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Structures of the *cis* and *trans* Isomers of the Bis(1-thia-4,7-diazacyclononane)cobalt(III) Cation

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Abstract. *trans*-Bis(1-thia-4,7-diazacyclononane)-cobalt(III) trifluoromethanesulfonate, (I), *trans*-[Co-$(C_6H_{14}N_2S)_2](CF_3SO_3)_3$, $M_r = 798.6$, triclinic, $P\bar{1}$, $a = 10.422$ (2), $b = 10.561$ (2), $c = 14.352$ (4) Å, $\alpha = 105.83$ (2), $\beta = 102.57$ (2), $\gamma = 103.29$ (2)°, $V = 1411.1$ Å^3, $Z = 2$, $D_x = 1.878$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 10.27$ cm^{-1}, $F(000) = 812$, $T = 294$ K. Final $R = 0.038$ for 4044 reflections. *cis*-Bis(1-thia-4,7-diazacyclononane)cobalt(III) tetraaqualithium(I) bromide monohydrate, (II), *cis*-[Co($C_6H_{14}N_2S)_2$]-[Li(H$_2$O)$_4$]Br$_4$.1H$_2$O, $M_r = 768.1$, monoclinic, C2, $a = 13.426$ (5), $b = 9.455$ (2), $c = 11.504$ (4) Å, $\beta = 113.15$ (2)°, $V = 1342.8$ Å^3, $Z = 2$, $D_x = 1.899$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 66.32$ cm^{-1}, $F(000) = 760$, $T = 294$ K. Final $R = 0.026$ for 1183 reflections. The two tridentate ligands coordinate with a *trans* arrangement of the S atoms and ring conformations ($\lambda\delta\lambda$, $\lambda\delta\lambda$) in (I) and a *cis* arrangement and ring conformations ($\lambda\lambda\lambda$, $\lambda\lambda\lambda$) in (II). The *trans* Co–S bonds in (I), 2.251 (1) and 2.246 (1) Å, are longer than the *cis* Co–S bonds in (II), 2.217 (2) Å. Molecular-mechanics calculations show that the *cis* isomer is slightly more stable than the *trans* and also suggest that the difference in Co–S bond lengths is a consequence of an electronic, rather than a steric, *trans* effect.

Introduction. Metal complexes of the macrocyclic ligand 1-thia-4,7-diazacyclononane (tasn), a nine-membered ring with one thioether-S and two amine-N donor atoms, have been the subject of much attention recently (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988, and references therein). Two geometric isomers are possible for octahedral |M(tasn)$_2$|$^{x+}$ complexes, designated *cis* and *trans* according to the arrangement of the S atoms about the metal. Structures of both |Cu(tasn)$_2$|(NO$_3$)$_2$ and |Ni(tasn)$_2$|(NO$_3$)$_2$ have revealed the *trans* isomer (Boeyens, Dobson & Hancock, 1985; Hart, Boeyens, Michael & Hancock, 1983). Preparation of the Co^{III} complex was first described by Gahan, Lawrance & Sargeson (1982) and they and Nonoyama & Ishida (1984) obtained spectroscopic evidence for the existence of more than one isomer. However, separation of the isomers could not be effected chromatographically. We recently reported the structure of the perchlorate salt of the Co^{III} complex obtained in the earlier preparation and showed that it too had the *trans* geometry (Hambley & Gahan, 1986). Extensive surveys of the crystals using visual, crystallographic and density separation techniques did not locate another crystal type. In order to investigate further the possible existence of the *cis* isomer an

HPLC study of the reaction mixture was undertaken (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988). This confirmed that both isomers were present and, subsequently, column chromatography using Sephadex cation-exchange resin was used to separate the isomers. It was found that isomerization in the system was facile in neutral or basic solution, so that the *cis* isomer, though the more thermodynamically stable, could be crystallized only from acidic solution (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988). This explained why only the *trans* isomer was found in the solid state in earlier studies, this being the less soluble isomer in the perchlorate and bromide salts. We now report the structure of the *cis* isomer of $|Co(tasn)_2|^{3+}$ as the bromide salt. The complex cation in the perchlorate salt of the *trans* isomer was found previously to be conformationally disordered, resulting in uncertainty of both the conformation and bond lengths (Hambley & Gahan, 1986). Therefore, we now report the structure of the *trans* isomer, as the trifluoromethanesulfonate (triflate) salt. A strain-energy minimization analysis has also been carried out to investigate the relative stabilities of the *cis* and *trans* isomers.

Experimental. Crystals were mounted on glass fibres with cyanoacrylate resin. Cell dimensions were determined by a least-squares fit to the setting parameters of 25 independent reflections ($8 < \theta < 12°$) measured and refined on an Enraf–Nonius CAD-4F four-circle diffractometer. Details of the data collection and structure refinement are given in Table 1.

The structures were solved by heavy-atom methods and refined on F by full-matrix least-squares procedures. All H atoms were included at calculated sites (C—H 0·97, N—H 0·91 Å) with individual or group isotropic thermal parameters, except for those of water molecules which were included at observed sites, and the H atom of $OW(3)$ which was refined. Non-H atoms were all, with the exception of the disordered F, O and C atoms of (I) and the Li atom of (II), refined anisotropically. The absolute configuration of (II) (*cis*) was established by refining the structure with all coordinates inverted. This converged with $R = 0·032$ (compared with 0·026 for the original configuration), confirming the original configuration at a confidence level of better than 99·5% (Hamilton, 1965). Positional and equivalent isotropic thermal parameters are given in Tables 2 and 3.* Bond distances and angles are in Tables 4 and 5.

