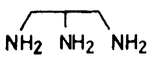
An Improved Synthesis of 1,2,3-Triaminopropane: *X*-Ray Structure of *s-fac*-Bis(1,2,3-triaminopropane)cobalt(III) Chloride

By **Kim Henrick, Mary McPartlin, Shelley Munjoma, Philip G. Owston, Roger Peters, Samuel A. Sangokoya,** and **Peter A. Tasker,*** Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB

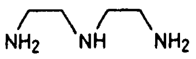
A convenient synthesis of 1,2,3-triaminopropane (ptn) has been achieved by the reduction of 1,2,3-triazidopropane. The triamine ptn gives a cobalt(III) complex $[Co(ptn)_2]Cl_3$, which has been characterised by ^{13}C n.m.r. and *X*-ray analysis. The crystals are monoclinic, space group *C*2/*c*, with *a* = 12.511(2), *b* = 8.196(1), *c* = 14.580(2) Å, β = 113.19(2)°, and *Z* = 4. 1 506 Unique observed reflections [$I > 3\sigma(I)$] have been used to solve and refine the structure down to *R* 0.0264.

1,2,3-TRIAMINOPROPANE (ptn) is the smallest tridentate aliphatic triamine.[1] However, its co-ordination chemistry [2] has received little attention since the 1920's because it has been difficult to prepare [3-5] in reasonable yields, and the most effective method reported previously [5] involves a laborious six-step synthesis.

The conversion of aliphatic polyalcohols into the corresponding polyamines *via* the scheme $R(OH)_n \longrightarrow R(OSO_2R')_n \longrightarrow R(NH_2)_n$ (R' = aryl group) has been described previously,[6] and an adaptation of this scheme to the preparation of 1,2,3-triaminopropane (ptn) is reported here. The crystal structure of the bis(triamine)-cobalt(III) complex, $[Co(ptn)_2]Cl_3$, has been undertaken to define the geometry of co-ordination of ptn, and to allow comparisons with other small bi- and tri-dentate ligands, *e.g.* dien (diethylenetriamine).



ptn



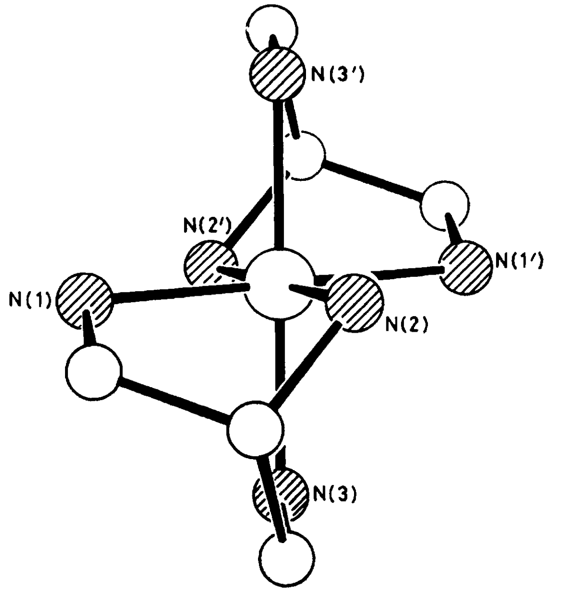
dien

RESULTS AND DISCUSSION

Reduction of 1,2,3-triazidopropane proves to be an effective method of preparation for 1,2,3-triaminopropane. Hydrazine hydrate–palladium–carbon is a particularly convenient reagent for this reduction, but $Li[AlH_4]$ and $Na[BH_4]$ may also be used, and do not appear to be accompanied by the undesired elimination reactions observed [7] in preparations of related aliphatic diamines.

