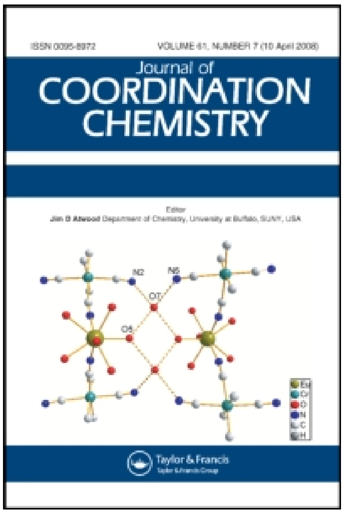

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 54. THE CRYSTALLIZATION MODES OF FIVE NEW COMPLEXES [*TRANS*-(3,2,3-TET)Co(III)X_2]*Y*, *X*=NO_2^-, CN^-, NCS^-

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 54. THE CRYSTALLIZATION MODES OF FIVE NEW COMPLEXES [*TRANS*-(3,2,3-TET)Co(III)X_2]Y, X=NO_2^-, CN^-, NCS^-

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A few complexes of formula [*trans*-Co(N_4)X_2]Y, where X = a monodentate ligand, N_4 = a tetraamine ligand and Y = a halide or oxy anion have been found to crystallize as conglomerates; however, the majority crystallize as racemates. The complexes are of such variety of composition and packing characteristics that it is difficult to ascertain why they crystallize in one form or the other. We decided to investigate a series of [*trans*-Co(N_4)X_2]Y compounds in which the amine was kept constant in order to limit the variables that affect the outcome.

Five different compounds of composition [*trans*-Co(3,2,3-tet)X_2]Y (3,2,3-tet = 1,10-diamino-4,7-diaza-decane, $X = NO_2^-$, CN^-, SCN^-, and $Y = BF_4^-$, Cl^-, Br^-, I^-) were prepared and their crystallization behavior examined by determining their crystal structures. In all cases, when crystallized from deionized water at 21°C, these substances are racemates. Suggestions regarding this crystallization mode are offered in the discussion.

Keywords: Crystal structure; Cobalt(III); Conglomerate crystallization; Tetraamine; Racemates; Cobalt amine derivatives; Cobalt cyanides; Cobalt thiocyanates

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INTRODUCTION

In earlier studies, we have shown [1–4] that a sizable group of *cis*-dinitro cobalt(III) and oxalato cobalt(III) compounds crystallize as conglomerates and provided persuasive evidence that the phenomenon is controlled by hydrogen bonds. We now wish to address the crystallization behavior of a series of *trans* compounds, as well as to introduce new ligands combined with some of the amines with which we succeeded in observing both racemic as well as conglomerate crystallization. We explored the Cambridge Structure Database to ascertain whether or not there were already cases of conglomerate crystallization of cobalt amine cyanides and cobalt amine thiocyanates. There are four examples of amine cyanides and thirteen amine thiocyanates of Co(III) which are genuine examples of conglomerate crystallization. Thus, we decided to explore those two series, using tetraamine ligands known from previous work to give *trans* geometries.

While [*trans*-Co(en)$_2$(NO$_2$)$_2$] X(X = I$^-$, NO$_3^-$, ClO$_4^-$, NCS$^-$) and [*trans*-Co(en)$_2$(NO$_2$)(NCS)]NCS [4–7] crystallize as racemates, compounds [*trans*-Co(en)$_2$(NO$_2$)(NCS)] X(X = I$^-$, ClO$_4^-$) and [*trans*-Co(en)$_2$(ONO)(NCS)] X(X = I$^-$, ClO$_4^-$) all crystallize as conglomerates [8]. Further, for a series of 3,2,3-tet amine compounds, we found that [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$] X(X = Br$^-$, I$^-$, Cl$^-$·(H$_2$O)$_3$, NO$_3^-$, ClO$_4^-$) [9–12] and [*trans*-Co(3,2,3-tet)Cl$_2$]NO$_3$ [10, 13] crystallize as conglomerates. By contrast, [*trans*-Ni(3,2,3-tet)(NO$_2$)$_2$] [14] and [*trans*-Co(2,3,2-tet)(NO$_2$)$_2$]NO$_3$ [15] crystallized as racemates. Thus far, we have not formed a clear explanation of the phenomenon of conglomerate crystallization of *trans* derivatives. To further investigate the conglomerate crystallization behavior of the *trans*-cobalt coordination compounds, single crystals of more *trans* 3,2,3-tet cobalt(III) compounds were obtained and their crystallization behavior are reported herein.

EXPERIMENTAL

Preparation of the Compounds

[Trans-Co(3,2,3-tet)(NO$_2$)$_2$]BF$_4$ (I)

To a water solution of [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]Cl, which was prepared according to the literature method [10], was added an excess of a saturated water solution of NaBF$_4$. After several days of slow evaporation, crystals of the desired complex were obtained and filtered. Single crystals suitable for X-ray diffraction were obtained upon recrystallization from water.

[Trans-Co(3,2,3-tet)(CN)$_2$]Cl$\cdot$H$_2$O (II)

[*trans*-Co(3,2,3-tet)Cl$_2$]Cl$\cdot$3/2H$_2$O (1.65 g, 0.05 mol) prepared according to the literature method [16], was dissolved in water (100 mL) and the solution was heated on a water-bath for 15 min. Then, NaCN (0.50 g, 0.1 mol) dissolved in 20 mL of water was added dropwise to the cobalt solution whereupon the color turns to yellowish-orange. The volume of the solution was reduced to ~40 mL and left to crystallize at room temperature. After one week, the orange crystalline complex separated, was collected by filtration, washed with ethanol and air-dried. Single crystals suitable for X-ray diffraction were obtained by dissolving the

TABLE I Summary of data collection and processing parameters for compound I, [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]BF$_4$

	Compound I
Space Group	P-1 (No. 2)
Cell Constants	$a = 6.457(4)$ Å
	$b = 7.792(3)$ Å
	$c = 9.019(6)$ Å
	$\alpha = 66.87(4)°$
	$\beta = 79.53(6)°$
	$\gamma = 81.75(4)°$
Cell Volume (Å^3)	409.1(4)
Molecular Formula	CoBC$_8$F$_4$H$_{22}$N$_6$O$_4$
Molecular Weight	412.03
F(000)	212.44
Z	1
Density (Mg$\cdot$m^{-3})	1.673
Radiation Employed	MoKα(0.70930 Å)
μ	1.11 mm^{-1}
h(min, max)	−8 9
k(min, max)	0 10
l(min, max)	−11 12
Absorption Correction	Yes
Relative Transmission Coefficients	0.6369, 0.7751
Data Collection Range	4−60
Scan Width	1.00+0.35tanθ
Total Data Collected	2516
Total Unique Data Collected	2516
Data Used in Refinement	897 ($I > 3\sigma(I)$)
Merging R-value	0.000
RF	0.104
Rw	0.116
GoF	0.58
Max shift/sigma Ratio	0.010
Deepest Hole (e/Å^3)	−0.950
Highest Peak (e/Å^3)	1.08
Weights Used	$W = \sigma[(F_0)]^{-2}$

RF = Σ(Fo − Fc)/Σ(Fo), Rw = [Σ(w(Fo − Fc)**2)/Σ(wFo**2)]$^{1/2}$, GoF = [Σ(w(Fo − Fc)**2)/(No. of reflns-No. of params.)]$^{1/2}$.

complex in a minimum of water, followed by slow evaporation at ambient temperature.