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* Lists of structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms, bond lengths for triflate anions of (I), close intermolecular contacts and force-field parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51649 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data-collection and processing parameters*

	(I) (*trans*)	(II) (*cis*)
Crystal habit	Needles	Prismatic
Dimensions (mm)	0·09 × 0·18 × 0·38	0·29 × 0·32 × 0·25
Transmission factors	0·83, 0·93	0·18, 0·28
Diffractometer	Enraf–Nonius CAD-4F, four circle	
Monochromator	Graphite	Graphite
Scan mode	ω–1·67θ	ω–1·33θ
2θ range (°)	1·0–50·0	1·0–50·0
Reflections measured	5269	1313
Unique reflections	4627	1228
Intensity controls	3	3
Intensity variation (%)	<3	<2
R_{int}	0·014	0·011
Range of hkl	0→12, –12→12, –17→17	0→15, 0→11, –13→13
Reflections used $|I > 2·5\sigma(I)|$	4044	1183
Parameters refined	481	136
R	0·038	0·026
wR	0·051	0·035
Weighting constants $g,k |w = g/(\sigma^2 F_o + kF_o^2)|$	3·14, 1·2 × 10^{-3}	1·51, 3·3 × 10^{-3}
Maximum shift/e.s.d.	0·5	0·02
Peaks in final map (e Å^{-3})	±0·6	±0·6

Programs used were *SUSCAD* (Guss, 1976a) for data reduction, *ABSORB* (Guss, 1976b) for absorption corrections using the numerical integration method described by Coppens, Leiserowitz & Rabinovich (1965), *SHELX76* (Sheldrick, 1976) for solution and refinement, and *ORTEP* (Johnson, 1965) for plotting. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

Molecular mechanics. The strain energy of a molecule can be described as the sum over all individual interactions of bond deformation (E_b), valence angle deformation (E_θ), torsion angle deformation (E_ω) and non-bonded interaction (E_{nb}) energies:

$$E_{total} = \Sigma E_b + \Sigma E_\theta + \Sigma E_\omega + \Sigma E_{nb}.$$

The present force field was developed from earlier force fields for modelling metal complexes, described previously for hexaaminecobalt(III) and triaminetrithioethercobalt(III) complexes (Hambley, Hawkins, Palmer & Snow, 1981; Hambley & Snow, 1986), by making changes which followed the philosophy of Allinger's *MM2* force field for organic compounds (Allinger, 1977). For the present force field, non-bonded interactions taken from *MM2* have also been included as detailed elsewhere (Hambley, 1988a,b).

Strain-energy minimization was achieved using a locally written program (*MOMEC*87; Hambley, 1987) based on the Newton–Raphson refinement method first described by Boyd (1968). All refinements were continued until shifts in positional parameters were less than 0·001 Å.

Discussion. *Structure* (I) (*trans*). This consists of the complex cation and three trifluoromethanesulfonate (triflate) anions. One of the triflate anions is highly disordered, both by rotation about the C—S axis and by end-over-end tumbling. The other two triflate anions are

Table 2. Positional parameters (× 10⁴) for (I) (trans)

$$B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

The triflate disorder results from rotation about the centre of the C—S bond to give sites (A) and (B) and then, for each of these, rotation about the C—S bond occurs to give the unprimed and primed sites for O and F. The occupancies of the primed and unprimed sites are constrained to sum to the occupancy of the associated S and C atoms and the total occupancies are constrained to unity.

