Supplementary Material Available: Table III, a listing of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of *uns-cis*-2,4-Pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) Iodide Monohydrate

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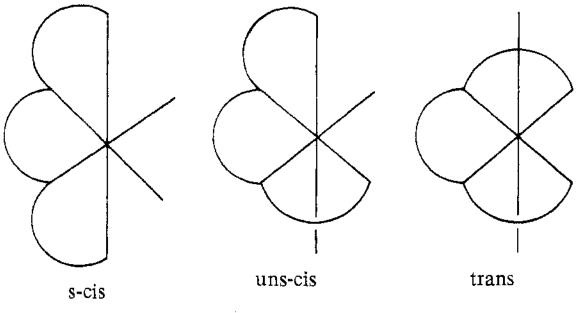
The complex *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) iodide monohydrate, $CoC_{13}H_{31}N_4O_3I_2$, crystallizes from water in the centrosymmetric space group $P2_1/c$ with $a = 10.833$ (1) Å, $b = 12.902$ (1) Å, $c = 17.558$ (1) Å, and $\beta = 117.57$ (1)°. The calculated density of 1.85 g cm^{-3} agrees with the experimental value of 1.84 g cm^{-3} for mol wt 604 and $Z = 4$. X-ray diffraction data to $2\theta = 50°$ (Zr-filtered Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved via the use of Patterson, Fourier, and least-squares refinement techniques to a final discrepancy index of 0.034 for the 3050 statistically significant ($|F_o| > 3\sigma(F_o)$) reflections. The metal ion is found at the center of a nearly regular octahedron. The structure is distinguished only by its striking similarity to that of the trans precursor and by the evidence it provides for a subtle but stereochemically significant conformation change within the ligand which must accompany trans–cis isomerization.

Introduction

As part of our continuing study of the stereochemistry of transition metal complexes with flexible tetradentate ligands, we have been impressed by the apparent stereoselectivity imparted to these species by increasing the length of the ligand chain between various pairs of donor atoms. Thus, in well-documented studies by Sargeson, Buckingham, and their co-workers,[1-3] complexes of cobalt(III) have been characterized with triethylenetetramine (3,6-diaza-1,8-octanediamine) (2,2,2-tet) in s-cis, uns-cis, and trans topologies.



Increasing the length of the chain between the secondary nitrogen donors, as in the case of 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and its derivatives, favors formation of trans complexes and also leads to the exclusive formation of the uns-cis isomer.[4-6] Lengthening the chain between the primary and secondary donors [4,7-diaza-1,10-decanediamine (3,2,3-tet) and its derivatives, for example] also favors the production of trans complexes; the cis topology has only been observed for mixed-ligand complexes involving 3,2,3-tet and bidentate chelating ligands. Since the earliest reports of complexes with 3,2,3-tet, there have appeared several synthetic and spectroscopic studies supporting the uns-cis geometry for the latter complexes.[7-11] More recently, DeHayes and Busch[12] have reported the details of a strain energy minimization calculation on the *trans*- and hypothetical *cis*-Cl_2(3,2′,3-tet)Co^{III} cation from which they conclude that the trans isomers are favored by some 2.5 kcal/mol over the cis isomer and that the uns-cis complex is lower in energy than the corresponding s-cis isomer.

We report the synthesis of the *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) cation and its electronic and ^1H NMR spectra in the context of the strain energy minimization calculation previously reported and of the structure of a crystal of the iodide salt.

Experimental Section

Synthesis of *uns-cis*-2,4-Pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) Iodide Monohydrate, *uns-cis*-[Co(3,2,3-tet)acac]I_2·H_2O. To 3.4 g of *trans*-dichloro(4,7-diaza-1,10-decanediamine)cobalt(III) chloride[7] and 0.56 g of KOH dissolved in 40 ml of water at 80 °C was added 1.0 g of 2,4-pentanedione in 5 ml of ethanol. At the end of 1 h of heating on a steam bath, 3 g of NaI was added and the solution was reduced in volume to about 20 ml under a steam of air. Upon cooling of the mixture overnight in a refrigerator (4 °C), red crystals were isolated by filtration and recrystallized twice from hot water.