Bis(triamine)cobalt(III) complexes were readily prepared under the conditions described by Mann and Pope.[2] The molecular structure of the cation in $[Co(ptn)_2]Cl_3$ is shown in the Figure, and selected interatomic distances and angles are given in Table 1. The complex has an *s-fac* configuration with a crystallographic centre of symmetry. The symmetrical nature of the complex in solution (D_2O) was confirmed by ^{13}C n.m.r. which showed only two signals [at 60.05 (CH) and 48.09 (CH_2) p.p.m., chemical shifts which are consistent with values [8-10] for related dien complexes].

The co-ordinate bond from the central nitrogen atom of



The centrosymmetric cation $[Co(ptn)_2]^{3+}$ with atom labels as in Tables 1—3

TABLE 1

Interatomic bond distances and angles in $[Co(ptn)_2]^{3+}$ *

(*a*) Bond distances/Å			
N(1)–Co	1.961(2)	N(3)–Co	1.964(2)
N(2)–Co	1.942(2)		
N(1)–C(1)	1.491(3)	N(3)–C(3)	1.492(3)
N(2)–C(2)	1.496(3)		
C(1)–C(2)	1.521(3)	C(3)–C(2)	1.512(3)
$N–H_{mean}$	0.847(16)		
$C–H_{mean}$	0.978(13)		
(*b*) Bond angles/°			
N(1)–Co–N(2)	84.9(1)	N(3)–Co–N(2)	83.9(1)
N(1)–Co–N(2')	95.1(1)	N(3)–Co–N(2')	96.1(1)
N(1)–Co–N(3)	85.9(1)		
N(1)–Co–N(3')	94.1(1)		
Co–N(1)–C(1)	109.4(1)	Co–N(3)–C(3)	109.9(1)
Co–N(2)–C(2)	100.6(1)		
N(1)–C(1)–C(2)	107.8(2)	N(3)–C(3)–C(2)	107.5(2)
N(2)–C(2)–C(1)	105.4(2)	N(2)–C(2)–C(3)	105.5(2)
C(1)–C(2)–C(3)	112.2(2)		

* Entries are arranged with chemically equivalent lengths or angles on the same lines.

ptn, N(2), is significantly shorter than bonds from the terminal atoms, N(1) and N(3) (see Table 1). A similar pattern has been observed for *fac* and *mer* complexes of dien, where in most cases the central (secondary) amine donor gives the shortest Co–N bond (see Table 2). There is close agreement between chemically equivalent bond lengths and angles in the two halves of the ligand, Table 1, and it can be concluded that 1,2,3-triaminopropane is capable of co-ordinating in a very regular manner, giving pseudo-mirror-plane symmetry between the two halves of the ligand in *fac*-octahedral complexes.

TABLE 2

Cobalt(III)–nitrogen bond lengths (Å) in dien complexes

Complex	Co–NH_2	Co–NH	Ref.
s-fac-$[Co(dien)_2]Br_3$	1.97(1)	1.95(1)	*a*
mer-$[Co(dien)_2][NO_3]_3 \cdot H_2O$	1.957—1.980(8)	1.946, 1.949(8)	10
mer-$[Co(dien)(en)Cl][ZnCl_4]$	1.960, 1.964(6)	1.930(6)	*b*
mer-$[Co(dien)(N_3)_3]$	1.954, 1.966(7)	1.922(7)	*c*
μ-fac-$[Co(dien)_2][Co(CN)_6] \cdot 2H_2O$	1.951, 1.970(4)	1.968(4)	*d*

[a] M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 1972, **28**, 470. [b] A. R. Gainsford, D. A. Honse, and W. T. Robinson, *Inorg. Chim. Acta*, 1971, **5**, 595; en = ethylenediamine. [c] L. F. Druding and F. D. Sancilio, *Acta Crystallogr., Sect. B*, 1975, **30**, 2386. [d] M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 1973, **29**, 739.

