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trans-Diamminebis[dimethylglyoximato(1−)]cobalt(III) Nitrate *and* Thiocyanate*

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Abstract. $[Co(C_4H_7N_2O_2)_2(NH_3)_2]NO_3$, *trans*-$[(NH_3)_2\,Co(Hdmg)_2]NO_3$, Hdmg = the monoanion of dimethylglyoxime, monoclinic, $P2_1/c$, a = 9·940 (2), b = 6·3847 (7), c = 12·558 (2) Å, β = 99·872 (3)°, U = 785·2 Å^3, Z = 2, d_m = 1·629 (12), d_c = 1·629 Mg m^{-3} R_1 = 0·026, R_2 = 0·038. $[Co(C_4H_7N_2O_2)_2(NH_3)_2]SCN.H_2O$, *trans*-$[(NH_3)_2Co(Hdmg)_2]SCN.H_2O$, orthorhombic, $Pmmn$, a = 7·0346 (8), b = 10·528 (2), c = 11·476 (3) Å, U = 849·9 Å^3, Z = 2, d_m = 1·563 (8), d_c = 1·568 Mg m^{-3}, R_1 = 0·036, R_2 = 0·022. The six-coordinate cobalt complexes have the expected *trans* geometry with coplanar Hdmg ligands joined by a strong hydrogen bond between oxime O atoms. There is no evidence favoring formulation as $[(NH_3)_2(H_2dmg)Co(dmg)]^+$. The two cation structures are essentially identical and the Co—N(NH$_3$) bonds are 1·951 (2) (NO_3^- salt) and 1·957 (2) Å (SCN$^-$ salt).

Introduction. To extend the 'Structural *trans* Effect' (STE) series which has been established (Heeg, Elder & Deutsch, 1980) for octahedral complexes of the type $[(NH_3)_5CoX]^{n+}$, we have begun a program to determine structures of the type $[(NH_3)Co(Hdmg)_2X]^{+,0,-}$. To define a zero for this STE series we determined the structures of *trans*-$[(NH_3)_2Co(Hdmg)_2]Br$ (Heeg & Elder, 1980) as well as *trans*-$[(NH_3)_2Co(Hdmg)_2]NO_3$ and *trans*-$[(NH_3)_2Co(Hdmg)_2]SCN.H_2O$ which we report here.

Amber-colored crystals of *trans*-$[(NH_3)_2Co(Hdmg)_2]NO_3$ were formed by simple metathesis from a solution of the Cl$^-$ salt (Nakatsuka & Iinuma, 1936) using NH_4NO_3. Replacement of the Cl$^-$ by NO_3^- was shown both by the lack of AgCl precipitate when $AgNO_3$ was added to a solution of the NO_3^- crystals and the presence of a strong NO_3^- absorption band in the IR spectrum. A crystal (0·21 × 0·15 × 0·30 mm) of the NO_3 salt was mounted and a Syntex $P\bar{1}$ diffractometer used with Mo radiation to measure unit-cell constants (14 pairs of reflections), systematic absences and intensity data in our usual manner (Heeg & Elder, 1980). Intensities for 1803 reflections (hkl, $hk\bar{l}$, $2·5 \le 2\theta \le 50°$) were averaged where necessary to yield 1295 unique, observed reflections $[I > 2\sigma(I)]$. Other details of data collection were as follows: scan rate 1·0–6·0° min^{-1}; scan range 1·5° in 2θ; max h 12; max k 8; max l 15. Examination of the intensity data showed systematic absences for $h0l$, l odd and $0k0$, k odd in agreement with space group $P2_1/c$. With Z = 2, this requires that both the complex cation and the NO_3^- anion have site symmetry $\bar{1}$ as found for a previous determination of this structure from projections (Viswanathan & Kunchur, 1961). An independent solution derived from a Patterson vector map was consistent with the published solution (Co at 0,0,0 and N at $\frac{1}{2}$,0,0), and confirmed the space-group assignment. Electron density maps showed positions for all non H atoms including six O atoms of one-half weight about N(4), yielding a static, disordered NO_3^-. This model was refined without difficulty. H atoms were found from a difference electron density map (ΔF map). Those on NH_3 and the oxime H atom were well behaved on refinement. A ΔF map at this point showed a second set of H atoms on CH_3 staggered between holes at the sites of the original H-atom positions for CH_3. Further investigation showed that the final model with six fixed H atoms each of half-weight on CH_3 was clearly

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* Dimethylglyoxime ≡ 2,3-butanedione dioxime.

