

Hg—I bond length = 2.617 (6) Å and the angle I—Hg—I = 178.3°, and in the 1:1 complex between 18-crown-6 and HgI₂ (Pears, Fraser Stoddart, Crosby, Allwood & Williams, 1986a) which contains a linear HgI₂ molecule where the Hg—I bond length = 2.622 (1) Å.

The geometry of the dimeric anion [Hg₂I₆]²⁻ is very similar to that found previously: Pears, Fraser Stoddart, Crosby, Allwood & Williams (1986b), Shibaeva & Kaminskij (1984) and Zacharie, Wuest, Olivier & Beauchamps (1985). In these structures, however, the bridging iodines are not equidistant from the bonded Hg atoms (2.906 and 2.944, 2.819 and 2.957, 2.864 and 2.962 Å), contrary to the present case [2.934 (1) Å]. Correspondingly, the angle Hg—I_{bridge}—Hg in the present structure [83.81 (4)°] is somewhat smaller than that in the references listed above: 88.0 (1), 87.2 (2) and 85.7 (2)°.

There are two van der Waals contacts [3.769 (2) Å] – see Fig. 2 – between iodines of HgI₂ and [Hg₂I₆]²⁻ [*r*_w(I) = 2.15 Å; *CRC Handbook of Chemistry and Physics* (1979)] and two van der Waals contacts between Hg(1) and two equivalent I(4) atoms [*r*_w(Hg) = 1.50 Å; Grdenić, 1965]. However, there are also two further distances Hg(1)—I(3) [Hg(1) belongs to the HgI₂ molecule] which exceed the sum of van der Waals radii of Hg and I, just completing the environment of the Hg(1) atom to form a very deformed octahedron.

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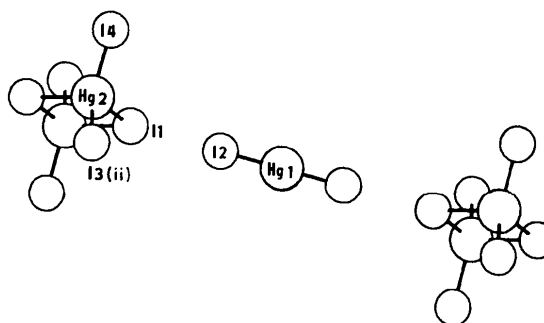


Fig. 2. A view of the [Hg₂I₆]²⁻ and HgI₂ molecules. The atoms Hg(1), I(2) and I(1) lie within a line parallel to the *c* axis.

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Structures of (β-Cyanoethyl)(3-ethylpyridine)bis(dimethylglyoximato)cobalt(III) (1) and (β-Cyanoethyl)(4-ethylpyridine)bis(dimethylglyoximato)cobalt(III) (2)

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Abstract. (1): [Co(C₃H₄N)(C₇H₉N)(C₄H₇N₂O₂)₂], *M*_r = 450.38, monoclinic, *P*2₁/*n*, *a* = 19.570 (2), *b* = 9.288 (2), *c* = 11.644 (2) Å, β = 92.37 (2)°, *V* =

2114.6 (6) Å³, *Z* = 4, *D*_x = 1.415 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.91 cm⁻¹, *F*(000) = 944, *T* = 298 K, *R* = 0.071 for 3079 independent reflections.

(2): [Co(C₃H₄N)(C₇H₉N)(C₄H₇N₂O₂)₂], $M_r = 450.38$, triclinic, $P\bar{1}$, $a = 11.247$ (6), $b = 11.230$ (4), $c = 9.416$ (2) Å, $\alpha = 93.17$ (7), $\beta = 114.20$ (2), $\gamma = 99.45$ (5)°, $V = 1060.0$ (8) Å³, $Z = 2$, $D_x = 1.416$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 7.91$ cm⁻¹, $F(000) = 472$, $T = 298$ K, $R = 0.057$ for 3241 independent reflections. In each crystal the β -cyanoethyl group adopts a conformation which is parallel to the cobaloxime plane. The size of the cavity for the β -cyanoethyl group in crystal (2) is significantly greater than that in crystal (1). This explains the greater isomerization rate of (2) than that of (1) on exposure to visible light.