	x	y	z	B_{eq}(Å²)	Occ.
Co(1)	3051 (1)	1960 (1)	2445 (1)	1·94	—
S(1)	2744 (1)	1813 (1)	813 (1)	2·33	—
S(2)	3360 (1)	2116 (1)	4076 (1)	2·58	—
N(1)	3442 (3)	3970 (2)	2811 (2)	2·36	—
N(2)	5025 (3)	2300 (3)	2526 (2)	2·62	—
C(1)	5209 (3)	1416 (4)	1592 (2)	3·29	—
C(2)	4375 (3)	1583 (3)	653 (2)	3·02	—
C(3)	2993 (4)	3633 (3)	959 (2)	3·01	—
C(4)	2821 (4)	4411 (3)	1952 (2)	2·88	—
C(5)	4957 (3)	4632 (3)	3295 (2)	2·64	—
C(6)	5711 (3)	3793 (3)	2729 (2)	2·80	—
N(3)	2655 (3)	−59 (3)	2177 (2)	2·64	—
N(4)	1066 (3)	1623 (3)	2268 (2)	2·47	—
C(7)	3611 (4)	−358 (3)	2970 (3)	3·67	—
C(8)	3591 (4)	439 (4)	4022 (3)	3·56	—
C(9)	1582 (4)	1891 (4)	4111 (2)	3·38	—
C(10)	733 (3)	2168 (4)	3237 (2)	3·03	—
C(11)	341 (3)	132 (3)	1689 (2)	2·69	—
C(12)	1178 (4)	−706 (3)	2073 (3)	2·94	—
S(3)	8473 (1)	2446 (1)	625 (1)	2·71	—
O(1)	8490 (3)	2648 (3)	1650 (2)	4·82	—
O(2)	7275 (2)	1408 (2)	−120 (2)	3·58	—
O(3)	9760 (2)	2385 (3)	435 (2)	4·18	—
C(13)	8264 (4)	4013 (4)	434 (4)	5·37	—
F(1)	9303 (3)	5102 (3)	1028 (3)	8·16	—
F(2)	7118 (3)	4212 (3)	595 (3)	8·38	—
F(3)	8204 (3)	3933 (4)	−518 (2)	9·73	—
S(4A)	3612 (2)	2319 (2)	8148 (1)	3·97	0·58 (1)
O(4A)	4500 (14)	3410 (16)	8317 (10)	5·24 (26)	0·35 (1)
O(5A)	4678 (16)	1677 (17)	8303 (10)	8·33 (30)	0·35 (1)
O(6A)	2631 (13)	2438 (11)	8697 (8)	3·25 (15)	0·35 (1)
O(4A')	3763 (22)	981 (21)	8117 (15)	5·82 (33)	0·23 (1)
O(5A')	4808 (31)	2759 (38)	8200 (21)	11·81 (85)	0·23 (1)
O(6A')	2961 (17)	2042 (22)	8791 (11)	5·63 (36)	0·23 (1)
S(4B)	2660 (2)	1066 (3)	6902 (2)	3·70	0·42 (1)
O(4B)	3228 (17)	395 (19)	7609 (15)	4·71 (29)	0·25 (1)
O(5B)	2331 (24)	17 (23)	6769 (15)	7·87 (44)	0·25 (1)
O(6B)	3619 (16)	1721 (13)	6332 (10)	2·52 (20)	0·25 (1)
O(4B')	3855 (27)	1329 (31)	6494 (18)	5·35 (53)	0·17 (1)
O(5B')	2921 (27)	−69 (24)	7202 (22)	4·56 (45)	0·17 (1)
O(6B')	1323 (20)	863 (24)	6305 (15)	3·29 (36)	0·17 (1)
C(14A)	2503 (13)	1732 (14)	6845 (9)	6·53 (24)	0·58 (1)
F(4A)	1460 (15)	495 (12)	6481 (10)	6·39 (31)	0·35 (1)
F(5A)	3281 (10)	1173 (10)	6181 (6)	4·28 (17)	0·35 (1)
F(6A)	2208 (12)	3095 (14)	6803 (11)	7·44 (25)	0·35 (1)
F(5A')	1154 (12)	831 (17)	6623 (11)	3·91 (25)	0·23 (1)
F(6A')	3073 (16)	1760 (15)	6159 (9)	4·65 (27)	0·23 (1)
C(14B)	2889 (12)	2690 (12)	7853 (8)	4·67 (21)	0·42 (1)
F(4B)	2099 (15)	2609 (11)	8446 (10)	3·77 (19)	0·25 (1)
F(5B)	4126 (17)	3708 (12)	8204 (11)	3·97 (23)	0·25 (1)
F(6B)	2364 (13)	3582 (11)	7421 (10)	4·93 (21)	0·25 (1)
F(4B')	4089 (24)	3618 (23)	8553 (16)	6·01 (50)	0·17 (1)
F(5B')	3295 (35)	3705 (24)	7838 (19)	7·98 (50)	0·17 (1)
F(6B')	2122 (24)	2428 (29)	6459 (17)	7·32 (53)	0·17 (1)
O(4)	1398 (24)	1634 (28)	6710 (17)	6·50 (51)	0·09 (3)
O(5)	2589 (95)	1968 (86)	8449 (65)	6·50 (51)	0·09 (3)
O(6)	1515 (33)	2651 (28)	7936 (27)	6·50 (51)	0·09 (3)
S(5)	2747 (1)	6719 (1)	4633 (1)	2·90	—
O(7)	2695 (3)	5335 (2)	4605 (2)	3·85	—
O(8)	3208 (4)	7085 (3)	3861 (3)	7·83	—
O(9)	3360 (3)	7745 (3)	5615 (2)	4·81	—
C(15)	973 (5)	6687 (5)	4346 (4)	5·56	—
F(7)	414 (4)	6412 (4)	5000 (4)	12·51	—
F(8)	861 (3)	7898 (3)	4310 (3)	8·79	—
F(9)	257 (4)	5726 (4)	3470 (4)	10·16	—

Table 3. Positional parameters (× 10⁴) for (II) (cis)

	x	y	z	B_{eq}(Å²)
Co(1)	0	5429 (1)	5000	1·81
S(1)	380 (1)	3796 (2)	3853 (1)	2·87
N(1)	−1525 (3)	5388 (5)	3772 (4)	2·37
N(2)	179 (4)	6887 (5)	3851 (4)	2·18
C(1)	−1772 (5)	4315 (8)	2725 (5)	3·16
C(2)	−979 (6)	3112 (7)	3079 (6)	3·36
C(3)	572 (5)	4939 (8)	2676 (5)	3·60
C(4)	909 (4)	6382 (7)	3235 (5)	2·91
C(5)	−899 (5)	7364 (7)	2891 (5)	2·63
C(6)	−1788 (4)	6852 (7)	3263 (6)	2·69
Br(1)	1386 (1)	0	4571 (1)	3·38
Br(2)	2950 (1)	934 (1)	9373 (1)	6·30
O(1)	4689 (5)	5418 (7)	8610 (5)	6·21
O(2)	3759 (4)	−2255 (7)	9871 (6)	5·75
O(3)	0	7921 (14)	0	9·13
Li(1)	5000	−3275 (20)	10000	4·16 (32)

Table 4. Bond lengths (Å) and angles (°) for (I) (trans)