[Trans-Co(3,2,3-tet)(CN)$_2$]Br·H$_2$O (III)

[*trans*-Co(3,2,3-tet)Cl$_2$]Cl·3/2H$_2$O (1.65 g, 0.05 mol) dissolved in water (100 mL) was heated on a water bath for 15 min, followed by addition of NaCN (0.50 gm, 0.1 mol) in 20 mL of water. To the resulting yellowish-orange solution, 2 mL of a saturated solution of NaBr, was added. The volume of the solution was reduced to ~60 mL and left to crystallize at room temperature. After several days orange single crystals were obtained. These were collected by filtration, washed with ethanol and air-dried.

TABLE II Summary of data collection and processing parameters for compounds **II**, [*trans*-Co(3,2,3-tet)(CN)$_2$]Cl·H$_2$O and **III**, [*trans*-Co(3,2,3-tet)(CN)$_2$]Br·H$_2$O

	Compound **II**	*Compound* **III**
Space Group	P2$_1$/c	P2$_1$/c
Cell Constants	$a = 8.244(2)$ Å $b = 14.355(9)$ Å $c = 13.292(7)$ Å $\beta = 99.86(3)°$	$a = 8.188(3)$ Å $b = 14.528(10)$ Å $c = 13.287(6)$ Å $\beta = 99.67(4)°$
Cell Volume (Å^3)	1549.8(13)	1558.1(14)
Molecular Formula	CoC$_{10}$ClH$_{24}$N$_6$O	CoBrC$_{10}$H$_{24}$N$_6$O
Molecular Weight	338.72	383.18
F(000)	714.00	783.76
Z	4	4
Density (Mg·m^{-3})	1.452	1.625
Radiation Employed	MoKα(0.70930 Å)	MoKα(0.70930 Å)
μ	1.28 mm^{-1}	3.64 mm^{-1}
h(min, max)	−10 10	−10 10
k(min, max)	0 11	0 18
l(min, max)	0 17	0 17
Absorption Correction	Yes	Yes
Relative Transmission Coefficients	0.6354, 0.7500	0.2450, 0.4561
Data Collection Range	4–55	4–55
Scan Width	$0.65 + 0.35\tan\theta$	$0.95 + 0.35\tan\theta$
Total Data Collected	2964	6124
Total Unique Data Collected	2860	3565
Data Used in Refinement	2067 ($I > 3\sigma(I)$)	1684 ($I > 4\sigma(I)$)
Merging R-value	0.018	0.081
RF	0.034	0.086
Rw	0.039	0.112
GoF	0.45	1.34
Max shift/sigma Ratio	0.000	0.000
Deepest Hole (e/Å^3)	−0.440	−1.72
Highest Peak (e/Å^3)	0.520	2.09
Weights Used	$W = \sigma[(F_0)]^{-2}$	$W = \sigma[(F_0)]^{-2}$

RF = Σ(Fo − Fc)/Σ(Fo), Rw = [Σ(w(Fo − Fc)**2)/Σ(wFo**2)]$^{1/2}$, GoF = [Σ(w(Fo − Fc)**2)/(No. of reflns-No. of params.)]$^{1/2}$.

[Trans-Co(3,2,3-tet)(NCS)$_2$]Cl (IV)

[*trans*-Co(3,2,3-tet)Cl$_2$]Cl·3/2H$_2$O (1.65 g, 0.05 mol) dissolved in water (100 mL) was heated on a water bath for 15 min, followed by addition of NaSCN (0.85 g, 0.1 mol) in 20 mL of water. Upon addition of the thiocyanate solution, the color turns dark purple and, after a few minutes, a green precipitate formed which was filtered quickly and discarded. The dark purple filtrate was allowed to stand at room temperature and a brown precipitate, which separated out of this solution, was filtered. The product obtained was dissolved in hot water and crystallized from charcoal. After one week the reddish-brown crystals separated out were collected by filtration, washed with ethanol and air-dried.

TABLE III Summary of data collection and processing parameters for compounds IV, [*trans*-Co(3,2,3-tet)(NCS)$_2$]Cl and V, [*trans*-Co(3,2,3-tet)(NCS)$_2$]I

	Compound IV	*Compound* V
Space Group	P2$_1$/n	P2$_1$/n
Cell Constants	$a = 11.030(18)$ Å	$a = 11.085(7)$ Å
	$b = 13.224(12)$ Å	$b = 13.286(6)$ Å
	$c = 13.35(3)$ Å	$c = 12.293(10)$ Å
	$\beta = 98.33(17)°$	$\beta = 97.51(6)°$
Cell Volume (Å^3)	1782(6)	1795.1(20)
Molecular Formula	CoC$_{10}$ClH$_{22}$N$_6$S$_2$	CoC$_{10}$H$_{22}$IN$_6$S$_2$
Molecular Weight	384.83	476.28
F(000)	802.86	943.55
Z	4	4
Density (Mg·m^{-3})	1.434	1.762
Radiation Employed	MoKα(0.70930 Å)	MoKα(0.70930 Å)
μ	1.34 mm^{-1}	2.88 mm^{-1}
h(min, max)	−13 12	−13 13
k(min, max)	0, 15	0 15
l(min, max)	0, 14	0 14
Absorption Correction	No	Yes
Relative Transmission Coefficients	N/A	0.3396, 0.5277
Data Collection Range	4−50	4−50
Scan Width	$0.75 + 0.35\tan\theta$	$1.00 + 0.35\tan\theta$
Total Data Collected	3308	3383
Total Unique Data Collected	3136	3182
Data Used in Refinement	739 ($I > 2.5\sigma(I)$)	893 ($I > 4\sigma(I)$)
Merging R-value	0.263	0.133
RF	0.175	0.051
Rw	0.202	0.058
GoF	0.65	0.35
Max shift/sigma Ratio	0.504	0.001
Deepest Hole (e/Å^3)	−1.46	−0.940
Highest Peak (e/Å^3)	1.99	0.830
Weights Used	$W = \sigma[(F_O)]^{-2}$	$W = \sigma[(F_O)]^{-2}$

RF = Σ(Fo − Fc)/Σ(Fo), Rw = [Σ(w(Fo − Fc)**2)/Σ(wFo**2)]$^{1/2}$, GoF = [Σ(w(Fo − Fc)**2)/(No. of reflns-No. of params.)]$^{1/2}$.

[Trans-Co(3,2,3-tet)(NCS)$_2$]I (V)

This compound was prepared as described for the corresponding chloride complex (IV) except for the addition of a saturated solution of NaI to the