Electronic Spectrum. The electronic spectrum of the *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) cation, as either the iodide or the nitrate salt, was obtained with a Beckman DBG spectrophotometer equipped with matched 10-mm silica cells and a 10-in. potentiometric recorder.

Proton Magnetic Resonance Spectra. Proton magnetic resonance spectra were recorded on a Varian A-60D spectrometer at ambient probe temperature. Saturated solutions in D_2O were employed with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.

Crystallography. A red, irregularly shaped crystal of the title compound (0.3-mm maximum dimension), cleaved from a larger crystal, was mounted with the $0\bar{2}5$ axis coincident with the ϕ axis of a Picker FACS-I four-circle diffractometer. The reciprocal lattice showed $2/m$ symmetry with extinctions $k = 2n + 1$ for $(0k0)$ and $l = 2n + 1$ for $(h0l)$, uniquely characterizing the space group as $P2_1/c$. Lattice constants were determined by a least-squares fit of 16 carefully measured values of the copper $K\alpha_1$ and $K\alpha_2$ doublet (1.540 50 and 1.544 33 Å) for reflections with $2\theta > 60°$ using a very narrow slit. The resultant lattice constants and their estimated standard deviations are $a = 10.833$ (1) Å, $b = 12.902$ (1), Å, $c = 17.558$ (1) Å, and $\beta = 117.57$ (1)°. The calculated density of 1.85 g/cm^3, assuming four molecules each of the title compound and water, agrees with the experimental density of 1.84 ± 0.03 g/cm^3 (by flotation methods in $CHCl_3$–$CHBr_3$).

Intensity data were collected on a Picker FACS-I fully automated diffractometer using Zr-filtered molybdenum radiation. The θ–2θ scan technique using a constant scan rate of 2°/min, a variable scan width $(1.6 + 0.3 \tan \theta)°$, and 10-s background measurements at each end of the scan was used to measure the 3863 unique reflections to a 2θ maximum of 50° ($d = 0.84$ Å). Of this total, 3050 were considered statistically significant by the criterion $|F_o| > 3\sigma(F_o)$

$$\sigma^2(F) = \frac{Q}{4}\left[\frac{I_s + (t_s/t_b)^2 I_b + (0.02 I_N)^2}{I_N}\right]$$

where Q contains corrections for crystal decay, Lorentz–polarization, and absorption, I_s and I_b are the scan and background intensities, t_s and t_b are the scan and background times, and I_N is the net integrated intensity. The intensities were corrected for Lorentz–polarization effects, a linear 6% crystal decay as a function of exposure time, and for absorption as a function of ϕ, with a transmission factor of 1.19:1.0 (linear $\mu = 37$ cm^{-1} for Mo $K\alpha$ radiation).

Structure Determination. The structure was initially determined using a set of data collected with copper radiation in a manner similar to that described above. A set of cobalt and iodine coordinates were found consistent with the larger vectors in a three-dimensional Patterson function. The coordinates and isotropic temperature factors of these three atoms were refined by block-diagonal least squares (minimizing $\sum w(\Delta F)^2$). The remainder of the nonhydrogen atoms were located by alternating Fourier synthesis and least squares. Isotropic refinements followed by anisotropic refinement, using $1/\sigma^2$ weights and molybdenum data, for these 23 atoms led to $R = 0.043$ ($R = \sum w|\Delta F|/\sum w|F|$).

A difference electron density map was then calculated to locate the hydrogen coordinates. Positive regions of electron density were found at most, but not all, of the anticipated hydrogen positions. Therefore, the nonmethyl hydrogen coordinates were calculated, based upon expected geometry, and included in subsequent structure factor calculations but not refined. Refinement was continued for the nonhydrogen atoms until the shifts were less than one-tenth the estimated standard deviations of the respective parameters. The final $R = 0.034$ and the "goodness of fit" $S = 1.9$.

