Inorganica Chimica Acta, 42 (1980) 271–275
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X-Ray Structure of *Mer*-Trichloro[N-(3-aminopropyl)-1,3-diaminopropane]-cobalt(III)

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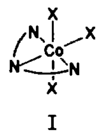
Received April 11, 1980

The single crystal X-ray structure of [Co(dpt)Cl$_3$] (dpt is N-(3-aminopropyl)-1,3-diaminopropane) is reported. The molecule crystallizes in space group $P2_12_12_1$ with four molecules in a cell of dimensions a = 9.290(3) Å, b = 6.782(3) Å, c = 18.620(4) Å; ρ_{calcd} = 1.679 g cm^{-3}, ρ_{exptl} = 1.66 g cm^{-3}. Full-matrix least squares refinement of 1129 reflections having $F > 3\sigma_F$ gave R = 0.029 and R_w = 0.032. The complex has the meridional stereochemistry with both chelate rings in the chair form. Cobalt–nitrogen and –chlorine distances are in the expected range. Carbon-13 NMR data is presented for [Co(TACN)-dpt]$^{+3}$ (TACN is 1,4,7-triazacyclononane), which is apparently the first complex to have dpt coordinated in facial form. Qualitative observations show that dpt is a much inferior ligand for Co(III) than diethylenetriamine.

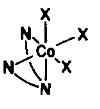
Introduction

Cobalt(III) complexes of N-(3-aminopropyl)-1,3-diaminopropane (hereafter, dpt) have been the subject of several investigations. In contrast to diethylenetriamine (dien) [1] only meridional isomers (I) of dpt have been characterized [2–4]. Structural data are available for two isomers of *mer*-[Co(dpt)(en)Cl]$^{+2}$ III [3] and IV [4] and [Ni-(dpt)$_2$](ClO$_4$)$_2$ [5]. No conclusive evidence for a facial form (II) has apparently been reported. In fact, a reported third isomer [2] of [Co(dpt)(en)Cl]$^+$ has been shown to be a mixture of two different compounds [6].



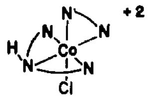
I

meridional

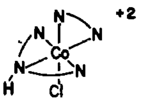


II

facial



III



IV

The similarity in absorption spectra of [Co(dpt)-Cl$_3$] and [(1,4,7-triazacyclononane)CoCl$_3$] suggested to us that the former might also have a facial stereochemistry although it had been earlier assigned as meridional [8]. This paper reports the single crystal X-ray structure of [Co(dpt)Cl$_3$], which shows that it, in fact, has the meridional (I) stereochemistry. Also presented is ^{13}C NMR evidence for a complex that contains dpt coordinated in a facial form and some observations that suggest dpt is a poor complexing agent for Co(III).

Experimental Section

[Co(dpt)Cl$_3$] and [Co(TACN)Cl$_3$] (TACN is 1,4,7-triazacyclononane), were prepared by literature procedures [7, 9]. Carbon-13 NMR spectra were obtained on a JEOL-PFT100 spectrometer operating at 25.15 MHz. Wilmad 592-E-10 microcells were used for samples from ion-exchange experiments.

Preparation of [Co(TANC)dpt]$^{+3}$

An aqueous solution generated from 0.3 g complex and 0.5 g dpt was evaporated to dryness on a steam bath and the oily residue heated for a further 6 hr. After this time, the dark colored material was placed on a C-25 Sephadex column and eluted with 0.5 M NaCl. An intermediate orange fraction was collected and concentrated by evaporation, addition of ethanol, and filtration until most of the sodium chloride was separated. No more than 50 mg of complex remained at this point. A ^{13}C NMR spectrum obtained on this material showed 9 approximately equally intense bands at δ (D$_2$O solution vs dioxane) = –15.23, –15.71, –16.08, –19.17, –21.78, –29.67, –30.09, –42.65 and –44.71. The sample was rechromatographed on a 1.7 m C-25 SP-Sephadex column with 0.5 *M* NaCl as eluent. No separation of

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TABLE I $[Co(C_6H_{17}N_3)Cl_3]$ Crystal Data

Mol wt	296 53
space group	$P2_12_12_1$
cell constants	
a, A	9 290(3)
b, A	6 782(3)
c, A	18 620(4)
No of reflections used to determine	15
cell constants and their 2θ limits, deg	4 9 < 2θ < 18
Z	4
ρ_{calcd}, g cm^{-3}	1 679
ρ_{exptl}, g cm^{-3} [a]	1 66
μ, cm^{-1}	21 5