TABLE IV Atomic parameters *x*, *y*, *z* and Biso for compound **I**, [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]BF$_4$ E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.08000	0.21000	0.69000	2.77 (17)
N1	0.033 (5)	0.055 (5)	0.905 (4)	3.9 (8)
N2	-0.140 (3)	0.403 (4)	0.717 (3)	1.0 (4)
N3	0.137 (4)	0.368 (4)	0.436 (3)	2.1 (6)
N4	0.300 (8)	-0.007 (8)	0.681 (7)	7.6 (14)
N5	0.308 (8)	0.358 (8)	0.731 (7)	8.6 (14)
N6	-0.134 (3)	0.091 (3)	0.656 (3)	1.0 (4)
O1	0.389 (10)	0.231 (8)	0.821 (8)	8.3 (17)
O2	0.282 (4)	0.522 (4)	0.660 (4)	5.4 (7)
O3	-0.182 (5)	-0.061 (4)	0.743 (4)	5.9 (7)
O4	-0.271 (6)	0.170 (5)	0.561 (4)	5.2 (8)
C1	-0.025 (8)	0.161 (7)	1.042 (6)	5.8 (12)
C2	-0.220 (5)	0.311 (5)	0.995 (4)	2.5 (6)
C3	-0.161 (7)	0.465 (6)	0.838 (5)	4.4 (10)
C4	-0.109 (5)	0.566 (5)	0.561 (5)	4.9 (8)
C5	-0.047 (5)	0.510 (5)	0.431 (4)	4.5 (7)
C6	0.173 (6)	0.305 (6)	0.329 (5)	2.9 (8)
C7	0.352 (6)	0.166 (6)	0.340 (5)	4.3 (9)
C8	0.334 (7)	-0.021 (6)	0.498 (6)	4.5 (10)
H12	-0.173	0.458	0.415	5.2
H13	-0.014	0.626	0.329	5.2
H1	0.168	-0.023	0.940	3.3
H2	-0.068	-0.030	0.929	3.3
H3	0.085	0.261	1.005	6.1
H4	-0.052	0.093	1.141	6.1
H5	-0.283	0.346	1.088	2.0
H6	-0.341	0.241	0.977	2.0
H7	-0.271	0.568	0.834	5.4
H8	-0.024	0.498	0.860	5.4
H9	-0.274	0.350	0.720	1.7
H10	-0.240	0.652	0.555	6.3
H11	0.008	0.638	0.575	6.3
H14	0.262	0.436	0.431	3.0
H15	0.050	0.255	0.306	2.1
H16	0.216	0.415	0.203	2.1
H17	0.368	0.116	0.233	4.7
H18	0.492	0.216	0.316	4.7
H19	0.471	-0.111	0.489	10.4
H20	0.214	-0.089	0.499	10.4
H21	0.255	-0.127	0.771	8.9
H22	0.441	0.017	0.705	8.9
F1	-0.506 (5)	0.599 (5)	0.296 (4)	10.2 (10)
F2	-0.367 (3)	0.871 (3)	0.134 (3)	5.6 (5)
F3	-0.259 (5)	0.695 (4)	0.368 (4)	10.1 (8)
F4	-0.191 (6)	0.604 (5)	0.156 (4)	12.5 (10)
B	-0.335 (6)	0.709 (7)	0.233 (6)	4.8 (8)

Biso is the mean of the principal axes of the thermal ellipsoid.

purple product. Brown-red needles were obtained by crystallizing the crude brown precipitate from hot water containing 0.5 g of activated charcoal.

Elemental analyses were not determined since the structure and the elemental analyses of the starting material [*trans*-Co(3,2,3-tet)Cl_2]Cl · 3/2H_2O was known [10].

TABLE V Atomic parameters *x*, *y*, *z* and Biso for compound II, [*trans*-Co(3,2,3-tet)-$(CN)_2$]Cl · H_2O E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.90045 (6)	0.24357 (4)	0.11703 (3)	1.550 (21)
N1	0.8565 (5)	0.3721 (3)	0.0642 (3)	2.60 (19)
N2	0.6976 (4)	0.2007 (3)	0.02505 (24)	2.18 (15)
N3	0.9355 (4)	0.1108 (3)	0.15801 (24)	2.33 (16)
N4	1.0992 (4)	0.2837 (3)	0.2138 (3)	2.26 (16)
N5	0.7082 (5)	0.2814 (3)	0.2921 (3)	3.30 (17)
N6	1.1035 (5)	0.2132 (3)	−0.0542 (3)	3.63 (20)
C1	0.6898 (7)	0.4124 (4)	0.0586 (4)	3.31 (23)
C2	0.5646 (6)	0.3567 (4)	−0.0144 (4)	3.64 (23)
C3	0.5448 (5)	0.2577 (4)	0.0199 (3)	3.32 (22)
C4	0.6661 (6)	0.1031 (4)	0.0541 (4)	3.21 (22)
C5	0.8286 (6)	0.0542 (4)	0.0782 (4)	3.23 (23)
C6	1.1053 (6)	0.0727 (4)	0.1783 (4)	3.07 (22)
C7	1.2166 (6)	0.1272 (4)	0.2603 (4)	3.51 (22)
C8	1.2503 (5)	0.2248 (4)	0.2273 (3)	3.08 (22)
C9	0.7757 (5)	0.2649 (3)	0.2258 (3)	2.16 (16)
C10	1.0297 (5)	0.2243 (3)	0.0097 (3)	2.28 (18)
H1	0.913 (4)	0.408 (3)	0.096 (3)	0.7 (8)
H2	0.884 (6)	0.373 (4)	−0.006 (4)	5.5 (14)
H3	0.652 (5)	0.415 (3)	0.136 (3)	2.9 (10)
H4	0.688 (6)	0.468 (4)	0.033 (4)	4.1 (13)
H5	0.463 (6)	0.390 (4)	−0.018 (4)	4.5 (12)
H6	0.595 (6)	0.366 (3)	−0.091 (4)	4.1 (11)
H7	0.516 (5)	0.256 (3)	0.096 (3)	2.6 (9)
H8	0.442 (7)	0.224 (4)	−0.018 (4)	5.4 (14)
H9	0.721 (5)	0.200 (3)	−0.040 (3)	3.4 (11)
H10	0.604 (5)	0.109 (3)	0.121 (3)	2.9 (9)
H11	0.577 (7)	0.073 (4)	0.001 (4)	6.3 (15)
H12	0.888 (6)	0.047 (3)	0.019 (4)	4.2 (12)
H13	0.822 (6)	−0.011 (4)	0.111 (4)	4.3 (12)
H14	0.894 (5)	0.100 (3)	0.218 (3)	2.6 (9)
H15	1.165 (6)	0.079 (4)	0.111 (4)	5.0 (13)
H16	1.102 (6)	0.011 (4)	0.206 (4)	3.5 (11)
H17	1.318 (6)	0.095 (3)	0.279 (3)	2.8 (9)
H18	1.171 (6)	0.125 (4)	0.322 (4)	4.9 (13)
H19	1.340 (5)	0.256 (3)	0.283 (3)	3.9 (11)
H20	1.309 (9)	0.218 (5)	0.145 (6)	10.8 (22)
H21	1.122 (6)	0.340 (4)	0.197 (4)	3.1 (12)
H22	1.061 (6)	0.292 (4)	0.272 (4)	4.7 (13)
O1W	0.4873 (7)	−0.0470 (4)	0.1882 (4)	6.3 (3)
H23	0.597 (14)	−0.048 (8)	0.211 (8)	15.1 (42)
H24	0.467 (13)	−0.103 (8)	0.190 (8)	14.0 (44)
Cl	0.82138 (15)	0.00098 (9)	0.34383 (8)	3.41 (5)

Biso is the mean of the principal axes of the thermal ellipsoid.