Introduction. It has been found that the β -cyanoethyl group bonded to the cobalt atom in some cobaloxime complex crystals isomerizes to α -cyanoethyl on exposure to visible light (Ohgo & Takeuchi, 1985). The isomerization rates are different among the cobaloxime complex crystals. Recently it has been reported that the complex with 3-methylpyridine as an axial base ligand exists in two crystal forms and that the rate of the isomerization is closely related to the size of the cavity available for the β -cyanoethyl group in the two forms of the crystals (Uchida, Danno, Sasada & Ohashi, 1987). A similar relationship between the reaction rate and cavity size occupied by the reactive group has been found for the crystalline-state racemization on exposure to X-rays (Ohashi, 1988). In order to examine if the above relationship holds good for crystals with different axial ligands, we have prepared several complexes with different axial base ligands. This paper reports the crystal structures of two complexes with 3-ethylpyridine and 4-ethylpyridine, and the relationship between reaction cavity and isomerization rate.

Experimental. (1) and (2) prepared in a similar way to that reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981); orange crystals recrystallized from aqueous methanol solutions. Crystal approximate dimensions 0.5 × 0.3 × 0.1 mm (1) and 0.3 × 0.3 × 0.1 mm (2). Rigaku AFC-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Systematic absences: $0k0$ $k = 2n + 1$, $h0l$ $h + l = 2n + 1$ (1) and no absence (2). Cell parameters refined by least-squares method on the basis of 15 (1) and 18 (2) independent 2θ values [$20 < 2\theta < 30^\circ$ (1) and $20 < 2\theta < 30^\circ$ (2), $\lambda = 0.71069$ Å]. Three-dimensional intensity data collected up to $2\theta = 50^\circ$; range of hkl , -23 to 23 , 0 to 11 and 0 to 13 (1) and -15 to 15 , -15 to 15 and 0 to 12 (2). ω - 2θ scan technique, scan speed 4° min^{-1} (θ). Three standard reflections showed no significant change in intensity. 3718 (1) and 3733 (2) intensities measured, 3079 (1) and 3241 (2) intensities with $|F_o| > 3\sigma(|F_o|)$ con-

Table 1. Final atomic coordinates ($\times 10^5$ for Co, and $\times 10^4$ for C, N and O) and equivalent isotropic thermal parameters for compounds (1) and (2)

