

Fig. 1. The structure of $\text{TlBr}_3 \cdot 2\text{OPPh}_3$.

atoms occupying equatorial positions and O atoms axial. Within the limits of error (0.05 Å) the Tl and Br atoms are coplanar. Bond distances and angles are given in Table 2; the Tl—Br distances are not significantly different [av. 2.505 (2) Å] and compare with those observed in other five-coordinate thallium(III) bromide complexes, e.g. av. 2.505 (2) Å in $\text{TlBr}_3 \cdot \text{dioxane}$ (Jeffs, Small & Worrall, 1983), av. 2.536 (9) Å in $\text{TlBr}_3 \cdot 2\text{pyridine}$ (Jeffs, Small & Worrall, 1984). The Tl—O distances 2.38 (2) and 2.39 (2) Å are similar to those observed in trichlorobis(4-pyridine-carbonitrile 1-oxide-*O*)thallium, 2.36 (1), 2.40 (1) Å

(Gutiérrez-Puebla, Vegas & García-Blanco, 1980) and in $[(p\text{-HC}_6\text{H}_4)_2\text{TiCl}(\text{OPPh}_3)]_2$, 2.391 (9) Å (Henrick *et al.*, 1980) but shorter than in $\text{TlBr}_3 \cdot \text{dioxane}$, 2.54 (1) Å. This difference may reflect the ligand strengths.

The relatively large U_{ij} of Br atoms may indicate disorder.

Angular distortions are observed both in the equatorial plane (116.4–124.2°) and along the axial direction of the trigonal bipyramid [O(1)—Tl—O(2) 174.8°]. Torsion angles (Table 3) show that P(1) and P(2) lie in a plane between Br(1) and Br(3) and this may explain the large angle. The P—O—Tl angles, 150, 152°, are smaller than in $[(p\text{-HC}_6\text{F}_4)_2\text{TiCl}(\text{OPPh}_3)]_2$, 168° (Henrick *et al.*, 1980). However, large variations in $M\text{—O—P}$ bond angles are well known, and it has been concluded that they are easily deformed and may be considerably affected by crystal-packing effects (Henrick *et al.*, 1980).

Centrosymmetrically related molecules are well separated, the closest distance involving Tl; Tl—Br(2') = 5.06 Å is too large to suggest a bridging role for the Br.

References

- BAXTER, J. & GAFNER, G. (1972). *Inorg. Chem.* **11**, 176–178.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GUTIÉRREZ-PUEBLA, E., VEGAS, A. & GARCÍA-BLANCO, S. (1980). *Acta Cryst.* **B36**, 145–147.
 HENRICK, K., MATTHEWS, R. W., MCPARTLIN, M., DEACON, G. B. & PHILLIPS, R. J. P. (1980). *J. Organomet. Chem.* **193**, 13–21.
 JEFFS, S. E., SMALL, R. W. H. & WORRALL, I. J. (1983). *Acta Cryst.* **C39**, 1628–1630.
 JEFFS, S. E., SMALL, R. W. H. & WORRALL, I. J. (1984). *Acta Cryst.* **C40**, 65–67.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of *s-fac*-[Bis(3-aminopropyl)amine](diethylenetriamine)cobalt(III) Dithionate Perchlorate Monohydrate, $[\text{Co}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{C}_6\text{H}_{17}\text{N}_3)]^{3+} \cdot \text{S}_2\text{O}_6^{2-} \cdot \text{ClO}_4^- \cdot \text{H}_2\text{O}$, and Comparison with the Geometry Calculated by Molecular Mechanics

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Abstract. $M_r = 570.9$, orthorhombic, $Pc2_1b$, $a = 9.592$ (3), $b = 13.454$ (3), $c = 16.748$ (9) Å, $Z = 4$, $U = 2161.3$ Å³, $D_m = 1.77$ (2), $D_x = 1.754$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.115$ mm⁻¹, $F(000) =$

1192, $T = 295$ K, $R = 0.037$ on 1058 observed [$I > 2.5\sigma(I)$] reflections. The two tridentate ligands coordinate to Co giving an *s-fac* topology. The two six-membered chelate rings adopt chair and flattened-

chair conformations. The detailed geometry of the complex cation as calculated by molecular-mechanics analysis agrees well with the geometry observed in the crystal, with distortions of bond lengths and angles well reproduced.

