

## Complexes of *N,N'*-di(2-hydroxyethyl)-2,4-pentanediiimine. Preparation and Structure of a Cobalt(III) Complex

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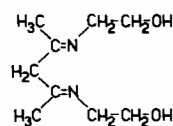
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A cobalt(III) complex of *N,N'*-di(2-hydroxyethyl)-2,4-pentanediiimine has been prepared from bis-2,4-pentanedionato)cobalt(II) and 2-aminoethanol and the structure of the complex has been determined by an X-ray diffraction study. The compound,  $\text{Co}(\text{C}_9\text{H}_{15}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_7\text{NO})_2$ , crystallized in triclinic space group  $\bar{P}1$  ( $a = 12.677(1) \text{ \AA}$ ,  $b = 9.187(1) \text{ \AA}$ ,  $c = 9.364(1) \text{ \AA}$ ,  $\alpha = 121.70(8)^\circ$ ,  $\beta = 81.26(8)^\circ$ ,  $\gamma = 115.64(8)^\circ$ ) with 2 molecules per unit cell ( $\rho_{\text{calc}} = 1.46 \text{ g cm}^{-3}$ ;  $\rho_{\text{obsd}} = 1.45(1) \text{ g cm}^{-3}$ ). A total of 3210 unique, non-zero reflections that were collected on an automated four-circle diffractometer were used to refine the structure by full-matrix least-squares methods. The structure, which was refined to a conventional *R* value of 0.060, consists of a cobalt(III) ion coordinated to the planar, tetradentate diimine ligand and to two monodentate 2-aminoethanol groups. The coordination geometry shows only small deviations from ideal octahedral geometry with the cobalt–donor atom distances ranging from 1.897(4) to 1.989(3)  $\text{\AA}$  and the angles at cobalt for *cis*-donor atoms ranging from 85.5° to 94.6°.

### Introduction

Although a large number of complexes of imines of 2,4-pentanedione have been reported,<sup>1</sup> there have been relatively few reports of complexes of diimines of 2,4-pentanedione. Most of the complexes that have been reported<sup>2–5</sup> were prepared by using the pre-formed ligand and only the complexes of the macrocyclic ligand formed from 2,4-pentanedione and diethylenetriamine were prepared directly by template reactions.<sup>3,4</sup> As part of a general study of transition metal complexes of aminoalcohols and their imines, we attempted the preparation of a series of complexes of *N,N'*-di(2-hydroxy-ethyl)-2,4-pentanediiimine, I, by direct reaction of 2-aminoethanol and bis(2,4-pentanedionato)metal(II) compounds in the presence of excess 2,4-pentanedione.



Since this tetradentate ligand contains three ionizable protons, it is possible for a trivalent metal ion to form neutral complexes ( $\text{ML}$ , where L represents the trianion of the ligand I,  $\text{H}_3\text{L}$ ) and for divalent metal ions to form anionic mononuclear complexes ( $\text{ML}^-$ ), neutral trinuclear complexes ( $\text{M}_3\text{L}_2$ ), or neutral, protonated complexes ( $\text{MLH}$ ). Employing a variety of metal ions and varying the reaction conditions, we have isolated a polynuclear nickel(II) complex which can be represented as  $\text{Ni}_3\text{L}_2(\text{EtaH})_4$  (where EtaH represents a neutral 2-aminoethanol), copper(II) and nickel(II) complexes with the empirical formula  $\text{MLH}$ , and a cobalt(III) complex with the empirical formula  $\text{CoL}(\text{EtaH})_2$ . Although all of these compounds could contain the tetradentate diimine, it is possible that one or more of the additional 2-aminoethanol molecules in the first and last compounds listed have added across the imine linkages to give a more complex ligand. The presence of both alcohol and alkoxide groups in each of the complexes creates the possibility of hydrogen bonding which could be intramolecular in nature. Intermolecular hydrogen-bonding could create infinite chains or networks of hydrogen-bonded molecules or it could involve “cooperative” hydrogen bonding as in the mixed cobalt(III)–nickel(II) complex of 2-aminoethanol.<sup>6</sup> In order to determine the nature and mode of coordination of the ligand or ligands and to determine the extent and type of hydrogen bonding present, we have carried out structure studies of all of the compounds isolated except the trinuclear nickel complex (for which suitable crystals have not been obtained). In this paper, we report the preparation and structure of the cobalt(III) complex.