S(1)—Co(1)	2·251 (1)	S(2)—Co(1)	2·246 (1)
N(1)—Co(1)	1·962 (3)	N(2)—Co(1)	1·977 (3)
N(3)—Co(1)	1·986 (3)	N(4)—Co(1)	1·963 (3)
C(2)—S(1)	1·826 (4)	C(3)—S(1)	1·826 (4)
C(8)—S(2)	1·826 (4)	C(9)—S(2)	1·827 (4)
C(4)—N(1)	1·503 (5)	C(5)—N(1)	1·488 (4)
C(1)—N(2)	1·489 (4)	C(6)—N(2)	1·491 (4)
C(2)—C(1)	1·513 (5)	C(4)—C(3)	1·510 (5)
C(6)—C(5)	1·505 (5)	C(7)—N(3)	1·496 (5)
C(12)—N(3)	1·489 (4)	C(10)—N(4)	1·500 (5)
C(11)—N(4)	1·486 (4)	C(8)—C(7)	1·522 (5)
C(10)—C(9)	1·509 (5)	C(12)—C(11)	1·503 (6)
S(2)—Co(1)—S(1)	179·8 (0)	N(1)—Co(1)—S(1)	88·6 (1)
N(1)—Co(1)—S(2)	91·1 (1)	N(2)—Co(1)—S(1)	84·8 (1)
N(2)—Co(1)—S(2)	95·2 (1)	N(2)—Co(1)—N(1)	86·2 (1)
N(3)—Co(1)—S(1)	95·5 (1)	N(3)—Co(1)—S(2)	84·8 (1)
N(3)—Co(1)—N(1)	175·9 (1)	N(3)—Co(1)—N(2)	94·8 (1)
N(4)—Co(1)—S(1)	91·3 (1)	N(4)—Co(1)—S(2)	88·7 (1)
N(4)—Co(1)—N(1)	93·4 (1)	N(4)—Co(1)—N(2)	176·1 (1)
N(4)—Co(1)—N(3)	85·9 (1)	C(2)—S(1)—Co(1)	100·6 (1)
C(3)—S(1)—Co(1)	99·3 (1)	C(3)—S(1)—C(2)	102·9 (2)
C(8)—S(2)—Co(1)	100·5 (1)	C(9)—S(2)—Co(1)	99·3 (1)
C(9)—S(2)—C(8)	103·6 (2)	C(4)—N(1)—Co(1)	113·6 (2)
C(5)—N(1)—Co(1)	108·2 (2)	C(5)—N(1)—C(4)	115·1 (3)
C(1)—N(2)—Co(1)	111·6 (2)	C(6)—N(2)—Co(1)	110·6 (2)
C(6)—N(2)—C(1)	111·0 (3)	C(2)—C(1)—N(2)	110·9 (3)
C(1)—C(2)—S(1)	110·1 (3)	C(4)—C(3)—S(1)	111·1 (3)
C(3)—C(4)—N(1)	112·6 (3)	C(6)—C(5)—N(1)	109·2 (2)
C(5)—C(6)—N(2)	108·6 (3)	C(7)—N(3)—Co(1)	111·7 (2)
C(12)—N(3)—Co(1)	110·4 (2)	C(12)—N(3)—C(7)	111·9 (3)
C(10)—N(4)—Co(1)	113·8 (2)	C(11)—N(4)—Co(1)	108·3 (2)
C(11)—N(4)—C(10)	114·7 (3)	C(8)—C(7)—N(3)	110·2 (3)
C(7)—C(8)—S(2)	111·1 (3)	C(10)—C(9)—S(2)	111·3 (3)
C(9)—C(10)—N(4)	112·6 (3)	C(12)—C(11)—N(4)	108·9 (2)
C(11)—C(12)—N(3)	108·7 (3)		

Table 5. Bond lengths (Å) and angles (°) for (II) (cis)

S(1)—Co(1)	2·217 (2)	N(1)—Co(1)	1·979 (4)
N(2)—Co(1)	1·988 (5)	C(2)—S(1)	1·807 (7)
C(3)—S(1)	1·828 (6)	C(1)—N(1)	1·509 (7)
C(6)—N(1)	1·490 (8)	C(4)—N(2)	1·495 (7)
C(5)—N(2)	1·504 (7)	C(2)—C(1)	1·501 (10)
C(4)—C(3)	1·500 (10)	C(6)—C(5)	1·498 (9)
Li(1)—O(1)	1·932 (13)	Li(1)—O(2)	1·880 (11)
N(1)—Co(1)—S(1)	88·7 (1)	N(2)—Co(1)—S(1)	88·3 (1)
N(2)—Co(1)—N(1)	84·3 (2)	C(2)—S(1)—Co(1)	96·8 (2)
C(3)—S(1)—Co(1)	99·3 (2)	C(3)—S(1)—C(2)	104·8 (3)
S(1)—Co(1)—S(1)	91·7 (1)	C(1)—N(1)—Co(1)	115·1 (4)
C(6)—N(1)—Co(1)	106·3 (3)	C(6)—N(1)—C(1)	111·5 (4)
N(1)—Co(1)—N(1)	177·8 (3)	C(4)—N(2)—Co(1)	111·5 (3)
C(5)—N(2)—Co(1)	111·3 (3)	C(5)—N(2)—C(4)	111·6 (4)
N(2)—Co(1)—N(2)	92·2 (3)	C(2)—C(1)—N(1)	112·6 (5)
C(1)—C(2)—S(1)	109·5 (5)	C(4)—C(3)—S(1)	109·1 (4)
C(3)—C(4)—N(2)	110·5 (5)	C(6)—C(5)—N(2)	109·8 (4)
C(5)—C(6)—N(1)	108·7 (5)	O(1)—Li(1)—O(1)	100·5 (9)
O(2)—Li(1)—O(2)	118·2 (11)	O(2)—Li(1)—O(1)	111·5 (3)

involved in moderately strong hydrogen bonds with the amine H atoms.

