one-step high-yield synthesis and have observed that the product separates in two forms. One consists of flat yellow needles whose infra-red spectrum is exactly superimposable on that of the material described previously [20] ("yellow" isomer). The other form consists of yellow-brown octahedra ("brown" isomer).* Repetition of the synthesis shows that the ratio of "yellow" to "brown" forms is variable. In one case the "yellow" form only was obtained. Recrystallisation of either form from hot dilute acetic acid gives varying mixtures of the two forms ** which are separated by hand.

The two crystal forms while having very different appearance, also give significantly different infra-red spectra and X-ray powder patterns. The infra-red spectra are shown in Fig. 1, where they are compared with spectra for *meridional*-$[Co(NO_2)_3(NH_3)_3]$ and *meridional*-$[Co(NO_2)_3dien]$. In particular in the region of the CH_2 rocking frequency (880—900 cm^{-1}) the "brown"

* These isomers have identical colours when finely ground. The apparent difference is due to crystal shape.

** There seems to be a latitude effect operating here. In Denmark the "brown" isomer predominates, while in Australia the compound crystallises almost exclusively in the "yellow" form.

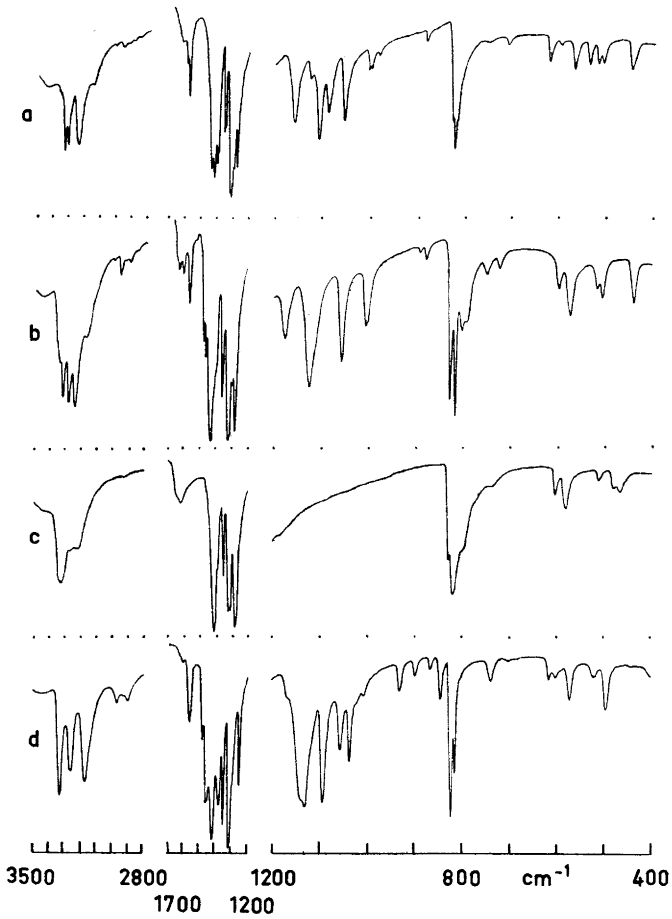

Fig. 1. IR-Spectra (a) "yellow" *meridional*-[$Co(NO_2)_3NH_3en$]; (b) "brown" *meridional*-[$Co(NO_2)_3NH_3en$]; (c) *meridional*-[$Co(NO_2)_3(NH_3)_3$]; (d) *meridional*-[$Co(NO_2)_3dien$].

isomer has a sharp doublet (885, 898 cm^{-1}) while the "yellow" isomer has a singlet at 885 cm^{-1}. This has been used to distinguish *cis* from *trans* diacido bis(diamine) metal complexes [21] and the observation of this phenomenon here initially suggested that the "brown" could be the *facial* and the "yellow" the *meridional* isomer. Such evidence is very like that cited above for the uncertain establishment of such isomerism in other similar systems. However, the solution studies on these isomers do not support this possibility of geometric isomerism.

The UV-visible spectra for these two isomers are identical. The maxima are listed in Table 1 wherein they are compared with other *meridional* trinitrotriamine complexes and also with *trans*-dinitrotetraamminecobalt(III) acetate.[16]

Table 1. Maxima of UV-visible absorptions.

meridional-$[Co(NO_2)_3NH_3en]$		*meridional*-$[Co(NO_2)_3dien]$		*meridional*-$[Co(NO_2)_3(NH_3)_3]$		*trans*-$[Co(NO_2)_2(NH_3)_4]CH_3COO$	
λ (mμ)	log ε	λ (mμ)	log ε	λ (mμ)	log ε	λ (mμ)	log ε
430	2.45	430	2.45	431	2.34	440	2.24
338	3.68	335	3.69	344	3.76	346	3.61
251	4.31	251	4.31	252	4.29	252	4.20
202	4.25	201	4.15	195	4.31	193	4.32