## Experimental

### Preparation

To a mixture of 50 ml of 2-aminoethanol and 25 ml of 2,4-pentanedione were added 0.56 g of potassium hydroxide and 3.2 g of bis(2,4-pentanedionato)cobalt (II). The resulting mixture was heated gently at 115°C until everything was dissolved and the solution was then allowed to stand overnight. The dark red needles that formed were separated by filtering.

Anal. Calcd. for  $\text{CoC}_{13}\text{H}_{29}\text{N}_4\text{O}_4$ : C, 42.85; H, 8.02; N, 15.37. Found: C, 42.92; H, 7.82; N, 15.38.

### Collection and Reduction of the Intensity Data

A crystal of approximate dimensions  $0.20 \times 0.20 \times 0.70$  mm was mounted in a glass capillary with the long dimension parallel to the fiber. After assigning cell parameters, it was found that the 1, -2, 1 vector of the reciprocal lattice was parallel to the spindle axis of the precession camera. Precession photographs indicated a triclinic crystal, space group  $P1$  or  $P\bar{1}$ . Space group  $P\bar{1}$  was assumed and the successful refinement of the structure has confirmed this choice.

The crystal was transferred to an automated Picker four-circle diffractometer and 22 reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained are:  $a = 12.677(1)$  Å,  $b = 9.187(1)$  Å,  $c = 9.364(1)$  Å,  $\alpha = 121.70(8)^\circ$ ,  $\beta = 81.26(8)^\circ$ ,  $\gamma = 115.64(8)^\circ$ , and  $V = 832.68$  Å<sup>3</sup> (25°C, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å). A Delaunay reduction using these cell parameters confirmed the triclinic description of the unit cell. The conventional reduced cell parameters obtained are:  $a' = 12.677$  Å,  $b' = 9.039$  Å,  $c' = 9.364$  Å,  $\alpha' = 120.13^\circ$ ,  $\beta' = 98.74^\circ$ , and  $\gamma' = 106.41^\circ$ . The transformation matrix is:

$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

The calculated density of 1.46 g/cm<sup>3</sup>, based on two formula units per unit cell, agrees well with the observed density of 1.45(1) g/cm<sup>3</sup> measured by the flotation method using a mixture of n-heptane and carbon tetrachloride.

Intensities were measured with a scintillation counter mounted 21 cm from the crystal by the  $\theta$ -2 $\theta$  scan technique, using a takeoff angle of 1.6° and a scan rate of 1° min<sup>-1</sup>. A symmetric scan of 2° was taken about the calculated peak position and stationary background counts of 20 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the attenuators were calibrated by collecting intensities on 30 different reflections of various magnitudes. The threshold point was set so that the counting rate would

not exceed 10,000 counts/second and the pulse height analyzer was set for approximately a 90% window centered on the Mo  $K\alpha$  peak. A total of 5114 reflections were collected. Corrected intensities (I) were obtained by subtracting three times the actual measured background from the total integrated peak count (CT),

$$I = CT - 3(\text{bgd1} + \text{bgd2}).$$

The factor of three in the calculation arises from the peak scan time being three times as long as the total background count time. The corrected intensities were assigned standard deviations according to the formula<sup>7</sup>

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(\text{bgd1} + \text{bgd2}) + (pI)^2]^{1/2}$$

where  $t_c$  is the scan time;  $t_b$  is the counting time of each background (either bgd1 or bgd2). The ignorance factor, p, was assigned a value of 0.01. A total of 3210 reflections were accepted as statistically above background on the basis that  $\sigma(I)/I$  was less than 0.30. The intensities were corrected for Lorentz and polarization effects but were not corrected for absorption. The calculated linear absorption coefficient,  $\mu$ , was 10.9 cm<sup>-1</sup> and the value of  $e^{-\mu t}$  ranged from 0.70 to 0.80; the actual range in integrated transmission factors is smaller than this. The intensities of two standard reflections (5,0,0 and -6,7,-6) were measured at intervals of 100 reflections and showed no significant variation during the data collection.

### Solution and Refinement of the Structure

Computations were carried out on a Burroughs B5500 computer and on a Univac 1108 computer. Programs employed included modified versions of F.L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy XFLS and ORFFE least-squares and function and error programs, the Johnson ORTEP thermal ellipsoid plotting program, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers<sup>8</sup> were employed for all atoms.