In the complex cation *trans*-[Co(tasn)₂]³⁺ (Fig. 1), the Co^{III} atom is coordinated facially to two tridentate

tasn ligands and the two S donor atoms occupy *trans* positions. The cation has approximate C_2 symmetry, with the axis passing through the Co atom and bisecting the N(1)—Co—N(4) and N(2)—Co—N(3) angles. The conformations of the five-membered rings in each of the macrocycles are ($\lambda\delta\lambda$). The two rings coupled by the S atom have opposite chiralities. In all complexes of the related ligand tacn (1,4,7-triazacyclononane), the conformation with all rings having the same chirality ($\lambda\lambda\lambda$ or $\delta\delta\delta$) is present, and this arrangement has also been found in |Ni(tasn)₂|(NO₃)₂ (Hart, Boeyens, Michael & Hancock, 1983). The conformation found here has been observed previously in the structure of |Cu(tasn)₂|(NO₃)₂ (Boeyens, Dobson & Hancock, 1985). In that report it was suggested that the mixed-chirality conformation was stabilized by the longer metal-to-donor-atom bond lengths of the copper complex compared to the nickel complex. Clearly this rationalization cannot be applied to the cobalt complex. H···H interactions within each ligand range from 2·18 to 2·27 Å, similar to those observed in the complex |Ni(tasn)₂|²⁺ (Hart, Boeyens, Michael & Hancock, 1983). It seems likely that the ($\lambda\lambda\lambda$) and ($\lambda\delta\lambda$) conformations of the tasn ring are of similar stability and which is adopted depends on external factors.

Coordination of the ligand involves considerable strain; this is most evident in the C—N—C angles at N(1) and N(4) which are opened from tetrahedral to *ca* 115°, and in the X—C—C—X torsion angles which are in the range 34 to 45°, considerably less than the value of 55° observed in 'unstrained' five-membered chelate rings.

The Co—N bond lengths are typical of those observed previously for cobalt(III) amine complexes. The Co—S bond lengths |2·251 (1), 2·246 (1) Å| are almost identical to those found in the structure of *unsym-fac*-|Co(daes)₂|³⁺ (Hammershoi, Larsen & Larsen, 1978) where daes |2,2'-di(aminoethyl)sulfide| is the

open-chain tridentate (*NSN*) analogue of tasn and in which the S atoms are *cis*. They are shorter than those in other Co^III complexes with *trans* Co—S bonds, Na|Co(L-met)₂|(ClO₄)₂ (L-met = L-methioninato) 2·301 (1) Å (Hambley, 1988b) and |Co{(S)-Me-L-cys}₂|ClO₄.H₂O 2·270 (2), 2·273 (2) Å (De Meester & Hodgson, 1976). Nevertheless, the Co—S bonds in *trans*-|Co(tasn)₂|³⁺ are significantly longer than those in the *cis* isomer |2·217 (2) Å|, discussed below, suggesting that there may be some *trans* effect.

Structure (II) (*cis*). This consists of the complex cation lying on a twofold axis, a tetraaqualithium cation also on a twofold axis, two Br anions at general sites and an H₂O molecule of hydration on a twofold axis. Amine and water H atoms are involved in hydrogen bonds with Br anions and there appears to be a strong hydrogen bond between two water molecules |O(1)··· O(3) 2·79 (1) Å| though an H atom could not be located in the region.

The geometry about the Li⁺ cation is approximately tetrahedral. The Li—O bond lengths are similar to those in other |Li(H₂O)₄|⁺ units; for example in LiGaO₂.6H₂O, Li—O is 1·97 (1)–2·00 (1) Å (Caranoni, Pepe & Capella, 1978).

The S donor atoms occupy *cis* positions in the approximately octahedral complex cation (Fig. 2). Co—N bond lengths are normal but the Co—S bond length |2·217 (2) Å| is at the short end of the reported range. The shortest Co—S(thioether) bond reported previously was 2·226 (1) Å in |Co(azacapten)|-ZnCl₄Cl (azacapten = 1-methyl-3,13,16-trithia-6,8,-10,19-tetraazabicyclo|6.6.6|icosane) (Gahan, Hambley, Sargeson & Snow, 1982) but in that case the ligand probably constrains the bond length to some extent.
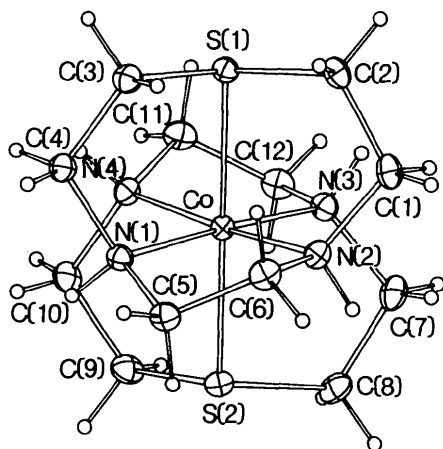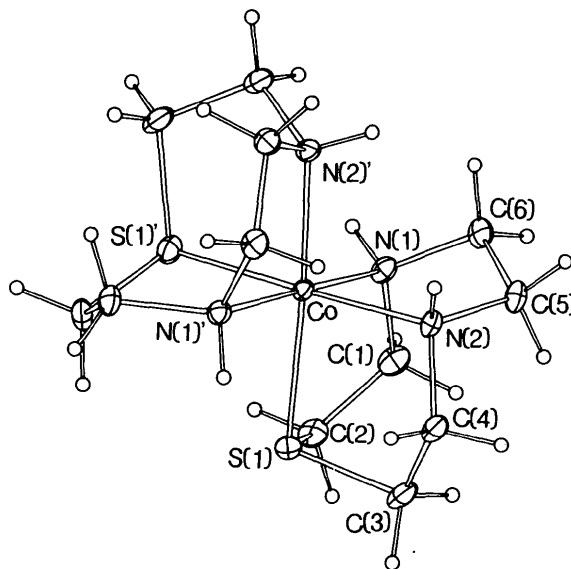