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superior (133 variables, R_1 = 0·026, R_2 = 0·038) to either model with three full-weight H atoms per CH_3 group (133 variables, R_1 = 0·035, R_2 = 0·043). In the final cycle of refinement the maximum shift was 0·13σ and the average shift was 0·028σ. A final ΔF map was essentially featureless with the highest peak corresponding to 0·25 e Å^{-3}. Neutral-atom scattering factors, corrected for anomalous dispersion, were used.

trans-[$(NH_3)_2Co(Hdmg)_2$]SCN.H_2O was formed as orange, plate-like crystals *via* metathesis of the Cl^- salt with KSCN. The presence of solvent in the crystal was detected through observation of the O—H stretch in the IR spectrum of a mineral oil mull. The formulation of the compound as a monohydrate is substantiated by the X-ray analysis. Preliminary precession photographs indicated an orthorhombic crystal with a single *n*-glide. Unit-cell constants (15 pairs of reflections) and intensity data were measured on a crystal fragment (0·18 × 0·19 × 0·20 mm). Measurement techniques were as above with the following exceptions: 1938 reflections (*hkl*, 2·5 ≤ 2θ ≤ 51·0°), 1018 unique observed reflections [$I \geq 3\sigma(I)$]; scan rate 1·0–4·0° min^{-1}; max *h* 9; max *k* 14; max *l* 15; empirical absorption correction* applied. A Patterson vector map yielded locations for nearly all non-H atoms in agreement with space group *Pmmn*. The Co was located at $\frac{1}{4},\frac{1}{4}$,0·0743 (*mm* symmetry) and all of the SCN^- atoms at $\frac{1}{4},\frac{3}{4},z$ (*mm* symmetry). Most H atoms and the remaining non-H atoms were found from a series of ΔF maps. Remaining H atoms were placed at their ideal locations. Refinement converged with R_1 = 0·036 and R_2 = 0·022. In the final cycle a scale factor, all variable atomic positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms were refined (102 variables). The maximum shift was 0·19σ and the mean shift was 0·05σ. A final ΔF map was essentially featureless; the highest peak, occurring between Co and NH_3, was less than 0·3 e Å^{-3}.

Final atomic positional parameters and $U_{eq.}$ values for both structures are given in Table 1. Bond lengths are listed in Table 2, and bond angles collected in Table

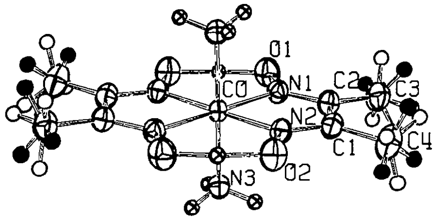

Fig. 1. The complex cation in *trans*-[$(NH_3)_2Co(Hdmg)_2$]NO_3. The two sets of disordered H atoms are shown as open and filled circles on C(3) and C(4).

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic thermal parameters* [$U_{eq} = (U_1U_2U_3)^{1/3}$ (×10^3)]

	x	*y*	*z*	U_{eq} (Å^2)
[$(NH_3)_2Co(Hdmg)_2$]NO_3				
Co	0	0	0	145
O(1)	865 (1)	2474 (2)	1884 (1)	194
O(2)	1113 (2)	−3811 (2)	−621 (1)	186
O(3)	6010 (5)	74 (10)	884 (6)	288
O(4)	4143 (7)	1098 (19)	214 (10)	309
O(5)	5329 (27)	−993 (21)	−608 (11)	409
N(1)	1091 (2)	700 (3)	1342 (1)	163
N(2)	1214 (1)	−2297 (2)	134 (1)	162
N(3)	1258 (2)	1592 (3)	−722 (1)	168
N(4)	5000	0	0	261
C(1)	2180 (2)	−2314 (3)	963 (1)	174
C(2)	2126 (2)	−488 (3)	1681 (2)	173
C(3)	3176 (2)	−88 (3)	2645 (2)	202
C(4)	3258 (2)	−3958 (4)	1174 (2)	215
[$(NH_3)_2Co(Hdmg)_2$]SCN.H_2O				
Co	2500	2500	743 (1)	184
O(1)	2500	4933 (2)	1829 (2)	241
O(2)	2500	4943 (2)	−323 (2)	231
O(3)	2500	7500	1603 (4)	263
N(1)	2500	3663 (2)	1998 (2)	195
N(2)	2500	3676 (3)	−507 (2)	205
N(3)	5283 (3)	2500	746 (3)	212
N(4)	2500	7500	6976 (4)	273
C(1)	2500	3197 (3)	3041 (2)	206
C(2)	2500	3204 (3)	−1547 (3)	221
C(3)	2500	3960 (4)	4128 (3)	244
C(4)	2500	3987 (6)	−2631 (3)	260
C(5)	2500	7500	5982 (4)	230
S	2500	7500	4584 (1)	276