TABLE VI Atomic parameters *x*, *y*, *z* and Biso for compound III, [*trans*-Co(3,2,3-tet)-$(CN)_2$]Br·H_2O E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.3953 (3)	0.24069 (16)	0.12170 (13)	1.52 (8)
N1	0.3489 (18)	0.3684 (10)	0.0732 (9)	2.4 (6)
N2	0.1891 (18)	0.1991 (11)	0.0303 (9)	2.4 (6)
N3	0.4326 (18)	0.1109 (10)	0.1587 (9)	2.4 (6)
N4	0.5969 (17)	0.2801 (10)	0.2184 (9)	2.3 (6)
N5	0.5988 (19)	0.2118 (14)	−0.0501 (10)	3.9 (9)
N6	0.2016 (20)	0.2754 (13)	0.2988 (10)	3.7 (8)
C1	0.186 (3)	0.4080 (15)	0.0677 (13)	3.7 (10)
C2	0.0544 (23)	0.3527 (16)	−0.0023 (13)	3.5 (9)
C3	0.0387 (21)	0.2541 (18)	0.0273 (12)	3.5 (9)
C4	0.1607 (25)	0.1028 (15)	0.0560 (13)	3.2 (9)
C5	0.322 (3)	0.0557 (13)	0.0801 (12)	3.1 (9)
C6	0.5984 (25)	0.0719 (14)	0.1782 (13)	3.2 (8)
C7	0.715 (3)	0.1261 (17)	0.2612 (13)	3.8 (9)
C8	0.7452 (23)	0.2212 (16)	0.2314 (12)	3.2 (9)
C9	0.5241 (21)	0.2232 (13)	0.0148 (11)	2.4 (8)
C10	0.2705 (21)	0.2608 (13)	0.2319 (10)	2.3 (7)
H1	0.372	0.370	0.006	3.2
H2	0.423	0.406	0.117	3.2
H3	0.155	0.411	0.138	4.4
H4	0.188	0.474	0.041	4.4
H5	0.084	0.353	−0.074	4.7
H6	−0.057	0.383	−0.006	4.7
H7	0.008	0.256	0.097	4.1
H8	−0.054	0.227	−0.022	4.1
H10	0.103	0.101	0.117	3.5
H11	0.088	0.072	−0.003	3.5
H12	0.308	−0.008	0.106	3.7
H13	0.373	0.051	0.016	3.7
H14	0.390	0.106	0.222	3.1
H15	0.591	0.005	0.200	4.1
H16	0.646	0.071	0.112	4.1
H17	0.664	0.130	0.325	4.5
H18	0.826	0.095	0.279	4.5
H19	0.790	0.219	0.166	4.1
H20	0.833	0.249	0.286	4.1
H21	0.566	0.289	0.284	3.2
H22	0.630	0.340	0.195	3.2
Br	0.6975 (3)	0.49524 (19)	0.15130 (16)	5.10 (12)
O	0.0266 (25)	0.4470 (15)	0.3170 (12)	7.3 (11)
H9	0.224	0.201	−0.045	3.2

Biso is the mean of the principal axes of the thermal ellipsoid.

X-ray Crystallography

For all five compounds, data were collected with an Enraf-Nonius CAD-4 diffractometer. The procedure used for crystal alignment, cell constant determination, space group determination and data collection were uniform for all five crystals.

A crystal of compound **I** was centered with data in the $4° \leq 2\theta \leq 60°$ range, compounds **II** and **III** in the $4° \leq 2\theta \leq 55°$ range, and compounds **IV** and **V** in $4° \leq 2\theta \leq 50°$ range. Examination of the cell constants, absences, and Niggli matrix [16] clearly showed compound **I** to crystallize in a triclinic lattice whose systematic absences indicate it belongs in

TABLE VII Atomic parameters *x*, *y*, *z* and Biso for compound **IV**, [*trans*-Co(3,2,3-tet)-$(NCS)_2$]Cl E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.5587 (9)	0.2771 (6)	0.1835 (5)	1.8 (4)
S1	0.655 (3)	0.3622 (19)	0.5509 (13)	7.5 (16)
S2	0.4963 (18)	0.2013 (13)	−0.1857 (11)	4.1 (10)
N1	0.704 (5)	0.302 (3)	0.137 (3)	2.3 (9)
N2	0.610 (4)	0.133 (3)	0.213 (3)	0.5 (7)
N3	0.410 (5)	0.248 (3)	0.235 (3)	2.5 (10)
N4	0.499 (6)	0.422 (4)	0.161 (4)	4.7 (14)
N5	0.637 (6)	0.309 (4)	0.331 (4)	4.5 (13)
N6	0.454 (8)	0.250 (5)	0.035 (6)	9.2 (22)
C1	0.785 (8)	0.238 (6)	0.084 (6)	6.1 (20)
C2	0.785 (8)	0.132 (6)	0.123 (6)	5.0 (17)
C3	0.677 (8)	0.080 (5)	0.141 (6)	4.8 (17)
C4	0.500 (6)	0.084 (4)	0.227 (4)	2.6 (12)
C5	0.411 (7)	0.147 (5)	0.287 (5)	4.9 (17)
C6	0.327 (6)	0.316 (4)	0.286 (4)	2.0 (11)
C7	0.319 (7)	0.417 (5)	0.239 (5)	3.9 (15)
C8	0.416 (6)	0.470 (4)	0.217 (4)	2.4 (12)
C9	0.648 (6)	0.335 (4)	0.425 (4)	1.9 (11)
C10	0.458 (9)	0.230 (7)	−0.061 (7)	7.3 (24)
H1	0.753	0.329	0.202	3.0
H2	0.685	0.357	0.087	3.0
H3	0.882	0.265	0.109	6.9
H4	0.777	0.243	0.004	6.9
H5	0.840	0.127	0.195	5.4
H6	0.821	0.089	0.068	5.4
H7	0.699	0.008	0.175	5.7
H8	0.621	0.065	0.070	5.7
H9	0.661	0.136	0.283	1.5
H10	0.453	0.066	0.153	3.6
H11	0.517	0.019	0.270	3.6
H12	0.449	0.151	0.367	5.9
H13	0.331	0.113	0.281	5.9
H14	0.356	0.234	0.166	3.5
H15	0.242	0.284	0.279	3.4
H16	0.359	0.319	0.367	3.4
H17	0.276	0.463	0.293	4.5
H18	0.258	0.416	0.169	4.5
H19	0.385	0.534	0.175	3.7
H20	0.461	0.494	0.291	3.7
H21	0.469	0.429	0.085	5.3
H22	0.574	0.464	0.173	5.3
Cl	0.7723 (19)	0.0425 (14)	0.4354 (12)	4.8 (11)

Biso is the mean of the principal axes of the thermal ellipsoid.

space group P1 (No. 1) or P-1 (No. 2). Compounds II and III crystallize in a primitive monoclinic lattice whose systematic absences indicate both belong in space group $P2_1/c$ (No. 14), and compounds IV and V, crystallize in a monoclinic lattice whose systematic absences belong to $P2_1/n$ (No.14).

TABLE VIII Atomic parameters *x*, *y*, *z* and Biso for compound V, [*trans*-Co(3,2,3-tet)-$(NCS)_2$]I E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.4495 (3)	0.2547 (3)	0.80079 (23)	1.83 (14)
N1	0.4944 (17)	0.3962 (16)	0.8262 (15)	2.7 (10)
N2	0.6108 (16)	0.2254 (16)	0.7571 (14)	2.5 (10)
N3	0.4186 (18)	0.1097 (16)	0.7827 (14)	3.2 (11)
N4	0.2859 (16)	0.2787 (15)	0.8364 (13)	2.9 (10)
N5	0.5070 (17)	0.2299 (17)	0.9503 (17)	3.2 (11)
N6	0.3903 (16)	0.2811 (15)	0.6529 (15)	2.6 (11)
C1	0.561 (3)	0.4511 (18)	0.7485 (22)	3.8 (14)
C2	0.6756 (24)	0.4022 (23)	0.7310 (21)	3.8 (15)
C3	0.6672 (21)	0.2963 (25)	0.6889 (18)	4.0 (16)
C4	0.6031 (21)	0.1251 (24)	0.7097 (21)	3.8 (15)
C5	0.533 (3)	0.0608 (24)	0.7731 (24)	5.2 (16)
C6	0.346 (3)	0.0586 (21)	0.8587 (20)	4.1 (14)
C7	0.225 (3)	0.1039 (22)	0.8626 (20)	4.1 (14)
C8	0.2282 (22)	0.2108 (21)	0.9067 (19)	3.5 (13)
C9	0.5144 (19)	0.2297 (18)	1.0463 (25)	2.7 (12)
C10	0.3751 (21)	0.3062 (20)	0.5641 (23)	3.5 (13)
S1	0.5107 (6)	0.2273 (7)	1.1763 (5)	4.0 (4)
S2	0.3576 (7)	0.3466 (7)	0.4375 (6)	6.1 (5)
H1	0.544	0.400	0.896	3.7
H2	0.420	0.433	0.833	3.7
H3	0.507	0.456	0.674	4.3
H4	0.577	0.524	0.774	4.3
H5	0.733	0.401	0.803	3.3
H6	0.721	0.444	0.678	3.3
H7	0.749	0.273	0.677	4.5
H8	0.613	0.301	0.616	4.5
H9	0.663	0.222	0.827	3.5
H10	0.689	0.094	0.711	4.3
H11	0.565	0.127	0.631	4.3
H12	0.578	0.045	0.847	5.4
H13	0.517	−0.009	0.734	5.4
H14	0.370	0.105	0.712	4.0
H15	0.390	0.062	0.934	4.6
H16	0.336	−0.015	0.837	4.6
H17	0.180	0.101	0.784	5.4
H18	0.178	0.056	0.907	5.4
H19	0.277	0.212	0.983	4.4
H20	0.144	0.236	0.914	4.4
H21	0.233	0.280	0.769	3.5
H22	0.286	0.344	0.869	3.5
I	0.74468 (17)	0.48392 (16)	1.03874 (14)	4.09 (9)