Fig. 1. *ORTEP* plot of *trans*-[Co(tasn)₂]³⁺ ($\lambda\delta\lambda$, $\lambda\delta\lambda$) cation showing the atom numbering. The δ rings are between N(1), S(1) and between N(4), S(2).

Fig. 2. *ORTEP* plot of the *cis*-|Co(tasn)₂|³⁺ ($\lambda\lambda\lambda$, $\lambda\lambda\lambda$) cation showing the atom numbering.

The ligand conformation is the more usual $(\lambda\lambda\lambda)$ and comparison of bond angles in the *cis* and *trans* isomers suggests this $(\lambda\lambda\lambda)$ conformation leads to lower internal strain. In the *cis* isomer the X—C—C—X torsion angles are in the range -40 to $-49°$, closer to ideal, and the C—N—C angles are not unusually opened. Intraring H$\cdots$H contacts are similar in the two isomers although those in the *cis* isomer ($2\cdot24$–$2\cdot28$ Å) are at the long end of the range observed for the *trans* isomer.

The crystallization of the *cis* isomer in a non-centrosymmetric space group shows that spontaneous resolution has occurred and raises the question of the definition of the configuration of the complex cation. The dissymmetry in the *cis*-$|Co(tasn)_2|^{3+}$ cation arises essentially from a configurational effect from the different donor atoms N and S in the macrocyclic ligand, and not from the chelate rings. Thus an absolute configuration cannot be assigned by the IUPAC rules based on chelate rings as skew pairs, and the vicinal effects of the four asymmetric donor N atoms also cancel. The absolute configuration of the cation in the particular crystal examined is defined by the diagram in Fig. 2. The ring conformations are in principle an independent source of chirality, and the conformations discussed in the text and in Table 7 refer to the absolute configuration shown in Fig. 2.

Chromatographic discrimination of the $|Co(tasn)_2|^{3+}$ *isomers.* Chromatography of the $|Co(tasn)_2|^{3+}$ complex by cation exchange has given unusually poor discrimination between the isomers (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988) and this can now be understood in terms of the detailed geometries found for the isomers. There is substantial evidence that chromatographic discrimination results from 'polydentate' interactions between a tetrahedral anion such as SO_4^{2-} or PO_4^{3-} and two or three H(amine) atoms of the complex cation (Keene & Searle, 1974; Searle, 1977; Sakagushi, Tsuge & Yoneda, 1983). In the case of the *trans* isomer (Fig. 1) only one H(amine) atom would be accessible by a single anion. For the *cis* isomer (Fig. 2) only one pair of H(amine) atoms is able to interact with a single anion, and the mutual orientation of these atoms is not ideal for strong hydrogen bonding to an anion. The thioether groups cannot participate in hydrogen bonding with basic anions. These observations can thus account for the poor chromatographic discrimination and the elution of the *cis* isomer before the *trans*.

Some chromatographic comparisons give support to these proposals. The elution of the complex down SP-Sephadex columns using the eluents Na_2SO_4/H^+ and Na_2(+)tartrate was examined in comparison with some related charged (3+) cobalt(III) complexes. These included the three geometric isomers of $|Co(dien)_2|^{3+}$ (dien = diethylenetriamine) whose relative elutions *sym-fac* $>>$ *unsym-fac* $>$ *mer* are reasonably understood on the basis of ion association (Searle, 1977), *unsym-*

Table 6. R_x *values for elution of complexes on SP-Sephadex C-25 with different eluents*

Eluent Complex	0·1 M Na₃PO₄ (pH 12)	0·3 M Na₂(+)tart (pH 6)	0·2 M Na₂SO₄/H⁺ (pH 2)
$\mid$Co(tasn)₂$\mid^{3+}$ (two isomers)	0·3ₐ*†‡	0·6₂†	0·5₆ *trans* 0·6₆ *cis*
mer-$\mid$Co(dien)₂$\mid^{3+}$	0·2ₕ	0·6ₕ	0·7₉
$\mid$Co(tacn)₂$\mid^{3+}$	0·4₃	0·7₀	0·8₉
u-fac-$\mid$Co(dien)₂$\mid^{3+}$	0·6ₕ	0·9ₓ	1·0₂‡
u-fac-$\mid$Co(daes)₂$\mid^{3+}$	0·7₃	1·0₃‡	0·9₆
$\mid$Co(en)₃$\mid^{3+}$	1·00	1·00	1·00
s-fac-$\mid$Co(dien)₂$\mid^{3+}$	1·6₅	1·4₂	1·4₃

* Moves as brown-red species.
† Isomers not separated due to rapid equilibration.
‡ Complex moves relatively faster with this particular eluent, so that there is a reversal of elution order of complexes.

fac-$|Co(daes)_2|^{3+}$ and $|Co(tacn)_2|^{3+}$. The elutions were quantified in terms of R_x (relative R_f) values referenced to $|Co(en)_3|^{3+}$ as described previously (Searle, 1977, 1987), and the results are shown in Table 6.