EXPERIMENTAL

1,2,3-*Tris(methylsulphonyloxy)propane*.—To a stirred solution of propane-1,2,3-triol (46 g, 0.50 mol) in dry pyridine (500 cm^3) at 0 °C was added methanesulphonyl chloride (229 g, 2 mol) over 1.5 h. The resulting mixture was stored at 2 °C for 42 h (during which time it turned deep red), and then poured into a mixture of MeOH (1 dm^3), water (1 dm^3), and concentrated HCl (1 dm^3). Water (1 dm^3) was added to the resulting hot (red) solution and the mixture set aside at room temperature for 18 h. The residue was washed with MeOH–water (3 : 1, 3 × 200 cm^3), water (3 × 200 cm^3), and MeOH (200 cm^3), giving the required compound as slightly pink needles (132 g, 81%), m.p. 78.5 °C (lit.,[11] 77.0—78.0 °C) (Found: C, 22.1; H, 4.4. Calc. for $C_{16}H_{14}O_9S_3$: C, 22.1; H, 4.30%), $\nu_{max.}$ at 3 037m, 3 014m, 2 978m, 2 944m, 1 350br, s, 1 280m, 1 248s, 1 186s, and 1 175s cm^{-1}. δ (C_5H_5N): 3.30 (s, 6 H, α-SO_3CH_3), 3.37 (s, 3 H, β-SO_3CH_3), and 4.67—4.88 (m, 5 H, α-CH_2 and β-CH) p.p.m.

1,2,3-*Tris(phenylsulphonyloxy)propane* was prepared using benzenesulphonyl chloride by a similar method except that ethanol was used instead of methanol in the work-up and washing. After drying *in vacuo* at 60 °C for 24 h, the required compound was obtained as a white solid (95%), m.p. 82.0 °C (Found: C, 49.4; H, 4.0. $C_{21}H_{20}O_9S_3$ requires C, 49.2; H, 3.95%); $\nu_{max.}$ at 3 176w, 1 589w, 1 455s, 1 373s, 1 355s, 1 249m, and 1 190br, s cm^{-1}. δ (^{1}H) ($CDCl_3$): 4.13 (d, 4 H, α-CH_2), 4.76 (qnt, 1 H, J = 5 Hz, β-CH), and 7.28—8.05 (m, 15 H, aryl H) p.p.m.

1,2,3-*Triazidopropane*.—*Method A*. A mixture of 1,2,3-tris(methylsulphonyloxy)propane (65 g, 0.20 mol), NaN_3 (59 g, 0.9 mol), and dimethyl sulphoxide (400 cm^3) was maintained at 85 °C under N_2 for 5 h. After cooling and adding to water (1 200 cm^3), the triazide was extracted into dichloromethane (4 × 200 cm^3). The extracts were washed with water (4 × 50 cm^3), dried ($Na_2[SO_4]$), and reduced to minimum volume on a rotary evaporator giving crude 1,2,3-triazidopropane as a brown liquid (29 g, 87%) [$\nu_{max.}$ at 3 370w, 2 940m, 2 870w, 2 520w, 2 120vs, 1 450s, 1 350s, and 1 285br, vs cm^{-1}. δ ($CDCl_3$): 3.15—3.90 (br m, centring at 3.47) p.p.m.].

Method B. A mixture of 1,2,3-tris(phenylsulphonyloxy)-propane (102 g, 0.20 mol), NaN_3 (59 g, 0.90 mol), and 2,2′-oxydiethanol (400 cm^3) was heated at 95 °C under N_2 for 5 h. After working up as for method A, except using Et_2O for extractions, 1,2,3-triazidopropane (29 g, 88%) was obtained as a golden yellow liquid.

CAUTION: Although no difficulties were experienced with the crude triazide, in view of the potentially explosive properties of organic azides no attempt was made to purify the material, and it is recommended that reduction to the triamine be attempted immediately after removal of solvent.