Biso is the mean of the principal axes of the thermal ellipsoid.

Data were corrected for absorption using empirical curves derived from Psi scans of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation [17].

Processing of the data was carried out with the PC version of the NRCVAX package [18]. The cobalt atoms were found using direct methods. After refining the scale factor and the positional parameters of the Co atoms, a difference Fourier map produced many of the non-hydrogen atoms in all five cases. The remaining atoms were found in subsequent difference maps. The positions and anisotropic thermal parameters of heavy atoms, including the waters of crystallization were refined. For compound **II**, all hydrogen atoms including the hydrogens of the water molecules were found experimentally in a difference map and used for least squares calculations. For the other four compounds, the hydrogen atoms were added to ideal positions and used for least squares calculations. The details of data collection for compound **I** are summarized in Table I. The details of data collection for compounds **II** and **III** are summarized on Table II. The corresponding data for compounds **IV** and **V** are listed on Table III. Fractional coordinates for compounds **I** through **V** are given in Tables IV through VIII.

RESULTS

The successful solution of the single crystal structure shows that compound **I** crystallizes in centrosymmetric space group P-1 (No. 2). There is one [*trans*-Co(3,2,3-tet)$(NO_2)_2]^+$ cation and one BF_4^- anion in the asymmetric unit (Fig. 1). The cobalt(III) is coordinated by four nitrogens of the 3,2,3-tet amine ligand, and two nitrite ligands bonded to the central cobalt atom through their nitrogens in a *trans* configuration. The two six-membered rings are in the classical chair conformation. Selected bond lengths and bond angles are listed in Table IX.

Compounds **II**, [*trans*-Co(3,2,3-tet)$(CN)_2]Cl\cdot H_2O$, and **III**, [*trans*-Co(3,2,3-tet)-$(CN)_2]Br\cdot H_2O$ both crystallize as racemates in monoclinic lattices. These compounds are isomorphous and isostructural and crystallize in space group $P2_1/c$. In both complex cations, the central cobalt ions are in an octahedral coordination environment, and coordinated by four nitrogens of the 3,2,3-tet amine ligand. The two CN^- ligands are bound to the central cobalt atom through carbon in a *trans* configurations (Figs. 2 and 3). Tables X and XI list selected bond lengths and bond angles.

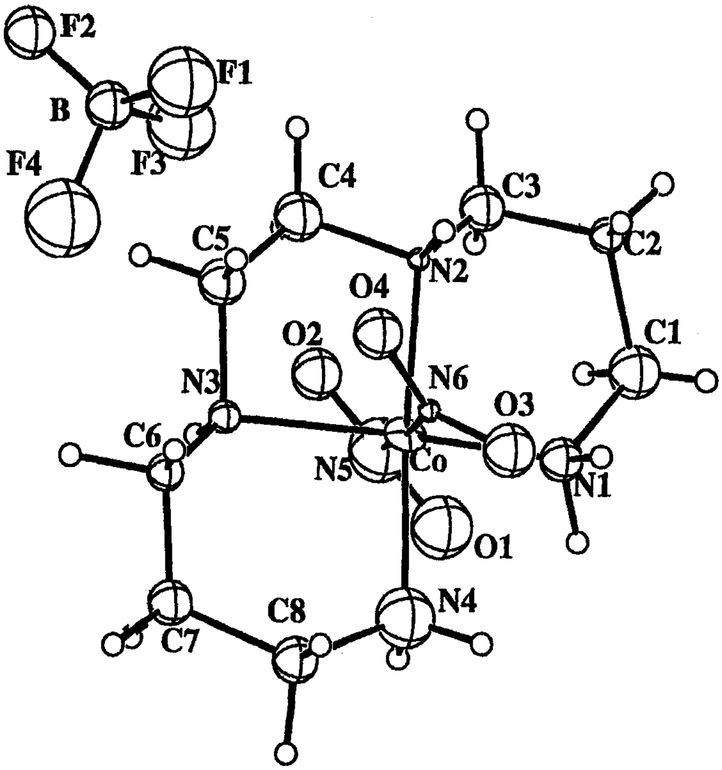

FIGURE 1 Molecular structure of compound I, [*trans*-Co(3,2,3-tet)$(NO_2)_2$]BF_4.

Compounds IV and V, [*trans*-Co(3, 2, 3-tet)$(NCS)_2$]Cl and [*trans*-Co(3, 2, 3-tet)-$(NCS)_2$]I crystallize in monoclinic lattices whose space groups are $P2_1/n$, and are isomorphous and isostructural. The two *trans* NCS^- ligands are N-bound. The molecular structures for these compounds are illustrated in Figures 4 and 5, with conformations of the 3,2,3-tet amine ligand the same as in compounds I, II and III with two six-membered rings in chair conformations and with a *pseudo* two-fold axis. Selected bond lengths and bond angles for compounds IV and V are shown in Tables XII and XIII, respectively.

DISCUSSION

Symmetrically substituted, *trans*-compounds such as [*trans*-$Co(en)_2$ $(NO_2)_2$]X ($X = Cl^-$ I^- and NCS^- and ClO_4^-), [*trans*-$Co(en)_2(NO_2)_2$]

TABLE IX Selected bond lengths and bond angles for compound I, [*trans*-Co(3,2,3-tet)-$(NO_2)_2$]BF_4

Co—N1	1.83 (4)	N5—O2	1.19 (7)
Co—N2	1.974 (24)	N6—O3	1.19 (4)
Co—N3	2.13 (3)	N6—O4	1.27 (4)
Co—N4	2.06 (5)	C1—C2	1.58 (6)
Co—N5	2.16 (5)	C2—C3	1.48 (6)
Co—N6	1.899 (22)	C4—C5	1.39 (5)
N1—C1	1.70 (6)	C6—C7	1.46 (6)
N2—C3	1.33 (5)	C7—C8	1.59 (6)
N2—C4	1.48 (5)	F1—B	1.39 (5)
N3—C5	1.50 (4)	F2—B	1.24 (5)
N3—C6	1.21 (5)	F3—B	1.35 (6)
N4—C8	1.67 (7)	F4—B	1.42 (6)
N5—O1	1.13 (9)		
N1—Co—N2	93.3 (13)	C5—N3—C6	118 (3)
N1—Co—N3	174.8 (13)	Co—N4—C8	110 (3)
N1—Co—N4	81.8 (19)	O1—N5—O2	151 (6)
N1—Co—N6	86.8 (13)	Co—N6—O3	123.6 (22)
N2—Co—N3	90.5 (11)	Co—N6—O4	126.1 (22)
N2—Co—N4	175.1 (17)	O3—N6—O4	109 (3)
N2—Co—N6	88.1 (10)	N1—C1—C2	108 (3)
N3—Co—N4	94.2 (17)	C1—C2—C3	110 (3)
N3—Co—N6	89.9 (10)	N2—C3—C2	109 (3)
N4—Co—N6	90.7 (17)	N2—C4—C5	111 (3)
Co—N1—C1	116 (3)	C5—C4—F3	62.8 (23)
Co—N2—C3	123.7 (24)	N3—C5—C4	119 (3)
Co—N2—C4	104.3 (19)	N3—C6—C7	116 (3)
C3—N2—C4	107 (3)	C6—C7—C8	115 (3)
Co—N3—C5	96.3 (20)	N4—C8—C7	118 (4)
Co—N3—C6	126 (3)		

[*trans*-$(NH_3)_2Co(NO_2)_2(ox)$] crystallize as racemates and the cations are chiral; but, internally compensated, inasmuch as the two five-membered rings are conformed either as $\delta\lambda$ or $\lambda\delta$.