Introduction. Three topological forms (*mer*, *u-fac* and *s-fac*) are possible for each of the complexes [Co(dien)₂]³⁺, [Co(dpt)₂]³⁺, and [Co(dien)(dpt)]³⁺ [dien = diethylenetriamine, dpt = bis(3-aminopropyl)-amine]. All three isomers have been separated and characterized for [Co(dien)₂]³⁺ (Searle, Lincoln, Keene, Teague & Rowe, 1977), while for [Co(dpt)₂]³⁺ only the *mer* isomer can apparently be isolated (Searle & Hambley, 1982a). We recently reported the isolation of all three isomers of [Co(dien)(dpt)]³⁺ and the crystal structure of the *mer* isomer (Searle & Hambley, 1982b).

Strain-energy-minimization (molecular-mechanics) calculations on the systems [Co(dien)₂]³⁺ (Hambley & Snow, 1982) and [Co(dpt)₂]³⁺ (Hambley, Searle & Snow, 1982) have reproduced the isomer distribution in the former case and explained the occurrence of only the *mer* isomer in [Co(dpt)₂]³⁺. The preparative study of the [Co(dien)(dpt)]³⁺ system indicated that the isomer stability order was *u-fac* > *mer* > *s-fac*, which was different from the order observed (*mer* > > *u-fac* > *s-fac*) for the two parent systems. X-ray structural analyses were thus undertaken on all three isomers of [Co(dien)(dpt)]³⁺ to confirm the assignments made from spectroscopic methods, and a molecular-mechanics analysis of the system was carried out to attempt to rationalize this unexpected difference in relative isomer stabilities. This article describes the structure of the *s-fac* isomer and gives a comparison of the detailed solid-state geometry with that obtained by the molecular-mechanics model.

Experimental. Plate-shaped orange-yellow crystals grown by ethanol vapour diffusion into a water solution of [Co(dien)(dpt)](ClO₄)₃ and lithium dithionate. *D_m* by flotation in chloroform/1,2-dibromoethane. Crystal 0.16 × 0.20 × 0.03 mm. Precession photography, orthorhombic space group, absences *l* = 2*n* + 1 for 0*kl* and *k* = 2*n* + 1 for *hk*0 consistent with *Pc*2₁*b* and *Pcmb*; the former, a non-standard setting of *Pca*2₁, confirmed by the analysis. Lattice parameters by least-squares fit to the setting parameters of 25 independent reflections. Enraf-Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo K α radiation, 1.2 < 2 θ < 24°, ω - θ scans, ω -scan angles and horizontal counter apertures (0.80 + 35tan θ)° and (2.40 + 0.5tan θ)mm, respectively. No systematic intensity variation in standard reflections. Lorentz, polarization, and absorption (Coppens, Leiserowitz & Rabinovich, 1965) corrections; transmission factors 0.81–0.96. 1473 independent reflections; 1058 with *I* > 2.5 σ (*I*) (index range *h* 0/10, *k* 0/15, *l* 0/15)

considered observed and used in the calculations. Structure solved by Patterson and Fourier methods. H atoms of the complex molecule included at calculated sites (C–H 0.97, N–H 0.91 Å) with group temperature factors. Perchlorate anion disordered over two orientations with the Cl atom stationary. A group multiplicity parameter modelling this disorder refined to 0.57 (6). Only full-occupancy non-hydrogen atoms were assigned anisotropic thermal parameters. Block-matrix least-squares refinement on *F*. *w* = 1.0/(σ_F^2 + 0.0019*F*_o²). Refinement converged (all shifts < 0.1 σ) with *R* = 0.037, *wR* = 0.048. Maximum residual electron density in final difference map ± 0.4 e Å⁻³. Scattering factors (neutral Co for Co^{III}) and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). All calculations performed on a Cyber-173 computer using *SHELX76* (Sheldrick, 1976).

Discussion. Final atomic parameters are given in Table 1.* The structure consists of the complex cation, dithionate and perchlorate anions, and a water molecule packed with all moieties involved in weak hydrogen-bonding interactions.

An *ORTEP* plot (Johnson, 1965) of the *s-fac*-[Co(dien)(dpt)]³⁺ complex cation with the atom-numbering scheme is shown in Fig. 1. The ring conformations of the coordinated dien are $\lambda\delta$, the same as observed in *s-fac*-[Co(dien)₂]Br₃ (Kobayashi, Marumo & Saito, 1972). However, unlike that structure the two five-membered rings here exhibit quite different N–C–C–N torsion angles of 49 (1) and –35 (1)°. This is presumably a consequence of the very different conformations which are observed for the two six-membered rings of the dpt. One of these rings [Co–N(5)–C(8)–C(9)–C(10)–N(6)] forms a quite regular chair geometry with Co and C(9) lying *ca* 0.9 and 0.7 Å respectively above and below the plane defined by the other four atoms. The other dpt ring adopts a conformation where five atoms [Co, N(4), N(5), C(5), C(7)] lie in a plane and C(6) lies *ca* 0.7 Å out of this plane. A similar conformation was observed for the facially coordinated dpt ligands in [(dpt)Co(OH)₃·Co(dpt)](ClO₄)₃ (Searle & Hambley, 1982a) and in *u-fac*-[Co(dien)(dpt)](ClO₄)₃ (Hambley & Searle, 1983).