The PMR spectrum in DMSO-d_6 solution, shown in Fig. 2, is the same for both isomers. Assignments of absorptions are readily achieved by reference to the 100 Mc spectrum of *meridional*-$[Co(NO_2)_3(NH_3)_3]$. For the latter com-

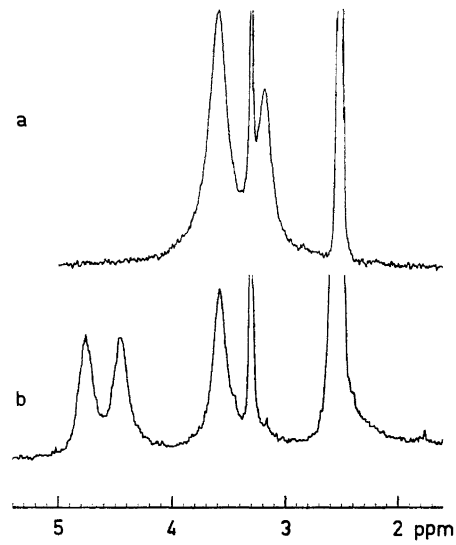

Fig. 2. 100 Mc PMR spectra (a) *meridional*-$[Co(NO_2)_3(NH_3)_3]$; (b) *meridional*-$[Co(NO_2)_3NH_3en]$.

pound the two peaks at 3.15 and 3.65 ppm are in the ratio 1:2. Clearly the upfield peak represents the ammonia group *trans* to a nitro group, and the downfield absorption represents the two ammonias *trans* to each other. For *meridional*-$[Co(NO_2)_3NH_3en]$ there are three absorptions at 3.60, 4.45 and 4.75 ppm, respectively, and they bear the ratio 3:2:2. The peak at 3.60 ppm clearly represents the ammonia group *trans* to one amine group. The other two

represent the amine protons of the ethylenediamine group. By comparison with *meridional*-$[Co(NO_2)_3(NH_3)_3]$ we assign the band at 4.45 to the amine group *trans* to a nitro group, and the band at 4.75 ppm to the amine group *trans* to the ammonia group. In this spectrum the ethylene chain is obscured by the DMSO absorption at 2.50 ppm.

Finally the chromatographic methods which have proved to be so successful [20] in separating geometric isomers in other similar systems, fail to achieve a separation in this instance.

Clearly it is not possible to draw conclusions from the above study concerning the relationship which exists between these isomeric forms of $[Co(NO_2)_3NH_3en]$. The problem has been solved by the recently completed X-ray studies on single crystals of both the "yellow" and "brown" forms,[22] where Gram Jensen, Soling and Thorup prove that the two compounds are Conformational Isomers of *meridional*-$[Co(NO_2)_3NH_3en]$. This excellent study has placed all atoms, including the protons, in both molecules, and makes it very clear that the oxygens of the 1 and 6-nitro groups are involved in hydrogen-bonding with the ammonia protons and also with the protons of the amine group in the 5-position. In an effort to ascertain the energy barrier to rotations between the two forms we have studied the Differential Thermal Analyses of both isomers in the hope of observing a phase transition for one of them. However, there is no endothermic change of any kind for either isomer below 200°C and at about 210°C both undergo a rapid exothermic reaction with a correspondingly rapid loss of weight (explosion).

The presence of hydrogen-bonding explains other features of these structures. The fact that the metal-ethylenediamine ring is considerably distorted in the "brown" form is compensated for by the short hydrogen-bonds formed by this ligand with the oxygen of the nitro group projecting directly below it. This distortion, furthermore, explains why the "brown" isomer has additional complexity in its infra-red absorption spectrum — especially why the CH_2 rocking band is split.

Finally, it is possible that Werner and Grun [23] have already described this phenomenon. In one of the early papers on this compound they describe two crystals forms — "yellow brown plates" and "flat feathery striped needles". These could possibly be the brown and yellow isomers, respectively, but more likely are two crystalline modifications of the "yellow" isomer which we have also obtained in poorly formed aggregated flat needles and well formed plates which appear somewhat browner in colour than the needles.

EXPERIMENTAL

PMR spectra were recorded on a Varian HA100 NMR spectrophotometer. The lock signal was external TMS and the solvent DMSO-d_6.

Infra-red spectra were recorded on a Perkin-Elmer 337 Infra-red (Grating) Spectrophotometer with samples in vacuum pressed potassium bromide discs.

UV-visible spectra were recorded using a Cary 14 Spectrophotometer. The 10^{-4} M aqueous solutions were measured within 10 min from the commencement of the dissolution process. In the visible region 10 cm cells were used and for the UV region 1 cm cells were employed.