1,2,3-*Triaminopropane*.—*Method A*. A solution of the triazide (32 g, 0.19 mol) in ethanol (600 cm^3) under N_2 was heated under gentle reflux and 99% hydrazine hydrate (284 cm^3) and 5% Pd/C (4 g) were added in four equal portions over a period of 1.5 h at 0.5-h intervals. The reaction mixture was heated at reflux for another 3 h, and then filtered through a Celite bed. Solvent was removed under reduced pressure and the residue short-path distilled to give 1,2,3-triaminopropane as a pale yellow oil (15 g, 89%), b.p. 100—104 °C (10 mmHg *) [lit.,[12] b.p. 92—93 °C (9 mmHg)]; $\nu_{max.}$ at 3 450—3 300br, 2 940br, s, 1 600br, s, and 975—900br cm^{-1}. δ (^{1}H) ($CDCl_3$): 1.10—1.50 (NH_2) and 2.15—2.94 (m, α-CH_2 and β-CH).

Method B. The triazide (29 g, 0.18 mol) was added over 1.5 h to a suspension of $Li[AlH_4]$ (24 g, 0.60 mol) in tetrahydrofuran (1 dm^3), and then the mixture was heated under reflux for 18 h. After cooling and addition of water (24 cm^3), 15% Na[OH] (24 cm^3), and water (72 cm^3), the resulting tacky precipitate was extracted for 18 h from Soxhlet thimbles using a refluxing isopropyl alcohol solution (500 cm^3) of the evaporated filtrate. After evaporation of the extract under reduced pressure (45 °C) and removal of water by azeotropic distillation with benzene, the triamine was obtained (14.5 g, 93%) by distillation as in method A.

Method C. A suspension of the triazide (25 g, 0.15 mol), $Na[BH_4]$ (17.1 g, 0.45 mol), and Pr^iOH (450 cm^3) was heated under reflux for 36 h. After cooling, most of the Pr^iOH was removed from the resulting gel under reduced pressure, water (150 cm^3) was added, and the mixture heated under reflux for 2 h. Most of the water was removed under reduced pressure at 45 °C, and the residue dried and distilled as in method B to give the triamine (11.6 g, 87%).

Bis(1,2,3-*triaminopropane*)*cobalt*(III) *Chloride*, $[Co(ptn)_2]Cl_3$.—A mixture of ptn (4.0 g, 45 mmol) in 15% Na[OH] (20 cm^3) and penta-amminechlorocobalt(III) chloride (5.0 g, 20 mmol) in water (150 cm^3) was heated at 80 °C for 3 h. The red-brown solution was concentrated to *ca*. 5 cm^3, made just acid with dilute HCl, and filtered. Evaporation of the filtrate produced a brown-yellow solid which was recrystallised from a small volume of hot water to give orange crystals of $[Co(ptn)_2]Cl_3$ (4.5 g, 58%) (Found: C, 20.8; H, 6.6; N, 2.45. $C_6H_{22}Cl_3CoN_6$ requires C, 21.0; H, 6.45; N, 2.45%).

The complex $[Co(ptn)_2]I_3$ was similarly prepared as brown-yellow crystals, in 81% yield, m.p. 308—310 °C

---

* Throughout this Note: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 3

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	0.25	0.25	0
Cl(1)	0.094 18(4)	0.196 00(6)	−0.469 90(5)
Cl(2)	0.5	0.061 71(10)	0.25
N(1)	0.375 5(1)	0.376 2(2)	0.099 5(1)
N(2)	0.147 9(1)	0.411 9(2)	0.020 0(1)
N(3)	0.234 9(1)	0.141 2(2)	0.114 4(1)
C(1)	0.326 2(2)	0.482 7(3)	0.156 0(2)
C(2)	0.201 5(2)	0.428 7(3)	0.131 1(2)
C(3)	0.195 2(2)	0.260 7(3)	0.171 5(2)
HN(11)	0.425 9(21)	0.309 2(34)	0.139 5(20)
HN(12)	0.408 5(20)	0.432 4(31)	0.068 6(20)
HN(21)	0.144 6(18)	0.503 2(28)	−0.007 4(17)
HN(22)	0.079 8(21)	0.377 1(32)	−0.001 8(19)
HN(31)	0.187 8(22)	0.059 2(35)	0.096 5(19)
HN(32)	0.299 7(19)	0.105 8(28)	0.150 5(18)
H(11)	0.325 5(20)	0.593 4(32)	0.131 6(20)
H(12)	0.370 8(20)	0.469 5(29)	0.225 9(20)
H(2)	0.158 6(18)	0.511 1(27)	0.153 0(18)
H(31)	0.114 3(22)	0.237 2(26)	0.159 1(19)
H(32)	0.247 6(22)	0.254 9(29)	0.241 1(21)