Lengths, and valence and torsion angles relating to the cation geometry are listed in Table 2. Some of the Co–N bonds are significantly longer than those

* Lists of structure factors, anisotropic thermal parameters, positional and thermal parameters of the H atoms, all bond lengths and angles, intermolecular contact distances, and least-squares-planes calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38993 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

typically observed (1.95–1.98 Å) in cobalt(III)–hexamine complexes. Such extended bond lengths were also observed in the solid-state structures of *mer*-[Co(dpt)₂](ClO₄)₃ (Hambley, Searle & Snow, 1982) and *mer*-[Co(dien)(dpt)]₂(S₂O₈)₃·EtOH·H₂O (Searle &

Hambley, 1982*b*), and for the former complex this extension of the bonds could be attributed to internal steric strain. Also, some bond angles, particularly the Co–N–C angles (Table 2), show quite severe distortions from tetrahedral, which is also typical of Co^{III}–dpt complexes. C–C and C–N bond lengths range from 1.46 (2) to 1.53 (2) Å and from 1.47 (2) to 1.52 (2) Å, respectively, and there is no statistically meaningful variation. Anion geometries are unexceptional.

The molecular-mechanics analysis undertaken to clarify the unexpected isomer distribution observed for [Co(dien)(dpt)]³⁺ is described elsewhere (Hambley & Searle, 1983). The minimization technique and the force field employed were as described previously (Hambley, Hawkins, Palmer & Snow, 1981). The calculations showed that the *u-fac* isomer has the lowest strain energy, in accord with the experimental observations.

Table 1. Positional parameters ($\times 10^4$) and isotropic temperature factors (Å^2)

$$B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
Co	2593 (1)	2500	269 (1)	1.52
N(1)	3778 (8)	1766 (6)	-475 (5)	2.45
N(2)	1509 (8)	2880 (6)	-702 (5)	2.24
N(3)	3729 (8)	3742 (6)	51 (5)	2.08
N(4)	1267 (8)	3358 (6)	903 (5)	2.24
N(5)	3858 (8)	2158 (5)	1186 (5)	2.29
N(6)	1359 (8)	1372 (5)	488 (5)	2.16
C(1)	3485 (12)	2043 (8)	-1313 (7)	3.42
C(2)	1916 (10)	2217 (8)	-1376 (6)	2.63
C(3)	1730 (10)	3954 (8)	-902 (7)	3.13
C(4)	3214 (10)	4269 (7)	-691 (6)	2.66
C(5)	1349 (11)	3386 (9)	1782 (7)	3.63
C(6)	2775 (12)	3448 (8)	2106 (7)	3.66
C(7)	3580 (11)	2534 (12)	2022 (7)	4.29
C(8)	4226 (9)	1060 (7)	1204 (7)	2.76
C(9)	2965 (12)	406 (8)	1340 (9)	3.97
C(10)	1972 (11)	382 (7)	646 (7)	3.42
S(1)	2541 (2)	2419 (3)	4777 (2)	2.66
O(1)	3164 (8)	1955 (6)	5454 (6)	4.26
O(2)	1244 (7)	2914 (6)	4956 (5)	3.32
O(3)	3524 (7)	3008 (6)	4309 (6)	4.55
S(2)	1979 (3)	1201 (2)	4017 (2)	2.68
O(4)	1008 (8)	635 (5)	4482 (5)	3.42
O(5)	3275 (9)	695 (7)	3888 (6)	5.26
O(6)	1345 (9)	1677 (7)	3320 (5)	4.42
Cl(1)	6969 (3)	4287 (2)	1794 (2)	3.53
O(7)	6069 (22)	4337 (16)	1093 (11)	4.1 (4)‡
O(8)	7492 (27)	3360 (15)	1956 (12)	5.5 (5)‡
O(9)	6061 (24)	4684 (13)	2434 (11)	4.7 (5)‡
O(10)	8195 (24)	4846 (19)	1832 (16)	6.9 (6)‡
O(7')†	6749 (30)	3278 (16)	2030 (13)	4.2 (7)‡
O(8')	8325 (36)	4536 (28)	1477 (25)	8.4 (10)‡
O(9')	6453 (30)	4622 (21)	1072 (16)	4.7 (6)‡
O(10')	6722 (30)	4989 (22)	2445 (17)	5.1 (6)‡
O(11)	-949 (11)	1287 (9)	1661 (6)	7.00

† Primes refer to the minor component of the disordered perchlorate, multiplier 0.43 (6).