In the case of conglomerates of species containing a *trans* pair of en ligands, such as in [*trans*-$Co(en)_2(NO_2)(NCS)$]X and [*trans*-$Co(en)_2$ $(ONO)(NCS)$]X where $X = I^-$ and ClO_4^-, it has been found that the two en rings are in $\delta\delta$ or $\lambda\lambda$ pairs; that is, they behave as if they are in an enantiomorphic environment and acquire conformations which render the en rings homochiral. The species in question lie at a general position of the space group $P2_1$ in which neither the symmetry requirements nor the cell contents impose symmetry conditions on the species in question.

Thus the en rings, in theory, acquire conformations attuned to their environment. They select to be in $\delta\delta$ or $\lambda\lambda$ pairs when in an enantiomorphic medium and in a $\delta\lambda$ or $\lambda\delta$ pair when in a centrosymmetric environment, even when located at general positions of the space group [19–22]. Therefore, it is clear that the conformation of en rings is acutely sensitive to

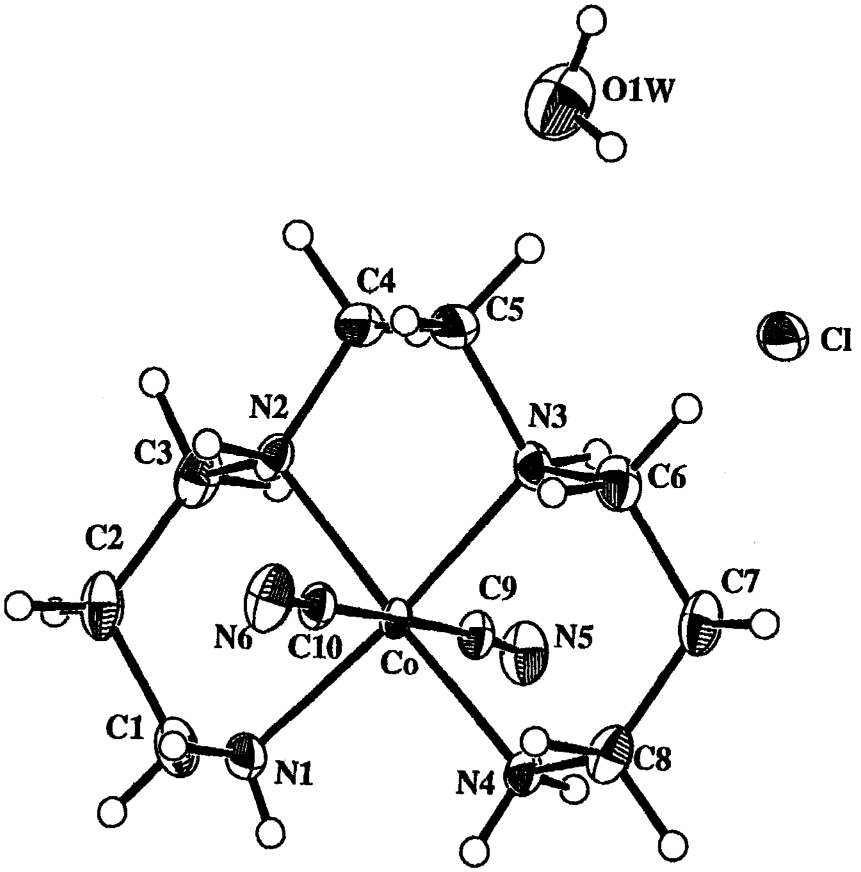

FIGURE 2 Molecular structure of compound II, [*trans*-Co(3,2,3-tet)$(CN)_2$]Cl.

the enantiomorphic or centrosymmetric properties of the lattice; and, while in most cases of enantiomorphic lattices the en rings are either $\Lambda(\delta\delta)$ or $\Delta(\lambda\lambda)$ in the case of [*cis*-Co$(en)_2(NO_2)_2$] [*trans*-Co$(NH_3)_2(NO_2)_4$] [20] and in [*cis*-Ru$(en)_2(NO_2)_2$]Cl [21], they are $\Lambda(\delta\lambda)$ or $\Delta(\lambda\delta)$ due to the fact that one ring is coerced to be *ob* by intramolecular hydrogen bonds [20, 21].

For the series of 3,2,3-tet compounds, [*trans*-Co(3,2,3-tet)$(NO_2)_2$]X and [*trans*-Co(3,2,3-tet)Cl_2]NO_3, the secondary nitrogens become chiral upon complexation, which must be of the same chirality in order for the secondary hydrogen to be at the structurally favorable axial positions. The crystal structural studies show that all the above compounds crystallize as conglomerates with ordered and conformationally chiral five- membered rings. Would this trend continue to be true regardless of the identity of the

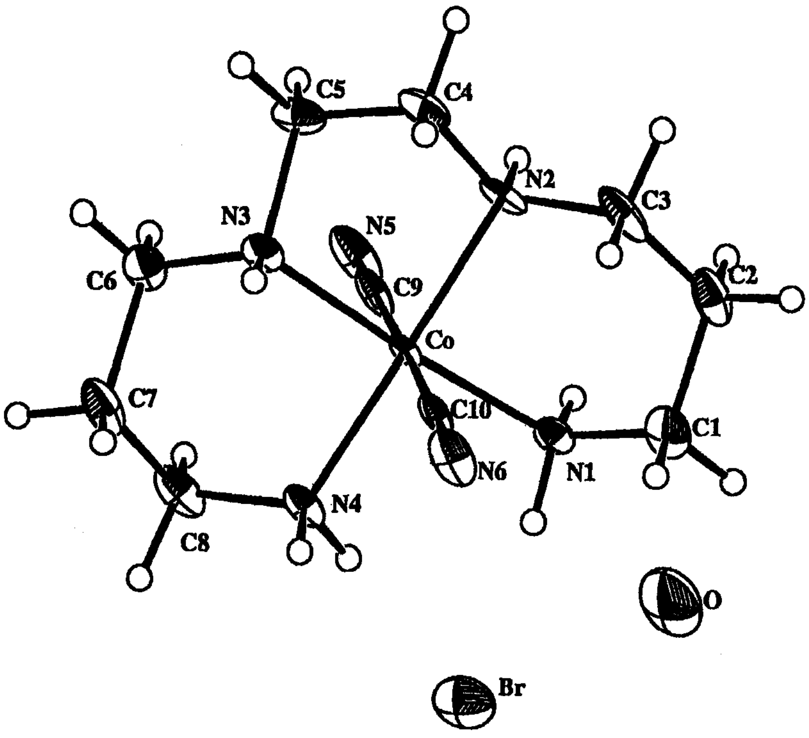

FIGURE 3 Molecular structure of compound III, [*trans*-Co(3,2,3-tet)(CN)$_2$]Br.

counter anion since the counter anion plays a very important role in the conglomerate crystallization of the *cis* compound? [1 – 3].