(Found: C, 11.7; H, 3.7; N, 14.1. $C_6H_{22}CoI_3N_6$ requires C, 11.65; H, 3.60; N, 13.6%).

Crystal Data.—$C_6H_{22}Cl_3CoN_6$, $M = 343.5$, Monoclinic, $a = 12.511(2)$, $b = 8.196(1)$, $c = 14.580(2)$ Å, $\beta = 113.19(2)°$, $U = 1\,374$ Å^3, $D_m = 1.641$ g cm^{-3}, $Z = 4$, $D_c = 1.659$ g cm^{-3}, $F(000) = 732$, space group $C2/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 17.26 cm^{-1}. 1 528 Reflections were recorded ($3.0 < \theta < 25.0°$) on a Philips PW1100 diffractometer, with graphite-monochromated Mo-K_α radiation, and a θ—2θ scan mode on a crystal of size 0.18 × 0.17 × 0.22 mm. Lorentz-polarisation corrections were applied, and equivalents were averaged to give 1 506 unique observed reflections [$I > 3\sigma(I)$].

The Co and Cl atoms were located from a Patterson function and positions of all the other atoms were found from subsequent Fourier-difference syntheses. The structure was refined[13] by full-matrix least-squares methods with complex neutral-atom scattering factors from ref. 14 and weights $w = 1/|\sigma^2(F)|$. The refinement converged to $R = 0.0264$ and $R' = 0.0272 = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$. The atomic co-ordinates are given in Table 3 and the vibration parameters and observed and calculated structure factors are in Supplementary Publication No. SUP 23136 (12 pp.).*

[1/726 *Received, 7th May*, 1981]

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

REFERENCES

[1] D. St. C. Black, *Coord. Chem. Rev.*, 1972, **9**, 219.

[2] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1925, 2675, 2681.

[3] E. Brackenbusch, *Ber. Bunsenges. Phys. Chem.*, 1873, **6**, 1289.

[4] S. Gabriel and W. Michels, *Ber. Bunsenges. Phys. Chem.*, 1892, **25**, 3056.

[5] F. G. Mann and W. J. Pope, *Proc. R. Soc. London, Ser. A*, 1925, **107**, 80.

[6] E. B. Fleischer, A. E. Gebala, A. Levey, and P. A. Tasker, *J. Org. Chem.*, 1971, **36**, 3042.

[7] J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley, and W. T. Robinson, *J. Am. Chem. Soc.*, 1973, **95**, 1656; K. Henrick and P. A. Tasker, *Inorg. Chim. Acta*, 1980, **47**, 47.

[8] L. F. Druding, H. C. Wang, R. E. Cohen, and F. D. Sancilo, *J. Coord. Chem.*, 1973, **3**, 105.

[9] G. H. Searle, S. F. Lincoln, F. R. Keene, S. G. Teague, and D. G. Rowe, *Aust. J. Chem.*, 1977, **30**, 1221.

[10] F. D. Sancilio, L. F. Druding, and D. M. Lukasezewski, *Inorg. Chem.*, 1976, **15**, 1626.

[11] A. G. Kostova and L. B. Leonteva, *Zh. Obsch. Khim.*, 1960, **30**, 3541.

[12] T. Curtius and A. Hesse, *J. Prakt. Chem.*, 1900, **62**, 232.

[13] G. M. Sheldrick, 'SHELX-76 Program System,' University Chemical Laboratory, Cambridge, 1976.

[14] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974.