Compound	$B_{eq} = (1/3)\sum_i B_{ij} a_i^* a_j^* a_i \cdot a_j$			B_{eq}
	x	y	z	
Compound (1)				
Co(1)	58878 (4)	28095 (8)	73767 (6)	2.9
N(1)	6032 (2)	866 (5)	7005 (4)	3.6
N(2)	5775 (2)	2946 (5)	5768 (4)	3.5
N(3)	5765 (2)	4770 (5)	7742 (4)	3.6
N(4)	6029 (3)	2673 (6)	8981 (4)	4.0
O(1)	6199 (3)	-148 (5)	7802 (5)	5.3
O(2)	5647 (2)	4190 (5)	5224 (4)	4.9
O(3)	5624 (3)	5767 (5)	6932 (4)	5.1
O(4)	6176 (3)	1420 (6)	9516 (4)	5.6
C(1)	5960 (3)	523 (7)	5920 (5)	4.0
C(2)	5807 (3)	1756 (7)	5197 (5)	3.8
C(3)	5828 (3)	5106 (7)	8816 (6)	4.2
C(4)	5984 (3)	3870 (8)	9552 (5)	4.5
C(5)	6073 (5)	-967 (8)	5471 (9)	6.6
C(6)	5732 (4)	1685 (11)	3902 (6)	6.1
C(7)	5753 (4)	6609 (9)	9247 (9)	6.6
C(8)	6105 (4)	3955 (12)	10828 (6)	6.9
N(5)	7461 (4)	1379 (11)	4912 (7)	9.2
C(9)	6890 (3)	3324 (8)	7274 (6)	4.3
C(10)	7427 (4)	2199 (11)	7034 (8)	6.6
C(11)	7422 (4)	1776 (11)	5794 (9)	7.3
N(6)	4850 (2)	2426 (5)	7529 (4)	3.2
C(12)	4383 (3)	3300 (7)	7037 (5)	3.8
C(13)	3682 (3)	3119 (8)	7142 (6)	4.8
C(14)	3474 (4)	1933 (8)	7793 (6)	5.2
C(15)	3949 (4)	1041 (8)	8299 (6)	4.7
C(16)	4632 (3)	1315 (7)	8157 (5)	4.0
C(17)	3163 (5)	4249 (12)	6623 (9)	6.8
C(18)	2791 (6)	3767 (15)	5580 (11)	12.2
Compound (2)				
Co(1)	31888 (5)	72829 (4)	67964 (6)	2.7
N(1)	3314 (3)	8970 (3)	7087 (4)	3.1
N(2)	3049 (4)	7624 (3)	4793 (4)	3.3
N(3)	3016 (4)	5582 (3)	6486 (4)	3.6
N(4)	3297 (4)	6966 (3)	8767 (4)	3.3
O(1)	3403 (3)	9573 (3)	8410 (4)	4.0
O(2)	2861 (4)	6733 (3)	3626 (4)	4.7
O(3)	2850 (4)	4974 (3)	5133 (4)	5.0
O(4)	3425 (4)	7842 (3)	9909 (4)	4.2
C(1)	3312 (4)	9560 (4)	5921 (5)	3.3
C(2)	3160 (4)	8741 (4)	4566 (5)	3.4
C(3)	3072 (5)	5015 (4)	7681 (6)	4.0
C(4)	3231 (4)	5847 (4)	9033 (5)	3.8
C(5)	3398 (7)	10894 (4)	5992 (8)	5.4
C(6)	3082 (6)	9184 (6)	3061 (6)	5.1
C(7)	2982 (8)	3678 (5)	7648 (9)	6.6
C(8)	3302 (7)	5418 (6)	10529 (7)	5.8
C(9)	1198 (5)	6916 (5)	5950 (7)	4.5
C(10)	452 (6)	7963 (6)	5813 (7)	5.5
C(11)	248 (5)	8587 (6)	4373 (7)	5.7
N(5)	67 (5)	9051 (5)	3353 (6)	4.9
N(6)	5223 (3)	7529 (3)	7619 (4)	2.7
C(12)	6048 (4)	8267 (4)	8963 (5)	3.2
C(13)	7409 (4)	8460 (4)	9547 (5)	3.4
C(14)	8007 (4)	7890 (4)	8737 (5)	3.7
C(15)	7147 (5)	7143 (4)	7341 (5)	3.7
C(16)	5802 (4)	6990 (4)	6832 (5)	3.2
C(17)	9504 (6)	8072 (6)	9327 (8)	5.3
C(18)	10012 (7)	6937 (8)	9593 (14)	9.4

sidered observed and used for the structure determination. Lorentz and polarization corrections, absorption corrections (1), and no absorption corrections (2). Structure solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares with SHELX76 (Sheldrick, 1976).

H atoms located on difference map. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + C(F_o)^2]^{-1}$, $C = 0.0040$ (1) and 0.0040 (2). Final $R = 0.071$ (1) and

Table 2. Selected bond distances (Å), bond angles (°) and torsion angles (°)

	(1)	(2)
Co(1)—N(1)	1.880 (5)	1.872 (4)
Co(1)—N(2)	1.881 (5)	1.894 (4)
Co(1)—N(3)	1.887 (5)	1.882 (4)
Co(1)—N(4)	1.882 (5)	1.867 (4)
Co(1)—C(9)	2.027 (7)	2.004 (6)
Co(1)—N(6)	2.076 (5)	2.056 (4)
N(1)—Co(1)—N(2)	81.3 (2)	81.2 (2)
N(1)—Co(1)—N(3)	178.7 (2)	178.6 (2)
N(1)—Co(1)—N(4)	98.4 (2)	98.0 (2)
N(1)—Co(1)—C(9)	93.3 (3)	93.4 (2)
N(1)—Co(1)—N(6)	90.6 (2)	90.7 (2)
N(2)—Co(1)—N(3)	98.6 (2)	98.9 (2)
N(2)—Co(1)—N(4)	178.3 (2)	178.7 (2)
N(2)—Co(1)—C(9)	90.0 (3)	89.7 (2)
N(2)—Co(1)—N(6)	91.2 (2)	90.3 (2)
N(3)—Co(1)—N(4)	81.7 (2)	81.9 (2)
N(3)—Co(1)—C(9)	85.3 (3)	85.2 (2)
N(3)—Co(1)—N(6)	90.7 (2)	90.7 (2)
N(4)—Co(1)—C(9)	88.4 (3)	89.3 (2)
N(4)—Co(1)—N(6)	90.5 (2)	90.7 (2)
C(9)—Co(1)—N(6)	176.0 (2)	175.9 (2)
N(1)—Co(1)—N(6)—C(12)	133.1 (5)	-48.4 (3)
N(1)—Co(1)—C(9)—C(10)	3.2 (7)	0.4 (4)
Co(1)—C(9)—C(10)—C(11)	-77.2 (9)	-80.6 (5)