Table 2. *Bond lengths* (Å)

[$(NH_3)_2Co(Hdmg)_2$]NO_3			
Co—N(1)	1·894 (1)	Co—N(2)	1·889 (1)
N(1)—O(1)	1·359 (2)	N(2)—O(2)	1·346 (2)
N(1)—C(2)	1·290 (3)	N(2)—C(1)	1·290 (2)
C(1)—C(4)	1·490 (3)	C(2)—C(3)	1·479 (3)
Co—N(3)	1·951 (2)	C(1)—C(2)	1·480 (3)
N(4)—O(3)	1·364 (6)	N(4)—O(4)	1·169 (10)
N(4)—O(5)	1·085 (17)		
[$(NH_3)_2Co(Hdmg)_2$]SCN.H_2O			
Co—N(1)	1·890 (2)	Co—N(2)	1·895 (3)
N(1)—O(1)	1·351 (3)	N(2)—O(2)	1·350 (4)
N(1)—C(1)	1·294 (4)	N(2)—C(2)	1·292 (4)
C(1)—C(3)	1·484 (5)	C(2)—C(4)	1·492 (6)
Co—N(3)	1·957 (2)	C(1)—C(1′)	1·468 (4)
S—C(5)	1·604 (5)	C(2)—C(2′)	1·483 (5)
N(4)—C(5)	1·141 (7)		

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* *PSICOR:* a FORTRAN program to calculate empirical data corrections was extensively modified by J. C. Barrick from a program by D. Tipton of the University of Southern California. Corrections are based on repetitive scans of a reflection as it is stepped around the diffraction vector. Several reflections at various values of 2θ are scanned. The program is used to preprocess the data tape written by the diffractometer, producing a corrected tape in the same format as the original.

Table 3. *Bond angles* (°)

$[(NH_3)_2Co(Hdmg)_2]NO_3$			
N(1)–Co–N(2)	81·0 (1)	N(1)–Co–N(2′)	99·0 (1)
N(1)–Co–N(3)	88·6 (1)	N(2)–Co–N(3)	89·7 (1)
Co–N(1)–C(2)	117·2 (1)	Co–N(2)–C(1)	117·0 (1)
Co–N(1)–O(1)	121·5 (1)	Co–N(2)–O(2)	121·7 (1)
O(1)–N(1)–C(2)	121·0 (2)	O(2)–N(2)–C(1)	121·2 (2)
N(1)–C(2)–C(3)	125·4 (2)	N(2)–C(1)–C(4)	124·2 (2)
N(1)–C(2)–C(1)	111·9 (2)	N(2)–C(1)–C(2)	112·7 (2)
C(1)–C(2)–C(3)	122·7 (2)	C(2)–C(1)–C(4)	123·1 (2)
$[(NH_3)_2Co(Hdmg)_2]SCN.H_2O$			
N(1)–Co–N(1′)	80·8 (1)	N(1)–Co–N(2)	98·8 (1)
N(1)–Co–N(3)	89·9 (1)	N(2)–Co–N(3)	90·1 (1)
Co–N(1)–C(1)	117·3 (2)	Co–N(2)–C(2)	116·6 (3)
Co–N(1)–O(1)	122·1 (2)	Co–N(2)–O(2)	121·8 (3)
O(1)–N(1)–C(1)	120·6 (2)	O(2)–N(2)–C(2)	121·6 (3)
N(1)–C(1)–C(3)	125·0 (3)	N(2)–C(2)–C(4)	123·9 (4)
N(1)–C(1)–C(1′)	112·3 (3)	N(2)–C(2)–C(2′)	112·6 (3)
C(1′)–C(1)–C(3)	122·8 (3)	C(2′)–C(2)–C(4)	123·5 (3)

3.* The structure of the complex cation is shown in Fig. 1, and exhibits the expected *trans* octahedral geometry.