Results and Discussion

Electronic Spectra. Electronic spectra of the *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) cation as either the iodide or nitrate salt exhibited a single, broad absorption at 512 nm (ϵ 135) and a shoulder at about 375 nm (ϵ ca. 243). Apart from higher molar extinction coefficients, which we attribute to the effects of low-lying electronic transitions within the delocalized 2,4-pentanedionato chelate ring, these spectra are quite similar to those of related oxalato complexes[13] and do not contribute materially to stereochemical characterization of the complex.

Proton Magnetic Resonance Spectrum. The complex *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) iodide is insufficiently soluble in D_2O to afford high sensitivity, yet certain features of the spectrum may be interpreted in the light of published spectra.

The 2,4-pentanedione methyl groups appear as a doublet with chemical shifts of 2.18 and 2.23 ppm, indicating magnetic nonequivalence. All previous experience with 2,4-pentanedionato complexes suggests that this nonequivalence arises from a difference in the orientation of each methyl group with respect to the adjacent chelate ring of the tetramine ligand and is expected only for the uns-cis topology. The remaining hydrogens of the ligand methylene groups were assigned to three broad lines at chemical shifts of 2.83, 2.42, and 1.90 ppm. The broadness of the lines is characteristic of NMR spectra of cobalt compounds.[14] An attempt to measure the area of the three peaks was made using a planimeter technique. The resulting area ratios were 1.9:1.1:1.0, respectively.

The assignments were made based on a comparison with the NMR spectrum of the free 3,2,3-tet ligand consisting of a broad unresolved resonance at 2.52 ppm and a pentet at 1.5 ppm. The pentet arises from the coupling of methylene groups 8 and 15 with the adjacent methylene groups at positions 7, 9, 14, and 16. The relative positions of the two peaks at 2.83 and 1.90 ppm in the complex were nearly the same as in the free ligand with a downfield shift of 0.4 ppm. Thus, the peak at 1.90 ppm was assigned to the methylene groups at positions 8 and 15, with the area under the peak representing four protons.

In the NMR spectra of other tetramine ligands,[15] the chemical shifts of the methylene groups located between two other methylene groups were dependent on the location of these methylene groups relative to the plane defined by N13, the cobalt ion, and N17. For the methylene group in the plane the shift was approximately 0.8 ppm upfield from the NMR line of the other methylene groups. The chemical shift was closer to that found in the free ligand in compounds with the methylene out of the plane. In the case of the 2,2,3-tet complex, the chemical shift was 0.9 ppm or intermediate between the two extremes. The low-field peak at 2.83 ppm was assigned to the remaining methylene groups least affected magnetically and/or sterically by the formation of the complex. These are probably the methylene groups at positions 7, 9, 14, and 16. The methylene groups at positions 11 and 12 are possibly under some steric stress which would cause an upfield shift; hence these groups were assigned to the peak at 2.42 ppm. Also, the area ratio of 2:1 agreed with the number of protons, 8 and 4. The amine hydrogens were not investigated because of exchange with the deuterium in the solvent.

Description of the Structure. Table I lists the final fractional coordinates and anisotropic temperature factors for all nonhydrogen atoms together with the estimated standard deviations for all parameters. Table II lists the calculated hydrogen coordinates. Table III compares selected intramolecular distances and angles for this study to those calculated by Busch[12] using semiempirical conformational analysis. Table IV lists the intermolecular contacts and Figure 1 is an ORTEP[16] stereodrawing of the complex showing its conformation and the atom numbering scheme.

In the context of published structures of cobalt(III) complexes with flexible tetradentate ligands, the present structure has no outstanding features. Thus, all of the bond distances and angles are found to lie within a "normal" range;