Two polymorphs of [*trans*-Co(2,3,2-tet)(NO$_2$)$_2$]NO$_3$ were obtained and their crystal structures were determined [23]. Their crystallization pathway is important because they have a pair of five-membered rings on opposite sites of the basal plane analogous to *trans*-bis(ethylenediamine)cobalt(III) cations. Models show that the secondary nitrogens should be a heterochiral pair, while those of 3,2,3-tet series compounds are a homochiral pair. It seems that these factors play a role in the selection of the crystallization path, since the X-ray crystallographic studies show that the two polymorphs of the compound [*trans*-Co(2,3,2-tet)(NO$_2$)$_2$]NO$_3$ crystallize as racemates with the two secondary nitrogens of each crystal structure as a heterochiral pair. Also, the two monodentate cyano ligands are decisive in the selection of racemate crystallization rather than conglomerate crystallization.

For the 3,2,3-tet series: [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]*X* and [*trans*-Co(3,2,3-tet)Cl$_2$]NO$_3$ all crystallize as conglomerates while [*trans*-Co(3,2,3-tet)

TABLE X Selected bond lengths and bond angles for compound II, [*trans*-Co(3,2,3-tet)(CN)$_2$]Cl·H$_2$O

Co—N1	1.985 (4)	C1—H4	0.87 (5)
Co—N2	1.993 (3)	C2—C3	1.509 (8)
Co—N3	1.990 (4)	C2—H5	0.96 (5)
Co—N4	1.987 (3)	C2—H6	1.09 (5)
Co—C9	1.937 (4)	C3—H7	1.08 (4)
Co—C10	1.942 (4)	C3—H8	1.03 (6)
N1—C1	1.482 (6)	C4—C5	1.498 (8)
N1—H1	0.76 (4)	C4—H10	1.11 (4)
N1—H2	0.99 (6)	C4—H11	1.02 (6)
N2—C3	1.494 (6)	C5—H12	1.01 (5)
N2—C4	1.487 (6)	C5—H13	1.03 (6)
N2—H9	0.92 (5)	C6—C7	1.516 (7)
N3—C5	1.497 (6)	C6—H15	1.09 (5)
N3—C6	1.484 (6)	C6—H16	0.96 (5)
N3—H14	0.93 (4)	C7—C8	1.509 (8)
N4—C8	1.491 (6)	C7—H17	0.95 (5)
N4—H21	0.87 (5)	C7—H18	0.96 (6)
N4—H22	0.90 (6)	C8—H19	1.05 (5)
N5—C9	1.145 (5)	C8—H20	1.28 (7)
N6—C10	1.137 (5)	O1W—H23	0.91 (11)
C1—C2	1.518 (8)	O1W—H24	0.82 (11)
C1—H3	1.12 (4)		
N1—Co—N2	89.25 (16)	Co—N2—C4	107.3 (3)
N1—Co—N3	175.00 (15)	C3—N2—C4	110.2 (4)
N1—Co—N4	92.30 (18)	Co—N3—C5	106.6 (3)
N1—Co—C9	91.68 (17)	Co—N3—C6	119.4 (3)
N1—Co—C10	87.85 (17)	C5—N3—C6	110.6 (4)
N2—Co—N3	86.51 (15)	Co—N4—C8	119.5 (3)
N2—Co—N4	177.49 (15)	N1—C1—C2	110.4 (4)
N2—Co—C9	90.56 (15)	C1—C2—C3	113.6 (4)
N2—Co—C10	90.79 (15)	N2—C3—C2	113.3 (4)
N3—Co—N4	92.03 (16)	N2—C4—C5	107.9 (4)
N3—Co—C9	91.02 (16)	N3—C5—C4	107.1 (4)
N3—Co—C10	89.55 (16)	N3—C6—C7	112.1 (4)
N4—Co—C9	87.43 (15)	C6—C7—C8	112.9 (4)
N4—Co—C10	91.24 (15)	N4—C8—C7	111.7 (4)
C9—Co—C10	178.57 (17)	Co—C9—N5	176.1 (4)
Co—N1—C1	119.5 (3)	Co—C10—N6	179.0 (3)
Co—N2—C3	118.1 (3)	H23—O1W—H24	99 (10)

(CN)$_2$]Cl and [*trans*-Co(3,2,3-tet)(CN)$_2$]I crystallize as racemates. The conformations of the 3,2,3-tet amine ligand for all of the above compounds are the same, but the *trans*-dinitro and *trans*-dichloro compounds crystallize as conglomerates, while *trans*-dicyano compounds crystallize as racemates suggesting that the homochiral amine ligand is not the only factor influencing the outcome. If this is not the only factor that controls conglomerate crystallization the two *trans* monodentate ligands must also play a role in the selection of the crystallization pathway.

TABLE XI Selected bond lengths and bond angles for compound III, [*trans*-Co(3,2,3-tet)-$(CN)_2$]Br · H_2O

Co—N1	1.979 (15)	N3—C6	1.453 (25)
Co—N2	2.000 (13)	N4—C8	1.471 (25)
Co—N3	1.960 (15)	N5—C9	1.149 (21)
Co—N4	1.997 (13)	N6—C10	1.151 (21)
Co—C9	1.923 (16)	C1—C2	1.53 (3)
Co—C10	1.943 (16)	C2—C3	1.50 (3)
N1—C1	1.44 (3)	C4—C5	1.47 (3)
N2—C3	1.46 (3)	C6—C7	1.55 (3)
N2—C4	1.47 (3)	C7—C8	1.47 (3)
N3—C5	1.497 (22)		
N1—Co—N2	89.4 (6)	Co—N2—C4	107.3 (10)
N1—Co—N3	175.4 (5)	C3—N2—C4	111.2 (15)
N1—Co—N4	91.9 (6)	Co—N3—C5	106.8 (11)
N1—Co—C9	89.0 (7)	Co—N3—C6	121.4 (12)
N1—Co—C10	90.5 (7)	C5—N3—C6	110.8 (14)
N2—Co—N3	86.7 (6)	Co—N4—C8	119.0 (11)
N2—Co—N4	177.4 (5)	N1—C1—C2	111.9 (16)
N2—Co—C9	91.3 (6)	C1—C2—C3	115.2 (15)
N2—Co—C10	90.3 (6)	N2—C3—C2	114.9 (15)
N3—Co—N4	92.1 (6)	N2—C4—C5	108.8 (15)
N3—Co—C9	88.7 (7)	N3—C5—C4	108.7 (15)
N3—Co—C10	92.0 (7)	N3—C6—C7	112.0 (15)
N4—Co—C9	90.9 (6)	C6—C7—C8	113.5 (15)
N4—Co—C10	87.4 (6)	N4—C8—C7	113.8 (16)
C9—Co—C10	178.2 (7)	Co—C9—N5	178.8 (16)
Co—N1—C1	121.0 (12)	Co—C10—N6	177.1 (17)
Co—N2—C3	118.2 (11)		

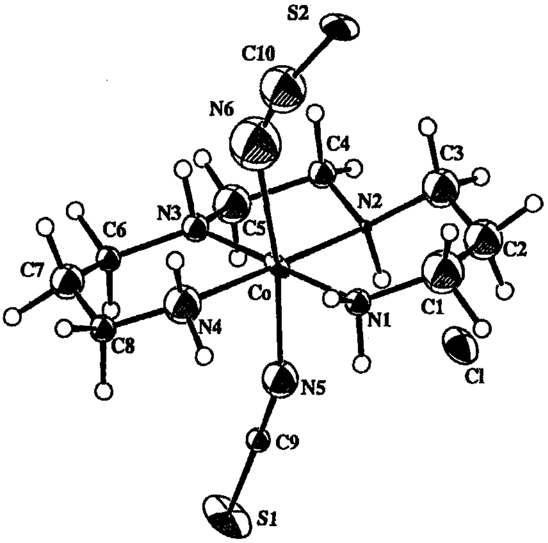

FIGURE 4 Molecular structure of compound IV, [*trans*-Co(3, 2, 3-tet)$(NCS)_2$]Cl.