[a] By flotation in hexane–1,2-dibromoethane

the band was apparent but it was collected in two fractions The second fraction, after concentrating as described above, was again examined by ^{13}C NMR The same nine resonances were present but those at −21 78, −29 67 and −42 71 were only ~½ as intense as in the first spectrum We conclude that the remaining six resonances are probably due to [Co(TACN)-(dpt)]$^{+3}$ λ_{max} values values for the compound are 482 and 348 nm

X-Ray Data Collection and Refinement

$[Co(dpt)Cl_3]$ was recrystallized by Curtis' procedure [9] For data collection a section ~0 3 mm long was cut from a well-shaped rod whose cross-section dimensions were about 0 3 x 0 34 mm Crystal data and information concerning diffraction data collection and refinement are given in Tables I and II The structure was solved by use of a Patterson synthesis and standard Fourier methods and refined by full matrix least-squares methods using Sheldrick's SHELX-76 program Scattering factors were Cromer

TABLE II Data Collection and Refinement Details for $[Co(C_6H_{17}N_3)Cl_3]$

diffractometer	Syntex $P2_1$
monochromator (Bragg 2θ angle, deg)	graphite (12 2)
radiation A	MoK$\bar{\alpha}$, 0 71069
take off angle, deg	6 75
scan method	θ–2θ
scan speed, min/max (deg min^{-1})	2 0(29 3)
scan width, deg	2 0
background/scan time ratio (TR)[a]	1 0
no of standards (monitoring freg , no of reflections)	3, (97)
2θ limits of data, deg	4 < 2θ < 50
h,k l limits	0,0,0 → +h, +k, +l
no of data	1227
no of data used in final refinement ($F > 3\sigma_F$)[b]	1129
no of data/no of variables	8 4
$R = (\Sigma \| \|F_o\| - \|F_c\| \|)/(\Sigma \|F_o\|)$[c]	0 029
$R_w = [\Sigma(\|F_o\| - \|F_c\|)(w^{1/2})/[\Sigma(\|F_o\|)(w^{1/2})]$	0 032

[a] Background counts measured before (BG1) and at the end (BG2) of the scan Intensities determined from total scan (CT) and background (BG) counts by I = CT-TR(BG1 + BG2) σ_I = [CT + (TR)^2(BG1 + BG2)]$^{1/2}$ [b] $F_o = (I/Lp)^{1/2}$, $\sigma_F = \sigma_I/2(F)(Lp)$ where Lp is the Lorentz and polarization correction An absorption correction was not applied [c] Function minimized = $\Sigma w(|F_o| - |F_c|)^2$ where $w = n/(\sigma_F^2 + mF^2)$, in the final cycle n was 0 692 and m was 1 6 × 10^{-3}

TABLE III Final Positional and Anisotropic Thermal Parameters[a] (with esd s) for Nonhydrogen Atoms of *mer*-Trichloro-[N-(3-aminopropyl)-1,3-diaminopropane)] cobalt(III)

Atom	X	Y	Z	U11	U22	U33	U23	U13	U12
Co	0 15420(6)	0 16458(9)	0 12538(3)	0 0192(3)	0 0233(3)	0 0219(3)	−0 0008(3)	0 0006(3)	−0 0001(3)
Cl1	0 3736(1)	0 2996(2)	0 11480(6)	0 0234(5)	0 0342(6)	0 0410(7)	0 0017(5)	0 0025(5)	−0 0050(5)
Cl2	0 0487(1)	0 4724(2)	0 13159(6)	0 0319(6)	0 0261(6)	0 0406(6)	−0 0019(5)	0 0022(6)	0 0052(5)
Cl3	−0 0651(1)	0 0159(2)	0 13287(6)	0 0239(6)	0 0357(7)	0 0452(7)	−0 0020(6)	0 0019(5)	−0 0046(5)
N1	0 1605(4)	0 1766(6)	0 2309(2)	0 033(2)	0 036(2)	0 024(2)	0 003(2)	0 000(2)	0 003(3)
N2	0 2411(4)	−0 1065(6)	0 1223(2)	0 023(2)	0 029(2)	0 027(2)	−0 001(2)	−0 000(2)	0 002(2)
N3	0 1245(4)	0 1932(7)	0 0208(2)	0 031(2)	0 037(2)	0 023(2)	−0 001(2)	−0 002(2)	0 007(2)
C1	0 2811(6)	0 0920(9)	0 2729(3)	0 038(3)	0 052(3)	0 028(3)	−0 001(2)	−0 008(2)	0 004(3)
C2	0 2953(7)	−0 1242(9)	0 2552(3)	0 046(3)	0 053(3)	0 035(3)	0 016(3)	−0 008(3)	0 002(3)
C3	0 3469(5)	−0 1582(8)	0 1796(3)	0 032(3)	0 037(3)	0 040(3)	0 003(2)	−0 009(2)	0 009(3)
C4	0 3059(6)	−0 1710(8)	0 0528(2)	0 039(3)	0 034(3)	0 038(3)	−0 003(2)	0 009(2)	0 008(3)
C5	0 2088(7)	−0 1387(9)	−0 126(3)	0 051(4)	0 052(4)	0 029(2)	−0 016(3)	−0 002(2)	0 004(4)
C6	0 2020(7)	0 0734(9)	−0 0345(3)	0 037(3)	0 069(4)	0 024(2)	−0 001(3)	0 003(2)	0 019(3)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE IV. Selected Interatomic Distances (A), Angled (deg), and Least-Squares Planes for *mer*-[$Co(C_6H_{17}N_3)Cl_3$].