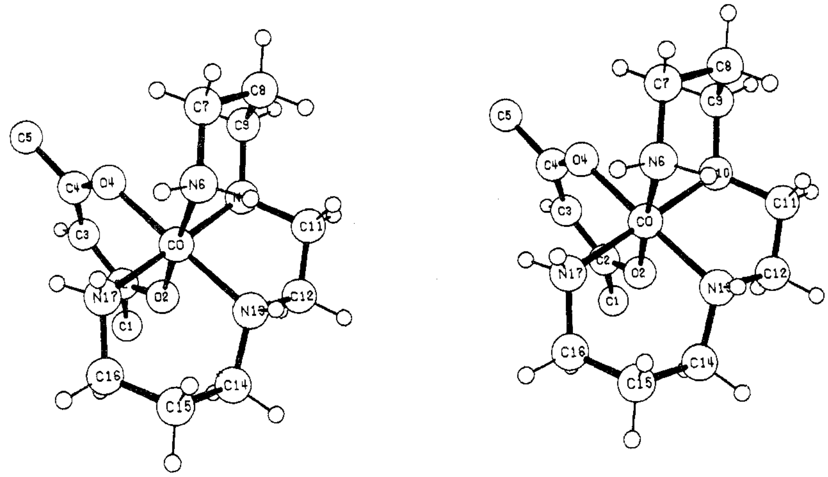


Figure 1. ORTEP[16] stereodrawing of the *uns-cis*-2,4-pentanedionato(4,7-diaza-1,10-decanediamine)cobalt(III) cation.

Table I. Fractional Coordinates and Anisotropic Temperature Factors[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I1	0.0107 (0)	0.2755 (0)	0.4306 (0)	131 (1)	62 (0)	48 (0)	6 (1)	57 (1)	8 (0)
I2	−0.2664 (0)	−0.1410 (0)	0.2464 (0)	77 (0)	105 (0)	44 (0)	−15 (1)	19 (1)	−11 (1)
Co	0.7763 (1)	0.2816 (1)	0.0939 (0)	57 (1)	35 (0)	24 (0)	0 (1)	21 (1)	−1 (1)
C1	0.4571 (8)	0.1458 (6)	0.1318 (5)	152 (11)	80 (6)	85 (5)	−31 (13)	84 (13)	5 (9)
C2	0.5661 (6)	0.2260 (5)	0.1384 (4)	89 (7)	62 (5)	42 (3)	−1 (10)	38 (8)	10 (7)
O2	0.6386 (4)	0.2000 (3)	0.1024 (3)	103 (5)	46 (3)	50 (2)	−14 (6)	48 (6)	−3 (4)
C3	0.5788 (7)	0.3193 (5)	0.1805 (4)	100 (8)	67 (5)	51 (4)	−3 (10)	50 (9)	−5 (7)
C4	0.6748 (6)	0.3955 (5)	0.1897 (3)	76 (7)	59 (4)	23 (2)	19 (9)	23 (7)	9 (5)
O4	0.7597 (4)	0.3937 (3)	0.1593 (2)	91 (5)	44 (3)	35 (2)	−5 (6)	35 (5)	−7 (4)
C5	0.6858 (7)	0.4915 (5)	0.2425 (4)	125 (9)	65 (5)	35 (3)	0 (11)	38 (9)	−16 (6)
N6	0.9190 (4)	0.3626 (4)	0.0810 (3)	66 (5)	45 (3)	28 (2)	−2 (7)	21 (5)	−2 (4)
C7	0.8898 (6)	0.4750 (4)	0.0578 (4)	91 (7)	47 (4)	33 (3)	−15 (9)	33 (8)	−7 (6)
C8	0.7665 (7)	0.4904 (5)	−0.0271 (4)	123 (9)	47 (4)	39 (3)	2 (10)	37 (9)	7 (6)
C9	0.6323 (6)	0.4529 (5)	−0.0302 (4)	80 (7)	55 (4)	32 (3)	14 (9)	18 (7)	6 (6)
N10	0.6311 (4)	0.3381 (4)	−0.0148 (3)	55 (5)	48 (3)	30 (2)	6 (7)	14 (5)	2 (4)
C11	0.6272 (6)	0.2765 (5)	−0.0869 (4)	77 (7)	70 (5)	34 (3)	1 (10)	15 (8)	−9 (7)
C12	0.6573 (6)	0.1664 (5)	−0.0584 (4)	105 (8)	58 (5)	37 (3)	−16 (10)	30 (8)	−11 (6)
N13	0.7880 (5)	0.1661 (4)	0.0248 (3)	83 (6)	43 (3)	37 (2)	0 (7)	28 (6)	−9 (5)
C14	0.8178 (7)	0.0618 (5)	0.0630 (4)	142 (9)	42 (4)	56 (4)	0 (11)	44 (10)	−2 (7)
C15	0.9487 (8)	0.0577 (5)	0.1474 (5)	148 (10)	55 (5)	58 (4)	27 (12)	36 (11)	−2 (7)
C16	0.9349 (8)	0.1138 (5)	0.2179 (4)	163 (11)	57 (5)	43 (3)	16 (12)	25 (10)	20 (7)
N17	0.9196 (5)	0.2268 (4)	0.2029 (3)	108 (7)	53 (4)	29 (2)	3 (8)	23 (6)	4 (5)
OH_2	0.3310 (5)	0.1978 (4)	0.4290 (4)	120 (7)	114 (5)	78 (3)	22 (9)	55 (8)	21 (6)