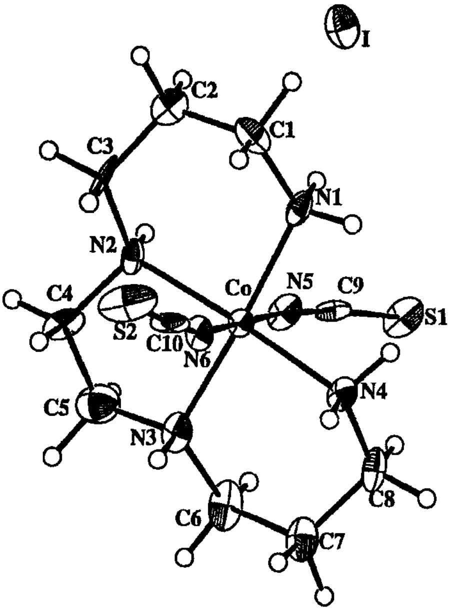

FIGURE 5 Molecular structure of compound V, [*trans*-Co(3, 2, 3-tet)(NCS)$_2$]I.

TABLE XII Selected bond lengths and bond angles for compound IV, [*trans*-Co(3,2,3-tet)(NCS)$_2$]Cl

Co—N1	1.80 (5)	N2—C4	1.41 (7)
Co—N2	2.00 (4)	N2—H9	0.96 (4)
Co—N3	1.88 (5)	N3—C5	1.48 (8)
Co—N4	2.03 (6)	N3—C6	1.49 (7)
Co—N5	1.95 (5)	N4—C8	1.39 (8)
Co—N6	2.06 (8)	N5—C9	1.19 (7)
S1—C9	1.59 (5)	N6—C10	1.22 (12)
S2—C101	1.70 (9)	C1—C2	1.48 (10)
N1—C1	1.46 (9)	C2—C3	1.42 (11)
N1—H1	0.97 (4)	C4—C5	1.55 (9)
N1—H2	0.96 (4)	C6—C7	1.45 (8)
N2—C3	1.42 (8)	C7—C8	1.35 (9)
N1—Co—N2	89.5 (18)	C3—N2—C4	112 (5)
N1—Co—N3	178.1 (20)	Co—N3—C5	112 (4)
N1—Co—N4	94.0 (22)	Co—N3—N6	129 (3)
N1—Co—N5	88.0 (22)	C5—N3—C6	109 (4)
N1—Co—N6	99 (3)	Co—N4—C8	126 (4)
N2—Co—N3	88.9 (17)	Co—N5—C9	159 (5)
N2—Co—N4	176.2 (19)	Co—N6—C10	143 (7)
N2—Co—N5	87.7 (19)	N1—C1—C2	111 (6)
N2—Co—N6	96.0 (23)	C1—C2—C3	123 (7)
N3—Co—N4	87.6 (21)	N2—C3—C2	112 (6)
N3—Co—N5	90.8 (22)	N2—C4—C5	114 (5)
N3—Co—N6	82 (3)	N3—C5—C4	104 (5)
N4—Co—N5	90.9 (22)	N3—C6—C7	113 (4)
N4—Co—N6	84 (3)	C6—C7—C8	123 (6)
N5—Co—N6	171 (3)	N4—C8—C7	117 (5)
Co—N1—C1	132 (4)	S1—C9—N5	175 (5)
Co—N2—C3	121 (3)	S2—C10—N6	168 (9)
Co—N2—C4	103 (3)		

TABLE XIII Selected bond lengths and selected bond angles for compound V, [*trans*-Co(3,2,3-tet)(NCS)$_2$]I

Co—N1	1.960 (21)	N4—C8	1.45 (3)
Co—N2	1.971 (18)	N5—C9	1.17 (4)
Co—N3	1.965 (22)	N6—C10	1.13 (3)
Co—N4	1.947 (18)	C1—C2	1.47 (4)
Co—N5	1.893 (21)	C2—C3	1.50 (5)
Co—N6	1.883 (19)	C4—C5	1.45 (4)
N1—C1	1.48 (4)	C6—C7	1.48 (4)
N2—C3	1.46 (3)	C7—C8	1.52 (4)
N2—C4	1.45 (4)	C9—S1	1.60 (3)
N3—C5	1.45 (4)	C10—S2	1.63 (3)
N3—C6	1.48 (3)		
N1—Co—N2	90.7 (8)	C3—N2—C4	111.7 (20)
N1—Co—N3	174.9 (8)	Co—N3—C5	107.9 (17)
N1—Co—N4	91.8 (8)	Co—N3—C6	118.7 (16)
N1—Co—N5	88.1 (9)	C5—N3—C6	113.9 (20)
N1—Co—N6	91.4 (8)	Co—N4—C8	121.8 (15)
N2—Co—N3	85.8 (9)	Co—N5—C9	161.4 (19)
N2—Co—N4	176.5 (8)	Co—N6—C10	167.0 (19)
N2—Co—N5	91.6 (8)	N1—C1—C2	113.2 (21)
N2—Co—N6	89.3 (7)	C1—C2—C3	116.8 (22)
N3—Co—N4	91.9 (8)	N2—C3—C2	114.9 (20)
N3—Co—N5	88.3 (8)	N2—C4—C5	109.5 (23)
N3—Co—N6	92.3 (8)	N3—C5—C4	108.4 (24)
N4—Co—N5	90.9 (8)	N3—C6—C7	114.1 (20)
N4—Co—N6	88.2 (7)	C6—C7—C8	114.3 (24)
N5—Co—N6	178.9 (9)	N4—C8—C7	111.1 (19)
Co—N1—C1	120.6 (15)	N5—C9—S1	174.5 (20)
Co—N2—C3	120.2 (15)	N6—C10—S2	177.4 (22)
Co—N2—C4	106.4 (14)		

The counter anion is very important in the control of conglomerate crystallization in some *cis* cobalt amine compounds, with a strong hydrogen bonding counter anion favoring racemic crystallization [1 – 3]. The previous results suggest that the counter anion is not uniquely important. While compounds with halide anions could crystallize as conglomerates, counter anions with strong hydrogen bonding ability such as NO_3^- and ClO_4^- also crystallize as conglomerates, which is not true in *cis*-dinitro and *cis*-oxalato compounds. In spite of these uncertainties, we think the counter anion is important in conglomerate crystallization because the crystal structure of the neutral complex [*trans*-Ni(3,2,3-tet)(NO$_2$)$_2$] [14], has almost the same configuration as the complex cation [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]$^+$ but crystallizes as a racemate.

For the compounds reported earlier, homochirality at the secondary nitrogens (that is RR or SS instead of RS) or at the two chelating rings ($\delta\delta$ or $\lambda\lambda$ instead of $\delta\lambda$ or $\lambda\delta$) are often important in holding homochiral molecules together. However, for the *trans* 3,2,3-tet series of compounds, this factor is not as important as the effect of replacement of the two *trans* ligands; that is, for series of compounds [*trans*-Co(3,2,3-tet)X_2]Y

conglomerates were obtained when $X = NO_2^-$ or Cl^-, while racemates were formed when $X = CN^-$ or NCS^-.

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