‡ *B*_{iso} values.

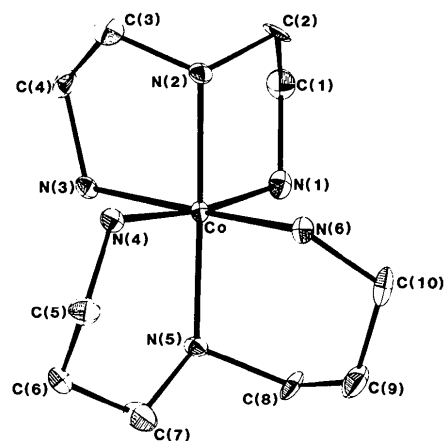


Fig. 1. Thermal-ellipsoid plot (50% probability) of the cation of *s-fac*-[Co(dien)(dpt)](S₂O₈)(ClO₄)·H₂O and the atom-numbering scheme.

Table 2. Comparison of observed and calculated structural parameters

	Solid state	Molecular mechanics		Solid state	Molecular mechanics		Solid state	Molecular mechanics
Co–N(1)	1.954 (8) Å	1.984 Å	Co–N(3)	2.028 (8) Å	1.978 Å	Co–N(5)	2.010 (8) Å	1.984 Å
Co–N(2)	1.997 (8)	1.984	Co–N(4)	2.020 (8)	1.986	Co–N(6)	1.959 (7)	1.968
N(1)–Co–N(2)	85.0 (3)°	83.1°	Co–N(5)–C(7)	121.7 (6)°	119.0°	Co–N(1)–C(1)–C(2)	-37 (1)°	-24°
N(2)–Co–N(3)	85.5 (3)	86.8	Co–N(5)–C(8)	112.2 (6)	116.4	Co–N(2)–C(2)–C(1)	-39 (1)	-45
N(1)–Co–N(3)	89.4 (3)	86.3	Co–N(6)–C(10)	119.4 (6)	119.7	Co–N(2)–C(3)–C(4)	34 (1)	33
N(2)–Co–N(4)	87.4 (3)	85.3	C(2)–N(2)–C(3)	111.8 (8)	114.2	Co–N(3)–C(4)–C(3)	20 (1)	29
N(3)–Co–N(4)	87.8 (3)	88.1	C(7)–N(5)–C(8)	110.4 (9)	109.2	Co–N(4)–C(5)–C(6)	43 (1)	40
N(1)–Co–N(5)	91.2 (3)	92.0	N(1)–C(1)–C(2)	106.9 (9)	106.5	Co–N(5)–C(7)–C(6)	-26 (1)	-35
N(3)–Co–N(5)	90.1 (3)	93.0	N(2)–C(2)–C(1)	107.4 (8)	108.6	Co–N(5)–C(8)–C(9)	-63 (1)	-64
N(4)–Co–N(5)	96.2 (3)	99.5	N(2)–C(3)–C(4)	110.4 (8)	110.6	Co–N(6)–C(10)–C(9)	57 (1)	62
N(1)–Co–N(6)	94.6 (3)	98.1	N(3)–C(4)–C(3)	111.3 (8)	109.3	N(1)–C(1)–C(2)–N(2)	49 (1)	44
N(2)–Co–N(6)	92.1 (3)	94.1	N(4)–C(5)–C(6)	114.7 (9)	112.1	N(2)–C(3)–C(4)–N(3)	-35 (1)	-40
N(4)–Co–N(6)	87.9 (3)	87.1	N(5)–C(7)–C(6)	117.7 (10)	115.0	N(4)–C(5)–C(6)–C(7)	-72 (1)	-74
N(5)–Co–N(6)	92.5 (3)	87.0	N(5)–C(8)–C(9)	112.4 (8)	114.0	N(5)–C(7)–C(6)–C(5)	62 (1)	72
Co–N(1)–C(1)	111.6 (6)	114.2	N(6)–C(10)–C(9)	111.7 (9)	112.2	N(5)–C(8)–C(9)–C(10)	69 (1)	59
Co–N(2)–C(2)	109.1 (6)	108.7	C(5)–C(6)–C(7)	114.1 (10)	111.1	N(6)–C(10)–C(9)–C(8)	-62 (1)	-57
Co–N(2)–C(3)	110.8 (6)	109.3	C(8)–C(9)–C(10)	113.7 (11)	113.7	C(1)–C(2)–N(2)–C(3)	84 (1)	77
Co–N(3)–C(4)	111.0 (6)	111.2				C(2)–N(2)–C(3)–C(4)	-87 (1)	-89
Co–N(4)–C(5)	120.4 (6)	120.3				C(6)–C(7)–N(5)–C(8)	-160 (1)	-172
						C(7)–N(5)–C(8)–C(9)	76 (1)	74