[a] Esd's refer to last digit. Anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Temperature factors are $\times 10^4$.

Table II. Positions Calculated for Hydrogen Atoms

	x	y	z
H3[a]	0.5123	0.3332	0.2056
H6	1.0074	0.3578	0.1366
H6′	0.9352	0.3281	0.0347
H7	0.9739	0.5082	0.0562
H7′	0.8734	0.5120	0.1026
H8	0.7823	0.4519	−0.0713
H8′	0.7586	0.5671	−0.0418
H9	0.5518	0.4720	−0.0870
H9′	0.6181	0.4915	0.0164
H10	0.5350	0.3335	−0.0190
H11	0.7010	0.3025	−0.1023
H11′	0.5342	0.2826	−0.1392
H12	0.6679	0.1224	−0.1029
H12′	0.5779	0.1363	−0.0504
H13	0.8716	0.1705	0.0132
H14	0.8243	0.0114	0.0212
H14′	0.7360	0.0398	0.0727
H15	1.0269	0.0910	0.1403
H15′	0.9754	−0.0171	0.1649
H16	1.0169	0.0974	0.2750
H16′	0.8479	0.0861	0.2201
H17	1.0129	0.2520	0.2100
H17′	0.9043	0.2583	0.2503

[a] Numbers refer to bonding atom.

there are no unusual intermolecular interactions and no extraordinary intramolecular "nonbonded" contacts. Indeed, the structure of *uns-cis*-$[Co(3,2,3\text{-tet})acac]^{2+}$ is perhaps most remarkable in its striking similarity to the published structures of related trans complexes including the synthetic precursor *trans*-$[Co(3,2,3\text{-tet})Cl_2]^+$.[7] Comparison of the intraligand bond distances and angles and the metal to ligand distances between the cis and trans isomers reveals *no* significant differences. Moreover, the corresponding structural parameters found for *uns-cis*-$[Co(2,3',2\text{-tet})(NO_2)_2]^{6+}$ are surprisingly similar to those of the structure we described here.

Our results closely agree with a "strain-free" configuration described by DeHayes and Busch[12] (Table III). We note that there are few significant differences between the x-ray and strain energy minimized coordinates; those discrepancies which do appear suggest that the DeHayes–Busch potential energy terms, U_R and U_{NB}, are slightly out of balance. Observed C–C and N–C distances are generally smaller than the calculated values.

Our study has revealed an interesting feature which, in turn, suggests some interesting modifications to the subject ligand. The chelate ring N6–C7–C8–C9–N10, which may be considered to be displaced from the plane of the precursor trans

Table III. Selected Intramolecular Distances (Å) and Angles (deg)