Chromatography. In a typical study downward elution with 2-butanol-pyridine-water-acetic acid (4:3:2:1) on Whatman 3MM paper caused both isomers to be displaced at the same rate. The R_F value was 0.43.

meridional-$[Co(NO_2)_3(NH_3)_3]$. A simple synthesis for this compound is as follows: Chloropentaamminecobalt(III) chloride (1.0 g) and sodium nitrite (1.0 g) are mixed with 20 ml of water and the mixture is heated rapidly on a hot plate. As the colour changes a black deposit forms. This may be removed by rapid hot-filtration through a cotton plug. The filtrate is further heated until it is quite yellow (several minutes) filtered again and cooled in ice. Crystallisation is initiated by rubbing the walls of the beaker a few times with a glass rod. Crystallisation is allowed to proceed for several hours and the product is collected at the pump, washed with cold aqueous ethanol and then ethanol and air dried. The infra-red spectrum is exactly superimposable on that for the compound described by Jørgensen.[6] The yield is 0.3 g (30 %). (Found: H 3.64; N 33.45. Calc. for $CoH_9N_6O_6$: H 3.63; N 33.87).

"Brown" and "yellow" forms of meridional $[Co(NO_2)_3NH_3en]$. Cobalt(II) acetate tetrahydrate (10 g, 0.04 mol) is dissolved in a solution of sodium nitrite (10 g, 0.14 mol) and ethylenediamine (2.5 g, 0.04 mol) in 25 % aqueous ammonia (50 ml, 0.75 mol). During this process the solution becomes warm. To this warm solution concentrated hydrogen peroxide (3 ml) is added as quickly as the effervescence will allow. The resulting solution is heated on a hot plate until a thick precipitate forms. It is then allowed to cool, collected on a suction filter, washed with a little water followed by ethanol and then acetone and air-dried. The yield of this crude product is 7 g, 70 %.

The crude product is mostly dissolved in a minimum of hot 5 % acetic acid and filtered. The solution is set aside and allowed to cool slowly. A mixture of brown octahedra and flat yellow plates form and these are easily separated by hand.

As pointed out above both isomers may be recrystallised from hot dilute acetic acid to yield sometimes pure isomers and sometimes a mixture of isomers. At no stage of the synthesis is the ratio of the two isomers predictable.

In another synthesis reactants were kept cool ($\sim$ 25°) and the solution stirred for five days. Similar yields were obtained but the infra-red spectrum indicated that the crude product was almost entirely in the "yellow" form.

A final example of how this synthesis can be varied is the process by which we first obtained good crystals of the "yellow" form:

Cobalt(II) acetate tetrahydrate (27 g), ethylenediamine (12 g), sodium nitrite (40.5 g), ammonium acetate (15 g), and ammonium hydroxide (150 ml 50 % solution) were mixed using a magnetic stirrer. Concentrated hydrogen peroxide (9 ml) was added slowly so that the temperature never rose above 40°C. The resulting mixture was stirred for seven days. The yellow powdery material which separated in this time was collected in the usual way (yield 9.5 g, 35 %). 5 g of this raw product was extracted with four aliquots of 1 % acetic acid preheated to 80–90°C (one of 80 ml and three of 120 ml). These filtered extracts were allowed to cool slowly by standing on the slowly cooling hot plate. The "brown" form was found in decreasing proportion from extracts 1 to 4. The crystals were large and could be separated by hand. (Found: ("Yellow" form [20]) C 8.66; H 4.22; N 30.70. ("Brown" form) C 8.64; H 4.09; N 30.72. Calc. for $CoC_2H_{11}N_6O_6$: C 8.76; H 4.05; N 30.67).

CONCLUSION

The solution of this problem established a new kind of isomerism for nitro complexes which we have called Conformational Isomerism. It is probable that such isomerism exists identifiably only in the solid state. As a result of this work it is clear that the assignment of geometric isomerism by reference only to infra-red spectra or X-ray powder patterns is unacceptable. In this regard we would emphasise the use of NMR spectroscopy (especially the N—H region in perdeutero-DMSO solution).[24]

Acknowledgements. We are particularly grateful to Professor Niels Hofman Bang for permission to use samples from the S. M. Jørgensen collection at the Technical University of Denmark. We also thank Mr. A. C. Arandjelovic for recording the PMR spectra, Professor Simonsen of the Danish Institute of Silicate Industries for recording and discussing the D.T.A. spectra and Professor F. Woldbye for helpful discussion. One of us (T.E.M.) wishes to thank the Technical University of Denmark for an appointment as Visiting Professor during the course of this work.

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Received June 29, 1969.