Also, the conformational geometry observed in the solid-state structure of each of the three isomers is either that with the calculated minimum energy or a conformation of energy close to the minimum. Table 2 gives a comparison of the solid-state structure with that calculated by the energy-minimization method for the same conformer of the *s-fac* isomer. The molecular-mechanics model represents an isolated complex molecule, so that some discrepancies can be expected because of the influence of packing and hydrogen bonding on the solid-state structure. However, good general agreement is observed, and in particular the above-mentioned distortions are well reproduced in the theoretical model.

In D₂O solution, the ¹³C NMR spectrum indicates that the complex cation has effective mirror symmetry (point group *C_s*) due to conformational averaging (Searle & Hambley, 1982*b*).

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References

- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
 HAMBLEY, T. W., HAWKINS, C. J., PALMER, J. A. & SNOW, M. R. (1981). *Aust. J. Chem.* **34**, 45–56.
 HAMBLEY, T. W. & SEARLE, G. H. (1983). *Aust. J. Chem.* Submitted.
 HAMBLEY, T. W., SEARLE, G. H. & SNOW, M. R. (1982). *Aust. J. Chem.* **35**, 1285–1295.
 HAMBLEY, T. W. & SNOW, M. R. (1982). Unpublished results.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KOBAYASHI, M., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* **B28**, 470–474.
 SEARLE, G. H. & HAMBLEY, T. W. (1982*a*). *Aust. J. Chem.* **35**, 1297–1309.
 SEARLE, G. H. & HAMBLEY, T. W. (1982*b*). *Aust. J. Chem.* **35**, 2399–2411.
 SEARLE, G. H., LINCOLN, S. F., KEENE, F. R., TEAGUE, S. G. & ROWE, D. G. (1977). *Aust. J. Chem.* **30**, 1221–1228, and references therein.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Studies on Tetramethylammonium Tetrabromometallates. I. Structures of Tetramethylammonium Tetrabromocuprate(II), [N(CH₃)₄]₂[CuBr₄], and -zincate(II), [N(CH₃)₄]₂[ZnBr₄], at Room Temperature

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Abstract. Cu isomorph: $M_r = 531.1$, orthorhombic, *Pnma*, $a = 12.600$ (4), $b = 9.326$ (2), $c = 15.825$ (6) Å, $V = 1860$ (2) Å³, $Z = 4$, $D_m = 1.92$ (1), $D_x = 1.898$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 103$ cm⁻¹, $F(000) = 1020$, $T = 293$ (2) K, final $R = 0.060$ for 585 observed reflections. Zn isomorph: $M_r = 533.0$, orthorhombic, *Pnma*, $a = 12.681$ (4), $b = 9.239$ (3), $c = 16.025$ (6) Å, $V = 1877$ (2) Å³, $Z = 4$, $D_m = 1.91$ (1), $D_x = 1.887$ g cm⁻³, $\mu = 104$ cm⁻¹, $F(000) = 1024$, final $R = 0.059$ for 898 observed reflections. The ZnBr₄ tetrahedron is slightly distorted as explained by the crystal-field effect; Br–Cu–Br angles of the CuBr₄ tetrahedron range from 102.0 to 126.6° due to a Jahn–Teller distortion. The mean bond length is 2.426 Å for Cu–Br and 2.447 Å for Zn–Br. The N(CH₃)₄ groups are affected by large oscillations.

Introduction. Recently, physical properties of tetramethylammonium tetrahalogenometallate crystals {[N(CH₃)₄]₂[MX₄], with $M = \text{Zn, Co, Ni, Fe, Cu, Hg}$ and $X = \text{Cl, Br, I}$ } have been intensively studied because of the existence of successive phase transitions. Some of these compounds show a modulated phase: [N(CH₃)₄]₂[ZnCl₄], [N(CH₃)₄]₂[CoCl₄] (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978), [N(CH₃)₄]₂[CuBr₄] (Gesi, 1982). These compounds are known to have an orthorhombic high-temperature phase with space group *Pnma*. But an important difference occurs between the members of this series for the modulated phase: for tetramethylammonium tetrachlorozincate and -cobaltate, the modulation direction is along **a*** and for tetramethylammonium tetrabromocuprate, it is along **c***.