	This study	Ref 12	Diff
	Distances		
Co–N17	1.956 (5)	2.06	−0.10
C16–N17	1.478 (9)	1.49	−0.01
C16–C15	1.501 (11)	1.55	−0.04
C15–C14	1.505 (12)	1.55	−0.04
C14–N13	1.472 (8)	1.49	−0.02
N13–C12	1.492 (9)	1.49	0.00
C12–C11	1.493 (9)	1.55	−0.06
C11–N10	1.479 (8)	1.50	−0.02
N10–C9	1.507 (8)	1.49	0.02
C9–C8	1.510 (9)	1.55	−0.04
C8–C7	1.484 (9)	1.55	−0.07
C7–N6	1.500 (7)	1.49	−0.01
	Angles		
N17–Co–N6	89.7 (2)	86	4
Co–N17–C16	120.3 (4)	121	−1
N17–C16–C15	112.0 (6)	113	−1
C16–C15–C14	112.7 (7)	112	1
C15–C14–N13	112.9 (6)	115	−2
C14–N13–Co	118.5 (4)	118	0
N13–Co–N6	93.1 (2)	86	7
Co–N13–C12	107.5 (4)	107	−0
N13–C12–C11	107.0 (5)	108	1
C11–N10–Co	109.0 (4)	108	1
N10–Co–N6	90.6 (2)	88	3
Co–N10–C9	118.0 (4)	121	−3
N10–C9–C8	113.4 (5)	113	0
C9–C8–C7	113.5 (6)	111	2
C8–C7–N6	112.4 (5)	111	1
C7–N6–Co	117.9 (4)	120	−2

Table IV. Intermolecular Contact Distances[a]

Atom 1	Atom 2	Transformation	Distance, Å
I1	N6	$x-1, {}^1/_2-y, {}^1/_2+z$	3.68
I1	N13	$x-1, {}^1/_2-y, {}^1/_2+z$	3.58
I1	C15	$1-x, {}^1/_2+y, {}^1/_2-z$	3.98
I1	N17	$x-1, y, z$	3.69
I1	OH_2	x, y, z	3.63
I2	N6	$1-x, y-{}^1/_2, {}^1/_2-z$	3.58
I2	C11	$-x, -y, -z$	4.00
I2	C12	$-x, -y, -z$	3.99
I2	N17	$1-x, y-{}^1/_2, {}^1/_2-z$	3.84
I2	OH_2	$-x, y-{}^1/_2, {}^1/_2-z$	3.51
N10	OH_2	$x, {}^1/_2-y, z-{}^1/_2$	2.96
C11	OH_2	$x, {}^1/_2-y, z-{}^1/_2$	3.36

[a] Heavy to light atom less than 4.0 Å; light atom to light atom less than 3.5 Å.

complex, is also inverted. Thus, the equatorial hydrogen atoms bonded to C7, C8, and C9 in the trans complex occupy axial positions in the uns-cis complex described here. (The chelate ring N13–C14–C15–C16–N17 is virtually unchanged (vide supra).) We anticipate, therefore, that a methyl substituent on C15 will control the stereochemistry of the trans–cis isomerism which we have described earlier[17] yet remain relatively stereochemically "innocent" during the course of ligand substitution reactions. In an unstrained trans complex, this substituent is expected to occupy an equatorial position placing it about 5 Å from the metal center and on the pseudosymmetry plane which bisects the six-membered chelate rings.[18] Indeed, we expect to find an unusually small "vicinal" contribution to the optical activity of appropriately resolved complexes. Transformation of this trans complex into a cis isomer requires that the unsubstituted chelate ring be displaced from the plane (to produce a species resembling Figure 1, if C15 is substituted and C8 unsubstituted)—the substituted ring cannot be displaced without a high-energy inversion of the methyl group into an axial position. Moreover, through N13, an equatorial methyl group on C15 is expected to determine the configuration of chelate ring N13–C12–C11–N10 which, in turn, will require that chelate ring N10–C9–C8–C7–N6 be displaced upward (Figure 1). Similarly, substituents on both C8 and C15 are expected to give rise to complexes which are fixed in the trans (for the racemic or *RR,SS* ligand) or in the cis (meso ligand) configuration. The latter may afford the only synthetic route to *cis*-diacido(3,2,3-tet)Co^{III} derivatives.

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Registry No. *uns-cis*-[Co(3,2,3-tet)acac]$I_2 \cdot H_2O$, 59109-97-6; *trans*-dichloro-(4,7-diaza-1,10-decanediamine)cobalt(III) chloride, 31842-33-8; 2,4-pentanedione, 123-54-6.

Supplementary Material Available: A listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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