With two formula units per unit cell, the asymmetric unit consists of one formula unit. From a three-dimensional Patterson function coordinates were obtained for the cobalt atoms. Successive electron density calculations, with initial phasing based on the contribution of the cobalt atoms to the structure amplitudes, revealed the positions of all remaining non-hydrogen atoms. Full-matrix least-squares refinement of a scale factor, coordinates, and anisotropic temperature factors for all atoms was carried out using a weighting scheme based on counting statistics ( $w_1 = 4I/\sigma(I)^2$ ) and minimizing  $w(|F_o| - |F_c|)^2$ ; the refinement converged to a weighted residual  $R_2 = (\sum w_i(|F_o| - |F_c|)^2 / \sum w_i(|F_o|)^2)^{1/2}$ , of 0.059 and a conventional residual  $R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|)$ , of 0.060. The positional parameters from the last cycle of least-squares refinement are presented

in Table I, and the final thermal parameters are presented in Table II. Observed and calculated structure factors are presented in Table III.

### Discussion

Figure 1 shows the asymmetric unit of the structure in which a cobalt(III) ion is octahedrally coordinated by the tetradentate diimine ligand and two monodentate 2-aminoethanol groups. Selected bond distances and bond angles for the structure are presented in Table IV. The coordination geometry shows only small deviations from an ideal octahedral arrangement with cobalt-donor atom distances ranging from 1.897 Å to 1.989 Å and the angles at cobalt for *cis*-donor atoms ranging from 85.5° to 94.6°. The diimine ligand occupies four coplanar coordination sites and creates two five-membered and one six-membered chelate rings. The charge of the trivalent cobalt ion is balanced by the loss of three protons from the ligand. Since alkoxide oxygen atoms are generally better coordinating groups than alcohol oxygen atoms, it is probable that protons have been lost from E1O and E2O; from the structure parameters observed, it appears that the third proton has been removed from the carbon, AC3, which is beta to the two imine nitrogen atoms. Within the six-membered chelate ring, which includes both imine groups and AC3, the two carbon-carbon distances are equivalent (1.39(1) Å) and the two carbon-nitrogen

TABLE I. Final positional parameters for Co(C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>7</sub>ON)<sub>2</sub>.

Atom <sup>a</sup>	x	y	z
Co	0.15793(5)	-0.07136(8)	-0.23311(7)
AC1	0.4810(5)	-0.127(1)	-0.272(1)
AC2	0.3944(3)	-0.0447(7)	-0.2503(5)
AC3	0.4381(4)	0.1264(7)	-0.2452(6)
AC4	0.3728(4)	0.2187(6)	-0.2375(5)
AC5	0.4394(5)	0.4048(9)	-0.2319(8)
E1N	0.2821(3)	-0.1376(5)	-0.2409(4)
E1C1	0.2386(5)	-0.3220(7)	-0.2535(8)
E1C2	0.1215(4)	-0.3520(7)	-0.1784(7)
E1O	0.0550(2)	-0.3018(4)	-0.2370(4)
E2N	0.2568(3)	0.1520(5)	-0.2353(4)
E2C1	0.1930(5)	0.2568(8)	-0.2237(7)
E2C2	0.0670(5)	0.135(1)	-0.257(1)
E2O	0.0297(2)	-0.0118(4)	-0.2294(4)
E3N	0.1699(3)	0.0773(5)	0.0158(4)
E3C1	0.2767(4)	0.1418(7)	0.1199(5)
E3C2	0.2770(4)	0.2726(8)	0.3052(5)
E3O	0.1879(3)	0.1892(7)	0.3822(5)
E4N	0.1260(3)	-0.2272(5)	-0.4830(4)
E4C2	0.1842(4)	-0.3544(6)	-0.7749(5)
E4C1	0.2177(4)	-0.1929(6)	-0.5949(5)
E4O	0.1646(3)	-0.5271(5)	-0.7911(4)

<sup>a</sup> The atom designations denote the origin of the particular atom; atoms from 2,4-pentanedione are preceded by A, those from the two 2-aminoethanol molecules that are incorporated into the diimine ligand are preceded by E1 and E2; the atoms of the 2-aminoethanol molecules are preceded by E3 and E4.

TABLE II. Final anisotropic thermal parameters<sup>a</sup> ( $\times 10^4$ ) for Co(C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>7</sub>ON)<sub>2</sub>.