The R_x data show that the $|Co(tasn)_2|^{3+}$ isomers elute more slowly with tartrate^{2-} and SO_4^{2-} eluents than the other complexes listed. This implies relatively weaker associations for $|Co(tasn)_2|^{3+}$, and the discriminations between the isomers would be smaller accordingly. These weaker associations may be attributed to a number of factors acting together.

(1) The slower movement of $[Co(tasn)_2]^{3+}$ than $|Co(tacn)_2|^{3+}$, where tacn is the imino analogue of tasn, shows that the replacement of the —NH— groups in $|Co(tacn)_3|^{3+}$ by nonassociating thioether groups is an important factor, at least with the macrocyclic complexes. However, *unsym-fac*-$|Co(daes)_2|^{3+}$ and *unsym-fac*-$|Co(dien)_2|^{3+}$, which are the open-chain analogues of $|Co(tasn)_2|^{3+}$ and $[Co(tacn)_2]^{3+}$ respectively, move similarly to each other which indicates that other factors are also important in determining the separations.

(2) The macrocyclic complexes move more slowly than their open-chain analogues. The two sets of complexes differ in that the chelate-ring conformations are expected to be more constrained in the macrocycles, so that —NH— bonds may not be optimally disposed for hydrogen bonding. As well, the additional rings in macrocyclic complexes hinder association sterically. The solid state structures of the $|Co(tasn)_2|^{3+}$ isomers support these proposals as mentioned. The availability of three —NH— pairs on $|Co(tacn)_2|^{3+}$ probably accounts for its faster elution.

(3) The macrocycle complexes and their open-chain analogues also differ in their types of amine groups: the macrocycles have only *sec*-NH groups, which couple the rings, whereas the open-chain complexes have —NH₂ groups available. Dreiding models show that some particular H atoms which are lost from —NH₂ groups in making the closure to a macrocycle, such as going from *unsym-fac*-$[Co(daes)_2]^{3+}$ to *cis*-$|Co(tasn)_2|^{3+}$, are those which are most favourable for hydrogen bonding in the open-chain complex. Thus

three H atoms including those from NH_2 are available from octahedron faces of the $|Co(dien)_2|^{3+}$ isomers, whose separation is *sym-fac*>>*unsym-fac*. However, in $|Co(tasn)_2|^{3+}$, where the $-NH-$ H atoms are available only in pairs (in *cis*) or singly (in *trans*), the isomers elute in the reverse-symmetry order *cis*>*trans*. These coordinated *sec*-NH and $-NH_2$ groups within the one complex have different acidities but it is unknown how this factor might affect hydrogen bonding.

(4) On elution with $0.1 M$ Na_3PO_4 eluent the $|Co(tasn)_2|^{3+}$ complex moves as the dark deprotonated species. The R_x value is very low (0.3_4), which reflects the great discrimination between this complex and $|Co(en)_3|^{3+}$ effected by this eluent, and this can be attributed in part to the reduced cation charge of the deprotonated species giving reduced complex–resin interaction.

Molecular mechanics. The aim of the molecular-mechanics calculations was threefold: to determine the relative stabilities of the *cis* and *trans* isomers, to determine the relative stabilities of the $(\lambda\lambda\lambda)$ and $(\lambda\delta\lambda)$ conformations, and to determine whether steric factors alone are responsible for the different Co–S bond lengths observed for the *cis* and *trans* isomers. Accordingly a number of conformations were modelled for both the *cis* and the *trans* isomers. Minimized strain energies are given in Table 7. The strain energies E_{total} of the most stable conformation for the *cis* and *trans* isomers are very similar, with the *cis* isomer $0.8 kJ mol^{-1}$ more stable than the *trans* isomer. The *cis* isomer is also stabilized by statistical effects; it can be formed in two ways corresponding to the two enantiomers, but the *trans* isomer can only be formed in one. Thus a *cis:trans* mixture of 73:27 would be expected under equilibrium conditions (calculated from $\Delta H = -0.8$, $T\Delta S = 1.72 kJ mol^{-1}$ at 298 K). This agrees well with the experimentally determined isomer distribution of 80:20 in solution (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988) so that the present study explains why the *cis* isomer is the more stable. Under neutral or basic conditions, however, only the *trans* isomer crystallizes, but this is due to lower solubilities of the *trans* salt (perchlorate and bromide). A similar situation is observed for the three isomers of $|Co(L-met)_2|^+$: molecular-mechanics calculations show that all the isomers have similar strain energies (Hambley, 1988b) and this is supported by preparative studies (Hidaka, Yamada & Shimura, 1974), yet in solution the *trans*-N and *trans*-O isomers convert to the isomer with *trans*-S(thioether) groups. Thus, it appears that the *trans*-S arrangement is favoured in the solid state.