Distances			
Co–Cl1	2.243(1)	Cl1–Co–Cl2	91.2(1)
Co–Cl2	2.309(1)	Cl1–Co–N1	92.5(1)
Co–Cl3	2.277(1)	Cl1–Co–N2	90.3(1)
		Cl1–Co–N3	90.0(1)
Co–N1	1.967(3)		
Co–N2	2.009(4)	Cl2–Co–N1	85.7(1)
Co–N3	1.976(4)	Cl2–Co–N3	84.3(1)
		N1–Co–N2	93.1(2)
N1–C1	1.482(7)	N2–Co–N3	96.8(2)
C1–C2	1.509(8)		
C2–C3	1.505(7)	Co–N1–C1	122.3(3)
C3–N2	1.492(5)	Co–N2–C3	117.3(3)
N2–C4	1.494(5)	Co–N2–C4	117.0(3)
C4–C5	1.531(7)	Co–N3–C6	123.9(3)
C5–C6	1.496(8)		
C6–N3	1.497(7)	N1–C1–C2	109.1(5)
		C1–C2–C3	112.4(5)
Angles		C2–C3–N2	115.0(4)
		C3–N2–C4	106.6(4)
Cl1–Co–Cl3	177.4(1)	N2–C4–C5	114.2(4)
Cl2–Co–N2	178.1(1)	C4–C5–C6	112.2(5)
N1–Co–N3	169.8(2)	C5–C6–N3	110.8(5)

Least Squares Planes

$0.085X + 0.006Y + 0.996Z = 2.439$		$-0.907X - 0.416Y + 0.065Z = 1.583$	
atom	dev, A	atom	dev, A
Cl1	−0.025	N1	0.013
Cl2	0.022	N2	0.002
Cl3	−0.026	N3	0.014
N2	0.026	Cl2	−0.001
Co	0.003	Co	−0.028

$-0.407X + 0.909Y + 0.086Z = 0.700$

atom	dev, A
Cl1	−0.081
Cl3	−0.142
N1	0.153
N3	0.054
Co	−0.067

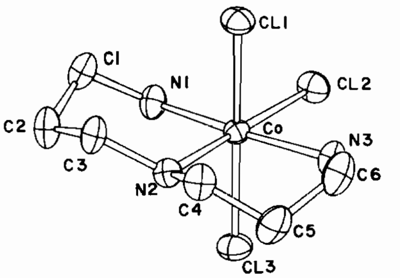


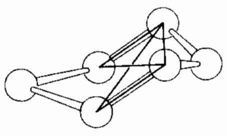
Fig. 1. ORTEP drawing of [$Co(dpt)Cl_3$]. Probability of ellipsoids are at the 50% level. Hydrogen atoms are not included.

and Waber's [10], those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components [11]. After all heavy atoms were located and their positional and anisotropic thermal parameters varied in three cycles of least squares refinement, hydrogen atom positions were calculated assuming sp^3 hybridization of carbon and nitrogen atoms. These atoms were included in fixed positions in the final cycles of refinement and only their isotropic thermal parameters were allowed to vary. Non-hydrogen atom atomic positions in fractional coordinates and their anisotropic thermal parameters are given in Table III. A listing of hydrogen atom coordinates and thermal parameters and observed and calculated structure factor amplitudes is available from the editor on request.