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co	35.3(4)	88(1)	65.3(8)	27.9(5)	13.4(3)	45.7(7)
AC1	67(4)	383(20)	299(16)	115(8)	37(6)	181(15)
AC2	43(3)	189(10)	110(7)	44(4)	11(3)	67(7)
AC3	43(3)	204(11)	154(8)	14(4)	12(4)	98(8)
AC4	66(3)	113(8)	82(6)	9(4)	10(3)	40(6)
AC5	98(5)	177(12)	240(13)	2(6)	31(6)	141(11)
E1N	45(2)	120(7)	107(5)	38(3)	15(3)	60(5)
E1C1	78(4)	150(10)	263(12)	64(5)	21(5)	123(9)
E1C2	65(3)	175(10)	239(11)	29(5)	2(5)	158(10)
E1O	49(2)	135(6)	140(5)	22(3)	5(2)	98(5)
E2N	59(3)	108(7)	77(5)	35(3)	20(3)	55(5)
E2C1	108(5)	180(10)	165(9)	90(6)	52(5)	122(9)
E2C2	72(5)	259(16)	546(25)	48(7)	-15(8)	280(3)
E2O	53(2)	205(7)	118(5)	68(3)	31(2)	109(5)
E3N	43(2)	148(7)	77(5)	42(3)	9(2)	61(5)
E3C1	53(3)	214(10)	97(6)	56(4)	-1(3)	60(7)
E3C2	64(3)	219(11)	92(6)	55(5)	4(3)	69(7)
E3O	77(3)	430(14)	143(6)	47(5)	5(3)	181(8)
E4N	50(2)	123(7)	69(5)	28(3)	18(2)	42(5)
E4C2	60(3)	157(9)	87(6)	40(4)	17(3)	57(6)
E4C1	66(3)	137(8)	81(6)	24(4)	27(3)	49(6)
E4O	69(2)	145(6)	176(6)	59(3)	33(3)	74(5)

<sup>a</sup> The anisotropic thermal parameter is defined as  $\exp[-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl]$ .

TABLE III. Observed and calculated structure factors (in Electrons) for Co(C9H15N2O2)(C2H7NO)2.

Table with 8 columns: H, K, FO, FC, H, K, FO, FC, H, K, FO, FC, H, K, FO, FC, H, K, FO, FC, H, K, FO, FC. It contains numerical data for structure factors and labels like L=1, L=2, L=3, L=4, L=5, L=6, L=7, L=8, L=9, L=10, L=11, L=12.

TABLE III. (Cont.)

Table with multiple columns of numerical data, likely representing bond lengths and angles for various atoms in a complex. The columns are organized into groups (e.g., H E F O FC, H K P O FC, etc.). The table includes various numerical values such as 1.32, 1.33, 1.34, etc., and some labels like L=1, L=2, L=3, L=4, L=5, L=6, L=7, L=8, L=9, L=10. The data is organized into 10 columns, each with a group of atoms and corresponding numerical values.

distances are equivalent (1.32(1) Å); there is, thus, complete delocalization of the negative charge and π-system over this portion of the ligand. As expected for a delocalized π-system, this portion of the ligand is essentially planar. The conformation of the ligand is indicated by the distance of each atom from the best least-squares plane of the coordinated atoms of the diimine, Table V. The carbons adjacent to the oxygen atoms, E1C2 and E2C2, are on opposite sides of the plane with distances of 0.49 Å and 0.23 Å from the plane, respectively. The only other atom of the diimine

ligand which is more than 0.05 Å out of the plane is the methyl carbon, AC1, which is 0.19 Å from the plane. It is interesting to compare the two halves of the ligand. Only one pair of corresponding bond distances shows a difference significantly greater than three times the standard deviation – the carbon-carbon distances in the five-membered rings differ by 0.060 Å, which is greater than seven times their standard deviations. This difference probably results from the effect of thermal motion on the atomic positions in the C<sub>2</sub>H<sub>4</sub> portions of the ligand.

TABLE IV. Interatomic distances (Å) and angles (deg.) for  $\text{Co}(\text{C}_9\text{H}_{15}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_7\text{NO})_2$ .