Discussion. The main purpose of these determinations of *trans*-$[(NH_3)_2Co(Hdmg)_2]^+$ structures has been to find a precise value for the Co–N(NH_3) length and to evaluate the reproducibility of this distance on changing counter ion, degree of hydration, crystal-packing forces, *etc.* In our previous study of the Br^- salt (Heeg & Elder, 1980), we found Co–N(NH_3) to be 1·960 (2) Å. Here, for the NO_3^- salt, we find 1·951 (2) Å and for the SCN^- monohydrate we obtain 1·957 (2) Å. Based on these three determinations the most likely value for Co–N(NH_3 *trans* to NH_3) in a $[(NH_3)_2Co(Hdmg)_2]^+$ complex is 1·956 (5) Å, where the estimated error is calculated from the variation in the three determinations. The relatively high reproducibility of this distance gives us confidence that we may define a meaningful STE for complexes of the type *trans*-$[(NH_3)Co(Hdmg)_2X]^{+,0,-}$ as STE = [Co–N(NH_3 *trans* to X)] – [Co–N(NH_3 *trans* to NH_3)] or STE = [Co–N(NH_3 *trans* to X)] – 1·956 (5) Å.

In general the detailed structure of the complex is invariant to changes in counter ion, degree of hydration, crystal packing, *etc.* Table 4 compares chemically equivalent bond lengths found for the three different salts. All three of the complexes appear to contain two monoanionic Hdmg ligands with bridging hydrogen bonds joining the ligands effectively into a macrocycle. Recent articles (Palenik, Sullivan & Naik, 1976; Bresciani-Pahor, Calligaris & Randaccio, 1978) have suggested that several complexes of this type should be formulated as containing one neutral dimethylglyoxime ligand, H_2dmg, and one dianionic dimethylglyoximato ligand, dmg. The differences between formulation as $[Co(Hdmg)_2]^+$ and $[(H_2dmg)Co(dmg)]^+$ are relatively subtle, depending principally on the location of the bridging H atoms. In the NO_3^- salt the complex has site symmetry $\bar{1}$ which requires two Hdmg ligands. The Br^- salt has $2/m$ symmetry for the complex with the twofold axis passing through Co and both oxime H atoms and thus also requires two Hdmg ligands. The SCN^- hydrate has mm symmetry for the complex. Each Hdmg ligand lies in the mirror plane at $x = \frac{1}{4}$ and is related to itself by a mirror at $y = \frac{1}{4}$ passing between the imine C atoms. Therefore in this complex the formulation as dmg, H_2dmg is at least possible. However, the refined position of the oxime H atom is not significantly different from midway between the two oxime O atoms ($<1\sigma$), whereas in the better documented cases formulated as $[(H_2dmg)Co(dmg)]^+$ the H atom is asymmetrically placed with a mean O–H distance of 1·05 (6) Å and a mean O···H distance to the O of the dmg ring of 1·46 (6) Å. Thus all three crystals discussed here contain $[(NH_3)_2Co(Hdmg)_2]^+$.

The previous report on the structure of $[(NH_3)_2Co(Hdmg)_2]NO_3$ described the NO_3^- as freely rotating about an axis through N and normal to the NO_3^- plane. We have chosen instead a static disorder of O atoms to describe the NO_3^-. The relatively low final values R_1 = 0·026 and R_2 = 0·038 indicate that this model is moderately successful in treating the data; however, the disparities in the N–O lengths (1·36, 1·17, 1·09 Å) indicate that the NO_3^- model is not chemically significant. The close similarity among the complex cations in the three different structures leads us to believe that the errors in the NO_3^- structure are largely confined to the anion. The fact that the NH_3 moiety