0.057 (2), $wR = 0.082$ (1) and 0.068 (2). In final least-squares cycle, $(\Delta/\sigma)_{\max}$ 0.2 (1) and 0.3 (2). Excursions in final difference map, +0.5 and -0.5 (1) and +0.4 and -0.4 $e \text{ \AA}^{-3}$ (2). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), are corrected for anomalous-scattering contribution. Calculations carried out on the FACOM-HITAC system M-680H computer at the University of Tokyo.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Molecular structures of (1) and (2) with numbering of atoms are shown in Figs. 1(a) and 1(b), respectively. Selected bond distances and angles and torsion angles are listed in Table 2. The Co—C distances, 2.027 (7) Å (1) and 2.004 (6) Å (2) and the Co—N(6) distances, 2.076 (5) Å (1) and 2.056 Å (2) are the same as the corresponding ones in the 3-methylpyridine complex, the Co—C distances, 2.016 (4) Å (Form 1) and 2.019 (3) Å (Form 2), and the Co—N(5) distances, 2.065 (3) Å (Form 1) and 2.075 (3) Å (Form 2), within experimental error. The Co—N(equatorial) distances are in the range 1.880 (5)–1.894 (4) Å, which are nearly equal to the corresponding ones in the cobaloxime complexes determined so far. The torsion angles of Co—C(9)—C(10)—C(11) are -77.2 (9)° (1) and -80.6 (5)° (2).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles of non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53282 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This causes the β -cyanoethyl groups of (1) and (2) to adopt a parallel conformation to the cobaloxime plane. Such a parallel conformation was also found in both forms of 3-methylpyridine crystals. The crystal structures of (1) and (2) are shown in Figs. 2(a) and 2(b), respectively. There are no unusually short contacts between the molecules in both crystals.

The reaction cavities (Ohashi, Uchida, Sasada & Ohgo, 1983) for the β -cyanoethyl groups of (1) and (2) were drawn and the volumes of the cavities were calculated to be 13.12 and 14.00 Å³ for (1) and (2), respectively. The rates of isomerization were obtained from the change of IR spectra due to C≡N stretching mode, assuming first-order kinetics in the early stages (Sekine, 1989). The rate constants for (1)

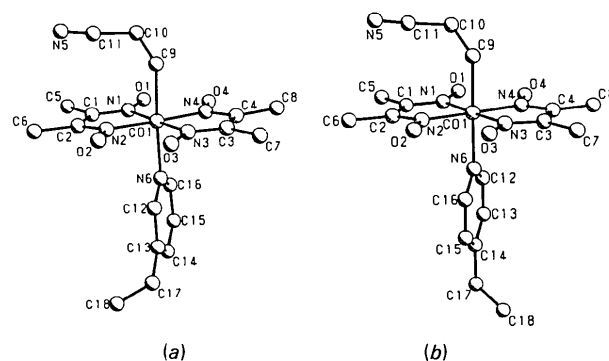


Fig. 1. Molecular structures of (a) compound (1) and (b) compound (2), with the numbering of the atoms.