Atoms	Distance, Å	Atoms	Angles, degrees	Atoms	Angles, degrees
Co-E1O	1.931(3)	E1O-Co-E1N	86.1(1)	Co-E2N-E2C1	112.8(3)
Co-E2O	1.917(3)	E2O-Co-E2N	86.7(1)	Co-E1N-AC2	126.4(3)
Co-E1N	1.898(4)	E1O-Co-E2O	92.6(1)	Co-E2N-AC4	126.1(3)
Co-E2N	1.897(4)	E1N-Co-E2N	94.6(2)	E1O-E1C2-E1C1	109.6(4)
Co-E3N	1.976(3)	E3N-Co-E1O	91.6(1)	E2O-E2C2-E2C1	116.4(5)
Co-E4N	1.989(3)	E3N-Co-E1N	94.6(1)	E3O-E3C2-E3C1	114.1(4)
E1O-E1C2	1.404(6)	E3N-Co-E2O	86.4(1)	E4O-E4C2-E4C1	112.4(3)
E2O-E2C2	1.389(7)	E3N-Co-E2N	89.8(1)	E1C2-E1C1-E1N	106.2(4)
E3O-E3C2	1.402(6)	E4N-Co-E1O	85.5(1)	E2C2-E2C1-E2N	109.1(4)
E4O-E4C2	1.421(6)	E4N-Co-E1N	91.3(2)	E3C2-E3C1-E3N	113.7(3)
E1N-E1C1	1.478(6)	E4N-Co-E2O	87.6(1)	E4C2-E4C1-E4N	112.1(3)
E2N-E2C1	1.458(6)	E4N-Co-E2N	93.0(1)	E1N-AC2-AC1	119.4(5)
E3N-E3C1	1.495(5)	E1O-Co-E2N	178.3(2)	E2N-AC4-AC5	119.3(5)
E4N-E4C1	1.486(5)	E2O-Co-E1N	178.4(2)	E1N-AC2-AC3	123.0(4)
E1C1-E1C2	1.520(8)	E3N-Co-E4N	173.3(1)	E2N-AC4-AC3	123.3(4)
E2C1-E2C2	1.460(9)	Co-E2O-E2C2	110.1(3)	AC1-AC2-AC3	117.6(4)
E3C1-E3C2	1.504(6)	Co-E1O-E1C2	108.4(3)	AC5-AC4-AC3	117.4(4)
E4C1-E4C2	1.505(6)	Co-E3N-E3C1	121.1(3)	AC2-AC3-AC4	126.5(4)
AC2-AC3	1.399(7)	Co-E4N-E4C1	121.8(3)	AC2-E1N-E1C1	121.3(4)
AC3-AC4	1.392(8)	Co-E1N-E1C1	112.1(3)	AC4-E2N-E2C1	121.0(4)
AC1-AC2	1.523(6)				
AC4-AC5	1.518(6)				
E1N-AC2	1.324(6)				
E2N-AC4	1.327(6)				
E3O-E2O'	2.679(5)				
E4O-E1O''	2.593(4)				

TABLE V. Equation of the best least-squares plane<sup>a</sup> of the coordinated atoms of the diimine ligand and distances of atoms from this plane.

Equation of the Best Least-Squares Plane for E1O, E2O, E1N, and E2N: $0.022X - 0.008Y + 1.000Z + 1.819 = 0$			
Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Co	0.021	E2C2	-0.234
AC1	-0.190	E2N	-0.004
AC2	-0.054	E3O	4.883
AC3	-0.027	E3C1	2.829
AC4	0.001	E3C2	4.283
AC5	0.036	E3N	1.981
E1O	-0.004	E4O	-4.345
E1C1	-0.080	E4C1	-2.821
E1C2	0.489	E4C2	-4.237
E1N	0.004	E4N	-1.952
E2O	0.004		
E2C1	0.054		

<sup>a</sup> The equation is referred to orthogonal axes with the orthogonal X axis coincident to *a* and the orthogonal Z axis coincident to *c*<sup>\*</sup>.

The two monodentate 2-aminoethanol groups occupy *trans*-positions and, since amines are generally better ligands than alcohols, they are assumed to be coordinated through nitrogen. With this assignment, the carbon–nitrogen distances (1.495(5) and 1.486(5) Å) and the carbon–oxygen distances (1.402(6) and 1.421(6) Å) are consistent with the values found for the carbon nitrogen distances (1.478(6) and 1.458(6) Å) and the carbon–oxygen distances (1.404(6) and 1.389(7) Å) of the five-membered chelate rings. The fact that the temperature factors of these atoms were normal is further support for the assignment.

The non-coordinated alcohol groups of the 2-aminoethanol ligands and the alkoxide oxygens of adjacent molecules are involved in hydrogen bonding. Infinite chains (Figure 2) are created along the diagonal of the *bc*-plane by the interaction of one alcohol group, E3O, with the alkoxide, E2O, of the molecule related by the inversion center at the origin and by interaction of the second alcohol group, E4O, with alkoxide, E1O, of the molecule related by the inversion center at 0, -1/2, -1/2. The oxygen–oxygen distances, 2.68(1) and 2.59(1) Å, respectively, indicate reasonably strong hydrogen bonding.