Table 4. *Comparison of bond lengths* (Å) *for* $[(NH_3)_2Co(Hdmg)_2]^+$

	NO_3^-	SCN^-	Br^-	Mean
Co–NH_3	1·951 (2)	1·957 (2)	1·960 (2)	1·956 (5)
Co–N(im)	1·894 (1), 1·889 (1)	1·890 (2), 1·895 (3)	1·893 (1)	1·892 (3)
N–O	1·359 (2), 1·346 (2)	1·351 (3), 1·350 (4)	1·347 (2)	1·351 (5)
N=C	1·290 (3), 1·290 (2)	1·294 (4), 1·292 (4)	1·294 (2)	1·292 (2)
=C–CH_3	1·490 (3), 1·479 (3)	1·484 (5), 1·492 (6)	1·487 (3)	1·486 (5)
=C–C=	1·480 (3)	1·468 (4), 1·483 (5)	1·474 (3)	1·476 (7)
O–H	1·224 (20), 1·266 (20)	1·207 (38), 1·265 (38)	1·235 (3)	

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* Lists of structure factors, thermal parameters, and hydrogen atomic parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35398 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

forms two hydrogen bonds to the oxime O atoms of adjacent [$(NH_3)_2Co(Hdmg)_2]^+$ cations [N(3)–H(2)$\cdots$O(2) at x, $1 + y$, z, N$\cdots$O = 2·94 Å, and N(3)–H(3)$\cdots$O(1) at x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$, N$\cdots$O = 3·02 Å] and only one comparable bond to the NO_3^- anion [N(3)–H(1)$\cdots$O(3) at $1 - x$, $\bar{y}$, $\bar{z}$, N$\cdots$O = 2·96 Å] may give some indication why the nitrate is not ordered in this structure.

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Sodium 5,6-Dihydrouracil-6-sulfonate Monohydrate

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Abstract. $C_4H_5N_2O_5S^-.Na^+.H_2O$, $P2_1/c$, a = 5·668 (1), b = 11·026 (2), c = 13·261 (2) Å, β = 94·62 (2)°, Z = 4, D_c = 1·884, D_o = 1·87 Mg m^{-3}, V = 826·1 Å^3, M_r = 234·1, λ(Mo $K\alpha$) = 0·71069 Å, T = 299 ± 1 K, $F(000)$ = 480. The intensity data were collected on an automated diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement, with the temperature factors of the non-hydrogen atoms allowed to refine anisotropically, yielded an R of 0·032 for the 1735 significant data. The modified pyrimidine anions are packed as hydrogen-bonded, centrosymmetrically related pairs, bridged by coordination bonds to the Na^+ ion and hydrogen bonds with the water molecule.

Introduction. The title compound was obtained as a by-product of the synthesis of N^4-semicarbazido-5,6-dihydrocytosine 6-sulfonate. Nitrogen nucleophiles, such as semicarbazide and bisulfite, are mutagenic, and are believed to induce mutations by reaction with cytosine residues in polynucleotides (Hayatsu, 1976*a*; Budowsky, 1976). Recently, Hayatsu has reported a ‘cooperative’ action in the induction of mutations by combinations of bisulfite and several nitrogen nucleophiles, including semicarbazide (Hayatsu, 1977). As the mechanism of mutation is in question, structure determinations of reaction products of these mutagens with cytosine can be important.

N^4-Semicarbazido-5,6-dihydrocytosine 6-sulfonate was synthesized according to Hayatsu (1976*b*). The identity of the resulting finely divided powder was confirmed by spectral analysis: UV, in water, λ_{max} 243 nm, λ_{min} 214 nm; in 0·1 M NaOH, λ_{max} 265 nm, λ_{min} 227 nm. Attempts to recrystallize the material from 0·2 M $NaHSO_3$–Na_2SO_3, pH 7, as suggested by Hayatsu, resulted, in our hands, in well formed crystals of 5,6-dihydrouracil-6-sulfonate. Recrystallization from water and from neutral solutions of semicarbazide also gave the elimination product. The identity of the crystalline material was established by its UV spectrum in water and by its reversal to uracil upon treatment with alkali (Hayatsu, 1976*b*).

As the apparent lability of the semicarbazide group suggests a significant role for the deaminated product in the mutagenic activity of semicarbazide–bisulfite reactions with cytosine, a structure determination of 5,6-dihydrouracil-6-sulfonate was undertaken.

A crystal 0·30 × 0·35 × 0·30 mm was selected for diffraction study. The space group and approximate cell dimensions were determined from precession and Weissenberg photographs. More-accurate cell dimensions were obtained by least-squares refinement of the first moments of 40 observed 2θ values in the range $45 < 2\theta < 53°$ [r.m.s. $(\theta_c - \theta_o)$ = 0·026°], measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was determined by flotation in mixtures of chloroform and

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