Calculations were carried out on three combinations of ligand conformation for the *trans* isomer: $(\lambda\lambda\lambda, \lambda\lambda\lambda)$ in which the ligands are related by a twofold rotation axis, $(\lambda\lambda\lambda, \delta\delta\delta)$ in which the ligands are related by a centre of symmetry and $(\lambda\delta\lambda, \lambda\delta\lambda)$ as observed in the crystal structure. Similar conformations were con-

Table 7. Minimized strain energies (kJ mol⁻¹) for the isomers of $|Co(tasn)_2|^{3+}$

Isomer	Conformer	E_b	E_{nb}	E_θ	E_ω	E_{total}
trans	$(\lambda\lambda\lambda, \lambda\lambda\lambda)$	27.9	75.3	23.0	33.3	159.5
	$(\lambda\lambda\lambda, \delta\delta\delta)$	28.5	78.8	23.0	35.5	165.8
	$(\lambda\delta\lambda, \lambda\delta\lambda)$	25.8	77.1	21.8	39.6	164.2
cis	$(\lambda\lambda\lambda, \lambda\lambda\lambda)$	28.2	75.5	22.9	32.8	159.4
	$(\delta\delta\delta, \delta\delta\delta)$	28.0	74.5	23.0	33.2	158.7
	$(\delta\delta\delta, \lambda\lambda\lambda)$	29.7	79.8	23.2	35.3	168.0
	$(\lambda\delta\lambda, \lambda\delta\lambda)$	26.7	78.9	23.2	40.4	169.2
	$(\delta\lambda\delta, \delta\lambda\delta)$	26.6	77.8	21.0	39.0	164.5

sidered for the *cis* isomer, although there is a greater number of arrangements as a result of the chirality of the *cis* isomer. Other arrangements with different ring conformations in the two ligands are possible, but it is clear from the calculations performed that these are unlikely to give lower energies. For both the *cis* and the *trans* isomers the most stable arrangements are those with all the five-membered rings having the same conformation. For the *cis* isomer the two possibilities with all rings adopting the same conformations have very similar strain energies, with the arrangement observed in the crystal structure $(\lambda\lambda\lambda, \lambda\lambda\lambda)$ being only $0.7 kJ mol^{-1}$ less stable than $(\delta\delta\delta, \delta\delta\delta)$. In the case of the *trans* isomer the crystal structure arrangement $(\lambda\delta\lambda, \lambda\delta\lambda)$ has a calculated energy substantially higher (by $4.7 kJ mol^{-1}$) than the most stable arrangement, though statistical entropy effects will favour this lower symmetry conformation by $1.7 kJ mol^{-1}$. The $(\lambda\delta\lambda, \lambda\delta\lambda)$ conformation has been observed in the structure of $|Cu(tasn)_2|(NO_3)_2$ (Boeyens, Dobson & Hancock, 1985). In that structure a much longer M–S bond $|2.745-2.772 (1) Å|$ was observed which would reduce the unfavourable inter-ring interactions which de-stabilize that conformation in the case of the Co^{III} structure.

The Co–S bond lengths in the energy-minimized geometries of the *cis* and *trans* isomers are similar, 2.243 and 2.235 Å respectively. The former is significantly longer than that observed in the crystal structure of the *cis* isomer, 2.217 (2) Å, and the latter is marginally shorter than the values in the *trans* isomer, 2.251 (1) and 2.246 (1) Å. Thus, the calculations do not provide a steric explanation for the observed differences in the Co–S bond lengths, so that it appears that the Co–S bond may exert a weak electronic *trans* effect. A similar conclusion was reached in a study of the isomers of $|Co(L-met)_2|^+$ (Hambley, 1988b).

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Structure of Oxobis(phenolato)[tris(3,5-dimethyl-1-pyrazolyl)-hydroborato]molybdenum(V)

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Abstract. $C_{27}H_{32}BMoN_6O_3$, $M_r = 595·34$, monoclinic, $P2_1/n$, $a = 16·376$ (6), $b = 10·438$ (5), $c = 17·016$ (8) Å, $\beta = 107·25$ (3)°, $V = 2777·8$ Å^3, $Z = 4$, $D_m = 1·37$, $D_x = 1·43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 5·02$ cm^{-1}, $F(000) = 1228$, $T = 296$ K, $R = 0·038$, $wR = 0·045$ for 2457 reflections. This molecule is the first structurally characterized mononuclear molybdenum complex containing a terminal aryl oxide ligand. The central molybdenum atom adopts a distorted octahedral coordination geometry with one face of the octahedron occupied by the tridentate pyrazolylborate ligand and the opposite face by the oxo and the two phenolato ligands. The structure is compared with that of the analogous benzenethiolate complex.

Introduction. We have been interested in the synthesis and characterization of molybdenum compounds as models for oxomolybdenum enzyme active sites, especially that of sulfite oxidase (Spence, 1983; Garner & Bristow, 1985). Sulfite oxidase has been shown to contain a mononuclear Mo center (Cramer, 1983), which cycles between the Mo^{VI}, Mo^V, and Mo^{IV} oxidation states (Rajagopalan, 1980; Kipke, Cusanovich, Tollin, Sunde & Enemark, 1988). Because the one-electron-reduced molybdenum site is readily characterized by EPR, the preparation of model complexes in the Mo^V oxidation state is of particular interest (Bray, 1980). Dimerization of oxo-Mo^V complexes in the presence of water has been circumvented in our studies by using the bulky tridentate ligand tris(3,5-dimethyl-1-pyrazolyl)hydroborate (L). The 3-methyl groups of the pyrazole rings project beyond the molybdenum, create a steric pocket, prevent dimerization and allow preparation of a series of mononuclear Mo^V complexes (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1987). Here we present the structure of one of these complexes, $LMoO(OPh)_2$.

Experimental. The complex was prepared by the method of Cleland et al. (1987). Ruby red blocks obtained by the slow evaporation of a benzene solution of $LMoO(OPh)_2$ at 298 K, dimensions 0·30 × 0·25 ×

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