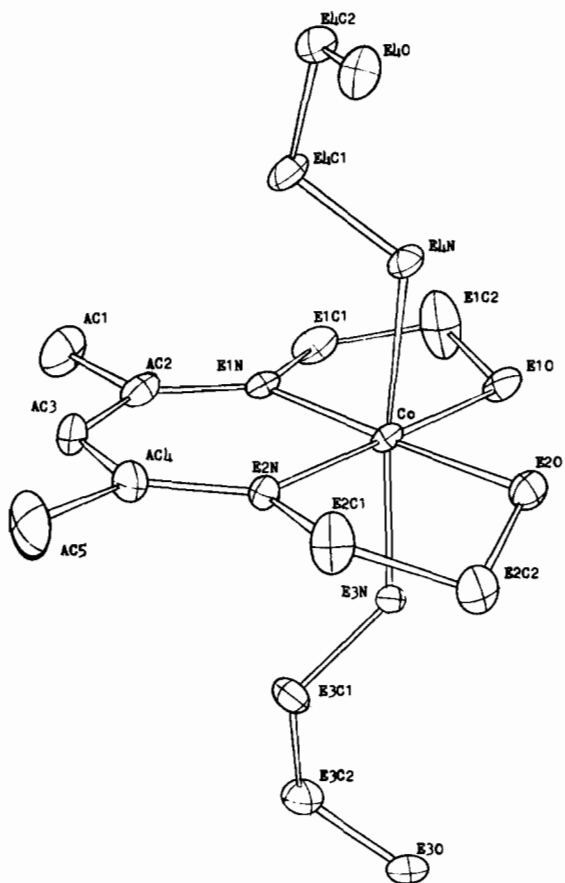


Figure 1. A perspective drawing of the asymmetric unit of  $\text{Co}(\text{C}_9\text{H}_{15}\text{N}_2\text{O}_2)(\text{C}_2\text{H}_7\text{NO})_2$ . Thermal ellipsoids are drawn at the 50% probability level. The atom designations denote the origin of the particular atom; atoms from 2,4-pentanedione are preceded by A, those from the two 2-aminoethanol molecules that are incorporated into the diimine ligand are preceded by E1 and E2; the atoms of the 2-aminoethanol molecules are preceded by E3 and E4.

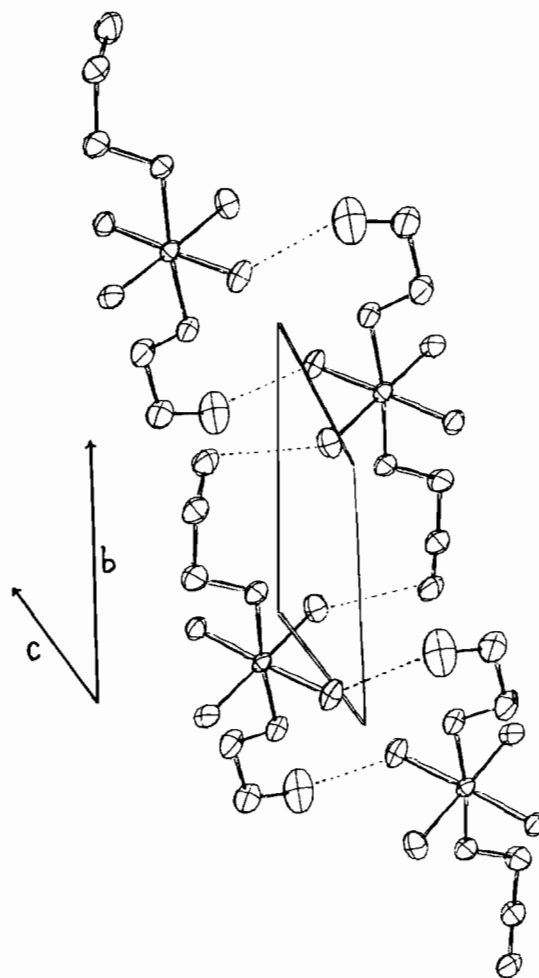


Figure 2. A portion of the structure showing the hydrogen bonding between molecules along the diagonal of the  $bc$ -plane. Only the cobalt coordination sphere and the 2-aminoethanol atoms are shown.

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