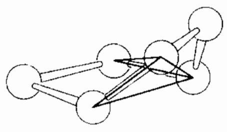
Results and Discussions

The crystal lattice of [$Co(dpt)Cl_3$] consists of non-interacting molecules, which have the triamine bonded with the primary amino groups *trans, i.e.,* the complex has the meridional stereochemistry (I) as previously assigned by Gainsford and House [8]. A perspective drawing of the complex is given in Fig. 1 and a listing of selected interatomic distances, angles and least-squares planes in Table IV. The axial chlorine–cobalt internuclear distances of 2.243(1) and 2.277(1) Å are slightly shorter than the equatorial distance of 2.309(1) Å; all three distances are within the expected range for Co(III)–chlorine interactions. *Trans* nitrogen–cobalt distances are 1.967(3) and 1.976(4) Å, with the third Co–N distance slightly longer at 2.009(4) Å. Again, these are typical bond distances for cobalt(III). All Cl(1)–Co–L and Cl(3)–Co–L interatomic angles are near 90° (with the Cl(1)–Co–Cl(3) angle at 177.4(1)°) but angles within the N(1), N(2), N(3), Cl(2), Co plane (the maximum deviation from the least-squares plane calculated for these atoms is 0.03 Å for the cobalt atom) deviate substantiallly from their ideal values. This is apparently a result of the large 'bite' of the six-membered chelate rings of the dpt ligand since the N(1)–Co–N(2) and N(2)–Co–N(3) angles are 93.1(2) and 96.8(2)°, respectively.

Unlike complexes III and IV, which have chair and boat conformations for the six-membered chelate rings, [$Co(dpt)Cl_3$] has both rings in the chair form. A measure of the distortion from the chair conformation can be defined in terms of the angle between two planes defined as shown below.



Chair



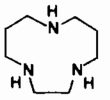
Skew-Boat

These angles are 2.3 and 3.6° for the two chelate rings of [Co(dpt)Cl$_3$]; for III, 3.3 and 47.5° [3] and for IV, 0.0 and 50.8° [4]. Thus [Co(dpt)Cl$_3$] has a much more symmetrical chelate ring structure. This is further reflected in the near pairwise equivalence of the Co–N–C angles in the present case whereas there are considerable differences within these pairs of angles for III and IV. It was suggested earlier, on the basis of conformational analysis studies, that the chair–chair forms of III and IV might be disfavored, in part, because of angle distortions at N(1) and N(3) since these appeared to increase above those values found in the chair–boat form. However, the Co–primary nitrogen–carbon angles observed in the present case (ave. 123°) are larger than those calculated for the chair–chair forms of III and IV [4]. One must conclude that the precise factors that determine chelate ring conformations for Co(III)–dpt complexes cannot be defined on the basis of information presently available.

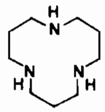
[Ni(dpt)$_2$](ClO$_4$)$_2$ also has chair chelate ring conformations [5] but significantly longer metal–nitrogen bond distances than for the cobalt(III) complexes (Ni–primary nitrogen, 2.14 Å; Ni–secondary nitrogen, 2.22 Å). It is interesting to compare the effect of this increased bond length on the structure of the dpt ligand. Two effects are most obvious; a decrease in N–M–N angles, which are 91.5° for the nickel complex (the complex has a crystallographically imposed center of symmetry), and decreases in the Ni–N–C angles which are 116.1° at the secondary nitrogen atom and 120.8° at the primary nitrogen donor. The overall result is a considerably greater flattening of the chair conformation in the cobalt complex. This is best described in terms of the dihedral angle between the N(primary), M, N(secondary) plane and the mean plane defined by the N(primary)–C and N(secondary)–C bonds. These dihedral angles are 156° for Ni(dpt)$_2^{+2}$ and 162 and 166° for the Co(III)–dpt complex.

Perhaps a less subtle question than what factors affect chelate ring conformations concerns those factors that determine the geometrical preferences of dpt in its metal complexes and particularly in Co(III) complexes.