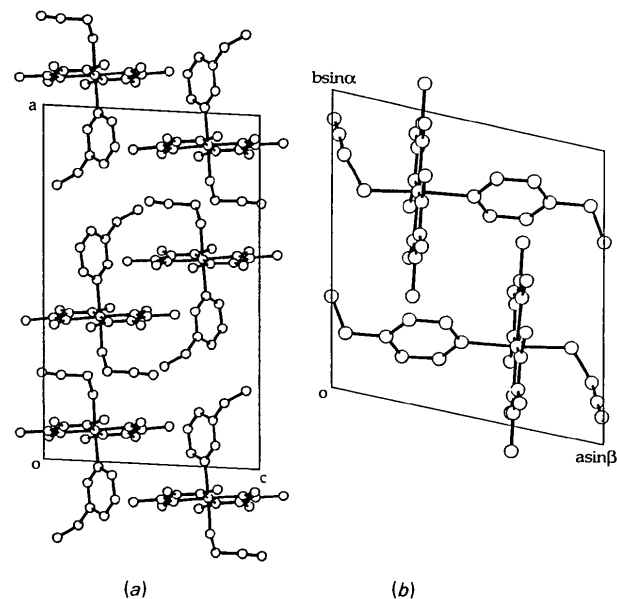


Fig. 2. Crystal structures (a) viewed along *b* for compound (1) and (b) viewed along *c* for compound (2).

and (2) are 1.4×10^{-4} and $1.6 \times 10^{-4} \text{ s}^{-1}$, respectively. It is clear that the larger the reaction cavity, the greater the rate constant. Such a relationship has been found for the polymorphic crystals of the 3-methylpyridine complex. This may indicate that the β - α photoisomerization is controlled by the crystal-line lattice in the early stages and that the size of the reaction cavity in the initial structure is a good guide when elucidating the reaction rate.

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Structure of [Hydrotris(3,5-dimethyl-1-pyrazolyl)borato]dipropyldithiocarbamatoxomolybdenum(IV)

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Abstract. C₂₂H₃₆BMoN₇OS₂, $M_r = 585.46$, monoclinic, $P2_1/n$, $a = 9.753$ (2), $b = 20.890$ (2), $c = 14.065$ (2) Å, $\beta = 106.07$ (1)°, $V = 2753.6$ Å³, $Z = 4$, $D_m = 1.41$, $D_x = 1.41 \text{ g cm}^{-3}$, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 6.4 \text{ cm}^{-1}$, $F(000) = 1216$, $T = 295 \text{ K}$, $R = 0.046$, $wR = 0.051$ for 3662 reflections. The central Mo atom adopts a distorted octahedral coordination geometry in which one face of the octahedron is occupied by the tridentate hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand and the opposite face by an oxo and dipropyldithiocarbamate ligand. The structure of the mononuclear complex is compared with that of the analogous diethyldithiocarbamate complex.

Introduction. Interest in metal oxo compounds has gained considerable momentum in recent years owing to the role of metal oxo species in certain catalytic processes of biological (Spiro, 1985) and industrial importance (Nugent & Mayer, 1988). These include the presence of mononuclear oxomolybdenum species in molybdenum hydroxylases (Bray, 1980; Spence, 1983; Cramer, 1983). The bulky hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (L)

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has been utilized to prepare oxomolybdenum complexes with unusual structural features and to prevent the formation of polynuclear species. Compounds such as $LMoOX_2$ ($X =$ halide, pseudohalide, alkoxide, thiolate) (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1987) and $LMoO(S_2CNR_2)$ ($R = \text{Me, Et, Pr, Bu}$) (Young, Roberts, Ortega & Enemark, 1987) have been prepared and characterized. We have recently prepared a series of vanadyl complexes of the form $LVO(S_2CNR_2)$ ($R = \text{Me, Et, Pr, Bu}$) (Sit, Collison, Mabbs & Cleland, 1989) and are investigating the detailed electron spin resonance spectra of these species in dilute single crystals. Crystals of the analogous $LMoO(S_2CNR_2)$ complexes serve as diamagnetic host lattices for these studies. We herein report the structure of one of these complexes, $LMoO(S_2CNPr_2)$.

Experimental. The complex was prepared by the method of Young *et al.* (1987). Emerald green crystals obtained by liquid–liquid diffusion of methanol into a methylene chloride solution of $LMoO[S_2CN(C_3H_7)_2]$ at 298 K, dimensions $0.4 \times 0.25 \times 0.20 \text{ mm}$, mounted on a glass fiber with cyanoacrylate glue, D_m by flotation ($ZnBr_2$ and

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