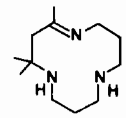
To our knowledge only complexes of triamines such as V–VII [12, 13], which may be considered as derivatives of dpt, appear to have the N–C$_3$–N–C$_3$–N unit in a facial form. This was confirmed for the Ni(II) complex of VII by an X-ray structure determination on NiL(NCS)$_2$ which has the triaza ligand coordinated to the axial and two basal positions of a distorted tetragonal pyramid. Both saturated chelate rings have the chair conformation. It is also interesting to note that Koyama and Yoshino were unable to prepare a Co(III) complex of VI [13] although a Co(III) complex of VII has been reported [12]. It was with these points in mind that we attempted to prepare [(dpt)(triamine)Co]$^{+3}$ complexes from [Co(dpt)Cl$_3$] and [Co(TACN)Cl$_3$], TACN = 1,4,7-triazacyclononane, in aqueous solution. These trichloro species dissolve in water upon heating to produce aquated forms that have not been characterized [14] so that these experiments are somewhat ill-defined; however, the results are nonetheless quite interesting and point to some interesting properties of dpt, especially relative to the homologous linear triamine, dien.



V



VI



VII

Initial spectrophotometric experiments (10^{-3} *M* complex, 10^{-2} *M* triamine, 50 °C) indicated that the mono-TACN and mono-dpt complexes produced CoN$_6$ products with dien but not with dpt. Several attempts involving higher reactant concentrations, higher amine to complex ratios and increased temperature failed to produce [Co(TACN)(dpt)]$^{+3}$ or [Co(dpt)$_2$]$^{+3}$. It might be noted that at least one person has indicated that he was unable to prepare Co(dpt)$_2^{+3}$ [9]. In a separate, preparative scale experiment the product of the dien reaction with the dpt complex was isolated and found by ^{13}C NMR to be a mixture of Co(dien)$_2^{+3}$ stereoisomers [16]. Reexamination of the absorption spectra of the earlier reaction mixtures indicated that this was also the product formed under more dilute conditions [17]. Thus, dien completely displaced dpt from cobalt. Although this result was reproducible, the absence of a catalytic amount of Co(II) cannot be insured.

A complex believed to be [Co(TACN)dpt]$^{+3}$ was ultimately isolated from a reaction mixture that consisted initially of [Co(TACN)Cl$_3$] and a large excess of dpt. This solution was evaporated to dryness on a steam bath and the oily residue heated for several more hours. Chromatography of the material gave several bands; a yellow-orange band traveling at an intermediate rate was concentrated and examined by ^{13}C NMR. The spectrum consisted of 9 resonances of roughly equal intensity. On the basis of our earlier work on TACN complexes [7], three of these [δ(*vs.* dioxane) = −15.23, −15.71, −16.08] could be assigned to TACN. After re-chromatographing the sample (see experimental section for details) the ^{13}C NMR spectrum showed these three absorptions and three of the remaining six (δ = –19.17, –30.09, –44.71) to be equally intense with the remaining three resonances being less than one-half as intense. On this basis we assign this spectrum to $[Co(TACN)dpt]^{+3}$, which must have dpt coordinated in a facial form. Unfortunately, we have not obtained crystals for X-ray analysis nor have we accumulated enough of the material to further characterize it. The species responsible for the three remaining resonances in the ^{13}C NMR spectrum, has not been examined further at this point.

Conclusion

Although $[Co(dpt)Cl_3]$ also contains the triamine in *mer* form, the ^{13}C NMR data for the complex assigned as $[Co(TACN)(dpt)]^{+3}$ suggest that it can bind to three *cis* coordination sites. In comparison with dien, dpt is a very poor ligand with our qualitative observations indicating that it will not substitute Co(III) in aqueous solution and that it may, in fact, be displaced by dien. These observations suggest that there is a great deal remaining to be learned about a ligand that might otherwise be expected to be very similar to dien but which obviously is not.

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14 Weigardt *et al.* (ref. 15) have shown that $[Co(TACN)Cl_3]$ reacts with aqueous base to give tri-μ-hydroxobis-[(TACN)Co(III)] cation and that this species gives *trans*-diaquo-di-μ-hydroxobis[(TACN)Co(III)] upon treatment with acid. Based on the absorption spectrum of the solution obtained by dissolving $[Co(TACN)Cl_3]$ in water, neither of these can be the major species present. The former is probably produced when $[Co(TACN)Cl_3]$ is heated with dpt in water.

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16 ^{13}C NMR spectra of the three geometrical isomers of $Co(dien)_2^{+3}$ have been reported. G. H. Searle, S. F. Lincoln, F. R. Keene, S. G. Teague and D. G. Rowe, *Aust. J. Chem., 30,* 1221 (1977). Our spectra correspond to a mixture of *mer, sym–fac* and *unsym–fac* isomers in the approximate ratio 2:1.5:1.

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